
Coloring of Plastics

Fundamentals – Colorants – Preparations

Albrecht Müller



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With 31 Figures and 66 Formulas

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The Author:

Dr. Albrecht Müller, Fontanestraße 51, 42657 Solingen, Germany

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Preface

The title *Coloring of Plastics* already points towards the two main subjects covered in this book – color and plastics.

Colors have a long history; in prehistoric time, colored minerals were used for rock and cave paintings and later on to decorate ceramic items, e. g., artifacts and household articles. In the last century, the production of color dyes for textiles laid the foundation for several chemical companies, which are well known worldwide today. Over the following decades these companies grew and started new fields of production, one of which was plastics.

At the beginning of the 20th Century the term *plastics* was originally used for modified natural occurring polymeric substances. Later, all synthetic produced polymers were called plastics and today plastics are well-known and very important raw materials to the extent that a modern society without plastics is unimaginable. The entertainment industry is a prime example with its CD's, video recorders, and cameras as key applications for plastic materials. In addition, the use of plastic materials was the key to miniaturize many technical and consumer parts, thus facilitating parts not only lighter but also much easier to handle, both very important advantages for the consumer. Many product designs only became technically and economically feasible by using thermoplastic materials rather than metal.

The field of “coloring of plastics” also includes other areas such as the construction of the processing machine, the processing technology, quality assurance of the raw materials and final products, toxicology of the raw materials, the legal aspects from the handling of all ingredients during the production of a color preparation to the processing of plastic parts, and the safe use of the products made of plastics in their specific applications. Because all these different fields are linked together they must be considered during the development of a color preparation for the customer. Only then will the customer be pleased with the color preparation and with the finished product.

This book was originally published in German under the title *Einfärben von Kunststoffen* and the translation was revised and adapted to the US market especially regarding legal aspects/rules and regulation. The basic principles of coloring of plastics are the same worldwide, including toxicological and ecological considerations. The standard methods for the evaluation of properties, the legal aspects, the equipment used etc. differ mainly in detail, but not fundamentally.

Which particular colorant is finally chosen for a specific application often depends on its country of origin, not only because of the (usually) better service by the manufacturer of the colorant but also for economical reasons.

My special thanks belong to Ms Jackie Powell for her most appreciated help in revising my translation.

Albrecht Müller

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1 Introduction

Everywhere in our environment we are surrounded by colors. These can be the natural colors of flora and fauna or synthetically colored clothing, furniture, or household goods to name just a few.

Many of the items we use daily are made of colored plastics. Yet although technical standards for the coloring of plastics have long been in place, questions, problems, and mistakes arise again and again. This is not surprising in view of all the different available raw materials (plastics and colors), rules and regulations, and the specific requirements of customers. These specific requirements especially can necessitate discussions between suppliers of the color preparation and their customers, because some requirements can exclude or counteract each other or cannot be fulfilled completely all the time.

Experience shows that processors of plastics often have limited knowledge regarding the complexity of a color preparation; likewise the colorist's knowledge of the processing of plastics is limited as well. An intensive exchange of information between both is therefore very important. In this way the understanding of each will improve considerably to make it possible to achieve a higher quality standard for the products of each.

In the following chapters all the different aspects of coloring of plastics are described in detail. The emphasis of course is on plastics and colorants, their specific properties, and their interactions. Several interactions are well known and can have adverse effects on certain properties; it is therefore very important to avoid these.

All the colorants are listed in the worldwide common Color Index. The Color Index number as such does not indicate the chemistry of a colorant. A detailed description should be consulted for this purpose. It is important for the colorist to know the chemistry of the colorant because this will enable him to estimate directly important properties of the colorant. For this reason the chemistry of each colorant, based on published data, is added to the description of each colorant.

Like other aspects of life, the coloring of plastics is governed by laws, rules, and regulations. On several occasions in the past a colorant that had been used successfully for many years was banned overnight because of new toxicological data and/or evidence of hazardous effects to the environment. Typical examples are lead and cadmium pigments and specific disazodiarylide pigments and azo dyes.

This book would be incomplete without a description of the theory of colors and our sense for colors. Only the main features are presented because an extensive literature on this topic [1, 2] is available.

2 Methods Used to Color Plastics

The processor of plastics has a choice between two different product lines to add color to his products: either he uses mass colored plastic material or he adds the color himself using a color preparation. Both methods have their technical and economic advantages and disadvantages.

The application of mass colored plastic materials is preferred for items for which certain properties need to be guaranteed such as mechanical strength during long-term use, requirements regarding noninflammability, or other properties in the field of electronic parts. This procedure is valid especially for all technical parts and pieces of equipment with certain required properties guaranteed by the processor of the item. In these cases the color as such is not so important because it is fixed at any rate by international standards. For those applications a mass colored plastic material is preferred. All manufacturers of plastics offer special grades within their range of products in standardized colors. In addition they supply special customer matched colors if the ordered quantity is large enough to allow an economical manufacturing. The reason for such a requirement very often is the wish of the processor of plastics to use their corporate colors as a marketing tool. Recently, the minimum quantities of customer matched colors have increased considerably, and this increase will continue in future. Because of this increase it becomes more and more difficult for the processor of plastics to receive the needed quantities within an acceptable price range. An alternative is the use of color preparations instead of mass colored plastic material. The manufacturer of color preparations can observe an increase in this trend.

The disadvantages and advantages of mass colored plastics are:

- *Disadvantages*
 - Expensive
 - Longer terms for delivery
 - Rather expensive stock
 - Only standard colors available
 - Minimum quantity in case of customer matched colors
 - Remaining stock
- *Advantages*
 - Optimum in color distribution
 - No additional equipment required
 - Guaranteed properties

- In case of complaints only one supplier, therefore easier handling of a complaint.

A completely different situation exists in the case of plastic articles made for daily use. In consumer goods the right color plays a very important role; in addition the color of these articles changes more or less yearly owing to always changing fashion. The processor of plastics can follow the latest color trends alone by using color preparations. Only by using color preparations is the processor of plastic material flexible enough to match his products to the fast changing color trends and fashion; at the same time he is also free to select the most suitable plastic grade for each article and/or can respond to different quotations of plastic materials that have more or less the same properties.

The disadvantages and advantages of self-coloration are:

- *Disadvantages*
 - Need of additional equipment, for example, metering unit, premixing devices, color check, and so forth
 - A good mixing screw profile
 - Intensive training of the workers
 - Greater requirements toward quality assurance
- *Advantages*
 - Short-term delivery of natural colored plastics
 - Low stock
 - Supply and storage of the natural colored plastic material in container or in bulk
 - Only small quantities of leftovers of color preparations
 - High degree of flexibility in color matching
 - Fast service and supply of new color preparations by the manufacturer of color preparations
 - Easy and fast change of color during production on the processing machine
 - Better possibilities to react to price increase

Considering all the advantages of self-coloration it is not surprising it is the standard procedure in manufacturing of consumer goods. The presupposition for self-coloration is the availability of color preparations. These are provided worldwide by a large number of manufacturers of color preparations. To develop a most favorable color preparation in terms of matching the desired color, its processing behavior and the properties of the colored article, it is necessary to consider all the different parameters, including all the specific requirements very often listed in detail by the customer. The complexity of a color preparation is considered in the following chapters.

3 Requirements for Color Preparations

The first step in designing a color preparation is the definition of the desired color. This can be done using different internationally common color systems such as Pantone or HSK, RAL (Germany), a piece of lacquered metal sheet, a colored plastic specimen, or simply a piece of printed paper. The most extreme pattern is to match a color according to a small piece of paper torn out of a magazine, catalog, or newspaper. Experience shows this is more common than imagined.

If it is possible to measure the color with a spectrophotometer, the colorist, combining this information with computer data, receives a kind of “guiding recipe” that he has to adapt to all the customer-specific requirements including a perfect color match in the intended plastic material. If it is impossible to measure the color, the colorist starts his work at the very beginning.

The next steps are to create an accurate color recipe, to prepare it, to produce a sample by injection molding, and finally to compare its shade with the color specimen. These steps have to be repeated if necessary until a successful matching of the color is achieved. If the sample accurately matches the color of the specimen a larger sample will be produced and sent to the customer together with a quotation and request for approval. At the same time the recipe will be transferred to the recipe archive (Fig. 3.1).

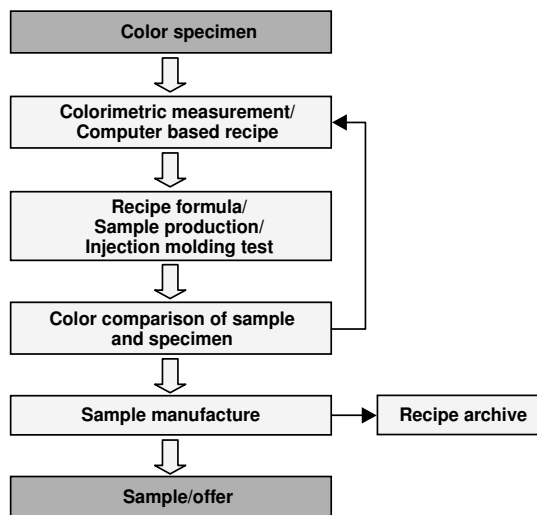


Figure 3.1: General color matching procedure

At first glance it seems to be rather easy to formulate a color recipe that will match the color specimen accurately. It is not as simple as it looks, especially when the color specimen is a piece of printed paper or a lacquered metal sheet. On one side printing inks normally contain a very high colorant concentration, a concentration that is impossible in plastics, and on the other hand many colorants suitable for printing inks cannot be applied because of their insufficient thermal stability in plastics. In addition, the binder of the printing ink is absolutely transparent and colorless; plastics, however, are more or less opaque with an individual tint. The behavior of lacquered metal sheets is basically very similar to pieces of printed paper. In such a situation only a dialogue between the supplier of the color preparation and the customer can solve the problem; a 100% match of the color specimen is absolutely impossible. The colorist is only able to approximate the color in the plastic material. Another problem arises from a structured surface of the color specimen. In such a case the colorist must have a mold with at least a very similar surface structure; otherwise the color match fails.

From the generalized diagram showing the color matching procedure, it is not evident which criteria have to be taken in account when formulating the recipe. The most important points are listed below.

- Desired type of color preparation
- Type of plastic to be colored
- Processing parameters
- Colorant concentration
- Choice of colorant (type, chemical and thermal stability, light fastness/weather resistance, shrinkage/warpage, migration fastness)
- Additives/fillers/stabilizers
- Legal requirements
- Customer-specific requirements

The list is indicative of the complexity of a color preparation. In the case of customer-specific requirements a dialogue with the customer may be unavoidable because often these requirements have not been adequately described and/or it is impossible to satisfy all the requirements because some of them, by necessity, exclude each other.

3.1 Chemical Stability

The importance of chemical stability is not always obvious at first but becomes evident if we look closer at the requirements a plastic article has to fulfill during

daily use. The requirements are manifold and sometimes very specific according to special utilization. Because of the large variety of requirements it is impossible for the supplier of colorants to check each colorant for every possible use.

In conformity to international standards the supplier of colorants checks the stability of pigments to acids (HCl , H_2SO_4 , HNO_3) and alkalis (NaOH , Na_2CO_3) and the resistance of dyestuff to peroxides. These test results cover a broad scope of possible applications. In the field of packaging plastic containers, bottles, boxes, films, and so forth are today very common. Many of the filling goods are at least slightly acidic or alkaline. Tests of resistance to peroxides have a twofold importance. First, unsaturated polyesters are polymerized by peroxides as catalysts; second, modern household detergents for the cleaning of textiles contain peroxides.

Chemical stability is a property of the whole system containing at least colorant and plastics. Because so many different types and grades of plastics and a very broad range of colorants are available it is impossible to run chemical stability tests of every possible combination. The test data of a colorant manufacturer are nothing other than an indication of what to expect. In practice running storage tests is unavoidable, especially in the field of packaging. Only the test can determine if an interaction is to be expected between the colored plastic container and the filling good during storage.

The test for thermal stability of a colorant is linked to the test for chemical stability. A typical example is polyamide (PA). Several colorants cannot be used in PA although they withstand much higher temperatures when applied in other types of polymer. The reason for the instability of colorants in PA is the reducible force of a PA melt. In this case the limitation of use is a question not only of heat stability, but also of a combination of thermal and chemical stability of the colorant at the temperatures of a PA melt. The following examples may give you an idea of the versatility of chemical stability.

- *Packaging.* A wide range of filling goods are packed in colored plastic containers, for example, medicine, food, cosmetics, household detergents, chemicals, and so forth. The list is nearly endless. In all these cases test runs to check the storage stability are an absolute "must." No forecast is possible because of the variety of feasible interactions. Chemical reactions between the packaging material (plastics/colorant/additives) and the filling good are one possibility of interaction; another is migration, because solvents as component of the filling good may dissolve the colorant and/or additives of the packaging material.
- *Gaskets.* A screw cap with gasket, made of polyethylene (PE) and colored with phthalocyanine blue, was used on a container holding sulfuric acid as the

filling good. The color had no real function; it was used only to make it easier to check the presence of the gasket. Because of a chemical interaction between the sulfuric acid and the phthalocyanine blue the gasket was discolored. By exchanging the organic blue for an inorganic blue the problem was solved immediately.

- *Battery container.* This type of container is basically the packaging of the battery acid. They are available in different colors, mainly black, gray, or yellow.
- *Bottle crates.* Colorants for bottle crates require not only good light fastness and weather resistance but also good resistance to alkaline detergents. Bottle crates, back to the filler (e.g., brewery), will be usually washed before refilling.
- *Textiles.* Colored textiles should not bleach during washing and/or dry cleaning. In this application the requirements for the colorants are resistance to bleaching substances, mainly peroxides, and resistance to solvents used during dry cleaning.
- *Automobile industry.* The use of plastic material within the automobile industry increases yearly. Under the hood, for example, many parts are made of colored plastics. These parts must be resistant to fuel, lubricants, gasoline, and refrigerants at higher temperatures. Because of these severe requirements most of the parts are black, colored with carbon black.

This list can be continued. According to the actual application the requirements for chemical stability vary considerably and are very specific for each application. Because of this only a storage test with the final part can determine if all requirements will be fulfilled by the whole system containing plastics, colorant, and additives. A forecast based on separate tests of each single component is not possible.

3.2 **Migration Fastness**

Migration fastness is a worldwide requirement for colorants. Many international rules and regulations are based on the “nonmigration principle.” By definition, for example, in Germany according to DIN 53 775 part 3 [17], blooming is differentiated from bleeding. (Note: The German standard DIN is the counterpart to the American ASTM-Methods.)

Blooming: The effect of blooming can occur when a dissolved colorant moves from the inside to the surface of a plastic article and recrystallizes there. Because pigments are defined as completely insoluble in plastics only dyestuff, soluble in plastics by definition, can bloom. In reality some organic pigments are partially soluble, and these can bloom also.

Bleeding. The effect of bleeding is manifold. Both pigments and dyestuff can show the effect of bleeding; it is a question of condition. Bleeding can occur in two ways.

Bleeding can be observed when a plastic article contains plasticizer, in which many organic pigments are partially soluble. Bleeding is observed in the case of migration of the plasticizer to the surface of the part. For this reason many organic pigments cannot be applied in plasticized plastics such as poly(vinyl chloride) (PVC) or polyurethane elastomers (PU).

The other possibility is that the plastic article itself does not contain any solvent or plasticizer but comes in contact with a solvent and/or plastic part containing plasticizer. The solvent and/or plasticizer can dissolve partially the organic colorant of the surface layer. The result is a transfer of color to the other medium, and this is bleeding also.

Bleeding can be a problem in the field of packaging. The liquid content of a package is based on solvents. In this connection the term solvent means not only the “classical” solvent but includes all liquid components of a formulation or product.

Many technical devices and household appliances, just to name two examples, are assembled of different plastic parts. If one part is made of a plasticized polymer it would be worthwhile to bear in mind the possibility of bleeding. Proper checks and storage tests are recommended in such cases.

Migration tests of colors are based on bleeding. A piece of a white colored film of plasticized PVC is pressed upon the colored plastic part to be checked for migration at elevated temperature. Not only is the composition of the plasticized PVC film accurately described and defined but also all parameters of the test, for example, the weight to be used, duration of the test, and the temperature. In Germany the migration test is described in DIN 53775 part 3; similar standardized test methods exist in other countries.

Migration fastness is no longer a requirement only for colorants. The term migration fastness has been widened to include any additive and/or impurity present in a consumer good, as a consequence of the fact that any substance migrating from a plastic article may be hazardous to health. To avoid any hazard to the customer the legal authorities of nearly all countries published specific rules and regulations that consumer goods have to fulfill. The list of regulated plastic articles varies slightly from country to country. All plastic materials and containers that come in contact with food and beverages during processing, transportation, or use in household items and toys are always listed, however.

In Germany, for example, the criteria for the composition of listed consumer goods are laid down in the *Lebensmittel- und Bedarfsgegenstandesgesetz*. In

paragraph 31 of this law it is specified: “It is forbidden to use any substance for consumer goods which may migrate, except impurities without any hazard to health, which are tasteless, odorless and technically unavoidable.” In other words, it is a strict “nonmigration principle.” Paragraph 5 contains the list of all the plastic articles subject to this regulation. The migration test method is published in the *BgVV-Empfehlungen* (Recommendations of the German Health Authorities), chapter B II/IX [18]. This chapter contains a detailed description of the test as such and a definition of the test liquids to be used to simulate the different kinds of food.

The test liquids are:

- Distilled water
- Acetic acid, 2% by weight
- Ethanol, 10% by volume
- Coconut oil, coconut fat or peanut oil

The recommendation to test the migration of toys differs from the methods for consumer goods in contact with food because of differences in usage. Children put toys in their mouth and very often perspire during play. The fastness to saliva and sweat is therefore the main criterion for the migration test of toys. In Germany the test is defined in DIN 53 160 [19], including the test liquids which are a simulation of saliva and sweat.

In the United States the Food and Drug Administration (FDA) enforces also the “nonmigration principle.” There are several regulations that are basically very similar to the German one. The migration test for plastic articles in food contact is described in FDA CFR 21 § 176.170. This regulation consists of several sections. One deals with the classification of food and beverages in nine categories according to their use and type of processing. Other sections define and describe the test procedures, apparatus to be used, time, temperature, and the liquids to simulate the different types of food.

Toys are regulated in “Standard Consumer Safety Specification on Toy Safety – ASTM F 963” and partially in FDA CFR 16 § 1501–1518, “Federal Hazardous Substances Act Regulations.” This regulation deals with hazardous substances, their limits, and restrictions regarding toy safety.

3.3 Shrinkage/Warpage

Any material, including plastics, expands with increasing temperature. The volume of a polymer melt is therefore larger in comparison to the solid state of the polymer and shrinks again during cooling. The degree of thermal expansion during the

manufacture of plastic articles on an injection molding machine depends on type and grade of the polymer. The amount of shrinkage is a very important parameter and must be taken in account during construction of the mold. The data sheets of the different natural colored polymers indicate that the shrinkage of the polymer in the direction of flow is usually larger than in the crossflow direction. Any additive, including colorants, to the original natural colored polymer will influence more or less the shrinkage. This effect becomes very obvious in the case of reinforced plastics. Reinforced plastics show a much smaller shrinkage in both directions and at the same time the shrinkage in each direction is nearly the same.

In the case of partial crystalline polymers, for example, polyethylene (PE) or polypropylene (PP), shrinkage is influenced to a certain extent by the degree of crystallization.

Colorants may affect the shrinkage. The degree of this effect depends on the chemistry of the colorant, type and grade of the polymer, the particle size of the colorant, and pigment concentration.

The amount of shrinkage and the dependency on the different parameters can be measured by using a model plate that is either rectangular or round. The results of such a test are displayed in Fig. 3.2. A rectangular plate with film gate was used, and the concentration of the color preparations applied in different grades of PP was 1.5%. The silvery, orange, and light blue color preparations were actual customer matched colors. The differences in width (dW) and length (dL) of the model plate in comparison to the natural colored PP was evaluated for each color. This test results show the dependence on the grade of polymer, the direction of flow of the melt, and of course on the type of pigment.

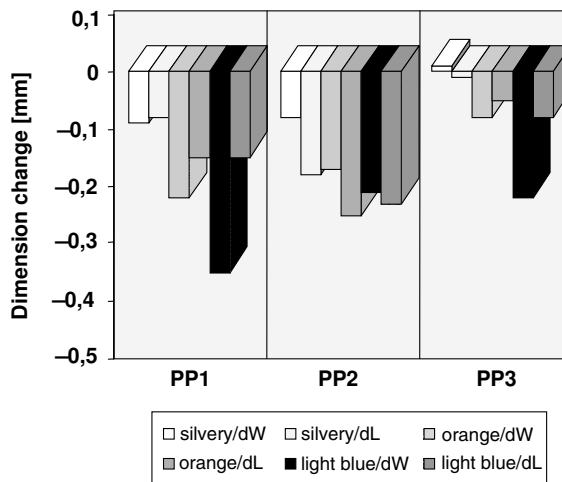


Figure 3.2: Dependence of shrinkage on the grade of PP

Shrinkage and warpage are tightly linked. In case the shrinkage of a partial crystalline polymer such as PE, for example, in the flow direction of the polymer melt is abnormally higher than in the crossflow direction, rotation-symmetric plastic articles become oval; non-rotation-symmetric plastic articles may show a devastating distortion or warpage. Differences in wall thickness of a plastic article are another cause of distortion, because plastics show a very low thermal conductivity. The cooling rate of the thick part is much slower in comparison to that of the thin part. This can be exemplified by large-surfaced, thick-walled, non-rotation-symmetric plastic containers such as bottle crates.

Many organic pigments influence shrinkage because they act as a nucleating agent in a partially crystalline polymer, whereas inorganic pigments do not show this effect. The very fine organic pigments in a polymer melt provide crystallization nuclei that initiate crystal growth. It is not only the crystallization rate that is influenced by the nucleating agent, but also the morphology and thus the mechanical properties of the polymer. The size and shape of the crystallized part of a partially crystalline polymer can be determined by optical methods. The mechanical properties of a partially crystalline polymer depend on its degree of crystallinity. In general, the tensile strength increases with increasing degree of crystallinity, while the tear strength decreases.

Effects on the pigment surface during contact with the polymer melt are likely the reason for the action of organic pigments as nucleating agents. Action as a nucleating agent does not immediately mean warpage. Only uncommon nucleating effects of organic pigments in a partially crystalline polymer lead to warpage. The shape of the pigment particle is a major factor. An acicular particle, for example, is normally oriented along the flow direction of the polymer melt and therefore gives rise to uncommon nucleating effects.

Nucleation is a surface effect, underlined by the following fact. The “normal” Pigment blue 15, for example, is famous for its warpage in PE. If this pigment is coated with a layer of wax, warpage is no longer observed during the coloring of PE, at least as long as the coat is not damaged by shear during processing. Coated grades of Pigment blue 15 (and other pigments) are marketed commercially for coloring of partially crystalline polymers.

In practice the influence of shrinkage by organic colorants plays a large role in all those cases where plastic articles have to be assembled, for example, screw caps, toothed wheels, assembled household ware such as coffee percolators, and so forth. The usual requirement is a very good dimensional stability independent of the color. Considering the wide variety of colors, this requirement cannot be fulfilled for *any* color, and compromises are sometimes unavoidable.

3.4 Toxicology

Every (new) chemical substance that is to be marketed requires not just identification of its (superior) technical, physical, and chemical properties, but also an evaluation of its toxicological properties. Today toxicological and ecological considerations have become a prime concern, and colorants are no exception. The internationally standardized tests evaluating any toxicological risk to human beings and environment are based on situations of daily life. These toxicological tests simulate the risk of a single exposure, repeated exposure, and exposure during pregnancy, and show possible effects on fertility and any possible toxicological risk to our environment.

Consequently the following tests are employed [21, 22]:

- Acute toxicity
- Chronic toxicity
- Mutagenicity
- Embryonic toxicity
- Generation tests
- Ecology

3.4.1 Acute Toxicity

The test for acute toxicity provides information on the effect of a possible short-term, single exposure on human health. Acute toxicity is defined as the toxic effect of a substance after a single oral, dermal, or inhalative application. LD₅₀ indicates the amount of substance expressed in milligrams per kilogram body weight that has a lethal effect on 50% of the test animals. Additional information includes the test animals (mainly rats) and method of application (mainly oral). In the past the exposure limit was 5 000 mg/kg body weight. Today the limit is 2000 mg/kg body weight in the rat by oral administration. This is the consequence of new definitions of acute toxicity, for example, by the European Union regulation 67/548 EU of hazardous substances.

LD ₅₀ , oral, rat	< 25 mg/kg	Very toxic
LD ₅₀ , oral, rat	25 – 200 mg/kg	Toxic
LD ₅₀ , oral, rat	200 – 2000 mg/kg	Hazardous to health

There are numerous publications of toxicological studies of colorants [21]. In no case an acute toxicity below 5000, respectively 2000 mg/kg was found. The risk of harmful toxicological effects of colorants to humans is rather low. In this connection it is certainly interesting to mention that our table salt has a LD₅₀ of 3000 mg/kg (oral, rat).

All these toxicological tests are carried out with the pure substance. Contact with the pure colorant is limited to manufacturing and/or processing. In addition, in plastic articles the colorant is not only very diluted but also bound in a polymer matrix; a customer therefore cannot come into direct contact with the colorant, even if a child swallows a colored plastic toy.

Another means of contact is inhalation of a gaseous or powdery substance. Gaseous substances play no role in coloring of plastics but powdery substances do. Very fine powders generally present a potential risk of harmful effects to health if inhaled. According to the latest publications it seems that every fine powder containing particle fraction of a certain size, a particle of a size that may settle in the lung, is harmful to health. Organic pigments are very finely ground to improve their application. Because of their potential toxicological risk it is recommended that proper safety devices be worn, for instance dust mask, gloves, and so forth, during processing of any powdery substance. The safety data sheets, supplied with every product, contain detailed information for safe handling, type of safety devices, and first aid measures in case of accidental intake.

A consequent avoidance of forming dust is an additional way to reduce any toxicological risk. This is important in another context. The third possibility of an acute toxicological effect is dermal contact, causing an irritation of the skin and/or mucous membrane. These data are also included in the safety data sheets. Although most colorants have not been shown to cause irritation of the skin or mucous membrane, it is advisable to avoid any dermal contact. Powders typically can desiccate the skin and skin in such a condition is susceptible to unrelated diseases.

3.4.2 *Chronic Toxicity*

Chronic toxicity studies involve the repeated application of a test substance to test animals, typically for a period of either 90 days (subchronic toxicity) or 2 years (chronic toxicity). Solid substances are applied by ingestion and gaseous substances by inhalation. A special breed of white mouse is normally used as the test animal; other species of test animals include rats, rabbits, and so forth. The prime objective of such a long-term feeding study is to learn of any chronic effect including the potential risk of causing cancer. Carcinogenicity studies are therefore of cardinal importance. As result of these long-term feeding studies, quite a

large number of chemical substances have to be classified as carcinogenic. A direct transferability to humans is, however, disputed. The large amount of the test substance relative to the body weight of the animal is one argument, because it is not always certain if the chronic effect can be traced back to chemical reactions of the substance in the body of the test animal or if it is just the reaction of the body to the large amount of this anomalous substance in the feed. Others argue this special breed of mouse is too sensitive, because many feeding studies document minor chronic effects in the control group of test animals although their feed is free of the test substance. Another argument is the result of epidemiological studies in companies handling the substances in question. They were all negative, with no sign of an increased risk of cancer.

A typical example for such a discussion are disazodiarylide pigments, which contain dichlorobenzidine as a substituent. Pure dichlorobenzidine is classified as carcinogenic. Long-term feeding studies of those disazodiarylide pigments, however, did not show any chronic toxicity in mice or rats; in addition no dichlorobenzidine or other metabolites could be detected in the urine of the test animals.

3.4.3 Mutagenicity

Many methods are available to test a chemical for mutagenicity. The purpose of these studies is to detect possible effects on the genetic material. Only a very few of these methods have gained a wider recognition. Best known is the Ames test, a bacterial test that is fast and requires only a limited expense. A correlation between the results of the Ames test and mutagenicity of mammals or even with carcinogenic effects remains controversial. Of 24 organic pigments that were Ames tested, only two showed a slightly positive result, and all the rest were negative [21].

3.4.4 Embryonic Toxicity

Another concern is the question of whether a chemical affects the development of an embryo and/or leads to malformations during pregnancy. Feeding studies answer this question. A chemical with a positive result has to be classified as a hazardous substance.

3.4.5 Generation Tests

Generation tests are carried out to answer the question of whether a chemical affects reproduction and/or fertility. Here, too, a chemical with a positive result has to be classified as a hazardous substance.

3.4.6 Ecology

Ecological considerations gained worldwide recognition as the protection of our environment became a major concern during the last several years. The test methods vary according to the different ways a substance may be released into our environment. Gaseous substances are checked, for example, for effects on the ozone layer. Solid substances will be tested for a possible toxicity to algae, bacteria, and fish. The test methods are standardized worldwide, including the species of algae, bacteria, and fish to be used as test specimens. The test results, respectively classification, are part of any safety data sheet.

In nearly every country there are specific regulations for transportation and disposal of waste, based on the classification.

Colorants for plastics are practically insoluble in water and largely biologically inert. The danger of contamination of water with colorants may be avoided with measures such as filtration, sedimentation, or adsorption. Pollution of waste water can be practically avoided.

Completely different is the situation for all the other components of a color preparation such as antistatic agents, plasticizers, stabilizers, flame retardants, and so forth. Several of these are classified as hazardous to the environment; therefore specific measurements are necessary during processing to avoid any pollution of the environment.

In this context it should be mentioned that a substance “completely harmless as a result of all toxicological studies” nevertheless can be very hazardous to our environment. Prime examples are certain types of fluorinated hydrocarbons that are classified as “ozone destroyers;” consequently their use is banned worldwide.

3.5 Thermal Stability

All manufacturers of plastic materials provide customers with detailed information regarding the properties and recommendations for processing of their different types and grades of plastics. The processing temperature depends on the type and grade of plastics and can vary considerably because of the chemistry of the plastic type and covers a range of 160–200 °C (320–392 °F) for PVC up to approximately 320 °C (608 °F) for polysulfone (PSU). At the same time the processing temperature represents the temperature a colorant has to resist to be applicable to this special type of plastic. In practice it would make no sense to ask for a heat stability of 320 °C (608 °F) for all colorants. Only a very few organic colorants could fulfill this stringent requirement.

Manufacturers of colorants follow another path. They check the application of each colorant in the different types of plastics. Their recommendations for the use of a colorant in different types of plastics are based on those test results.

The thermal stability, also denoted as heat stability, of a colorant depends on:

- The chemistry of the colorant
- The crystal structure, respectively crystal modification of pigments
- The effective concentration of the colorant in the plastic material
- The type and grade of plastics to be colored
- The processing parameter, for example, residence time, use of a hot runner, and so forth
- Additives present, for example, filler, stabilizer, flame retardant, and so forth

The thermal stability is – like many others – a system-related parameter that cannot be determined in connection with a pure pigment only.

The necessity to standardize the test methods resulted from the manifold dependencies. Only then is the colorist able to compare several colorants and to choose the right one for the project he works on.

The standardized test methods vary from country to country only in detail. Most of the European manufacturers of colorants follow by agreement more or less the German standard method DIN 53 772 [20].

All test parameters are defined and described in DIN 53 772. A standard type and grade of plastic is used. The concentration of the colorant is according to 1/3 respectively 1/25 standard depth of shade in pure tone as well as in white reduction (1% titanium dioxide). The result would be a series of four tests. The test starts at the lowest possible processing temperature of the standard plastic material and is increased step by step. At each step there is an increase of 20 °C (68 °F). The residence time is always 5 minutes. Each time a test specimen is injection molded and it is inspected not only visually but also by a colorimetric measurement for a change in color. The measurement data are recorded in a graph. By definition the temperature that gives a difference in color of $dE^* = 3$, is the heat stability of the tested colorant in the type of standard plastic applied.

The increase of the processing temperature step by step leads in the case of a thermostable organic colorant to a temperature near which the plastic itself shows signs of discoloration. This discoloration can and must be taken in consideration while fixing the limit of thermal stability.

Most inorganic pigments are reaction products of high-temperature calcination, for example, between 700 and 900 °C (1292 and 1652 °F). The thermal stability

of calcined inorganic pigments is far beyond the thermal stability of every plastic material and any determination of the thermal stability by a strict application of the standardized test method would give unrealistic data.

In Fig. 3.3 the procedure of fixing the limit of thermal stability is shown schematically, and this imaginary colorant would have a thermal stability of 260 °C (500 °F).

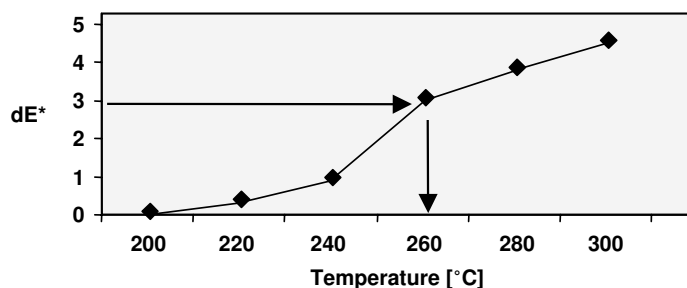


Figure 3.3: Schematic presentation of fixing the thermal stability

Each temperature reading is round off to the nearest 10°. In theory the results of the four tests are four temperatures. Manufacturers of colorants, however, list in their data sheets of colorants just two temperatures, the thermal stability in the pure tone and in the white reduction.

In the standardized test methods for thermal stability the concentration of the pigment in the plastic material is defined and fixed; however, in practice the effective concentration of a colorant in a plastic article is quite different from the standard depth of the shade. Besides the heat stability depends on the effective concentration of the colorant in plastics. It is well known that the thermal stability of an organic pigment decreases with decreasing concentration, but there is no general rule on how much. This is the reason why several manufacturers of colorants supply data based on a gradation of concentration. The gradation is either 1%, 0.1%, 0.01% and 0.001% or 1.0%, 0.1%, 0.05%, 0.025% and 0.01% in the pure tone and the white reduction. The tests are carried out in reference to the standardized test method. The test results, supplied as a graph, show in an impressive manner the dependence of the thermal stability on the actual concentration. These data are very important for the daily work of a colorist. A very low concentration of a colorant is not only required for pastel color shades but also when it is necessary to match a special nuance in the shade. Pigments can be used for such applications when they show no or just a minor decrease of thermal stability with decreasing concentration.

In reality, all these supplied data are solely a guideline because the grade of plastic material to be colored is normally different from the standard type of polymer used in the test, and the composition of an actual color preparation is much more complicated than that of a test system containing only plastic and colorant. A color preparation may contain in addition filler, plasticizer, dispersing agent, antioxidant, stabilizer, and flame retardant. Chemically all these components are not inert; each of them can influence the thermal stability of the colorant and polymer.

Any discoloration of an organic substance is in fact a function of temperature multiplied by the residence time. In the standard test method the residence time is fixed at 5 minutes, a time that is much longer than the processing time of plastics under normal circumstances. Consequently experience shows that an organic colorant can be processed at a slightly higher temperature than indicated in the data sheets for the thermal stability, provided that the residence time is very short.

In this context, for example, it is important that the size of the injection molding machine corresponds to the size and weight of the plastic article to be manufactured, in which case an economic production is possible. This assumption is usually fulfilled but not always, especially in the case of tiny articles. For technical reasons the size of a plastic processing machine cannot be reduced indefinitely. For the molding of very tiny plastic articles, it is therefore unavoidable to use a machine that is really too big in comparison to the size of the parts. In such a case the residence time of the colored polymer melt in the injection molding machine may be well above 5 minutes with the consequence that discoloration and degradation of the plastic material and/or organic colorant start at a lower temperature than indicated in the data sheets.

Another reason for discoloration can be the use of a hot runner. The residence time in the hot runner must be added to the time in the injection molding machine. The resulting residence time is usually short enough to avoid any discoloration. However, a careful consideration of this parameter is recommended. Unfavorable features in the construction of a hot runner such as too small dimension of the hot runner nozzle or other parts of the hot runner are the main reason for discoloration. Today every machine is powerful enough to push the melt through every hot runner that is too small in some dimension. The resulting frictional heat cannot be calculated or controlled and is normally high enough to begin to cause thermal damage of the organic colorant and/or plastic material.

Thermal damage of organic colorants is possible not only during the manufacture of plastic articles but also during the production of a granulated color preparation, a so-called masterbatch. Prime examples are the daylight fluorescent pigments. Within the scope of quality assurance any thermal damage is detectable and precaution measures can be arranged.

The thermal stability of organic colorants depends on type and grade of the polymer. The extent of dependence is demonstrated by means of Pigment red 149, a perylene pigment. Its chemical formula is shown in Fig. 3.4.

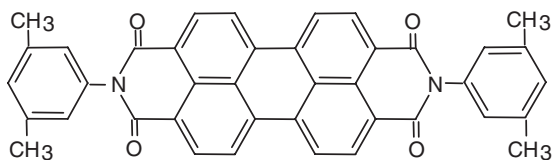


Figure 3.4: Chemical formula of Pigment red 149

The thermal stability of Pigment red 149 in different polymers is listed in Table 3.1.

Table 3.1: Thermal Stability of Pigment red 149 in Different Polymers

Polymer	Thermal stability	
	(°C)	(°F)
Polycarbonate (PC)	310	590
Polyolefins (POs)	300	572
Polystyrene (PS)/ Poly(methyl methacrylate) (PMMA)/ Polyethylene terephthalate (PET)	280	536
Acrylonitrile-butadiene- styrene (ABS)	250	482

3.6 Light Fastness/Weather Resistance

The light fastness of a material is defined by the ability of a given pigment – polymer system to retain its initial color values on exposure to daylight. It is consequently a system-related parameter.

Weather resistance is defined as the simultaneous or alternating effect of irradiation with daylight and atmospheric impacts such as humidity (rain), atmospheric oxygen, and industrial exhaust.

In simple terms, weather resistance is light fastness plus humidity, because humidity is usually the most important atmospheric parameter.

In no other field of coloring of plastics is the question of interpretation of test results more often up for discussion between customer and supplier of the color preparation. This is partly due to requirements of the customer that cannot always be completely fulfilled. On the other hand, in no field of coloring of plastics does such a large discrepancy between theory and practice exist. One of the main reasons is the dependence of light fastness and weather resistance on the actual climate of the place where the plastic article is presumably to be used. The climate varies considerably from region to region. In the far north, in Alaska for example, there is a rather moderate summertime and very cold winter, in the far south, for example, in Arizona, it is very dry and very hot, while in the southeast it is very humid and hot.

Except a few inorganic pigments, all other colorants change their shade more or less readily upon irradiation. A combined influence of light and weather (humidity) will generally damage an organic colorant and polymer much faster than light alone. The adverse effect of humidity is well known in chemistry and may be demonstrated with an everyday example. A paint or lacquer for wood can be stored in a tightly sealed container for quite a while. After application to wood the paint will cure within a short while because of the humidity in the air.

Several organic colorants show good light fastness but insufficient weather resistance. Their use is then limited to the wide field of indoor applications. The data sheet of colorants contains detailed information regarding light fastness/ weather resistance.

Two methods are applied to determine light fastness/weather resistance:

- Natural irradiation with and without humidity on outdoor experimental stations
- Artificial irradiation with and without humidity in the laboratory

The test stations for weathering, for example in Florida, Arizona, and in Bandol (South of France) are well known. A series of experiments in each location proved that the results are not strictly comparable but the tendency of fastness is the same everywhere. This is not surprising when we consider the differences in the climatic conditions of each experimental station. In Florida it is very humid and hot, in Arizona it is very dry and very hot, whereas in Bandol, at moderate humidity and temperature, the impact of atmospheric components due to nearby industrial exhaust plays a major part.

Tests done under natural climatic conditions require a long period of time. No customer, however, is willing to wait so long. Consequently methods were developed to determine the light fastness in the laboratory under artificial and accelerated

conditions. The basis of any accelerated test is an adequate simulation of the different climatic conditions in the test apparatus and in addition a sufficient correlation between both test principles.

For the sake of comparison the test methods had to be standardized. The World-wide Federation of National Standard Institutes published the method *ISO 4892 – Plastics – Methods of exposure to laboratory light sources*, and the Germany institute published *DIN 53378 – Künstliches Bewittern oder Bestrahlen in Geräten – Beanspruchung durch gefilterte Xenonbogenstrahlung* [3]. In other countries similar standards are applied.

At first glance all the different standards may appear confusing, but on a closer look it can be noticed that all are basically the same, differing only in detail.

The test conditions are well defined each time. The main parameters are the intensity and length of irradiation, the source of light, size and shape of the test specimen, the temperature of the specimen, kind and duration of wetting, and of course the evaluation techniques [9, 10]. According to the literature the kind and duration of wetting is of special importance for test results of weather resistance.

The blue scale, also known as blue wool scale, was originally developed for the evaluation of colored textiles exposed to light. It consists of eight blue colored woolen samples, which differ in their fastness to light. These standardized woolen samples are prepared with chemically defined blue dyes. Number 1 indicates the lowest and number 8 the highest degree of fastness. The fastness of each blue dye is graduated in such a manner that the time required for a significant change in color doubles from step to step. If testing the light fastness the colored plastic specimen and these samples are together exposed to light until the standard shows a significant change in color. The change may be in the shade, the brightness, and/or intensity of color. A color change is considered to be significant when it equals step 3 or 4 on the gray scale for evaluation of color change. The gray scale consists of five steps, with 1 the lowest and 5 the highest value and is defined, for example, in the German standards DIN 54001 [4].

Extremely light-fast materials, which correspond to step 7 or 8 on the blue scale, can show some uncommon effects because the woolen sample – the textile carrier – cotton by definition, may not be sufficiently stable in comparison to the plastic material of the test specimen; in addition in this range of fastness it is difficult to determine accurately differences in color.

It is probably not by chance that the standard ISO 4892 recognizes only seven steps on the blue scale. At stage 7/1 the first blue standard will be discarded and replaced by a fresh sample (stage 7/2) when the blue standard shows a contrast equal to step 4 on the gray scale under the condition that the colored plastic

specimen does not yet show a visible color change. This procedure is repeated as often as required (stage 7/n).

In the past there were several attempts to develop a new standard based on physical methods, but all of them failed. One of the main reasons may be the fact that over decades manufacturers of colorants accumulated a very extensive archive of data, which in case of a radical change of evaluation would become more or less worthless.

For the daily work of a colorist the blue scale is not so important in comparison to the manufacturer of colorants. The question a colorist has to answer usually is how the light fastness of his sample compares with the competitor's sample and/or how much of which stabilizer is necessary to improve the light fastness to the level of the competitor. As the work involves the comparison of samples, physical methods, for example, the use of a spectrophotometer can be applied to evaluate the test specimen. In contrast to this, the colorant manufacturer's data have an absolute value.

Light fastness/weather resistance depends on:

- Chemistry of the colorant
- Crystal modification (organic pigments)
- Concentration of the colorant (organic colorants)
- Type and grade of the polymer
- Additives such as filler, stabilizer, flame retardant, and so forth
- Processing parameter
- Intensity and duration of irradiation
- Temperature impact during use of the plastic article
- Atmospheric conditions of the surroundings

When considering all these factors it is obvious that the light fastness data are valid only for the tested system in combination with the test conditions, and are no statement of universal validity. This is just as true with respect to the colorant manufacturer's data, but nevertheless these supplied data are very important hints for the colorist.

3.6.1 *Chemistry of the Colorant*

Generally speaking, many properties of a substance depend on its chemistry, and colorants are no exception. This includes possible positive or negative effects of crystal modification. Differences in light fastness according to crystal modification are well known, for example, titanium dioxide and the blue phthalocyanine pigments.

The light fastness/weather resistance of the majority of *inorganic pigments* is excellent. In the case of the widely used titanium dioxide the light fastness depends on its crystal modification, the rutile modification shows much better light fastness properties in comparison to the anatase modification. In addition to this white pigment there are no limitations of applications of inorganic pigments attributable to insufficient light fastness. In contrast with the inorganic pigments, all organic colorants, not only organic pigments but also organic dyes, exhibit a strong dependence on chemical structure. Consequently limitations of their use are quite common when good light fastness properties are required.

The variation of light fastness of chemically different colorants is shown in Fig. 3.5. For these standard tests PE was colored with different organic pigments at a concentration of 0.05 % in pure tone [5].

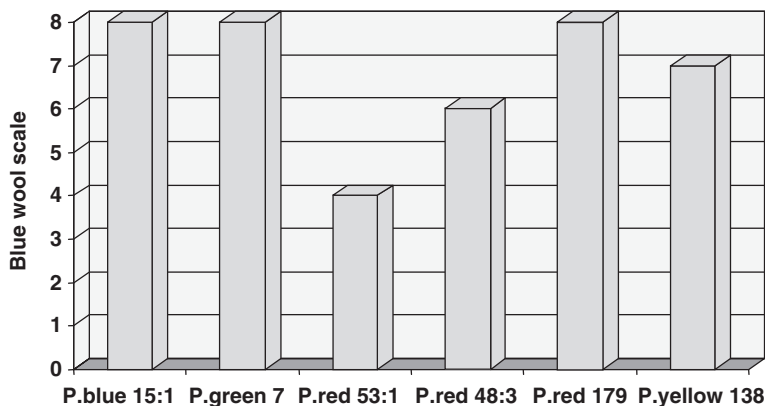


Figure 3.5: Dependence of light fastness on the chemical structure of different organic pigments

The catalog of requirements for any new color preparation contains, besides others, statements of the customer regarding the wanted and/or expected light fastness. The task of the colorist is not only to match the color exactly but also to choose the right colorants to fulfill all other requirements. The data supplied by each manufacturer of colorants are very helpful in this context.

3.6.2 Concentration of the Colorant

The dependence of light fastness on the concentration of a colorant is rather straightforward. In case of a high concentration it is visually not very obvious

when single molecules of a large number are damaged or uncolored by the impact of light. At low concentrations, however, the damage of each single molecule is much more noticeable relative to the small number of total molecules.

Manufacturers of colorants supply detailed data regarding the light fastness of organic colorants at different concentrations in standard plastics. All these data indicate a decrease of light fastness with decreasing concentration. The organic colorants are differentiated with respect to the concentration at which the decrease starts and how pronounced the decrease is. When the decrease starts at a very low concentration the colorant can be used for nonfading pastel shades and/or to match a special nuance in the shade.

In many cases the customer requires a color preparation with a good hiding power to avoid any visibility of the underlying layer of the top part or the content of a package. Titanium dioxide is the pigment of choice for this purpose. Such a color preparation consists of titanium dioxide as opacifier and a colorant. The need of colorant is then relatively high because the white of the titanium dioxide first must be covered before the color matching can take place.

As described in the standard test methods, the light fastness of a colorant is determined not only in pure tone but also in white reduction. It is rather common that the light fastness differs corresponding to both kinds of coloring. The difference is sometimes considerable; the dependence of light fastness on the concentration may vary as well. In white reduction the decrease of light fastness starts quite often at a higher concentration in comparison to the pure tone. The reasons are not quite clear. It is a matter for discussion if this is the consequence of adverse affects of the titanium dioxide or just a visual effect. In white reduction a damaged single molecule of colorant can no longer contribute to the color and at the same moment the brightening effect of the titanium dioxide increases. The answer to this question is of no importance for the daily work of a colorist, but merely of scientific interest.

The Pigment red 48:2 was chosen to demonstrate the difference of fastness properties between a coloring in pure tone and in white reduction (Fig. 3.6). The light fastness of a coloration in pure tone with Pigment red 48:2 is independent of the concentration within the wide range of 0.05–0.2% pigment and in addition a light fastness of 7 on the blue scale would be sufficient for many plastic articles of indoor use. On the other hand a coloration in white reduction shows a strong dependence of light fastness on the concentration and degree of white reduction [5]. The low light fastness would allow only applications without any special requirements regarding light fastness.

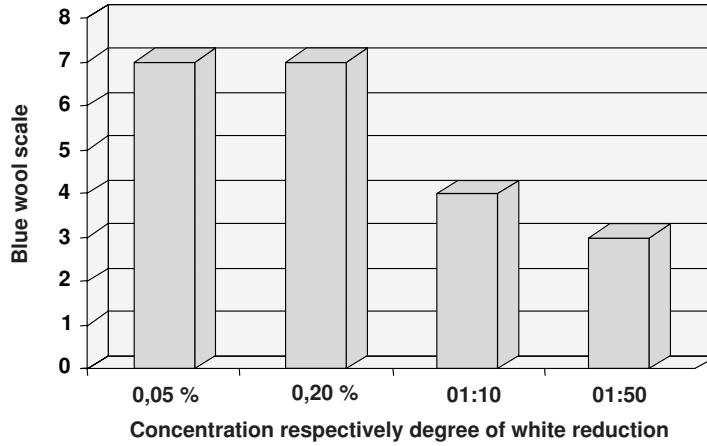


Figure 3.6: The light fastness depends on the concentration and degree of white reduction. Pigment red 48:2, polymer PE, pigment concentration in pure tone 0.05% and 0.2%, in white reduction 1:10, respectively 1:50

The weather resistance of this pigment is too low to allow any outdoor application (Fig. 3.7). From a scientific point of view it is interesting that the weather resistance of a coloration in pure tone, contrary to the light fastness, depends at least at early stages of weathering on the concentration of the pigment [5].

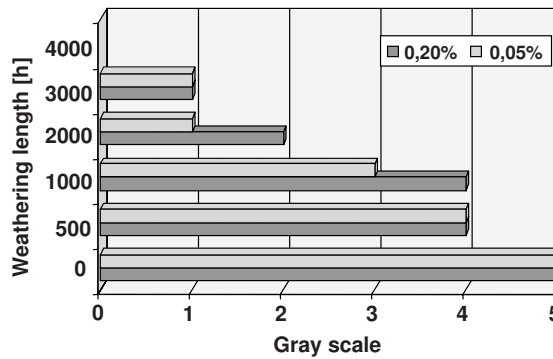


Figure 3.7: Dependence of weather resistance on the pigment concentration and length of weathering. Pigment red 48:2, polymer PE, concentration 0.2 respectively 0.05%

3.6.3 *Type and Grade of Polymer*

Fastness properties are always related to the whole system. Polymers used as matrices for colorants differ in the chemistry of their monomers, method of production, and in the presence of additives. The consequence of this variety is a large number of different types and grades of plastics with concrete differences in their properties, including light fastness/weather resistance.

To start any photochemical reaction in a polymer chain several conditions must be fulfilled, the most important ones are [11–13]:

- Absorption of energy
- Conversion of a reactive group in the polymer in a stimulated stage
- Start of the reaction before the absorbed energy is released again

Because of the filtering effects of the atmosphere the highest energy radiation, reaching the surface of the earth, has a wavelength of 290 nm. The energy of this UV radiation is in the range of the bonding energy of the different atoms in a polymer chain such as C-H, C-C, C-N, and so forth, but this radiation is not absorbed by the polymers. The wavelength of maximum absorption by polymers lies in a range that is filtered completely by the atmosphere and therefore does not reach the surface of the earth. Without absorption no light-induced degradation of polymers should occur but in reality polymers suffer from it. At a first glance this seems to be a contradiction between theory and practice. Numerous tests proved there is no discrepancy between both. The two polymers polyethylene (PE) and poly(methyl methacrylate) (PMMA) functioned as test models. They were polymerized in the laboratory at well controlled conditions; the results were very pure grades of both polymers.

Corresponding to theoretical prediction, these pure grades of PE and PMMA did not show a light-induced degradation. Analytical investigations of technical grades of the same polymers proved the presence of defects such as double bonds, leftovers of the catalysts, chain scissions, and others. These flaws absorb energy, and at the same time they are the real reason for light-induced damages. In spite of all efforts of polymer manufacturers a certain number of defects are unavoidable in the technical grades of their polymers. The production methods vary considerably between the single manufacturer and this is the explanation for differences in light fastness between single grades of the same type of polymer supplied by different manufacturers.

The very common Pigment yellow 180, a benzimidazolone pigment, can be used as an example to demonstrate the dependence of light fastness on the type of polymer (Table 3.2) [6].

Table 3.2: *Dependence of Light Fastness on the Type of Polymer. Pigment Yellow 180, Concentration 1/3 Standard Depth of Shade in Pure Tone, Respectively 0.1%, in White Reduction 1/3 Standard Depth of Shade with Titanium Dioxide Respectively 0.1% + 1% Titanium Dioxide*

Type of polymer	Light fastness pure tone/white reduction
PA-6	7–8/6
PC	5–6/5–6
PET	6–7/7–8
PMMA	5–6/3–4
Polyolefins (POs)	6–7/6–7
PS, ABS	6–7/6–7
PVC	6–7/6–7

3.6.4 Additives

Additives are quite commonly present in plastic materials. Their function is the improvement of properties. Which property should be improved depends on the requirements a plastic article has to fulfill. Substances can be added in one of two ways: either as components of the color preparation or previously incorporated in the polymer by the manufacturer.

The most important additives are:

- Antistatic agents
- Flame retardant
- Filler
- Dispersing agents / lubricant / release agent
- Nucleating agent
- Stabilizer
- Blowing agent
- Plasticizer

All these additives are chemically not inert and interactions with colorants cannot be excluded. The interaction can be either positive or negative and any prediction

is impossible. Stabilizers show by nature a positive effect on the light fastness/ weather resistance of the plastic article. Plasticizers may enhance migration and nucleating agents influence shrinkage. If because of customer requirements the addition of additives becomes necessary it is recommended to check the fastness and other properties of the whole system consisting of polymer, colorant, and additive to avoid any surprises caused by unexpected interactions.

3.6.5 Processing Parameters

Processing parameters are another important feature to be taken into consideration of possible adverse effects on light fastness. Cycle times lately have been shortened because of economic considerations. The presupposition for such a step was a distinct increase of the processing temperature and the use of a hot runner. At the same time the residence time declined. An increase of the processing temperature may lead to a predamage of the colorant, which is not detectable by quality assurance methods but may affect light fastness. When the customer requires a definite statement regarding light fastness it is necessary to run those tests with specimens manufactured on the production machine and the later processing parameter. The colored plastic plaques of a laboratory extruder, used for color matching, are not suited for such a purpose. For a number of technical reasons, the actual processing parameters of a production machine cannot be simulated on a laboratory machine.

3.6.6 Intensity of Irradiation

We know from our own experience that the tanning of our skin depends on the intensity of the sun's rays. This observation is transferable without any restriction to light fastness, there too the intensity of irradiation is a very important parameter in all standard test methods for light fastness. In method ISO 4892 as well as in the German standard DIN 53387 it is stated that the intensity of irradiation is a point of discussion between supplier and customer and should be chosen in such a manner that the intensity of irradiation corresponds to the solar radiation of the region of intended use of the plastic article.

For decades the solar radiation has been recorded by meteorological stations worldwide. The measured sun intensity of each day is averaged to a mean value for the month and further on to a mean value for the year [14]. These data are known as global radiation.

The global radiation is not a constant value, but is variable according to the daily change of the position of the sun, the geographic position of the location, and

other climatic factors such as clouds or fog. The daily variations will be leveled more and more the longer the recorded period is.

In the Northern hemisphere the months with the highest global radiation are June and July, the minimum occurs during December and January. In the Southern hemisphere it is just opposite.

In the so-called climate atlas all locations with the same global radiation are linked up. When you know the region of the intended use of the plastic article, the intensity of irradiation, to be used in the test of light fastness, should correspond to the value of the global radiation for this area. A certain complication can arise when the same article will be used in regions with quite different global radiation. In such a case it may be more economic to have two articles with different stabilizations instead of one for the most stringent condition.

Every test of light fastness ends in a result of step n on the blue scale. In case of accelerated laboratory tests the question at once arises as to what this result means for the practice. A definite answer in the sense of a guarantee is unfortunately impossible. This explicit statement is made in several standard test methods, for example, in the German standard DIN 53 387 in paragraph 1 *“Range of application and purpose: An general valid correlation between an accelerated laboratory test and natural strain cannot be expected because of the versatility of parameters ...”*

The above mentioned question can be answered therefore only in the following way: “It can be expected that...”

The main reasons for such an indefinite answer become apparent considering some parameters of the test in detail.

- From our own experience we know that the climate can change considerably every year, and a long-term weather forecast is impossible. In a hot summer with very intensive sunshine the natural stress of the plastic article is much higher than during a summer with many clouds and rainy periods.
- The intensity of irradiation for the light fastness test is based on the median of global radiation for the region in question. A large variation of the global radiation on a monthly basis may demonstrate the meteorological data of the German city Hamburg. The records cover a range of 40 years. The global radiation for the months June/July was in the hottest, most sunny summer more than 10 times higher than in the coolest, very cloudy and rainy summer. The monthly global radiation of the hottest summer was twice the amount of the 40-year median [14].
- Environmental factors, for example, pollution of the atmosphere by industrial exhausts, can cause abnormal effects.

3.6.7 *Temperature of the Environment*

The parameter temperature is of importance for any aging process, and plastic articles are no exception. The aging of plastic articles during their use is a chemical reaction. In chemistry a general rule of thumb postulates that an increase of a temperature by 10° accelerate a chemical reaction by a factor of 2. At the same time every increase of temperature speeds up the rate of diffusion of oxygen, humidity, and other gaseous components of the environment into the plastic material. All these components are responsible for an oxidative degradation of the plastic material.

The temperature of a surface area depends not only on the temperature of the surroundings and/or the temperature of use but also on the color. The last point is a consequence of the process leading to color. When light falls on an object some part of it will be absorbed and another part will be reflected. The absorbed part of light is converted to heat, and is practically "lost." The reflected part of light will hit our eyes and according to its wavelength we see a color. Light colors reflect much larger fractions of the incident light than dark ones; therefore the temperature of a light colored object is lower in comparison to a dark colored one. It is not by chance that we prefer light-colored garments in the summertime.

3.6.8 *Environmental Factors*

Our atmosphere is no longer made up of pure air but is polluted with industrial exhausts and exhaust gases of cars. The main pollutants are nitric oxides (NO_x), sulfuric oxide (SO_2), and ozone (O_3). All these substances can accelerate a light-induced aging of any plastic material as proven by several series of tests [15, 16]. During irradiation of the test specimen the air in the apparatus was purposely polluted by these substances at precisely defined concentrations. The magnitude of the observed interactions depends on their concentration in the air and the sensitivity of the chemically different types of plastic materials and colorants to this kind of substance.

4 Composition of Color Preparations

A color preparation is composed of plastics as carriers, colorants, and additives. Additives can be incorporated into plastics in two different ways. One possibility is to incorporate the additive in the color preparation, which is preferred when the required concentration of the additive is relatively low in the final part. If a high concentration is necessary the additive must be added directly at the plastics manufacturer's plant; examples are fillers and flame retardants. The concentration of filler can reach 60%.

4.1 Color as a Design Element

4.1.1 *The Basis of Color Sensation*

Any book about colors would be incomplete without a description of at least the essential features of the process of seeing, especially seeing colors.

Daylight, both natural and artificial, belongs to the wide range of electromagnetic waves such as radio waves, infrared, ultraviolet, and X-rays. Physically they are all the same, differing solely in their wavelength and frequency. From this wide spectrum of wavelengths only the very small fraction between 400 and 780 nm is visible.

Visible, white sunlight (Fig. 4.1) consists of a mixture of the colors red up to violet. When sunlight falls on an object, some of it is absorbed and some is reflected. The absorbed part is transformed to heat and practically speaking is "lost" for the sensation of color. After passing through the pupil and lens, the reflected part of the light impinges on the retina, where an image of the object is formed. The retina contains two different types of cells, the so-called rods and cones. The rods are not sensitive to colors; they only allow a differentiation between light and dark, important for seeing at twilight or dawn. The cones, however, are sensitive to colors. There are three different types of cones, which differ in their maximum spectral sensibility for the colors green, blue, and red-orange. In this context it should be mentioned that all methods of colorimetric measurement are based on these three colors plus a light-dark differentiation.

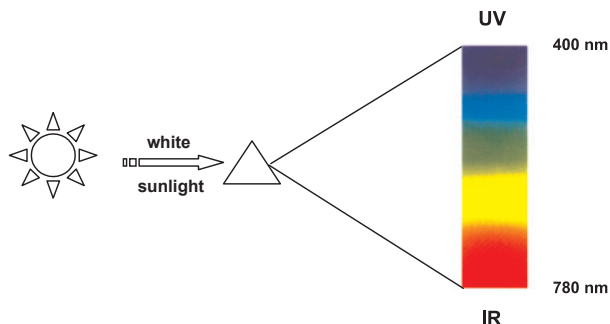


Figure 4.1: *Colors of the solar spectrum*

The reflected part of sunlight is just a fraction of the whole spectrum, and corresponding to the wavelength of the reflected light we see a definite color.

An ideal white object reflects 100% of the light, in practice however we notice a “white with a light tint,” very often a bluish or yellowish tint.

An ideal black object absorbs 100% of the light, consequently no light is reflected and therefore the object appears black.

Analogous with our other senses such as hearing or tasting, color vision differs from person to person, sometimes very distinctly. The most serious deficiency of color vision is color-blindness. Statistically more men than women suffer from some type of a defect in color vision, with a reduced ability to distinguish between red and green being among the most common of these. The capability to perceive colors is very closely related to individual differences in the sensitivity of the eyes. This important fact is sometimes the reason for long discussions between supplier and customer if the presented plastic specimen of a matched color is inspected only visually. Another matter for discussion is the question of accuracy of a produced color preparation. This discussion can take place not only with the customer but also in the supplier’s own plant within the scope of quality assurance. Because of this “personal factor” it is recommended that the same person is always involved in the visual check of color.

The necessity of an objective method was very obvious. The development led to different colorimetric systems. The system used most often is the CIE-LAB system; others are the Munsell, respectively ISCC-NBS systems. All of them have the disadvantage that they are not able to describe in a *perfect* manner what we see, therefore all these systems cannot replace completely visual judgment, but they are very valuable tools nonetheless.

A very extensive literature is available dealing with all aspects of colorimetry; the measurement of colors, therefore it is done without a detailed description in this context [1, 2].

4.1.2 Metamerism

Nearly every customer specifies in his requirements that the color to be matched should show no signs of metamerism. This phenomenon can be noticed nearly daily, but we are unaware of its physical background. It is not by chance that we go to a window in a department store with artificial lighting when we are about to buy clothing or accessories to check if the colors of the different pieces match. Slight differences in their shades are not infrequent.

We speak of metamerism when two colored objects show the same color in sunlight but a slight difference in shade in artificial light (or vice versa) (Fig. 4.2).

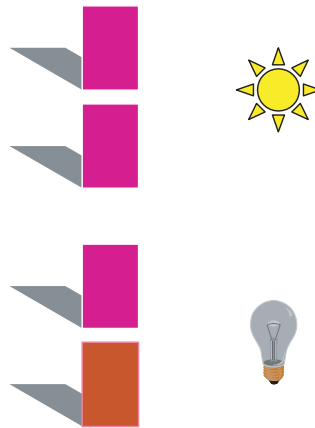


Figure 4.2: Schematic demonstration of metamerism

The origin of metamerism lies in the physical process of generating colors. The color of an object is the sum of several, simultaneously used colorants. The interrelation of reflection and absorption is specific for each single colorant and depends on the wavelengths of the source of light. On the other hand every source of light exhibits its own specific spectrum of wavelengths. Detailed measurements of sunlight and artificial sources of light proved quite significant differences not only in the spectra of wavelengths but also in their intensities. These differences are responsible for the phenomenon of metamerism.

Metamerism is a serious problem, and avoiding metamerism is usually a very important goal in color matching. In practice the colorist can only minimize metamerism but cannot avoid it totally. Colorists of different companies quite often will use at least partly other colorants to match the same color. Only an absolutely identical selection of colorants for both samples of the matched color would prevent any metamerism.

Nearly all spectrophotometers allow measurements with different standardized sources of light. By means of this tool the spectral-reflectance curves of the specimen in question can be recorded for every source of light. Usually both curves are not identical but will show distinct variations. The variation, a criterion of metamerism, can be minimized by exchanging one or more colorants.

4.1.3 Use of Colors

Although seeing colored objects is a pleasant sensation, colors are used for more than this, as they must fulfill specific tasks. One function that immediately comes to mind, is the application of color to all objects in our lives, while other functions of color are not so obvious. The most important tasks are to use color as an:

- Element of design
- Element of marking
- Element of protection

The majority of colors are used undoubtedly as *elements of design*. An object can be modeled in a perfect way, and can be very functional, but if it has the “wrong” color we are not pleased with it. On the other hand an object not so perfectly modeled will please us when it has the “right” color.

Another, but less obvious, use of colors is as an *element of marking*. Several industries, such as electrical engineering and car manufacturing, to name just two, apply colored articles to prevent mistakes. Every single electrical cable is isolated and specifically color-linked to its function, with the colors to be used standardized more or less worldwide. The purpose of this marking is to avoid dangerous short circuits. In the car industry the colored cables should indicate the different electrical circuits typically used in a car.

The third application of colors, no less important than the others, is as an *element of protection*. We notice these types of colored objects nearly daily, as they warn us of dangerous situations, for example, driving through construction sites on a highway or marking of emergency exits.

In nature, too, colors are important in many respects. Two examples alone demonstrate this. The bright colors of flowers attract bees and insects to ensure

pollination and ultimately reproduction. Animals typically adapt to the colors of the environment through camouflage as protection from their natural enemies. Some species of frogs living in the Brazilian tropical rain forest have an unusual and striking bright coloring that signals to their natural enemies, “careful, we are poisonous.”

4.2 Types of Color Preparations

There are three states of aggregation – gaseous, liquid, and solid. Gaseous colorants are not known; consequently either a liquid or a solid color preparation can be chosen for the coloring of plastics. There are two possibilities for a solid color preparation, either a powdery or a granulated form, the latter known as a masterbatch.

Each type of preparation shows typical properties according to the state of aggregation, and this should be considered carefully during the process of coloring. Lack of careful observation may result in production of defective plastic articles. This is explained in detail in Chapter 7, *Processing Errors*.

To color *thermoplastic resins* fundamentally all three types of preparation can be used, although many customers prefer a masterbatch, the granulated form. The other two forms, liquid and powdery color preparations, are used occasionally by customers specializing in these types.

For *thermosets* only the liquid or powder form is applicable. A thermoset consists usually of two liquid components, a reactive and a hardening component. After blending and curing a cross-linked product is formed, which cannot be manipulated later by thermoplastic methods. This is the reason why one of the two components has to be colored before the cure. In practice the hardener is usually colored, because it is fairly inert. Liquid preparations are preferred because of easier blending and handling; in addition, the binder of a liquid color preparation may function as a hardener, for example, in epoxy resins.

The cure of liquid lacquers depends on whether system is a multi-component or a single-component type. A single-component lacquer hardens by absorption of humidity. Two types are marketed: either the whole system is already colored or a liquid color preparation is added prior to application. Which system is used finally depends on several conditions, one of the most important being the chemical structure of the lacquer components. In both cases the color preparation must be completely free of water to avoid a premature cure (single-component systems) or a cure that is too fast (during blending of the lacquer with the color preparation).

The speed of cure of thermosets or lacquers can be changed considerably by colorants, because colorants are not necessarily chemically inert. They can accelerate or slow down the cure; therefore the right choice of colorant is very important. Another possibility is to alter slightly the composition of the thermoset or lacquer, but this method is not always successful. In the worst case the desired color shade must be altered.

For the coloring of *elastomers* quite analogous statements are valid, here, too, the color must be added before the cure, consequently only a liquid or powdery formulation can be applied.

4.2.1 Granulated Color Preparations/Masterbatch

A masterbatch is today the most preferred type of preparation, well documented by the large volume of sales.

A masterbatch consists of:

- Polymer as carrier
- Colorants
- Dispersing agent
- If necessary, additives such as stabilizers, nucleating agents, antistatic agents, lubricants, and so forth

The concentration of the components varies corresponding with the desired intensity of color and/or hiding power. Very intensive colors with a good hiding power require a high concentration, which very often lies in the range of 50% colorant, 40–45% polymer, and 5–10% dispersing agent. When the presence of an additive is required in a color preparation, there is no other way than to reduce the concentration of the colorants. The consequence of this is a higher addition of the preparation during the coloring of the polymer. On the other hand a wide range of additive preparations are commercially available. In such a case whether to incorporate the additive in the color preparation or apply two separate preparations is a question of economics.

For pastel shades and/or transparent colors a few percent of colorant in the preparation are enough, especially when a colorant with a high tinting strength can be used to match the desired color. The result is a very diluted masterbatch. In this case it is not the concentration of the masterbatch that defines the quantity of addition for the later coloring of a polymer but technical considerations. Very small amounts of a masterbatch are difficult to blend homogeneously in a polymer melt, therefore the coloring of a polymer melt demands a minimum of addition. The size of the pellets of a masterbatch is usually 2–3 mm (0.075–0.11 in.) in length

and 1.5–2.5 mm (0.05–0.09 in.) in diameter and the addition of such a masterbatch should be not smaller than approx. 1%. Much finer pellets or granules, of course, would allow an addition below 1%, but such types of masterbatches are not yet common for technical and economical reasons.

Considering these two extremes it is understandable that there is no general rule for the concentration of colorants in a masterbatch.

The manufacture of a masterbatch is a multistep process (Fig. 4.3).



Figure 4.3: Scheme of production of a masterbatch

- Step 1: All powdery components of the recipe are weighed out accurately and premixed.
- Step 2a: Homogenization of the powdery components in a mixer. Different constructed types of mixer can be used.
- Step 2b: The homogeneous blend is added to the weighed polymer and blended carefully. The same type of mixer as in step 2a can be used.
- Step 3: Extrusion of the mix. This step requires the use of a twin-screw extruder, because a high shear is necessary for a complete dispersion of the colorants in the polymer melt. There are two types of twin-screw extruder, the corotating and the counterrotating extruder. Both types of extruder have advantages and disadvantages; the choice of the most suited extruder corresponds to the properties of the colorants. Very hard organic pigments demand a high shear for a complete dispersion in the polymer melt; a corotating extruder is therefore preferred because of its higher shear. In contrast, pigments very sensitive to shear, such as pearlescent pigments, should be extruded on a corotating extruder because of its lower shear.
- Step 4: Granulation. There are principally two different methods. One method is to draw cords of colored melt, formed at the die face of the extruder head, cooling down in a water bath, and cutting. The results are cylindrical pellets. The other method is to cut the melt directly the moment it leaves the borings in the extruder head by rotating knives and cooling in a water bath (die face pelletizer). The results are lens-shaped pellets.

The most preferred method of granulation is to form a cord of colored melt, to cool it in a water bath, and to cut it into cylindrical pellets. The main advantage of this procedure is the flexibility in production, because the manufacture of customer matched color batches is not a continuous process but batchwise. The batchwise production is a consequence not only of the great variation of desired colors but also of the variety of polymers to be used as carriers. The size of such a batch can vary between 25 kg (55 lb) and several tons. Exceptions, however, are standard batches in white and black and a few other standard colors. In this case the second method of granulation is usually applied.

The diameter of the cylindrical pellets amounts usually to 1.5–2 mm (0.05–0.075 in.) and the length to 2–3 mm (0.075–0.11 in.). The effective size of these pellets depends on the one hand on the size of the borings in the extruder head and on the other hand on the degree of expansion of the colored polymer melt. In the compression section in front of the extruder head the polymer melt will be compressed and the degree of this compression varies accordingly to the type of polymer and the concentration of colorants and additives in the melt. The moment the melt leaves the borings in the extruder head the melt is relieved of the pressure and takes on its original volume. In case of much smaller diameters of the borings in the extruder head the cord can no longer be drawn satisfactorily whereas significant larger diameters lead to problem during cutting. Polymers are known as poor heat conductors and therefore the inside of the cord will not be cool, that is, solid enough, after passing through the water bath for a sufficient cutting. The heat transfer is too slow in such a case.

Lens-shaped pellets are quite common for several types of natural colored polymers and typical for batches in the standard colors white and black. In these color preparations the concentration of the colorant is as high as 60–75% while the amount of polymer drops to 15–25% in comparison to a customer-matched color preparation. Such a highly concentrated batch cannot be granulated by the usual method but only with the aid of a die face pelletizer. The operating principle of such a pelletizer is the following: the melt is pressed through the borings in the extruder head into fast running water, where rotating knives cut the discharged melt directly into small pieces. The speed of the running water must be high enough to guarantee a complete separation of each single, still soft pellet. In the fast running water the original cylindrical pellets try to reach the spherical form, which is in physical terms the most stable form. On the other hand the water directly cools down the surface of the pellets. Both reactions counteract each other and the results are lens-shaped pellets.

This process has been modified in such a way that now very fine, nearly spherical granules, so-called “micropellets,” can be produced. The main disadvantage of such fine granules is the high cost of production. The most important advantage is

an extremely larger number of particles per weight unit in comparison to the normal cylindrical pellet. Such a very fine granule can be metered well below 1% if it is done directly on the plasticizing screw. Even then the dispersion of the micropellets in the polymer melt is homogeneous and streaks of color are unlikely to occur. In the case of pastel shades and/or transparent colors the concentration of the colorants in the preparation need to be very low to avoid streaks of colors during the coloring process. Here is another advantage of the micropellets because preparations for pastel shades and/or transparent colors can be more highly concentrated compared to a normal masterbatch. In this context it would be interesting to compare the costs of coloring between a normal masterbatch and micropellets. A masterbatch is cheaper in production but it requires a larger addition; on the other hand micropellets are more expensive in production but the required quantity for the coloring of polymers is significantly lower.

Technically considered there are further methods to manufacture pellets or granules. One of these is, for example, the modification of the spray drying process. The spray drying process is used to produce very fine granules starting from an aqueous slurry. The fine droplets, produced by a spraying nozzle or by a fast rotating disk, are dried in a stream of hot air. The results are very fine spherical, often hollow granules. Instead of an aqueous solution a melt, consisting of colorants and binder, can be sprayed into a stream of cold air. Here, too, the results are very fine spherical but full granules. The spraying nozzle requires a light-flowing melt; therefore the normal polymers cannot be used as binder. Possible binders are oligomers (waxes) or resins. Color preparations, based on this process, are commercially available and sometimes used for the coloring of polymers.

A masterbatch is the most expensive color preparation of all types because of the high expenditure of work (many steps) and energy (extrusion). Another disadvantage to some extent is the known incompatibility of polymers when blended with each other. It is therefore recommended that one use the same type of polymer as carrier for the color preparation that will be colored later, and vice versa.

Sometimes so-called “universal batches” are offered on the market. The word “universal” is derived from the Latin and means all-embracing; in other words the carrier of such a universal batch should be *compatible with any other polymer*. Our own practical experience denies this, which is not surprising when we consider the variety of chemical different types of polymer. Another restriction is the fact that not all colorants can be applied in every type of polymer for many reasons such as heat stability, light fastness, or weather resistance, or in the case of dyes the migration in partially crystallized polymers. This becomes very evident if, for example, the coloring of polyethylene (PE) and polyamide (PA) is compared. In PE much more colorants are applicable than in PA, in which the range of colorants is very limited. Consequently no universal batches are possible

in the true sense of the word. On the other hand it is known that in practice sometimes PA is colored with (special) color preparations based on PE as carrier, but only if there are no special requirements regarding the quality of the plastic article. For such types of batches the correct term would be “partial universal batches.”

Besides some disadvantages the advantages of a masterbatch predominate especially with respect to handling (Table 4.1). The most important advantages are: a very good metering, dust-free handling, and a very low expenditure of work changing colors in production.

In addition the pigments are dispersed completely in the polymer during the extrusion, and the result is an optimal utilization of the tinting strength of the colorants, probably one of the reasons why a masterbatch is the most preferred type of color preparation.

Table 4.1: *Disadvantages and Advantages of a Granulated Color Preparation*

Disadvantages	Advantages
Not universally applicable (incompatibility of polymers) High expenditure of work during production Most expensive type of color preparation	Dust-free handling Smallest expenditure of work when changing colors during production Very good metering No problems when high amounts have to be used for coloring Optimal utilization of the tinting strength of the colorants

4.2.2 *Liquid Color Preparations*

The composition of a liquid color preparation is quite similar to that of a masterbatch; the main difference is that instead of a polymer a liquid binder is used as carrier. Besides the two main components – binder and colorants – a liquid preparation may contain additives such as antissettling agents, stabilizer, nucleating agent, antistatic agent, filler, and so forth. Typical binders are fatty acid ester, ethoxylated fatty acid ester), paraffin oil, plasticizer, polyvalent alcohol, polyvalent amine, ethoxylated alcohol, or other components related to the system to be colored. The binders are used either alone or in combination.

The choice of binder depends on the type of polymer to be colored or in case of thermosets and elastomers on the chemistry of their liquid components. As binder for the coloring of thermoplastic resins fatty acid ester, ethoxylated fatty acids, or paraffin oil are usually used; for plasticized poly(vinyl chloride) (PVC), of course a plasticizer. In thermosets binders that contain still reactive groups at the end of the molecule are preferred because as a secondary effect the binder functions as a hardener during the cure of the thermosets. To color epoxy resins, for example, polyvalent alcohol, polyvalent amine is the most preferred binder.

The manufacture of a liquid color preparation is relatively easy (Fig. 4.4). The metered components of the recipe are mixed in the binder, loosely dispersed, and finally the whole system is milled. Strictly considered it is not a milling in the true sense of the process but only a complete dispersing of the colorants in the binder. The result of the grinding process should be a complete desagglomeration but no breakdown of the primary particle size of the colorants, which would lead to a color change. The tinting strength and other properties of colorants depend on the primary particle size; therefore the marketed colorants are milled already to a standardized particle size distribution by the manufacturer of colorants. The particle size of the dispersed colorants should be below 10 μm in a liquid color preparation.

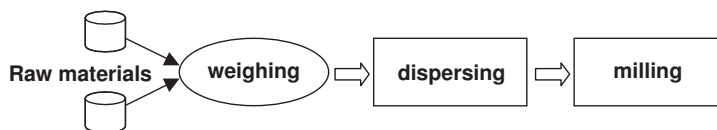


Figure 4.4: Scheme of production of a liquid color preparation

For the grinding process any machine can be used that is constructed to handle liquids and develops enough shear for the desagglomeration, for example, ball mills.

Analogous to the other types of color preparations, liquid color preparations, too, show disadvantages and advantages in coloring of thermoplastic resins (Table 4.2). One disadvantage is the high expenditure of cleaning at a color change during production, except if the liquid preparation is metered directly on the plasticizing screw. The main disadvantage is that a coloring concentration above 1.5–2.5% may cause an “oversmearing” effect. The polymer pellets, covered with the liquid color preparation, are no longer drawn in correctly from the metering zone of the plasticizing screw, resulting in defective plastic parts. This problem may come up

especially in the case of very bright colors with a good hiding power in thin-walled plastic parts. At the worst case a coloring with a liquid color preparation is impossible.

The specific surface area is a characteristic physical property of any solid particle. Typical values for organic pigments range between 10 and 140 m²/g, while in high absorptive grades of inorganic pigments the specific surface area can reach values up to 1200 m²/g and even higher, for example, special grades of carbon black, which is by definition in many countries an inorganic pigment, and silica as filler. The chemical structure of the substance and its particle size distribution, besides other factors, influence the specific surface area. Hence the amount of binder, necessary to wet the colorants and all other solid additives of a liquid color preparation, depends on the specific surface area of each component, and therefore at a given concentration the viscosity of the preparation varies. Considering the variety of colorants and their essential concentration to match the required colors, the resulting viscosity of any color preparation may vary considerably. For practical reasons the viscosity must be adjusted within a certain range. At a too low viscosity a relatively fast sedimentation of the colorants, especially of inorganic pigments, occurs. One method of prevention is to choose a higher concentration of the colorants and/or the incorporation of a high absorptive filler; in both cases the viscosity increases. On the other hand a too viscous liquid formulation causes metering problems during the coloring process.

Even at a constant composition of the preparation the viscosity can fluctuate within a limited range because the specific surface area of colorants is not constant but varies from batch to batch, what is quite normal for any technical product.

Table 4.2: *Advantages and Disadvantages of Liquid Color Preparations*

Disadvantages	Advantages
High expenditure of cleaning at color change in production No high coloring concentrations possible because of risk of oversmearing effects Variable viscosities because of different behavior of colorants and temperature Risk of sedimentation of (heavy) pigments	Dust-free handling Excellent distribution; each polymer pellet is wetted by color Good utilization of the tinting strength of the colorants Good metering Nearly partial-universal in thermoplastic resins Favorable costs of production

One advantage of a liquid color preparation is the very good wetting of each polymer pellet prior to extrusion, which is especially important for pastel color shades or transparent color shades. By the way this is the most important advantage of a liquid color preparation in comparison to a masterbatch.

Further advantages are the utilization of the full tinting strength because of the complete dispersed colorants, a good metering behavior, dust-free handling, and favorable costs of production.

Thermosets and elastomers are colored by blending of one of their liquid components with the liquid color preparation.

4.2.3 Powdery Color Preparations

The simplest form of a powdery color preparation is the pure colorant. But as processing aids a powdery color preparation contains usually at least diluting and dispersing agents, which improve the wetting of the colorants by the polymer melt. If required any other additive can be added provided that the substance is solid or at least absorbed on a carrier in the case of liquid substances.

For the homogenization of a blend consisting of colorants and additives a variety of mills are available. The best type of mill should be determined by pilot experiments. Great care should be taken to avoid a breakdown of the primary particle size of the colorants, on the other hand the mill should provide enough shear to destroy the agglomerates of the colorants (Fig. 4.5). In this context attention must be paid to the fact that pure, very fine powdery organic substances are sensitive to dust explosions.



Figure 4.5: Scheme of production of powdery color preparations

In a powdery color preparation the colorants are not yet dispersed but must first be dispersed in the polymer melt during the processing of the polymer. Injection molding machines are single-screw extruder types that in comparison to the twin-screw extruder used for the production of masterbatches usually do not develop enough shear for a complete dispersing of the colorants, especially in case of the so-called “hard” pigments, which are difficult to disperse. Prime examples of

such colorants are chromium oxide green and the blue and green phthalocyanine pigments. The results of an incomplete dispersing of pigments in a polymer melt are color specks and/or differences in the color related to an imperfect utilization of the tinting strength. By addition of more or another dispersing agent the number and size of color specks can be reduced but often not completely avoided. Another method is the use of a mixing head, available in different constructions.

A direct metering of powders on the plasticizing screw is very problematic because of their bad flowing properties, powders tend to stick very easily and any inconstant flow of a powder produces defective plastic parts.

The usual way to handle a powdery color preparation is to blend the color and the polymer in a drum. First the surface of the polymer granules is slightly wetted with a coupling agent, for example, a dispersing agent or paraffin oil, then the color preparation is added and the whole mixture blended for a couple of minutes. The result should be a nearly dry surface of the polymer, and technical problems during extrusion are then unlikely to occur. This procedure limits of course the quantity of powdery color preparation that can be applied. This is certainly a disadvantage in the case of very intensive, bright colors with a good (required) hiding power in thin-walled plastic parts.

Important advantages are the highest possible concentration of colorants in any color preparation, and the low costs of production (Table 4.3).

Table 4.3: *Advantages and Disadvantages of Powdery Color Preparations*

Disadvantages	Advantages
Dusty High expenditure of cleaning at color change in production Direct metering problematic Risk of inconsistent colors during coloring process Limitation of the quantity applicable during the coloring process No complete dispersing of colorants, therefore no full utilization of the tinting strength Use of coupling agents necessary	Highest possible concentration of colorants in any color preparation (Nearly) universal application Very economic because of low costs of production

4.2.4 Valuation of Color Preparations

The market is ruled undoubtedly by masterbatch. The reasons for its dominant role are the various advantages in handling during the process of coloring thermoplastic resins. These advantages counterbalance the higher costs of a masterbatch in comparison to the other types of color preparations.

By volume the liquid and powdery color preparations follow far behind for coloring of thermoplastic resins. The marketed volumes of these two types are in the range of 10% in comparison to masterbatch.

An exception, however, is PVC. The large PVC processors produce their own compounds, including coloring. When they use color preparations they usually prefer liquid color preparations based on a plasticizer.

As mentioned before a masterbatch cannot be used for coloring of thermosets and elastomers; in this case only liquid or powdery color preparations are applicable. By volume the quantities of these two types of polymers are of minor importance in comparison to the thermoplastic resins; consequently the need of liquid or powdery color preparations is very limited. A preference for one of these two possible types of color preparations is not apparent.

4.3 Types of Polymers and Their Processing

4.3.1 Types of Polymers

Plastics belong to the large group of macromolecules usually called polymers. Polymers are subdivided according to their chemistry into inorganic and organic polymers. A further subdivision marks their occurrence as natural or modified natural substance or as synthesized products (Fig. 4.6).

In early historic times the first articles for household and daily life were made of inorganic and organic natural substances. In the further course of development these substances were at least partly modified, and at the same time they became valuable raw materials for many other goods. Much later, in comparison to the long history of natural substances, the first synthetic polymers were invented relatively recently. A large variety of polymers became available, and there is no end of development in sight. The properties of different polymers are improved continuously to fulfill all requirements of their sometimes very specific applications. These improvements are achieved by using new catalysts, new combinations of monomers and polymers (blends), and/or altered production methods.

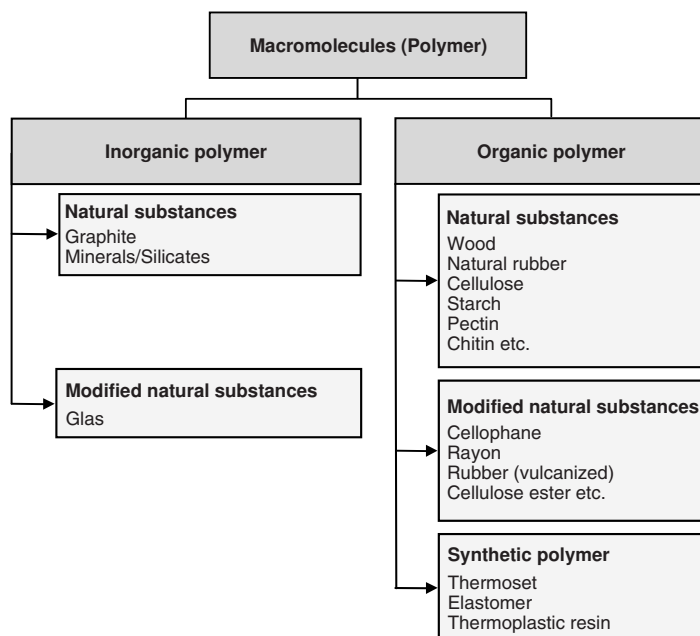


Figure 4.6: Classification of macromolecules

Polymers can be subdivided based on their properties in thermosets, elastomers, and thermoplastic resins or according to their production method in polycondensation products, polyaddition products, and polymerization products.

Thermosets are manufactured by cross-linking of linear or branched multifunctional raw materials. The real cross-linking reaction is also called cure. Thermosets are highly cross-linked. After cure these polymers can no longer be processed by thermoplastic methods; only a mechanical process is still possible. For the coloring of thermosets, only a powdery or liquid color preparation can be used, and should be added to one of the liquid raw materials before curing. In practice the more inert hardener is usually colored. The curing time can be influenced by the composition of the color preparation, and can be slowed down or speeded up.

Elastomers are loosely irreversible cross-linked polymers, which are elastic like rubber within a large temperature range. Small tension causes a high degree of elongation, which is reversible when the tension eases. The cross-linking reaction is also called vulcanization. Analogous to the thermosets, elastomers must be colored before the vulcanization, and only powdery or liquid color preparations can be used. Here, too, the speed of vulcanization may be influenced by the composition of the color preparation.

Thermoplastic elastomers are reversible cross-linked polymers. The cross-linking is raised during a thermoplastic processing and reestablished afterwards at the cooling of the processed part.

According to the literature no strict differentiation between thermosets and elastomers is possible, as both are cross-linked polymers. They differ only in the degree of cross-linking, and the borderline between both types is therefore fluent.

Thermoplastic resins, by far the largest group of polymers, consist of a long, linear, usually unbranched chain. They melt at higher temperatures and are processed by several thermoplastic methods, for example, injection molding, blow molding, film blowing, rotational molding, and so forth. For the coloring of thermoplastic resins all three types of color preparations can be applied principally, although the masterbatch is usually preferred.

Besides this subdivision, based on a characteristic property of the polymers, another possibility is to subdivide the polymers based on their characteristic production methods. Polymers are produced by polyaddition, polycondensation, and polymerization (Fig. 4.7).

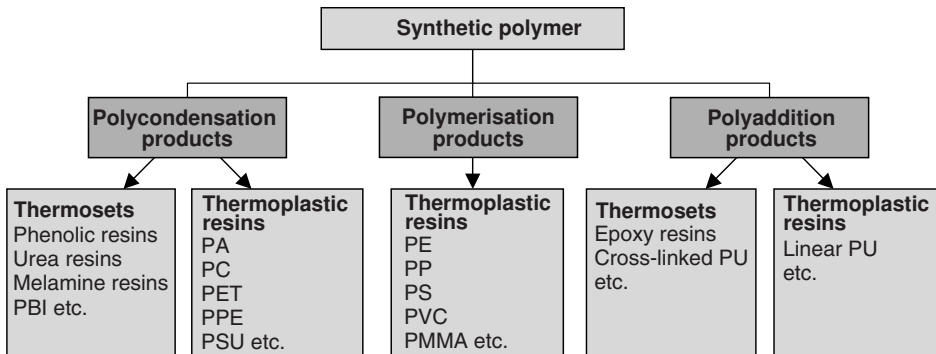


Figure 4.7: Subdivision of polymers according to their production method

Polycondensation is a step-by-step reaction of a monomer producing initially dimers and trimers, which then combine progressively to produce longer chains. The reaction is combined with an elimination of a small molecule, very often water. A monomer with two functional groups produces thermoplastic resins while a multifunctional monomer produces thermosets.

Polyaddition is a step-by-step reaction of a monomer producing initially dimers and trimers, which then combine progressively to produce longer chains. In contrast

to polycondensation this reaction is not combined with an elimination of a small molecule. A monomer with two functional groups produces thermoplastic resins while a multifunctional monomer produces thermosets.

Polymerization is a step-by-step reaction of a monomer producing longer chains. A polymerization process requires as starting material monomers with (at least) one double bond. Only thermoplastic resins can be produced by polymerization.

The type and grade of polymer is set by the customer and depends on the required properties of the final part. For color matching, it is important to receive a sample of the intended polymer, together with its data sheet. Only then is the colorist able to compose in a perfect manner the color preparations appropriate for this polymer. The reasons for this procedure are manifold, the more important being:

- The tint of the natural polymer and its transparency/opacity
- A precise color matching in this specific grade of polymer
- The presence of additives, for example, optical brightener, filler, and so forth
- To check the wanted hiding power and the mechanical and/or physical properties
- The processing behavior of the new color preparation in this grade of polymer

The first four reasons are related to the color as such, while the last point determines the type and grade of the polymer to be used as carrier of the masterbatch. The colorist normally uses a grade of polymer with a light flowing melt, because the melt viscosity increases with incorporation of higher amounts of colorants anyway. By test runs on an injection molding machine, the colorist checks the processing behavior of his color preparation in the customer supplied polymer, and of course the matched color. If problems occur the composition of the color preparation needs to be changed.

An important criterion regarding the selection of colorants to be used in the intended polymer is the processing temperature of the polymer to be colored. The processing temperatures vary within a wide range (Fig. 4.8). The processing temperature ranges from 160–200 °C (320–392 °F) for PVC; 200–250 °C (392–482 °F) for PE; 250–290 °C (482–554 °F) for PA; 320–340 °C (608–644 °F) for PSU.

With a few exceptions the heat stability of inorganic pigments is excellent, especially for all those pigments produced by high-temperature calcination. The calcination requires temperatures in the range of 700–1000 °C (1292–1832 °F).

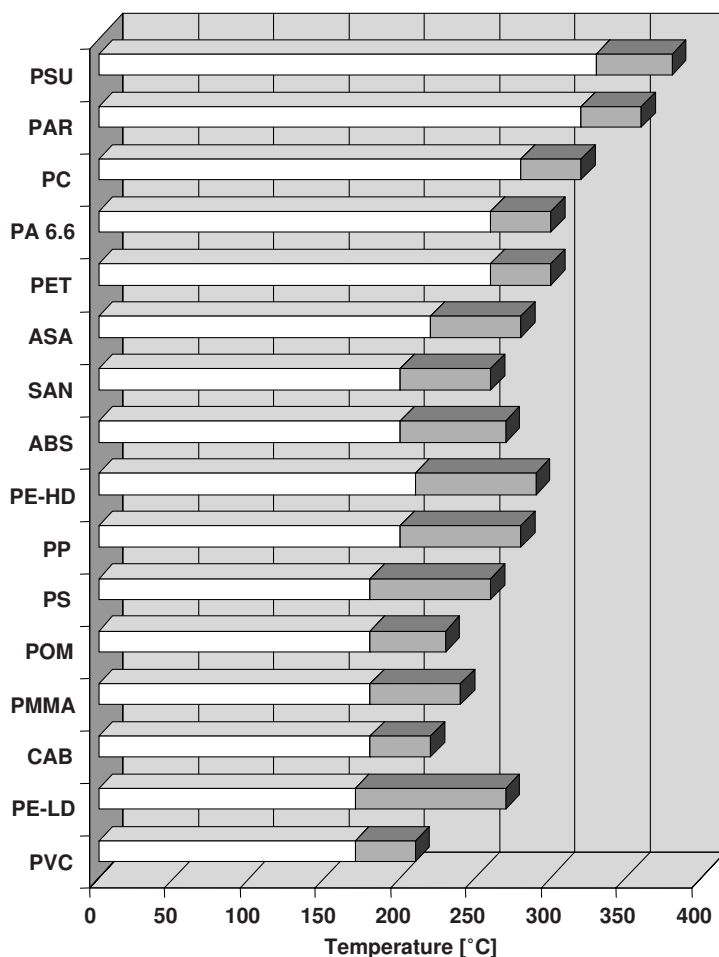


Figure 4.8: Processing temperatures for several plastics

The thermal stability of organic colorants is more or less limited, for two reasons. In the case of an organic pigment not only must the molecule as such be stable but also the crystal modification. There are well known examples in which the molecule is stable but not the crystal modification. Sometimes a substance forms more than one crystal modification, in which case the most thermodynamic stable modification is used as colorant for polymers, for example, phthalocyanine blue.

In comparison to organic pigments, many organic dyes show a higher thermal stability in spite of the fact that the structure of the molecule is chemically “simpler.” Dyes dissolve in polymers, and their thermal stability is determined solely by the stability of the molecule.

The number of organic pigments with a very high thermal stability is rather small. The coloring of engineering plastics with their sometimes extremely high processing temperatures can cause problems if very specific colors are requested. In those cases, it is not always possible to match *every* color.

It would be beyond the scope of the book to describe all plastics and their applications, with the exception of biodegradable polymers. There are very specific problems in connection with the coloring of biodegradable polymers.

4.3.2 *Biodegradable Polymers*

For several years biodegradable polymers have been discussed and some products tested. Biodegradable polymers are products that contain in their chains groups that are accessible to a natural decomposition. There are two possible mechanisms of breakdown, biodegradability or photochemical degradability.

Biodegradability can be defined as the tendency to undergo degradation by living microorganisms (e.g., bacteria, fungi) present in the natural environment. It occurs through reaction between the chemical enzymes secreted by the organism and the polymer chains. The result of such a degradation is water, carbon dioxide, and biomass (humus) and takes place within a manageable period of time.

The mechanism of photochemical degradation is very similar. The first step, however, is a breakdown of the polymer chain into smaller fractions caused by sunlight (UV irradiation). These fractions are then biodegradable. Here too, the degradation should take place within a manageable period of time.

For the use of biodegradable polymers it is of note that the decomposition reaction starts after the normal handling, which means either in the soil (compost) or in a disposal site.

Potential fields of application are:

- Packaging materials, for example, hollow bodies, shopping bags, packaging film, and so forth
- Horticulture, for example, flowerpots, films
- Agriculture, for example, agricultural films
- Household, for example, for articles with a short life span

The main idea of biodegradable polymers is to save valuable and limited disposal site space. Agricultural films are used when the growth of plants is still too slow because of unfavorable weather conditions at the beginning of a growing season. The agricultural film retains warmth during the night and the plants grow faster and ripen earlier. The use of biodegradable films is advantageous because they can be plowed into the soil after the harvest, a very ecofriendly means of waste disposal.

The idea of biodegradable polymers is not new, as cellophane was already developed in the 1920s. The original cellophane is a transparent, degradable film based on a modified cellulose. Later on cellophane was coated or lacquered to improve certain disadvantageous properties during its use. The result of these “improvements” was a loss of its biodegradability.

Further development followed two routes; the first was the development of a directly biodegradable polymer, and the other the development of biodegradable additives. The result of the first are polymers based on further modified cellulose or on polyhydroxy fatty acids, for example, poly(β -hydroxybutyrate). The other types are blends of a plastic, for example, PE, with starch as biodegradable additive. The concentration of the starch should be well below 50% in such a blend.

The biodegradable polymers available to date can be processed on any injection molding machine. All three types of color preparations can be principally used for coloring, but there are a few specific items to be considered regarding the composition of the preparation and during processing. Biodegradable polymers based on modified cellulose and/or starch contain a larger amount of plasticizer, mainly water and/or in a mixture with a high-boiling alcohol to reduce the brittleness of the part. The boiling point of these plasticizers lies somewhere below the processing temperature, therefore precautionary methods need to be implemented. Only then can an unintentional loss of plasticizer be avoided.

The natural color of biodegradable polymers is not attractive, and they are colored to have a pleasing appearance. The ideal scenario is certainly to ask for biodegradability of the whole system consisting of polymer, colorants, and additives. This cannot be realized for several reasons, and certain compromises are unavoidable.

The main reasons are:

- The naturally occurring colors of plants cannot be applied during any thermoplastic processing because of their insufficient heat stability and light fastness.
- The synthesized organic colorants are considered as nonbiodegradable; in addition it needs to be taken into account that organic colorants may form fragments detrimental to the environment. Any results regarding biodegradability of organic colorants have not yet been published.
- Inorganic pigments are generally not biodegradable as a consequence of their chemistry. On the other hand our entire surrounding, the soil, mountains, and so forth consist of a large amount of minerals, the raw material for inorganic pigments. Inorganic pigments are insoluble, and therefore most of the inorganic pigments cannot endanger our environment. The compromise is to use certain inorganic pigments for the coloring of biodegradable polymers.

Table 4.4: Limits of Heavy Metals in Dry Weight of Humus

Country	Standard/ norm	Heavy metal (mg/kg dry weight of humus)							
		Cr	Ni	Cu	Zn	Cd	Hg	Pb	As
Austria	ÖNorm S2200 Quality I	70	42	70	210	0.7	0.7	70	
Belgium	Urban waste	150 up to 200	50 up to 100	100 up to 500	up to 1500	5	5	up to 1000	
Belgium	VLACO	70	20	90	300	1.5	1.0	120	
Denmark	Status 1995	100	45	1000	4000	0.8	0.8	60	
Finland			100	600	1500	3.0	2.0	150	50
France	Category I–II	100 up to 200	20 up to 80	100 up to 200	250 up to 1000	2 up to 4	0.5 up to 3	140 up to 500	
Germany		400 up to 666	66 up to 100	400 up to 666	up to 1666	6.6 up to 11	8.4 up to 14	400 up to 666	
Germany	RAL GZ 251	100	50	100	400	1.5	1.0	150	
Spain		750	400	1750	4000	40	25	1200	
Switzer- land		150	50	150	500	3	3	150	
Euro- pean Com- munity	CENTC261 SC4 WG2 (50% of most strict norm)	35	10	35	105	0.4	0.4	30	25

Not every inorganic pigment can be used as a colorant. The ideal disposal procedure for biodegradable materials is to compost them. The composition of a compost is regulated by standards and/or legal requirements in many countries, which limit or exclude certain heavy metals in the compost (Table 4.4). The listed heavy metals are very similar in the different countries, but their limits vary some-

times considerably. The limits of heavy metals in compost do not differentiate if the substance is present in a soluble or insoluble stage. The significant figure is the total amount in 1 kg (2.2 lb) dry weight of humus.

4.4 Colorants

Color preparations are used to color polymers. For the development of a color preparation it is important to choose the right colorant. Only then will you be able to fulfill all the different requirements of your customer. The main requirement is of course the right shade; other also very important criteria are fastness properties, migration, warpage, and toxicological safety.

Colorant is the principal definition of all substances that can color polymers. Chemically they can be divided into two groups, the inorganic and organic colorants. If the colorant is insoluble in the polymer it is a pigment by definition, and if the colorant dissolves in the polymer it is a dye (Fig. 4.9) [23].

Inorganic dyes play no role in the coloring of polymers, but are mentioned here only for the reason to complete the classification.

The classification of a colorant as pigment is not always absolutely clear. There are several examples of an organic pigment that dissolves in some polymers. A good example is Pigment red 254 (DPP-Red). This pigment is insoluble in most polymers; it behaves like a pigment and gives brilliant red shades. In polycarbonate (PC), however, at temperatures above approx. 330 °C (626 °F) it dissolves and gives a fluorescent yellow shade. In PC the Pigment red 254 behaves like a dye. Further examples are described in the literature.

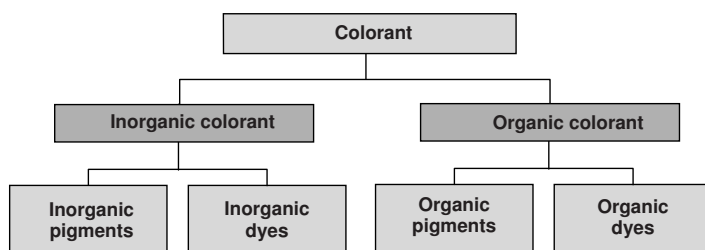


Figure 4.9: Classification of colorants

A substance can be used as a colorant for polymers when several requirements are fulfilled by the substance. The requirements for pigments are listed in Table 4.5 and those for dyes in Table 4.6. The requirements for pigments and dyes differ in some

criteria, owing to there specific physical behavior in a polymer. All colorants should have good heat stability, high tinting strength, and good fastness properties; the colorant should not migrate and should be toxicologically safe. Specific requirements for pigments are a good hiding power, they should be easy to disperse in a polymer melt, and should not cause warpage. Specific requirements for dyes are a clear transparent shade, and they should dissolve and spread rather fast in a polymer melt.

The requirements listed in Tables 4.5 and 4.6 represent the ideal situation, which is almost never achieved in practice.

Table 4.5: *Requirements for Pigments*

Requirements for pigments
High hiding power
Good dispersibility
High heat stability
High tinting strength
Good fastness properties (light/weather)
No migration
No warpage
Toxicologically safe

Table 4.6: *Requirements for Dyes*

Requirements for dyes
High heat stability
High tinting strength
Good fastness properties (light/weather)
Good solubility
No sublimation
No migration
Toxicologically safe

Most of the colorants do not fulfill *all* the requirements listed. If you would insist on it, the range of colorants would be very limited together with a paucity of avail-

able shades. On the other hand practice shows that not every colored polymer item truly requires the fulfillment of *all* requirements. Depending on the intended use, compromises are possible and quite normal. Each colorant has a weak and a strong side, caused partially by their different chemistries. These differences become very obvious when comparing the inorganic and organic colorants (Table 4.7).

Table 4.7: *Comparison of the Properties of Inorganic and Organic Pigments*

Property	Organic pigment	Inorganic pigment
Density	Low, mostly $< 2.5 \text{ g/cm}^3$	High, mostly $> 2.5 \text{ g/cm}^3$
Particle size	Mostly $< 1 \text{ }\mu\text{m}$, thereby high specific surface area	Mostly $> 1 \text{ }\mu\text{m}$, thereby low specific surface area
Tendency to form Agglomerates	High	Low
Dispersibility	Not very good	Much better
Solubility	Partial solubility, depends on concentration	Totally insoluble
Transparency	High, thereby low hiding power	Low, thereby high hiding power
Tinting strength	High, good brilliance	Low, mostly not brilliant
Heat fastness	Limited, sometimes low	Very high
Light fastness	Limited, sometimes low	Very good
Warpage	Sometimes very strong	None

Generally speaking, organic pigments have a lower hiding power in comparison to inorganic pigments, which is, however, an advantage in the case of transparent colors. The tinting strength and brilliance of a shade of an organic pigment are much higher than those of inorganic pigments, which are very often dull. The difference in tinting strength between organic and inorganic pigments is the consequence of different mechanisms in generating the color, caused by the fundamental differences in their chemical structures. In both types of pigments the interrelation of absorption and reflection is responsible for the color, but the physical processes involved differ in detail.

An unalterable condition for the appearance of color is the presence of chromophores, a system of conjugated double bonds (π -electronic system), in an

organic colorant. The electrons of the conjugated double bonds are elevated from the ground state energy level to an excited state by absorbing selected frequencies of the incident visible light, thereby giving the molecule the shade of the resulting complementary color. The type of conjugated double bonds depends on the chemistry of the organic colorant and is influenced by substituents with lone electron pairs. Substituents such as alkoxy, hydroxy, alkyl, and arylamino groups are known as electron donors. Electron acceptors are substituent functional groups such NO_2 , COOH , COOR , SO_2 , and others. The energy necessary to excite the whole electronic system, consisting of double bonds and substituents, varies according to the chemical structure of each molecule. Different energy levels mean at the same time different shades of color. The two pigments Pigment yellow 109 and Pigment yellow 110 differ only by one substituent and are therefore a good example to demonstrate the importance of a substituent for the color shade.

Inorganic pigments do not contain any double bonds or chromophores, therefore another principle leads to color. All chemical elements consist of a positive nucleus (protons), which is encircled by (negative) electrons. The size of the nucleus and consequently the number of electrons is determined by its placement in the periodic table of elements. In the periodic table all elements are placed according to their periodic repeated properties according to their atomic number, which defines the number of electrons and the electron shells.

The electrons rotate on definite energy levels, the so-called orbitals. The known orbitals are *s*, *p*, *d*, *f*, and *g* orbitals. By input of energy, for example, by absorption of sunlight, the electrons, preferably those of the higher electron shells, are elevated from the ground energy level to a higher energy level (excited state), whereby each energy level requires a definite amount of energy to elevate electrons to higher electron shells. The transition from a series of excited states to a common lower state (ground energy level) is responsible for a series of spectral emission lines. We can see a color when the wavelength of these spectral emission lines is in the range of visible light [24, 25]. The intensity of this emitted light is usually much lower in comparison to the conjugated double bonds of the organic colorants, which is why the tinting strength of inorganic pigments is quite often low.

A large number of substances act as nucleating agents in partially crystalline polymer such as polyolefins. Several organic pigments are no exception and provide crystallization nuclei in a polymer melt. Certain surface effects are responsible for this activity. The single crystals grow together to larger units, the spherulites, increasing the degree of crystallinity. The shrinkage of a polymer melt depends, besides other factors such as processing temperature, cooling rate, and pigment concentration, on the degree of crystallinity. Any distortion in the crystallization leads to warpage; among the many reasons are acicular crystals of

the colorant or large differences in wall thickness of nonrotational symmetric plastic parts.

Plastics are known as poor heat conductors, and the cooling rate of a molded plastic article is therefore slow. To reduce the amount of shrinkage, it would be logical to extend the cooling time during the injection molding. However this is not done in practice because of the expense involved. The amount of shrinkage and/or warpage of colored plastic articles is impossible to forecast, and should be tested by trials.

The appearance of shrinkage is not limited to injection molding; it plays an important part in blow molding as well. The large blue barrels (100 or 200L content) for hazardous goods must be put in special cooling stations directly after blow molding; otherwise the barrel would shrink too much, and consequently the container would no longer hold the required content.

The nucleating activity of several organic pigments is said to be a surface effect of the crystals; therefore the crystal surface should be coated and usually special types of wax are used for this purpose. The coat prevents direct contact of the crystal surface with the polymer melt and such a coated pigment prevents the appearance of warpage. The first coated pigment on the market was a special grade of phthalocyanine blue for injection molding of polyolefins, and others followed. The coat is sensitive to shear, which should be considered during the dispersal of those coated pigments in a color preparation and also later during the manufacture of plastic parts made of partially crystalline polymers such as polyolefins. In case of damage of the coat by too high shear a direct contact of the crystal surface and the polymer melt is no longer prevented and the warpage starts again.

The majority of inorganic pigments are produced by calcination at very high temperatures (approx. 700–900 °C) [1292–1652 °F]. These pigments possess very good heat stability. Other inorganic pigments, manufactured by different methods, usually show sufficient heat stability, with only a very few inorganic pigments with a limited heat stability.

The heat stability of organic colorants, however, is more or less limited.

Inorganic and organic pigments can be used to color all types of polymers, provided that the heat stability of the organic pigment is sufficient in the polymer to be colored.

The use of dyes is limited to amorphous polymers with a rather high glass transition temperature such as polystyrene (PS), polycarbonate (PC), poly(methyl methacrylate) (PMMA), and others. In partially crystalline polymers dyes would migrate directly.

The evaluation of toxicological safety of all colorants is subject to a continuous change. Possible reasons for a change might be the result of new toxicological studies, improved analytical methods in detection of hazardous impurities, or environmental considerations.

The very common lead chromates, lead sulfochromates, cadmium pigments, and disazodiarylide pigments used in the past have since been banned because of toxicological considerations. Other colorants may follow in the future.

5 Colorants for Polymers

5.1 Inorganic Pigments

The palette of inorganic pigments suitable to color polymers is relatively small in comparison to the organic colorants. There are only a few basic chemical formulas but they are available in numerous variations; therefore the palette seems larger than it really is. One example of many variations of a fundamental type are the so-called *complex inorganic color pigments* (formerly known as mixed phase metal oxide pigments). By adding other metal oxides and/or a variable ratio of the main metal oxides the exact shade is modified within a certain range. These variations are not always noticeable in the color index number of an inorganic pigment because very often only the basic chemical formula is listed there.

In Table 5.1 the most important inorganic colorants are listed, including those inorganic products that have a color index number but are not used as colorants in coloring of polymers; they are used mainly as fillers or processing aids.

Table 5.1: List of Inorganic Pigments

Product	Formula	Color index	Color	Remarks
1) Pigments consisting of pure elements				
Aluminum	Al	P. Metal 1	Silvery shiny	Effect pigment
Bronze	Cu-Zn Alloys	P. Metal 2	Golden shiny	Effect pigment
Carbon black (pigment)	C	P. black 7	Black	
2) Oxide pigments and hydroxide pigments				
Zinc white/ zinc oxide	ZnO	P. white 4	White	
Titanium dioxide (rutile/anatase)	TiO ₂	P. white 6	White	

Table 5.1: Continuation

Product	Formula	Color index	Color	Remarks
Antimony oxide	Sb_2O_3	P. white 11	White	No longer used because of toxicological concerns
Zirconium oxide	ZrO_2	P. white 12	White	No longer used as pigment
	SnO_2	P. white 15	White	Not used as a pigment
Iron oxide yellow	α -resp. γ - $\text{FeO}(\text{OH})$	P. yellow 42	Yellow	
Chromium oxide	Cr_2O_3	P. green 17	Green	
Iron oxide red	α - Fe_2O_3	P. red 101	Red	
Iron oxide black	Fe_3O_4	P. black 11	Black	
3) Complex inorganic pigments (previously: mixed phase metal oxide pigments)				
Nickel anti-mony titanium yellow rutile	$(\text{Ti}, \text{Ni}, \text{Sb})\text{O}_2$	P. yellow 53	Yellow	
Zinc ferrite brown spinel	ZnFe_2O_4	P. yellow 119	Yellow-brown	
Nickel barium titanium primrose priderite	$2\text{NiO} \cdot 3\text{BaO} \cdot 17\text{TiO}_2$	P. yellow 157	Yellow	
Nickel niobium titanium yellow rutile	$(\text{Ti}, \text{Ni}, \text{Nb})\text{O}_2$	P. yellow 161	Yellow	
Chromeniobium titanium buff rutile	$(\text{Ti}, \text{Cr}, \text{Nb})\text{O}_2$	P. yellow 162	Yellow	
Chrome tungsten titanium buff rutile	$(\text{Ti}, \text{Cr}, \text{W})\text{O}_2$	P. yellow 163	Yellow	

Table 5.1: Continuation

Product	Formula	Color index	Color	Remarks
Manganese antimony titanium buff rutile	$(\text{Ti}, \text{Mn}, \text{Sb})\text{O}_2$	P. yellow 164	Yellow-brown	
Bismuth vanadate molybdate	$\text{BiVO}_4/\text{Bi}_2\text{MoO}_6$	P. yellow 184	Yellow	
Nickel tungsten yellow rutile	$(\text{Ti}, \text{Ni}, \text{W})\text{O}_2$	P. yellow 189	Yellow	
Cobalt aluminate blue spinel Cobalt chromite blue-green spinel	CoAl_2O_4 $\text{Co}(\text{Al}, \text{Cr})_2\text{O}_4$	P. blue 28 P. blue 36	Blue/ reddish Blue/ greenish	
Cobalt tin blue-gray spinel	Co_2SnO_4	P. blue 35	Blue	
Cobalt zinc aluminate blue spinel	$(\text{Co}, \text{Zn})\text{Al}_2\text{O}_4$	P. blue 72	Blue	
Cobalt chromite green spinel	CoCr_2O_4	P. green 26	Green	
Cobalt titanate green spinel	$(\text{Co}, \text{Ni}, \text{Zn})_2\text{TiO}_4$	P. green 50	Green	
Iron manganese brown	$\text{Mn}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ $\text{Fe}(\text{OH})_2$	P. brown 7 + 8	Brown	
Chrome antimony titanium buff rutile	$(\text{Ti}, \text{Cr}, \text{Sb})\text{O}_2$	P. brown 24	Orange-yellow	
Iron chromite brown	$(\text{Fe}, \text{Cr})_2\text{O}_3$	P. brown 29	Brown	
Zinc iron chromite brown spinel	$(\text{Zn}, \text{Fe})(\text{Fe}, \text{Cr})_2\text{O}_4$	P. brown 33	Brown	
Iron chromite brown spinel	$\text{Fe}(\text{Fe}, \text{Cr})_2\text{O}_4$	P. brown 35	Brown	

Table 5.1: Continuation

Product	Formula	Color index	Color	Remarks
Manganese niobium titanium brown rutile	$(\text{Ti}, \text{Mn}, \text{Nb})\text{O}_2$	P. brown 37	Brown	
Chrome manganese zinc brown spinel	$(\text{Zn}, \text{Mn})\text{Cr}_2\text{O}_4$	P. brown 39	Brown	
Manganese chrome anti-mony titanium brown rutile	$(\text{Ti}, \text{Mn}, \text{Cr}, \text{Sb})\text{O}_2$	P. brown 40	Brown	
Iron manganese brown	Iron manganese oxide	P. brown 43	Brown	
Iron titanium brown spinel	Fe_2TiO_4	P. black 12	Black	
Copper chrome iron oxide	$\text{Cu}(\text{Cr}, \text{Fe})_2\text{O}_4$	P. black 22	Black	
Manganese ferrite black spinel	$(\text{Fe}, \text{Mn})_2\text{O}_4$	P. black 26	Black	
Iron cobalt chromite black spinel	$(\text{Co}, \text{Fe})(\text{Fe}, \text{Cr})_2\text{O}_4$	P. black 27	Black	
Copper chromite black spinel	$\text{Cu}(\text{Cr}, \text{Fe})_2\text{O}_4$	P. black 28	Black	
Iron cobalt black spinel	$(\text{Fe}, \text{Co})\text{Fe}_2\text{O}_4$	P. black 29	Black	
Chrome iron nickel black spinel	$(\text{Ni}, \text{Fe})(\text{Cr}, \text{Fe})_2\text{O}_4$	P. black 30	Black	
4) Sulfide prigmments and sulfide-selenium pigments				
Zinc sulfide	ZnS	P. white 7	White	
Lithopone	$\text{ZnS} + \text{BaSO}_4$	P. white 5	White	

Table 5.1: Continuation

Product	Formula	Color index	Color	Remarks
Cerium sulfide	Cerium sulfide (exact formula not yet published)	P. orange 75 P. orange 78 P. red 265 P. red 275	Orange Red-orange Red Red	
Cadmium yellow	(Cd,Zn)S CdS	P. yellow 35 P. yellow 37	Yellow Yellow	No longer used because of toxicological concerns
Cadmium red	Cd(S,Se)	P. red 108 P. orange 20	Yellow/red Orange	
5) Chromate mixed phase pigments and chromate-molybdates mixed phase pigments				
Lead chromate yellow	Pb(Cr,S)O ₄	P. yellow 34	Yellow	No longer used because of toxicological concerns
Lead chromate molybdate orange/red	Pb(Cr,Mo,S)O ₄	P. red 104	Orange-red	
6) Silicate pigments				
Silica	SiO ₂	P. white 27	White	Not used as pigment, filler
Aluminum silicate	Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	P. white19	White	Filler
Ultramarine	Na ₆₋₈ Al ₆ Si ₆ O ₂₄ S _n (n = 2-4)	P. blue 29 P. violet 15 P. violet 15	Blue Violet Red	
7) Diverse other pigments				
Cobalt violet phosphate	Co ₃ (PO ₄) ₂	P. violet 14	Violet	
Manganese violet	NH ₄ MnP ₂ O ₇	P. violet 16	Violet	
Cobalt lithium violet phosphate	CoLiPO ₄	P. violet 47	Violet	

Table 5.1: Continuation

Product	Formula	Color index	Color	Remarks
Cobalt magnesium red-blue borate	$(\text{Co,Mg})_2\text{B}_2\text{O}_5$	P. violet 48	Violet	
Barium sulfate	BaSO_4	P. white 21	White	Filler, processing aid
Chalk/calcium carbonate	CaCO_3	P. white 18	White	Filler, processing aid
Pearlescent pigments	Mica coated with TiO_2	–	Pearlescent – silvery shiny	Effect pigment
Colored pearlescent pigments	Mica coated with TiO_2 and metal oxide	–	Different colors	Effect pigment
Phosphorescent pigments	ZnS with traces of Cu or Ag	–	Greenish yellow phosphorescent	Effect pigment
“Flop-Pigments”	Aluminum flake pigments coated with iron oxide and SiO_2	–	Color depends on angle of vision	Effect pigment

The two most important colorants for the colors white and black belong to the inorganic pigments, namely titanium dioxide and carbon black. Carbon black is nearly pure carbon, which is one of the main components of the whole of organic chemistry. Nevertheless, however, carbon black is by definition an inorganic pigment, for example, the German standard DIN 55944 [23]. Titanium dioxide and carbon black are used not only for the pure white and black hues but also for shading, such as brightening or darkening of a color tint.

A worldwide discussion on “heavy metals in our environment” came up during the last decade. As a consequence, nearly every customer requires explicitly that color preparations must be *free of heavy metals*.

But what are heavy metals?

In the chemical dictionary *Römpp* [26] (published in Germany) all metals with a density above $3.5\text{--}5\text{ g/cm}^3$ are characterized as heavy metals, including the colored metals and lanthanide. Only the precious metals are a separate group, which play no role as a component of inorganic pigments.

In the dictionary *Umwelt und Chemie von A–Z*, published by the German association of the Chemical Industry, all metals with a density above 4.5 g/cm^3 are considered heavy metals, including all kinds of metals as well as the precious metals.

The same situation exists in other countries, where no clear definition of the term *heavy metal* can be found. This lack of a clear definition is astonishing because nearly everything else in industry is well defined and standard methods are published by the different associations in all countries. In our own experience, the interpretation of the term heavy metal varies from customer to customer. Some customers require only “free of lead and cadmium pigments,” while others exclude all heavy metals listed, for example, in the European Resolution AP (89)1 or in the German *BgVV-Empfehlung*, Chapter IX and – as an extreme case – a few customers exclude all heavy metals. In practice many discussions between the supplier of the color preparation and the customer were the logical consequence.

The description of heavy metals only says something about the density of the metal but nothing about toxicological and/or environmental aspects. Heavy metals are widespread in our environment, even in our food, because plants absorb them. In addition, several heavy metals are essential trace elements in our bodies, such as iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), chromium (Cr), molybdenum (Mo), and cobalt (Co). The daily requirement is in the range of 0.1–20 mg, depending on the heavy metal. If our bodies are not sufficiently supplied with those heavy metals then deficiency diseases occur.

The most important inorganic pigments were examined very carefully with regard to both toxicological and ecological effects. Summarizing the results, the most important inorganic pigments, with the exception of the harmful and banned lead chromates and cadmium pigments, are harmless toxicologically as well as ecologically [28, 29]. This results from, among other factors, the insolubility of inorganic pigments; they are not bioavailable in our stomachs (accidental swallowing) or in the environment. The toxicological effects of the lead chromates and cadmium pigments are based on their solubility in acids, for example, in gastric acid, and because of this these pigments are bioavailable.

The consequence of this situation is a further customer requirement that “the color preparation must be free of lead and cadmium.” Lead and cadmium are widespread in nature and minerals. Minerals are the raw material for most of the inorganic pigments, and it is therefore unavoidable that inorganic pigments are

contaminated with traces of lead and cadmium, in the range of a few milligrams per kilogram of pigment, a quantity that is concurrent with all national and international regulations regarding the purity of colorants. The customer requirement can specify only “free of lead and cadmium pigments,” because the requirement “free of lead and cadmium” would exclude even traces of these two heavy metals. An absolute absence of lead and cadmium in inorganic pigments is neither technically feasible nor required by any legal regulation.

Based on the description of heavy metals by the German Association of the Chemical Industry all inorganic pigments except aluminum flakes, carbon black, and ultramarine blue and violet contain heavy metals.

5.1.1 White Pigments

White pigments are used for pure white coloring, for shading (brightening) of colors, and for covering shades. For opaque shades titanium dioxide is preferred because of its very good hiding power. Covering shades are requested whenever a showthrough of the content of a package and/or of the underground is to be avoided. In those opaque colors the white pigment must be covered by color first before the color matching can begin. The result is a rather large need for colorant, which has a negative effect on the costs of the color preparation. It is therefore advisable to check first the efficiency of different additions of the color preparation with regard to its hiding power in the planned plastic article. Sometimes it may be more economical to increase slightly the amount of color preparation during the coloring process and/or to increase slightly the wall thickness instead of increasing the concentration of the white pigment in the color preparation. The result of these considerations should be a balance between costs and hiding power.

By definition, all substances with a refractive index higher than 1.7 are classified as white pigments. If the refractive index is lower than 1.7 they are classified as fillers (Table 5.2).

Strictly considered, the limiting value of 1.7 is not a constant but depends on the matrix of the pigments, because every matrix has its own specific refractive index. Polymers are no exception; therefore the refractive indices of pigments vary from polymer to polymer, and are consequently different for materials such as plastics, alkyd resins, cellulose, poly(ethylene terephthalate) (PET) fibers, and so forth.

Good optical properties are expected from white pigments, for example, high scattering power, a high degree of hiding power, good lightening power, a high degree of lightness, only an insignificant undertone (preferably none), and a high degree of whiteness. The most important property is the scattering power, which depends on the refractive index, particle size, and distribution and degree of dispersion.

Because of these dependencies the scattering power is a relative value and not an absolute value. The other parameters, such as hiding power, lightness, undertone and whiteness depend more or less on the scattering power of the white pigment.

Table 5.2: *Refractive Indices of Several White Pigments and Fillers*

Pigment	Color index number	Refractive index
Antimony oxide (Sb_2O_3)	Pigment white 11	2.19
Barium sulfate (BaSO_4)	Pigment white 21	1.64
Basic lead carbonate [$(\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3]$	–	2.01
Silica (SiO_2)	Pigment white 27	1.55
Chalk (CaCO_3)	Pigment white 18	1.58
Titanium dioxide – anatase (TiO_2)	Pigment white 6	2.55
Titanium dioxide – rutile (TiO_2)	Pigment white 6	2.70
Zinc oxide (ZnO)	Pigment white 4	2.00
Zinc sulfide (ZnS)	Pigment white 7	2.37
Zirconium oxide (ZrO_2)	Pigment white 12	2.40

Inorganic pigments are relatively easy to disperse in a polymer melt, much easier than organic pigments. They nevertheless undergo an aftertreatment. The treatment consists of coating the individual pigment particles with colorless inorganic and/or organic substances. The purpose of such an aftertreatment is to improve the dispersibility in a polymer matrix, the light fastness, and weather resistance. A complete dispersion of any pigment in the polymer matrix is important because only then can the optimum of tinting strength be exploited, which affects the economics of a color preparation.

The following description of the white pigments and fillers and/or processing aids is in alphabetic order for systematic reasons.

Aluminum silicate ($\text{Al}_2\text{Si}_2\text{H}_4\text{O}_9$) – Pigment white 19 / 77005

Filler and raw material for the synthesis of ultramarine blue and violet.

Antimony (III) oxide (Sb_2O_3) – Pigment white 11 / 77052

This white pigment is no longer used for coloring of plastics because of its toxicological effects. In technical plastic parts it is still used as a co-flame retardant.

Barium sulfate (BaSO₄) – Pigment white 21 / 77120 / CAS 7727.43.7

Properties: The mineral barite (barium sulfate) is very common in nature. Its density is in the range of 4.3–4.6 g/cm³. Owing to its low Mohs hardness of 3.5 it is not very abrasive in comparison to other inorganic pigments, which is favorable in regard to abrasion of plastic processing machines. Barium sulfate is practically inert toward acids, alkalis, and organic solvents; in addition, the light fastness and weather resistance are very good. The heat stability is high (above 300 °C [572 °F]). Because of its low tendency to form agglomerates it is easy to disperse.

Application: Owing to its low refractive index of 1.64 it is not considered a white pigment. The main use is as a filler and/or processing aid in color preparations. Barium sulfate is used, for example, in lamp covers made of plastic. In this case its low opacity is advantageous – on the one hand it is transparent enough for the light, and on the other hand a certain amount of light is scattered. The result of this combined effect is the required diffuse light scattering of lamp covers.

Two types of barium sulfate are marketed. One type is a very fine milled, natural barite and the other is a precipitated, synthetic barium sulfate. The synthetic type, available in different particle sizes, is preferred as a component of color preparations. Barium sulfate improves the flowing properties of the premixed colorants, especially in the case of a high concentration of organic pigments, and in addition it helps to disperse the pigments in the polymer melt during production of a color preparation.

Another very specific application of barium sulfate is in toys, a use that is not very obvious at first glance. In the past barium sulfate was the classic X-ray contrast medium. There are currently better ones in use. Still, barium sulfate can help to locate a toy swallowed accidentally by a child.

Pure barium sulfate is harmless toxicologically, and its use in plastics in contact with food is therefore permitted in many countries, including the United States (according to the FDA) and in most European countries.

In addition, barium sulfate is a component of Lithopone, Pigment white 5.

Basic lead carbonate [Pb(OH)₂·2PbCO₃] / – / CAS 1319.46.6

This pigment is no longer in use for coloring of plastics owing to its toxicological problems.

Chalk (CaCO₃) – Pigment white 18 / 77220 / CAS 1317.65.3

Properties: Calcium carbonate is besides quartz the most common mineral on earth. There are several types according to its formation and appearance.

- Calcite – colorless, transparent, translucent or opaque, dense crystals with perfect rhombohedral cleavage. Some varieties are fluorescent in UV light. Soluble in acids.
- Chalk – Chalk is a very pure limestone formed during the cretaceous period of fine calcite crystals consisting mainly of shells and skeleton of microscopic small fossils. There are many deposits that are exploited commercially.
- Limestone – Limestone is a compact form of chalk, formed also from the accumulation of calcareous skeletons of marine organisms.
- Marble – Marbles are produced by the metamorphism of limestone around igneous intrusions. Marble is essentially calcite but may contain greater or lesser amounts of dolomite and other minerals. It is a very coarse compacted mineral.

A chalk deposit can be commercially exploited if the purity of the calcium carbonate is higher than 99%. The lightness of chalk increases with decreasing amount of impurities. The most common impurities are iron oxides and carbonates of magnesium, strontium, and barium.

Besides the natural deposits, calcium carbonate is produced synthetically by precipitation. These grades, however, are much more expensive than the natural types.

Calcium carbonate is semihard and not very abrasive. The Mohs hardness is 3, and the density is between 2.6 and 2.8 g/cm³. Calcium carbonate is soluble in weak acids and insoluble in alkali. The properties can be adjusted by aftertreatment.

Application: Calcium carbonate is not a white pigment because of its low refractive index of 1.58. The main application is to reinforce plastics, and another use is as a processing aid. Similarly to barium sulfate, it improves the flowing properties of premixed colorants, especially at high concentrations of organic pigments, and the dispersing of the pigments in the polymer melt during the production of a masterbatch. Other applications are as a diluent in powdery color preparations and in the form of specially treated grades as antisedimentation agent in liquid color preparations.

Lithopone (ZnS/BaSO₄) – Pigment white 5 / – / CAS 1345.05.7

Properties: Lithopone is produced by coprecipitation and subsequent calcination of a mixture of zinc sulfate and barium sulfate. The ratio between both components varies, for example, a type with 60% ZnS and 40% BaSO₄ is marketed. The use of zinc sulfide and barium sulfate in contact with foods is permitted by the US FDA and in most European countries. Soluble zinc is toxic in large amounts, but the human body requires small quantities for metabolism. Owing to its low

solubility it is harmless in the human. Studies showed that there was no case of poisoning or chronic damage to health in the manufacture of this pigment despite exposure to dust during handling of the very finely ground pigment.

Application: Lithopones are used in many plastics, especially in glass fiber reinforced plastics, because the soft texture of lithopone prevents mechanical fiber damage during the coloring of the reinforced polymer. This is the main advantage in comparison to titanium dioxide, which damages the glass fiber of reinforced plastics during the coloring process.

Mica {K/Na/Al₂[(OH,F)₂Si₃O₁₀]} – Pigment white 20 / 77019 / CAS 12001.26.2

A raw material for the production of pearlescent pigments. Mica is the collective term for a whole series of minerals chemically known as hydrous alkaline aluminum silicates. The most important members of this group of silicates are muscovite, phlogopite, biotite, and paragonite. They differ in their content of potassium, sodium, and fluorine, and their characteristic feature is an appearance as very thin sheets.

Mainly muscovite and phlogopite are coated with a thin layer of metal oxides. The silvery pearlescent pigments result from a coat of titanium dioxide, colored pearlescent pigments result from iron and/or chromium oxide as a coat.

Silica or Silicon dioxide (SiO₂) – Pigment white 27 / 77811 / CAS 7631.86.9 respectively 112945.52.5

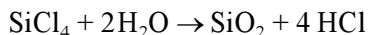
(Remark: The term Pigment white 27 is valid only for the naturally occurring silica, not for the synthetic grade, which is normally used in coloring of plastics.)

Owing to its low refractive index of 1.55, silica is not used as a white pigment but is a very important processing aid. The main functions of silica are:

- Improvement of the flow properties of organic pigments in a premix prior to the extrusion of color preparations (masterbatch production)
- Improvement of the flow properties of a powdery color preparation, including a stabilizing effect on storage
- Use as a thickening or antisedimentation agent in a liquid color preparation and to adjust the viscosity
- Grades of silica with an extremely high specific surface applied as carriers for liquid additives, for example, antistatic agents
- Filler in rubber and sealing compounds based on plastic
- Matting agent in plastic films
- Antiblocking agent in plastic films

Synthetic amorphous silica is produced either by precipitation or by a thermal process. Precipitated silica is manufactured by hydrolysis of an aqueous sodium silicate solution with an acid.

There are two variations of the thermal process, either silicon tetrachloride is combusted with steam according to the formula



or by reaction of quartz and coke in an electric furnace at high temperature.

The properties of silica are usually adjusted by aftertreatments to fulfill all requirements and to fit all applications. There are hydrophobic and hydrophilic grades, and grades with a broad variation of specific surface and/or particle size distribution.

Silica is chemically inert, soluble only in hydrogen fluoride (HF). The fastness properties are excellent.

Synthetic silica is amorphous, a very important fact. Naturally occurring silica is crystalline and toxicologically harmful. Crystalline silica causes silicosis through inhalation. The MAK value (Maximale Arbeitsplatz Konzentration = maximal allowed concentration of a harmful substance on the workplace; list of harmful products and substances in Germany) of silica dust is limited to 6 mg/m³ of air. The LD₅₀ is > 5000 mg/kg body weight, rat, oral application, and not irritating to skin and mucous membrane.

Talc [$\text{Mg}_6(\text{Si}_8\text{O}_{20})(\text{OH})_4$] – Pigment white 26 / – / CAS 14807.96.6

Properties: This magnesium silicate is chemically inert, very soft, no white pigment, excellent heat stability.

Application: Talc is used mainly to reinforce plastics, similar to glass fiber and chalk. Specially treated types are applied as nucleating agents in polyolefins.

Tin dioxide (SnO_2) – Pigment white 15 / 77861 / CAS 18282.10.5

Tin dioxide occurs in nature as cassiterite (tinstone), which is a very dense (density 6.8–7.1 g/cm³) and hard substance (Mohs hardness 6–7). It is not used as a white pigment, but it plays an important role in the production of the silvery pearlescent pigments. The pearlescent pigments are manufactured by precipitation of titanium dioxide on thin mica platelets. Anatase is formed during the subsequent calcination. This grade of pearlescent pigments shows an insufficient light fastness and weather resistance. If the mica platelets, however, are treated with tin dioxide prior to the precipitation of titanium dioxide, rutile is formed during the calcination. This grade of pearlescent pigments shows a good light fastness and weather resistance. They contain approx. 1–2% tin dioxide.

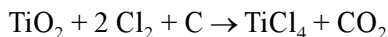
Titanium dioxide (TiO₂) – Pigment white 6 / 77891 / CAS 13463.67.7

Properties: Titanium dioxide dominates the market of white pigments and is the most important inorganic pigment in terms of quantity. Titanium dioxide occurs in nature in the crystal modifications rutile (tetragonal), anatase (tetragonal), and brookite (rhombic). Rutile and anatase are produced industrially in large quantities. Brookite is difficult to produce and therefore it plays no role in the pigment industry. Rutile is the most thermodynamically stable modification and has the most compact atomic structure and therefore the highest density. The density of anatase is approx. 3.9 g/cm³ and that of rutile approx. 4.2 g/cm³. Rutile is the hardest modification with a Mohs hardness of 6.5–7. Anatase is softer, with a Mohs hardness of 5.5–6. Not only are the optical properties of rutile superior to those of anatase (refractive index of rutile is 2.70, of anatase 2.55), but also the light fastness and weather resistance of the rutile modification are superior to those of anatase.

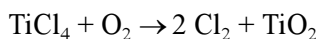
Titanium dioxide pigments are produced by two different processes, the sulfate process and the chloride process. The anatase modification can be produced only by the sulfate process, while the rutile modification is produced by both processes.

Sulfate process is the older of the two processes. Titanium containing raw materials such as the mineral ilmenite (FeTiO₃) or titanium slag is broken down with concentrated sulfuric acid at higher temperatures. In the resulting solution the dissolved Fe³⁺ (of the ilmenite or the titanium slag) must be reduced to Fe²⁺; the solution is then cooled to crystallize the FeSO₄, which is separated by filtration or centrifugation. The reduction of the iron is important, because a trivalent iron sulfate is too soluble in sulfuric acid. The next step is the precipitation of titanium oxide hydrate by hydrolysis, which is filtered off the solution and the filter cake washed several times with water or dilute acid to remove further impurities. To produce specific pigment grades the hydrate must be treated prior to calcination. Depending on the kind and substances of treatment either rutile or anatase is formed during the subsequent calcination.

The *chloride process* requires a concentrated titanium slag. The titanium of the raw material is converted to titanium tetrachloride in a reducing atmosphere at high temperature. The following reaction takes place:



The titanium tetrachloride is first purified by fractional distillation and then combusted with oxygen at high temperature to form titanium dioxide and chlorine.



Because of the high temperature of 900–1400 °C (1652–2552 °F) during the combustion of titanium tetrachloride only the thermodynamically stable rutile modification is formed.

An aftertreatment of the titanium dioxide is essential for its fastness properties. Titanium dioxide absorbs water, and accordingly its surface is saturated by coordinately bonded water, which forms hydroxyl ions. The presence of hydroxyl groups makes photochemical induced reactions possible. The treatment consists of coating each individual pigment particle with colorless inorganic compounds by precipitating them onto the surface. Zirconium (Zr), tin (Sn), aluminum (Al), and silicon (Si) compounds are used as coating, sometimes followed by an additional coating with specific organic compounds [30]. By choosing the right organic compound the final surface can be made either hydrophobic or hydrophilic [31, 32].

The coat prevents direct contact between the plastic matrix and the reactive surface of the titanium dioxide, consequently the light fastness and weather resistance are improved.

Titanium dioxide is inert, insoluble (except in concentrated sulfuric acid and hydrogen fluoride), and very stable. It is regarded as completely nontoxic, which is underlined by its application in tooth paste and in the coat of medical pills.

Application: Rutile, the preferred type, is applied to color nearly all types of plastics, either for pure white shades or for the lightening of colored shades including colors with a good hiding power. There is, however, one restriction. The high hardness of the rutile is disadvantageous in glass fiber reinforced plastics, because the rutile can damage the glass fiber during the coloring process combined with a severe loss of mechanical strength of the final plastic part. In spite of the inferior optical properties the much softer lithopone or zinc sulfide is the white pigment of choice to color glass fiber reinforced plastics.

Another application is for matting of plastic fibers, in this case the anatase modification is preferred because its lower abrasion.

Zinc oxide (Zinc white – ZnO) – Pigment white 4 / – / CAS 1314.13.2

Properties: Zinc oxide is a very fine white powder. The chemical stability is not very good because zinc oxide is amphoteric; it reacts with acids and is soluble in alkaline solutions. This is an disadvantageous in the field of packaging material. The density is approx. 5.67 g/cm³; the Mohs hardness is 4–4.5. The optical properties are inferior to those of titanium dioxide. Zinc oxide is easy to disperse and the light fastness is good.

Zinc oxide is manufactured by two different processes, either by the direct or American process or by the indirect or French process.

The *direct or American process* is a very simple one at low cost. A mixture of coal as reducing agent and zinc oxide containing raw materials or zinc ores are heated up to 1000–1200 °C (1832–2192 °F). Under this condition the zinc oxide (of the raw material) is reduced to metal, which evaporates. The zinc vapor is then oxidized to zinc oxide. The purity of the zinc oxide is determined by the composition of the raw materials used.

The *indirect or French process* starts from metallic zinc, which is boiled and the resulting vapor oxidized to zinc oxide.

Zinc ores are contaminated usually with several other metal oxides, mainly cadmium, lead, iron, and aluminum oxides. Various separation techniques are therefore necessary to purify the zinc vapor before oxidation.

Zinc oxides with different degrees of purity are commercially available; some types still contain a few percent of lead. Before use the colorist should check the quality of the zinc oxide to enable him to fulfill all customer requirements regarding impurities of heavy metals.

Zinc is an essential trace element for humans, animals, and plants. Lack of sufficient zinc causes deficiency diseases, for example, it affects the growth of hair and reproduction.

Zinc oxide is not considered to be toxic or dangerous, although a few early studies showed some toxic effects. These toxic effects were probably the result of impurities, especially of lead, in the zinc oxide used for the studies.

Zinc oxide is insoluble in water and can be separated from waste water rather easily. Because of the toxicity of zinc ions in water to fish and other aquatic living things the concentration of zinc ions in waste water is limited.

Application: The most important use is in the rubber industry and in molding compounds. It plays no important role in coloring of thermoplastic resins.

Zinc sulfide (ZnS) – Pigment white 7 / 77975 / CAS 1314.98.3

Properties: Zinc sulfide is the second most important white pigment after titanium dioxide. The refractive index is 2.37. It is a soft pigment, and the Mohs hardness is 3; therefore the pigment is not very abrasive, which makes it especially suitable for coloring of glass fiber reinforced plastics. The light fastness of zinc sulfide is good but the weather resistance is insufficient. UV radiation in combination with humidity oxidizes zinc sulfide to the colorless zinc sulfate (ZnSO_4) in several plastics. In contrast, however, zinc sulfide improves the light fastness and weather resistance of polyolefins. The use of zinc sulfide in poly(vinyl chloride) (PVC) is restricted depending on the system of stabilization. In lead containing systems zinc sulfide reacts with lead forming the dark lead sulfide.

Because of its low solubility it is harmless in human. Studies have shown there was no case of poisoning or chronic damage to health in the manufacture of this pigment despite exposure to dust during handling of the very finely ground pigment. Zinc sulfide is permitted in contact with food by the US FDA and in most European countries. Soluble zinc, however, is toxic in large amounts, although as the human body requires small quantities for metabolism, zinc belongs to the essential trace elements.

Zinc sulfide is the main component of lithopone, Pigment white 5, and the base of some luminescent pigments. One form of luminescent pigments consists of zinc sulfide doped with silver (Ag) or copper (Cu). This type of effect pigment is described in the chapter on additional inorganic effect pigments.

Application: The optical properties of zinc sulfide are obviously inferior to those of titanium dioxide and therefore its use is restricted. Similar to the use of lithopone, zinc sulfide is applied especially in systems that require a low abrasion of the pigment, and in glass fiber reinforced plastics, because the soft texture of zinc sulfide prevents a mechanical fiber damage during the coloring process. This is the main advantage in comparison to titanium dioxide, which damages the glass fiber of reinforced plastics during extrusion.

Zirconium dioxide (ZrO_2) – Pigment white 12 / 77990

Zirconium dioxide is completely substituted by the superior titanium dioxide. It is used, together with other substances, during the aftertreatment of titanium dioxide to improve the fastness properties of rutile.

5.1.2 Black Pigments

Similar to the role of titanium dioxide for white shades, carbon black dominates the market for black shades. Black pigments are used either for pure black shades or for darkening of colored shades. Strictly considered there are only three basic formulas of black inorganic pigments: carbon black (Pigment black 7), iron oxide black (Pigment black 11) and iron titanium brown (Pigment black 12). The other black pigments, Pigment black 22, and Pigment black 26 through 30, are variations of iron oxide black, Fe_3O_4 , (Pigment black 11). In these pigments the iron is partly substituted by other metals such as copper (Cu), manganese (Mn), chromium (Cr), cobalt (Co), and nickel (Ni), either alone or in combination (Table 5.3).

Carbon black (C) – Pigment black 7 / 77266 / CAS 1333.86.4

Properties: Carbon black, pure carbon, is a very fine pigment with a very high tinting strength. Carbon black is classified as an inorganic pigment, for example,

in the German standard DIN 55944, in spite of the fact that carbon is one of the main components in the whole of organic chemistry [23].

Table 5.3: List of Black Pigments for Coloring of Plastics

Product	Formula	Color Index Number
Carbon black	C	Pigment black 7
Iron oxide black	Fe_3O_4	Pigment black 11
Iron titanium brown spinel	Fe_2TiO_4	Pigment black 12
Copper iron chromite black	$\text{Cu}(\text{Cr},\text{Fe})_2\text{O}_4$	Pigment black 22
Manganese ferrite black spinel	$(\text{Fe},\text{Mn})_2\text{O}_4$	Pigment black 26
Iron cobalt chromite black spinel	$(\text{Co},\text{Fe})(\text{Fe},\text{Cr})_2\text{O}_4$	Pigment black 27
Copper chromite black spinel	$\text{Cu}(\text{Cr},\text{Fe})_2\text{O}_4$	Pigment black 28
Iron cobalt black spinel	$(\text{Fe},\text{Co})\text{Fe}_2\text{O}_4$	Pigment black 29
Chrome iron nickel black spinel	$(\text{Ni},\text{Fe})(\text{Cr},\text{Fe})_2\text{O}_4$	Pigment black 30

Carbon black is manufactured by several production processes. The most important are the furnace black process and the channel black process; other processes of less importance are the lamp black process, the thermal black process, and the acetylene black process. They differ in technical details and the raw materials used. Most common are gaseous (natural gas) or liquid hydrocarbons (oil). The basis of all processes is a partial combustion of hydrocarbons.

The properties of carbon black are determined by the particle size distribution, the structure (coalescence of primary particle into aggregates), the specific surface area and the chemical composition of the pigment surface [34, 35].

The *primary particle size* of carbon black is in the range of 10–300 nm, it is a very fine grained pigment.

The *specific surface area* varies widely. A coarse grade of carbon black has a specific surface area as small as $10\text{m}^2/\text{g}$, while the finest grades can have a specific surface area as large as $1200\text{m}^2/\text{g}$. During the handling of very fine grades of carbon black it is necessary to take precautions. One aspect is to avoid a heavy soiling of the workers, machines, and the surroundings by the fine dust, and another involves wetting problems during incorporation in a polymer melt. Very fine carbon black is difficult to wet with the polymer melt, as this requires not only very effective dispersing agents but also a high shear during incorporation. Only in the case of a complete dispersal is it possible to make the most of the full color depth of carbon black, which is an important feature when carbon black is

used to darken a colored shade in addition to maintaining consistency of the exact shade from production to production. The color depth of carbon black increases with decreasing particle size. On the other hand, a coarser carbon black is easier to disperse in a polymer melt than a very fine grade. In the case of dispersal problems it may be advisable to use a coarser carbon black. Although the color depth of a coarser carbon is lower the visual impression is a higher color depth because of the more complete dispersion. The dependencies of typical properties of carbon black on the particle size are shown in Fig. 5.1.

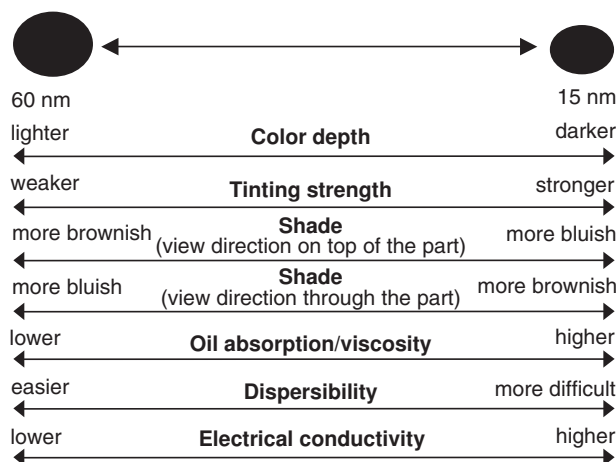


Figure 5.1: Dependencies of typical properties of carbon black on the particle size

As mentioned previously the color depth of carbon black increases with decreasing particle size. At constant concentration the number of pigment particles increases at the same time, which results in a higher light absorption and less scattering. The absorption rate of very fine grades of carbon black can reach nearly 99.5%, which is a very “deep” black. Consequently a coarser carbon black absorbs less light and is scattered more; the visual impression is that of a “lighter” black. The bluish or brownish tone of carbon black is the result of this interaction between light absorption and light scattering, which depends on the particle size. Whether a bluish or brownish tone is noticeable depends on the angle of vision. A bluish tone appears when looking through a transparent part, colored with a coarse carbon black, and the brownish tone appears when looking on top of the surface of the same part. In case of a very fine grade of carbon black it is the reverse.

The exact shade depends not only on the particle size but also on its *structure*. During the production process the primary particles of carbon black, almost

spherically shaped, coalesce into aggregates in the form of chains or clusters. The type of aggregates is called the structure of carbon black.

The dependence of some typical properties of carbon black on the structure is shown in Fig. 5.2.

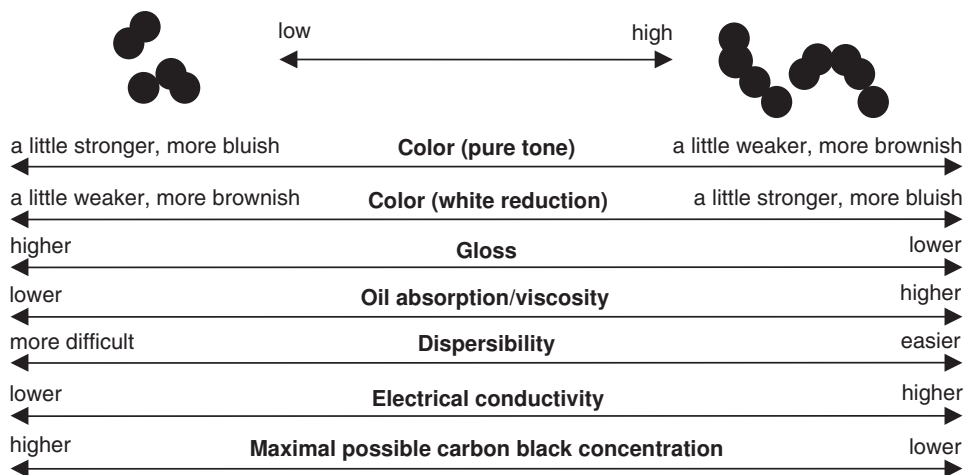


Figure 5.2: Dependence of some typical properties of carbon black on its structure

Carbon black is manufactured by a partial combustion of hydrocarbons; therefore the surface of the particles contains oxygen, bound to the surface in the form of acidic or basic functional groups. The amount of surface oxides and their composition depends on the production process and the raw material. The amount of surface oxides can be increased by an oxidative aftertreatment. The structure and number of oxygen-containing functional groups on the surface of carbon blacks influence the application properties. The chemical composition of the carbon black surface is called *surface chemistry*.

Many polymers are degraded by UV radiation under atmospheric conditions. In those plastics, especially in polyolefins, carbon black acts as a stabilizer by absorbing the UV radiation. The stabilizing action of carbon black increases with decreasing particle size and with increasing concentration up to approx. 2–3%. A medium-fine and highly structured grade of carbon black is the preferred grade for such an application.

Another property of carbon black is its electrical conductivity. Depending on the requirements the plastic part has to fulfill, this electrical conductivity is either dis-

ruptive or required. The electrical conductivity depends on the type of production process, as well as on the specific surface area and structure, and of course on the concentration of carbon black in the finished part. If required, special grades of carbon black are marketed to lend polymers antistatic or electrically conductive properties. The necessary concentrations, however, are much higher than usually applied for the coloring of polymers.

Every substance with a very high specific surface area adsorbs larger amounts of gaseous or liquid components. Grades of carbon black with a large specific surface area have a remarkable adsorption capacity for solvents, binders, polymers, and additives; therefore interactions cannot be excluded. The adsorption of stabilizer or antioxidants can cause problems in polymer systems, such as a reduced light fastness or weather resistance. The adsorption of dispersing agents leads to problems regarding wetting and dispersing of carbon black, and an adsorption of the polymer melt increases its viscosity. In rubber carbon black can influence the speed of vulcanization.

In Fig. 5.3 is shown how a combination of particle size and structure influences the properties of a finished part.

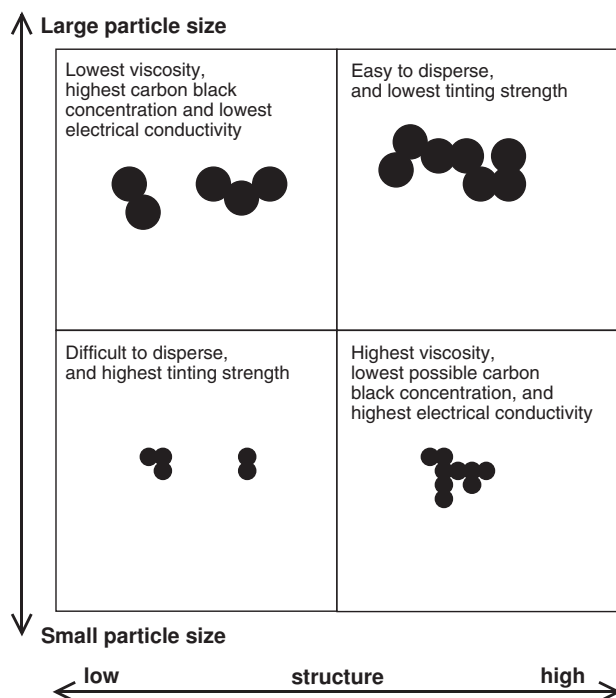


Figure 5.3: Dependence of properties on the combination of particle size and structure of carbon black

The LD₅₀ of carbon black is > 5 000 mg/kg body weight, rat, oral application, it is not irritating to the skin or mucous membranes. Carbon black is used to color household article, toys, packaging material, and so forth. The legal requirements regarding purity of the carbon black differ from country to country. The main aspect is the content of polycyclic aromatic hydrocarbons as impurities, evaluated by an extraction with toluene. A special grade of carbon black has been approved by the US FDA for plastic articles in contact with food.

Application: More than 90% of the total amount of the carbon black produced is used as reinforcing filler in rubber for tires and other technical rubber goods. The use as colorant is approx. 2–4% of the produced quantity, nevertheless this is a large quantity considering that the yearly production is about 6 million tons of carbon black.

In comparison to carbon black the *other black pigments* play no important role in coloring of plastics. Their main disadvantage is the low tinting strength. They are used if carbon black cannot be used for any reason or for tinted shades. Generally considered, for the tinting of a color only very small amounts of a colorant are necessary, and on the other hand a very even distribution of a small quantity in a larger mixture is difficult to achieve. In such a case a low tinting strength can even be an advantage. If such a pigment is used for tinting, the necessary quantity increases and mixing problems decrease. In addition, these other black pigments, based on metal oxides, are much easier to disperse in a polymer melt than carbon black.

The heat stability of these pigments is very good with the exception of iron oxide black, which is oxidized (to red iron oxide) at temperatures above 250 °C (482 °F). The light fastness and weather resistance are good. They are insoluble and chemically inert.

Iron oxide black (Fe₃O₄) – Pigment black 11 / – / CAS 1317.61.9

Iron oxide black occurs in nature in the form of the mineral magnetite. At present, the natural material cannot be used as a colorant because of impurities. In prehistoric times it was used, together with other minerals, for rock and cave paintings.

Iron oxide black is synthesized by oxidation of iron and is a mixture of Fe²⁺ and Fe³⁺ oxide. The divalent iron (Fe²⁺) is sensitive to oxygen, and is easily oxidized to the trivalent iron (Fe³⁺). The heat stability of iron oxide black is therefore limited to about 250 °C (482 °F).

Iron titanium brown spinel (Fe_2TiO_4) – Pigment black 12 / 77543 / CAS 68187.02.0

This pigment is produced by high-temperature calcination of iron oxide (FeO) and titanium dioxide (TiO_2). As a modifier it may contain one or a combination of the following oxides: Al_2O_3 , CoO, Cr_2O_3 , Fe_2O_3 , MnO, or ZnO [33]. The color varies between brown, dark brown, and brownish black, depending on the kind and quantity of the modifier. Crystal modification: spinel.

Copper iron chromite black [$\text{Cu}(\text{Cr},\text{Fe})_2\text{O}_4$] – Pigment black 22 / 77429 / CAS 55353.02.1

This pigment is produced by high-temperature calcination. The metals copper and chromium are ionically interdiffused in the crystalline matrix of spinel, therefore copper and chromium lose their own typical chemical, physical, and physiological properties.

Manganese ferrite black spinel [$(\text{Fe},\text{Mn})(\text{Fe},\text{Mn})_2\text{O}_4$] – Pigment black 26 / 77494 / CAS 68186.94.7

This pigment is the reaction product of high-temperature calcination of manganese (II) oxide (MnO), manganese (III) oxide (Mn_2O_3), iron (II) oxide (FeO), and iron (III) oxide (Fe_2O_3). As a modifier it may contain one or a combination of the following oxides: Al_2O_3 , CoO, CuO, NiO, SiO_2 , or TiO_2 [33]. Crystal modification: spinel.

Iron cobalt chromite black spinel [$(\text{Co},\text{Fe})(\text{Fe},\text{Cr})_2\text{O}_4$] – Pigment black 27 / 77502 / CAS 68186.97.0

Produced by high-temperature calcination of iron (II) oxide (FeO), cobalt (II) oxide (CoO), iron (III) oxide (Fe_2O_3), and chromium (III) oxide (Cr_2O_3). As a modifier it may contain one or a combination of the following oxides: Al_2O_3 , B_2O_3 , CuO, MnO, NiO, or SiO_2 [33]. Crystal modification: spinel.

Copper chromite black spinel [$\text{Cu}(\text{Cr},\text{Fe})_2\text{O}_4$] – Pigment black 28 / 77428 / CAS 68186.91.4

This pigment is the reaction product of high-temperature calcination of copper (II) oxide (CuO) and chromium (III) oxide (Cr_2O_3). Many grades contain iron (III) oxide (Fe_2O_3) as a modifier.

Iron cobalt black spinel [$(\text{Fe},\text{Co})\text{Fe}_2\text{O}_4$] – Pigment black 29 / 77498 / CAS 68187.50.8

Produced by high-temperature calcination of iron (II) oxide (FeO), cobalt (II) oxide (CoO), and iron (III) oxide (Fe_2O_3). As a modifier it may contain one or a

combination of the following oxides: Al_2O_3 , B_2O_3 , MnO , NiO , or SiO_2 [33]. Crystal modification: spinel.

Chrome iron nickel black spinel $[(\text{Ni},\text{Fe})(\text{Cr},\text{Fe})_2\text{O}_4]$ – Pigment black 30 / 77504 / CAS 71631.15.7

This pigment is the reaction product of high-temperature calcination of chromium (III) oxide (Cr_2O_3), iron (II) oxide, iron (III) oxide, and nickel (II) oxide in varying amounts. Several grades are marketed. As a modifier it may contain CuO , MnO , or Mn_2O_3 [33]. Crystal modification: spinel.

5.1.3 Colored Pigments

The most colored inorganic pigments are complex mixed metal oxides. They can be classified according to various aspects, based on either coloristic or on chemical considerations. In contrast to the organic pigments, the properties of which depend on their chemistry to a large extent, this is not noticeable in the case of inorganic pigments. The classification scheme for inorganic colored pigments therefore follows coloristic considerations.

5.1.3.1 Blue Pigments

Chemically considered there are only three inorganic blue pigments: ultramarine blue (Pigment blue 29), cobalt tin blue-gray spinel (Pigment blue 35), and cobalt aluminate blue spinel (Pigment blue 28). The other three pigments (Pigment blue 36:1, blue 36, and blue 72) are modification of Pigment blue 28, in which parts of the cobalt are substituted either alone or in combination with chromium and zinc. These variations differ in their tinting strength and color shade (Table 5.4).

Table 5.4: List of Inorganic Blue Pigments

Product	Formula	Color index number
Cobalt aluminate blue spinel	CoAl_2O_4	Pigment blue 28
Ultramarine blue	$\text{Na}_{6-8}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_n$ ($n = 2-4$)	Pigment blue 29
Cobalt tin blue-gray spinel	Co_2SnO_4	Pigment blue 35
Cobalt chromite blue-green spinel	$\text{Co}(\text{Al},\text{Cr})_2\text{O}_4$	Pigment blue 36
Zinc chrome cobalt aluminum spinel	$(\text{Zn},\text{Co})(\text{Cr},\text{Al})_2\text{O}_4$	Pigment blue 36:1
Cobalt zinc aluminate blue spinel	$(\text{Co},\text{Zn})\text{Al}_2\text{O}_4$	Pigment blue 72

Cobalt aluminate blue spinel (CoAl_2O_4) – Pigment blue 28 / 77346 / CAS 68186.86.7

Cobalt chromite blue-green spinel [$\text{Co}(\text{Al},\text{Cr})_2\text{O}_4$] – Pigment blue 36 / 77343 / CAS 68187.11.1

Zinc chrome cobalt aluminum spinel [$(\text{Zn},\text{Co})(\text{Cr},\text{Al})_2\text{O}_4$] – Pigment blue 36:1 / 77343:1 / CAS 74665.01.3

Cobalt zinc aluminate blue spinel [$(\text{Co},\text{Zn})\text{Al}_2\text{O}_4$] – Pigment blue 72 / 77347 / CAS 68186.87.8

Properties: These four pigments can be summarized because they have the same chemical basis. The basic product, Pigment blue 28, is produced by high-temperature calcination of cobalt (II) oxid (CoO) and aluminum oxide (Al_2O_3). The other variations are produced by a partial substitution of the cobalt by chromium and zinc, either alone or in combination. According to the literature [33] each single pigment can be modified additionally by other metal oxides. The result is a large variety of marketed products. These blue pigments differ in their tinting strength and shades (reddish or greenish blue) depending on the exact chemical composition.

All of them form the crystalline modification of spinel during calcination. They are chemically inert, absolutely insoluble, have a good hiding power and an excellent heat stability, show very good light fastness and weather resistance, and they do not cause warpage in partially crystalline polymers. All toxicological studies showed no signs of toxicity to humans or the environment [5, 29].

In this connection something else should be mentioned. In Germany as well as in some other countries *cobalt as metal, as cobalt oxide or cobalt sulfide* are classified as carcinogenic, for example, in Germany by the “Gefahrstoffverordnung” (dangerous goods ordinance) dated August 16, 1986. The cobalt, however, is incorporated into the crystal lattice of spinel so tightly that it completely loses its typical chemical, physical, and physiological properties. Several toxicological studies proved this [29], and there are no signs of any toxicological or carcinogenic effects. These cobalt-containing blue pigments are consequently not considered as *hardly soluble cobalt compounds* in the sense of this ordinance. This statement is important because many customer requirements prohibit any colorants containing cobalt.

Application: The main use is for light blue colors or pastel shades.

Ultramarine blue ($\text{Na}_{6-8}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_n$) – Pigment blue 29 / 77007 / CAS 57455.37.5

Properties: Ultramarine blue is the most frequently used blue inorganic pigment. The mineral lazurite is chemically very closely related to ultramarine blue, a rock rich in lazurite called lapis lazuli, a semiprecious stone. Powdered lazurite was once the source for the pigment ultramarine. Today it is synthesized by a multistage process. The raw materials are china clay, feldspar, anhydrous sodium carbonate, sulfur, and a reducing agent (oil or coal). The first step is the activation of the clay by heating up to about 700 °C (1292 °F). Then the activated clay is blended with the other raw materials and heated to about 750 °C (1382 °F) under reducing conditions. At this stage the sodium carbonate reacts with the sulfur and in combination with the reducing agent sodium polysulfides are formed. Finally the “raw” ultramarine is purified from byproducts and refined. The refinement is of special importance because the content of free sulfur should be below 5 ppm, otherwise the typical “sulfur smell” occurs during the processing of plastics colored with ultramarine.

The forming of the two sulfur groups S_3^- and S_2^- is responsible for the color. Both groups show the character of a radical, stabilized by lattice entrapment.

Violet ultramarine is produced by heating the blue grade with ammonium chloride at approx. 240 °C (464 °F) in the presence of air. Treating the violet grade with hydrogen chloride (HCl) gas at 140 °C (284 °F) gives the *pink* ultramarine.

Consequently synthetic ultramarine is commercially available in three colors:

- Reddish blue ultramarine – Pigment blue 29 / 77007 / CAS 57455.37.5
- Violet ultramarine – Pigment violet 15 / 77007 / CAS 12769.96.9
- Pink ultramarine – Pigment red 259 / 77007 / CAS 12769.96.9

The color of ultramarine blue is a reddish blue with high tinting strength. Ultramarine blue is insoluble, most grades are easy to disperse in polymer melts, it has a good heat stability, shows a good light fastness and weather resistance, and causes no warpage in partially crystalline polymers [36]. The normal grades of ultramarine blue are sensitive to acids. Acid-resistant grades are coated by silica and are commercially available. The density is 2.35 g/cm³. The ultramarine particles are hard and can cause abrasion.

Ultramarine is safe, and the only known hazard is the evolution of the (poisonous) hydrogen sulfide in contact with acid. The LD₅₀ is > 10,000 mg/kg body weight, rat, oral application; it is nonmutagenic, nonirritant, and nonsensitizing to skin. Because of its insolubility it is not toxic to fish.

Application: Ultramarine blue can be used to color any polymer. In the case of packaging material it is recommended to check the storage stability, because

interactions between the pigment and the filling good cannot be excluded always. This depends on the composition of the filling good.

Cobalt tin blue-gray spinel (Co_2SnO_4) – Pigment blue 35 / 77368 / CAS 68187.05.3

This pigment is produced by high-temperature calcination of cobalt (II) oxide and tin (IV) oxide. It may contain as modifier for the shade Al_2O_3 , Fe_2O_3 , or NiO [33]. Crystal modification: spinel. Its main use is for coloring of ceramic glazes, and is very seldom used in plastics.

5.1.3.2 Brown Pigments

There are numerous brown inorganic pigments on the market. The large number of brown pigments, however, can be synthesized by three processes:

- The rutile crystal lattice (TiO_2) is modified by incorporation of color giving metals such as chromium, nickel, or manganese and to maintain the valence of four the colorless antimony, niobium, or tungsten. The results are yellowish or brownish color shades. Depending on the exact chemical composition they are listed in the color index either as yellow or brown pigment. Figure 5.4 contains the pigments produced according to this principle, and for the purpose of completeness the yellow and brown pigments are listed together.
- The brownish red shade of iron (III) oxide (Fe_2O_3) can be shifted into a dark brown by a partial substitution of the iron by other metals, for example, chromium, manganese, or zinc.
- The result of a partial replacement of chromium by iron, zinc, or manganese (either alone or in combination) in chromium (III) oxide (Cr_2O_3) is a color shift from a dull green to a dark brown.

All these pigments differ in color, color shade, and tinting strength. They are absolutely insoluble, chemically inert, have excellent heat stability, show good light fastness and weather resistance, and do not cause any warpage in partially crystalline polymers. By the incorporation in the host crystal lattice the metals lose their typical chemical, physical, and physiological properties. This is important in the case of the metal oxides of antimony and nickel, which are harmful. The chromium is in the trivalent stage, which is – in contrast to chromium-VI – harmless.

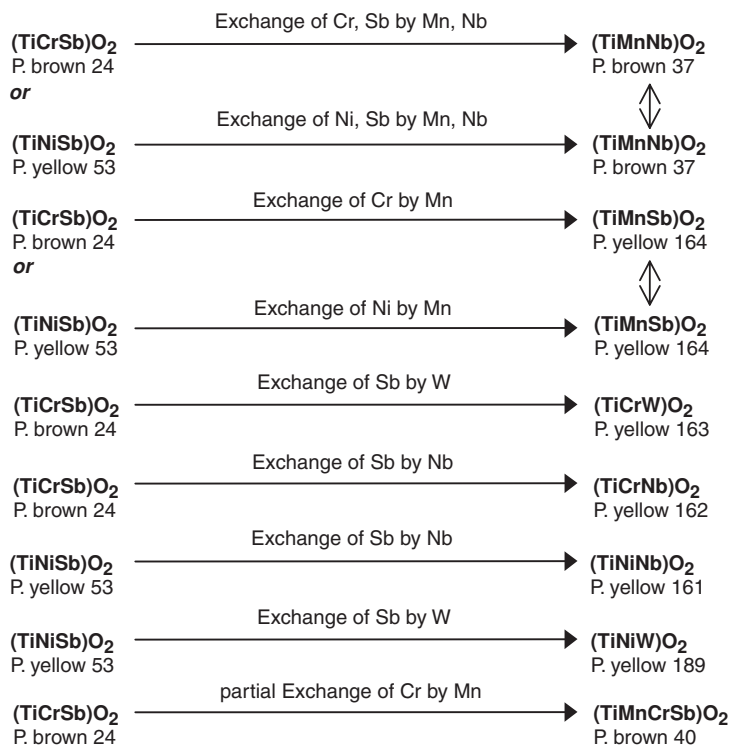


Figure 5.4: Principle of synthesis of inorganic yellow and brown mixed metal oxide pigments

In the past this type of pigment was called a *mixed metal oxide pigment*. This term is misleading, because it is not a mixture in the true sense of the word but is a homogeneous incorporation of colored cations in the crystal lattice. The American Dry Color Manufacturers' Association denotes these colorants now as *complex inorganic color pigments* [33], a term that describes this type of pigment more accurately.

On the other hand intensive brown colors can be achieved by mixing of red and black colorants. Whether it is more favorable to use a brown pigment or a mixture of red and black colorants depends on the shade to be matched. In practice both methods are common.

The commercially available brown pigments for coloring of plastics are listed in Table 5.5.

Table 5.5: List of Inorganic Brown Pigments

Product	Formula	Color index number
Chrome antimony titanium buff rutile	$(\text{Ti,Cr,Sb})\text{O}_2$	Pigment brown 24
Iron chrome oxide	$(\text{Fe,Cr})_2\text{O}_3$	Pigment brown 29
Zinc iron chromite brown spinel	$(\text{Zn,Fe})(\text{Fe,Cr})_2\text{O}_4$	Pigment brown 33
Iron chromite brown spinel	$\text{Fe}(\text{Fe,Cr})_2\text{O}_4$	Pigment brown 35
Manganese niobium titanium brown rutile	$(\text{Ti,Mn,Nb})\text{O}_2$	Pigment brown 37
Chrome manganese zinc brown spinel	$(\text{Zn,Mn})\text{Cr}_2\text{O}_4$	Pigment brown 39
Manganese chrome antimony titanium brown rutile	$(\text{Ti,Mn,Cr,Sb})\text{O}_2$	Pigment brown 40
Iron manganese oxide	$(\text{Fe,Mn})_2\text{O}_3$	Pigment brown 43

Chrome antimony titanium buff rutile $[(\text{Ti,Cr,Sb})\text{O}_2]$ – Pigment brown 24 / 77310 / CAS 68186.90.3

Properties: This pigment is produced by a high-temperature calcination of titanium dioxide (TiO_2), chromium (III) oxide (Cr_2O_3), and antimony (V) oxide (Sb_2O_5) in varying amounts. The chromium cation is responsible for the color shift from the white of the titanium dioxide to this yellow-brown, and the colorless antimony is used to maintain the valence of four. Both metals are incorporated in the crystal matrix of rutile, and at the same time they lose their own typical properties [28, 38]. This is important for antimony because antimony oxide is classified as carcinogenic. This pigment is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are excellent.

All studies showed no toxicological effects [38], and it is considered to be safe in handling and use. Nevertheless the usual precautionary methods for handling of fine powders should be applied to avoid a drying out of the skin, which may open the way for other skin diseases.

Application: Can be used in any type of polymer.

Iron chrome oxide $[(\text{Fe,Cr})_2\text{O}_3]$ – Pigment brown 29 / 77500 / CAS 12737.27.8

Properties: This pigment is produced by a high temperature calcination of chromium (III) oxide (Cr_2O_3) and iron (III) oxide (Fe_2O_3) in varying amounts. It is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are excellent.

Application: Can be used in any type of polymer.

Zinc iron chromite brown spinel $[(\text{Zn},\text{Fe})(\text{Fe},\text{Cr})_2\text{O}_4]$ – Pigment brown 33 / 77503 / CAS 68186.88.9

Properties: This spinel is produced by a high-temperature calcination of zinc oxide (ZnO), iron (II) oxide (FeO), iron (III) oxide (Fe_2O_3), and chromium (III) oxide (Cr_2O_3) in varying amounts [33]. Numerous grades of this pigment are the result of this variation in composition, differing in shade.

This pigment is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

Application: Can be used in any type of polymer.

Iron chromite brown spinel $[\text{Fe}(\text{Fe},\text{Cr})_2\text{O}_4]$ – Pigment brown 35 / 77501 / CAS 38187.09.7

Properties: This pigment is produced by a high-temperature calcination of iron (II) oxide (FeO), iron (III) oxide (Fe_2O_3), and chromium (III) oxide (Cr_2O_3) in varying amounts. It forms the crystal matrix of a spinel. Chemically it could be considered as Pigment brown 33 without zinc.

This pigment is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

Application: Can be used in any type of polymer.

Manganese niobium titanium brown rutile $[(\text{Ti},\text{Mn},\text{Nb})\text{O}_2]$ – Pigment brown 37 / 77890 / CAS 70248.09.8

Properties: This pigment is one of the variations of Pigment brown 24 or yellow 53 (refer to Fig. 5.4). Chromium or nickel are substituted by manganese and antimony by niobium. Crystal matrix: Rutile.

This pigment is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

Application: Can be used in any type of polymer.

Chrome manganese zinc brown spinel $[(\text{Zn},\text{Mn})\text{Cr}_2\text{O}_4]$ – Pigment brown 39 / 77312 / CAS 71750.83.9

Properties: It is produced by high-temperature calcination of chromium (III) oxide (Cr_2O_3), manganese (II) oxide (MnO), and zinc (II) oxide (ZnO) by varying amounts. Spinel. Chemically it may be considered as a kind of variation of Pigment brown 33.

This pigment is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

Application: Can be used in any type of polymer.

Manganese chrome antimony titanium brown rutile $[(\text{Ti}, \text{Mn}, \text{Cr}, \text{Sb})\text{O}_2]$ –
Pigment brown 40 / 77891 / CAS 69991.68.0

This pigment is closely related to Pigment brown 24 and is the result of a partial substitution of chromium by manganese (refer to Fig. 5.4). The properties and use are similar to those of Pigment brown 24.

Iron manganese oxide $[(\text{Fe}, \text{Mn})_2\text{O}_3]$ – *Pigment brown 43* / 77536 /
 CAS 12062.81.6

Properties: This pigment can be considered as a variation of Pigment red 101, Fe_2O_3 . By a partial substitution of iron by manganese the color is shifted from a brownish red to brown. This pigment is insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good. The LD_{50} is > 5000 mg/kg body weight, rat, oral application, and it is not irritating the skin or mucous membrane.

Application: Can be used in any type of polymer. It is recommended, however, to check the grade for soluble manganese ions, because soluble manganese may accelerate the aging of polypropylene.

5.1.3.3 Yellow Pigments

In the past the color yellow was dominated by lead chromate (Pigment yellow 34) and the cadmium pigments (Pigment yellow 35 and yellow 37). Because of toxicological considerations the use of these pigments was banned by several regulations.

Lead chromate is chronically toxic; therefore in the European community it is classified as *category one substance*, which means any part containing more than 0.5% lead must be labeled with the death's head indicating a poison [21].

Guideline EU 91/338 of the European Community bans the use of cadmium pigments in many plastic materials, which are listed in detail. The list includes most of the plastics usually used for packaging material or household goods [39]. For safety reasons, cadmium pigments can be used only if absolutely required.

The use of cadmium, without naming these pigments, is in fact banned by the CONEG-regulation (USA) and the European guideline EU 94/62 in any packaging material in contact with food. These two guidelines limit the total amount of cadmium, lead, chromium (VI), and mercury to 100 ppm in 1 kg (2.2 lb) of the plastic packaging material. This limiting value is far below the concentration required for tinting of plastics. The origin of traces of these elements consequently can be only as impurities of (mainly inorganic) pigments.

As a result of this ban many colors had to be matched anew. The alternative color preparations no longer showed the same properties, such as hiding power and/or fastness properties. In addition the colorist was forced to use organic pigments, which are significantly more expensive than the previously used cadmium and lead pigments. All this caused much work and many discussions with the customer, but finally all problems were solved.

The greenish yellow bismuth vanadate molybdate (Pigment yellow 184) can be considered as a kind of replacement because its coloristic properties resemble those of the cadmium and lead pigments.

The inorganic yellow pigments for coloring of plastics are listed in Table 5.6. For the purpose of completeness the banned cadmium and lead pigments are mentioned also, and in addition it is noticeable that several pigments are variations of Pigment brown 24 or Pigment yellow 53 (refer to Fig. 5.4).

Table 5.6: List of Inorganic Yellow Pigments for Coloring of Plastics

Product	Formula	Color index number
Lead chromate	$\text{Pb}(\text{Cr,S})\text{O}_4$	Pigment yellow 34
Cadmium yellow	CdS	Pigment yellow 35
Cadmium yellow	$(\text{Cd,Zn})\text{S}$	Pigment yellow 37
Iron oxide yellow	$\alpha\text{- or } \gamma\text{-FeO}(\text{OH})$	Pigment yellow 42
Nickel antimony titanium yellow rutile	$(\text{Ti,Ni,Sb})\text{O}_2$	Pigment yellow 53
Zinc ferrite brown spinel	ZnFe_2O_4	Pigment yellow 119
Nickel barium titanium primrose priderite	$2\text{NiO} \cdot 3\text{BaO} \cdot 17\text{TiO}_2$	Pigment yellow 157
Nickel niobium titanium yellow rutile	$(\text{Ti,Ni,Nb})\text{O}_2$	Pigment yellow 161
Chrome niobium titanium buff rutile	$(\text{Ti,Cr,Nb})\text{O}_2$	Pigment yellow 162
Chrome tungsten titanium buff rutile	$(\text{Ti,Cr,W})\text{O}_2$	Pigment yellow 163
Manganese antimony titanium buff rutile	$(\text{Ti,Mn,Sb})\text{O}_2$	Pigment yellow 164
Bismuth vanadate molybdate	$\text{BiVO}_4 / \text{Bi}_2\text{MoO}_6$	Pigment yellow 184
Nickel tungsten yellow rutile	$(\text{Ti,Ni,W})\text{O}_2$	Pigment yellow 189

Lead chromate [$\text{Pb}(\text{Cr,S})\text{O}_4$] – Pigment yellow 34 / 77603 / CAS 1344.37.2

No longer used.

Cadmium yellow [CdS respectively $(\text{Cd,Zn})\text{S}$] – Pigment yellow 35 respectively yellow 37

No longer used.

Iron oxide yellow [α - or γ -FeO(OH)] – Pigment yellow 42 / 77492 / CAS 20344.49.4

Properties: α -FeO(OH) occurs in nature in the form of the mineral goethite and γ -FeO(OH) as lepidocrocite. They differ in their crystal lattices. These iron oxides are synthesized by precipitation and oxidation. The starting material is iron (II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), a byproduct of the titanium dioxide production (sulfate process) or from other sources. The solution of the iron salt is first mixed with alkali and then oxidized, usually with air. The total amount of alkali, reaction time, and temperature are controlled very carefully. This method is one of several processes that yield the yellow pigment α -FeO(OH).

This pigment has limited heat stability, because at higher temperatures it loses water forming the red iron (III) oxide Fe_2O_3 . To improve heat stability, the pigment is coated by a mixture of aluminum and silicon oxides. Such a coated, stabilized pigment shows a heat stability of approx. 260 °C (500 °F), while the heat stability of the unstabilized grade is only approx. 200 °C (392 °F).

Application: The use of this pigment for coloring of plastics is very limited because of the unusual low heat stability of an inorganic pigment. It can be used to color PE-LD or other polymers with similar low processing temperatures.

Nickel antimony titanium yellow rutile [(Ti,Ni,Sb)O₂] – Pigment yellow 53 / 77788 / CAS 71077.18.4

Properties: This pigment is produced by high temperature calcination of titanium dioxide (TiO_2), nickel (II) oxide (NiO), and antimony (V) oxide (Sb_2O_5). It can be considered as base material for other yellow pigments, which are produced by substitution of nickel and/or antimony by other metals (refer to Fig. 5.4).

This pigment is absolutely insoluble and chemically inert, shows a good hiding power, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

The LD_{50} is higher than 5000 mg/kg body weight, rat, oral application, and it does not irritate the skin or mucous membrane [38].

In this connection something else should be mentioned. In Germany but also in some other countries *nickel as metal, as nickel oxide, or as nickel sulfide* is classified as carcinogenic, for example, in Germany by the “Gefahrstoffverordnung” (dangerous goods ordinance) dated August 16, 1986. In addition, nickel is known to be allergenic. The nickel, however, is incorporated into the crystal lattice of rutile so tightly that it completely loses its typical chemical, physical, and physiological properties. Several toxicological studies proved this [28, 29, 38], there are no sign of any toxicological or carcinogenic effects. These nickel-containing

pigments are consequently not considered as *hardly soluble nickel compound* in the sense of this ordinance. This statement is important because many customer requirements prohibit any colorants containing nickel.

Application: Can be used in any type of polymer.

Zinc ferrite brown spinel [(Zn,Fe)Fe₂O₄] – Pigment yellow 119 / 77496 / CAS 68187.51.9

Properties: This pigment is produced by high-temperature calcination of zinc oxide (ZnO), iron (II) oxide (FeO), and iron (III) oxide (Fe₂O₃) in varying amounts. As modifier it may contain in addition Al₂O₃, In₂O₃, NiO, SiO₂, or TiO₂ [33]. Crystal matrix: Spinel.

This pigment is absolutely insoluble and chemically inert, shows a good hiding power, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

The LD₅₀ is higher than 2000 mg/kg body weight, rat, oral application, and it does not irritate the skin or mucous membrane [5].

Nickel barium titanium primrose priderite (2NiO·3BaO·17TiO₂) – Pigment yellow 157 / 77900 / CAS 68610.24.2

Properties: This pigment is produced by high-temperature calcination of nickel oxide (NiO), barium oxide (BaO), and titanium oxide (TiO₂) in varying amounts. Crystal matrix: Priderite.

This pigment is absolutely insoluble and chemically inert, shows a good hiding power, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

Application: Can be used in any type of polymer.

The following five yellow pigments can be considered as variations of Pigment brown 24 and/or Pigment yellow 53. They are the result of a partial or complete substitution of the coloring metals chromium, nickel, or antimony, which is necessary to maintain the valence of four, by other metals (refer to Fig. 5.4). These pigments differ in their shades and tinting strength. All pigments form the crystal matrix of rutile. All other properties are very similar and comparable to Pigment brown 24 and Pigment yellow 53.

Nickel niobium titanium yellow rutile [(Ti,Ni,Nb)O₂] – Pigment yellow 161 / 77895 / CAS 68611.43.8

In this pigment the antimony of Pigment yellow 53 is substituted by niobium. Its tinting strength is slightly higher than those of Pigment yellow 53.

Chrome niobium titanium buff rutile $[(\text{Ti,Cr,Nb})\text{O}_2]$ – Pigment yellow 162 / 77896 / CAS 68611.42.7

In this pigment the antimony of Pigment brown 24 is substituted by niobium.

Chrome tungsten titanium buff rutile $[(\text{Ti,Cr,W})\text{O}_2]$ – Pigment yellow 163 / 77897 / CAS 68186.92.5

In this pigment the antimony of Pigment brown 24 is substituted by tungsten.

Manganese antimony titanium buff rutile $[(\text{Ti,Mn,Sb})\text{O}_2]$ – Pigment yellow 164 / 77899 / CAS 68412.38.4

The substitution of the coloring metal chromium (Pigment brown 24) or nickel (Pigment yellow 53) by manganese leads to this pigment.

Nickel tungsten yellow rutile $[(\text{Ti,Ni,W})\text{O}_2]$ – Pigment yellow 189 / 77902 / CAS 69011.05.8

In this pigment the antimony of Pigment yellow 53 is substituted by tungsten.

Bismuth vanadate molybdate $(\text{BiVO}_4/\text{Bi}_2\text{MoO}_6)$ – Pigment yellow 184 / – / CAS 14059.33.7

Properties: Two types of pigments are marketed commercially. The composition varies between a modified BiVO_4 and a two-phase pigment bismuth vanadate molybdate, $4\text{BiVO}_4 \cdot 3\text{Bi}_2\text{MoO}_6$, depending on the supplier. The grades for coloring of plastics are stabilized by coating mainly with silicates but also in combination with other inorganic oxides (boron, aluminum, and zinc oxides). These oxides form a glasslike coat, which improves the heat stability. During the production of a color preparations but also later during the coloring of plastics it is important to avoid excessive shear, otherwise the heat stability decreases. The data for heat stability varies between 280 °C (536 °F) and 300 °C (572 °F) depending on the supplier and type of stabilization. Bismuth vanadate is a pigment with a brilliant greenish yellow color, and shows a high tinting strength and good hiding power. The light fastness and weather resistance (4–5 on the gray scale, 2 years Florida) is good both in pure tone and in white reduction with titanium dioxide. The density is approx. 7.7 g/cm³; it is a rather heavy pigment. The refractive index is approx. 2.45. Bismuth vanadates are insoluble and resistant to acids and alkalis. This pigment does not cause warpage in partially crystalline polymers.

The LD₅₀ value is higher than 5000 mg/kg body weight, rat, oral application; it does not irritate the skin or mucous membrane, and it is not sensitizing (test animal guinea pigs). Long-term inhalation studies (3 months) showed some toxic effects in the lungs of rats, probably caused by the content of Vanadium (V) oxide

[5, 7]. Minimizing any risk, it is delivered in a relative coarse, dust-free form; in addition the usual precaution methods for handling of dusts are recommended. The pigment is insoluble and therefore it can be easily separated from waste water.

Application: It can be used in many plastics but not in the engineering plastics because of the limited heat stability of this pigment. In case of doubt it is recommended that a heat stability test be run in the intended plastic material prior to color matching.

5.1.3.4 Green Pigments

Green colorants for coloring of plastics are rare, regardless of their chemistry. There are only three inorganic pigments and one organic green pigment (phthalocyanine green, two different shades). The most important inorganic green pigment is chromium (III) oxide (Table 5.7).

Table 5.7: List of Inorganic Green Pigments

Product	Formula	Color index number
Chromium green-black hematite	Cr_2O_3	Pigment green 17
Cobalt chromite green spinel	CoCr_2O_4	Pigment green 26
Cobalt titanate green spinel	$(\text{Co,Ni,Zn})_2\text{TiO}_4$	Pigment green 50

Green shades can be achieved also by a subtractive color mixing, which means by mixing of a yellow and blue pigment.

Chromium oxide green (DCMA designation: Chromium green-black hematite)
 $[\text{Cr}_2\text{O}_3]$ – Pigment green 17 / 77288 / CAS 68909.79.5

Properties: This pigment is produced by reduction of alkali dichromate or by thermal decomposition of ammonium dichromate and subsequent calcination. If potassium dichromate is used as the starting material instead of sodium dichromate, a green pigment with a more bluish tint is obtained. In addition the pigment can be modified by precipitation of hydroxides of, for example, titanium or aluminum before the calcination. The result is a green pigment with a more yellowish shade. Regardless of the production method used, the resulting chromium (III) oxide pigment must be free of chromium (VI), which is harmful. The grades of chromium (III) oxide for coloring of plastics contain usually < 5 ppm of chromium (VI).

In this connection it is very important to accentuate that the chromium of this green chromium oxide is trivalent. Trivalent chromium oxide is considered harmless. No toxicological or carcinogenic effects were detected in rats receiving up to 5% chromium (III) oxide in their feed [54]. The LD_{50} value of chromium (III) oxide is > 5000 mg/kg body weight, rat, oral application, and it does not irritate the skin or mucous membrane. Trivalent chromium belongs to the essential trace elements for humans and animals. Animal experiments proved that a shortage of chromium leads to deficiency symptoms and even deficiency diseases.

Sixvalent chromium compounds, the so-called chromates (e.g., lead chromates) are classified as toxicological and carcinogenic.

The toxicity of chromium compounds depends on the valence of the chromium; therefore it is of great importance to differentiate always between the safe chromium (III) and the harmful chromium (VI) valence.

Chromium (III) oxide is insoluble and chemically inert. The green shade is rather dull, and therefore it cannot be used for brilliant green color shades. The pigment has a high tinting strength and good hiding power. The heat stability, light fastness, and weather resistance are very good. It does not cause any warpage in partially crystalline polymers.

Chromium (III) oxide crystallizes in the rhombohedral structure of the corundum type. This type of crystal lattice is known for its hardness, consequently chromium (III) oxide is a very hard (Mohs hardness ca. 9) and abrasive pigment. This must be taken into account in its use as a colorant, especially at higher concentrations in a color preparation. Wear and tear take place not only during the production of the color preparation but also during the coloring process of plastics.

Application: Can be used in any type of polymer.

Cobalt chromite green spinel ($Co_2Cr_2O_4$) – Pigment green 26 / 77344 / CAS 68187.49.5

Properties: This pigment is produced by high-temperature calcination of cobalt (II) oxide (CoO) and chromium (III) oxide (Cr_2O_3) in varying amounts. To modify the color shade, this pigment may contain also aluminum oxide (Al_2O_3), magnesium oxide (MgO), silica (SiO_2), zinc oxide (ZnO), or zirconium dioxide (ZrO_2), either alone or in combination. These variations are included in the designation Pigment green 26. Depending on the exact composition the commercially available pigments differ in tinting strength and shade.

These pigments are insoluble and chemically inert. Their tinting strength is low, but their hiding power is good. The heat stability, light fastness, and weather resistance are very good. They do not cause any warpage in partially crystalline polymers.

Application: Can be used in any type of polymer for light green colors or pastel shades.

Cobalt titanate green spinel $[(Co,Ni,Zn)_2TiO_4]$ – Pigment green 50 / 77377 / CAS 68186.85.6

Properties: The basic formula is Co_2TiO_4 , but in the commercially available pigments for the coloring of plastics, parts of the cobalt are substituted by other metals, mainly nickel and zinc, but also by iron and other oxides. The marketed grades differ by their shades.

These pigments are insoluble and chemically inert. Their tinting strength is low, but their hiding power is good. The heat stability, light fastness, and weather resistance are very good. They do not cause any warpage in partially crystalline polymers.

Application: Can be used in any type of polymer for light green colors or pastel shades.

5.1.3.5 Red/Orange Pigments

For many years these two colors were dominated by cadmium pigments and lead chromates, which have been banned because of toxicological and ecological considerations. The reasons for this ban were explained in section 5.1.3.3.

Today the red iron (III) oxides and the newly developed cerium sulfide pigments are the only commercially available inorganic red and orange pigments for coloring of plastics (Table 5.8).

Table 5.8: List of Inorganic Red/Orange Pigments

Product	Formula	Color index number
Cadmium red	$Cd(S,Se)$	Pigment orange 20
Cerium sulfide	*	Pigment orange 75
Cerium sulfide	*	Pigment orange 78
Iron brown hematite	$\alpha-Fe_2O_3$	Pigment red 101
Lead chromate molybdate	$Pb(Cr,Mo,S)O_4$	Pigment red 104
Cadmium red	$Cd(S,Se)$	Pigment red 108
Cerium sulfide	*	Pigment red 265
Cerium sulfide	*	Pigment red 275

* The exact chemical composition is not yet published.

Cadmium red [Cd(S,Se)] – Pigment orange 20 and Pigment red 108

No longer used.

Lead chromate molybdate [Pb(Cr,Mo,S)O₄] – Pigment red 104 / 77605 / CAS 12656.85.8

No longer used.

Iron brown hematite (Fe₂O₃) – Pigment red 101 / 77491 / CAS 1309.37.1

Properties: Iron oxide is widespread in nature; whole regions are colored red by iron oxide in the soil. In prehistoric times naturally occurring iron oxides were used, together with other oxides, for rock and cave paintings. Today the natural iron oxide cannot be used as a colorant because of its impurities, for example, crystalline silicon dioxide and other heavy metals. The synthesized iron oxide is produced by two different processes:

- Precipitation and hydrolysis of solutions of iron salts
- Laux process involving reduction of nitrobenzene

The starting material for the *precipitation process* is very often an aqueous solution of FeSO₄, which is a byproduct of the titanium dioxide sulfate process. The bivalent iron is oxidized first, then hydrolyzed, and the yellow FeO(OH) precipitated. A subsequent high-temperature calcination transforms the FeO(OH) into the red iron oxide by separation of water [40].

In the *Laux process* nitrobenzene is reduced by metallic iron. It was used to produce aniline and the iron oxide had more the character of a (valuable) byproduct. Aniline has lost much of its former importance because of its classification as a carcinogenic substance.

The shade of the iron oxide depends on the purity of the iron, the process parameter, and particle size. It varies between red and red-brown.

Iron oxide is insoluble. It does not cause any warpage in partially crystalline polymers. It has an excellent heat stability, a high tinting strength and a good hiding power, and very good light fastness and weather resistance. Iron oxide is considered to be safe for humans, and belongs to the essential trace elements for the body, as proved by many toxicological studies.

Application: Iron oxide can be used in almost every polymer. One exception is poly(vinyl chloride) (PVC), especially in outdoor applications. Iron oxide in combination with traces of HCl, always present in PVC, and humidity causes a decomposition of PVC.

Cerium sulfide – Pigment red 265 / 77283-2 / CAS 12014.93.6

Pigment red 275 / 77283-0 / CAS 12014.93.6

Pigment orange 75 / 77283-1 / CAS 12014.93.6

Pigment orange 78 / 772850 / CAS 12014.93.6 + 12031.49.1

Properties: Cerium sulfide pigments are a very new development and have been commercially available for about 2 years. Their exact chemical structure is not yet published. The different color index numbers and CAS numbers indicate chemical differences, but the exact types of differences are not quite clear.

The thermal stability of *pure* cerium sulfide is not sufficient for coloring of plastics, but the supplier found a possibility to stabilize them. According to their data sheets the heat stability of those stabilized grades is about 290–310 °C (554–560 °F), which is sufficient for several plastics [41]. Cerium sulfide has a good tinting strength and hiding power, shows good light fastness and weather resistance, and does not cause warpage in partially crystalline polymers. It is a relatively hard pigment, with a Mohs hardness of 4–5.

Cerium sulfide is not stable in (strong) acids; one reaction product is the gaseous, poisonous hydrogen sulfide (H_2S). This sensitivity to acids should be taken into consideration during storage, handling, and processing, and also when cerium sulfide is used as a colorant in packaging material. It is recommended to check the packaging material in combination with the filling good prior to use.

Application: It can be used in several polymers but not in all types because of the limited heat stability. In case of doubt preliminary tests are recommended.

5.1.3.6 Violet Pigments

The most important violet pigment is ultramarine violet, the other pigments can be used only for light violet colors or pastel shades owing to their lack of a high tinting strength. Some of the violet pigments are used as *decolorizers* of plastics. Owing to the synthesis of polymers, they very often have a very weak, mainly yellowish tint as their own color, which can be covered by these violet pigments. The result is a “colorless polymer” (Table 5.9).

Table 5.9: List of Inorganic Violet Pigments

Product	Formula	Color index number
Cobalt violet phosphate	$\text{Co}_3(\text{PO}_4)_2$	Pigment violet 14
Ultramarine violet	$\text{Na}_{6-8}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_n$ ($n = 2-4$)	Pigment violet 15
Manganese ammonium polyphosphate	$\text{NH}_4\text{MnP}_2\text{O}_7$	Pigment violet 16
Cobalt lithium violet phosphate	CoLiPO_4	Pigment violet 47
Cobalt manganese red-blue borate	$(\text{Co,Mg})_2\text{B}_2\text{O}_5$	Pigment violet 48

Cobalt violet phosphate [$\text{Co}_3(\text{PO}_4)_2$] – Pigment violet 14 / 77360 / CAS 13455.36.2

Properties: It is produced by a high-temperature calcination of cobalt (II) oxide (CoO) and phosphorus (V) oxide (P_2O_5). The pigment is stable in acids and alkalis, but unstable in water (hydrolysis). It possesses a very low tinting strength.

Application: Can be used only for light violet shades and/or pastel shades in various polymers, and is used as decolorizer.

Ultramarine violet ($\text{Na}_{6-8}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_n$) – Pigment violet 15 / 77007 / CAS 12769.96.9

Properties: Ultramarine pigments were described in the section on blue pigments (compare Pigment blue 29). It is the most important violet pigment. It has a good tinting strength and good light fastness and weather resistance.

Violet ultramarine is produced by heating the blue grade with ammonium chloride at approx. 240 °C (464 °F) in the presence of air. The heat stability of the violet ultramarine is, however, slightly lower in comparison to the blue grade, but still high enough for various polymers.

Application: Analogous to the blue grade, it can be used for coloring of many polymers.

Manganese ammonium polyphosphate ($\text{NH}_4\text{MnP}_2\text{O}_7$) – Pigment violet 16 / 77742 / CAS 10101.66.3

Properties: This pigment was used already about 1900. It is produced by heating a suspension of manganese salts, manganese oxide, phosphorus acid, and ammonium salts of phosphorus acids and a subsequent calcination.

It is insoluble in water and organic solvents. It is stable in acids but not very stable in alkali. The sensitivity to alkali should be taken into consideration when it is

used as a colorant in packaging materials. The heat stability is good ($> 300^{\circ}\text{C}$), it shows a good light fastness. The tinting strength is on the weak side. It is considered to be safe for humans, which is underlined by its use as colorant in cosmetics, for example, in lipsticks.

Application: The use is limited owing to its low tinting strength, it is used for light violet shades and/or pastel shades, and can be applied in various polymers.

Cobalt lithium violet phosphate (CoLiPO_4) – Pigment violet 47 / 77363 / CAS 68610.13.9

Properties: It is produced by a high-temperature calcination of cobalt (II) oxide (CoO), lithium oxide (LiO), and phosphorus (V) oxide (P_2O_5). It can be considered as a variation of Pigment violet 14. The tinting strength is very low.

Application: Can be used in very light violet shades, and predominantly as a decolorizer.

Cobalt magnesium red-blue borate $[(\text{Co,Mg})_2\text{B}_2\text{O}_5]$ – Pigment violet 48 / 77352 / CAS 68608.93.5

Properties: It is produced by a high-temperature calcination of cobalt (II) oxide (CoO), magnesium oxide (MgO), and boron (III) oxide (B_2O_3). Its tinting strength is very low.

Application: Can be used in very light violet shades, and predominantly as a decolorizer.

5.1.4 Pearlescent Pigments

Pearlescent pigments are produced by coating of mica with titanium dioxide (silvery shiny pearlescent pigments) or other metal oxides, for example, iron oxide, either alone or in combination with titanium dioxide. The results of the second method are the colored pearlescent pigments.

The idea behind the pearlescent pigments is to imitate the natural pearl luster. A pearl is formed when a grain of sand enters a mussel. The grain of sand is a foreign body in the mussel, and as a kind of resistance, the mussel coats the grain of sand with alternating layers of calcium carbonate and protein. These layers differ in their refractive indices. Parts of the light are reflected, and other parts pass on to the next layer, and this is repeated on each following layer. The visual effect of pearl luster is produced by this multiple reflection and transmittance of the (sun) light on these thin layers (Fig. 5.5) [42].

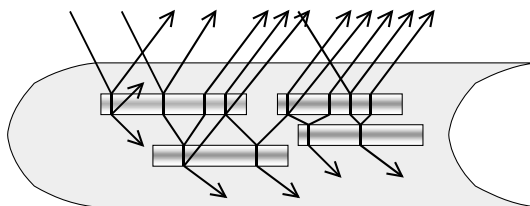


Figure 5.5: Schematic drawing of the process of multiple reflection and transmittance

The pearlescent pigments are produced by coating of thin mica platelets with an exactly defined and controlled layer of titanium dioxide. During the subsequent calcination the titanium dioxide forms the anatase modification. The light fastness of this grade of pearlescent pigments is not sufficient for several applications, for example, for a nonfading coloring of polymers. Pearlescent pigments with a good light fastness are produced when the mica is first coated by a thin layer of tin dioxide (SnO_2), which catalyzes the formation of the rutile modification. This grade of pearlescent pigments contains between 1 % and 2 % of tin dioxide.

The effect of pearlescent pigments depends on the particle size distribution of the mica used as carrier. The optical impression varies from a silvery pearl luster to a bright sparkling.

The commercially available pearlescent pigments for coloring of polymers usually have the following particle size distribution:

- 5–25 μm $\Rightarrow$ silvery shining with a distinct pearl luster
- 10–50 μm $\Rightarrow$ brilliant shining
- 30–150 μm $\Rightarrow$ bright sparkling

The thickness of the titanium dioxide layer is between 40 and 60 nm in these silvery pearlescent pigments.

An increase of the TiO_2 layer thickness leads to *interference pearlescent pigments*. In this case the color effects depend on the angle of vision. This kind of pigment plays no role in the coloring of plastics, and is used mainly in cosmetics.

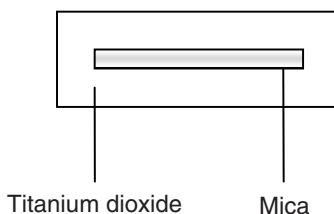
Colored pearlescent pigments are produced by exchange of the titanium dioxide by another metal oxide, for example, iron oxide. Depending on the layer thickness of the iron oxide the color varies with increasing layer thickness from bronze, over copper-red, red, red-violet to a red-green. The color effect is the result of a combination of light absorption and interference.

Besides these monolayer pearlescent pigments, there are multilayer pigments, which are called *combination pearlescent pigments*. They are produced by a stepwise process. First the mica is coated with titanium dioxide, and on top of it a

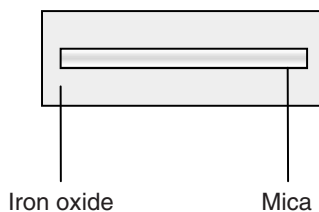
second layer is applied. Iron oxide as a second coat gives gold-colored pigments, while chromium (III) oxide gives green-colored pigments with varying shades of green. The intensity of the golden shade increases with increasing layer thickness of the iron oxide (Fig. 5.6).

Monolayer pearlescent pigments

Silvery pearlescent pigments



Colored pearlescent pigments



Combination pigments

Golden colored pigments

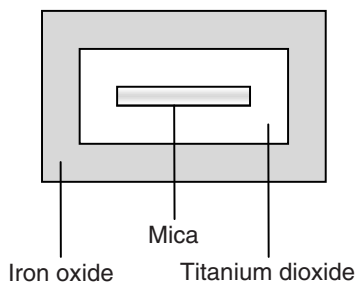


Figure 5.6: Principles of composition for different pearlescent pigments

All three types of pigments, the silvery, the colored monolayer, and the colored combination pearlescent pigments are applied for coloring of plastics, either alone or in combination. Very interesting color effects can be achieved by mixing them with organic colorants, with metal effect pigments, and/or with traces of carbon black. There are really no limits to the creativity of the colorist.

The intensity of luster and sparkling effect are greater the better the transparency of the polymer is. In opaque or reinforced plastics it is very hard to achieve a really satisfying effect. As a kind of compromise a very opaque polymer can be painted with a lacquer-containing pearlescent pigment, but this is very seldom done because of the cost.

The mica platelets are fragile, and therefore a few precautions methods are unavoidable. A critical point is the production of a masterbatch. For a good dispersing of any pigment in a polymer melt a certain amount of shear is absolutely necessary. On the other hand any excessive shear will damage the original particle size distribution of the pearlescent pigment. For the manufacture of a masterbatch containing pearlescent pigments the use of a corotating extruder is recommended, because the shear in such an extruder is less than in a counterrotating extruder. In addition the processing parameter of the extruder must be adjusted to avoid unintentional damage. The danger of unintentional damage increases with increasing particle size of such an effect pigment.

The damage of pearlescent pigments in a extruder is noticed very easily. The silvery pigments lose their silvery luster, which turns to a more or less dull gray, and a colored pearlescent pigment changes its shade, which can be noticed in comparison to the original pigment. The practice shows that the damage of pearlescent pigments can be minimized but not completely avoided during the production of a masterbatch.

The next critical point is the addition of such a masterbatch during the coloring of the final product, especially when a pin gate and/or a hot runner is used. The diameter of the pin gate and/or the channel of the hot runner must be large enough to avoid excessive shear, otherwise a damage of the pigments is unavoidable. If needed the diameters should be adjusted to the particle size of the pearlescent pigment.

An incomplete dispersion of pearlescent pigments in a masterbatch causes specks of agglomerated pigments later on during the manufacture of the final product. This is not only a visual defect, but also can cause holes in a thin-walled packaging material, and liquid filling goods may leak out.

The pearlescent pigments are tiny platelets. To reach an optimum of optical effect, special care has to be given to ensure a parallel alignment of the platelets during application. This can be influenced by the mold construction. One important point

is the position of the gate, and another is the design of the part as such. In practice, however, the normal procedure is to use an already existing mold. Many colors of plastic articles, especially for household and personal use, depend on the fashionable colors, which change on a yearly basis. In the worst case the use of an existing mold can exclude the application of pearlescent pigments because the effect is not satisfying enough.

All effective pigments, pearlescent pigments are no exception, possess an unpleasant property, the occurrence of flow lines. Parallel alignment of the pigment is hindered in the front area of a polymer melt, and a disorientation of the platelets takes place. The result is flow lines. All shapes, except the spherical, show this physical phenomenon.

Experience shows that plastic articles with functional gaps are usually not colored with pearlescent pigments. The polymer melt is divided at the gap, and both parts join again behind it. In this area of confluence the flow lines are too clearly visible.

Flow lines are a disturbing visual effect. Their appearance can be minimized but not completely avoided. Several methods are described, and the most important one are:

- Use of a polymer with a higher melt viscosity
- Increase of pigment concentration
- Change the position of the feed point in such a way that the flow line moves toward an invisible part
- Increase the injection rate in combination with a larger gate
- Change processing parameters (temperature, time, etc.)

In many cases first a combination of these actions is successful in minimizing the visually disturbing flow lines.

5.1.5 Metal Effect Pigments

More and more, plastics are replacing metals as constructing materials. The reasons are manifold, but the result is always an improvement. Possible reasons are:

- Saving of weight – plastic parts are much lighter than metallic parts, they are easier to handle and to manufacture; in addition they save energy because of the weight reduction (e.g., car industry).
- Fulfilling of specific mechanical, physical and/or chemical requirements of the part – an important fact within many industries.
- Question of design – many items of our daily life, household appliances, entertainment equipment, today are made of plastics.

In connection with colors the last reason is of special importance. The thermo-plastic processing of plastics allows well designed items that please our senses in addition to other advantages, for example, lighter weight, easier to handle, more convenient, and so forth. Now shapes are possible that previously had been impossible in metal as constructing materials because of the comparable difficult processing of metal. On the other hand the new plastic goods should resemble the earlier metal parts. This goal is reached by a coloring of plastics with metal effect pigments. There are two chemical different types, pure aluminum and copper alloys, mainly bronze (copper/tin alloy) and brass (copper/zinc alloy).

Aluminum (Al) – Pigment metal 1 / 77000 / CAS 7429.90.5

Aluminum is marketed in two different shapes, as a powder and as tiny platelets. The particle size of the powder ranges from approx. 15 μm up to approx. 200 μm . The platelets are produced by stamping out different shapes, and their thickness depends how thin the original aluminum foil is rolled out. The shape chosen can be a polygon, rectangle, or square, in varying sizes.

Very fine aluminum is sensitive to oxygen, and on the surface a thin layer of aluminum oxide is formed by oxidation. In this way the aluminum loses its rich luster, and it becomes matte. To protect the surface for oxidation, the aluminum is coated by a thin layer of a transparent lacquer, and it keeps its rich luster.

Another type of effect pigment is based on this technique. The aluminum platelets can be coated also with a colored lacquer instead of a transparent type. The result is a colored *speckled effect pigment*. This type of effect pigments is available in all primary colors, including black. These platelets are sensitive to shear and temperature; therefore precautionary methods have to be implemented to avoid any damage. Analogous to pearlescent pigments one method is to avoid excessive shear, therefore the use of a corotating extruder is recommended during the manufacture of a masterbatch containing this type of pigment. Excessive shear can cause a separation of the colored layer from the aluminum platelets, and the shiny aluminum appears again. This can be noticed very easily under a microscope. Another kind of damage is caused by (excessive) temperature.

The heat stability of the lacquer is not always sufficient, especially in plastics that require higher processing temperatures. The colored lacquer layer weakens, separates from the aluminum platelets, and is dispersed in the polymer melt. The result is a discoloration of the basic color of the plastic part, for example, a white as basic color turns into a gray.

Very fine, pure aluminum powder is explosive. To reduce the risk of explosion during handling, the grades for the coloring of plastics are delivered in a harmless form. There are several possibilities to reach this goal. One possibility of stabili-

zation is to mix the aluminum powder with solvents such as paraffin oil. These pastes contain between 60% and 80% aluminum. Another method, specially developed for the coloring of plastics, is the incorporation of the aluminum powder in a plastic matrix at the site of the supplier. Such concentrates contain 70–80% aluminum in different types of polymer matrix, and corresponding to the production method the results are longish, cylindrical pellets. The type of polymer matrix has to be considered when such a concentrate is applied in a masterbatch. In addition to these stabilized grades of aluminum, unstabilized, pure, dust-free grades of aluminum powder are marketed.

There is no general guideline for the selection of the most suitable grade of aluminum effect pigment for a masterbatch. The grade depends on the intended effect. For the manufacture of a highly concentrated masterbatch an aluminum paste and/or the concentrate is advantageous. For specific effects sometimes only a small amount of aluminum effect pigment is required in combination with an organic colorant. In such a case the pure aluminum powder may be advantageous. The coarse concentrate (the pellets) can cause problems in regard to a homogeneous distribution of the aluminum in a masterbatch, and the paraffin oil of a paste may hinder a complete dispersing of the organic colorant.

The intensity of luster and sparkling effect is greater the better the transparency of the polymer is. In opaque or reinforced plastics it is very difficult to achieve a really satisfying effect. As a kind of compromise a very opaque polymer may be painted with a lacquer containing these aluminum pigments, but this is very seldom done because of the costs.

All effect pigments, including aluminum pigments, possess an unpleasant property, the occurrence of flow lines (compare pearlescent pigments).

The heat stability, hiding power, and fastness properties of aluminum pigments are very good.

Copper alloys (bronze / brass) – Pigment metal 2 / 77400

The two copper alloys, bronze (copper/tin alloy) and brass (copper/zinc alloy), are applied as metallic effect pigments. Similar to aluminum they are sensitive to oxygen and in addition to gaseous contamination of the environment. By attack of oxygen and other gases, oxides and sulfides are formed on the surface of these pigments, which cause a discoloration and loss of luster. But there is also another reason for discoloration. These pigments may react with other components of a color preparation.

In theory this sensitivity can be eliminated by a change of the composition of these alloys. In practice, however, this is not possible. One reason is the color shade of those alternative alloys would move from the wanted “warm” copper

shade to an unpleasant “cold” white shade. The other reason is a technical one. The hardness of those alternative alloys increases considerably, and they are too hard for milling or other ways of cutting into a powdery form.

The bronze and brass pigments are coated with a thin layer of a transparent lacquer or are incorporated in a polymer matrix [43], the same methods of protection that are applied to stabilize the aluminum pigments. The behaviors of these bronze and brass pigments are consequently the same regarding handling, concentration, and application in a masterbatch.

Bronze and brass pigments are marketed in different particle sizes, which varies between very fine (approx. 5–10 μm) and very coarse (approx. 200–300 μm).

Their shades differ depending on the composition. Their heat stability, hiding power, and fastness properties are very good. The intensity of luster and sparkling effect is greater the better the transparency of the polymer is. In opaque or reinforced plastics it is very difficult to achieve a really satisfying effect. As a kind of compromise a very opaque polymer may be painted with a lacquer containing these pigments, but this is very seldom done because of the costs.

All effect pigments, including copper alloys, possess an unpleasant property, the occurrence of flow lines (compare pearlescent pigments).

The intensity of the metallic effect depends on the particle size, and therefore it can be adjusted. Very fine metal effect pigments create a very homogeneous optical impression, combined with a very good hiding power, while coarse metal effect pigments give a lighter color with a clear sparkling effect.

5.1.6 Conductive Pigments

In many fields of technology electrostatic electricity is a large security risk. Plastics are known as very poor conductors of electricity, including of course also the electrostatic electricity. To avoid any risk, the plastic parts must be equipped with antistatic and/or conductive substances. This includes plastic objects such as floors, floor coverings, cases, instruments, packaging material, container, pipes, and so forth, to name only a few. Whether an antistatic or conductive supplementation of the object is necessary depends on the classification of the area of use and the legal conductivity requirements, for example, any part in an ex area has to be conductive equipped. One way of course is to replace plastics as constructing material with metal. This is seldom possible, and therefore the plastics have to be supplemented with either an antistatic or conductive substance. Several inorganic substances, including inorganic pigments, can be used for this purpose:

- *Metal effect pigments* – their application as conductive pigment requires concentrations in plastics that are considerably higher in comparison to a use

as colorant. The concentration must be in a range in which the pigments touch each other; the part is then conductive.

- *Carbon black* – various conductive grades of carbon black are marketed. Such objects have a visual disadvantage, as they are always black.
- *Coated mica platelets* – using the technology of pearlescent pigment manufacture, mica can be coated principally with any metal oxides. Two types of conductive pigments are marketed, a gray and a transparent type. Gray conductive types are made by coating the mica with titanium dioxide and silicon dioxide and on top a layer of tin dioxide doped with antimony oxide. In the case of transparent conductive types the mica platelets are coated directly with tin dioxide doped with antimony oxide. Pure tin dioxide is an isolator, but becomes a semiconductor by doping with antimony oxide. These pigments do not have the disadvantage of the black color, and can be used in objects with light colors. At a minimal concentration of 3% there are already effects of conductivity, but higher concentrations are recommended [52]. Mica platelets are sensitive to shear. As described previously in the section on pearlescent pigments, the same precautionary methods should be used during the incorporation in a polymer melt.
- *Metal fibers* – glass fibers are very common to reinforce plastics. Using the same technology of incorporation, the glass fibers can be replaced by metal fibers. This replacement leads to a conductive object provided that the concentration is high enough for the fibers to touch each other.

The best way to achieve the required conductivity cannot be predicted, as too many applications and specific requirements are involved.

5.1.7 Pigments for Laser Marking

There are several reasons why technical components have to be marked, and the question of product liability is certainly one of them. The use of a laser for labeling and marking has gained much acceptance, especially if the traditional printing process cannot be applied because of the surface shape, size, and/or construction of the part. At first glance the marking, labeling, and decorating of plastic products with a laser seems to be rather easy. The laser beam is focused by an optics, which through computer control directs the beam toward the component to be marked. Under the influence of the heat, generated by the impact of the laser beam, the surface of the plastic component is changed, and the result is a marking in this area. In practice, however, it is more complicated. For a successful application of a laser several preconditions must be fulfilled, and in addition all parameters must be coordinated with each other.

The most important parameters are:

- Type of plastic to be marked
- Colorants in the plastic
- Additives in the plastic
- Construction and operating mode of the laser
- Size and shape of the component to be marked
- Type and size of the required marking

The surface of the plastic component is changed by the impact of the laser beam. The following three alterations of the surface can occur:

- A thin layer of foam is formed by the heat, developed during the impact of the laser beam.
- A thin layer is cleared away; the result is an engraving.
- The absorbed energy of the laser beam damages the surface of the plastic component. This process is called carbonization.

These three alterations are shown schematically in Fig. 5.7.

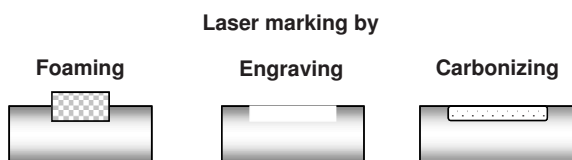


Figure 5.7: Alterations of the plastic surface by a laser beam

Carbonization is not only the simplest method of marking but also the most frequently used one. By carbonizing a dark writing is created on a preferably light colored plastic component. The maximal contrast appears on a white background. Suitable plastics for this method are polymers containing aromatic groups, for example, polycarbonate (PC) and polyester (PET, PBT). The intensity of the writing can be increased by special additives, and the marking then appears nearly black. One additive frequently used for laser marking is modified pearlescent pigments. In the presence of a modified pearlescent pigment other polymers such as polyolefins (PO) and acrylonitrile-butadiene-styrene (ABS) can be marked by carbonization. The marking of these polymers requires a concentration of at least 0.1% of these modified pearlescent pigments. Higher concentrations are preferred because the legibility of the marking then increases.

Besides these modified pearlescent pigments there are still other additives in use, for example, modified aluminum flakes.

A colored marking is possible when the polymer contains two colorants with different sensitivities to laser light. One possibility is to color the plastic component with a combination of a colorant that is not sensitive to laser light and a special grade of carbon black that is sensitive to laser light. The carbon black is cleared away completely by the impact of the laser beam, and the colored background appears. This process, however, requires that no carbonization occurs, which would cover the colored mark. This method is applied preferably to mark polyacetal (POM), in the case of polyolefins the marking is not very clear.

Another possibility to achieve a white writing on a black background is to apply a thin layer of a black foil on top of a white colored component. By a complete clearing away of the black foil by the laser the white writing appears.

A multicolored marking is not possible at the present state of technology.

Different laser types and processes are available for laser marking (Table 5.10).

Table 5.10: *Laser Types and Processes of Marking*

Properties	Nd:YAG laser	Excimer laser
Wavelength	1064 nm or 532 nm	351 nm
Operating mode	Pulsed	Pulsed
Energy	50–80 Watt	50–200 Watt
Mode of marking	Vector mode	Mask mode
Speed of marking	Up to 1000 mm/s	Up to 100 symbols/s
Size of the field to be marked	150 mm diameter	200 mm ²

The *Nd:YAG laser* operates in the vector mode. With the help of two deflecting mirrors the beam of laser light is diverted by computer control, and a special optics focuses the beam on the surface of the component to be marked. The laser “writes” symbol by symbol. This method produces the best flexibility, and the writing can be changed any time with the use of a computer. This flexibility is significant when serial numbers, date of production, and/or other important dates are to be integrated in the marking.

The *excimer laser* operates in the mask mode. Between the laser and the component to be marked, a mask is positioned, and only those parts of the laser light that

pass the mask, containing gaps in form of symbols and/or a complex decoration, can mark the component. This technology produces a complex decoration with extensive proportions within a very short time. One disadvantage is that any change in the marking requires a change of the mask, and another disadvantage is the high price of an excimer laser.

Laser marking is a process without any contact; therefore inaccessible surfaces and/or bend components can be marked without any difficulty. This is the decisive advantage of laser technology, because every printing technology fails in these cases.

Further advantages of laser technology in comparison to the traditional printing technology are:

- No printing colors necessary
- No preparation of the plastic surface prior to printing
- No equipment for the drying of the print necessary and/or other typical precautions
- The marking is forgery-proof

For laser marking, polyolefins should contain at least 0.1% of the modified pearlescent pigments; a higher concentration is advisable to achieve a clearer marking. For the handling and incorporation of these pigments the same precautionary methods should be implemented as described in the section on pearlescent pigments.

5.1.8 Additional Inorganic Effect Pigments

Two different types of pigments are marketed for very specific effects:

- Luminescent pigments
- So-called “color flop pigments”

5.1.8.1 Luminescent Pigments

Inorganic luminescent pigments are synthetically produced substances absorbing energy (light), which is emitted subsequently as light, either immediately or over a longer period of time. These pigments shine for a certain time even in complete darkness. This phenomenon is also called phosphorescence. Chemically they belong to the following groups:

- Zinc sulfide doped with metals, for example, silver (Ag) or copper (Cu). The results are pigments with the following formula: $\text{ZnS} \cdot \text{Ag}$ or $\text{ZnS} \cdot \text{Cu}$.
- Aluminates doped with lanthanides, for example, $\text{Al}_2\text{O}_3 \cdot \text{Sr} \cdot \text{Eu}$.

- Alkaline earth metal sulfides, doped with lanthanides or other metals, for example, SrS·Eu or SrCaS·Bi.

The emitted color and the intensity and duration of luminescence depend on the chemistry of these pigments. The doped zinc sulfide and the aluminates emit a yellowish green light, while the alkaline earth metal sulfides shine in a orange (SrS·Eu) or blue (SrCaS·Bi) [44].

The heat stability of these pigments is good ($> 400\text{ }^{\circ}\text{C}$ [$752\text{ }^{\circ}\text{F}$]). Sulfides are generally sensitive to strong acids. For a distinct effect the particle size of these pigments has to be between 20 and 60 μm , which means they are very coarse in comparison to a typical colorant and therefore not suitable for thin-walled plastic components.

No problems are reported during production and handling of a masterbatch, and luminescent pigments can be processed like any other inorganic pigment.

Many uses are imaginable and practiced, for example, in toys and to mark emergency exits or other safety related items.

5.1.8.2 Color Flop Pigments

This is as yet not an official designation of this very new group of pigments; it describes only the effect. The characteristic of these pigments is that they change color depending on the angle of vision – basically the appearance of interference. One type of pearlescent pigments shows this effect too, but it is very weak. The goal of further development was to achieve pigments with a strong effect of interference, and it took a long time before the first pigments appeared on the market.

The first two colors, a golden and a red shade, are now available. They are produced by the BASF corporation in Ludwigshafen, Germany, and their trade name is Variochrome. Chemically it is a multilayer pigment, and the bases are aluminum platelets coated with silicon dioxide and iron oxide in varying thickness. The color varies between golden and red depending on the thickness of the iron oxide. This is just the beginning, and it can be expected that in the near future further colors will follow. The fastness properties are very good.

Similar pigments produced by other companies are available at least as experimental pigments, for example, by E. Merck in Darmstadt, Germany.

5.2 Organic Pigments

In comparison to the inorganic pigments there is a large variety of organic colorants. This diversity is the consequence of their chemistry, because within organic chemistry there are not only much more fundamental components but in addition

they can be varied by replacement of their substituents, which are nearly unlimited. The results are many colorants with slightly different shades. In practice the number of commercially marketed colorants is limited. Limitations are present in terms of economic, technical, toxicological concerns, and/or other disadvantageous properties.

The organic pigments can be subdivided either according to the chemical structure or the color. Both systems are practiced in the literature, and both have advantages and disadvantages besides the tendency to overlap. Overlapping occurs especially in the colors red, yellow, and violet. For the purpose of this book it may be useful to list the organic pigments according to the chemical constitution. One reason is the fact that several properties, for example, light fastness, weather resistance, and heat stability, are very similar within a group of pigments with the same basic chemical structure. The organic pigments are therefore subdivided according to the basic formula, which predicts to a certain extent the expected, typical properties. New pigments without published formulas can be classified only when at least their assignment is known.

Not all marketed colorants can be used for the coloring of plastics. One reason that excludes their use for the coloring of plastics is insufficient heat stability. The main fields of application then are printing paints and lacquers. These pigments are not described in this book. Analogous to inorganic pigments those pigments, which are no longer in use because of, for example, toxicological concerns, are just mentioned but not described in detail.

Each organic pigment that is suitable for the coloring of plastics is described with its characteristic properties. In this context it should be emphasized that several data can be used only as guidelines and not as exact data for any color preparation. Data such as heat stability, light fastness, and weather resistance are based on standardized test methods in standard plastics. In practice, however, the composition of an actual color preparation and/or the final product is much more complex.

Several colorants are marketed by more than one supplier. Those pigments differ usually in their optical and physical properties, and consequently the shades are not absolutely identical. The main reasons for those differences are different particle size distribution and different aftertreatments to improve the stability of the crystal and the dispersing in the polymer melt. As a result the data regarding heat stability and/or light fastness may differ also.

All marketed organic pigments, including those that are applied only in printing paints or lacquers, are described in detail in the publication *Industrial Organic Pigments* by W. Herbst and K. Hunger [45].

In view of the many types of plastics and their manifold applications in combination with all the specific requirements for the final product, it would be far beyond

the scope of this book to describe every plastic in detail, including all suitable colorants. An additional restriction is given by the fact that the manufacturer of colorants checks the performance of his colorants usually only in the most important types of plastics. This alone is very laborious and time consuming. The supplied data sheets contain this information together with a sample of the color shade.

Another reason for this restriction is the variety of requirements for the final product based on the intended application. A technical part has to fulfill many specific requirements, while those of a disposable item are relatively limited. The colorist recognizes which properties are required of the new color preparation on the basis of the customer supplied requirements specification. In case of doubt it is recommended to check with the manufacturer whether the colorant is suitable for the intended use.

The organic pigments can be divided into two main groups, azo pigments and nonazo pigments, which are also known as polycyclic pigments. Both main groups can be subdivided further according to structural characteristics, for example, by the number of azo groups or the type of disazo component, and the type of rings that constitute the aromatic structure of the polycyclic pigments (Fig. 5.8). In addition to these two main groups single organic pigments are marketed that cannot be classified in one of these main groups, for example, the metal complex pigments and the isoindolinone or isoindoline pigments.

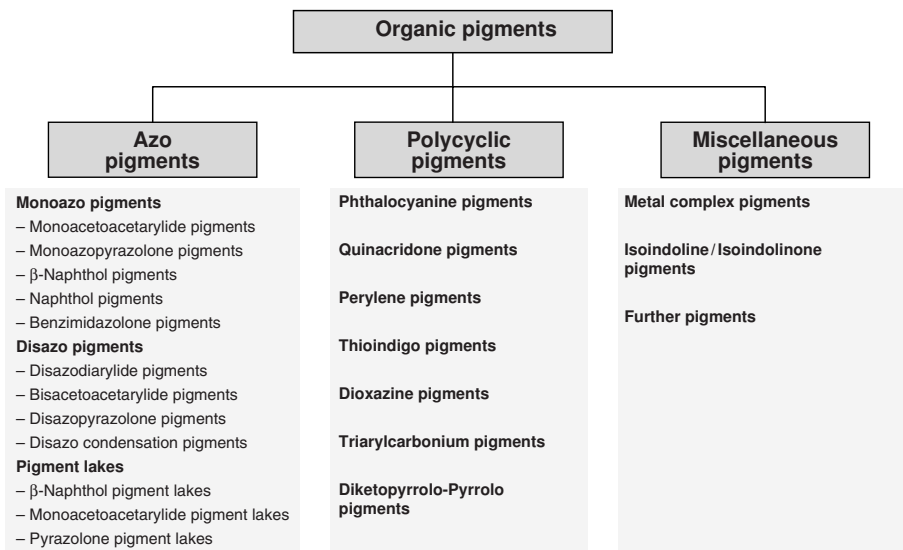


Figure 5.8: Classification of organic pigments based on the chemical structure

The characteristic of organic colorants is the presence of chromophores, a system of conjugated double bonds (π -electron system). The appearance of color is associated with electronic excitation caused by an absorption of selected wavelengths of the incident visible light, thereby giving the molecule the shade of the resulting complementary color.

5.2.1 Azo Pigments

The characteristic of all azo pigments is the azo group $[-N=N-]$. Monoazo pigments contain one azo group, the disazo pigments contain two azo groups, and there are no products on the market with more than two azo groups.

The basic formula of a monoazo pigment is $[R'-N=N-R'']$ and of a disazo pigments it is $[R'-N=N-R'''-N=N-R'']$. R' , R'' , and R''' are different components with varying substituents. The chemical constitution of the components can be used for a further subdivision of azo pigments. When an azo pigment contains as a substituent an acidic group, for example, a sulfo or carboxy group, then it forms by precipitation azo pigment lakes. Metal cations such as calcium, strontium, barium, magnesium, or manganese are used usually for precipitation. This leads to a further subdivision of azo pigments, in nonlaked azo pigments and laked azo pigments.

The azo pigments can be subdivided the following way:

- Monoazo pigments
 - Monoacetoacetarylide pigments
 - Monoazopyrazolone pigments
 - β -Naphthol pigments
 - Naphthol pigments
 - Benzimidazolone pigments
- Disazo pigments
 - Disazodiarylide pigments
 - Bisacetoacetarylide pigments
 - Disazopyrazolone pigments
 - Disazo condensation pigments
- Pigment lakes
 - β -Naphthol pigment lakes
 - Monoacetoacetarylide pigment lakes
 - Pyrazolone pigment lakes

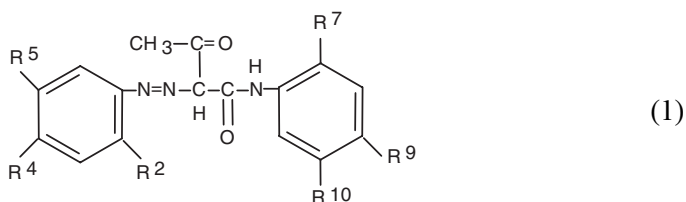
Numerous combinations of the different components are possible, including varying substituents, which result in a large number of azo pigments. The color of azo pigments is usually in the range of yellow, orange, red, and brown with many

different shades. No green or blue azo pigments are marketed; these two colors are covered by polycyclic pigments.

5.2.1.1 Monoazo Pigments

Monoacetoacetarylides Pigments

This group of azo pigments has a certain historical importance, because the very first marketed azo pigment belongs to this group with basic formula 1. Many other pigments followed, and consequently this is numerically the largest group of azo pigments.



In spite of the large number of pigments only a few can be used for the coloring of plastics (Table 5.11). Most of them cannot be applied because of a too low heat stability and/or other disadvantageous properties, for example, migration.

Pigment yellow 49 / 11 765 / CAS 2904.04.3

Properties: Greenish yellow, good light fastness.

Application: For viscose spin dyeing and for the mass coloration of viscose foils [45].

Pigment yellow 97 / 11 767 / CAS 12225.18.2

Properties: Medium yellow, average tinting strength, tendency to migrate in plasticized PVC at low concentrations, pigment does not affect shrinkage.

Average heat stability: 240 °C (464 °F) in PE-HD. At commonly used concentrations the pigment dissolves almost completely at temperatures about 200 °C (392 °F) in PS, combined with a color shift.

Good light fastness: 6–7 (pure tone) / 8 (white reduction) in rigid PVC, 7/7 in PE, and 7–8 / 5 in PS.

Application: It can be used in several polymers, for example, rigid poly(vinyl chloride) (PVC-U), polyolefins (PO), polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), poly(methyl methacrylate) (PMMA), and epoxy resins, unsaturated

polyester resin. In the case of plasticized polyvinyl chloride (PVC-P), it is recommended to consider the possibility of migration.

Pigment yellow 116 / 11790 / CAS 30191.02.7

Properties: Reddish yellow, a slight tendency to migrate in plasticized PVC.

Low heat stability: approx. 180 °C (356 °F).

Good light fastness: 7–8 (pure tone) / 6 (white reduction) in PVC.

Application: Its use is restricted to PVC; the insufficient heat stability limits the application in other polymers, for example, PO, PS.

Table 5.11: List of Substituents of Azo Pigments According to Basic Formula 1

Color index number	Substituent					
	R ²	R ⁴	R ⁵	R ⁷	R ⁹	R ¹⁰
P. yellow 49	CH ₃	Cl	H	OCH ₃	Cl	OCH ₃
P. yellow 97	OCH ₃	SO ₂ NH-C ₆ H ₅	OCH ₃	OCH ₃	Cl	OCH ₃
P. yellow 116	Cl	CONH ₂	H	H	NHCOCH ₃	H

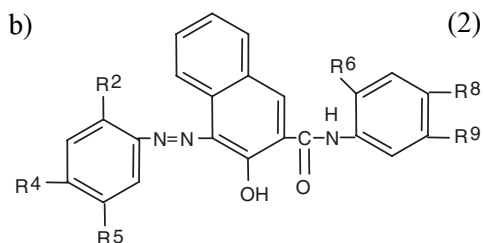
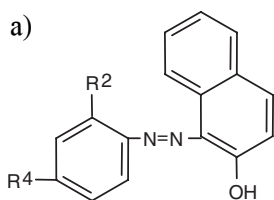
Monoazopyrazolone Pigments

The nonlaked monoazopyrazolone pigments play no role in the coloring of plastics.

β-Naphthol Pigments/Naphthol Pigments

These two groups can be summarized because their chemical structures are very closely related. The β-naphthol pigments show no further substituents on the β-naphthol group, and their chemical structure is relatively simple (basic formula 2a). The naphthol pigments are much more complex (basic formula 2b). They show substituents on the β-naphthol group in the *m*-position to the azo group, and an additional substituent on the coupling component (R⁵).

From the β-naphthol pigments (basic formula 2a) only two pigments can be applied to some extent (Table 5.12). All the other pigments of this group are not suitable for the coloring of plastics because of their disadvantageous properties, for example, insufficient heat stability, tendency to migrate, and others disadvantages.



Pigment orange 5 / 12075 / CAS 3468.63.1

Properties: Insufficient heat stability, strong tendency to migrate because of its solubility in many solvents.

Good light fastness: 8 (pure tone) / 6 (white reduction) in rigid PVC.

Application: Its use is limited to rigid PVC.

Pigment red 3 / 12120 / CAS 2425.85.6

Properties: Insufficient heat stability, strong tendency to migrate because of its solubility in many solvents, but fair light fastness.

Application: Its use is limited to rigid PVC.

Table 5.12: List of Substituents of β -Naphthol Pigments According to Basic Formula 2a

Color index number	Substituent	
	R ²	R ⁴
P. orange 5	NO ₂	NO ₂
P. red 3	NO ₂	CH ₃

The naphthol pigments with their more complex chemical structure (basic formula 2b) possess a much better profile of properties in comparison to the relatively simple β -naphthol pigments. Consequently many pigments of this group are applied for the coloring of plastics, among them some widely used pigments (Table 5.13).

Pigment red 5 / 12490 / CAS 6410.41.9

Properties: bluish red (carmine), insufficient heat stability, strong tendency to migrate, therefore cannot be applied in plasticized PVC.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in rigid PVC.

Application: Its use is limited to rigid PVC, and it is used for spin dyeing of viscose rayon.

Pigment red 31 / 12360 / CAS 6448.96.0

Properties: Bluish red (bordeaux).

Good heat stability: 280 °C (536 °F) in PS and PMMA.

Good light fastness: 7 (pure tone) in PMMA.

Application: It can be applied in several polymers, for example, rubber, PS, PMMA, unsaturated polyester resin, and so forth. This pigment is used primarily in the United States and Japan, and is not very common in Europe.

Pigment red 112 / 12370 / CAS 6535.46.2

Properties: Brilliant red shade, not completely fast to migration, insufficient heat stability.

Good light fastness: 8 (pure tone) in rigid PVC, but only 5–6 in white reduction.

Application: Its use is limited to rigid PVC, and it is used for spin dyeing of viscose rayon.

Pigment red 146 / 12485 / CAS 5280.68.2

Properties: Bluish red, not completely fast to migration.

Insufficient heat stability: Below 200 °C (392 °F).

Good light fastness: 8 (pure tone) in rigid PVC, but only 6 in white reduction.

Application: Its use is limited to rigid PVC.

Pigment red 150 / 12290 / CAS 56396.10.2

In the past this pigment was used to color PVC, but it has now more or less been completely replaced by other pigments with better properties.

Pigment red 164 / – / 12216.95.4

Properties: Yellowish red, little tinting strength, not completely fast to migration. The chemical constitution has not yet been published.

Heat stability: The heat stability varies and depends on the polymer to be colored. The heat stability is about 270 °C (518 °F) (pure tone) and 250 °C (482 °F) (white reduction) in PS, but only 220–200 °C (428–392 °F) in polyolefins.

Average light fastness.

Application: This pigment can be used in several polymers, for example, polyurethanes, PS, rigid PVC, and PE with low processing temperature (PE-LD).

Pigment red 170 / 12475 / CAS 2786.76.7

Properties: Bluish red, good tinting strength, not completely fast to migration. Pigment red 170 is polymorphous, there are two crystal modification, which differ slightly in terms of opacity and color shade.

Average heat stability which in addition depends on the concentration in the polymer: 240 °C (464 °F) in PE at a concentration of 0.1%, but only 220 °C (428 °F) in PE at a concentration of 0.05%.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE

Application: The use of this pigment is limited to polyolefins, rigid PVC, and spin dyeing of viscose rayon. Because of its solubility in several solvents, including plasticizer, it should not be applied in polymers containing plasticizer, for example, plasticized PVC and polyurethane. It is not recommended for the coloring of polystyrene and acrylonitrile butadiene styrene copolymers.

Pigment red 187 / 12486 / CAS 59487.23.9

Properties: Pigment red 187 is polymorphous, and two crystal modifications are known, which differ considerably in fastness properties and color shade. Only the bluish red modification is commercially available. The pigment does not migrate in plasticized PVC. The shrinkage of PE is only slightly affected by this pigment.

Good heat stability: 300 °C (572 °F) in PS and PC; 290 °C (554 °F) in ABS; 260 °C (500 °F) in PE. The heat stability is independent of the concentration within a wide range, therefore it can be used to nuance shades.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE; 7 / 7 in PVC.

Application: It can be used in many polymers, for example, PVC, PO, PS, ABS, and for spin dyeing of PP and PAN.

Pigment red 188 / 12467 / CAS 61487.48.1

Properties: Yellowish red, it tends to bloom in plasticized PVC at low concentrations.

Heat stability: Approx. 220 °C (428 °F) in PE.

Application: Its use is limited to rigid PVC and grades of PE with a low processing temperature, mainly PE-LD.

Pigment red 222 / – / CAS 71872.63.4

Properties: Bluish red, average tinting strength, tends to migrate in plasticized PVC. The chemical constitution is not yet published, but it is classified as member of this pigment group.

Average heat stability: 240 °C (464 °F) in PE, at higher temperatures the color shifts toward the bluish side.

Application: Its use is more or less limited to rigid PVC, POs, and PU.

Pigment orange 22 / 12470 / CAS 6358.48.1

Properties: Reddish orange, good fastness properties.

Application: Its use is limited to spin dyeing.

Pigment orange 38 / 12367 / CAS 12236.64.5

Properties: Yellowish red, fast to migration, only a slight effect on the shrinkage of polyethylene.

Good heat stability: 260–280 °C (500–536 °F) in PE, which decreases at concentrations below 0.05%, and is only 240 °C (464 °F) at 0.005%.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC, similar fastness in PE.

Application: It is used primarily in PVC, PO, PS, and for spin dyeing.

Pigment brown 1 / 12480 / CAS 6410.40.8

Properties: Neutral brown, not stable in many organic solvents, which limits its use considerably.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in rigid PVC.

Application: This pigment has lost much of its importance, but it is still used for brown transparent PVC bottles. The pigment dissolves in PS at the processing temperature, giving an orange shade.

Table 5.13: List of Substituents of Naphthol Pigments According to Basic Formula 2b

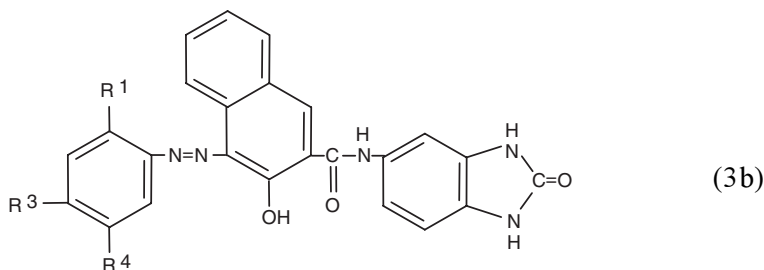
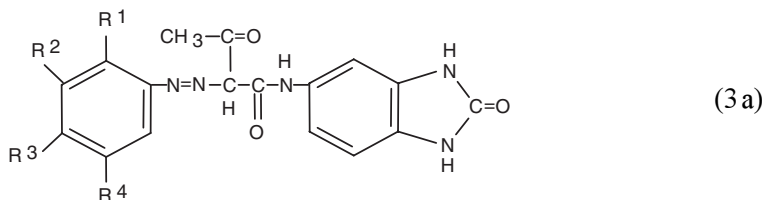
Color index number	Substituents					
	R ²	R ⁴	R ⁵	R ⁶	R ⁸	R ⁹
P. red 5	OCH ₃	H	SO ₂ N(C ₂ H ₅) ₂	OCH ₃	OCH ₃	Cl
P. red 31	OCH ₃	H	CONHC ₆ H ₅	H	H	NO ₂
P. red 112	Cl	Cl	Cl	CH ₃	H	H
P. red 146	OCH ₃	H	CONHC ₆ H ₅	OCH ₃	Cl	OCH ₃
P. red 150	OCH ₃	H	CONHC ₆ H ₅	*		
P. red 164	**					
P. red 170	H	CONH ₂	H	OC ₂ H ₅	H	H
P. red 187	OCH ₃	H	CONHC ₆ H ₄ - (p)CONH ₂	OCH ₃	OCH ₃	Cl
P. red 188	COOCH ₃	H	CONHC ₆ H ₃ - Cl ₂ (2,5)	OCH ₃	H	H
P. red 222	**					
P. orange 22	Cl	H	Cl	OC ₂ H ₅	H	H
P. orange 38	Cl	H	CONH ₂	H	NHCOCH ₃	H
P. brown 1	Cl	H	Cl	OCH ₃	H	OCH ₃

* The substituent is only CONH₂, no additional benzene ring.

** Chemical constitution not yet published.

Benzimidazolone Pigments

The shades of benzimidazolone pigments are either yellow and orange or red and brown. All pigments contain the 5-aminocarbonyl benzimidazolone group, but there are differences in detail. In the case of the yellow and orange shades the coupling component is 5-acetoacetylaminobenzimidazolone, and this leads to basic formula 3a, which parallels the acetoacetarylides of the monoazo pigments (the benzene ring is replaced by the benzimidazolone group; refer to basic formula 1). The red and brown pigments can be considered as a variation of the naphthol pigments (refer to basic formula 2b), where the benzene ring is replaced by the benzimidazolone group, which leads to the basic formula 3b.



The following benzimidazolone pigments are based on basic formula 3a (Table 5.14):

Pigment yellow 120 / 11783 / CAS 29920.31.8

Properties: Greenish yellow, no tendency to migrate, no effect on the shrinkage of PE-HD.

Good heat stability: 270 °C (518 °F) in PS; 260 °C (500 °F) in PO; and 250 °C (482 °F) in ABS. In PE the heat stability decreases only at a concentration below 0.01%.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC, PE, and PS.

Good weather resistance: 4–5 in PE.

Application: It can be used in many polymers.

Pigment yellow 151 / 13980 / CAS 61036.28.0

Properties: Greenish yellow, no tendency to migrate, only a slight effect on the shrinkage of PE-HD.

Good heat stability: 280 °C (536 °F) in ABS; 260 °C (500 °F) in PS and PO. The heat stability decreases only slightly with decreasing concentration in PE.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC, similar data in PS and PE.

Application: It can be used in many polymers.

Pigment yellow 154 / 11 781 / CAS 63 661.02.9

Properties: Greenish yellow, no tendency to migrate.

Low heat stability: 210 °C (410 °F) in PE

Good light fastness and weather resistance in PVC, which makes it suitable for exterior use in this polymer.

Application: The low heat stability limits the use of this pigment to PVC and grades of polyethylene with a low processing temperature (PE-LD).

Pigment yellow 175 / 11 784 / CAS 35 636.63.6

Properties: Greenish yellow, low tinting strength, no effect on the shrinkage of PE-HD; although insoluble in most solvents it may be advisable to check the migration in plasticized PVC.

Good heat stability: 270 °C (518 °F) in PE.

Good light fastness and weather resistance in PVC-U.

Application: It can be used in several polymers.

Pigment yellow 180 / 21 290 / CAS 77 804.81.0

Properties: Greenish yellow, no tendency to migrate, no effect on the shrinkage of PE-HD. In contrast with the other pigments of this group it is a disazobenzimidazolone pigment.

Good heat stability: 300 °C (572 °F) in PS and PC; 290 °C (554 °F) in PO; 280 °C (536 °F) in PMMA and PET; 260 °C (500 °F) in PA 6. The heat stability in PE is independent of the concentration within a wide range, and decreases only below 0.005%, which means this pigment can be used to nuance color shades.

Good light fastness: 6–7 (pure tone) / 6–7 (white reduction) in PVC; 6–7 / 6 in PE, 7–8 / 6 in PA 6; 6–7 / 7–8 in PET; 5–6 / 3–4 in PMMA.

Application: It can be used in many polymers, including POM (minimum concentration > 0.1%).

Pigment yellow 181 / 11 777 / CAS 74 441.05.7

Properties: Reddish yellow, low tinting strength, no tendency to migrate, no effect on the shrinkage of PE-HD.

Good heat stability: 300 °C (572 °F) in PO and PS, 280 °C (536 °F) in ABS. In PE there is only a slight decrease in heat stability at a concentration between 0.1% and 0.005%.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC, PE, and PS.

Good weather resistance: 4 in PE.

Application: It can be used in many polymers, including POM (minimum concentration > 0.1%). It is not recommended for the coloring of PA and PC.

Pigment yellow 194 / – / CAS 82199.12.0

Properties: Medium yellow, good tinting strength, tendency to migrate in plasticized PVC.

Medium heat stability: 250 °C (482 °F) in PS; 230 °C (446 °F) in PE. It is noticeable that the heat stability decreases in PE rather fast at a concentration < 0.1%.

Medium to good light fastness: 6 (pure tone) / 5–6 (white reduction) in PVC; 7 / 7 in PE and PS.

Application: The relative low heat stability limits its use to polymers with a low processing temperature, for example, PVC, PE-LD, PS. It is not recommended for the coloring of ABS.

Pigment orange 36 / 11780 / CAS 12236.62.3

Properties: Reddish orange, no tendency to migrate in plasticized PVC, no effect on the shrinkage of PE-HD.

Low heat stability: 220 °C (428 °F) in PE.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC.

Application: The low heat stability limits its use to polymers with a low processing temperature, for example, PVC, PE-LD.

Pigment orange 62 / 11775 / CAS 75601.68.2

Properties: Yellowish orange.

Low heat stability: 200–220 °C (392–428 °F) in PE.

Good light fastness in rigid PVC.

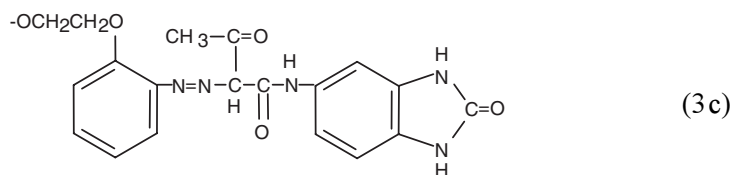
Application: The low heat stability limits its use to polymers with a low processing temperature, for example, PVC, PE-LD; in addition it is used for spin dyeing of PP grades with good flow behavior.

Table 5.14: List of Substituents of Benzimidazolone Pigments According to Basic Formula 3a

Color index number	Substituent			
	R ¹	R ²	R ³	R ⁴
P. yellow 120	H	COOCH ₃	H	COOCH ₃
P. yellow 151	COOH	H	H	H
P. yellow 154	CF ₃	H	H	H
P. yellow 175	COOCH ₃	H	H	COOCH ₃
P. yellow 180	*	H	H	H
P. yellow 181	H	H	-OCNH-C ₆ H ₄ -CONH ₂	H
P. yellow 194	OCH ₃	H	H	H
P. orange 36	NO ₂	H	Cl	H
P. orange 62	H	H	NO ₂	H

* This substituent has the following chemical constitution:

Substituent R¹ of P. yellow 180:



The following benzimidazolone pigments are based on basic formula 3b (Table 5.15):

Pigment red 171 / 12512 / CAS 6985.95.1

Properties: Bluish red, high tinting strength, no migration in plasticized PVC.

Medium heat stability: 240 °C (464 °F) in PE.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PVC; 6–7 / 6 in PE.

Application: The low heat stability limits its use to polymers with a low processing temperature, for example, PVC, PE-LD; in addition it is used in unsaturated polyester and for spin dyeing of PAN.

Pigment red 175 / 12513 / CAS 6985.92.8

Properties: Dull red, no migration in plasticized PVC, only a very slight effect on the shrinkage of PE-HD.

Good heat stability: 300 °C (572 °F) in PS; 290 °C (554 °F) in ABS; 270 °C (518 °F) in PE. The heat stability decreases with decreasing concentration in PE.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC; 8 / 8 in PE and PS.

Good weather resistance: It is used in combination with carbon black for brown PVC window frames.

Application: It can be used in many polymers, for example, PVC, PO, PET, PUR, and for spin dyeing of PP. It is not recommended for the coloring of PC.

Pigment red 176 / 12515 / CAS 12225.06.8

Properties: Bluish red, no migration in plasticized PVC.

Good heat stability: 300 °C (572 °F) in PS; 270 °C (518 °F) in PO; 260 °C (500 °F) in PMMA. It should be taken into consideration that the heat stability decreases in some polymers with increasing amounts of titanium dioxide.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in PVC; 7 / 7 in PO; 7 / 4 in PMMA.

Application: It can be used in many polymers, for example, PVC, PO, PS, and for spin dyeing of PP and PAN. It is not recommended for the coloring of ABS.

Pigment red 185 / 12516 / CAS 61951.98.2

Properties: Bluish red, nearly no migration in plasticized PVC.

Medium heat stability: 270 °C (518 °F) in PS; 250 °C (482 °F) in PE. The heat stability is more or less independent of the concentration within a range between 0.1 and 0.005% (pure tone) in PE, but the heat stability decreases with increasing amounts of titanium dioxide (white reduction).

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC; 6 / 5–6 in PE; 7 / 6–7 in PS.

Application: Its use is limited to polymers with low processing temperatures, for example, PVC, PUR, PVCD, PE-LD, and PP.

Pigment red 208 / 12514 / CAS 31778.10.6

Properties: High tinting strength, no migration in plasticized PVC.

Low heat stability: Approx. 220–200 °C (428–392 °F). The heat stability is higher in a transparent specimen (pure tone) than in a white reduction.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in PVC.

Application: Because of the insufficient heat stability it can be used only in PVC and for spin dyeing of PP and PAN, provided that the processing temperature is < 200 °C (< 392 °F). It cannot be used in polyolefins.

Pigment violet 32 / 12517 / CAS 12225.08.0

Properties: Bluish red, high tinting strength, no migration in plasticized PVC.

Low heat stability: < 210 °C (< 410 °F) in PE.

Good light fastness: 7–8 (pure tone) / 6–7 (white reduction) in PVC.

Application: Because of insufficient heat stability it can be used only in PVC and for spin dyeing of viscose rayon. It may be used in some light-flowing PE-LD grades, provided that the processing temperature is < 210 °C (< 410 °F). A preliminary examination is recommended.

Pigment brown 25 / 12510 / CAS 6992.11.6

Properties: Reddish brown, high tinting strength, nearly no migration in plasticized PVC (depending on the concentration), only a slight effect on the shrinkage of PE-HD.

Good heat stability: 280 °C (536 °F) in PET and PS. The heat stability depends clearly on the concentration in PE; it is 290 °C (554 °F) at a concentration of 0.1%, but only 240 °C (464 °F) at a concentration of 0.005%.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 8 in PE; 7 / 6–7 in PET.

Good weather resistance: The pigment meets the requirements for long-term exposure, for example, in window frames composed of PVC.

Application: It can be used in many plastics, for example, PVC, PO, PS, PET, and for spin dyeing of PP and PAN.

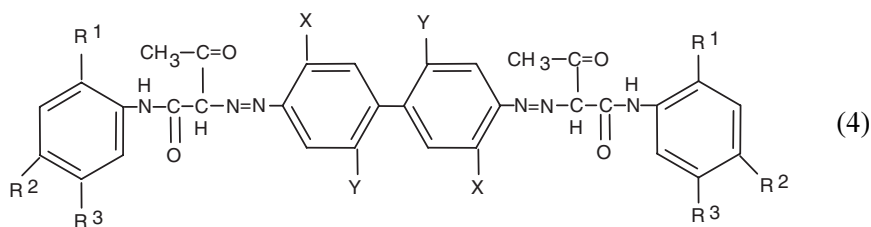
Table 5.15: List of Substituents of Benzimidazolone Pigments According to Basic Formula 3b

Color index number	Substituent		
	R ¹	R ³	R ⁴
P. red 171	OCH ₃	NO ₂	H
P. red 175	COOCH ₃	H	H
P. red 176	OCH ₃	CONHC ₆ H ₅	H
P. red 185	OCH ₃	SO ₂ NHCH ₃	CH ₃
P. red 208	COOC ₄ H ₉ (n)	H	H
P. violet 32	OCH ₃	SO ₂ NHCH ₃	OCH ₃
P. brown 25	Cl	H	Cl

5.2.1.2 Disazo Pigments

Disazodiarylide Pigments

The chemical constitution of the disazodiarylide pigments follows basic formula 4. In the past most members of this group were very important and very often used pigments, for example, Pigment yellow 12, yellow 13, yellow 14, yellow 17, and yellow 83. The characteristic of this pigment group is the content of dichlorobenzidine as component.



The substituent X consists mainly of chlorine, and the substituent Y of hydrogen. A further variation of the substituent X is either a CH₃ or OCH₃ group. Studies done in 1989 and 1990 showed that these pigments may decompose during

processing in polymers at temperatures above 200 °C (392 °F). The first decomposition products are a monoazo substance and an aromatic amine, and the decomposition of the monoazo substance continues at temperatures > 240 °C (464 °F), especially after a prolonged exposure to this temperature, and dichlorobenzidine is formed. The result of analytical investigations proved that only traces of dichlorobenzidine (a few ppm) were formed. Dichlorobenzidine and some other benzidine derivatives are classified as carcinogenic according to toxicological studies (in Germany dichlorobenzidine is listed as a group III A2 compound = proved carcinogenic effects in animals). As consequence of these studies the processing temperature of these pigments was limited to 200 °C (392 °F). The processing temperature of polymers is usually higher; therefore these pigments cannot be used any longer for the coloring of polymers, except PVC, which is normally processed below 200 °C (392 °F).

In Amendment 2 of the German *Bedarfsgegenständeverordnung* [46], dated 1994, all azo colorants were banned that decompose under specified test methods forming a listed amine. The list contains 20 amines that are classified as carcinogenic, including dichlorobenzidine and other benzidine derivatives. Many dyes and pigments cannot be used any longer for coloring of polymers. Numerous colors had to be matched anew which caused some problems because the properties of alternative colorants were quite different, for example, with respect to their hiding power and price.

Bisacetoacetarylide Pigments

From this group of pigments only Pigment yellow 155 is of commercial interest for coloring of plastics.

Pigment yellow 155 / – / CAS 68516.73.4

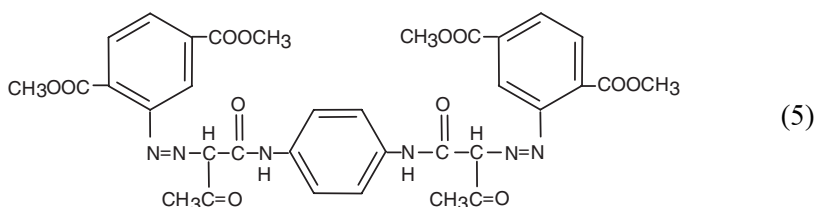
Properties: Greenish yellow, good tinting strength, not completely fast to migration in plasticized PVC.

Good heat stability: 260 °C (500 °F) in PE.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE, similar fastness in PVC and PS.

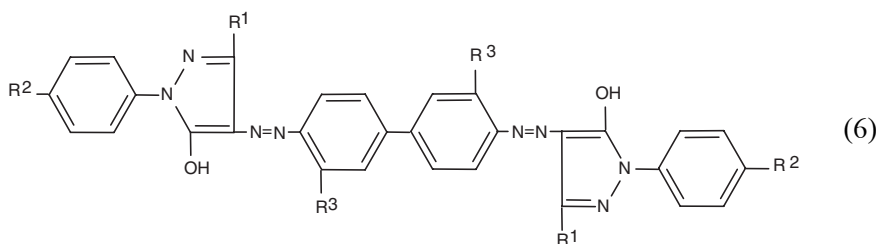
Application: It can be used in many polymers, for example, PVC, PO, PMMA, and PS. It is not recommended for the coloring of ABS and SAN.

Pigment yellow 155 has the following chemical constitution:



Disazopyrazolone Pigments

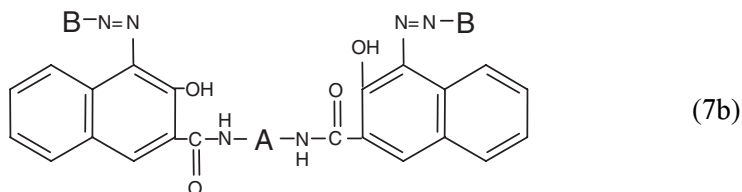
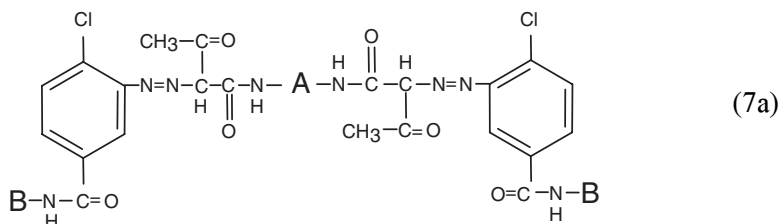
The disazopyrazolone pigments are based on basic formula 6.



Basic formula 6 indicates that this type of pigments also contains benzidine derivatives as a central component. The substituent R^3 is either chlorine or the methoxy group. These two benzidine derivatives are banned accordingly to Amendment 2 of the German Bedarfsgegenständeverordnung (refer to the chapter on disazodiarylide pigments). In the past Pigment orange 13, orange 34, and Pigment red 37, red 38, and red 41 played an important role in the coloring of plastics, but today they are insignificant.

Disazo Condensation Pigments

The pigments of this group are either yellow or red, as a consequence of their different chemical constitutions, which however is very close related to each other. The pigments based on formula 7a are yellow, whereas pigments with the basic formula 7b are red. A general characteristic of these pigments is a good heat stability and high light fastness in several polymers; they therefore play an important role in the coloring of plastics.



The following disazo condensation pigments are based on the formula 7a (Table 5.16):

Pigment yellow 93 / 20710 / CAS 5580.57.4

Properties: Greenish yellow, good tinting strength, no migration in plasticized PVC, only a slight effect on the shrinkage of PE-HD.

Good heat stability: 250–280 °C (482–536 °F) in PE, depending on the concentration.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC; 7–8 / 6–7 in PE; providing the processing time is short. The light fastness decreases when the processing time is up to 5 minutes.

Medium weather resistance: 3–4 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, and for spin dyeing of PP.

Pigment yellow 94 / 20038 / CAS 5580.58.5

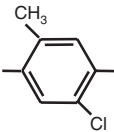
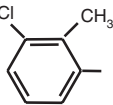
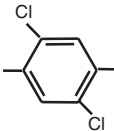
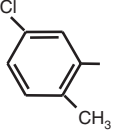
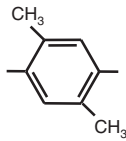
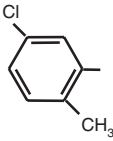
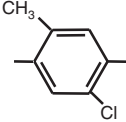
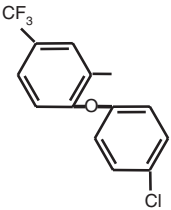
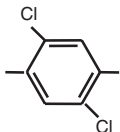
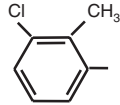
Properties: Greenish yellow, medium tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Good heat stability: 290 °C (554 °F) in PE; it should be mentioned that the heat stability depends on the amount of titanium dioxide in the color preparation. In pure tone the heat stability decreases at a concentration < 0.1%, but is constant in white reduction down to 0.001%.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, and for spin dying of PP and PAN.

Table 5.16: List of Substituents of Disazo Condensation Pigments Based on Formula 7a

Colour Index Number	Substituent	
	A	B
P. yellow 93		
P. yellow 94		
P. yellow 95		
P. yellow 128		
P. yellow 166		

Pigment yellow 95 / 20034 / CAS 5280.80.8

Properties: Reddish yellow, high tinting strength, no migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good heat stability: 260–280 °C in PE, depending on the concentration.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC; 7 / 6–7 in PE.

Medium weather resistance: Only 2–3 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, PUR, and for spin dyeing of PP.

Pigment yellow 128 / 20037 / CAS 57971.97.8

Properties: Greenish yellow, medium tinting strength, no migration in plasticized PVC, only a slight effect on the shrinkage of PE-HD.

Medium heat stability: 240 °C (464 °F) in PE.

Good light fastness: 7–8 (pure tone) / 8 (white reduction) in PVC, 8 / 7–8 in PE.

Application: The use of this pigment is limited to polymers with a low processing temperature, for example, PVC, PE-LD, and for spin dyeing of PP and PAN, provided the required processing temperature is low enough.

Pigment yellow 166 / 20035 / CAS 76233.82.4

The pigment is available only in Japan [45].

The following disazo condensation pigments are based on formula 7b (Table 5.17):

Pigment orange 31 / 20050 / CAS 12286.58.7

Properties: Reddish orange, good to medium tinting strength, not completely fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD. It is used very often in combination with carbon black for brown shades.

Good heat stability: 300 °C (572 °F) in PE.

Medium light fastness: Approx. 6 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, and for spin dyeing of PP.

Pigment red 144 / 20735 / CAS 5280.78.4

Properties: Bluish red, high tinting strength, not completely fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD. This pigment is marketed by several manufacturers, and differs mainly in its crystal size. This is probably the reason why the data regarding fastness properties differ.

Good heat stability: 280–290 °C (536–554 °F) in PE.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PE.

Good weather resistance: 4 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, PS, PUR, and for spin dyeing of PP and PAN.

Pigment red 166 / 20730 / CAS 12225.04.6

Properties: Yellowish red, high tinting strength, not completely fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Good heat stability: 280–290 °C (536–554 °F) in PE, depending on the concentration.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 7 in PE; 7 / 6–7 in PP.

Good weather resistance: 4 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, PS, PUR, and for spin dyeing of PP and PAN.

Pigment red 214 / – / CAS 40618.31.3

Properties: Bluish red, high tinting strength, not completely fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Good heat stability: 300 °C (572 °F) in PE, PS, acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC).

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 7–8 in PE; 6 / 7 in ABS; 6–7 / 6–7 in PS; 7–8 / 7 in PC.

Application: It can be used in many polymers, but is not recommended for the coloring of polyamide (PA).

Pigment red 220 / 20055 / CAS 57971.99.0

Properties: Yellowish red, medium tinting strength, only slight effect on the shrinkage of PE-HD (> 260°C [>500 °F]).

Good heat stability: 280–290 °C (536–554 °F) in PE, depending on the concentration.

Good light fastness: 7 (pure tone) / 7 (white reduction) in PVC; 7 / 6–7 in PE.

Medium weather resistance: Approx. 3 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, and for spin dyeing of PP and PAN.

Pigment red 221 / 20065 / CAS 61815.09.6

Properties: Bluish red, high tinting strength, not completely fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD (warpage).

Good heat stability: Approx. 280–290 °C (536–554 °F) in PE.

Good light fastness: 7–8 (pure tone) / 6–7 (white reduction) in PVC.

Application: It is recommended especially for the coloring of PVC and PUR. An application in PE may be problematic because of the strong effect on the shrinkage (warpage).

Pigment red 242 / 20067 / CAS 118440.67.8 (CAS 52238.92.3)

Properties: Yellowish red, medium tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD (warpage).

Good heat stability: 290–300 °C (554–572 °F) in PE, PS, PC.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 7–8 in PE; 7–8 / 7 in PS; 7 / 7 in ABS; 7–8 / 7–8 in PC.

Application: It can be used in many polymers.

Pigment red 248

Properties: Bluish red, high tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD depending on the processing temperature (warpage). The chemical constitution is not yet published, but it is classified as a disazo condensation pigment.

Good heat stability: 290 °C (554 °F) in PE

Good light fastness: 8 (pure tone) / 7 (white reduction) in PVC, similar data for PE.

Application: It can be used in many polymers, for example, PVC, PE, PS.

Pigment red 262

Properties: Bluish red. The chemical constitution is not yet published, but it is classified as disazo condensation pigment.

Good heat stability: 290–300 °C (554–572 °F) in PE, PS, PC.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 7–8 in PE; 5–6 / 5 in PS; 6 / 6 in ABS; 7–8 / 7 in PC.

Application: It can be used in many polymers, for example, PVC, PE, PS, ABS, PC. It is not recommended for PA.

Pigment brown 23 / 20060 / CAS 57972.00.6

Properties: Reddish brown, medium to good tinting strength, not completely fast to migration in plasticized PVC (depending on the plasticizer), medium effect on the shrinkage of PE-HD. Because of its good weather resistance this pigment is used in combination with carbon black in PVC window frames.

Good heat stability: 280 °C (536 °F) in PE and PS.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC.

Application: It can be used in many polymers, for example, PVC, PE, PS, and for spin dyeing of PP and PAN.

Pigment brown 41

Properties: Yellowish brown, medium tinting strength, not completely fast to migration in plasticized PVC. The chemical constitution is not yet published, but it is classified as a disazo condensation pigment.

Good heat stability: 300 °C (572 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE.

Application: It can be used in many polymers, for example, PVC, PE, PS, PMMA, ABS, and SAN. It is not recommended for the coloring of PA.

Pigment brown 42

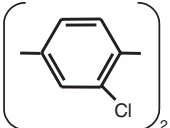
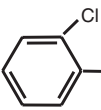
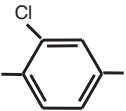
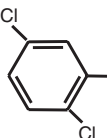
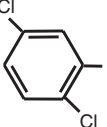
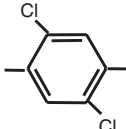
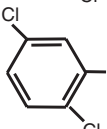
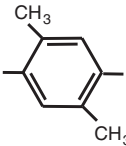
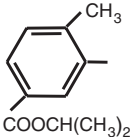
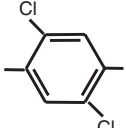
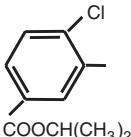
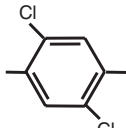
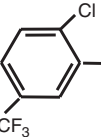
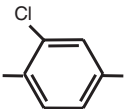
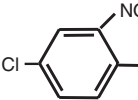
Properties: Yellowish brown, medium tinting strength, not completely fast to migration in plasticized PVC. The chemical constitution is not yet published, but it is classified as disazo condensation pigment.

Good heat stability: 280 °C (536 °F) in PE.

Good light fastness and weather resistance in PVC.

Application: This rather new pigment is recommended especially for the coloring of PVC, but it can be used also in other polymers.

Table 5.17: List of Substituents of Disazo Condensation Pigments Based on Formula 7b

Colour Index Number	Substituent	
	A	B
P. orange 31		
P. red 144		
P. red 166		
P. red 214		
P. red 220		
P. red 221		
P. red 242		
P. brown 23		

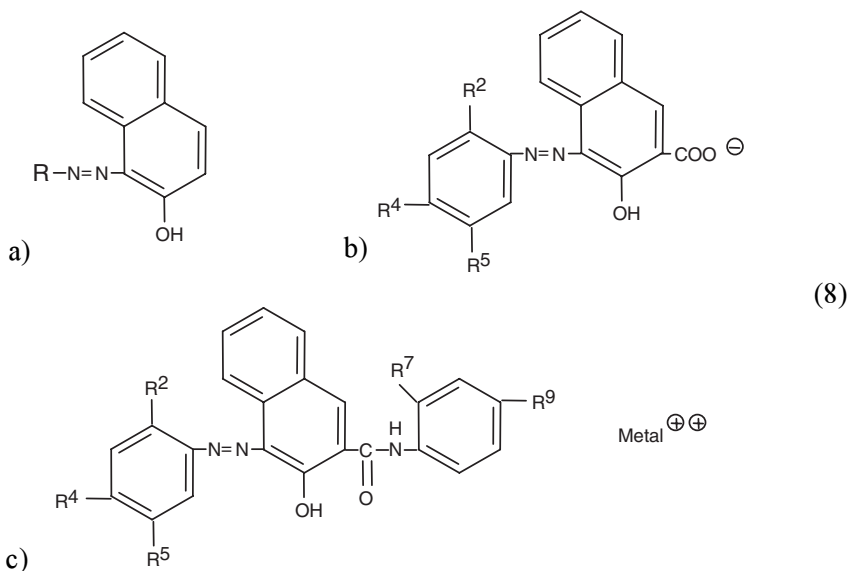
5.2.1.3 Azo Pigment Lakes

β -Naphthol Pigment Lakes

Analogous to the nonlaked naphthol pigments there are several variations. The defining characteristic is the presence of at least one acidic group (sulfonic acid and/or carboxylic acid) as a substituent. The simplest molecule is a diazo component and β -naphthol as coupling component; the disazo component contains the acid group (basic formula 8a).

The replacement of the β -naphthol component by **beta-oxynaphthoic acid (BONA)** as coupling component leads to basic formula 8b. The coupling component contains an additional acid group ($-\text{COO}^-$).

This acidic group can be used to add a further benzene ring with substituents, which gives basic formula 8c.



The following naphthol pigment lakes are based on formula 8a (Table 5.18):

Pigment red 53 / 15585 / CAS 2092.56.0

Pigment red 53:1 / 15585:1 / CAS 5160.02.1

Properties: Medium to good tinting strength, nearly completely fast to migration in plasticized PVC, no effect on the shrinkage of PE-HD. The pigment is today marketed mainly as barium salt (Pigment red 53:1), in the past also as sodium salt

(Pigment red 53) and as strontium salt (Pigment red 53:–), but both disappeared more or less completely from the market. There are only slight differences between these salts.

Soluble barium as an impurity in colorants is limited in many countries, for example, in Germany according to the BgVV-Recommendations, chapter IX, and in the European community according to the EU-Resolution AP (89) 1. The *normal* quality of Pigment red 53:1 does not fulfill these requirements regarding the content of soluble barium impurities. *Special* qualities of this pigment are, however, marketed that fulfill these requirements. This goal was reached by modifying the synthesis process of this pigment in combination with special cleaning steps. In using this pigment for color matching it is important to choose the right quality depending on the customer requirements. This pigment is marketed by many manufacturers, and therefore it is not surprising that the supplied data vary more or less, but basically they are the same.

Good heat stability: 250–280 °C (482–536 °F) in PE; 290 °C (554 °F) in PS; 270 °C (518 °F) in ABS. The heat stability decreases considerably below a pigment concentration of 0.05–0.1%.

Medium to insufficient light fastness: 6 (pure tone) / 2 (white reduction) in PVC; 3–4 / 2–3 in PE; 4 / 3–4 in PS; 3 / 2–3 in ABS.

Application: This pigment can be used only when there are no special requirements regarding light fastness.

Pigment red 68 / 15525 / CAS 5850.80.6

Properties: Yellowish red (scarlet), medium tinting strength, not completely fast to migration in plasticized PVC, no effect on the shrinkage of PE-HD, calcium salt.

Good heat stability: 290–300 °C (554–572 °F) in PE

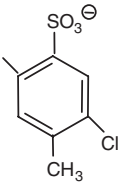
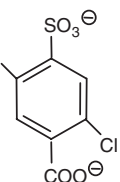
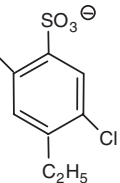
Medium light fastness: 4–5 (pure tone) / 3–4 (white reduction) in PE.

Application: This pigment can be used only when there are no special requirements regarding light fastness; it no longer plays any role in the coloring of plastics.

Pigment orange 46 / 15602 / CAS 67801.01.8

This pigment no longer plays any role in the coloring of plastics owing to its insufficient light fastness.

Table 5.18: List of the Substituents of the Pigments According to Basic Formula 8a

Color Index Number	R	Metal
P. red 53 P. red 53:1 P. red 53:-		$\text{Na}^{\oplus}$ $\text{Ba}^{\oplus\oplus}$ $\text{Sr}^{\oplus\oplus}$
P. red 68		$\text{Ca}^{\oplus\oplus}$
P. orange 46		$\text{Ba}^{\oplus\oplus}$

The following naphthol pigment lakes (BONA) are based on formula 8b (Table 5.19):

Pigment red 48

This pigment is marketed as barium, calcium, strontium, manganese, and magnesium salt. The properties of the different salts differ only slightly. Their application is limited to PVC and PE-LD owing to the low heat stability. In addition the light fastness is not good; consequently these pigments can be used only when there are no high requirements regarding the light fastness for the final product.

Pigment red 48:1 / 15865:1 / CAS 7585.41.3

Properties: Barium salt, medium tinting strength, no migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Low heat stability: 200–240 °C (392–464 °F) in PE.

Low light fastness.

Application: As a barium salt this pigment does not fulfill the requirements regarding soluble barium as an impurity in colorants, therefore and in connection with the insufficient light fastness, it does not play any role in the coloring of plastics.

Pigment red 48:2 / 15865:2 / CAS 7023.61.2

Properties: Calcium salt, good tinting strength, no effect on the shrinkage of PE-HD. The heat stability and the light fastness are slightly better than those of the barium salt.

Medium heat stability: 220–250 °C (428–482 °F) in PE, 250 °C (482 °F) in PS.

Medium light fastness: 7 (pure tone) / 4 (white reduction) in PVC, 6 / 4–5 in PE.

Application: This pigment can be used only when there are no special requirements regarding light fastness of the final product, especially in white reduction.

Pigment red 48:3 / 15865:3 / CAS 15782.05.5

Properties: Strontium salt, no migration in plasticized PVC, no effect on the shrinkage of PE-HD. Within the Pigment red 48 group it is the most stable salt and consequently used most frequently.

Medium heat stability: 240 °C (464 °F) in PE, 250 °C (482 °F) in PS, 260 °C (500 °F) in ABS.

Medium light fastness: 6–7 (pure tone) / 5–6 (white reduction) in PVC; 6–7 / 6 in PE; 6 / 4–5 in PS; 4–5 / 4–5 in ABS.

Application: This pigment can be used only when there are no strict requirements regarding light fastness for the final product.

Pigment red 48:4 / 15865:4 / CAS 5280.66.0

Properties: Manganese salt, high tinting strength, no effect on the shrinkage of PE-HD.

The manganese salt should not be used for the coloring of PP, because manganese ions accelerate the aging of this polymer (depending on the type), and the PP becomes brittle very fast.

The heat stability and the light fastness are inferior to those of Pigment red 48:3, therefore this manganese salt more or less disappeared from the market.

Pigment red 48:5 / 15865:5

Properties: Magnesium salt. According to the literature the properties of this salt are similar to those of Pigment red 48:2.

Pigment red 57:1 / 15850:1 / CAS 5281.04.9

Properties: Calcium salt, bluish red, good tinting strength, slight effect on the shrinkage of PE-HD.

Low heat stability: 220–240 °C (428–464 °F) in PE. The heat stability decreases considerably at a pigment concentration below 0.1%, therefore this pigment can be used only for intensive colors.

Medium light fastness: 6–7 (pure tone) / 5–6 or 3–4 (white reduction) in PVC; 4 / 5 or 6 / 3 in PE. The supplied data vary in detail between the different manufacturers, but they show basically the same tendency.

Application: The use of this pigment for the coloring of plastics is limited owing to its low heat stability. In addition, it can be used only if there are no strict requirements regarding the light fastness of the final product.

Pigment red 200 / 15867 / CAS 58067.05.3

Properties: Calcium salt.

Application: The use of this rather new bluish red pigment is limited to plastic parts without special requirements regarding light fastness.

Table 5.19: List of the Substituents of the Pigments According to Basic Formula 8b

Color index number	Substituent			
	R ²	R ⁴	R ⁵	Metal ion
P. red 48:1	SO ₃ [−]	CH ₃	Cl	Ba ⁺⁺
P. red 48:2	Same substituents			Ca ⁺⁺
P. red 48:3	Same substituents			Sr ⁺⁺
P. red 48:4	Same substituents			Mn ⁺⁺
P. red 48:5	Same substituents			Mg ⁺⁺
P. red 57:1	SO ₃ [−]	CH ₃	H	Ca ⁺⁺
P. red 200	SO ₃ [−]	Cl	C ₂ H ₅	Ca ⁺⁺

The following naphthol pigment lakes are based on formula 8c (Table 5.22):

Pigment red 151 / 15890 / CAS 61013.97.6

Properties: Barium salt, bluish red, medium tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Good heat stability: 260 °C (500 °F) in PE. The pigment can dissolve partially in PS and ABS at temperatures above 260 °C (500 °F), combined with a slight color change.

Medium to good light fastness: 7 (pure tone) / 6 (white reduction) in PVC; 6–7 / 5–6 in PE.

Application: It is used in several polymers, for example, PVC, PE, PP, PS, ABS. Another use is the coloring of cast resins such as methylmethacrylate and unsaturated polyesters because of its good resistance to peroxide catalysts, which are usually used for the polymerization.

Pigment red 237

Properties: Yellowish red, medium tinting strength, no migration in plasticized PVC. The exact chemical structure has not yet been published.

Application: This rather new pigment is recommended especially for coloring of PVC.

Pigment red 239

Properties: Bluish red, medium tinting strength, no migration in plasticized PVC. The exact chemical structure has not yet been published.

Good heat stability: 270 °C (518 °F) in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, and others.

Pigment red 240

Properties: Bluish red, low tinting strength. The exact chemical constitution has not yet been published.

Good heat stability: 300 °C (572 °F) in PE.

Application: It can be used in several polymers. At this time it is only of regional importance (Japan) [45].

Pigment red 243 / 15910 / CAS 50326.33.5

Properties: Barium salt, yellowish red, nearly completely resistant to migration in plasticized PVC, affects the shrinkage of PE-HD.

Low light fastness: 4 (pure tone) / 3 (white reduction) in PVC.

Application: It is recommended for PVC and PE-LD, but owing to its low light fastness this pigment can be used only if there are no strict requirements regarding the light fastness of the final product.

Pigment red 247 / 15915 and Pigment red 247:1 / 15915:1 / CAS 43035.18.3

Properties: Both pigments have the same chemical composition but a different crystal modification; consequently their properties differ slightly. Calcium salt, bluish red, medium tinting strength, not completely resistant to migration in plasticized PVC, only a very slight effect on the shrinkage of PE-HD.

Both grades of this pigment are marketed.

Good heat stability (independent of the pigment concentration) (Table 5.20):

Table 5.20: Heat Stability of Pigment Red 247 and 247:1

Pigment	Polymer				
	PE	PS	ABS	PET	PC
P. red 247	300 ° (572 °F)	300 °C (572 °F)	300 °C (572 °F)		310 °C (590 °F)
P. red 247:1	280–300 °C (536–572 °F)	300 °C (572 °F)	300 °C (572 °F)	280 °C (536 °F)	310 °C (590 °F)

Medium to good light fastness (Table 5.21):

Table 5.21: Light Fastness of Pigment Red 247 and 247:1

Pigment	Polymer				
	PE	PS	ABS	PET	PC
P. red 247	6–7/6	6–7/6	6/5–6		5/4–5
P. red 247:1	6–7/5–6	6/6	6/6–7	7/4–5	5/5–6

Application: Both crystal modifications can be used in many polymers, but they are not recommended for the coloring of PA.

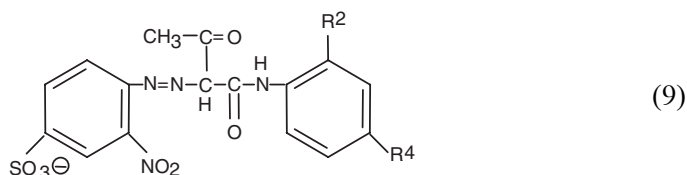
Table 5.22: List of the Substituents of the Pigments According to Basic Formula 8c

Color index number	Substituents					
	R ²	R ⁴	R ⁵	R ⁷	R ⁹	Metal ion
P. red 151	SO ₃ ⁻	H	H	H	SO ₃ ⁻	Ba ⁺⁺
P. red 237	*	*	*	*	*	*
P. red 239	*	*	*	*	*	*
P. red 240	*	*	*	*	*	*
P. red 243	SO ₃ ⁻	CH ₃	Cl	OCH ₃	H	Ba ⁺⁺
P. red 247	CH ₃	H	CONHC ₆ H ₄ SO ₃ ⁻ (p)	H	OCH ₃	Ca ⁺⁺

* chemical constitution not yet published

Monoacetoacetarylide Pigment Lakes

The chemical constitution of these pigments is analogous to that of the nonlaked pigments; the only difference is that the lakes contain an additional SO₃ group as a substituent. This leads to the basic chemical formula 9.



A further consequence of the analogous chemical constitution is the color of these monoacetoacetarylide pigment lakes, which are also yellow pigments (Table 5.23).

Pigment yellow 61 / 13880 / CAS 12286.65.6

Properties: Calcium salt, greenish yellow, low tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Medium heat stability: 250 °C (482 °F) in PE.

Medium light fastness: 5–6 (pure tone) / 5–6 (white reduction) in PE.

Application: Owing to its medium heat stability the use of this pigment is limited to polymers with a rather low processing temperature, for example, PVC, PE, and PP.

Pigment yellow 62:1 / 13940:1 / CAS 12286.66.7

Properties: Calcium salt, reddish yellow, low tinting strength, nearly completely resistant to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Medium heat stability: 240–260 °C (464–500 °F) in PE

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC and PE.

Application: Owing to its medium heat stability the use of this pigment is limited to polymers with a relative low processing temperature, for example, PVC, PE, PP, PS, PUR.

Pigment yellow 133 / – / CAS 132821.92.2

Properties: Strontium salt, greenish yellow, low tinting strength. The exact chemical constitution has not yet been published.

Medium heat stability: 260 °C (500 °F) in PE

Application: This pigment is only of regional importance (Asia) [45].

Pigment yellow 168 / 13960 / CAS 71832.85.4

Properties: Calcium salt, greenish yellow, low tinting strength, no migration in plasticized PVC, affects the shrinkage of PE-HD.

Low heat stability: 240 °C (464 °F) in PE.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC and PE

Application: Owing to its low heat stability the use of this pigment is limited to polymers with a low processing temperature, for example, PVC, and light-flowing grades of PE and PP.

Pigment yellow 169 / 13955 / CAS 73385.03.2

Properties: Calcium salt, reddish yellow.

Properties and applications very similar to Pigment yellow 168.

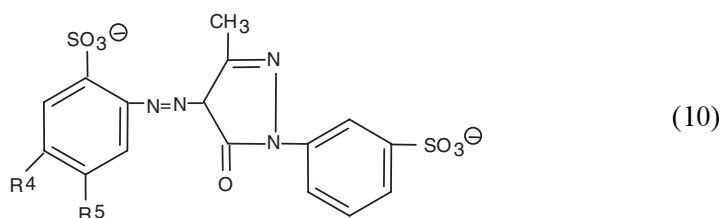
Table 5.23: List of the Substituents of Pigments According to Basic Formula 9

Color index number	Substituents		
	R ² ,	R ⁴	Metal ion
P. yellow 61	H	H	Ca ⁺⁺
P. yellow 62:1	CH ₃	H	Ca ⁺⁺
P. yellow 133	*	*	Sr ⁺⁺
P. yellow 168	Cl	H	Ca ⁺⁺
P. yellow 169	H	OCH ₃	Ca ⁺⁺

* chemical constitution not yet published

Pyrazolone Pigment Lakes

The nonlaked monoazopyrazolone pigments play no role in the coloring of plastics, but the situation is completely different in case of the laked pyrazolone pigments. They are very important and often used pigments (Table 5.24). The chemical constitution of this group of pigments is according to basic formula 10.



Pigment yellow 183 / 18792 / CAS 65212.77.3

Properties: Calcium salt, reddish yellow, low tinting strength, no migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good heat stability: 300 °C (572 °F) in PE.

Medium to good light fastness: 6 (pure tone) / 6–7 (white reduction) in PVC, 8 / 5 in PE. The light fastness decreases in PE depending on the degree of white reduction.

Application: This pigment can be used in many polymers, for example, PVC, PE, PP, PS, ABS, SAN, PMMA. It is not recommended in PA and PC.

Pigment yellow 190 / – / CAS 141 489.68.1

Properties: Calcium salt, low tinting strength. Owing to a very slight solubility in water there might be a slight coloring of the water bath during the manufacture of a masterbatch (granulation step). The exact chemical constitution has not yet been published.

Good heat stability: 300 °C (572 °F) in PE, 270 °C (518 °F) in PA.

Application: This pigment can be used in many polymers, for example, PVC, PE, PP, PS, ABS, and others, including PA.

Pigment yellow 191 / 18795 / CAS 129423.54.7

Properties: Calcium salt, reddish yellow, medium tinting strength, no migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good heat stability: 260–280 °C (500–536 °F) in PE, PS, ABS; 280 °C (536 °F) in PET, PMMA; 260 °C (500 °F) in PA; 320 °C (608 °F) in PC. The heat stability is independent of pigment concentration within a wide range in PE.

Good light fastness: 7 (pure tone) / 6 (white reduction) in PVC; 7–8 / 6–7 in PE; 7–8 / 7–8 in PET; 7 / 6–7 in PA; 7 / 7 in PS and ABS; 4–5 / 3–4 in PMMA; 6 / 4–5 in PC.

Medium weather fastness: 4/3 in PE.

Application: The pigment can be used to color a wide range of polymers.

Table 5.24: List of the Substituents of the Pigments According to Basic Formula 10

Color index number	Substituents		
	R ⁴	R ⁵	Metal ion
P. yellow 183	Cl	Cl	Ca ⁺⁺
P. yellow 190	*	*	Ca ⁺⁺
P. yellow 191	CH ₃	Cl	Ca ⁺⁺

* chemical constitution not yet published

5.2.2 Polycyclic Pigments

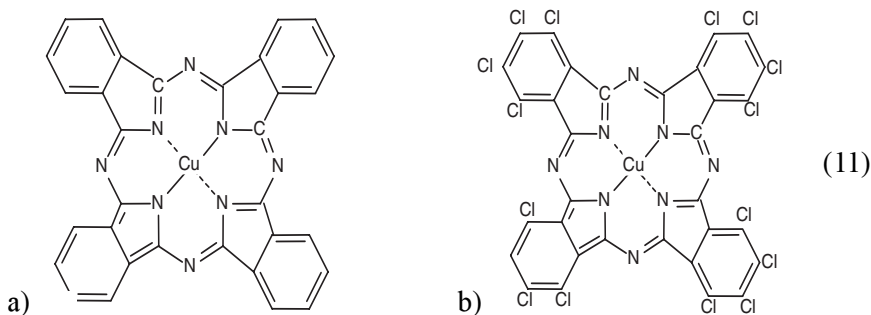
The name of this pigment group indicates the basic chemistry. Polycyclic pigments are made of several condensed aromatic and/or heterocyclic ring systems. The

many different colors are the result of variations of the ring system in combination with a large variety of possible substituents. The exact color and several properties depend on the crystal modification and/or isomerism (*cis*, *trans*). Generally speaking their main characteristics are good fastness properties and good resistance to solvents. On the other hand they are more costly than azo pigments, apart from the phthalocyanine pigments.

5.2.2.1 Phthalocyanine Pigments

The unsubstituted copper phthalocyanine pigments are blue (basic formula 11 a), while a nearly complete halogenation produces the green copper phthalocyanine pigments (basic formula 11 b). The commercially available green copper phthalocyanine pigments contain either (approximately) 15 chlorine atoms per molecule (Pigment green 7) or a mixture of chlorine and bromine (Pigment green 36). The ratio of the mixture of chlorine and bromine varies between the different manufacturers of green phthalocyanine pigments. The most yellowish green pigment contains (approximately) 11–12 bromine and 4–5 chlorine atoms as substituents. Pigments with only a partial halogenation gained no commercial interest.

The unsubstituted blue copper phthalocyanine pigment is polymorphous and five crystal modifications are known, whereas the green pigment shows only one crystal modification.



Copper can be exchanged by other metals, for example, zinc, iron, cobalt, but those products play no role in the coloring of plastics.

A detailed description of the blue and green phthalocyanine pigments, history, and production methods and properties is available in form of a company leaflet [47].

The copper phthalocyanine pigments are difficult to disperse in a polymer melt; therefore the use of an effective dispersing agent and sufficient shear during the

manufacture of a masterbatch are essential. Otherwise insufficiently dispersed pigments produce the visual disturbing color specks in the final product.

The coloring of plastics with a powdery color preparation, containing a higher concentration of phthalocyanine pigment, is very problematic because the single screw extruder, normally used for the injection molding of plastic parts, does not develop enough shear. The result can be that intensive blue or green colors without color specks are more or less impossible.

The unsubstituted blue copper phthalocyanine pigment (Pigment blue 15) is polymorphous. There are five crystal modifications (α , β , γ , δ , ϵ). The thermodynamic stability depends on the crystal modification; the β -modification shows the highest and the α -modification the lowest thermodynamic stability. The thermodynamic stability of these crystal modifications decreases in the following order: $\beta > \epsilon > \delta > \alpha \approx \gamma$.

The β - and the stabilized α -modifications are commonly used in the coloring of plastics. Special steps during the manufacture of this pigment produce the desired crystal modification. Each modification differs slightly in the exact shade.

The α -modification is thermodynamically not stable enough at the processing temperatures of polymers and would be converted into the stable β -modification. To avoid this the α -modification is stabilized by adding 0.5–1 atom chlorine; another method of stabilization is to treat the crystal surface with special substances.

Pigment blue 15 / 74160 / 147.14.8

Properties: α -modification, unstabilized, reddish blue. It plays no role in the coloring of plastics because at temperatures above 200 °C (392 °F) it is converted to the thermodynamic stable β -modification.

Pigment blue 15:1 / 74160 / 147.14.8

Properties: α -modification, stabilized with 0.5–1 atom chlorine, reddish blue, high tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD, hard to disperse in a polymer melt.

Good heat stability: 300 °C (572 °F) in PE, ABS, and PC; 280 °C (536 °F) in PET; 270 °C (500 °F) in PS; 260 °C (500 °F) in PA 6.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC, PE, PP; and PA-6; 7 / 8 in PET.

Application: Nearly every polymer can be colored with this blue pigment. Some problems were reported while coloring some grades of ABS and PC; in this case preliminary trials are recommended. For the coloring of natural rubber, special available grades of this pigment should be used, because the *normal* qualities may

show detrimental effects on the vulcanization and/or aging of this polymer. These detrimental effects are caused by impurities of “free” copper ions. Applied in unsaturated polyester resins the speed of curing may be reduced considerably.

Pigment blue 15:2 / 74160 / 147.14.8

Properties: α -modification, stabilized with 0.5–1 atom chlorine, reddish blue. This grade is stabilized in addition against flocculation in lacquers and printing inks. The properties and applications correspond closely to those of Pigment blue 15:1.

Pigment blue 15:3 / 74160 / 147.14.8

Properties: β -modification, no stabilization necessarily, because this modification is thermodynamically the most stable form. Greenish blue, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD, hard to disperse in a polymer melt.

Good heat stability: 320 °C (608 °F) in PC; 300 °C (572 °F) in PE, PP, and PS; 280 °C (536 °F) in ABS and PET; 240–280 °C (464–536 °F) in PMMA; 260 °C (500 °F) in PA-6. Applied in PE, the heat stability decreases only at pigment concentrations below 0.01% (pure tone) and 0.05% (white reduction).

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC, and PA-6; 7–8 / 7–8 in PE, PP, PET, PS, and PC.

Good weather resistance: 5 in PE.

Application: Nearly every polymer can be colored with this blue pigment. For the coloring of natural rubber special, available grades of this pigment should be used, because the *normal* qualities may show detrimental effects on the vulcanization and/or aging of this polymer. These detrimental effects are caused by impurities of “free” copper ions. Applied in unsaturated polyester resins the speed of curing may be reduced considerably.

Pigment blue 15:4 / 74160 / 147.14.8

Properties: β -modification. This grade is stabilized in addition against flocculation in lacquers and printing inks. The properties and applications correspond closely to those of Pigment blue 15:3.

Pigment blue 15:6 / 74160 / 147.14.8

Properties: ϵ -modification, stabilized, strong reddish blue. In comparison to Pigment blue 15:1 and blue 15:3 this grade plays no role in the coloring of plastics. This is partly due to the fact that a strong reddish tint can be matched by mixing of a blue and a red pigment.

Pigment blue 16 / 74100 / CAS 574.93.6

This pigment is the metal-free variation of the blue copper phthalocyanine pigment (Pigment blue 15). It plays no role in the coloring of plastics, but is mentioned here because of the reason of completeness.

Pigment green 7 / 74260 / CAS 1328.53.6

Properties: Bluish green, contains typically (approximately) 14–15 atoms chlorine, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD, hard to disperse in a polymer melt. It occurs in only one crystal modification.

Good heat stability: 300 °C (572 °F) in PE; 260–300 °C (500–572 °F) in PMMA; 290 °C (554 °F) in PS; 280 °C (536 °F) in PET; 260 °C (500 °F) in PA-6. The heat stability is independent of the pigment concentration within a wide range.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC; 7–8 / 7–8 in PE, PP, PS, ABS, and PC.

Good weather resistance: 5 in PE.

Application: Nearly every polymer can be colored with this green pigment, however preliminary tests are recommended when applying color to PA, PET, and PC.

Pigment green 36 / 74265 / CAS 14302.13.7

Properties: Yellowish green. This pigment contains a mixture of chlorine and bromine; the ratio is variable, depending on the manufacturer. Typically it contains two to eight atoms chlorine and nine to four atoms bromine. The yellowish tint increases with increasing number of bromine atoms. It occurs only in one crystal modification. It is hard to disperse in a polymer melt, and affects strongly the shrinkage of PE-HD. No migration in plasticized PVC.

Good heat stability: 300 °C (572 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE and other polymers.

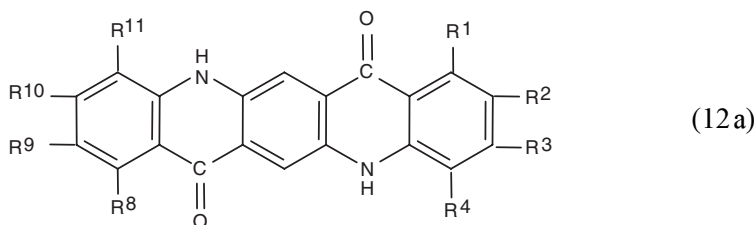
Good weather resistance: 5 in PE.

Application: Nearly every polymer can be colored with this green pigment, however, preliminary tests are recommended when applying color to ABS, PA, and PC.

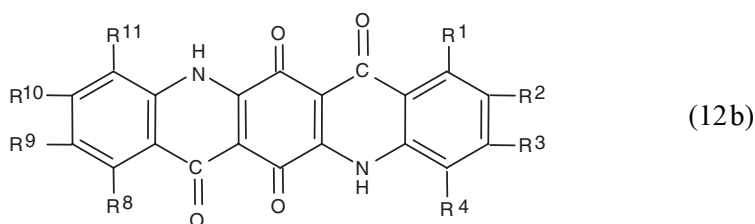
5.2.2.2 Quinacridone Pigments

The typical quinacridone structure is a five-ring polycyclic system, consisting of three benzene and two pyridone rings (as bridge between the benzene rings). The combination of the five rings can be either in an angular or linear form, and the arrangement of the heterocyclic pyridone rings can be either in *trans*- or *cis*-position. This gives four possible constitutions of quinacridone pigments, but only the

linear, *trans*-quinacridone pigment is of commercial interest for the coloring of plastics (basic formula 12a).



The central benzene ring can be oxidized, which gives the quinacridone quinone pigments (basic formula 12b).



The linear, *trans*-quinacridone exhibits several crystal modifications; the known ones are the α -, β -, δ -, and γ -modifications. Most synthetic methods produce the α -modification, which, however, shows insufficient fastness properties. This is the reason why the α -modification must be converted to the more stable β - or γ -modifications.

The exact shade of quinacridone pigments depends not only on the crystal modification but also on the substitution pattern. Experience shows that the substituents lighten the shade; therefore commercially available substituted quinacridone pigments contain no more than two substituents, either chlorine or the CH_3 group, on the peripheral benzene rings (Table 5.25).

Another method to change the shade is the formation of mixed crystal phases, containing a mixture of an unsubstituted and a substituted quinacridone pigment or a mixture of an unsubstituted quinacridone with a quinacridone quinone pigment. Several variations are commercially available.

The quinacridone pigments are difficult to disperse in a polymer melt; therefore the use of an effective dispersing agent and sufficient shear during the manufacture of a masterbatch are essential. Otherwise incomplete dispersed pigments produce visually disturbing color specks in the final product.

The coloring of plastics with a powdery color preparation, containing a higher concentration of quinacridone pigment, is very problematic, because the single screw extruder, normally used for the injection molding of plastic parts, does not develop enough shear. The result can be that intensive colors without any color specks are more or less impossible.

Pigment violet 19 – β -modification / 73900 / CAS 1047.16.1

Properties: Reddish violet, medium tinting strength, no migration in plasticized PVC, medium effect on the shrinkage of PE-HD.

Good heat stability: 290–300 °C (554–572 °F) in PE, PS, and ABS; 290 °C (554 °F) in PC; 280 °C (536 °F) in PET; 260 °C (500 °F) in PA-6. The heat stability is independent from the pigment concentration within a wide range.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE, PET, and PS; 7–8 / 7 in PVC, 7 / 6 in PA 6; 8 / 6–7 in PC.

Good weather resistance: 5 or 4–5 in PE.

Application: A wide range of polymers can be colored with this pigment. When applied to color POM the formation of a deposit on the surface of the mold is possible at concentrations below 0.1%.

Pigment violet 19 – γ -modification / 73900 / CAS 1047.16.1

Properties: Bluish red, medium tinting strength, no migration in plasticized PVC, medium effect on the shrinkage of PE-HD.

Good heat stability and light fastness, which are not completely independent of the particle size.

Application: A wide range of polymers can be colored with this pigment, including PA. When applied to color PET the pigment might dissolve at very low concentrations.

Pigment red 122 / 73915 / CAS 980.26.7

Properties: Bluish red, medium tinting strength, no migration in plasticized PVC, affects the shrinkage of PE-HD.

Good heat stability: 310 °C (560 °F) in PC; 300 °C (572 °F) in PE, PS, and ABS; 280 °C (536 °F) in PET; 260 °C (500 °F) in PA-6. The heat stability is independent of the pigment concentration within a wide range.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE, PS, PC, and PET; 8 / 7–8 in ABS, 7–8 / 7 in PVC; 7–8 / 6 in PA-6.

Good weather resistance: 5 in PE.

Application: A wide range of polymers can be colored with this pigment. When applied to color POM the formation of a deposit on the surface of the mold is possible at concentrations below 0.1%.

Pigment red 202 / 73907 / CAS 68859.50.7

Properties: Bluish red, strong effect on the shrinkage of PE-HD.

Good heat stability: 290–300 °C (554–572 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC; 7–8 / 8 in PE.

Good weather resistance: 5 in PE.

Application: A wide range of polymers can be colored with this pigment.

Pigment red 207 / 73900 + 73908 / CAS 1047.16.1 + 3089.16.5

Properties: Yellowish red. Mixed phase pigment of an unsubstituted quinacridone and 4,11-dichloroquinacridone.

The fastness properties correspond to the individual components.

Application: A wide range of polymers can be colored with this pigment.

Pigment red 209 / 73905 / CAS 3089.17.6

Properties: Yellowish red, low tinting strength, no migration in plasticized PVC, medium effect on the shrinkage of PE-HD. Mixed phase pigment of chlorinated quinacridone pigments (3,10-, 1,8-, and 1,10-dichloroquinacridone).

Good heat stability: 320 °C (608 °F) in PC; 300 °C (572 °F) in PE. The heat stability is independent of the pigment concentration within a wide range.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE, PC, and PS; 7–8 / 7–8 in PVC.

Application: A wide range of polymers can be colored with this pigment.

The following three pigments are mixed phase pigments of an unsubstituted quinacridone and a quinacridone quinone. The exact ratio between the single components is not yet published.

Pigment red 206 / 73900 + 73920 / CAS 1047.16.1 + 1503.48.6

Properties: Yellowish red.

Application: It is seldom applied for the coloring of plastics.

Pigment orange 48 / 73900 + 73920 / CAS 1047.16.1 + 1503.48.6

This pigment plays no role in the coloring of plastics because it may dissolve in PA and some other polymers. It is used to some extent in spin dying.

Pigment orange 49 / 73900 + 73920 / CAS 1047.16.1 + 1503.48.6

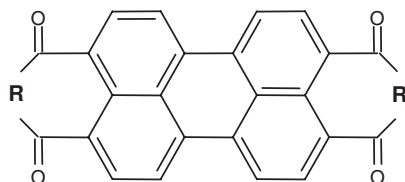
This pigment plays no role in the coloring of plastics.

Table 5.25: List of Substituents of Pigments According to Basic Formulas 12a and 12b

Color index number	Substituent							
	R ¹	R ²	R ³	R ⁴	R ⁸	R ⁹	R ¹⁰	R ¹¹
P. violet 19	H	H	H	H	H	H	H	H
P. red 122	H	CH ₃	H	H	H	CH ₃	H	H
P. red 202	H	Cl	H	H	H	Cl	H	H
P. red 207	H	H	H	Cl	H	H	H	Cl
<i>Mixed phase pigment with an unsubstituted quinacridone</i>								
P. red 209	H	H	Cl	H	H	H	Cl	H
<i>Mixed phase pigment with 1,8- and 1,10-dichloroquinacridone</i>								
P. red 206	Mixed phase pigment of unsubstituted quinacridone and quinacridone quinone							
P. orange 48	Mixed phase pigment of unsubstituted quinacridone and quinacridone quinone							
P. orange 49	Mixed phase pigment of unsubstituted quinacridone and quinacridone quinone							

5.2.2.3 Perylene Pigments

Perylene pigments are derivatives of basic formula 13; the component R is rather variable.



(13)

Depending on the chemical constitution of R, the perylene pigments exist in a wide range of colors, providing red, bordeaux, violet, brown, and black shades. Although the brown and black shades are chemically interesting pigments, they do not play a role in the coloring of plastics; only the red and violet pigments are of special commercial interest.

The application of perylene pigments in HALS (**H**indered **A**mine **L**ight **S**tabilizer) stabilized polyolefins, e.g., PE, is problematic. Depending on the perylene pigment concentration the HALS stabilizer might be inactivated or even destroyed; consequently the plastic part would fail to fulfill its requirements. If the use of perylene pigments in stabilized PE cannot be avoided, it is recommended to run preliminary tests to evaluate a possible interaction.

Perylene pigments offer a high tinting strength and provide very good fastness properties, not only in plastics but also in automobile paints, the other important field of application (Table 5.26).

Pigment red 123 / 71145 / CAS 24108.89.2

Properties: Medium red shade (scarlet-red), not entirely fast to bleeding in plasticized PVC (dependent on the plasticizer system), affects the shrinkage of PE-HD considerably.

Good heat stability: 300 °C (572 °F) in PE.

Application: This pigment is seldom used because of its inferior properties in comparison to Pigment red 149.

Pigment red 149 / 71137 / CAS 4948.15.6

Properties: Bluish red, high tinting strength, no migration in plasticized PVC, affects the shrinkage of PE, however, this influence decreases with increasing temperature.

Good heat stability: 310 °C (560 °F) in PC; 300 °C (572 °F) in PE; 280 °C (536 °F) in PS, PMMA and PET; 250 °C (482 °F) in ABS. The heat stability is independent of the pigment concentration within a wide range.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 7 in PE and PS; 8 / 6–7 in PMMA; 6–7 / 7–8 in PET.

Application: A wide range of polymers can be colored with this pigment, including cast resins such as methacrylic acid methylester or unsaturated polyesters, which are polymerized with peroxide catalysts. In polymers, stabilized with HALS, a possible interaction between the pigment and the stabilizer should be considered.

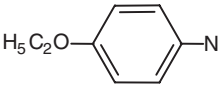
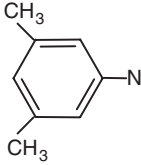
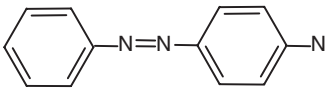
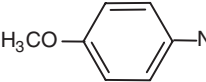
Pigment red 178 / 71155 / CAS 3049.71.6

Properties: The pigment crystallizes in two modifications, but only one is commercially available. The pigment is fast to migration in plasticized PVC, affects the shrinkage of HD-PE.

Good heat stability: 300 °C (572 °F) in PE.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PE.

Table 5.26: List of the Substituents of Pigments According to Basic Formula 13

Color Index Number	Substituent R
P. red 123	
P. red 149	
P. red 178	
P. red 179	CH ₃ —N
P. red 190	
P. red 224	O
P. violet 29	HN

Application: A wide range of polymers can be colored with this pigment. In polymers, stabilized with HALS, a possible interaction between the pigment and the stabilizer should be considered.

Pigment red 179 / 71130 / CAS 5521.31.3

Properties: In comparison to the other pigments of this class, the heat stability of Pigment red 179 is rather low.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE.

Good weather resistance: 5 (pure tone) / 4 (white reduction) in PE.

Application: Owing to its low heat stability the use is limited to polymers with a low processing temperatures, for example, PVC and PE-LD.

Pigment red 190 / 71140 / CAS 6424.77.7

The use of this bluish red pigment is preferably in automobile paints. In spite of its good heat stability it is seldom used as colorant for polymers.

Pigment red 224 / 71127 / CAS 128.69.8

Owing to its low heat stability the use of this bluish red pigment as colorant for polymers is very limited. One application is, for example, in spin dyeing of polyacrylonitrile.

Pigment violet 29 / 71129 / CAS 12236.71.4

Properties: A rather dull, dark violet, no migration in plasticized PVC.

Good heat stability: 300 °C (572 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE.

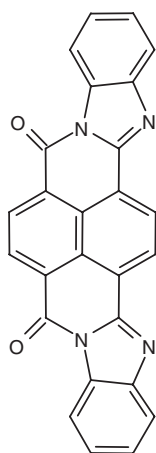
Medium weather fastness: 4 (pure tone) / 3 (white reduction) in PE.

Application: A wide range of polymers can be colored with this pigment. It is recommended to run preliminary tests in ABS, PA, PC, and PET.

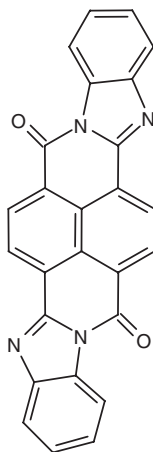
5.2.2.4 Perinone Pigments

The chemical constitution of perinone pigments (basic formula 14) indicates the existence of two isomeric forms, a *cis*- and a *trans*-isomer.

At present, only unsubstituted perinone pigments are commercially available as colorants for polymers. There are three products, a pure *cis*- and *trans*-isomer and a mixture of both. These isomers differ in color and properties.



cis-Form



trans-Form

(14)

Pigment orange 43 – trans-isomer / 71105 / CAS 4424.06.0

Properties: Reddish orange, high tinting strength, no migration in plasticized PVC, affects strongly the shrinkage of PE-HD.

Good heat stability: 280 °C (536 °F) in PE and PET. The heat stability in PE decreases considerably at concentrations < 0.1 %. The pigment dissolves in PET at very low pigment concentrations accompanied by a change of its shade to yellow.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE; 8 / 7–8 in PVC; 6 / 5–6 in PET.

Good weather resistance: 5 in PE.

Application: A wide range of polymers can be colored with this pigment.

Pigment red 194 – cis-isomer / 71100 / CAS 4216.02.8

Properties: Bluish red. At higher temperatures this *cis*-isomer dissolves in several polymers, for example, PVC, and PS, combined with a color shift.

Good heat stability: 270 °C (518 °F) in PE.

Application: The pigment is seldom used to color plastics.

Vat red 74 – mixed phase of both isomers / 73305

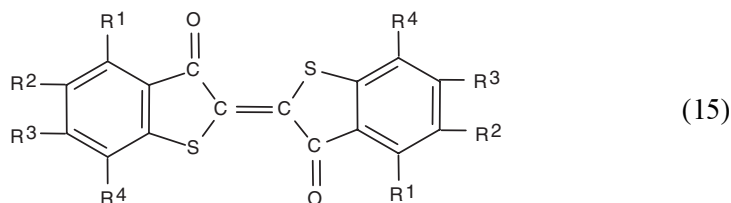
Properties: Scarlet.

Good heat stability: 300 °C (572 °F).

Application: Mainly used in spin dyeing of PP.

5.2.2.5 Thioindigo Pigments

The chemical structure of thioindigo (basic formula 15) indicates the possibility of several derivatives, which were marketed in the past. Today only two pigments (Pigment red 88 and red 181) and one dye (Vat red 41) are still commercially available (Table 5.27).



A characteristic feature of thioindigo pigments is the tendency to dissolve, depending on the polymer and processing temperature.

Pigment red 88 / 73312 / CAS 14295.43.3

Properties: Red-violet, affects considerably the shrinkage of PE-HD. Several grades of this pigment are marketed, differing in their tendency to migrate in plasticized PVC and in their fastness properties as result of different aftertreatments.

Good heat stability: 260–280 °C (500–536 °F) in PE. The pigment dissolves in PS depending on the processing temperature, combined with a color shift.

Good to medium light fastness: 8 (pure tone) / 6 (white reduction) in PVC; 8 / 5 in PE.

Insufficient weather resistance: 3 (pure tone) / 2 (white reduction) in PE.

Application: It is mainly used to color PVC, PUR, PE, PP, and for spin dyeing.

Pigment red 181 / 73360 / CAS 2379.74.0

Properties: Bluish red, good light fastness, dissolves in PS and similar polymers. It is a special purpose product for PS. In other polymers it is not applied.

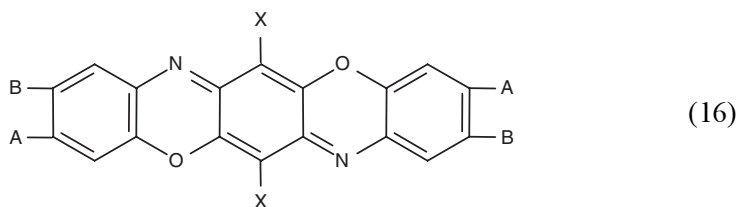
Vat red 41 – unsubstituted thioindigo. It is a dye.

Table 5.27: List of Substituents of Colorants According to Basic Formula 15

Color index number	Substituent			
	R ¹	R ²	R ³	R ⁴
P. red 88	Cl	H	H	Cl
P. red 181	CH ₃	H	Cl	H
Vat red 41	H	H	H	H

5.2.2.6 Dioxazine Pigments

In the past this group of pigments were important dyes to color textiles, but they have lost their former importance. This is partly due to certain deficiencies in their properties. Regarding the coloring of plastics, only two violet products of commercial importance are left. The general chemical constitution shows the basic formula 16.



Pigment violet 23 / 51319 / CAS 6358.30.1

Properties: Bluish violet, high tinting strength, not completely fast to migration in plasticized PVC, affects the shrinkage of PE-HD. The supplied data vary partly considerably among manufacturers, probably due to different particle sizes and/or aftertreatments.

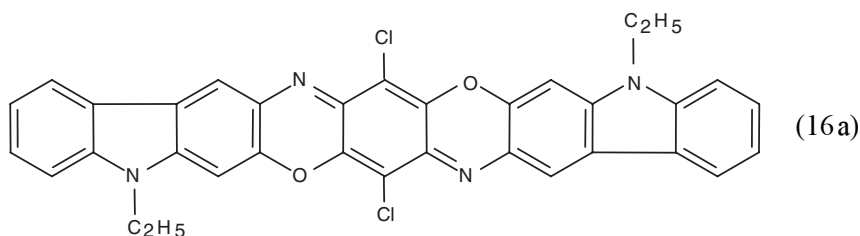
Good to medium heat stability: 280 °C (536 °F) in PE. It is remarkable that the heat stability depends strongly on the degree of white reduction. The heat stability drops in PE to 240 °C (464 °F) at a 1/25 standard pigment concentration; in addition a concentration below 0.5% should be avoided in PE. The pigment dissolves in PS and PET at processing temperatures above 250 °C (482 °F). The heat stability in PA-6 is 260 °C (500 °F).

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC; 6–7 / 4–5 and 8 / 7–8 in PE (depending on the manufacturer); 8 / 7–8 in PA-6; 7 / 7 in PS.

Good weather resistance: 4–5 in PE.

Application: The pigment can be used in many polymers, including spin dying.

Chemistry: In case of Pigment violet 23 the substituents A and B (basic formula 16) are not single components but are used to add a further ring system. The result is formula 16a, the chemical constitution of Pigment violet 23.



Pigment violet 37 / 51 345 / CAS 57971.98.9

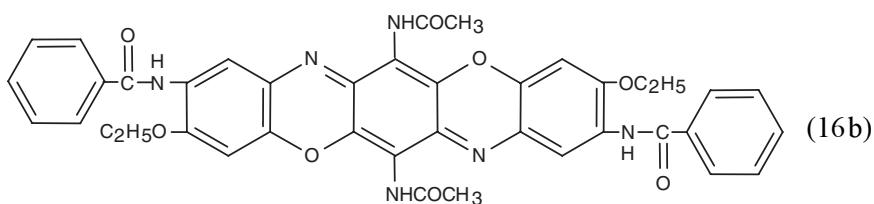
Properties: Reddish violet, high tinting strength, not completely fast to migration in plasticized PVC, affects considerably the shrinkage of PE-HD.

Good heat stability: 280–300 °C (536–572 °F) in PE, which decreases clearly with increasing white reduction.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE, which decreases clearly with increasing white reduction (1/25 standard pigment concentration).

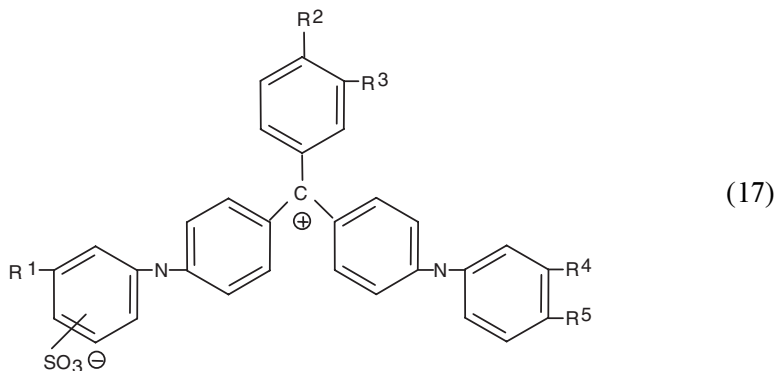
Application: The pigment can be used in many polymers, including spin dying.

Chemistry: The chemical constitution of Pigment violet 37 shows formula 16b.



5.2.2.7 Triarylcarbonium Pigments

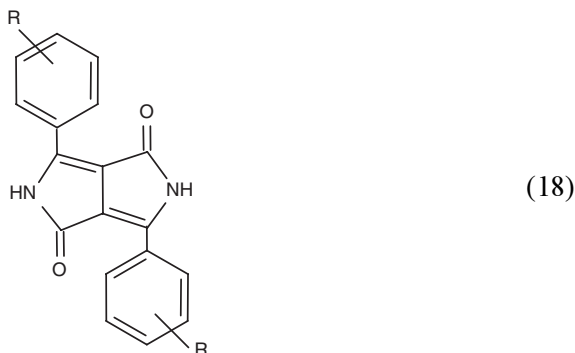
The chemical constitution of triarylcarbonium pigments is based on the general formula 17.



Miscellaneous triarylcation pigments are commercially available, which are applied exclusively in printing inks. They play no role in the coloring of plastics, but are mentioned here for the purpose of completeness.

5.2.2.8 Diketopyrrolo-Pyrrolo (DPP) Pigments

Although the constitution of this molecule has been known for a long time, industrial production started only in the last decade. The first member of this group was the Pigment red 254, and several other derivatives have since become available. The general chemical constitution of DPP pigments shows formula 18. The chemistry and number of the substituent R have not yet been published. In the case of Pigment red 254 the substituent R is chlorine (because of the chlorine content) and probably in the *p*-position.



Pigment red 254 / 56110 / CAS 122390.98.1

Properties: Red, high tinting strength, no migration in plasticized PVC, affects more or less the shrinkage of PE-HD (depending on the PE grade).

Good heat stability: 280–300 °C (536–572 °F) in PE; 290 °C (554 °F) in PS; 260 °C (500 °F) in PMMA. The pigment dissolves in PC at temperatures above 320 °C (608 °F), giving a bright fluorescent yellow.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC, PE, and ABS.

Good weather resistance: 5 in PE.

Application: The pigment can be used in many polymers.

Pigment red 255 / – / CAS 120500.90.5

Properties: Scarlet, nearly completely fast to migration in plasticized PVC.

Medium heat stability: 240 °C (464 °F) in PE.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PE.

Application: The use of this pigment is limited because of its low heat stability.

Pigment red 264 / – / –

Properties: Ruby, no effect on the shrinkage of PE-HD.

Good heat stability: 280–300 °C (536–572 °F) in PE. The heat stability decreases clearly in PE with increasing white reduction.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE.

Good weather resistance: 5 in PE.

Application: The pigment can be used in many polymers.

Pigment red 272 / – / –

Properties: Flame-red, no migration in plasticized PVC, slight effect on the shrinkage of PE-HD.

Good heat stability: 300 °C (572 °F) in PE.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PE.

Medium weather resistance: 2–3 in PE.

Application: The pigment can be used in many polymers.

Pigment orange 71 / – / –

Properties: Orange, slight effect on the shrinkage of PE-HD.

Good heat stability: 280–300 °C (536–572 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE; 7–8 / 7–8 in PVC.

Good weather resistance: 4–5 in PE.

Application: The pigment can be used in many polymers.

Pigment orange 73 / - / -

Properties: Orange, not completely fast to migration in plasticized PVC.

Good heat stability: 280–300 °C (536–572 °F) in PE.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PE; 7–8 / 6–7 in PVC.

Application: The pigment can be used in many polymers.

5.2.3 Miscellaneous Pigments

In this section all the pigments are described that can not be categorized in one of the other pigment groups. Some pigments have a chemical composition that resembles one of the previously described pigment groups but nevertheless they are single pigments. Here, too, the chemical structure is shown (if published).

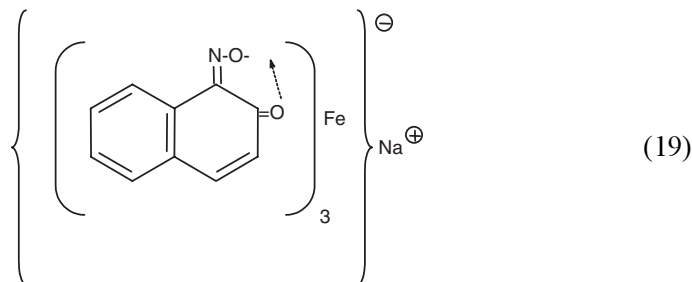
5.2.3.1 Metal Complex Pigments

A main feature of these pigments is the possibility of an interaction between the metal of the pigment and metal containing additives in the polymer, for example, metal containing stabilizer in PVC. The result of an interaction might be a darkening and/or color shift in the plastic part.

Pigment green 8 / 10006 / CAS 16143.80.9

Properties: Yellowish green.

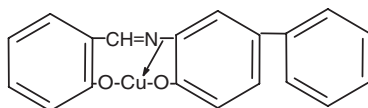
Application: This pigment is mainly used to color rubber. Owing to its low heat stability (220 °C [428 °F]) it can be applied only in polymers with a low processing temperature, for example, PVC and PE-LD. Another disadvantage that limits its use is the low light fastness of approx. 2–3. The pigment lost much of its former importance in comparison to the superior Pigment green 7.



Pigment yellow 117 / 48043 / CAS 21405.81.2

Properties: Greenish yellow, high tinting strength.

Application: In case of use in PVC, stabilized, for example, with tin compounds, the possibility of an interaction should be considered. The pigment is used mainly to color thermosets, where it shows a good light fastness and weather resistance.

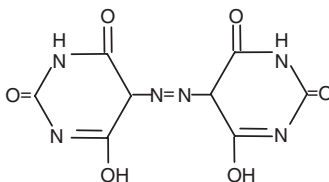


(20)

Pigment yellow 150 / 12764 / CAS 68511.62.6

Properties: Good fastness properties. When the color matching requires a white pigment to brighten the shade, the use of zinc sulfide (Pigment white 7) should be avoided because of a possible interaction that would result in a darkening of the shade (formation of dark nickel sulfide).

Application: The main use of this pigment is the spin dyeing of PP and PA, but also at the injection molding of PA and other polymers.

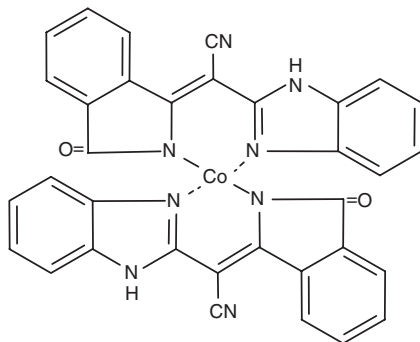


Ni-complex

(21)

Pigment yellow 177 / 48120 / CAS 60109.88.8

Application: This pigment was developed especially for spin dyeing of PP and PA. In other fields of coloring of plastics it is not applied.

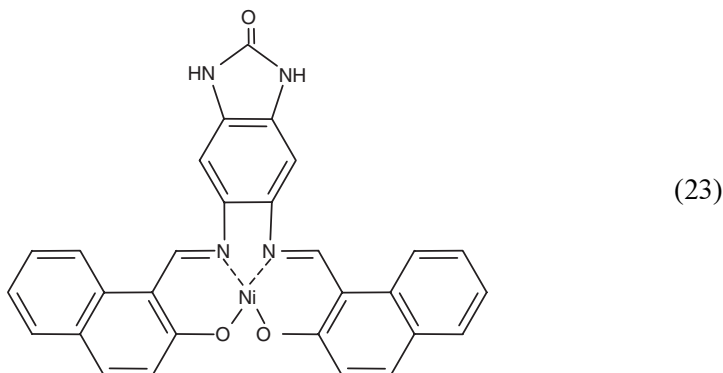


(22)

Pigment orange 68 / – / CAS 42844.93.9

Properties: The pigment is marketed in different particle sizes, which differ in the shades.

Good heat stability: 320 °C (608 °F) in PC; 300 °C (572 °F) in PE, PS, and ABS. The heat stability is independent of the pigment concentration within a wide range.



Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PE; 8 / 7 in PC; 7 / 7 in PS, PMMA, and PA-6; 6–7 / 6–7 in ABS and SAN.

Application: The pigment can be used in many polymers, including PA and PC.

5.2.3.2 Isoindoline / Isoindolinone Pigments

Pigment yellow 109 / 56284 / CAS 12769.01.6

Properties: Greenish yellow, low tinting strength, fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

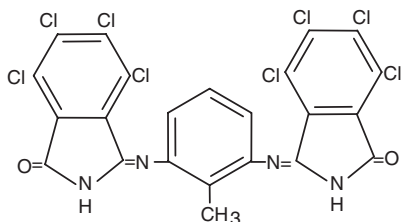
The two pigments Pigment yellow 109 and yellow 110 differ only by one substituent, a CH₃ group on the central benzene ring. This is a good example of the importance and effect of a substituent on the shade of a pigment.

Good heat stability: 280 °C (536 °F) in PE. The heat stability depends clearly on the pigment concentration. At a concentration of 0.1% the heat stability is 280 °C (536 °F), but only 240 °C (464 °F) at a concentration of 0.01% (in PE).

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE; 7–8 / 7–8 in PVC.

Good weather resistance: 4–5 in PE.

Application: The pigment can be used in many polymers, including for the spin dyeing.



(24)

Pigment yellow 110 / 56280 / CAS 5590.18.1

Properties: Reddish yellow, medium tinting strength, fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

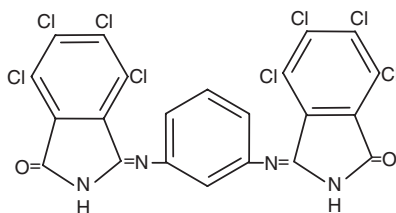
The two pigments Pigment yellow 110 and yellow 109 differ only by one substituent, a CH₃ group on the central benzene ring. This is a good example of the importance and effect of a substituent on the shade of a pigment.

Good heat stability: 270–280 °C (518–536 °F) in PE, depending on the pigment concentration.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC and PE.

Good weather resistance: 4–5 in PE.

Application: The pigment can be used in many polymers, including for the spin dyeing.



(25)

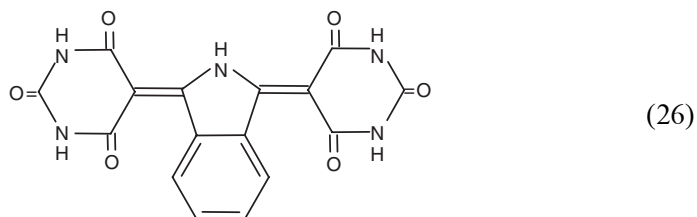
Pigment yellow 139 / 56298 / CAS 36888.99.0

Properties: Reddish yellow, medium tinting strength, fast to migration in plasticized PVC.

Medium heat stability: 250–260 °C (482–500 °F) in PE.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PE.

Application: The main fields of use are the coloring of PVC, PO, and PUR.



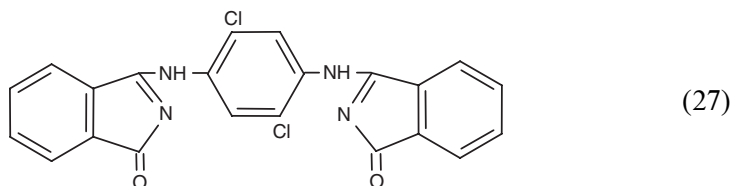
Pigment yellow 173 / – / CAS 51016.63.8

Properties: Greenish yellow, low tinting strength, nearly completely fast to migration in plasticized PVC (depending on the plasticizer).

Good heat stability: 290–300 °C (554–572 °F) in PE.

Good light fastness: 7–8 in PVC.

Application: The pigment can be used in many polymers.



Pigment orange 61 / 11265 / CAS 76168.74.6

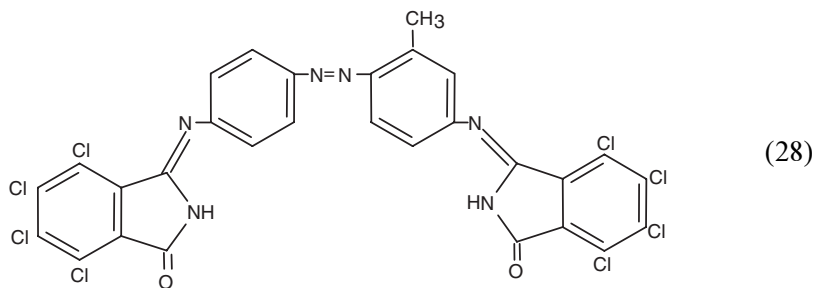
Properties: Orange, low tinting strength, fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Good heat stability: 270–290 °C (518–554 °F) in PE. The heat stability decreases clearly at a pigment concentration of < 0.01% (pure tone) and < 0.05% (white reduction).

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PE.

Good weather resistance: 4–5 in PE.

Application: The pigment can be used in many polymers, including for the spin dyeing.



Pigment brown 38 / – / CAS 126338.72.5

Properties: Yellowish brown, low tinting strength, not completely fast to migration in plasticised PVC. It is classified as an isoindoline pigment, although its exact chemical constitution has not yet been published.

Medium heat stability: 240 °C (464 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC.

Application: Due to its low heat stability the use of this pigment is limited to polymers with a rather low processing temperature, for example, PVC and PE-LD.

5.2.3.3 Aminoanthraquinone Pigments

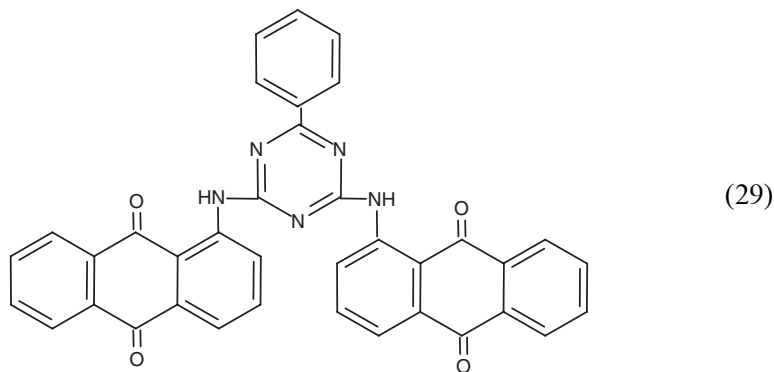
Pigment yellow 147 / 60645 / CAS 76168.75.7

Properties: Reddish yellow, low tinting strength, fast to migration in plasticized PVC.

Good heat stability: 300 °C (572 °F) in PE, PS, PET, and PC.

Good light fastness: 7 (pure tone) / 7 (white reduction) in PC.

Application: The pigment can be used in many polymers, including for the spin dyeing of PP.



Pigment red 177 / 48120 / CAS 60109.88.8

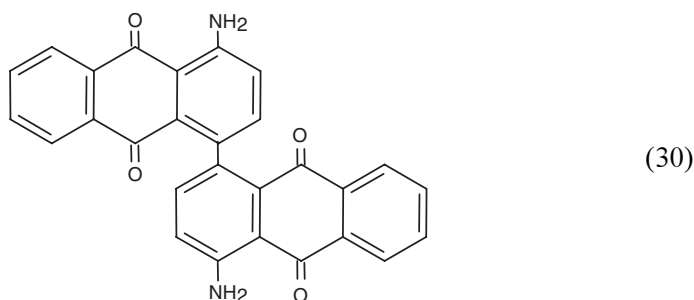
Properties: Red, low tinting strength, not completely fast to migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good heat stability: 270–280 °C (518–536 °F) in PE, the heat stability decreases clearly at pigment concentration < 0.1%.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC, 8 / 7 in PE.

Medium weather resistance: 3–4 in PE.

Application: The pigment can be used in many polymers, including for the spin dyeing of PP, PAN, and PA.



5.2.3.4 Indanthrone Pigments

Pigment blue 60 / 69800 / CAS 81.77.6

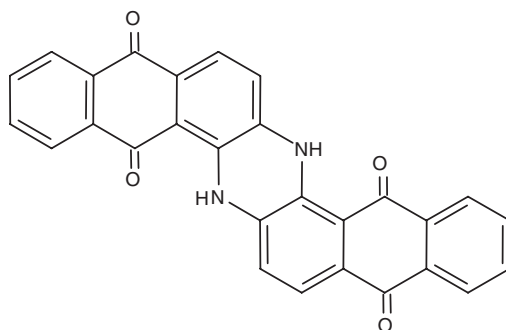
Properties: Blue, medium tinting strength, not completely fast to migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good heat stability: 270 °C (518 °F) in PE, depending on the pigment concentration.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC, 7–8 / 7–8 in PE.

Good weather resistance: 5 in PE.

Application: The pigment can be used in many polymers, including rubber and for the spin dyeing, but it is not recommended for the coloring of PA, PC, and PET.



(31)

5.2.3.5 Flavanthrone Pigments

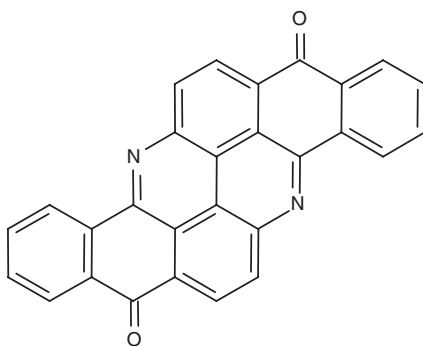
Pigment yellow 24 / 70600 / CAS 475.71.8

Properties: Reddish yellow, medium tinting strength.

Good heat stability: 270 °C (518 °F) in PE. The heat stability decreases clearly with increasing white reduction.

Good light fastness:

Application: The pigment can be used in several polymers, including for the spin dyeing (PAN). It should be noted that the pigment may dissolve partially in some polymers at higher processing temperatures combined with a color shift to a more greenish yellow.



(32)

5.2.3.6 Pyranthrone Pigments

Pigment red 216 / 59710 / CAS 1324.33.0

Properties: A tribromopyranthrone derivative, bluish red, low tinting strength, not completely fast to migration in plasticized PVC.

Medium heat stability: 250 °C (482 °F) in PE.

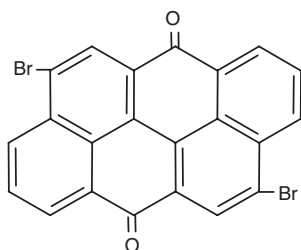
Good light fastness: 8 (pure tone) / 6 (white reduction) in PE; 8 / 8 in PVC.

Application: Owing to its medium heat stability the use of this pigment is limited to polymers with a rather low processing temperature, for example, PVC and PE-LD.

5.2.3.7 Anthanthrone Pigments

Pigment red 168 / 59300 / CAS 4378.61.4

Application: Owing to its low heat stability (approx. 180 °C [356 °F]) it can be used only to color PVC. The main fields of use are coatings and paints, where the pigment shows very good fastness properties.



(33)

5.2.3.8 Quinophthalone Pigments

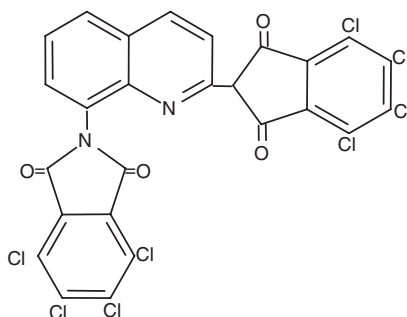
Pigment yellow 138 / 56300 / CAS 56731.19.2

Properties: Greenish yellow, medium to good tinting strength, affects the shrinkage of PE-HD (depending on the processing temperature).

Good heat stability: 290 °C (554 °F) in PE.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE. The light fastness decreases with increasing white reduction.

Application: The pigment can be used in many polymers.



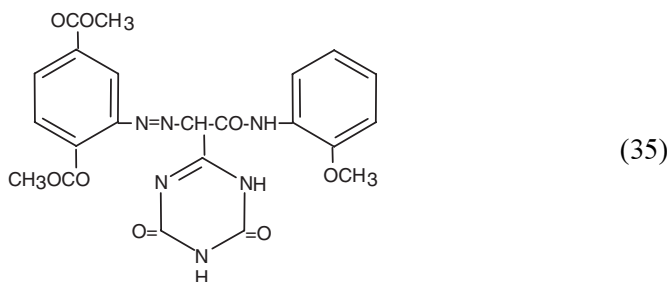
(34)

5.2.3.9 Additional Pigments with Known Chemical Structure

Pigment yellow 182 / – / CAS 67906.31.4

Properties: Reddish yellow, high tinting strength, not completely fast to migration in plasticised PVC, no effect on the shrinkage of PE-HD.

Good to medium heat stability: 280–250 °C (536–482 °F). The heat stability depends on the degree of white reduction and drops with increasing white reduction. The pigment dissolves in PS at temperatures > 200 °C (392 °F) combined with a significant color shift. The same behavior can be observed in ABS.



Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE.

Application: The use of this pigment is more or less limited to PVC-U and polyolefins.

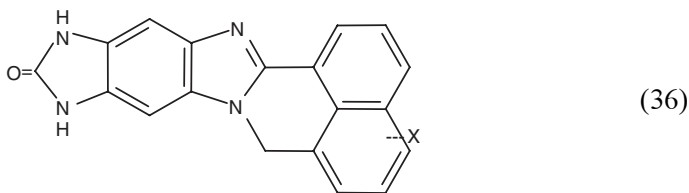
Pigment yellow 192

Properties: The chemistry of the substituents has not yet been published, only the general constitution is known. The pigment dissolves in PA, PC, and PMMA at a pigment concentration < 0.3%; at concentrations > 0.3% the dissolution is incomplete, which causes differences in the shade.

Good heat stability: 300 °C (572 °F) in PA.

Good light fastness: 8 in PA.

Application: The pigment was developed especially for the spin dyeing of PA, but because of the good fastness properties it is used also in other polymers.



Pigment orange 64 / 12760 / CAS 72102.84.2

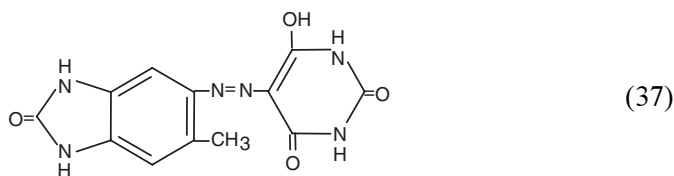
Properties: Orange, medium tinting strength, fast to migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good to medium heat stability: 280–240 °C (536–482 °F) in PE, depending on the pigment concentration.

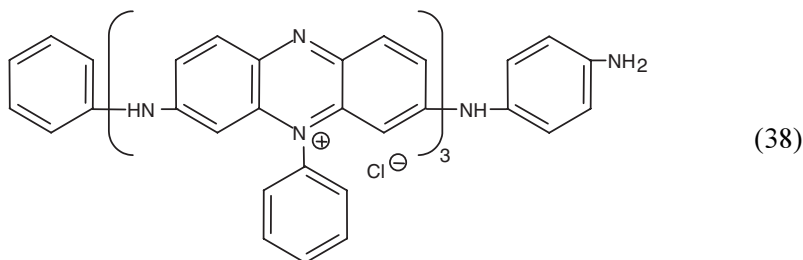
Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC, 7 / 7 in PE.

Good weather resistance: 4 in PE.

Application: The pigment can be used in many polymers.

*Pigment black 1 / 50440 / CAS 13007.86.8*

Pigment black 1 is also known as aniline black, its use is discontinued to color polymers because of the content of aniline, which is classified as carcinogenic.

**5.2.3.10 Additional Pigments with Unknown Chemical Structure***Pigment yellow 99 / – / 12225.20.6*

Properties: Reddish yellow, low tinting strength, good heat stability. It is described as anthraquinone pigment, but without chemical details.

Application: The pigment is recommended for textile printing and to color plastics. At present the pigment has only regional importance (Japan) [45].

Pigment yellow 187

Properties: Greenish yellow.

Good heat stability: 320 °C (608 °F) in PA.

Medium light fastness: Approx. 4 in PA.

Application: The pigment was developed especially to color PA.

5.3 Dyes

Dyes are defined as colorants that are (completely) soluble in a polymer at the processing temperature. The result is a solution of the dye, a molecular distribution of the dye in the polymer, and a crystalline structure is no longer noticeable. Contrary to dyes, pigments are defined as (completely) insoluble in a polymer at the processing temperature. The practice, however, shows that this differentiation between dyes and organic pigments is not always clear. It is known that some organic pigments dissolve at least partially in a polymer melt, depending on the polymer and the processing temperatures. A typical example is the DPP-Red, Pigment red 254. In most of the polymers it acts as pigment, giving a brilliant red shade. In PC, however, Pigment red 254 dissolves completely at a temperature above 320 °C (608 °F), giving a brilliant fluorescent yellow. In PC Pigment red 254 shows the typical behavior of a dye.

Analogous to pigments, dyes are subdivided into inorganic and organic substances, but in contrast to the inorganic pigments inorganic dyes do not exist for the coloring of plastics for systematic reasons. Consequently only organic dyes can be used to color plastics.

The dye must be soluble in a polymer melt, but should be insoluble in water. The insolubility in water is a very important requirement for dyes; otherwise it may migrate in contact with humidity. Any migration of color is not only a detrimental effect, for example, in the case of toys and/or packaging material, but generally banned by legal requirements (“non-migration principle”, followed by FDA and the European countries).

Dyes may be soluble, at least partially, in several solvents, fats, and oils. This property demands caution depending on the intended use of the colored plastic article. In case of packaging material it is recommended to run preliminary storage tests to evaluate a possible migration of the color into the filling good. Colored textiles should be fast during dry cleaning. There are many other occasions in which a colored plastic article may come in contact with solvents, for example, during decoration with printing inks and/or household goods and cleaner.

The general product profile of colorants, including dyes, was described in section 4.4, but there are still some other features specific for dyes. In a plastic article colored with pigments, the impression of color is due to an interplay of absorption and reflection in combination with a scattering of light on the surface of the pigment particles (crystals), the so-called Tyndall effect, whereas transparent plastic articles colored with dyes show only the interplay between absorption and reflection (Fig. 5.9).

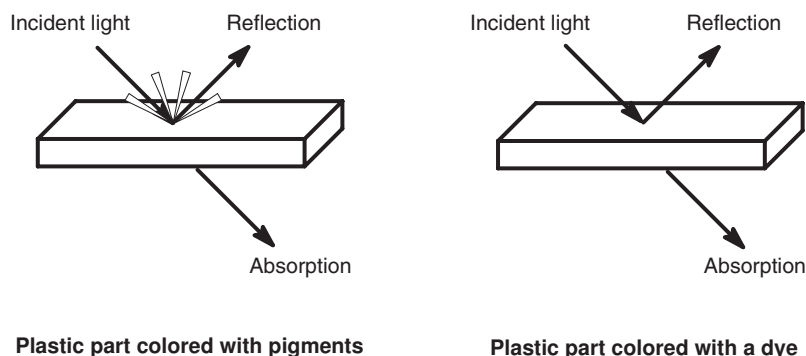


Figure 5.9: Differences in the optical behavior of pigments and dyes

The use of dyes is limited to amorphous polymers, which are polymers with a high glass transition temperature (Table 5.28). Dyes, applied in partial crystalline polymers, for example, polyolefins, would migrate directly.

Table 5.28: Glass Transition Temperature of Several Polymers

Polymer	Glass transition temperature
Glass	500–700 °C (932–1292 °F)
PS	98–100 °C (208–212 °F)
SB / ABS / SAN	80–105 °C (176–221 °F)
PMMA	105 °C (221 °F)
PC	143–150 °C (289–302 °F)
PVC-U	80 °C (176 °F)
PA 6	60–70 °C (140–158 °F)
PE (amorphous)	–80 °C (–112 °F)
PP (isotactic, 55% crystalline texture)	+3 °C (–37 °F)
PP (atactic, 5% crystalline texture)	–5 °C (–23 °F)

Dyes do not migrate from amorphous polymers under normal conditions of use, for example, at room temperature. This temperature is well below the glass transition temperature, and in a range in which the polymer chains as well the dye molecules are totally restricted in their molecular motion. In this solid dye solution in an amorphous polymer, there is no recrystallization or moving of the dye to the surface of the plastic possible. This behavior is proven by the following experiment: A plastic part, colored with a dye, was kept for a longer time clearly above its glass transition temperature. At temperatures above the glass transition temperature the polymer chain as well the dye molecules are no longer restricted in their molecular motion; consequently a migration of the dye was observed.

Originally the use of dyes was limited to transparent polymers, for example, PS, SAN, PMMA, PC, and PET. The necessary dye concentration for a transparent coloration is usually in the range of 0.01–0.1%, depending on the required intensity of the coloration. At those low concentrations migration does not occur. Dyes are applied also in opaque systems, systems containing an inorganic pigment with a good hiding power (e.g., titanium dioxide) and a dye as colorant. Analogous to the colored pigments the white component must be colored first before the color can be matched according to the customer supplied specimen. In opaque systems the necessary dye concentration is consequently clearly higher than in the case of a transparent coloration. At the same time the possibility of migration increases. When a dye is applied in an opaque system it is recommended to check beforehand the migration to ensure that the plastic article fulfills the “non-migration requirements.”

The real reason for the increasing use of dyes in opaque systems is their comparatively higher heat stability, which is very often in the range of 300 °C (572 °F). Analogous to pigments, the heat stability of dyes depends on the concentration in the plastic, on the type of polymer, and on the processing temperature and residence time during the processing of the amorphous polymer. The heat stability of dyes is very often higher than of chemically similar pigments. Only the dissolved dye molecule must be thermal stable in the polymer melt, while pigments must have not only a thermostable molecule but also a thermostable crystal modification.

The chemical structure of dyes is very similar to those of organic pigments; therefore it would be possible to subdivide the dyes analogously. However, the dyes are described according to their color because of the limited number of still usable products for the coloring of plastics. In the last few years many frequently used dyes were banned because of toxicological considerations.

A closer examination of the chemical constitution of dyes proves that their molecular structure is much simpler in comparison to pigments of the same chemical group. Two examples may demonstrate this (Fig. 5.10 and 5.11).

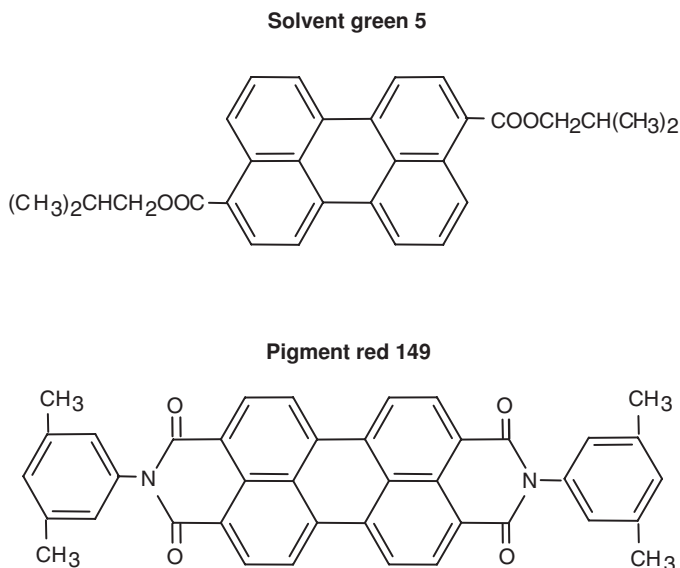


Figure 5.10: Comparison of the chemistry of perylene colorants

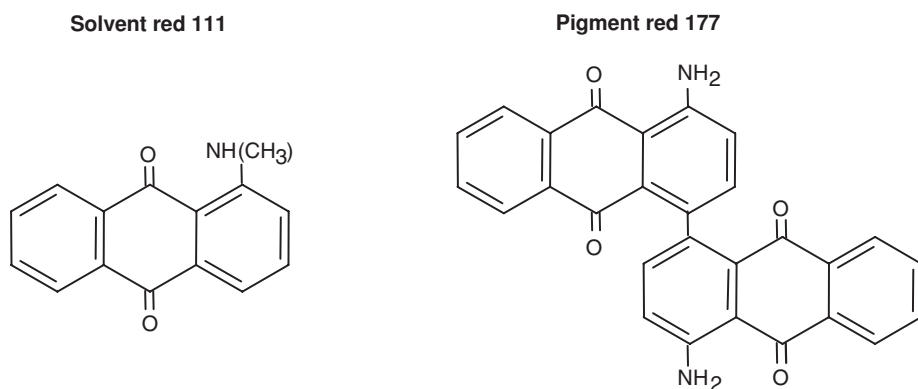


Figure 5.11: Comparison of the chemistry of anthraquinone colorants

At the same time these two examples show clearly the importance of chromophores, a system of conjugated double bonds that are responsible for the

absorption of light and finally responsible for the color. The first example is characterized by a color shift from green to red. The additional ring system of the Pigment red 149 causes another orientation of the conjugated double bonds (in comparison to Solvent green 5), associated with a different need of energy to excite the π -electrons. Different energies mean different wavelengths of the absorbed light, and consequently different colors. The second example does not show a color shift. Simplified expressed the molecule of Solvent red 111 is doubled in Pigment red 177; therefore the orientation of the conjugated double bonds is more or less the same in both colorants, and consequently there is no color shift. The Color Index differentiates between *solvent* and *disperse dyestuffs*. These two different terms do not express any differences in the chemical structure of a colorant but indicate the field of application – a nontextile and a textile application. This is one of the reasons why several chemical identical colorants are listed both as solvent and disperse dyestuff (Fig. 5.12).

Solvent yellow 114

Disperse yellow 54

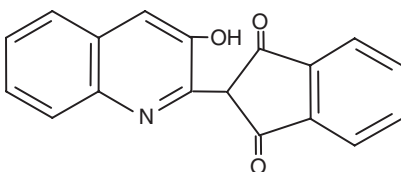


Figure 5.12: *Identical chemistry but different terms of dyes*

At the very beginning the only field of application of dyes was the coloring of textiles. Decades later, other fields of application for colorants were discovered, the nontextile applications. New colorants, synthesized by different manufacturers, were listed according to the intended field of application. At this stage the exact chemical structure was not always known and/or was not published for reasons of competition. This is probably another reason for the double term of “older” dyes.

Detailed data regarding the solubility of dyes in a polymer melt are not available. A certain assessment, however, is possible because the solubilities of several dyes in monomers, for example, methyl methacryl acid ester and styrene, were deter-

mined and additionally, as comparison in the rather polar solvent ethanol. The solubilities vary considerably, and a general idea is given in Table 5.29 [48].

Table 5.29: *Solubility of Dyes in the Monomers of PMMA and PS*

Dye	Solubility (in g/L)		
	Methyl metacryl acid ester	Styrene	Ethanol
Solvent yellow 160:1	2.4	4.7	0.3
Disperse yellow 201	110	400	1.3
Disperse yellow 54	1.8	3.1	0.7
Solvent yellow 130	0.1	0.2	< 0.1
Solvent orange 86	8.5	13	1
Disperse orange 47	4	6	21
Solvent red 111	7.5	13	0.7
Solvent red 179	1.6	4.5	0.1
Disperse violet 31	35	25	1
Solvent blue 97	18	55	< 0.1
Solvent green 3	4	11	< 0.1
Solvent green 28	10	25	< 0.1

In this context another physical phenomenon, sublimation, should be mentioned. Sublimation takes place when at increasing temperature a substance changes from the solid state directly into the gaseous one, leaving out the liquid state. Several dyes show this phenomenon. At high processing temperatures parts of the dye dissolved in the polymer melt go over into the gaseous state at the moment the colored polymer melt leaves the die to fill the mold. The gaseous dye deposits directly on the comparatively cool surface of the mold, slowly forming an increasing deposit. This deposit can cause flaws on the surface of the injection molded plastic part if it is not removed in time. In theory sublimation can be avoided by a decrease of the processing temperature, but in practice this is impossible, because each polymer requires for this type a typical (high) processing

temperature. The only possibility to avoid those deposits is therefore to exchange the dye applied for the color matching.

Sublimation takes place not only during the injection molding of plastics but also already during the drying of a masterbatch in a recirculating air dryer, for example, which is essential for PA or PET prior to their processing

A typical example of such a disturbing sublimation is Solvent red 111, which sublimates at the normal processing temperatures of amorphous polymers. On the other hand sublimation does not disturb the processing of a polymer if the dye sublimates at a temperature well above its processing temperature. A typical example for such a dye is Solvent red 135 (Fig. 5.13).

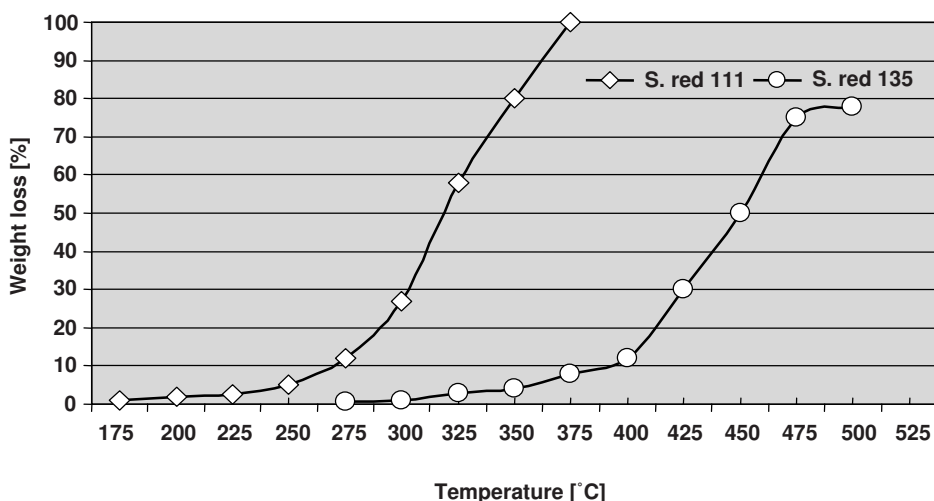


Figure 5.13: Sublimation temperatures of two dyes

The phenomenon sublimation is exploited in smoke signal rockets for military and/or civil purposes, which is another important field of application of Solvent red 111. The importance of the criterion *sublimation fastness* increased steadily in the past, because of:

- The necessary concentration of dyes increased clearly in opaque colors.
- The processing of plastics takes place at higher temperatures (faster cycles, pin gate, hot runner).
- Higher degree of automation (cleaning of the mold is no longer possible because of the construction of the mold and/or economic reasons).

The processing of dyes differs only slightly from those of pigments. There are of course no dispersing problems, because the dyes dissolve in the polymer melt. Dyes reach their maximum color intensity when they are completely dissolved. The completeness of the solution and in addition a homogeneous distribution of the molten dye in the polymer melt are essential to avoid any flaws in the final product. An incomplete solution of a dye would cause color specks and/or color streaks during the coloring of plastics. The result of an inhomogeneous distribution of the dissolved dye in the polymer melt would be color streaks. Both flaws are visually very disturbing and must be avoided.

The manufacture of a dye containing granular color preparation (masterbatch) requires relatively high processing temperatures to accelerate the dissolving, an increase of residence time to allow a complete dissolving, and a good mixing screw profile to reach a homogeneous distribution of the molten and/or dissolved dye in the polymer matrix. A fast distribution of the molten dye in the polymer melt is very important, not only because of the large differences in viscosity between the low-viscous dye melt and the high-viscous polymer melt but also to avoid a local oversaturation, which would negatively influence the speed of dissolving of the dye. The last point requires special attention at a higher dye concentration, which occurs in color preparations with a good covering property.

The melting point of several dyes is listed in Table 5.30.

Table 5.30: *Melting Points of Several Dyes*

Dye	Melting point
Solvent yellow 160:1	209 °C (408 °F)
Disperse yellow 201	115 °C (239 °F)
Solvent yellow 93	181 °C (359 °F)
Disperse yellow 54	264 °C (507 °F)
Solvent yellow 130	300 °C (572 °F)
Solvent orange 60	230 °C (446 °F)
Solvent orange 86	180 °C (356 °F)
Solvent red 179	255 °C (491 °F)
Solvent red 135	318 °C (604 °F)
Solvent red 52	280 °C (536 °F)
Disperse violet 31	186 °C (367 °F)

Table 5.30: Continuation

Dye	Melting point
Solvent violet 13	189 °C (372 °F)
Solvent violet 36	213 °C (415 °F)
Solvent blue 97	200 °C (392 °F)
Solvent green 3	213 °C (415 °F)
Solvent green 28	245 °C (473 °F)

The melting point of some dyes is higher or within the range of the processing temperature of polymers. In such a case the dissolving speed of the dye in the polymer melt is the time-determined process. To ensure a complete dissolving of the dye, the residence time during the manufacture of a masterbatch demands special attention. An incomplete solution of the dye would cause the visually very disturbing color specks and/or color streaks in the final product.

The available palette of dyes for the coloring of plastics diminished considerably in the last few years. In Amendment 2 of the German *Bedarfsgegenständeverordnung* [46], dated July 15, 1994, all azo colorants were banned that decompose under defined specific test conditions forming a listed amine. The list contains 20 amines that are classified as carcinogenic. The reason for this ban was originally the dying of textile, but later on it was extended to the whole field of coloring of plastics.

The shade of chemically identical pigments depends, besides other criteria, on the crystal size and crystal modification; therefore pigments produced by different manufacturers, show differences in their shades. They cannot be exchanged with each other without a new color matching. In contrast to the pigments, the shade of a dye depends only on the chemical structure. Assuming the same purity, chemically identical dyes, synthesized by different manufacturers, can be exchanged without any problems.

Considering the limited number of dyes, they are subdivided according to their color and not their chemistry, which was the subdivision of the organic pigments. Most of the dyes consist of a polycyclic ring system, and are mainly anthraquinone derivatives.

The exact chemical constitution of the dye is added, when this is known. Practice has proven that knowledge of the structure composition can be very helpful in answering all customer questions, for example, content of chlorine in a colorant.

5.3.1 Blue

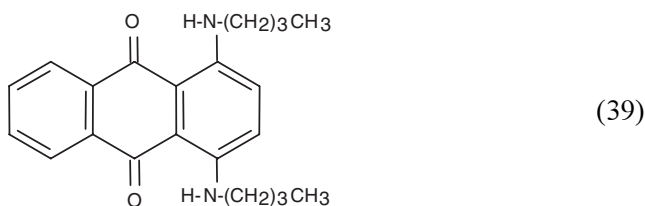
Solvent blue 35 / 61554 / CAS 17354.14.2 – Anthraquinone derivative

Properties: Blue, melting point 127 °C (260 °F), no migration at concentrations < 0.1%.

Good heat stability: 280–300 °C (536–572 °F) in PS; 280 °C (536 °F) in PET; 250 °C (482 °F) in PMMA and ABS.

Good to medium light fastness: 7 (pure tone) / 4–5 (white reduction) in PMMA and PET, 7 / 4 in PC, 6 / 4 in PS. The light fastness decreases with increasing degree of white reduction.

Application: The dye can be used in many amorphous polymers.



Solvent blue 67 – a copper phthalocyanine sulfamid

Properties: Blue, exact chemical constitution has not yet been published

Good heat stability: 280 °C (536 °F) in PET.

Medium light fastness: 6 in PET.

Application: The product was developed specially for the coloring of PET.

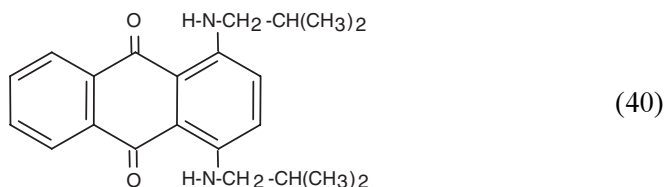
Solvent blue 78 – Anthraquinone derivative

Properties: Blue, melting point 160 °C (320 °F).

Good heat stability: 280–300 °C (536–572 °F) in PS.

Medium to low light fastness: 6 (pure tone) / 3–4 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers.



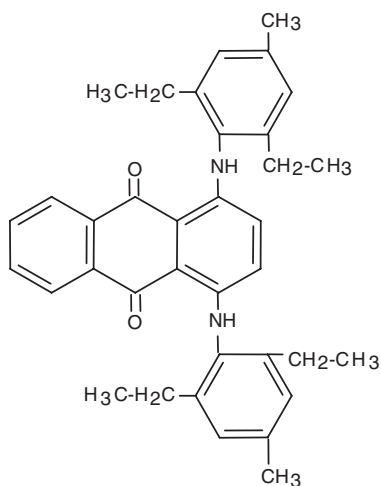
Solvent blue 97 / – / CAS 32724.62.2 – Anthraquinone derivative

Properties: Blue, melting point 200 °C (392 °F), no migration at concentrations < 0.1%.

Good heat stability: 340 °C (644 °F) in PC; 300 °C (572 °F) in PS, PMMA, and PA-6; 290 °C (554 °F) in PET; 260–280 °C (500–536 °F) in ABS.

Good light fastness: 7 (pure tone) / 6 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.



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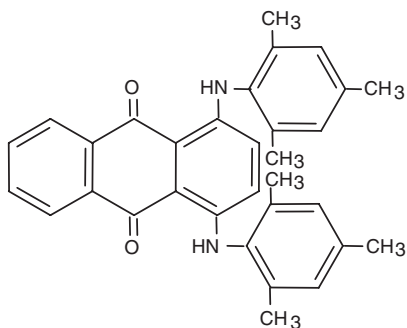
Solvent blue 104 – Anthraquinone derivative

Properties: Blue, melting point 240 °C (464 °F).

Good heat stability: 300 °C (572 °F) in PS.

Good light fastness: 7–8 (pure tone) in PS, SAN, PC, and PMMA.

Application: The dye can be used in many amorphous polymers.



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Solvent blue 132 – Anthraquinone derivative

Properties: Blue, exact chemical constitution has not yet been published.

Good heat stability: 300 °C (572 °F) in PA-6.

Good light fastness: 7 in PA-6.

Application: This dye was developed especially to color PA-6.

5.3.2 Brown

At present no brown dyes are commercially available. The previously marketed dyes were banned according to Amendment 2 of the German *Bedarfsgegenständeverordnung*. This lack of brown dyes is no real problem, because brown shades can be matched easily by a combination of a red and a black colorant.

5.3.3 Yellow

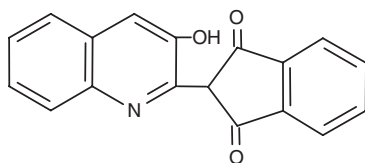
Disperse yellow 54 = Solvent yellow 114 / 47020 / CAS 17772.51.9 – Quinophthalone derivative.

Properties: Yellow, melting point 264 °C (507 °F), no migration at concentrations < 0.1%.

Good heat stability: 340 °C (646 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–280 °C (572–536 °F) in SAN; 290 °C (554 °F) in PET.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of PA-6.



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Disperse yellow 201 = Solvent yellow 179 / – / CAS 54079.53.7 – Methine derivative

Properties: Yellow, melting point 115 °C (239 °F), no migration at concentrations < 0.1%. The exact chemical constitution has not yet been published.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS, SAN, and PMMA; 290 °C (554 °F) in PET; 240–260 °C (464–500 °F) in ABS.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of PA-6.

Disperse yellow 241 – Azo dye

Properties: Yellow, melting point 254 °C (489 °F), no migration at concentrations < 0.1%. The exact chemical constitution has not yet been published.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS; 290 °C (554 °F) in PET; 300–260 °C (572–500 °F) in PMMA; 260 °C (500 °F) in SAN.

Good light fastness: 7 (pure tone) / 5–6 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of ABS and PA-6.

Solvent yellow 93 / 48160 / CAS 4174.09.8 – Pyrazolone derivative

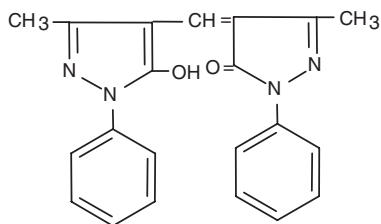
Properties: Yellow, melting point 181 °C (358 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–270 °C (572–518 °F) in SAN; 280 °C (536 °F) in PET.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PS.

Medium weather resistance: 4 (pure tone) / 3 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of ABS and PA-6.



(44)

Solvent yellow 98 / 56238 / CAS 27870.92.4 – Amino ketone derivative

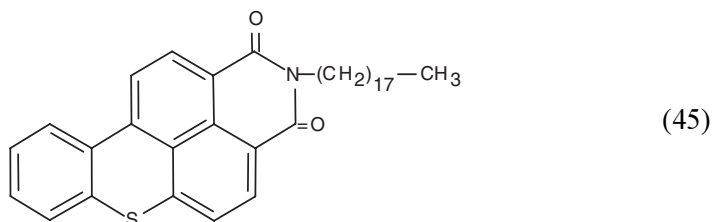
Properties: Yellow, fluorescent, melting point 98 °C (208 °F).

Good heat stability: 300 °C (572 °F) in PS, PMMA, PC, and PET.

Good to medium light fastness: 7 (pure tone) / 4–5 (white reduction) in PMMA.

The light fastness decreases with increasing degree of white reduction.

Application: The dye can be used in many amorphous polymers.



Solvent yellow 135 – Coumarin derivative

Properties: Greenish yellow, fluorescent, melting point 289 °C (552 °F).

Good heat stability: 300 °C (572 °F) in PS and PMMA; 280–300 °C (536–572 °F) in SAN; 240–260 °C (464–500 °F) in ABS.

Medium light fastness: 6 (pure tone) / 3–4 (white reduction) in PS. The light fastness decreases with increasing degree of white reduction.

Application: The dye can be used in many amorphous polymers, including the coloring of PA-6.

Solvent yellow 145 – Methine derivative

Properties: Yellow, melting point 240 °C (464 °F), at processing temperatures > 280 °C (536 °F) there is the tendency to sublime.

Heat stability: 300 °C (572 °F) in PC; 260 °C (500 °F) in PA-6. The heat stability varies considerably depending on the type of polymer to be colored.

Light fastness: 7 (pure tone) in PC, 3 (pure tone) in PA-6. The light fastness varies considerably depending on the polymer to be colored.

Application: The use of this dye is clearly limited due to its dependencies of fastness properties on the type of polymer.

Solvent yellow 160:1 / – / CAS 35773.43.4 – Coumarin derivative

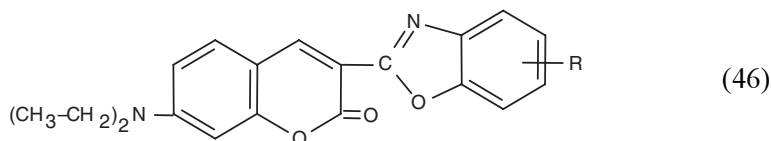
Properties: Greenish yellow, fluorescent, melting point 209 °C (408 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS, PMMA, and PA-6; 300–280 °C (572–536 °F) in SAN; 280 °C (536 °F) in PET; 240–260 °C (464–500 °F) in ABS.

Medium light fastness: 6 (pure tone) / 3–4 (white reduction) in PS. The light fastness decreases with increasing degree of white reduction.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.

Remark: Only the basic formula of this dye is known; the exact chemical constitution of the substituent is not (yet) published.



Solvent yellow 163 / 58840 – Anthraquinone derivative

Properties: Yellow, melting point 180 °C (356 °F).

Good heat stability: 340–360 °C (644–680 °F) in PC; 300 °C (572 °F) in PS.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in PS; 7 / 7 in PET.

Application: The dye can be used in many amorphous polymers, it is not recommended for the coloring of PA-6.

5.3.4 Green

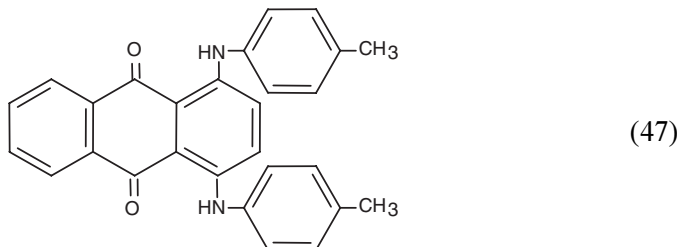
Solvent green 3 / 61585 / CAS 128.80.3 – Anthraquinone derivative

Properties: Bluish green, melting point 213 °C (415 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–280 °C (572–536 °F) in SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in PA-6 and ABS.

Good to medium light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PS; 7 / 6–7 in PC; 7 / 5 in PET; 6 / 5 in PA-6.

Application: The dye can be used in many amorphous polymers.



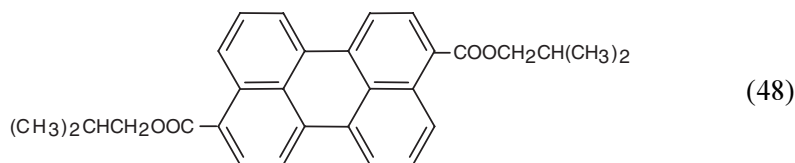
Solvent green 5 / 59075 / CAS 2744.50.5 – Perylene derivative

Properties: Greenish yellow, fluorescent, melting point 210 °C (410 °F).

Good heat stability: > 300 °C (572 °F) in PS.

Light fastness: 7 (pure tone) / 3 (white reduction) in PS. The light fastness decreases strongly with increasing white reduction, while a transparent shade (pure tone) shows a good light fastness.

Application: This dye is recommended especially for the coloring of PS, SAN, PMMA, and PC; preliminary tests are recommended for the coloring of SB, ABS, ASA, and PET. It is not recommended for the coloring of PA-6.

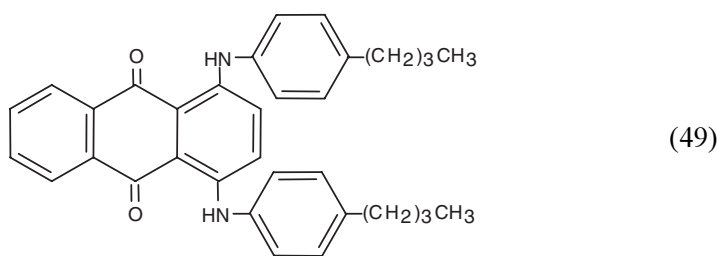
*Solvent green 20 – Anthraquinone derivative*

Properties: Green.

Good heat stability: 300 °C (572 °F) in PS and PC, 280 °C (536 °F) in PET.

Good light fastness: 7 (pure tone) / 7 (white reduction) in PET; 7 / 6–7 in PS; 7 / 6 in PC.

Application: The dye can be used in many amorphous polymers; it is not recommended for the coloring of PA-6.

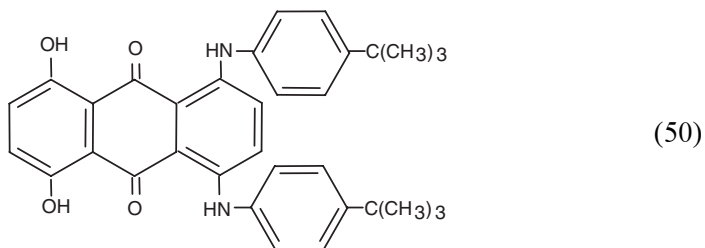
*Solvent green 28 / – / CAS 4851.50.7 – Anthraquinone derivative*

Properties: Yellowish green, melting point 245 °C (473 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–280 °C (572–536 °F) in SAN; 290 °C (554 °F) in PET; 260–280 °C (500–536 °F) in ABS.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers; it is not recommended for the coloring of PA-6.



5.3.5 Orange

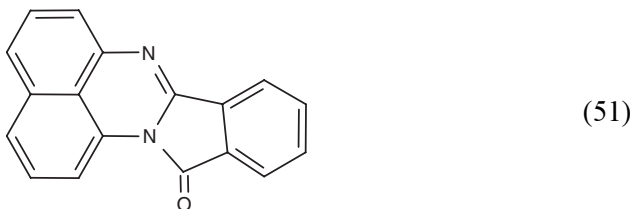
Disperse orange 24 = Solvent orange 60 / – / CAS 6925.69.5 – Perinone derivative

Properties: Yellowish orange, melting point 230 °C (446 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 280–300 °C (536–572 °F) in SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in ABS and PA-6.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.



*Disperse orange 47 = Solvent orange 107 / – / CAS 5718.26.3 –
Methine derivative*

Properties: Reddish orange, melting point 225 °C (437 °F), no migration at concentrations < 0.1%.

Good heat stability: 320 °C (608 °F) in PC; 300 °C (572 °F) in PS and SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in ABS and PMMA.

Good light fastness: 7–8 (pure tone) / 5–6 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of PA-6.

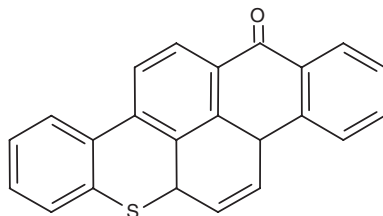
Solvent orange 63 / 68550 / CAS 16294.75.0 – Modified anthraquinone derivative

Properties: Red, fluorescent, melting point 260 °C (500 °F).

Good heat stability: 320 °C (608 °F) in PC; 300 °C (572 °F) in PS, PMMA, and PET.

Good to medium light fastness: 7–8 (pure tone) / 4 (white reduction) in PMMA; 5–6 / 6–7 in PC.

Application: The dye can be used in many amorphous polymers. A dye concentration < 0.3% is recommended.



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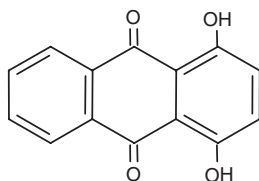
Solvent orange 86 / 58050 – Anthraquinone derivative

Properties: Orange, melting point 180 °C (356 °F).

Good heat stability: 300 °C (572 °F) in PS, PMMA, and SAN.

Good light fastness: 7 (pure tone) in PS.

Application: This dye no longer plays a role in coloring of plastics, because it can be used only for transparent colors.



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5.3.6 Red

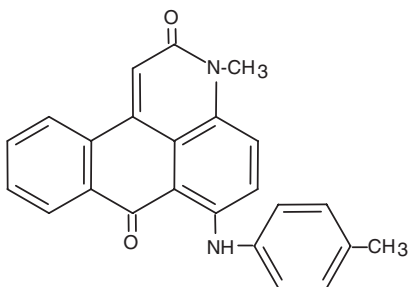
Solvent red 52 / 68210 / CAS 81.39.0 – Anthraquinone derivative

Properties: Bluish red, melting point 280 °C (536 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PMMA and PA-6; 280–300 °C (536–572 °F) in SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in PS and ABS.

Good to medium light fastness: 7 (pure tone) / 3–4 (white reduction) in PS. The light fastness decreases strongly with increasing degree of white reduction.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.



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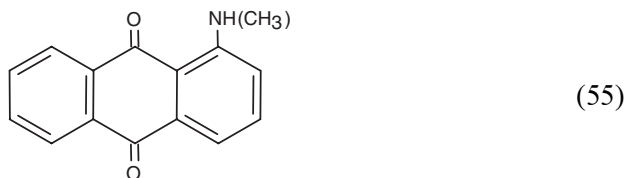
Solvent red 111 / 60505 / CAS 82.38.2 – Anthraquinone derivative

Properties: Red, melting point 170 °C (338 °F), no migration at concentrations < 0.1%. Strong tendency to sublime at the usual processing temperatures of amorphous polymers.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PMMA; 300–280 °C (572–536 °F) in PS and SAN; 270–280 °C (518–536 °F) in PA-6; 260–280 °C (500–536 °F) in ABS.

Good light fastness: 7 (pure tone) / 6 (white reduction) in PS, 7 / 4–5 in PC.

Application: In spite of its good fastness properties the use of this dye is limited because of its strong tendency to sublime.



Solvent red 135 / – / CAS 20749.68.2 – Perinone derivatives

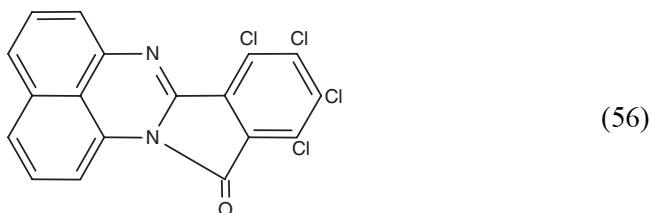
Properties: Yellowish red, melting point 318 °C (604 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PMMA; 280–300 °C (536–572 °F) in PS and SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in PA 6, 260–280 °C (500–536 °F) in ABS.

Good light fastness: 8 (pure tone) / 6 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.

Remark: This dye tends to sublime but only at temperatures well above the processing temperatures of amorphous polymers.



Solvent red 179 / – / CAS 6829.22.7 – Perinone derivative

Properties: Yellowish red, melting point 255 °C (491 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS, PA-6, and PMMA; 300–260 °C (572–500 °F) in SAN; 280 °C (536 °F) in PS.

Good light fastness: 8 (pure tone) / 6 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.

Solvent red 195 – Monoazo derivative

Properties: Red.

Good heat stability: > 300 °C (572 °F) in PS.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PS.

Weather resistance: 4 (pure tone) / 2 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers.

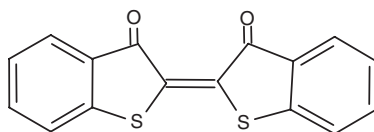
Vat red 41 / 73300 / CAS 522.75.8 – (unsubstituted) Thioindigo

Properties: Red, fluorescent, melting point > 300 °C (572 °F).

Good heat stability: 300 °C (572 °F) in PC and PMMA; 280 °C (536 °F) in PS.

Medium light fastness: 5–6 (pure tone) / 5–6 (white reduction) in PC; 4 / 3 in PMMA.

Application: The dye can be used in many amorphous polymers, but only when there are no strict requirements regarding the light fastness of the final product.



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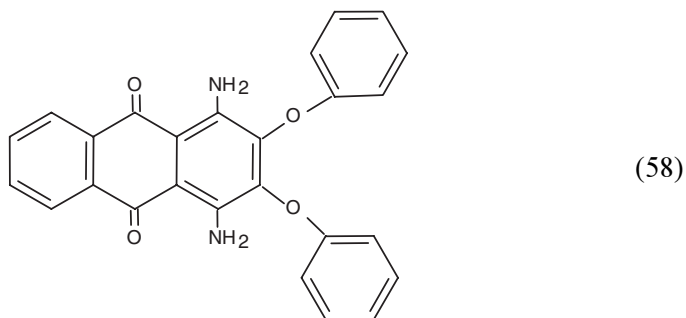
5.3.7 Violet*Disperse violet 26 = Disperse violet 31 / 62025 / CAS 6408.72.6 – Anthraquinone derivative*

Properties: Bluish violet, melting point 186 °C (366 °F), no migration at concentrations < 0.1%.

Good heat stability: 300 °C (572 °F) in PC and PS; 300–280 °C (572–536 °F) in SAN; 280 °C (536 °F) in ABS; 270–260 °C (518–500 °F) in PET.

Good light fastness: 7–8 (pure tone) / 6–7 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of PA-6 and PMMA.



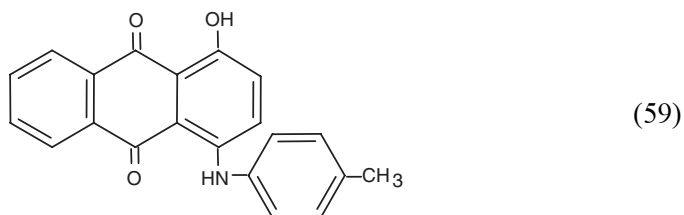
Solvent violet 13 / 60725 / CAS 81.48.1 – Anthraquinone derivative

Properties: Bluish violet, melting point 190 °C (374 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–280 °C (572–536 °F) in SAN; 290 °C (554 °F) in PET; 280–260 °C (536–500 °F) in ABS.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) and 8 / 5 in PS, depending on the supplier of this dye.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of PA-6.



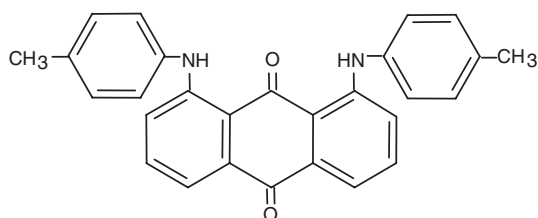
Solvent violet 36 / – / CAS 82.16.6 – Anthraquinone derivative

Properties: Reddish violet, melting point 213 °C (415 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–280 °C (572–536 °F) in SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in PA-6; 280–260 °C (536–500 °F) in ABS.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.



Solvent violet 37 – Anthraquinone derivative

Properties: Violet.

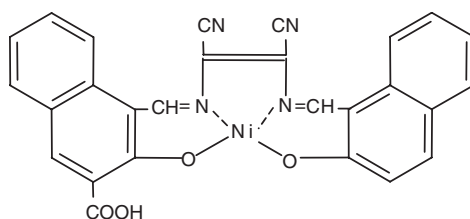
Good heat stability: 300 °C (572 °F) in PS.

Good light fastness: 7–8 (pure tone) in PS.

Application: The dye can be used in many amorphous polymers.

Solvent violet 49 / 48520 – Nickel complex

Application: This dye was developed especially for the spin dyeing.



5.3.8 Black

The commercially available black dyes are always a mixture of several (colored) dyes; a single black substance is not marketed at present.

5.4 Effect Colorants

One of the main functions of colors is their use as design elements; therefore designers look for new effects all the time. Analogous to the inorganic pigments, there are also organic effect pigments. The organic effect pigments can be subdivided into:

- Daylight fluorescent pigments
- Optical brighteners

- Speckled effect pigments
- Thermal colors
- Marble batches

5.4.1 Daylight Fluorescent Colors

This type of colorant consists of fluorescent dyes dissolved in a polymer matrix. A modified polyamide is used mainly as polymer matrix, but other polymers as carriers for the daylight fluorescent dyes are also quite common. The daylight fluorescent dyes are dissolved in a polymer matrix, and the product obtained is milled to a fine powder. These colorants therefore show the typical behavior of a pigment, and can be applied consequently also in partially crystalline polymers. Polyolefins (PO) are the main field of application of daylight fluorescent pigments.

Chemically the two principal classes of fluorescent dyes are the rhodamines, which reinforce the red region, and the greenish yellow aminonaphthalimide derivatives.

The concentration of these dyes in the polymer matrix is said to be in the range of 5%. The data sheets of the different manufacturers/suppliers of daylight fluorescent pigments do not contain details regarding the type of fluorescent dye involved or the effective concentration of the dye in the polymer matrix. Only the type of the polymeric carrier is mentioned.

The daylight fluorescent colors absorb not only visible light but also the ultraviolet (UV) fraction of daylight. The absorption of daylight is responsible for the basic color, while the absorbed UV light is transformed and emitted in the visible range. The result is a very high degree of reflectance, and the colored material appears to glow.

The daylight fluorescent dyes are sensitive to heat and duration of the heat impact. This requires special attention during manufacture of a masterbatch, but also later on during the production of the colored final product. The processing temperature should be as low as possible in combination with a short residence time. In practice there are limits, because every processing of a polymer requires a typical temperature range defined for the polymer to achieve a proper polymer melt. In addition the melting of a polymer takes a certain time, depending on the temperature. At a too low temperature and/or too short residence time a plasticizing screw has enough power to force an incomplete molten polymer through the extruder; at the same time an unknown amount of frictional heat is developed. The result might be thermal damage of the daylight fluorescent dye. A thermal damage of

the fluorescent dye is easily discernible, as the color loses more or less its high degree of brightness.

Owing to the limited heat stability of daylight fluorescent pigments, their application is limited to polymers with a rather low processing temperature, for example, PE-LD and light flowing grades of PP.

It is quite common during the injection molding to recycle directly flawed parts and/or the sprue parts. In the case of daylight fluorescent pigments this might be problematic because every additional impact of heat can increase the degree of thermal damage.

The concentration of a daylight fluorescent dye in the polymer matrix is rather low, which amounts to a high concentration of the daylight fluorescent pigment in the final product. The recommendations vary between 1% and 2% of the pigment. In practice such a high concentration causes slowly growing deposits on the mold and/or screw during injection molding. An addition of chalk during the processing of daylight fluorescent pigments may reduce the deposition but cannot prevent it completely. The reason for the formation of a deposit is an incompatibility between the polymer matrix of the daylight fluorescent pigment, for example, modified polyamide, and the polymer to be colored, mainly polyolefins.

Another disadvantage of daylight fluorescent pigments is the low degree of light fastness; the UV part of daylight is especially harmful. To improve gradually their light fastness, some suppliers recommend the addition of an UV absorber during the production of the colored final product and/or the application of a transparent UV absorber containing protective coat. The lacquering of colored plastic parts is practiced in case of safety related products, but this is too expensive for consumer goods. On the other hand the high brightness of a daylight fluorescent dye is the result of the transformation of absorbed UV light into visible light. The use of an UV absorber to improve light fastness would consequently reduce the high brightness. This is a typical example of the mutual exclusion of requirements.

Daylight fluorescent pigments are marketed in the colors yellow, green, red, blue, and violet. The yellow pigments are quantitatively the main product, certainly because yellow is used worldwide as a warning color.

5.4.2 Optical Brighteners

The optical brighteners are closely related to the daylight fluorescent dyes. They are colorless substances, emitting a bluish visible light after the transformation of absorbed UV light. Optical brighteners are applied as pure substances. The application concentration in the final part is in the range of 25–250 ppm.

Optical brighteners must behave like dyes, and dissolve in the polymer to show their effect. Contrary to organic dyes, optical brighteners can be used also in partially crystalline polymers. This is possible because of the extremely low application concentration. In this range of concentration they are fast to migration.

There are two fields of application of these substances. One is use as a decolorizer in polymers. Naturally colored polymers very often possess a very slight yellowish tint, which can be eliminated by the incorporation of an optical brightener. For this use the necessary concentration is in the range of 10–50 ppm. In this context it should be mentioned that the manufacturers of polymers do not release any information regarding the type and concentration of the incorporated optical brightener. The lack of such information considerably complicates the work of a colorist.

The other field of application is the coloring of polymers. The addition of an optical brightener to any color creates the impression of a higher brightness and cleanness of the color. Experience shows that colored plastic articles do not infrequently contain an optical brightener, but it is difficult to determine its source. There are two principal possibilities – the source is either the color preparation or the polymer.

A typical example of the use of an optical brightener is the color white. The addition of a small amount of an optical brightener to a white colored plastic part enhances the impression of white; the part is “whiter than white.” Depending on the type and grade of polymer the necessary concentration is in the range of 50–250 ppm.

We come across this application nearly daily. It is quite common that white colored textiles contain an optical brightener. To create special effects, the light in a disco changes in short intervals to all possible colors, including a pure UV light. In this case the white shirts and blouses glow with a bluish tint.

The absorption of UV light is the common method to detect the presence of an optical brightener in polymers. A light cabinet, used for the exact assessment of colors during the process of color matching and/or of colored specimen, contains in addition an UV lamp.

The work of a colorist is complicated by the presence of an optical brightener, for example, if the supplied color specimen does not contain an optical brightener but is present in the supplied polymer sample. A 100% matching of the color is impossible in such a case, and only a dialogue between the colorist and the customer can solve the problem.

The other possibility is that the supplied color specimen contains an optical brightener. This case, too, is very complicated. The basic color can be matched but an identical brightness and cleanness of the color is impossible to achieve as

long as the colorist does not know the colorants and the type of optical brightener used in the color specimen.

Generally speaking color can be matched by using quite different colorants, but on the other hand each colorant reacts differently to the presence of an optical brightener. Differences in brightness and cleanness are therefore quite normal. Another reason for differences in brightness and cleanness of a color is of course the type of optical brightener applied, because its efficiency to brighten a color varies from type to type. Several types of optical brightener are marketed for application in polymers.

Considering the large number of colorants and optical brighteners it is impossible to check all possible combinations to receive an identical color match.

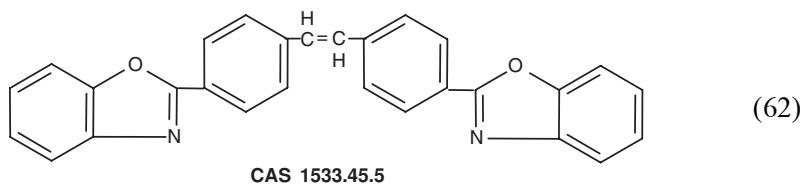
Here, too, only a dialogue between the colorist and the customer can solve the problem.

The incorporation of an optical brightener into a color preparation does not require special precaution methods, just a generally valid one. If blending a small quantity into a large one, it is advisable to check the homogeneity of the mixture.

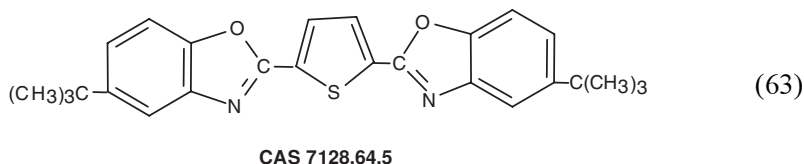
The chemical structures of optical brighteners for use in polymers resemble those of organic polycyclic colorants, but not exclusively. The chemical structure of some often applied optical brighteners are shown below.

They have the following structures:

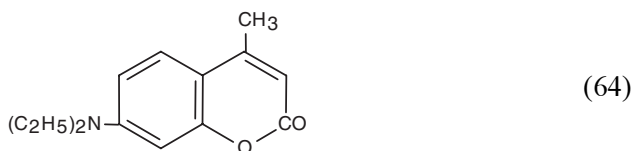
a) Benzoxazolyl derivatives



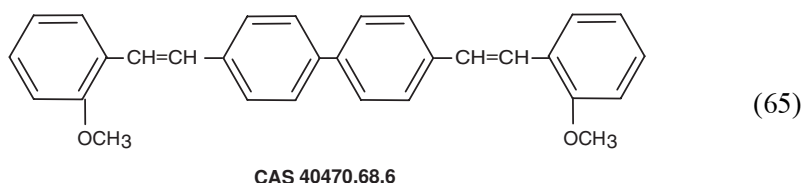
and



b) Coumarin derivatives



c) Ethylenediarylide derivatives



Additional products with similar or different chemical structures are known and commercially available.

5.4.3 Speckled Effect Pigments

There are many possibilities to create a speckled effect. Some of these possibilities are described in the section on *inorganic pigments*, for example, the different types of aluminum flakes. Organic speckled effect pigments are also known. They consist of textile fibers, available in the colors black, white, and colorful. The speckled effect increases with increasing size of the fibers, but the diameter and length of those fibers is limited for technical reasons. On one hand, the production methods of fibers limit the sizes, and on the other hand the fibers should not be so coarse and long that they may cause weak spots and/or defects in the final product, especially in thin-walled plastic articles.

Different types of polymers are used as fiber matrices. The requirements for the fiber matrix are a good heat stability, and no softening or melting at the processing temperature of the polymer to be colored. For the coloring of the fiber, colorants with a good heat stability and light fastness are usually applied. One example of often used speckled effect pigments are fibers based on a modified and cross-linked cellulose as matrix, and commercially available in the colors white, black, and colorful, mainly in blue, green, and red.

Considering the large number of polymers it may be necessary to check if the fiber can be applied in the selected type of polymer. A rather fast method is to add

the fiber to a homogeneous white or black colored plastic specimen (the choice depends on the color of the fiber). An insufficient heat stability of the fiber at the processing temperature of the selected polymer can be recognized by a visual comparison of the shape of the processed fiber with the raw fiber. A melting or softening of the fiber causes a visible color shift. Black, insufficient stable fibers will tint a white specimen gray, while white fibers will lighten a black specimen. Colorful fibers will tint a white specimen in the color of the fiber.

The concentration of those fibers in the final part depends on the desired intensity of the speckled effect; consequently the effective concentration can vary considerably.

5.4.4 Thermal Colors

A colored cup becomes colorless as a hot liquid is poured in, a straw takes on a new color when a cold beverage is sipped, a baby spoon becomes red when the food is still too hot. These are but a few examples of the process of thermochromism, the generic name for temperature-sensitive colors. Thermal colors are colorants that change their color if exposed to a higher temperature. This process is *reversible*, for example, such a colorant can be colorless at room temperature (20 °C [68 °F]) and colored at 40 °C (104 °F). After cooling down to room temperature the product will be colorless again. This process can be repeated many times.

Another group of substances shows an *irreversible* color change. They are used, for example, for the calibration of temperatures. These chemicals are not used in polymers, because there is no demand (not yet) for an irreversible color change in plastic parts; therefore they are not described in this context.

Thermal colors are a two-component system, consisting of an electron acceptor and an electron donor. Both substances are together microencapsulated in a polymer shell. At increasing temperatures at least one of the two substances melts, which causes a change in the force of attraction between the electron acceptor and electron donor. At the same time a change in the force of attraction means different energies (wavelengths of the light) to excite the electrons. The appearance of color depends on the wavelength of the absorbed light; consequently differences in the absorbed wavelength produces different colors. A similarity to organic pigments is very obvious. An organic pigment shows also a color shift in the case of a partial solubility at a too high processing temperature. An extreme case is the Pigment red 254, which dissolves in PC completely at a temperature of 320 °C (608 °F), giving a bright fluorescent yellow color, while the pigment colors other polymers a brilliant red.

Different colors can be produced by selection of appropriate dyestuff intermediates with different definite melting points. This second point is important for the predetermined temperature range of the color change. The commercially available thermal colors cover a temperature range of -25°C (-77°F) up to $+55^{\circ}\text{C}$ (131°F), in increments of approx. 5°C (41°F). The difference in temperature between a “cold” and a “hot” color is approx. 10°C (50°F).

The color change is a relatively slow process, because plastics are known as poor heat conductors. Thermal colors are available in the colors yellow, orange, red, green, brown, and black. The heat stability of the thermal colors marketed today is in the range of $180\text{--}200^{\circ}\text{C}$ ($356\text{--}392^{\circ}\text{F}$); therefore they can be applied only in polymers with a low processing temperature, for example, PE-LD, and light-flowing grades of PP or PS. The light fastness of thermal colors is not very good. The shell of the microcapsules is made of PE, PP, or PS.

The tinting strength of thermal colors is low; therefore high pigment concentrations, approx. 5–20%, are necessary. Interesting effects can be created when a very small amount of a “normal” colorant is added as basic color.

The incorporation of thermal colors in a color preparation, for example, masterbatch, causes no specific problems; they behave like normal pigments. Attention must be paid only to the low heat stability.

5.4.5 *Marble Batches*

Designers look for new effects all the time. The imitation of the natural marble effect in plastics was one of their objectives. In contrast to the other effects the imitation of the marble effect cannot be produced by a single substance, but requires a mixture of (mostly) two differently designed masterbatches.

An appropriate designed masterbatch does not cause any color streaks during the coloring of plastics. This goal is achieved by a good choice of the carrier, preferably of the same type of polymer that is to be colored, and selection of additional components, for example, waxes to influence the melt flow properties of the masterbatch. A well designed masterbatch possesses a processing temperature and melt viscosity comparable to those of the polymer to be colored. On the other hand color streaks occur when the melt viscosity of the masterbatch is much higher than those of the polymer and/or the masterbatch requires a clearly higher processing temperature. A masterbatch with such properties is rejected for the “normal” coloring of plastics, but this is the basis for the marble effect.

A marble batch consequently contains two different designed masterbatches, a normal, appropriately designed masterbatch for the basic color of the plastic article, and a second one for the marble effect. The second masterbatch is

designed in such a way that its use causes purposely color streaks. One possibility is that the second masterbatch contains a carrier that requires a higher processing temperature in comparison to the polymer to be colored; another possibility is to increase the melt viscosity of the second masterbatch.

In theory the designing of a marble batch seems easy, but in practice it requires a good balance between the processing parameters of the second masterbatch and the polymer to be colored. A too large difference in their properties can lead to the problem of incompatibility of both components, and the result would be faulty parts. A too small difference gives an insufficient marble effect.

The normal procedure is to run preliminary tests with differently designed marble batches on the production machine, the only way to check the marble effect and the quality of the colored final product. The small plastic specimens, used during the color matching are worthless in this context.

The principle of a marble batch is well defined. But in consideration of the numerous polymers in combination with the varieties of design it is difficult to create at once a sufficient marble effect. Usually it takes several test runs before the desired result is achieved. In addition it should be mentioned that a marble effect is not always possible, for example, when the mold contains gaps and/or is very rugged. In such a case the marble effect can be unsightly and therefore impossible.

6 Additives for Polymers

During the processing of polymers several selected substances are added to optimize specific properties of a polymer, because only after the incorporation of an additive can the polymer in question fulfill those specific requirements. Supplementation of polymers with additives is quite common.

The additives can be:

- Antimicrobiological substances
- Antistatic agents
- Flame retardants
- Fillers
- Lubricants / dispersing agents / release agents
- Nucleating agents
- Stabilizers
- Blowing agents
- Plasticizers

There are principally two methods of adding the additives either as a component of a color batch or as a separate additive batch.

Some additives must be incorporated by the manufacturer of the polymer because of the large concentration necessary. One example of such a case are fillers; some specific grades of polymers contain up to 55–60% filler, e. g., the glass fiber reinforced grades. On the other hand it is quite common that the customer requests the incorporation of an additive in the color preparation, for example, the use of stabilizer to improve the light fastness of the plastic article.

A combination of color plus additive in *one* batch can be problematic. There are several reasons for this. Any additive needs space in the recipe of the color preparation. As a result, the concentration of the colorant in the batch must be reduced, especially in the case of very intensive colors. The result is a higher coloring concentration for the final product. Another reason is the fact that some additives are not colorless, and consequently they also must be colored, which further increases the amount of colorant in the recipe.

Some additives are marketed as batches. In these cases it is certainly worthwhile to check if using two separate batches, a color batch and an additive batch, or a combination batch, color plus additive, is more economical.

Additives can be inorganic as well as organic substances. An interaction between additive and colorant cannot be excluded right away, and such an interaction can be negative or positive.

The function of an additive is the optimization of a specific property of a polymer. This requires tailor-made substances for each polymer depending on its chemical structure. The consequence is a large number of additives. The following sections contain only a general description of the additives. It would be beyond the scope of this book to go into too much detail.

6.1 Antimicrobiological Substances

Tests proved that bacteria and/or fungi can settle on plastics and even penetrate into the surface of the polymer. A mechanical cleaning of the surface is therefore not sufficient to remove them. A harmful contamination of the surface with bacteria and/or fungi can be avoided by adding an antimicrobiological substance to the polymer. The supplementation of polymers with an antimicrobiological substance is an additional precautionary measure, and it shall not and cannot replace the usual rules of hygiene.

Examples for fields of application are:

- Hospitals – floors, walls, appliances / equipment, protective gloves, bed linens, mattress, packaging material for medical equipment, and so forth.
- Household – kitchen, bathroom, bedroom
- Textile – work clothes of some occupational groups

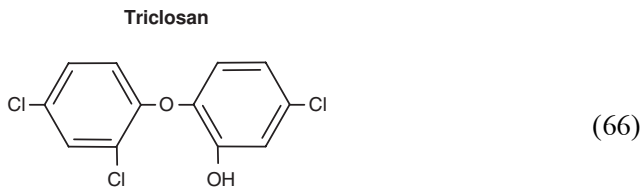
Antimicrobiological substances for application in polymers are not new substances, but well known substances, previously applied successfully in disinfectants for many years.

An antimicrobiological substance is suited to application in polymers, when several requirements are fulfilled.

The main requirements are:

- Good activity in polymers
- Good heat stability to withstand the processing temperatures of polymers
- Insoluble in water to avoid removal during cleaning or washing

An example of such a substance is 2,4,4'-trichloro-2'-hydroxydiphenylether, a phenol derivative with the generic name Triclosan.



2,4,4'-Trichloro-2'-hydroxydiphenylether

A concentration of 0.1–1.0% Triclosan is recommended for use in polymers. Additional substances are known.

6.2 Antistatic Agents

Many polymers possess good electrical insulating properties, and this makes them susceptible to the accumulation of static electricity. Static electricity is generated when two materials with different susceptibilities to electron loss are rubbed against each other; these can be two different polymers or two different materials. The friction from rubbing causes the natural balance of electrons to shift; one material loses electrons and becomes positively charged, and the other material gains electrons and, with them, a negative charge. In contact with a conductive material a discharge (spark) occurs. Dryness is an important factor for the buildup of static electricity; therefore especially in wintertime any static electricity can cause serious problems. The buildup of static electricity can be reduced considerably by adding antistatic agents to the polymer. The effect of an antistatic agent is the formation of a very thin layer of humidity on the surface of the polymer, which is to a certain extent conductive.

The fields of application of antistatic agents include:

- Packaging – reducing the collection of dust on consumer goods, causing poor customer appeal
- Electronics – safety at work, avoidance of faulty circuits or short circuits
- Industry – general precaution method (safety) to avoid problems associated with the presence of static electricity, for example, danger of dust explosions, during handling of inflammable liquids, and so forth
- Processing of plastics – processing aid to avoid bridging of resins during conveying and feeding operations

Practice shows that especially the last point causes problems during the processing of polymers without being discernible right away. For the feeding of a color batch

it is quite common to use a volumetric metering unit. Each cavity of this unit is filled and emptied in a rhythm defined by calibration. The cavity and the color batch normally consist of different polymers. Rotation during the feeding can cause a buildup of static electricity, and an incomplete emptying of the cavity is the result. This is clearly visible at an inhomogeneous and/or weak coloring of the polymer.

It is quite common that polymers and additives, for example, color batch, are not fed directly on the plasticizing screw but first in a hopper with a small window to control the flow of the materials. The window is often made of a transparent polymer. The rotation in the hopper, necessary for a good premix of the polymer pellets and the color batch, can also cause static electricity, and the color batch sticks to the window. The results are faulty colored parts. Another reason for a static electricity is the severe drying of polymers, which is required for the processing of polymers such as polycarbonate (PC) and poly(ethylene terephthalate) (PET).

Problems during the coloring of polymers related to static electricity can be solved by adding an antistatic agent to the color preparation. For this purpose the addition of 0.1–0.3% antistatic agent is sufficient.

In this context it should be mentioned that several dispersing agents show a side effect of antistatic activity.

The primary compounds used as antistatic agents are:

- Fatty acid esters
- Ethoxylated fatty acid esters
- Alkylamine derivatives
- Ethoxylated alkylamine derivatives
- Alkylsulfonates

The effect of an antistatic agent is the formation of a very thin layer of humidity, but this requires that the antistatic agent migrate to the surface of the polymer. The application concentration depends on the chemistry of the antistatic agent and the type of polymer.

The necessary concentration in a partial crystalline polymer is in the range of 0.1–0.5%, while amorphous polymers require a higher concentration, in range of 1.0–1.5%. The direction of migration is of course not only to the outer surface of the polymer but also to the inner surface, which could cause a harmful contamination of the filling good.

The use of an antistatic agent in a consumer good in contact with food and/or packaging of other sensitive products, for example, cosmetics, requires the observance of legal regulations. Restrictions exist in many countries for the purpose of preventing any harm to the consumer.

All listed types of consumer goods must fulfill several legal requirements. Which plastic part is listed as a consumer good varies from country to country, but generally it includes everything in contact with food, beverages, products for the household, and other sensitive products such as cosmetics and toys. In Germany, for example, all plastic articles in contact with food, packaging material for food, smoking materials, products for the household, cosmetics, and everything in contact with the skin for a longer time are listed. In those items the use of an antistatic agent is limited, and only approved and listed antistatic agents are allowed within a defined concentration; for example, ethoxylated alkylamine derivatives are allowed only up to a concentration of 0.15% in the final product. In the United States, only FDA-approved antistatic agents are allowed to be used in consumer goods.

Many antistatic agents are either liquid at room temperature or have a melting point well below any processing temperature of polymers, for example, the ethoxylated alkylamine derivatives and the ethoxylated fatty acids. The incorporation of a liquid substance in a solid color preparation requires special precaution methods, especially at higher concentrations. On the other hand, often used liquid antistatic agents are commercially available as solid concentrates, either absorbed on a high absorptive carrier such as silica or as a highly concentrated batch. Addition of these concentrates causes no problems during the production of a solid color preparation and they are therefore the preferred types.

6.3 Flame Retardants

The majority of polymers are more or less combustible. High standards in fire protection are responsible for the use of flame retardants. To comply with rules/laws polymers must be equipped with a flame retardant.

The main fields of application are:

- Electrical/electronic appliances, for example, TV compounds, fuse boxes, switches, plugs, and so forth
- Interior decor of public transport systems, such as busses, railways, and airplanes
- Protection of buildings (inside/outside), for example, airport buildings, railway stations, and so forth

In the past chlorinated/brominated substances were preferred because of their effectiveness at relatively low concentrations. But they showed a very significant disadvantage. In case of fire they release gaseous halogen hydrides, which in combination with water are highly corrosive. Even if the fire is small, the smoke fumes

can destroy entire installations by attacking the sensitive electronic components. The consequential damage was very often higher than the damage of the fire as such. The importance of this group of flame retardants diminished considerably in the last decade, and today they no longer play a role as flame retardants in polymers. A modern flame retardant is halogen-free. Their disadvantage is the high concentration necessary to reach the commonly used standard in industry, UL 94V-0. The addition can reach then 25–30%, and in extreme cases even higher.

Supplementation of the polymer with a flame retardant is done by the manufacturer of the polymer, for several reasons:

- The necessary concentration of a modern halogen-free flame retardant is too high as a component of a color preparation.
- Question of guarantee. The different fields of application are governed by several statutory regulations, and include the type of allowed flame retardant, its concentration, test methods, approval procedures for the final part, and so forth. The manufacturer of the plastic part has to document this to his customer in the industry.

The last point is clearly beyond the scope of a manufacturer of color preparations. Flame-resistant types of polymers usually are available only in standard colors. But there is an increasing demand for colors specific for the manufacturer of a flame-resistant plastic part (e.g., for color as trademark). The design of a color preparation for the coloring of a flame-resistant polymer is difficult because:

- No loss of the flame retardancy is permitted.
- Several flame retardants are not colorless; they first must be colored, which can increase the demand of color preparation considerably.
- A high concentration of color preparation can cause problems in highly filled polymers (filled with flame retardant) during the processing.
- Negative interactions between flame retardant and colorant cannot be excluded.

Because of these problems it is recommended to develop any color preparation for the coloring of flame-resistant polymers only in cooperation with the manufacturer of this type to be colored.

In the electrical/electronic industry an international standard for the classification of flame-resistant plastic parts is UL 94. The following practical experience may demonstrate how tricky the coloring of a flame-resistant polymer can be. Pure, powdery titanium dioxide (Pigment white 6), absolutely not flammable, was added as a colorant during the injection molding of a flame-resistant polymer. The result was a loss of the flame resistance of the part. At first this seemed a very

astonishing result. But a detailed examination of the UL 94 method explained this result. One very important criterion for the classification is the behavior of the ignited specimen. The hot melt should not form droplets, which when falling down ignite the wad of cotton wool. When this happens the plastic part does not fulfill the strict UL 94 requirements. Titanium dioxide is a “heavy” substance, which increased the weight of the polymer melt, and droplets were formed.

Substances of the following groups are applied as flame retardants:

- Aluminum hydroxide
- Zinc borates
- Red phosphorus
- Melamine derivatives (borates, cyanurates, phosphates)
- Phosphate derivatives (ammonium polyphosphates, aryl phosphates)
- Phosphorous acid ester (chlorinated and chlorine-free grades)
- Antimony pentoxide
- Chlorinated aliphatic hydrocarbons

The concentration depends on the chemistry of the flame retardant, the type of polymer, and the classification group (UL 94V-0, V-1, and so forth).

6.4 Fillers

Many technical plastic parts must have a high mechanical strength, sometimes in combination with a good durability at higher temperatures of use. This goal is achieved by the addition of fillers. The supplementation of polymers with fillers is usually done by the manufacturer of polymers. The concentration varies between 5% and 60%. Which filler is added depends on the type of filler, the type of polymer, and the specific requirements the final product has to fulfill during its entire life span. For many applications there are grades available that have been developed especially for this purpose.

The following fillers are usually applied to reinforce polymers:

- Glass fibers and glass spheres
- Carbon fibers
- Calcium carbonate (chalk)
- Talcum (silicates)
- Barium sulfate

During the color matching for the coloring of reinforced polymers some characteristic properties must be considered. The most important points probably are:

- Possible damage of the glass fibers. In accordance with their crystal modification several inorganic pigments are very hard and can break the glass fiber during the coloring procedure; these pigments should therefore be avoided, at least when a decrease of the mechanical strength is not acceptable. A typical example of such damage is titanium dioxide (Pigment white 6, rutile modification). When applied in a glass fiber reinforced polyamide, for example, a breakage of the glass fiber was observed, combined with a significant, unacceptable decrease of the mechanical strength of the final product. In this case there was no other possibility than to substitute the titanium dioxide by the optically inferior, but “softer” Pigment white 7 (Zinc sulfide) or Pigment white 5 (Lithopone). This danger of breakage should be considered not only in case of a pure white coloring but also when the pigment is used in white reduction. Another example is the very hard, abrasive chromium green hematite (Pigment green 17). In comparison to the titanium dioxide this pigment is seldom used, and can be substituted relatively easy by an organic pigment.
- Heat stability. A high concentration of filler causes a clear increase of the processing temperature of the polymer and a higher melt viscosity. A higher melt viscosity means a longer cycle time and residence time. The result of such a combined effect can be that the heat stability of an organic colorant, still applicable in the naturally colored polymer, is no longer sufficient for the coloring of the same, but reinforced polymer.
- Pigment concentration in the color preparation. Most fillers are not colorless. They first must be colored, which increases the necessary amount of colorant in the color preparation. The additional amount of colorant can be considerable, especially in the case of very intensive, brilliant colors. Several organic pigments are difficult to disperse, and a higher concentration of these increases the risk of an incomplete dispersion. Color specks in the final product are the logical consequence of an incomplete dispersion, and therefore precautionary methods are a necessity to avoid them.
- Melt viscosity of the color preparation. The melt viscosity of a reinforced polymer is higher in comparison to the naturally colored grade of the same polymer. This must be taken in consideration. The melt viscosity of the color preparation must be adjusted to those of the reinforced polymer; otherwise color streaks and/or other problems during the coloring process may occur.
- Intensive, brilliant colors. Not *every* intensive, brilliant color is possible in a reinforced polymer, especially in the case of highly filled grades of polymer. The fillers show the side effect of lightening colors. In an extreme case the necessary amount of color preparation can exceed the capacity of the reinforced polymer for an additional, large amount of color preparation.

- Use of dyes as colorants. Dyes can be used to color reinforced polymers. In a reinforced polymer, the proportion of the polymer in the product is lower (in comparison to the naturally colored grade). This may cause a migration of the dye at a very low but otherwise safe concentration.
- Interactions. Interactions between the filler and the colorants cannot be excluded. Interactions were reported in the case of glass fibers.

The design of a color preparation for the coloring of a reinforced polymer is not especially difficult when the specific properties and behavior of a reinforced polymer are taken into consideration.

6.5 Dispersing Agents/Lubricants/Release Agents

During the processing of polymers various difficulties can arise, ranging from problems in demolding a part during the injection molding to a sticking together of films during film blowing. Another difficulty may be the reproduction of a structured surface of the mold on the plastic part. In many cases a fast remedy is possible by adding a lubricant and/or release agent.

A strict differentiation between a lubricant and a release agent is impossible because the physical phenomena of adherence and glide merge into one another. The substances usually applied show both effects, and the effect that predominates depends on the polymer and the concentration. An application as release agent normally requires a higher concentration than for use as a lubricant. The concentration varies between 0.1 and 2.0%, depending on the efficiency of the substance, the intended effect, and the type of polymer. Specific grades of polymers are already equipped with those additives by the manufacturers of the polymer, but sometimes it may be advantageous to add it later.

The following substances are recommended as lubricants/release agents:

- Fatty acids, for example, stearic acid, palmitic acid.
- Fatty acid ester, for example, sorbitan tristearate, pentaerythritol fatty acid ester
- Fatty acid amides, for example, oleic acid amide, stearic acid amide, erucic acid amide
- Fatty alcohol, linear and branched grades
- Paraffin oil
- Waxes and their derivatives

A comparison of the chemical structures of these substances with dispersing agents shows that several of these substances are chemically identical. Every

color preparation contains dispersing agents in a variable concentration, and quite often their concentration is high enough to show positive side effects as lubricants and/or release agents. If the side effect is not yet sufficient it is not a problem to increase their concentration.

A substance is effective as a lubricant/release agent when it migrates at least partially to the surface of the polymer. This must be considered when the plastic part is used “in contact with food.” In many countries there are limits for global migration, which of course includes also lubricants, release agents, and dispersing agents. When the extent of the global migration exceeds the allowed limit, it is recommended to determine the chemical structure of each migrated substance, as only in this way is it possible to differentiate between the sources, the polymer, or the color preparation.

6.6 Nucleating Agents

Before an injection molded plastic part can be demolded, it must be cooled down. During this step of injection molding, partial crystalline polymers, for example, polyethylene (PE) and polypropylene (PP), start to crystallize, to form the so-called crystallites. The crystallization is a two-stage process. The first step is the formation of a stable nucleus, which occurs by local ordering of polymer chains. This is followed by the growth stage, which is governed by the rate of addition of other chains to the nucleus. Dust, impurities, remainders of catalysts, and so forth influence the first stage, because they can function as nuclei. The crystal growth takes several days before it is completed. The results are relative large crystals, known as spherulites that are visible in polarized light.

The presence of dust and other impurities is a coincidence, varying from batch to batch. The result would be a variable amount of shrinkage, which is influenced, among other factors, by the size and number of the spherulites. This effect would make it more difficult to reproduce the exact measurements in each injection molded plastic part; therefore nucleating substances are added to avoid this source of irregularities. If a nucleating agent is added to the system, crystallization can be induced at higher temperatures. With more nuclei available and the growth rate unaffected, crystallization is completed sooner. The availability of many nuclei also leads to more and smaller spherulites.

As described in section 3.3 *Shrinkage/Warpage*, several organic pigments act as nucleating agents, and cause the known problems regarding shrinkage and warpage in partially crystalline polymers, preferably in PE-HD and PP.

Experience shows that even in these cases the addition of a nucleating agent to the color preparation helps to reduce these problems. The nucleating agent seems to

be “faster.” The reason for this behavior is not clear, but the key is probably the first step of crystallization, the formation of a stable nucleus.

Although special grades of polymers, equipped with a nucleating agent, are commercially available, it is quite common to add a nucleating agent to the color preparation. In contrast with other additives, only a very small number of nucleating agents are known, and in addition their effectiveness is strictly related to the type of polymer.

The known nucleating agents have the following chemical structures:

- DBS (dibenzylidensorbitol) – in PP
- Aluminum benzoate – in polyolefins
- Calcium and lithium salts of higher aliphatic carbon acids – in PA
- Talcum (special grades) – in polyolefins

The necessary concentrations are in the range of 0.1–0.2% in the final product. Incorporation in color preparations causes no problems at all.

6.7 Stabilizers

Like every other organic substance, polymers age. The addition of a stabilizer to polymers can slow down the aging process, but a complete prevention is impossible. Any aging of polymers is combined with a significant loss of mechanical and physical properties, including change of color. Aged polymers are often very brittle, and the surface is no longer shiny.

Aging occurs for various reasons. Among these are thermodynamically unstable conditions in the material (internal factors), but the majority of causes are environmental effects on the material (external factors). Some typical examples of the influence of the environment on aging are:

- Impact of ionized rays – for example, medical technology, the sterilization of medical appliances by γ -rays
- Impact of weather – for example, outdoor use of polymers
- Biological impacts – for example, by bacteria and fungi. The basis for the decomposition of biodegradable polymers is this impact, and therefore in this special case a positive effect
- Chemical impacts – for example, interactions between the content and the packaging material, in chemical plants, industrial exhaust
- Mechanical impact – for example, rotation/movement of plastic parts, pressure (conveyor belts)

- Thermal impacts – for example, high temperatures during the processing of polymers and during the use (in chemical plants, in cars under the hood, etc.).

Analytical investigations very often showed that a combination of different impacts caused the aging. In Section 3.6 *Light Fastness / Weather Resistance* it was discussed that these fastness properties depend on the whole system, consisting of colorants and polymer. It is impossible to differentiate between the light fastness of an organic colorant and the polymer. The addition of stabilizers to the whole system is necessary if there are strict demands with respect to fastness. Fastness properties are essential requirements; therefore the stabilization of polymers is described in more detailed.

Model tests showed that a PE, consisting of a perfect chain $[-CH_2-CH_2-CH_2-]$, does not need any stabilization, as such an ideal PE is stable and withstands the damaging effects of the environment [49]. The chain of technical grades of PE is by far not perfect, and contains defective spots of a different nature and even double bonds. These defective spots are the real reason for the need of stabilization with a light stabilizer.

The aging of PE caused by the influence of weather is a photooxidative degradation. The first step, the formation of a polymer radical, is initiated by the absorption of energy, for example, intensive UV light. This radical reacts at once with atmospheric oxygen to create a peroxide radical, which starts a chain reaction. The most important steps of reaction are shown in Fig. 6.1.

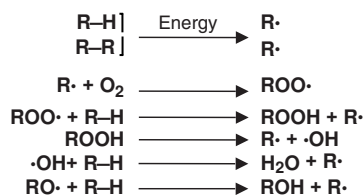


Figure 6.1: Chain reactions of peroxide radicals

The peroxide radical reacts with another molecule of the polymer, and the result is a peroxide hydroxide and a new polymer radical. The polymer radical can react either with itself, with a resulting breaking off of the chain reaction, or with atmospheric oxygen, in which case the chain reaction starts again. By the impact of energy the peroxide hydroxide disintegrates into a hydroxide radical and a polymer oxide radical, which react with further molecules of the polymer, and the chain reaction starts again.

These are only the most important steps of reaction, but further reactions are possible, for example, a reaction with double bonds and/or other defective spots in the polymer chain.

The reaction mechanism indicates that any impact of energy should be avoided: without energy no formation of radicals can be initiated, and without radicals the chain reaction cannot start. In practice, however, this is impossible. Energy in the form of heat is essential for the processing of polymers, and the absorption of light is unavoidable during the use of plastic parts. Consequently an effective stabilization against heat, light, and atmospheric oxygen is necessary for polymers to withstand prolonged exposure to the damaging effects of the environment.

The damaging effect of sunlight can be reduced, but not completely avoided, by the addition of an ultraviolet (UV) absorber to the polymer. Tests showed that the surface of a polymer cannot be protected by the addition of UV absorber, as they are effective first in deeper layers. The primary goal therefore must be the deactivation of the radicals before they can start a chain reaction.

During development of stabilizers it was recognized very early that the different reactions of decomposition require very specific substances for an optimized protection of the polymer during the entire life span. The results of all these efforts are the following groups of stabilizers:

- Processing stabilizers
- Long-term thermal stabilizers
- Light stabilizers

The *processing stabilizers* are added directly after the synthesis of the polymer by the manufacturer. Their function is the stabilization of a polymer during the processing. A minimum temperature of $> 130\text{ }^{\circ}\text{C}$ ($266\text{ }^{\circ}\text{F}$) is required to be effective. The optimal effectiveness of processing stabilizers is within the usual range of the processing temperatures of polymers. They protect the polymer against a heat-initiated decomposition.

Processing stabilizers are derivatives of the following chemical groups:

- Phosphites
- Hindered phenols
- Hydroxylamines
- Lactones

At temperatures below $130\text{ }^{\circ}\text{C}$ ($266\text{ }^{\circ}\text{F}$) the processing stabilizers are not effective (with the exception of the hindered phenols). Technical applications of plastic parts require a good thermal stability for a long time. These parts have to withstand the attack of elevated temperatures during the intended use. These tempera-

tures are clearly lower than the processing temperatures. But nevertheless the polymer must be stabilized, otherwise it is damaged before the expected time. This temperature range requires another type of stabilizer, the long-term thermal stabilizer.

Long-term thermal stabilizers are also added by the manufacturer of the polymer. They reach their optimal effectiveness at temperatures below 130 °C (266 °F).

Long-term thermal stabilizers belong to the following chemical groups:

- Hindered phenoles
- Hindered amines stabilizer (HAS)
- Thiosynergist (in combination with hindered phenoles)

The long-term thermal stabilizers are not effective at the processing temperatures of polymers (with the exception of the hindered phenoles).

The processing stabilizers and the long-term thermal stabilizers protect the polymer against the damaging attack of heat, while the third group, the light stabilizers, reduces the damaging effect of light and atmospheric oxygen.

The *light stabilizers* are the stabilizers that are applied to improve the light fastness and weather resistance of colored and natural polymers. Although there are special grades of polymers on the market that already contain light stabilizers, added by the manufacturer, it is a common practice to add light stabilizers to color preparations.

There are two types of light stabilizers according to the different function they have to fulfill. The *UV absorber* absorbs those wavelengths of the light that are responsible for the initial step of the formation of radicals in a polymer, while the *HALS* (**H**indered **A**mine **L**ight **S**tabilizer) deactivate any radical before it can start a chain reaction. A combination of UV absorber and HALS shows the chemical phenomenon of synergy, in which interaction of two active components of a mixture is such that the total effect is greater than the sum of the individual effects.

Chemically the UV absorbers belong to the following groups:

- Benzotriazoles
- Benzophenones
- Cyanoacrylates
- Oxanilides
- Phenylsalicylic acid esters

Besides the different chemical structures they differ in the wavelength of maximal absorption and consequently in the area of activity.

UV light is commonly subdivided according to the wavelengths:

- UV-A range – 315 to $\leq$ 400 nm
- UV-B range – 280 to $\leq$ 315 nm
- UV-C range – 100 to $\leq$ 280 nm

Consequently the UV absorbers can be assigned to one of these ranges depending on the wavelength of maximal absorption.

The term HALS already indicates the primary chemical principle. They consist of a heterocyclic, nitrogen-containing ring system, containing bulky substituents neighboring to the nitrogen. The diversity of commercially available products proves the variability of this principle.

The stabilization of a polymer against the damaging attack of light always requires the addition of a HALS. The type depends on the polymer to be stabilized. The concentration should be adjusted to the intensity of irradiation at the area of use and demanded light fastness; consequently the concentration is variable. The addition of a UV absorber as costabilizer is recommended because of the synergistic effect. Typical concentrations for the stabilization of a polyolefin are approx. 0.2–0.4% in the final product.

The majority of light stabilizers are solid substances, and an incorporation into a solid color preparation is uncomplicated. In the case of a liquid color preparation liquid light stabilizers are preferred, however, this is not always possible depending on the polymer to be colored. The liquid stabilizer is not necessarily the first choice for the stabilization of this polymer.

All stabilizers, including the light stabilizers, are naturally not inert substances, and therefore negative interactions with other components of the recipe, for example, filler, colorant, flame retardant, cannot be excluded. Several interactions are well known:

- The use of perylene pigments for the coloring of polymers stabilized with HALS should be avoided, as the perylene pigments can deactivate the HALS.
- HALS are alkaline and may interact with other alkali-sensitive components in the polymer, for example, colorants, flame retardants.
- HALS are alkaline and may interact with acidic substances, for example, thiosynergists and colorants.
- HALS may be absorbed on the surface of components with a high absorptive capacity, for example, carbon black and special grades of silica.
- HALS can be deactivated by environmental influences. The deactivation of HALS in agricultural films is known, caused by the contact with certain insecticides.

These and other possible negative interactions should always be taken into consideration during the process of color matching.

The stabilization of consumer goods “in contact with food” requires the consideration of legal aspects. Not all commercially available stabilizers are approved in every country; there are considerable differences, sometimes only in the allowed concentration. This aspect gains importance because of the increasing export of plastic items. The manufacturers of stabilizers are very helpful, and supply all necessary data for each country.

Finally, specific problems a colorist encounters should be mentioned. One problem is that usually the manufacturer of polymers does not release the type of processing stabilizer and long-term thermal stabilizer added. The colorist is therefore not able to estimate the possibility of negative interactions with components of his color preparation. There are grades of polymers available that are already equipped with light stabilizers. Here, too, the manufacturer of this grade does not release the type and concentration of the added stabilizer. On the other hand the customer of the colorist demands a statement regarding the light fastness to be expected from the colored plastic item. Without the knowledge of the type and concentration of the light stabilizer in this grade of polymer the colorist is not able to calculate if a further addition of light stabilizer is necessary, and if so, the additional quantity needed. These problems can be solved only in cooperation with the customer and a series of experiments to determine the light fastness. Another possibility is an analytical determination of the stabilizers, but this is not only time consuming but also rather costly.

6.8 Blowing Agents

The production of a foam requires the addition of a blowing agent to the polymer melt. In the past fluorinated hydrocarbons were used, but these substances were banned after their ozone layer depleting effect became known. Substances can be used as blowing agents when they are either light volatile or release a large quantity of gaseous products as a result of a thermal decomposition at the processing temperature. Examples of the second type of blowing agents are azodicarbonamide and toluene sulfohydrazide. Blowing agents are very seldom added to a color preparation, and possible only in the case of a powdery or liquid color preparation. The addition to a masterbatch is excluded because of the thermal instability of the blowing agents.

The coloring of a foam is not more difficult than the coloring of a solid polymer, if some specific properties of a foam are taken into consideration, for example:

- A homogeneous coloring of a foam demands a homogeneous cellular structure of the foam, which includes the size and wall thickness of each cell.
- The coloring of a foam demands a much higher concentration of color preparation, comparable to the coloring of a film.
- Colorants may influence the cellular structure of the foam.
- The color of a foam may slightly differ from the shade in a solid polymer. The cells are hollow, variable in size and wall thickness. All this may lead to differences in light absorption and reflection (comparatively to the solid polymer).

6.9 Plasticizers

The classical field of application of plasticizers is PVC, but this is not exclusive. Plasticizers are also added to other polymers, for example, PUR and several grades of rubber, to increase the flexibility of a polymer. Numerous plasticizers are marketed. Chemically they belong to the following groups:

- Phthalic acid ester
- Trimellitic acid ester
- Adipic acid ester
- Sebacic acid ester
- Fatty acid polyglycolester
- Chlorinated paraffin

Toxicological animal experiments point to a certain carcinogenic potential, if a high dosage of diethylhexylphthalic acid ester (DEHP) is repeatedly given in the animal food [50]. Other studies, however, showed that this effect is not applicable to humans. Nevertheless in many European countries the use of this specific phthalic acid ester is banned in those plastic items that may come in contact with food and similar applications. Although only this single substance is banned, many customers require polymers and/or color preparations to be “free of *any* phthalic acid ester.” This is not justified at all.

The design of a color preparation for the coloring of a plasticized polymer is not difficult if some specific properties of a plasticizer are taken into consideration.

Migration. The choice of organic colorants is restricted because many organic colorants are not completely fast to migration. In this case it is recommended to check the migration under the condition of the intended use of the colored plastic article. In the worst case the exact desired shade is impossible.

Influence on the hardness (Shore hardness). It is not uncommon that colorants and/or the carrier of the color preparation influence the shore hardness. In such a case it

is not always possible to adjust the shore hardness by varying the quantity of the plasticizer. The choice of the colorant and/or carrier requires special attention.

Plasticizers as carriers in liquid color preparations. The simplest way to color a plasticized polymer is the use of a liquid color preparation based on the plasticizer of the polymer. This is common practice in the case of plasticized PVC. The concentration of the color preparations depends on the quantity of the plasticizer in the final product.

Interactions. The possibility of interactions between the stabilizers of PVC and colorants should be considered.

Experience shows that every problem encountered so far could be solved in cooperation with the customer.

7 Processing Errors and Their Elimination

Everywhere where people work, errors are made, and the coloring of polymers is no exception. Each type of polymer processing of, for example, injection molding, blow molding, film blowing, and transfer molding, has typical technical problems. These problems are not considered in this chapter, but only those that are related more or less directly to the coloring of polymers. The spectrum of errors starts with problems during the production of a color preparation and ends with problems during the coloring of polymers. In the event of problems during the processing of polymers, very often the first thing is to blame the color for it, “*Without the color there was no problem, it started after adding the color...*”. There are many examples in which as a result of a successful error analysis the implicated color was proved “innocent.” This remark should not give the impression that color preparations do not cause any problems, because they do. On the other hand, the fact is that several processing problems first become apparent after addition of the color, which leads to citing the color as the cause.

Table 7.1 contains the most frequent errors related directly or indirectly to colors, the possible reasons and corresponding possible methods of elimination.

Table 7.1: List of Possible Processing Errors, Reasons, and Possible Methods of Elimination

Error	Possible reason	Possible method of elimination
Color specks in the color preparation	• <i>Masterbatch</i> – No optimal dispersion of the pigments	• <i>Masterbatch</i> – Increase the quantity of dispersing agent. – Increase the shear in the extruder. – Add processing aids.
	– Inhomogeneous premix	– More intensive mixing of the premix
	– Humidity in the polymer and/or other components of the recipe	– Use of dry products and/or drying of the humid component
	– Worn out plasticizing screw	– Replace the screw.
	– Incompletely dissolved dyes	– Change the processing parameter of the masterbatch.

Table 7.1: Continuation

Error	Possible reason	Possible method of elimination
Color specks in the color preparation	• <i>Liquid color preparation</i> – No optimal milling	• <i>Liquid color preparation</i> – Check the milling parameters. – Check the milling device; replace worn parts.
	– Humidity in the binder and/or other components of the recipe	– Use of dry products and/or drying of the humid component
Color specks in the final product	• <i>Masterbatch</i> – Incomplete dispersion of pigments – Incomplete dissolving of dyes	• <i>Masterbatch</i> – Use another batch. – Use another batch.
	• <i>Liquid color preparation</i> – Incomplete dispersion of pigments	• <i>Liquid color preparation.</i> – Use another batch
	• <i>Powdery color preparation</i> – Not enough or wrong coupling agent	• <i>Powdery color preparation</i> – Add more or another coupling agent.
	– No or not enough dispersing agent	– Add a dispersing agent or increase the quantity.
	– Not enough shear during the manufacture of the final part	– Increase the shear or use a mixing head or a similar device.
Color streaks in the final product	– Incomplete mixing of polymer melt and color preparation melt – a) Mechanical – b) Thermal – c) Too large difference in the melt viscosity of both components (masterbatch) – d) Too low coloring concentration (masterbatch)	– Use a mixing head or similar devices. – Check the function of each heating band of the extruder. – Check/adjust the temperature settings of the barrel heating zones. – Check/adjust the residence time. – Use a batch with a better adjusted melt viscosity. – Increase the coloring concentration.

Table 7.1: Continuation

Error	Possible reason	Possible method of elimination
Color streaks in the final product	– Contaminated with other colors – a) Contaminated color preparation – b) Later contamination by handling errors (drying, cleaning of hopper, contaminated recycled material, etc.)	– use another batch of color preparation. – Check the source of contamination (improve the handling, more care, better cleaning at color change, avoid contamination of recycled material, etc.).
Black spots	– Thermally damaged colorants	– Change/reduce the processing temperature. – Reduce the residence time. – Avoid dead spots in nozzle or hot runner. – Avoid the production of small parts in a too large extruder (too high screw volume = too long residence time).
	– Thermally damaged polymer	– Change/reduce the processing temperature. – Reduce the residence time. – Avoid dead spots in nozzle or hot runner. – Reduce the sticking of the melt on barrel, screw, etc. (add lubricant or use another alloy).
	– Contaminated colorants and/or polymer (dirt, impurities, foreign bodies, etc.)	– Use clean material. – Check the source for the contamination.
	– Worn screw, barrel, etc.	– Replace the worn parts.
	– Oxidation through compressed air (Diesel effect)	– Provide/improve venting. – Inject more slowly.
	– Contaminated recycled material	– Use clean material.

Table 7.1: Continuation

Bubbles/ streaks in flow direction (color- less)	– Humidity in the raw material	– Check moisture content of all components. – Check drying (increase the drying time or temperature). – Check the function of the dryer.
	– Later contamination with humidity (during storage, condensed water, leakage, etc.)	– Store all raw materials at room temperature and in a dry place. – Check cooling system on leakage.
Bubbles/ streaks (brownish)	– Too high processing temperature or too long residence time (begin of damage) – Too high shear (frictional heat because of too small feeding system)	– Reduce the processing temperature. – Reduce the residence time. – Check the temperature of the hot runner. – Check the hot runner diameter, if necessary enlarge it. – Reduce the injection rate.
Flow lines (pearlescent pigments and other effect pigments)	– Disorientation of effect pigments in the melt	No complete elimination possible, improvement by: – Adjusting the processing parameter – Changing the gate position

To summarize Table 7.1 the most common processing errors are:

- Color specks
- Color streaks
- Thermal damage
- Impurities
- Humidity streaks

Color specks in the final product are caused by incompletely dispersed pigments and sometimes by incompletely dissolved dyes. The source of these is absolutely clear if a masterbatch or a liquid color preparation was used for the coloring of the polymer. Color specks may occur preferably when these two types of color prepa-

ration contain a high concentration of organic, “hard to disperse” pigments, for example, the blue and green phthalocyanine pigments. It requires a great deal of shear to break up their agglomerates in a polymer melt as well as in a liquid color preparation during milling. The possibilities of elimination were described in an earlier chapter. Another reason for color specks in a color preparation is humidity. Humid pigments are very hard to disperse in a polymer melt; a typical example are the pearlescent pigments. In the case of a liquid color preparation a later contamination with humidity may cause a partial flocculation of the formerly well dispersed pigments, and the results are also color specks.

A very detailed error analysis, however, is necessary if a powdery color preparation was used for the coloring of the polymer. The pigments are not dispersed, determined by the system, and can be dispersed first during the coloring process. The reason for color specks can be not enough shear in the single-screw extruder, not enough coupling agent, and/or not enough dispersing agent. It is quite common that a combination of these reasons is responsible for the color specks.

Color streaks in the final part are caused mainly by an incomplete mixture of the molten polymer with the masterbatch melt. The reasons are manifold, for example, a too short mixing zone of the screw, too low processing temperature, too short residence time, too large difference in the viscosity of both melts, and a too small coloring concentration of the masterbatch. In addition color streaks in amorphous polymers can be caused by dyes that are not completely dissolved in the masterbatch. The elimination of color streaks usually requires a detailed error analysis.

An error analysis should not immediately exclude “impossible” causes, as the following example shows. Color streaks occurred during the coloring of PC on an injection molding machine, and without color there were no visible problems. The same problem arose in a new batch, and of course the color was blamed. After a while the real reason was found. A defective heating band in the middle of the barrel caused an incomplete plasticizing (this heating zone was too cold), which was not visible in the natural polymer but became visible when the color was added. After replacement of the defective heating band there were no further coloring problems, not even with the rejected batch. The customer was very fair and did send a letter of apology.

The consequences of *thermal damage* are mainly either brownish color streaks or black (dark) spots.

Brownish color streaks are the sign of a (beginning) thermal damage of the molten polymer. Hot runners and their construction (dead spots, too small dimensions etc.) are very often the source of this problem, but not exclusively. Thermal damage can also be caused by incorrect processing parameters, for example, too

long residence time, too fast injection, and/or faulty construction regarding the position and dimension of the gate.

If the thermally damaged part of the polymer melt is not replaced with every shot, the thermal damage continues, and black spots (carbonized polymer) are the final result.

This process takes more or less a longer time, therefore the appearance of black spots after a longer processing time indicates thermal damage. Black spots, directly visible at the beginning of a processing, are impurities in the polymer and/or other components.

In this context something else should be mentioned. In the case of very intensive dark colors it is possible to confuse dark spots with color specks. Even a colorist sometimes has difficulties in differentiating between both possibilities. As an example, the crystals of the blue phthalocyanine pigment are nearly black.

A (too) long residence time cannot be avoided all the time. One example of this is the production of tiny technical parts. The construction of every injection molding machine requires a minimum size and screw volume, but this can still be too large for those parts. Another reason for a prolonged residence time is the fact that some polymers tend to stick to the wall of the barrel; consequently this thin layer is not replaced with every shot, and a slow damage of this layer is unavoidable. The addition of lubricants and/or the use of other alloys as linings for the barrel may reduce those problems.

The sources of *impurities* are also manifold. Impurities can be present in the raw materials, and those can be detected rather quickly. It is more difficult to detect the source of impurities caused by a later contamination. They are quite often caused by “bad” handling habits and/or not enough care, for example, during the cleaning of peripheral devices during a color change. Contamination with other colors may cause color streaks.

Impurities can also be caused by abrasion. Every barrel and screw of an extruder should be replaced in time. Any worn barrel and/or screw can cause not only impurities, including a gray tinting of the color, but also problems during the processing, either during the production of a masterbatch or during the coloring of the polymer on the injection molding machine.

Humidity streaks are typical for technical polymers. Technical polymers, for example, PC and PET, must be dried very thoroughly prior to their processing. Another reason for humidity streaks is condensation, mainly in the winter. Warehouses are usually cold, while production halls are warm, with the heat developed by the many extruders alone contributing to this in large part. A contamination with condensation occurs if the “cold” raw materials (polymer and color preparation) are processed directly without the possibility of taking the temperature of the

production hall. To avoid this problem, it is recommended to store some quantities of the raw materials prior to processing in the production hall to allow an adjustment of the temperatures. Another, less frequent source of condensation are the pipes of the cooling system (dripping water) and/or a leakage of this system.

Another point must be mentioned in this context, the *accuracy of the color* from batch to batch. Differences are not necessarily a processing error. Every technical product varies in its properties from batch to batch, and a certain difference must be tolerated within limits. During color matching a certain color batch and polymer was used for the specimen. On the other hand the approval of the colored plastic item by the final customer takes time, usually several months. In the meantime other batches are in use. It is quite common that the shade of the specimen and that of the first production differs slightly; a *slight* difference cannot be avoided. It is therefore important to fix the tolerance limits right away with the customer. Only if the shade of the color preparation is outside of the agreed tolerance limit is it a production error. (For further details refer to Chapter 8 Quality Assurance)

8 Quality Assurance

Any new product can be marketed successfully only if the quality is good. To reach this goal it is necessary to run numerous tests during the development of the new product, to define its specifications, and to establish a quality assurance for the investigation of the quality [51].

All these tasks can be subdivided into three closely related fields of work:

- Determination of specifications, including the (agreed) tolerance limits
- Inspection of incoming products
- Inspection of finished products

A new product goes through several stages. It starts with the design and ends with the production of the new product. Intermediate stages are mold construction, prototype production, a check as to whether all requirements are fulfilled, and of course an early fixing of the color. Production will be repeated from time to time depending on the sales. In practice, however, the situation differs somewhat from this ideal, especially in regard to the color. An early fixing of the color, preferably before the production of the prototype starts, is infrequent. Typically all test runs of a new mold are done with natural polymer, including the check of all properties of the new product, and before production starts the color is fixed. While this is done there is failure to notice that any additive to a natural polymer influences several properties of the finished part. Colorants can affect shrinkage considerably, especially in partially crystalline polymers. In the worst case the size of the part or parts is no longer within the tolerance, a serious problem if parts are assembled to the final product. The result may be an expensive reworking of the mold.

The color of basic consumer items is a question of design, while the color of technical parts is determined by national or international agreements. The manufacturer of a color preparation asks his customer for approval of the supplied colored specimen. At the same time that the approval is given, this specimen acquires the status *specimen of origin*. The same procedure is also valid for each type and grade of polymer to be used in the new product, and may be repeated if there is more than one supplier of the polymer. This situation is quite usual for economic reasons.

For later purposes all relevant processing parameters of the colored specimen must be well documented, as well as, on the customer side, its processing parameters of the prototype production. The specimen of origin should be stored very

carefully. Special attention needs to be paid to the conditions of storage. The specimen should be stored in a dark, lightproof, and well sealed container. The packaging material should not contain any plasticizer, optical brightener, or other additives that may migrate. The condition “well sealed” excludes the influence of gaseous pollutants in the industrial environment and of dust. These requirements are important to avoid an adulteration of the specimen during storage.

As all polymers age, the storage time is limited even under these strict conditions of storage. The recommendation is therefore to replace the specimen approximately every 2 years; otherwise a misinterpretation of a new delivery may occur. It has proven successful to store a larger quantity of the color preparation and the polymer (1–5 kg [2.2–12 lb]), which guarantees the periodical replacement of the specimen.

The next step is the agreement of tolerances between supplier and customer. The tolerance limits should allow on one hand an economic production of the color preparation and on the other hand a constant color for each production of the final product. These contrary interests may cause a clash of interests.

Supplier = large tolerance $\Leftrightarrow$ customer = small (no) tolerance

Experience shows that a direct comprehensive dialogue between both parties can avoid such a clash of interests.

Before the tolerance can be fixed several parameters must be defined:

- Product properties
 - Color
 - Field of application
 - Material (polymer)
 - Surface structure
 - Further specific requirements
- Conditions of visual inspection
 - Source of light
 - Geometry of light reflection
 - Viewing geometry
- Conditions of inspection with a color measuring instrument
 - Type of color measuring instrument
 - Measuring geometry
 - Source of light
 - Color system (usually CIELAB)
 - Preparation of the specimen

Usually suppliers and customers have different color measuring devices. The common practice in such a case is to measure the *same* colored specimen on both

color measuring instruments. By comparison of the data, a tolerance can be determined separately for each instrument. The results are two tolerances, one for each color measuring instrument of the same colored specimen, and each party must agree to the tolerance of the other color measuring instrument. This procedure should cause no problems, because ultimately it is the same color, only measured on two different instruments. This procedure is recommended even if both parties have the same color measuring instrument. Color measuring instruments are a technical product with certain tolerances in spite of all efforts of the manufacturer to minimize them as far as possible.

The tolerance should be smaller than $\Delta E = 0.8-1.0$. Such a difference is just still visible depending on the shade, especially if the entire difference lies on one coordinate. This indicates it is usually not enough to fix only a ΔE , but fixing a tolerance limit for each coordinate is recommended. The sensitivity of our eyes to a specific color varies according to the shade. In accordance with the different sensitivities the tolerance can vary on each coordinate, therefore it is not necessary to ask for the same tolerance on each coordinate.

During the *inspection of the incoming products* each delivery must be checked carefully, and the data compared with the specification. This procedure helps to avoid the use of faulty raw material. It is recommended to check during the inspection of the incoming products only those properties that are relevant for the quality of the product. The costs of inspection can thereby be limited. A complete check of all data would be too cost intensive.

Quality-relevant points of a specification are, for example:

- Polymer – natural color, melt flow index, visual check (impurities, etc.)
- Colorant – colorimetric examination, humidity, visual check (impurities, etc.)
- Color preparation – color (colorimetric examination), melt flow index, humidity, visual check (impurities, contamination with other colors, etc.)

A specimen mold is usually used for this purpose. The production of each specimen must be in accordance with the processing parameter, fixed and documented in the specification. This is necessary to avoid misinterpretations, because slight differences in the processing parameter may cause slightly different shades. The data for each batch can be drawn in a diagram. With increasing amounts of data the diagram shows very well the variation within the tolerance field. In a data sheet or diagram something else is very discernible. The distribution of the data within the tolerance field can occur just by pure chance or the data may move more or less in one direction. An example of such a data sheet is given in Fig. 8.1.

Data sheet (Inspection of incoming goods and/or of finished products)

Article:
Article-No.:
Color:

Colorimetric Data

Date	Target	Standard	Tolerance/Difference
		L* a* b*	ΔL^* Δa^* Δb^* ΔE^*

Batch-No. _____

Figure 8.1: Example of a data sheet for color preparations

The tolerance can be enlarged if a batch just outside of the tolerance limit did not show any negative influence on the quality. On the other hand the tolerance must be reduced if a batch just inside of the tolerance limit influenced the quality of the final product.

The same basic principle is valid for the *inspection of the final product*. The quality assurance of a final product requires not only specifications of the raw materials and the final product but also a specification of the processing parameters. The last point is very important, because a change in a processing parameter can cause a difference in color or quality. A specification of processing parameter should therefore contain all parameters that are relevant to the color or quality. To

work out such a specification or in other words to define the processing “window,” it is necessary to change each processing parameter and to check its influence on the quality. The result is a list of those parameters that are relevant to the quality. It is quite normal if the list of the manufacturer of a color preparation differs in detail from the list of the producer of the final product. Such a difference is the consequence of a different significance of a single processing parameter in the quality. But the importance of a processing specification is in principle the same for both manufacturers. Analogous to the inspection of incoming products the data of the inspection of the final product must be compared with the specification. The same or a very similar data sheet can be used for the documentation of those results (Fig. 8.1).

The manufacturer of the color preparation checks the quality of his product by injection molding of a specimen and a colorimetric examination. These data together with the specimen are supplied to the customer.

The producer of the final product checks its quality, for example, the color, by comparison with the specimen and his own former productions, and this includes visual as well a colorimetric examination. Depending on the design of the product it is possible to measure the color direct on the product, which, however, requires an even part on it, or a separate specimen is produced, using a bypass on its extruder.

These basic features of quality assurance do not indicate the practical problem. It starts with the production of the specimen. The mold and laboratory injection molding extruder for the production of the specimen differ from the mold of the final product and the production extruder; consequently both parts are produced with different processing parameters. The color preparation is in both cases the same, but not the batch of the polymer. In addition the (small) samples for the approval of a color and color preparation are produced on a laboratory scale extruder, while the production is done on a production extruder. These different quantities of a color preparation are produced necessarily under different processing parameter. These facts may underline the importance of specifications and agreed tolerances. It is common practice to establish besides the specimen of origin a second one, a *specimen of (the first) production*, including all specifications.

The influence of processing parameters on the color (and other properties) is very often underestimated in spite of many publications that prove their importance. A technical college in Germany (KIMW – **K**unststoff**i**nstitut der **m**ittelst**ä**ndischen **W**irtschaft) is very active in this respect. Several theses proved the influence of processing parameters on the color and quality. These studies showed that the change of one processing parameter causes directly or indirectly a different strain on the molten polymer by temperature and time. On the other hand these two pa-

rameters are very important factors with regard to the heat stability of polymers and colorants and the fastness properties of the final product. These studies proved that the following processing parameters are relevant for the color and quality:

- Melting temperature
- Residence time
- Temperature of the mold
- Injection rate
- Revolutions of the screw
- Back pressure

In practice a change of processing parameter is quite common, usually caused by the production process. If the number of pieces is reached, production stops and the mold is dismantled. It would be ideal to use the same extruder for all further production runs, but this is not always possible. Often a similar injection molding extruder must be used for the next production of the same article, which causes at least slightly different processing parameters. This requires a special careful investigation of the first produced parts to avoid production flaws.

Finally a practical example may demonstrate the importance of processing parameters in combination with the construction of the mold. If a manufacturer of technical devices needs a very large number of pieces, usually two independent processors of polymers will produce them. They use different injection molding machines and differently constructed molds. At the beginning one processor had problems with the exact shade of his parts, while the other processor, using the same batch of color preparation, had no color problems. This problem was solved by a slight adjustment of the recipe of the color preparation for the processor with problems.

9 Mold Construction

Polymers and colorants are subject to the impact of temperature during processing. This thermal strain is not only the result of the processing parameter, but also a consequence of the construction of the mold. A suboptimally constructed mold may cause such an additional thermal strain that the sum of all thermal strains is already in the range of a beginning thermal damage. To avoid this, several points should be considered for the construction of the mold.

Special attention should be paid to the following points:

- Gate system. The diameter of the gate should not be too small, or a too high frictional heat may be the consequence. Another important point is the right position of the gate.
- Mold cooling system. Polymers are poor heat conductors. The cooling system must be not only efficient but also should ensure that the surface temperature of the mold is correct everywhere, because uneven heat dissipation in the mold can lead to differential shrinkage with all the detrimental effects on the quality of the molded part; in addition a poor heat dissipation in some regions of the mold can cause a substantial lengthening of the cycle time, leading to increased costs of the injection molding. A correct surface temperature of the mold is also important for a perfect surface finish of the molded part, for example, gloss, reproduction of surface structures.
- Surface finish of the mold. All parts of the mold should have the same surface finish, including the same alloy for the lining of all (at least visible) parts of the mould. Different alloys, for example, may cause a differential reproduction of the surface structure.
- Good venting of the mold. This is important to avoid black spots caused by the Diesel effect.
- Sharp edges. Generally sharp edges should be avoided, as they may cause a too high shear with a detrimental effect on the quality of the molded part.
- “Dead” spots. They must be avoided principally to prevent a thermal damage of polymer and/or colorant

The choice of the right hot runner system determines the function of the mold and the quality of the molded parts. Unsuitable hot runner systems usually cause high pressure losses, and they should be operated, if used at all, only at a very high temperature. But this high temperature usually will cause the polymer and/or col-

orant to degrade, and therefore their use should be avoided. The construction of a hot runner should avoid sharp edges, “dead” spots, too small dimensions, and should allow a good temperature control.

Problems related to the construction of a mold and/or hot runner are usually recognized during the test program. Whether a complete elimination of the problem is possible depends on the kind of problem, and of course on the expenditure of time and costs of elimination.

Most problems can be excluded if the above described critical points of construction are taken into consideration during the planning phase of the new mold and hot runner.

10 Legislation

Our everyday life is governed by laws and regulations, and new ones or at least amendments are added constantly. In recent years, the number of laws providing protection during the manufacture, use, storage, and transport of chemicals has risen worldwide. The same is true for regulations concerning waste removal. It is therefore no wonder that the processing of polymers is also subject to many laws and regulations. They vary from country to country, sometimes in substance, and sometimes only in detail. Today it is no longer sufficient to know the laws and regulations of one's own country. The increasing export of goods requires in addition the knowledge of the laws of the receiving country or even countries. Without exceeding the scope of this book, only an outline of the most important laws and regulations related to the coloring of polymers can be given. Generally considered all laws pursue the same aim, namely the protection of the consumer against any harm during the intended use of plastic items and the protection of workers during transportation, storage, handling, and processing. The way to reach this aim varies from country to country. In case of doubt it is recommended that one always check the latest status of the original text of the law or regulation. The most important laws and regulations are:

Unites States

- Toxic Substances Control Act (TSCA) (1976)
- Occupational Safety and Health Act (OSHA) (1970)
- Superfund Amendments and Reauthorization ACT (SARA) (1986)
- FDA, Code of Federal Regulations

CFR 21 § 178.3297 – Colorants for polymers

CFR 21 § 170.39 – Threshold of regulation for substances used in food-contact articles

CFR § 176.170 – contains the methods for the evaluation of migration

CFR 16 § 1501-1518 – Federal hazardous substances act regulations (toy safety)

- Standard Consumer Safety Specification on Toy Safety – ASTM F 963 – 92, 96a
- CONEG Regulation

European Community (EC)

- Guidelines for the Classification, Packaging, and Labeling of Dangerous Substances with Several Amendments (1967), (67/548 EC, 91/325 EC, etc.)
- General Preparations Directive (88/379 EC, amendment 93/18 EC)
- Safety of Toys (87/C343/EC), EN 71 part 3: chemical properties)
- Directive for Materials and Articles Intended to Come into Contact with Foodstuff (89/109 EC)
- Directive for Plastic Material Intended to Come into Contact with Foodstuff (90/128 EC, amendments 92/39 EC, 95/3 EC, 96/11 EC)
- Safety Data Sheets (93/112 EC, in combination with 88/379 EC and 91/115 EC)
- Packaging Regulation 94/62 EC (the European version of the CONEG regulation)
- EC Resolution AP (89) 1 – Impurities in colorants

Germany

- Chemical Law (1980), several amendments
- Hazardous Substances Ordinance (1986)
- 178th Communication of the BGA
- “Lebensmittel- und Bedarfsgegenständegesetz” (Consumer good ordinance)
- DIN EN 71, part 3 – Safety of toys

Other Countries

Every other country has its own laws and regulations, which sometimes correspond to those of the European Community, sometimes to US FDA regulations, and sometimes they are very specific for the country.

At the first glance this number of different laws is confusing. In reality, however, it is not as overwhelming as it looks. To describe important details of all the different laws and regulations, a completely different kind of description is chosen instead. In this way it is easier to work out similarities but also differences of the numerous regulations. The “guideline” will be on one hand the consumer goods and their requirements, and on the other hand the requirements all components of a colored plastic article are required to fulfill.

10.1 Consumer Goods: Definition and Requirements

The general idea of all regulations is to protect the consumer against any harm during the intended use of a specific item. All the different regulations vary therefore more or less only in detail.

First, the question of what is a consumer good must be answered. In Germany [Consumer good ordinance § 5 (1), dated 10.4.1992] a consumer good is defined in the following way:

- All articles, that are intended to be used in the production, processing, trading and consumption of foodstuffs and thereby come into contact with foodstuffs or have an effect on these
- All container and packaging material for cosmetics and smoking materials
- Devices for dental and oral hygiene, except medical instruments
- Devices (and products) for personal hygiene
- Toys and joke articles
- All articles that come in contact with the body (skin) for a longer time, for example, wigs, glasses, bed linen, clothes, jewelry, artificial eyelashes, and so forth
- Cleansing agents, including impregnating agents, and others products for consumer goods

In principle, these statements are valid for all other countries.

The US FDA defines consumer goods very similarly, but they differentiate in addition between household goods (“Housewares Exemption,” CFR 39 § 13285, dated 12.04.1974) that come in contact with food only for a *short time* and packaging material for food that stays in contact with food for a *long time*.

The *universal* requirement is that consumer goods must be free of any toxicological substance, must be odorless and tasteless, and must be free of impurities except those that are technically unavoidable [e.g., German consumer good ordinance § 31 (1), similar statement by the US FDA]. This goal can be reached only if every component of the plastic article fulfills specific requirements, and this is the original reason for all the requirements and regulations. For the production of consumer goods only approved components are allowed to be used; only then can it be expected there will be no harmful effects.

The condition “free of any toxicological harmful substance” is obviously the reason for several regulations, for example, the CONEG regulation, the European version 94/62 EC, and the Amendment 2 of the German consumer good ordinance.

CONEG Regulation (Coalition of Northeastern Governors): This regulation bans de facto the use of the toxicological cadmium pigments and lead chromates, but without naming them. Any packaging material for consumer goods is not allowed to contain totally more than 100 ppm of cadmium, lead, mercury, and chromium VI in 1 kg (2.2 lb) of packaging material. This low limit was chosen because on one hand at such a low concentration the pigments in question cannot yet develop any tinting strength, and on the other hand the amount is in the range of a permissible content of these substances as technical unavoidable impurities.

The *European packaging regulation 94/62 EC* is absolutely identical with the CONEG regulation; in other words it is the European version of it.

The *Amendment 2 (and 3) of the German Consumer Good Ordinance*, dated 15.7.1994, bans the use of those azo colorants that can separate one of 20 listed carcinogenic amines under certain test conditions. These conditions, including the analytical method for the evaluation, are defined. The list of these amines contains, for example, dichlorobenzidine, which is a component of the formerly very often used disazodiarylide and disazopyrazolone pigments (refer also to the chapter on azo pigments). Originally only the use of these azo pigments in textiles was banned, the ban has been broadened for all consumer goods.

10.2 Safety of Toys

Generally speaking, toys are defined as consumer goods, and consequently all the requirements applying to consumer goods must be fulfilled. There are, however, further regulations regarding the safety of toys. The requirements for a consumer good are just one part of the safety of toys. The term “intended use” varies considerably between a consumer good and a toy. A toy has to withstand very rough treatment, and in case of breakage the broken parts cannot cause any harm to children. To achieve this goal, all the different potential dangers must be considered in the construction and properties of toys. This is the reason for the regulations “safety of toys,” which consist of several parts. In this context only the part dealing with chemical properties, migration of impurities, is relevant.

The European Toys Standard EN 71 (1988) consists of three parts. The first two parts deal with the construction and handling properties of a toy, while the third part (EN 71-3), relevant in this context, defines the limits of regulated, soluble, technically unavoidable impurities in colorants or other components. In Table 10.1 the limits for plasticine and modeling clays and fingerpaints are added, which play no role in this regard.

Table 10.1: Limits of Regulated Impurities in Toys

Element	Limit – EN 71-3	Plasticine/fingerpaints
Antimony	60	10
Arsenic	25	5
Barium	1000	350
Lead	90	25
Cadmium	75	15
Chromium	60	25
Mercury	60	5
Selenium	500	50
Amount in ppm, soluble in 0.07 N hydrochloric acid (HCl), based on 1 kg (2.2-lb) toy.		

This strength of the hydrochloric acid, 0.07 N HCl, corresponds more or less with the strength of the gastric acid, and is chosen to calculate possible risks when a toy is accidentally swallowed. The impurities must be *soluble*, a very important condition. In this way inorganic pigments, consisting of insoluble oxides containing antimony, barium, or chromium, are not banned. The pigments in question are approved and considered to be nontoxic (refer also to the chapter on inorganic pigments).

The safety of toys includes still another condition, the *fastness to saliva and sweat*. Contact with saliva and/or sweat is another, very common potential risk for children.

The different regulations therefore contain standard test methods to investigate this route of a possible contamination, for example, the German standard DIN 53 160 “Prüfung von bunten Kinderspielwaren auf Speichel- und Schweißsechtheit” (test method to check the fastness to saliva and sweat) [19]. The test liquids are simulated saliva and sweat. The test method contains a detailed description of the composition of these test liquids and all other test parameters. This test, too, must be done on the final toy.

In other countries the rules and regulations are basically the same, but differ in detail. It is recommended to check in every case the original text, and always the latest status, for the country in question.

10.3 Requirements for Components of Consumer Goods

Worldwide any component of each consumer good must be approved for its specific application. The differences are just the list of the approved substances, their limits of concentration, and methods/conditions for their approval. This starts with polymers and colorants and ends with any additive.

10.3.1 Polymers

Any polymer for such an application must comply with the specific regulations of each country. These regulations usually contain a list of allowed monomers, the catalysts for the polymerization, including their maximal concentration as impurities in a polymer, any production-based impurity, and any additive necessary for the production of a polymer. Additional test methods, any restriction regarding the concentration of a substance or impurity, and migration limits are described. The application for approval requires a long list of physical, chemical, and toxicological data. Approved additives are sometimes only listed, because their approval is done by separate regulations. The basic requirements are more or less the same in each country, varying mainly only in details.

The relevant requirements for polymers are published in the following regulations:

USA: Published by FDA in the Code of Federal Register (CFR). Several paragraphs deal with the specific requirements for polymers.

European Community: 90/128 EC with the amendments 92/39 EC, 95/3 EC, and 96/11.

Germany: There are two independent regulations, the consumer good ordinance and the 178th recommendations of BGA; the latter is updated periodically.

Consumer good ordinance (dated 10.4.1992), including several amendments. This ordinance is partly a carryover of several EC regulations into a German regulation, and contains a general list of monomers and other substances allowed in polymers, including the ban of some substances.

The 178th *Recommendation of the German Health Authority* (formerly BGA, now BgVV) contains (besides other chapters) for each type of polymer a separate chapter, in which the requirements for this specific polymer are described in detail, including a list of approved substances.

10.3.2 Colorants

In comparison to the regulations for polymers and additives, the regulations for colorants differ considerably in some aspects. Common for all regulations is the “non-migration principle,” in which any migration of a colorant is not permitted. The differences are a consequence of a different way of looking at things. In the United States only those colorants may be used for the coloring of consumer goods that are approved and listed by their chemical constitution; it is a positive list. In contrast, the European Community allows generally all colorants that fulfill specific requirements regarding purity, and that are toxicological harmless. It is consequently not a positive list. The basic idea is, the authorities do not want to hinder the development of new colorants and their (fast) application. At the same time the responsibility for the safety of a new colorant clearly rests with the manufacturer.

The situation in France is confusing. A positive list exists (still) in France (the only positive list in Europe); on the other hand France agreed to the European Resolution AP (89) 1, which allows generally all colorants that fulfill specific requirements regarding purity, and that are toxicological harmless.

The relevant requirements for colorants are published in the following regulations:

USA: Published by FDA in the Code of Federal Register (CFR), *CFR 21 § 178.3297 – Colorants for Polymers*, which contains the positive list of approved colorants [part (e) – list of substances]. The colorants are listed with their chemical terms, color index number, and CAS number, except in the case of commodities such as chalk or iron oxide. In addition the list contains limitations in spite of the general definition given in § 178.3297. Paragraph 178.3297 defines the colorants and use in the following way: “*The substances, listed in paragraph (e) of this section may be safely used as colorants in the manufacture of articles or components of articles intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding food, subject to the provisions and definitions set forth in this section: ...*” Paragraph 178.3297 (c) says: “*Colorants in this section must conform to the description and specifications indicated...*”

Strictly speaking, the approval is valid only for the quality of the registered colorant and within the published limitations. This does not mean that all chemically identical colorants, manufactured by a company different from the company that asked for the approval, are automatically also approved. This is given only if the quality corresponds closely to the quality of the listed colorant.

Table 10.2 contains a list of approved colorants, but it must be emphasized that the list can be only incomplete, because several colorants are registered for approval. New approvals of colorants are published in the regular revision of CFR.

Table 10.2: *List of Colorants Approved by § 178.3.297 (Status 2001)*

Color index number	Color index formula	CAS number	Limitations
P. blue 15:1, 15:2, 15:3, 15:4	74160	147.14.8	
P. blue 28	77346	68186.86.7	Yes (see original text)
P. blue 29	77007	57455.37.5	Yes
P. black 7	77266	1333.86.4	Yes
P. black 28	77428	68186.91.4	Yes
P. green 7	74260	1328.53.6	
P. green 17	77288	68909.79.5	Yes
P. orange 64	12760	72102.84.2	
P. red 101 (approved as iron oxide)	77491	1309.37.1	
P. red 177	65300	4051.63.2	
P. red 187	12486	59487.23.9	Yes
P. red 220	20055	57971.99.0	
P. red 254	56110	122390.98.1	Yes
P. violet 15	77007	12769.95.9	Yes
P. violet 19	73900	1047.16.1	
P. white 4	—	1314.13.2	Yes
P. white 6	77891	13463.67.7	
P. white 7	77975	1314.98.3	Yes

Table 10.2: Continuation

Color index number	Color index formula	CAS number	Limitations
P. white 18 (approved as calcium carbonate)	77 220	1317.65.3	
P. white 20 (approved as aluminum and potassium silicate)	—	—	
P. white 21 (approved as barium sulfate)	77 120	7727.43.7	
P. white 26 (approved as magnesium silicate)	—	14807.96.6	
P. yellow 95	20034	5280.80.8	
P. yellow 110	56280	5590.18.1	
P. yellow 138	56300	56731.19.2	Yes
P. yellow 147	60645	76168.75.7	Yes
P. yellow 151	13980	61036.28.0	Yes
P. yellow 180	21290	77804.81.0	
P. yellow 181	1177	74441.05.7	
P. yellow 191	—	129423.54.7	Yes
P. Metal 1 (approves as aluminum)	—	7429.90.5	

The original list also contains some optical brighteners, but the list does not contain dyes. This is probably the consequence of a very strict application of the “non-migration principle,” because tiny traces of dyes may be detectable under the required test conditions.

There is another possibility for the approval of colorants, *CFR 21§ 170.39 – Threshold of Regulation for Substances Used in Food-Contact Articles*. This paragraph states: “Exemptions to regulation as a food additive are granted under this regulation, if the use of the substance in a food-contact article results in a dietary concentration at or below 0.5 ppb, or if the use of a regulated direct food additive is at or below 1% of the acceptable dietary intake.” In other words, the migration limit is 0.5 ppb. It is obvious that under these conditions only very pure inorganic pigments have a chance of approval.

The following inorganic pigments are approved at levels up to 2% in all types of food contact polymers according to this paragraph:

- Pigment brown 24
- Pigment green 50
- Pigment yellow 53

In this context another paragraph is important, *CFR 21 § 176.170*. This paragraph describes the method for an evaluation of any migration for consumer goods in food contact.

In view of the large number of available colorants only a few colorants can be used for the coloring of consumer goods, if “FDA conformity” is requested. This limits the number of possible shades.

European Community: Within the EC any colorant can be used if it fulfills the specific requirements regarding purity, if it does not migrate under the condition of the intended use, and if it is toxicologically safe. The colorants must fulfill the conditions described in: *Resolution AP (89) 1 – On the use of colorants in plastic materials coming in contact with food*. This resolution is accepted from the majority of the European countries in the meantime. The resolution contains the following sections:

- Field of application
- General principles
 - Migration
 - Specification
 - Soluble metals as impurities
 - Aromatic amines as impurities
 - Carbon black – extractable fraction in toluene
 - Polychlorinated biphenyls as impurities
 - Toxicological tests
- Description of the analytical method, including definition of the test liquids

The importance of each section varies depending on the type of colorant, for example, soluble metals as impurities are relevant in the case of inorganic pigments but not a problem in the case of organic pigments (except barium lakes) and dyes, while aromatic amines and polychlorinated biphenyls cannot be present in a calcinated inorganic pigment. A special case is carbon black with the extractable fraction, a consequence of the specific production method.

Table 10.3 contains the limits of regulated metals and aromatic amines. For the purpose of a better comparison with still existing national regulations, the valid limits of other countries are included in the table. The comparison clearly shows the similarity of all national regulations, which differ only in a few details.

Table 10.3: *Limits of Impurities by (Regulated) Metals and Aromatic Amines (Status 2/1999)*

Metal	Resolution AP (89) 1	Germany	Belgium	England	Netherlands	Spain
Lead	100	100	100	100	100	100
Arsenic	100	100	50	100	100	50
Mercury	50	50	50	50	50	50
Cadmium	100	100	2000	100	1000	2000
Zinc	—	—	—	2000	—	2000
Selenium	100	100	100	100	100	100
Barium	100	100	100	100	100	100
Antimony	500	500	2000	500	2000	2000
Chromium	1000	1000	1000	1000	1000	1000
Aromatic amines – all countries 500 mg/kg (0,1 n HCl)						

Amount in ppm, soluble in 0.1N hydrochloric acid (HCl), based on 1 kg (2.2 lb) of colorant

The impurities must be *soluble*, a very important condition. In this way inorganic pigments consisting of insoluble oxides containing antimony, barium, or chromium are not banned. These pigments in question are approved and considered to be toxicologically safe (refer also to the chapter on inorganic pigments).

The list of regulated metals is the same for toys (Table 10.1) and consumer goods, but the limits differ. A first glance may create the impression that the require-

ments for toys are stricter, but this is not the case. The explanation lies in the different points of reference. The limits of impurities in toys are based on 1 kg (2.2-lb) toy, while the limits of impurities for consumer goods are based on 1 kg of colorant. The usual concentration of a colorant in plastics, including toys, is in the range of a few percent, and because of this dilution effect it is no problem to fulfill the requirements of toys with these qualities.

The section on *test methods* describes the procedure for checking the migration. The test liquids to be used are defined and should simulate different types of food. Which test liquid should be used depends on the type of food.

There are the following test liquids:

- Distilled water
- Acetic acid, 2% by weight
- Ethanol, 10% by volume
- Coconut fat or oil or peanut oil

Germany: The German regulations are published in the 178th Recommendations of the health authorities. Chapter A IX describes the requirements of colorants for polymers and chapter B II/IX the test methods. The German regulation corresponds de facto to Resolution AP (89) 1.

10.3.3 Additives

Similar to polymers and colorants every additive must be approved for use in consumer goods. The conditions for approval are very similar to those for polymers and colorants. The approved additives can be found in different regulations depending on the characteristic of the additive, for example, optical brighteners and some fillers are considered as colorants, while antistatic agents, dispersing agents, lubricants, and so forth are usually listed in regulations regarding polymers.

A special case are the *flame retardants*. The risk of a fire is ubiquitous, and this is the reason for many specific regulations [53]. These regulations cover the potential risks in the different fields of application, for example:

- Electrical appliances / electronics – in Germany the VDE (Association of the German electrical engineers) – regulations, for example, VDE 0304, VDE 0471, VDE 0472, and so forth
- Building industry – in Germany the DIN standards, for example, DIN 4102 part 1–7, DIN 66081, DIN 66082, and so forth
- Automobile industry – for example, in the United States regulation MVSS 302 (Federal Motor Vehicle Safety Standards) and in Germany the standard DIN 75200.

- Aircraft industry – for example, in the United States regulation FAR 25853 (Federal Aviation Regulations) and in Germany regulation LTV 1500-850 (Luft-Tauglichkeits-Vorschrift)
- Plastics – the standard is UL 94

All these regulations differ in detail, but all regulations pursue the same goal: the prevention of a fire. The basic principle of all regulations is the test of fire behavior of any piece of equipment. The different test methods describe in detail the way to set light to the piece of equipment, and it is classified on the basis of its fire behavior.

11 References

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The successful coloring of plastic parts, beginning with the formulation of the color preparation and ending with the manufacture of the final product, is the result of the interaction of chemical, physical, and technological factors. In-depth knowledge of these factors and their interrelation and the consideration of national and international regulations are prerequisite for anyone working in this field.

This book describes the various aspects of coloring plastics. The reader is enabled to identify the color preparation that meets given product requirements. Only if color preparation, polymer material, and final product design and requirements are well coordinated will the customer be pleased with the colored plastic product.

Contents

- Methods for Coloring of Plastics
- Requirements for Color Preparations
- Composition of Color Preparations
- Colorants and Additives
- Processing Errors and Troubleshooting
- Quality Assurance
- National / International Regulations

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4 Composition of Color Preparations

A color preparation is composed of plastics as carriers, colorants, and additives. Additives can be incorporated into plastics in two different ways. One possibility is to incorporate the additive in the color preparation, which is preferred when the required concentration of the additive is relatively low in the final part. If a high concentration is necessary the additive must be added directly at the plastics manufacturer's plant; examples are fillers and flame retardants. The concentration of filler can reach 60%.

4.1 Color as a Design Element

4.1.1 *The Basis of Color Sensation*

Any book about colors would be incomplete without a description of at least the essential features of the process of seeing, especially seeing colors.

Daylight, both natural and artificial, belongs to the wide range of electromagnetic waves such as radio waves, infrared, ultraviolet, and X-rays. Physically they are all the same, differing solely in their wavelength and frequency. From this wide spectrum of wavelengths only the very small fraction between 400 and 780 nm is visible.

Visible, white sunlight (Fig. 4.1) consists of a mixture of the colors red up to violet. When sunlight falls on an object, some of it is absorbed and some is reflected. The absorbed part is transformed to heat and practically speaking is "lost" for the sensation of color. After passing through the pupil and lens, the reflected part of the light impinges on the retina, where an image of the object is formed. The retina contains two different types of cells, the so-called rods and cones. The rods are not sensitive to colors; they only allow a differentiation between light and dark, important for seeing at twilight or dawn. The cones, however, are sensitive to colors. There are three different types of cones, which differ in their maximum spectral sensibility for the colors green, blue, and red-orange. In this context it should be mentioned that all methods of colorimetric measurement are based on these three colors plus a light-dark differentiation.

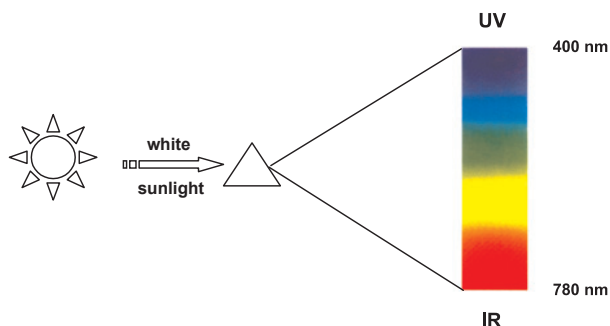


Figure 4.1: *Colors of the solar spectrum*

The reflected part of sunlight is just a fraction of the whole spectrum, and corresponding to the wavelength of the reflected light we see a definite color.

An ideal white object reflects 100% of the light, in practice however we notice a “white with a light tint,” very often a bluish or yellowish tint.

An ideal black object absorbs 100% of the light, consequently no light is reflected and therefore the object appears black.

Analogous with our other senses such as hearing or tasting, color vision differs from person to person, sometimes very distinctly. The most serious deficiency of color vision is color-blindness. Statistically more men than women suffer from some type of a defect in color vision, with a reduced ability to distinguish between red and green being among the most common of these. The capability to perceive colors is very closely related to individual differences in the sensitivity of the eyes. This important fact is sometimes the reason for long discussions between supplier and customer if the presented plastic specimen of a matched color is inspected only visually. Another matter for discussion is the question of accuracy of a produced color preparation. This discussion can take place not only with the customer but also in the supplier’s own plant within the scope of quality assurance. Because of this “personal factor” it is recommended that the same person is always involved in the visual check of color.

The necessity of an objective method was very obvious. The development led to different colorimetric systems. The system used most often is the CIE-LAB system; others are the Munsell, respectively ISCC-NBS systems. All of them have the disadvantage that they are not able to describe in a *perfect* manner what we see, therefore all these systems cannot replace completely visual judgment, but they are very valuable tools nonetheless.

A very extensive literature is available dealing with all aspects of colorimetry; the measurement of colors, therefore it is done without a detailed description in this context [1, 2].

4.1.2 Metamerism

Nearly every customer specifies in his requirements that the color to be matched should show no signs of metamerism. This phenomenon can be noticed nearly daily, but we are unaware of its physical background. It is not by chance that we go to a window in a department store with artificial lighting when we are about to buy clothing or accessories to check if the colors of the different pieces match. Slight differences in their shades are not infrequent.

We speak of metamerism when two colored objects show the same color in sunlight but a slight difference in shade in artificial light (or vice versa) (Fig. 4.2).

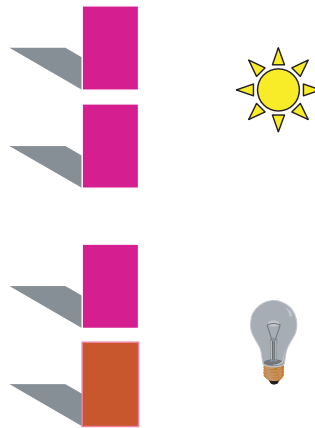


Figure 4.2: Schematic demonstration of metamerism

The origin of metamerism lies in the physical process of generating colors. The color of an object is the sum of several, simultaneously used colorants. The interrelation of reflection and absorption is specific for each single colorant and depends on the wavelengths of the source of light. On the other hand every source of light exhibits its own specific spectrum of wavelengths. Detailed measurements of sunlight and artificial sources of light proved quite significant differences not only in the spectra of wavelengths but also in their intensities. These differences are responsible for the phenomenon of metamerism.

Metamerism is a serious problem, and avoiding metamerism is usually a very important goal in color matching. In practice the colorist can only minimize metamerism but cannot avoid it totally. Colorists of different companies quite often will use at least partly other colorants to match the same color. Only an absolutely identical selection of colorants for both samples of the matched color would prevent any metamerism.

Nearly all spectrophotometers allow measurements with different standardized sources of light. By means of this tool the spectral-reflectance curves of the specimen in question can be recorded for every source of light. Usually both curves are not identical but will show distinct variations. The variation, a criterion of metamerism, can be minimized by exchanging one or more colorants.

4.1.3 Use of Colors

Although seeing colored objects is a pleasant sensation, colors are used for more than this, as they must fulfill specific tasks. One function that immediately comes to mind, is the application of color to all objects in our lives, while other functions of color are not so obvious. The most important tasks are to use color as an:

- Element of design
- Element of marking
- Element of protection

The majority of colors are used undoubtedly as *elements of design*. An object can be modeled in a perfect way, and can be very functional, but if it has the “wrong” color we are not pleased with it. On the other hand an object not so perfectly modeled will please us when it has the “right” color.

Another, but less obvious, use of colors is as an *element of marking*. Several industries, such as electrical engineering and car manufacturing, to name just two, apply colored articles to prevent mistakes. Every single electrical cable is isolated and specifically color-linked to its function, with the colors to be used standardized more or less worldwide. The purpose of this marking is to avoid dangerous short circuits. In the car industry the colored cables should indicate the different electrical circuits typically used in a car.

The third application of colors, no less important than the others, is as an *element of protection*. We notice these types of colored objects nearly daily, as they warn us of dangerous situations, for example, driving through construction sites on a highway or marking of emergency exits.

In nature, too, colors are important in many respects. Two examples alone demonstrate this. The bright colors of flowers attract bees and insects to ensure

pollination and ultimately reproduction. Animals typically adapt to the colors of the environment through camouflage as protection from their natural enemies. Some species of frogs living in the Brazilian tropical rain forest have an unusual and striking bright coloring that signals to their natural enemies, “careful, we are poisonous.”

4.2 Types of Color Preparations

There are three states of aggregation – gaseous, liquid, and solid. Gaseous colorants are not known; consequently either a liquid or a solid color preparation can be chosen for the coloring of plastics. There are two possibilities for a solid color preparation, either a powdery or a granulated form, the latter known as a masterbatch.

Each type of preparation shows typical properties according to the state of aggregation, and this should be considered carefully during the process of coloring. Lack of careful observation may result in production of defective plastic articles. This is explained in detail in Chapter 7, *Processing Errors*.

To color *thermoplastic resins* fundamentally all three types of preparation can be used, although many customers prefer a masterbatch, the granulated form. The other two forms, liquid and powdery color preparations, are used occasionally by customers specializing in these types.

For *thermosets* only the liquid or powder form is applicable. A thermoset consists usually of two liquid components, a reactive and a hardening component. After blending and curing a cross-linked product is formed, which cannot be manipulated later by thermoplastic methods. This is the reason why one of the two components has to be colored before the cure. In practice the hardener is usually colored, because it is fairly inert. Liquid preparations are preferred because of easier blending and handling; in addition, the binder of a liquid color preparation may function as a hardener, for example, in epoxy resins.

The cure of liquid lacquers depends on whether system is a multi-component or a single-component type. A single-component lacquer hardens by absorption of humidity. Two types are marketed: either the whole system is already colored or a liquid color preparation is added prior to application. Which system is used finally depends on several conditions, one of the most important being the chemical structure of the lacquer components. In both cases the color preparation must be completely free of water to avoid a premature cure (single-component systems) or a cure that is too fast (during blending of the lacquer with the color preparation).

The speed of cure of thermosets or lacquers can be changed considerably by colorants, because colorants are not necessarily chemically inert. They can accelerate or slow down the cure; therefore the right choice of colorant is very important. Another possibility is to alter slightly the composition of the thermoset or lacquer, but this method is not always successful. In the worst case the desired color shade must be altered.

For the coloring of *elastomers* quite analogous statements are valid, here, too, the color must be added before the cure, consequently only a liquid or powdery formulation can be applied.

4.2.1 Granulated Color Preparations/Masterbatch

A masterbatch is today the most preferred type of preparation, well documented by the large volume of sales.

A masterbatch consists of:

- Polymer as carrier
- Colorants
- Dispersing agent
- If necessary, additives such as stabilizers, nucleating agents, antistatic agents, lubricants, and so forth

The concentration of the components varies corresponding with the desired intensity of color and/or hiding power. Very intensive colors with a good hiding power require a high concentration, which very often lies in the range of 50% colorant, 40–45% polymer, and 5–10% dispersing agent. When the presence of an additive is required in a color preparation, there is no other way than to reduce the concentration of the colorants. The consequence of this is a higher addition of the preparation during the coloring of the polymer. On the other hand a wide range of additive preparations are commercially available. In such a case whether to incorporate the additive in the color preparation or apply two separate preparations is a question of economics.

For pastel shades and/or transparent colors a few percent of colorant in the preparation are enough, especially when a colorant with a high tinting strength can be used to match the desired color. The result is a very diluted masterbatch. In this case it is not the concentration of the masterbatch that defines the quantity of addition for the later coloring of a polymer but technical considerations. Very small amounts of a masterbatch are difficult to blend homogeneously in a polymer melt, therefore the coloring of a polymer melt demands a minimum of addition. The size of the pellets of a masterbatch is usually 2–3 mm (0.075–0.11 in.) in length

and 1.5–2.5 mm (0.05–0.09 in.) in diameter and the addition of such a masterbatch should be not smaller than approx. 1%. Much finer pellets or granules, of course, would allow an addition below 1%, but such types of masterbatches are not yet common for technical and economical reasons.

Considering these two extremes it is understandable that there is no general rule for the concentration of colorants in a masterbatch.

The manufacture of a masterbatch is a multistep process (Fig. 4.3).



Figure 4.3: Scheme of production of a masterbatch

- Step 1: All powdery components of the recipe are weighed out accurately and premixed.
- Step 2a: Homogenization of the powdery components in a mixer. Different constructed types of mixer can be used.
- Step 2b: The homogeneous blend is added to the weighed polymer and blended carefully. The same type of mixer as in step 2a can be used.
- Step 3: Extrusion of the mix. This step requires the use of a twin-screw extruder, because a high shear is necessary for a complete dispersion of the colorants in the polymer melt. There are two types of twin-screw extruder, the corotating and the counterrotating extruder. Both types of extruder have advantages and disadvantages; the choice of the most suited extruder corresponds to the properties of the colorants. Very hard organic pigments demand a high shear for a complete dispersion in the polymer melt; a corotating extruder is therefore preferred because of its higher shear. In contrast, pigments very sensitive to shear, such as pearlescent pigments, should be extruded on a corotating extruder because of its lower shear.
- Step 4: Granulation. There are principally two different methods. One method is to draw cords of colored melt, formed at the die face of the extruder head, cooling down in a water bath, and cutting. The results are cylindrical pellets. The other method is to cut the melt directly the moment it leaves the borings in the extruder head by rotating knives and cooling in a water bath (die face pelletizer). The results are lens-shaped pellets.

The most preferred method of granulation is to form a cord of colored melt, to cool it in a water bath, and to cut it into cylindrical pellets. The main advantage of this procedure is the flexibility in production, because the manufacture of customer matched color batches is not a continuous process but batchwise. The batchwise production is a consequence not only of the great variation of desired colors but also of the variety of polymers to be used as carriers. The size of such a batch can vary between 25 kg (55 lb) and several tons. Exceptions, however, are standard batches in white and black and a few other standard colors. In this case the second method of granulation is usually applied.

The diameter of the cylindrical pellets amounts usually to 1.5–2 mm (0.05–0.075 in.) and the length to 2–3 mm (0.075–0.11 in.). The effective size of these pellets depends on the one hand on the size of the borings in the extruder head and on the other hand on the degree of expansion of the colored polymer melt. In the compression section in front of the extruder head the polymer melt will be compressed and the degree of this compression varies accordingly to the type of polymer and the concentration of colorants and additives in the melt. The moment the melt leaves the borings in the extruder head the melt is relieved of the pressure and takes on its original volume. In case of much smaller diameters of the borings in the extruder head the cord can no longer be drawn satisfactorily whereas significant larger diameters lead to problem during cutting. Polymers are known as poor heat conductors and therefore the inside of the cord will not be cool, that is, solid enough, after passing through the water bath for a sufficient cutting. The heat transfer is too slow in such a case.

Lens-shaped pellets are quite common for several types of natural colored polymers and typical for batches in the standard colors white and black. In these color preparations the concentration of the colorant is as high as 60–75% while the amount of polymer drops to 15–25% in comparison to a customer-matched color preparation. Such a highly concentrated batch cannot be granulated by the usual method but only with the aid of a die face pelletizer. The operating principle of such a pelletizer is the following: the melt is pressed through the borings in the extruder head into fast running water, where rotating knives cut the discharged melt directly into small pieces. The speed of the running water must be high enough to guarantee a complete separation of each single, still soft pellet. In the fast running water the original cylindrical pellets try to reach the spherical form, which is in physical terms the most stable form. On the other hand the water directly cools down the surface of the pellets. Both reactions counteract each other and the results are lens-shaped pellets.

This process has been modified in such a way that now very fine, nearly spherical granules, so-called “micropellets,” can be produced. The main disadvantage of such fine granules is the high cost of production. The most important advantage is

an extremely larger number of particles per weight unit in comparison to the normal cylindrical pellet. Such a very fine granule can be metered well below 1% if it is done directly on the plasticizing screw. Even then the dispersion of the micropellets in the polymer melt is homogeneous and streaks of color are unlikely to occur. In the case of pastel shades and/or transparent colors the concentration of the colorants in the preparation need to be very low to avoid streaks of colors during the coloring process. Here is another advantage of the micropellets because preparations for pastel shades and/or transparent colors can be more highly concentrated compared to a normal masterbatch. In this context it would be interesting to compare the costs of coloring between a normal masterbatch and micropellets. A masterbatch is cheaper in production but it requires a larger addition; on the other hand micropellets are more expensive in production but the required quantity for the coloring of polymers is significantly lower.

Technically considered there are further methods to manufacture pellets or granules. One of these is, for example, the modification of the spray drying process. The spray drying process is used to produce very fine granules starting from an aqueous slurry. The fine droplets, produced by a spraying nozzle or by a fast rotating disk, are dried in a stream of hot air. The results are very fine spherical, often hollow granules. Instead of an aqueous solution a melt, consisting of colorants and binder, can be sprayed into a stream of cold air. Here, too, the results are very fine spherical but full granules. The spraying nozzle requires a light-flowing melt; therefore the normal polymers cannot be used as binder. Possible binders are oligomers (waxes) or resins. Color preparations, based on this process, are commercially available and sometimes used for the coloring of polymers.

A masterbatch is the most expensive color preparation of all types because of the high expenditure of work (many steps) and energy (extrusion). Another disadvantage to some extent is the known incompatibility of polymers when blended with each other. It is therefore recommended that one use the same type of polymer as carrier for the color preparation that will be colored later, and vice versa.

Sometimes so-called “universal batches” are offered on the market. The word “universal” is derived from the Latin and means all-embracing; in other words the carrier of such a universal batch should be *compatible with any other polymer*. Our own practical experience denies this, which is not surprising when we consider the variety of chemical different types of polymer. Another restriction is the fact that not all colorants can be applied in every type of polymer for many reasons such as heat stability, light fastness, or weather resistance, or in the case of dyes the migration in partially crystallized polymers. This becomes very evident if, for example, the coloring of polyethylene (PE) and polyamide (PA) is compared. In PE much more colorants are applicable than in PA, in which the range of colorants is very limited. Consequently no universal batches are possible

in the true sense of the word. On the other hand it is known that in practice sometimes PA is colored with (special) color preparations based on PE as carrier, but only if there are no special requirements regarding the quality of the plastic article. For such types of batches the correct term would be “partial universal batches.”

Besides some disadvantages the advantages of a masterbatch predominate especially with respect to handling (Table 4.1). The most important advantages are: a very good metering, dust-free handling, and a very low expenditure of work changing colors in production.

In addition the pigments are dispersed completely in the polymer during the extrusion, and the result is an optimal utilization of the tinting strength of the colorants, probably one of the reasons why a masterbatch is the most preferred type of color preparation.

Table 4.1: *Disadvantages and Advantages of a Granulated Color Preparation*

Disadvantages	Advantages
Not universally applicable (incompatibility of polymers) High expenditure of work during production Most expensive type of color preparation	Dust-free handling Smallest expenditure of work when changing colors during production Very good metering No problems when high amounts have to be used for coloring Optimal utilization of the tinting strength of the colorants

4.2.2 Liquid Color Preparations

The composition of a liquid color preparation is quite similar to that of a masterbatch; the main difference is that instead of a polymer a liquid binder is used as carrier. Besides the two main components – binder and colorants – a liquid preparation may contain additives such as antissettling agents, stabilizer, nucleating agent, antistatic agent, filler, and so forth. Typical binders are fatty acid ester, ethoxylated fatty acid ester), paraffin oil, plasticizer, polyvalent alcohol, polyvalent amine, ethoxylated alcohol, or other components related to the system to be colored. The binders are used either alone or in combination.

The choice of binder depends on the type of polymer to be colored or in case of thermosets and elastomers on the chemistry of their liquid components. As binder for the coloring of thermoplastic resins fatty acid ester, ethoxylated fatty acids, or paraffin oil are usually used; for plasticized poly(vinyl chloride) (PVC), of course a plasticizer. In thermosets binders that contain still reactive groups at the end of the molecule are preferred because as a secondary effect the binder functions as a hardener during the cure of the thermosets. To color epoxy resins, for example, polyvalent alcohol, polyvalent amine is the most preferred binder.

The manufacture of a liquid color preparation is relatively easy (Fig. 4.4). The metered components of the recipe are mixed in the binder, loosely dispersed, and finally the whole system is milled. Strictly considered it is not a milling in the true sense of the process but only a complete dispersing of the colorants in the binder. The result of the grinding process should be a complete desagglomeration but no breakdown of the primary particle size of the colorants, which would lead to a color change. The tinting strength and other properties of colorants depend on the primary particle size; therefore the marketed colorants are milled already to a standardized particle size distribution by the manufacturer of colorants. The particle size of the dispersed colorants should be below 10 μm in a liquid color preparation.

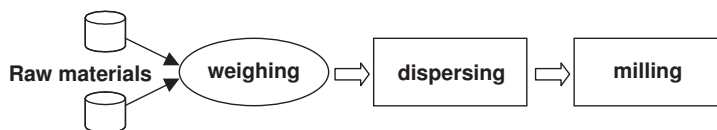


Figure 4.4: Scheme of production of a liquid color preparation

For the grinding process any machine can be used that is constructed to handle liquids and develops enough shear for the desagglomeration, for example, ball mills.

Analogous to the other types of color preparations, liquid color preparations, too, show disadvantages and advantages in coloring of thermoplastic resins (Table 4.2). One disadvantage is the high expenditure of cleaning at a color change during production, except if the liquid preparation is metered directly on the plasticizing screw. The main disadvantage is that a coloring concentration above 1.5–2.5% may cause an “oversmearing” effect. The polymer pellets, covered with the liquid color preparation, are no longer drawn in correctly from the metering zone of the plasticizing screw, resulting in defective plastic parts. This problem may come up

especially in the case of very bright colors with a good hiding power in thin-walled plastic parts. At the worst case a coloring with a liquid color preparation is impossible.

The specific surface area is a characteristic physical property of any solid particle. Typical values for organic pigments range between 10 and 140 m²/g, while in high absorptive grades of inorganic pigments the specific surface area can reach values up to 1200 m²/g and even higher, for example, special grades of carbon black, which is by definition in many countries an inorganic pigment, and silica as filler. The chemical structure of the substance and its particle size distribution, besides other factors, influence the specific surface area. Hence the amount of binder, necessary to wet the colorants and all other solid additives of a liquid color preparation, depends on the specific surface area of each component, and therefore at a given concentration the viscosity of the preparation varies. Considering the variety of colorants and their essential concentration to match the required colors, the resulting viscosity of any color preparation may vary considerably. For practical reasons the viscosity must be adjusted within a certain range. At a too low viscosity a relatively fast sedimentation of the colorants, especially of inorganic pigments, occurs. One method of prevention is to choose a higher concentration of the colorants and/or the incorporation of a high absorptive filler; in both cases the viscosity increases. On the other hand a too viscous liquid formulation causes metering problems during the coloring process.

Even at a constant composition of the preparation the viscosity can fluctuate within a limited range because the specific surface area of colorants is not constant but varies from batch to batch, what is quite normal for any technical product.

Table 4.2: *Advantages and Disadvantages of Liquid Color Preparations*

Disadvantages	Advantages
High expenditure of cleaning at color change in production No high coloring concentrations possible because of risk of oversmearing effects Variable viscosities because of different behavior of colorants and temperature Risk of sedimentation of (heavy) pigments	Dust-free handling Excellent distribution; each polymer pellet is wetted by color Good utilization of the tinting strength of the colorants Good metering Nearly partial-universal in thermoplastic resins Favorable costs of production

One advantage of a liquid color preparation is the very good wetting of each polymer pellet prior to extrusion, which is especially important for pastel color shades or transparent color shades. By the way this is the most important advantage of a liquid color preparation in comparison to a masterbatch.

Further advantages are the utilization of the full tinting strength because of the complete dispersed colorants, a good metering behavior, dust-free handling, and favorable costs of production.

Thermosets and elastomers are colored by blending of one of their liquid components with the liquid color preparation.

4.2.3 Powdery Color Preparations

The simplest form of a powdery color preparation is the pure colorant. But as processing aids a powdery color preparation contains usually at least diluting and dispersing agents, which improve the wetting of the colorants by the polymer melt. If required any other additive can be added provided that the substance is solid or at least absorbed on a carrier in the case of liquid substances.

For the homogenization of a blend consisting of colorants and additives a variety of mills are available. The best type of mill should be determined by pilot experiments. Great care should be taken to avoid a breakdown of the primary particle size of the colorants, on the other hand the mill should provide enough shear to destroy the agglomerates of the colorants (Fig. 4.5). In this context attention must be paid to the fact that pure, very fine powdery organic substances are sensitive to dust explosions.



Figure 4.5: Scheme of production of powdery color preparations

In a powdery color preparation the colorants are not yet dispersed but must first be dispersed in the polymer melt during the processing of the polymer. Injection molding machines are single-screw extruder types that in comparison to the twin-screw extruder used for the production of masterbatches usually do not develop enough shear for a complete dispersing of the colorants, especially in case of the so-called “hard” pigments, which are difficult to disperse. Prime examples of

such colorants are chromium oxide green and the blue and green phthalocyanine pigments. The results of an incomplete dispersing of pigments in a polymer melt are color specks and/or differences in the color related to an imperfect utilization of the tinting strength. By addition of more or another dispersing agent the number and size of color specks can be reduced but often not completely avoided. Another method is the use of a mixing head, available in different constructions.

A direct metering of powders on the plasticizing screw is very problematic because of their bad flowing properties, powders tend to stick very easily and any inconstant flow of a powder produces defective plastic parts.

The usual way to handle a powdery color preparation is to blend the color and the polymer in a drum. First the surface of the polymer granules is slightly wetted with a coupling agent, for example, a dispersing agent or paraffin oil, then the color preparation is added and the whole mixture blended for a couple of minutes. The result should be a nearly dry surface of the polymer, and technical problems during extrusion are then unlikely to occur. This procedure limits of course the quantity of powdery color preparation that can be applied. This is certainly a disadvantage in the case of very intensive, bright colors with a good (required) hiding power in thin-walled plastic parts.

Important advantages are the highest possible concentration of colorants in any color preparation, and the low costs of production (Table 4.3).

Table 4.3: *Advantages and Disadvantages of Powdery Color Preparations*

Disadvantages	Advantages
Dusty High expenditure of cleaning at color change in production Direct metering problematic Risk of inconsistent colors during coloring process Limitation of the quantity applicable during the coloring process No complete dispersing of colorants, therefore no full utilization of the tinting strength Use of coupling agents necessary	Highest possible concentration of colorants in any color preparation (Nearly) universal application Very economic because of low costs of production

4.2.4 Valuation of Color Preparations

The market is ruled undoubtedly by masterbatch. The reasons for its dominant role are the various advantages in handling during the process of coloring thermoplastic resins. These advantages counterbalance the higher costs of a masterbatch in comparison to the other types of color preparations.

By volume the liquid and powdery color preparations follow far behind for coloring of thermoplastic resins. The marketed volumes of these two types are in the range of 10% in comparison to masterbatch.

An exception, however, is PVC. The large PVC processors produce their own compounds, including coloring. When they use color preparations they usually prefer liquid color preparations based on a plasticizer.

As mentioned before a masterbatch cannot be used for coloring of thermosets and elastomers; in this case only liquid or powdery color preparations are applicable. By volume the quantities of these two types of polymers are of minor importance in comparison to the thermoplastic resins; consequently the need of liquid or powdery color preparations is very limited. A preference for one of these two possible types of color preparations is not apparent.

4.3 Types of Polymers and Their Processing

4.3.1 Types of Polymers

Plastics belong to the large group of macromolecules usually called polymers. Polymers are subdivided according to their chemistry into inorganic and organic polymers. A further subdivision marks their occurrence as natural or modified natural substance or as synthesized products (Fig. 4.6).

In early historic times the first articles for household and daily life were made of inorganic and organic natural substances. In the further course of development these substances were at least partly modified, and at the same time they became valuable raw materials for many other goods. Much later, in comparison to the long history of natural substances, the first synthetic polymers were invented relatively recently. A large variety of polymers became available, and there is no end of development in sight. The properties of different polymers are improved continuously to fulfill all requirements of their sometimes very specific applications. These improvements are achieved by using new catalysts, new combinations of monomers and polymers (blends), and/or altered production methods.

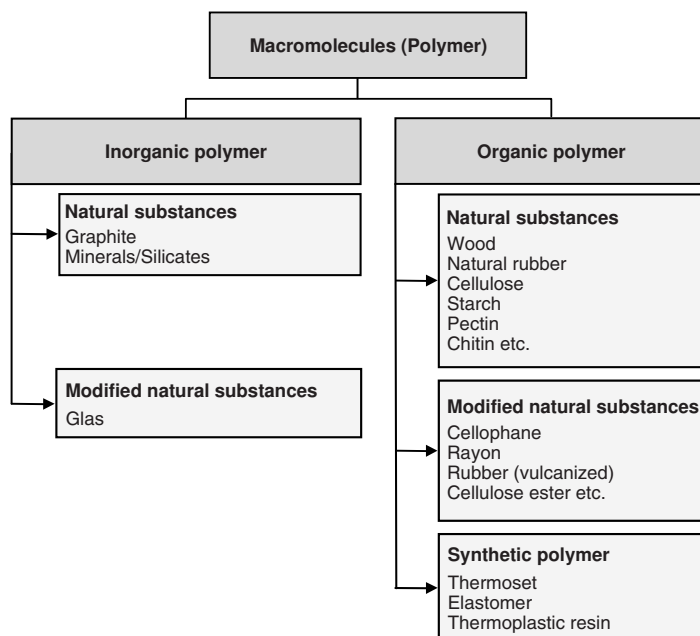


Figure 4.6: Classification of macromolecules

Polymers can be subdivided based on their properties in thermosets, elastomers, and thermoplastic resins or according to their production method in polycondensation products, polyaddition products, and polymerization products.

Thermosets are manufactured by cross-linking of linear or branched multifunctional raw materials. The real cross-linking reaction is also called cure. Thermosets are highly cross-linked. After cure these polymers can no longer be processed by thermoplastic methods; only a mechanical process is still possible. For the coloring of thermosets, only a powdery or liquid color preparation can be used, and should be added to one of the liquid raw materials before curing. In practice the more inert hardener is usually colored. The curing time can be influenced by the composition of the color preparation, and can be slowed down or speeded up.

Elastomers are loosely irreversible cross-linked polymers, which are elastic like rubber within a large temperature range. Small tension causes a high degree of elongation, which is reversible when the tension eases. The cross-linking reaction is also called vulcanization. Analogous to the thermosets, elastomers must be colored before the vulcanization, and only powdery or liquid color preparations can be used. Here, too, the speed of vulcanization may be influenced by the composition of the color preparation.

Thermoplastic elastomers are reversible cross-linked polymers. The cross-linking is raised during a thermoplastic processing and reestablished afterwards at the cooling of the processed part.

According to the literature no strict differentiation between thermosets and elastomers is possible, as both are cross-linked polymers. They differ only in the degree of cross-linking, and the borderline between both types is therefore fluent.

Thermoplastic resins, by far the largest group of polymers, consist of a long, linear, usually unbranched chain. They melt at higher temperatures and are processed by several thermoplastic methods, for example, injection molding, blow molding, film blowing, rotational molding, and so forth. For the coloring of thermoplastic resins all three types of color preparations can be applied principally, although the masterbatch is usually preferred.

Besides this subdivision, based on a characteristic property of the polymers, another possibility is to subdivide the polymers based on their characteristic production methods. Polymers are produced by polyaddition, polycondensation, and polymerization (Fig. 4.7).

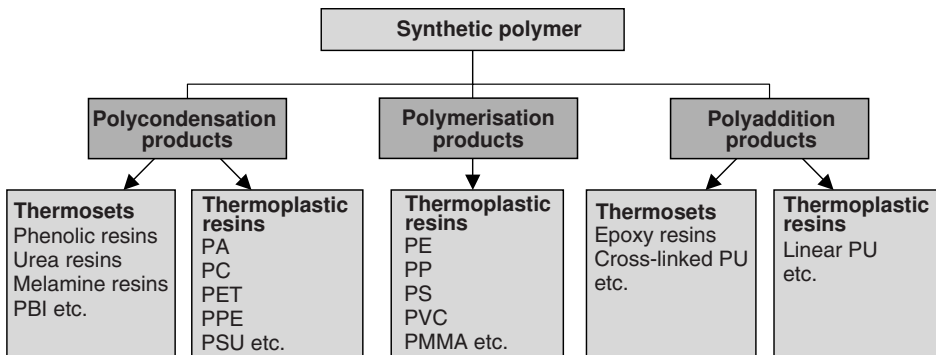


Figure 4.7: Subdivision of polymers according to their production method

Polycondensation is a step-by-step reaction of a monomer producing initially dimers and trimers, which then combine progressively to produce longer chains. The reaction is combined with an elimination of a small molecule, very often water. A monomer with two functional groups produces thermoplastic resins while a multifunctional monomer produces thermosets.

Polyaddition is a step-by-step reaction of a monomer producing initially dimers and trimers, which then combine progressively to produce longer chains. In contrast

to polycondensation this reaction is not combined with an elimination of a small molecule. A monomer with two functional groups produces thermoplastic resins while a multifunctional monomer produces thermosets.

Polymerization is a step-by-step reaction of a monomer producing longer chains. A polymerization process requires as starting material monomers with (at least) one double bond. Only thermoplastic resins can be produced by polymerization.

The type and grade of polymer is set by the customer and depends on the required properties of the final part. For color matching, it is important to receive a sample of the intended polymer, together with its data sheet. Only then is the colorist able to compose in a perfect manner the color preparations appropriate for this polymer. The reasons for this procedure are manifold, the more important being:

- The tint of the natural polymer and its transparency/opacity
- A precise color matching in this specific grade of polymer
- The presence of additives, for example, optical brightener, filler, and so forth
- To check the wanted hiding power and the mechanical and/or physical properties
- The processing behavior of the new color preparation in this grade of polymer

The first four reasons are related to the color as such, while the last point determines the type and grade of the polymer to be used as carrier of the masterbatch. The colorist normally uses a grade of polymer with a light flowing melt, because the melt viscosity increases with incorporation of higher amounts of colorants anyway. By test runs on an injection molding machine, the colorist checks the processing behavior of his color preparation in the customer supplied polymer, and of course the matched color. If problems occur the composition of the color preparation needs to be changed.

An important criterion regarding the selection of colorants to be used in the intended polymer is the processing temperature of the polymer to be colored. The processing temperatures vary within a wide range (Fig. 4.8). The processing temperature ranges from 160–200 °C (320–392 °F) for PVC; 200–250 °C (392–482 °F) for PE; 250–290 °C (482–554 °F) for PA; 320–340 °C (608–644 °F) for PSU.

With a few exceptions the heat stability of inorganic pigments is excellent, especially for all those pigments produced by high-temperature calcination. The calcination requires temperatures in the range of 700–1000 °C (1292–1832 °F).

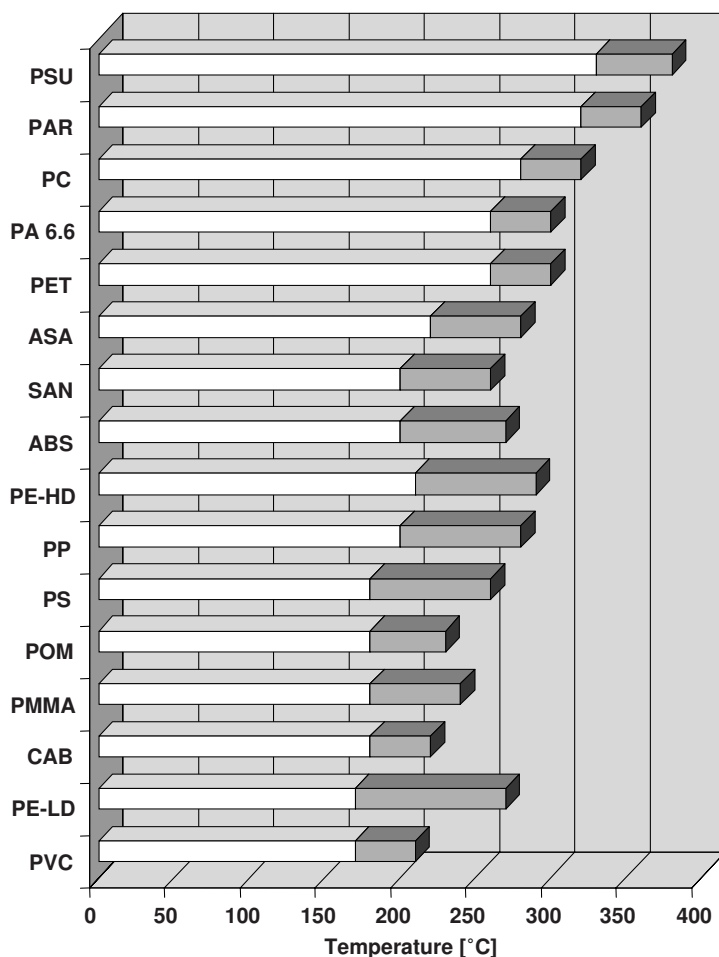


Figure 4.8: Processing temperatures for several plastics

The thermal stability of organic colorants is more or less limited, for two reasons. In the case of an organic pigment not only must the molecule as such be stable but also the crystal modification. There are well known examples in which the molecule is stable but not the crystal modification. Sometimes a substance forms more than one crystal modification, in which case the most thermodynamic stable modification is used as colorant for polymers, for example, phthalocyanine blue.

In comparison to organic pigments, many organic dyes show a higher thermal stability in spite of the fact that the structure of the molecule is chemically “simpler.” Dyes dissolve in polymers, and their thermal stability is determined solely by the stability of the molecule.

The number of organic pigments with a very high thermal stability is rather small. The coloring of engineering plastics with their sometimes extremely high processing temperatures can cause problems if very specific colors are requested. In those cases, it is not always possible to match *every* color.

It would be beyond the scope of the book to describe all plastics and their applications, with the exception of biodegradable polymers. There are very specific problems in connection with the coloring of biodegradable polymers.

4.3.2 *Biodegradable Polymers*

For several years biodegradable polymers have been discussed and some products tested. Biodegradable polymers are products that contain in their chains groups that are accessible to a natural decomposition. There are two possible mechanisms of breakdown, biodegradability or photochemical degradability.

Biodegradability can be defined as the tendency to undergo degradation by living microorganisms (e.g., bacteria, fungi) present in the natural environment. It occurs through reaction between the chemical enzymes secreted by the organism and the polymer chains. The result of such a degradation is water, carbon dioxide, and biomass (humus) and takes place within a manageable period of time.

The mechanism of photochemical degradation is very similar. The first step, however, is a breakdown of the polymer chain into smaller fractions caused by sunlight (UV irradiation). These fractions are then biodegradable. Here too, the degradation should take place within a manageable period of time.

For the use of biodegradable polymers it is of note that the decomposition reaction starts after the normal handling, which means either in the soil (compost) or in a disposal site.

Potential fields of application are:

- Packaging materials, for example, hollow bodies, shopping bags, packaging film, and so forth
- Horticulture, for example, flowerpots, films
- Agriculture, for example, agricultural films
- Household, for example, for articles with a short life span

The main idea of biodegradable polymers is to save valuable and limited disposal site space. Agricultural films are used when the growth of plants is still too slow because of unfavorable weather conditions at the beginning of a growing season. The agricultural film retains warmth during the night and the plants grow faster and ripen earlier. The use of biodegradable films is advantageous because they can be plowed into the soil after the harvest, a very ecofriendly means of waste disposal.

The idea of biodegradable polymers is not new, as cellophane was already developed in the 1920s. The original cellophane is a transparent, degradable film based on a modified cellulose. Later on cellophane was coated or lacquered to improve certain disadvantageous properties during its use. The result of these “improvements” was a loss of its biodegradability.

Further development followed two routes; the first was the development of a directly biodegradable polymer, and the other the development of biodegradable additives. The result of the first are polymers based on further modified cellulose or on polyhydroxy fatty acids, for example, poly(β -hydroxybutyrate). The other types are blends of a plastic, for example, PE, with starch as biodegradable additive. The concentration of the starch should be well below 50% in such a blend.

The biodegradable polymers available to date can be processed on any injection molding machine. All three types of color preparations can be principally used for coloring, but there are a few specific items to be considered regarding the composition of the preparation and during processing. Biodegradable polymers based on modified cellulose and/or starch contain a larger amount of plasticizer, mainly water and/or in a mixture with a high-boiling alcohol to reduce the brittleness of the part. The boiling point of these plasticizers lies somewhere below the processing temperature, therefore precautionary methods need to be implemented. Only then can an unintentional loss of plasticizer be avoided.

The natural color of biodegradable polymers is not attractive, and they are colored to have a pleasing appearance. The ideal scenario is certainly to ask for biodegradability of the whole system consisting of polymer, colorants, and additives. This cannot be realized for several reasons, and certain compromises are unavoidable.

The main reasons are:

- The naturally occurring colors of plants cannot be applied during any thermoplastic processing because of their insufficient heat stability and light fastness.
- The synthesized organic colorants are considered as nonbiodegradable; in addition it needs to be taken into account that organic colorants may form fragments detrimental to the environment. Any results regarding biodegradability of organic colorants have not yet been published.
- Inorganic pigments are generally not biodegradable as a consequence of their chemistry. On the other hand our entire surrounding, the soil, mountains, and so forth consist of a large amount of minerals, the raw material for inorganic pigments. Inorganic pigments are insoluble, and therefore most of the inorganic pigments cannot endanger our environment. The compromise is to use certain inorganic pigments for the coloring of biodegradable polymers.

Table 4.4: Limits of Heavy Metals in Dry Weight of Humus

Country	Standard/ norm	Heavy metal (mg/kg dry weight of humus)							
		Cr	Ni	Cu	Zn	Cd	Hg	Pb	As
Austria	ÖNorm S2200 Quality I	70	42	70	210	0.7	0.7	70	
Belgium	Urban waste	150 up to 200	50 up to 100	100 up to 500	up to 1500	5	5	up to 1000	
Belgium	VLACO	70	20	90	300	1.5	1.0	120	
Denmark	Status 1995	100	45	1000	4000	0.8	0.8	60	
Finland			100	600	1500	3.0	2.0	150	50
France	Category I–II	100 up to 200	20 up to 80	100 up to 200	250 up to 1000	2 up to 4	0.5 up to 3	140 up to 500	
Germany		400 up to 666	66 up to 100	400 up to 666	up to 1666	6.6 up to 11	8.4 up to 14	400 up to 666	
Germany	RAL GZ 251	100	50	100	400	1.5	1.0	150	
Spain		750	400	1750	4000	40	25	1200	
Switzer- land		150	50	150	500	3	3	150	
Euro- pean Com- munity	CENTC261 SC4 WG2 (50% of most strict norm)	35	10	35	105	0.4	0.4	30	25

Not every inorganic pigment can be used as a colorant. The ideal disposal procedure for biodegradable materials is to compost them. The composition of a compost is regulated by standards and/or legal requirements in many countries, which limit or exclude certain heavy metals in the compost (Table 4.4). The listed heavy metals are very similar in the different countries, but their limits vary some-

times considerably. The limits of heavy metals in compost do not differentiate if the substance is present in a soluble or insoluble stage. The significant figure is the total amount in 1 kg (2.2 lb) dry weight of humus.

4.4 Colorants

Color preparations are used to color polymers. For the development of a color preparation it is important to choose the right colorant. Only then will you be able to fulfill all the different requirements of your customer. The main requirement is of course the right shade; other also very important criteria are fastness properties, migration, warpage, and toxicological safety.

Colorant is the principal definition of all substances that can color polymers. Chemically they can be divided into two groups, the inorganic and organic colorants. If the colorant is insoluble in the polymer it is a pigment by definition, and if the colorant dissolves in the polymer it is a dye (Fig. 4.9) [23].

Inorganic dyes play no role in the coloring of polymers, but are mentioned here only for the reason to complete the classification.

The classification of a colorant as pigment is not always absolutely clear. There are several examples of an organic pigment that dissolves in some polymers. A good example is Pigment red 254 (DPP-Red). This pigment is insoluble in most polymers; it behaves like a pigment and gives brilliant red shades. In polycarbonate (PC), however, at temperatures above approx. 330 °C (626 °F) it dissolves and gives a fluorescent yellow shade. In PC the Pigment red 254 behaves like a dye. Further examples are described in the literature.

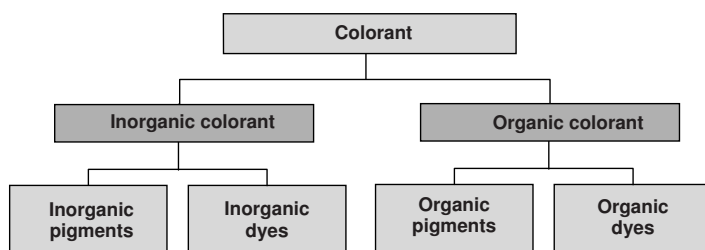


Figure 4.9: Classification of colorants

A substance can be used as a colorant for polymers when several requirements are fulfilled by the substance. The requirements for pigments are listed in Table 4.5 and those for dyes in Table 4.6. The requirements for pigments and dyes differ in some

criteria, owing to there specific physical behavior in a polymer. All colorants should have good heat stability, high tinting strength, and good fastness properties; the colorant should not migrate and should be toxicologically safe. Specific requirements for pigments are a good hiding power, they should be easy to disperse in a polymer melt, and should not cause warpage. Specific requirements for dyes are a clear transparent shade, and they should dissolve and spread rather fast in a polymer melt.

The requirements listed in Tables 4.5 and 4.6 represent the ideal situation, which is almost never achieved in practice.

Table 4.5: *Requirements for Pigments*

Requirements for pigments
High hiding power
Good dispersibility
High heat stability
High tinting strength
Good fastness properties (light/weather)
No migration
No warpage
Toxicologically safe

Table 4.6: *Requirements for Dyes*

Requirements for dyes
High heat stability
High tinting strength
Good fastness properties (light/weather)
Good solubility
No sublimation
No migration
Toxicologically safe

Most of the colorants do not fulfill *all* the requirements listed. If you would insist on it, the range of colorants would be very limited together with a paucity of avail-

able shades. On the other hand practice shows that not every colored polymer item truly requires the fulfillment of *all* requirements. Depending on the intended use, compromises are possible and quite normal. Each colorant has a weak and a strong side, caused partially by their different chemistries. These differences become very obvious when comparing the inorganic and organic colorants (Table 4.7).

Table 4.7: *Comparison of the Properties of Inorganic and Organic Pigments*

Property	Organic pigment	Inorganic pigment
Density	Low, mostly $< 2.5 \text{ g/cm}^3$	High, mostly $> 2.5 \text{ g/cm}^3$
Particle size	Mostly $< 1 \text{ }\mu\text{m}$, thereby high specific surface area	Mostly $> 1 \text{ }\mu\text{m}$, thereby low specific surface area
Tendency to form Agglomerates	High	Low
Dispersibility	Not very good	Much better
Solubility	Partial solubility, depends on concentration	Totally insoluble
Transparency	High, thereby low hiding power	Low, thereby high hiding power
Tinting strength	High, good brilliance	Low, mostly not brilliant
Heat fastness	Limited, sometimes low	Very high
Light fastness	Limited, sometimes low	Very good
Warpage	Sometimes very strong	None

Generally speaking, organic pigments have a lower hiding power in comparison to inorganic pigments, which is, however, an advantage in the case of transparent colors. The tinting strength and brilliance of a shade of an organic pigment are much higher than those of inorganic pigments, which are very often dull. The difference in tinting strength between organic and inorganic pigments is the consequence of different mechanisms in generating the color, caused by the fundamental differences in their chemical structures. In both types of pigments the interrelation of absorption and reflection is responsible for the color, but the physical processes involved differ in detail.

An unalterable condition for the appearance of color is the presence of chromophores, a system of conjugated double bonds (π -electronic system), in an

organic colorant. The electrons of the conjugated double bonds are elevated from the ground state energy level to an excited state by absorbing selected frequencies of the incident visible light, thereby giving the molecule the shade of the resulting complementary color. The type of conjugated double bonds depends on the chemistry of the organic colorant and is influenced by substituents with lone electron pairs. Substituents such as alkoxy, hydroxy, alkyl, and arylamino groups are known as electron donors. Electron acceptors are substituent functional groups such NO_2 , COOH , COOR , SO_2 , and others. The energy necessary to excite the whole electronic system, consisting of double bonds and substituents, varies according to the chemical structure of each molecule. Different energy levels mean at the same time different shades of color. The two pigments Pigment yellow 109 and Pigment yellow 110 differ only by one substituent and are therefore a good example to demonstrate the importance of a substituent for the color shade.

Inorganic pigments do not contain any double bonds or chromophores, therefore another principle leads to color. All chemical elements consist of a positive nucleus (protons), which is encircled by (negative) electrons. The size of the nucleus and consequently the number of electrons is determined by its placement in the periodic table of elements. In the periodic table all elements are placed according to their periodic repeated properties according to their atomic number, which defines the number of electrons and the electron shells.

The electrons rotate on definite energy levels, the so-called orbitals. The known orbitals are *s*, *p*, *d*, *f*, and *g* orbitals. By input of energy, for example, by absorption of sunlight, the electrons, preferably those of the higher electron shells, are elevated from the ground energy level to a higher energy level (excited state), whereby each energy level requires a definite amount of energy to elevate electrons to higher electron shells. The transition from a series of excited states to a common lower state (ground energy level) is responsible for a series of spectral emission lines. We can see a color when the wavelength of these spectral emission lines is in the range of visible light [24, 25]. The intensity of this emitted light is usually much lower in comparison to the conjugated double bonds of the organic colorants, which is why the tinting strength of inorganic pigments is quite often low.

A large number of substances act as nucleating agents in partially crystalline polymer such as polyolefins. Several organic pigments are no exception and provide crystallization nuclei in a polymer melt. Certain surface effects are responsible for this activity. The single crystals grow together to larger units, the spherulites, increasing the degree of crystallinity. The shrinkage of a polymer melt depends, besides other factors such as processing temperature, cooling rate, and pigment concentration, on the degree of crystallinity. Any distortion in the crystallization leads to warpage; among the many reasons are acicular crystals of

the colorant or large differences in wall thickness of nonrotational symmetric plastic parts.

Plastics are known as poor heat conductors, and the cooling rate of a molded plastic article is therefore slow. To reduce the amount of shrinkage, it would be logical to extend the cooling time during the injection molding. However this is not done in practice because of the expense involved. The amount of shrinkage and/or warpage of colored plastic articles is impossible to forecast, and should be tested by trials.

The appearance of shrinkage is not limited to injection molding; it plays an important part in blow molding as well. The large blue barrels (100 or 200L content) for hazardous goods must be put in special cooling stations directly after blow molding; otherwise the barrel would shrink too much, and consequently the container would no longer hold the required content.

The nucleating activity of several organic pigments is said to be a surface effect of the crystals; therefore the crystal surface should be coated and usually special types of wax are used for this purpose. The coat prevents direct contact of the crystal surface with the polymer melt and such a coated pigment prevents the appearance of warpage. The first coated pigment on the market was a special grade of phthalocyanine blue for injection molding of polyolefins, and others followed. The coat is sensitive to shear, which should be considered during the dispersal of those coated pigments in a color preparation and also later during the manufacture of plastic parts made of partially crystalline polymers such as polyolefins. In case of damage of the coat by too high shear a direct contact of the crystal surface and the polymer melt is no longer prevented and the warpage starts again.

The majority of inorganic pigments are produced by calcination at very high temperatures (approx. 700–900 °C) [1292–1652 °F]. These pigments possess very good heat stability. Other inorganic pigments, manufactured by different methods, usually show sufficient heat stability, with only a very few inorganic pigments with a limited heat stability.

The heat stability of organic colorants, however, is more or less limited.

Inorganic and organic pigments can be used to color all types of polymers, provided that the heat stability of the organic pigment is sufficient in the polymer to be colored.

The use of dyes is limited to amorphous polymers with a rather high glass transition temperature such as polystyrene (PS), polycarbonate (PC), poly(methyl methacrylate) (PMMA), and others. In partially crystalline polymers dyes would migrate directly.

The evaluation of toxicological safety of all colorants is subject to a continuous change. Possible reasons for a change might be the result of new toxicological studies, improved analytical methods in detection of hazardous impurities, or environmental considerations.

The very common lead chromates, lead sulfochromates, cadmium pigments, and disazodiarylide pigments used in the past have since been banned because of toxicological considerations. Other colorants may follow in the future.

5 Colorants for Polymers

5.1 Inorganic Pigments

The palette of inorganic pigments suitable to color polymers is relatively small in comparison to the organic colorants. There are only a few basic chemical formulas but they are available in numerous variations; therefore the palette seems larger than it really is. One example of many variations of a fundamental type are the so-called *complex inorganic color pigments* (formerly known as mixed phase metal oxide pigments). By adding other metal oxides and/or a variable ratio of the main metal oxides the exact shade is modified within a certain range. These variations are not always noticeable in the color index number of an inorganic pigment because very often only the basic chemical formula is listed there.

In Table 5.1 the most important inorganic colorants are listed, including those inorganic products that have a color index number but are not used as colorants in coloring of polymers; they are used mainly as fillers or processing aids.

Table 5.1: List of Inorganic Pigments

Product	Formula	Color index	Color	Remarks
1) Pigments consisting of pure elements				
Aluminum	Al	P. Metal 1	Silvery shiny	Effect pigment
Bronze	Cu-Zn Alloys	P. Metal 2	Golden shiny	Effect pigment
Carbon black (pigment)	C	P. black 7	Black	
2) Oxide pigments and hydroxide pigments				
Zinc white/ zinc oxide	ZnO	P. white 4	White	
Titanium dioxide (rutile/anatase)	TiO ₂	P. white 6	White	

Table 5.1: Continuation

Product	Formula	Color index	Color	Remarks
Antimony oxide	Sb_2O_3	P. white 11	White	No longer used because of toxicological concerns
Zirconium oxide	ZrO_2	P. white 12	White	No longer used as pigment
	SnO_2	P. white 15	White	Not used as a pigment
Iron oxide yellow	α -resp. γ - $\text{FeO}(\text{OH})$	P. yellow 42	Yellow	
Chromium oxide	Cr_2O_3	P. green 17	Green	
Iron oxide red	α - Fe_2O_3	P. red 101	Red	
Iron oxide black	Fe_3O_4	P. black 11	Black	
3) Complex inorganic pigments (previously: mixed phase metal oxide pigments)				
Nickel anti-mony titanium yellow rutile	$(\text{Ti}, \text{Ni}, \text{Sb})\text{O}_2$	P. yellow 53	Yellow	
Zinc ferrite brown spinel	ZnFe_2O_4	P. yellow 119	Yellow-brown	
Nickel barium titanium primrose priderite	$2\text{NiO} \cdot 3\text{BaO} \cdot 17\text{TiO}_2$	P. yellow 157	Yellow	
Nickel niobium titanium yellow rutile	$(\text{Ti}, \text{Ni}, \text{Nb})\text{O}_2$	P. yellow 161	Yellow	
Chromeniobium titanium buff rutile	$(\text{Ti}, \text{Cr}, \text{Nb})\text{O}_2$	P. yellow 162	Yellow	
Chrome tungsten titanium buff rutile	$(\text{Ti}, \text{Cr}, \text{W})\text{O}_2$	P. yellow 163	Yellow	

Table 5.1: Continuation

Product	Formula	Color index	Color	Remarks
Manganese antimony titanium buff rutile	$(\text{Ti}, \text{Mn}, \text{Sb})\text{O}_2$	P. yellow 164	Yellow-brown	
Bismuth vanadate molybdate	$\text{BiVO}_4/\text{Bi}_2\text{MoO}_6$	P. yellow 184	Yellow	
Nickel tungsten yellow rutile	$(\text{Ti}, \text{Ni}, \text{W})\text{O}_2$	P. yellow 189	Yellow	
Cobalt aluminate blue spinel Cobalt chromite blue-green spinel	CoAl_2O_4 $\text{Co}(\text{Al}, \text{Cr})_2\text{O}_4$	P. blue 28 P. blue 36	Blue/ reddish Blue/ greenish	
Cobalt tin blue-gray spinel	Co_2SnO_4	P. blue 35	Blue	
Cobalt zinc aluminate blue spinel	$(\text{Co}, \text{Zn})\text{Al}_2\text{O}_4$	P. blue 72	Blue	
Cobalt chromite green spinel	CoCr_2O_4	P. green 26	Green	
Cobalt titanate green spinel	$(\text{Co}, \text{Ni}, \text{Zn})_2\text{TiO}_4$	P. green 50	Green	
Iron manganese brown	$\text{Mn}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ $\text{Fe}(\text{OH})_2$	P. brown 7 + 8	Brown	
Chrome antimony titanium buff rutile	$(\text{Ti}, \text{Cr}, \text{Sb})\text{O}_2$	P. brown 24	Orange-yellow	
Iron chromite brown	$(\text{Fe}, \text{Cr})_2\text{O}_3$	P. brown 29	Brown	
Zinc iron chromite brown spinel	$(\text{Zn}, \text{Fe})(\text{Fe}, \text{Cr})_2\text{O}_4$	P. brown 33	Brown	
Iron chromite brown spinel	$\text{Fe}(\text{Fe}, \text{Cr})_2\text{O}_4$	P. brown 35	Brown	

Table 5.1: Continuation

Product	Formula	Color index	Color	Remarks
Manganese niobium titanium brown rutile	$(\text{Ti}, \text{Mn}, \text{Nb})\text{O}_2$	P. brown 37	Brown	
Chrome manganese zinc brown spinel	$(\text{Zn}, \text{Mn})\text{Cr}_2\text{O}_4$	P. brown 39	Brown	
Manganese chrome anti-mony titanium brown rutile	$(\text{Ti}, \text{Mn}, \text{Cr}, \text{Sb})\text{O}_2$	P. brown 40	Brown	
Iron manganese brown	Iron manganese oxide	P. brown 43	Brown	
Iron titanium brown spinel	Fe_2TiO_4	P. black 12	Black	
Copper chrome iron oxide	$\text{Cu}(\text{Cr}, \text{Fe})_2\text{O}_4$	P. black 22	Black	
Manganese ferrite black spinel	$(\text{Fe}, \text{Mn})_2\text{O}_4$	P. black 26	Black	
Iron cobalt chromite black spinel	$(\text{Co}, \text{Fe})(\text{Fe}, \text{Cr})_2\text{O}_4$	P. black 27	Black	
Copper chromite black spinel	$\text{Cu}(\text{Cr}, \text{Fe})_2\text{O}_4$	P. black 28	Black	
Iron cobalt black spinel	$(\text{Fe}, \text{Co})\text{Fe}_2\text{O}_4$	P. black 29	Black	
Chrome iron nickel black spinel	$(\text{Ni}, \text{Fe})(\text{Cr}, \text{Fe})_2\text{O}_4$	P. black 30	Black	
4) Sulfide pigments and sulfide-selenium pigments				
Zinc sulfide	ZnS	P. white 7	White	
Lithopone	$\text{ZnS} + \text{BaSO}_4$	P. white 5	White	

Table 5.1: Continuation

Product	Formula	Color index	Color	Remarks
Cerium sulfide	Cerium sulfide (exact formula not yet published)	P. orange 75 P. orange 78 P. red 265 P. red 275	Orange Red-orange Red Red	
Cadmium yellow	(Cd,Zn)S CdS	P. yellow 35 P. yellow 37	Yellow Yellow	No longer used because of toxicological concerns
Cadmium red	Cd(S,Se)	P. red 108 P. orange 20	Yellow/red Orange	
5) Chromate mixed phase pigments and chromate-molybdates mixed phase pigments				
Lead chromate yellow	Pb(Cr,S)O ₄	P. yellow 34	Yellow	No longer used because of toxicological concerns
Lead chromate molybdate orange/red	Pb(Cr,Mo,S)O ₄	P. red 104	Orange-red	
6) Silicate pigments				
Silica	SiO ₂	P. white 27	White	Not used as pigment, filler
Aluminum silicate	Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	P. white19	White	Filler
Ultramarine	Na ₆₋₈ Al ₆ Si ₆ O ₂₄ S _n (n = 2-4)	P. blue 29 P. violet 15 P. violet 15	Blue Violet Red	
7) Diverse other pigments				
Cobalt violet phosphate	Co ₃ (PO ₄) ₂	P. violet 14	Violet	
Manganese violet	NH ₄ MnP ₂ O ₇	P. violet 16	Violet	
Cobalt lithium violet phosphate	CoLiPO ₄	P. violet 47	Violet	

Table 5.1: Continuation

Product	Formula	Color index	Color	Remarks
Cobalt magnesium red-blue borate	$(\text{Co},\text{Mg})_2\text{B}_2\text{O}_5$	P. violet 48	Violet	
Barium sulfate	BaSO_4	P. white 21	White	Filler, processing aid
Chalk/calcium carbonate	CaCO_3	P. white 18	White	Filler, processing aid
Pearlescent pigments	Mica coated with TiO_2	–	Pearlescent – silvery shiny	Effect pigment
Colored pearlescent pigments	Mica coated with TiO_2 and metal oxide	–	Different colors	Effect pigment
Phosphorescent pigments	ZnS with traces of Cu or Ag	–	Greenish yellow phosphorescent	Effect pigment
“Flop-Pigments”	Aluminum flake pigments coated with iron oxide and SiO_2	–	Color depends on angle of vision	Effect pigment

The two most important colorants for the colors white and black belong to the inorganic pigments, namely titanium dioxide and carbon black. Carbon black is nearly pure carbon, which is one of the main components of the whole of organic chemistry. Nevertheless, however, carbon black is by definition an inorganic pigment, for example, the German standard DIN 55944 [23]. Titanium dioxide and carbon black are used not only for the pure white and black hues but also for shading, such as brightening or darkening of a color tint.

A worldwide discussion on “heavy metals in our environment” came up during the last decade. As a consequence, nearly every customer requires explicitly that color preparations must be *free of heavy metals*.

But what are heavy metals?

In the chemical dictionary *Römpp* [26] (published in Germany) all metals with a density above $3.5\text{--}5\text{ g/cm}^3$ are characterized as heavy metals, including the colored metals and lanthanide. Only the precious metals are a separate group, which play no role as a component of inorganic pigments.

In the dictionary *Umwelt und Chemie von A–Z*, published by the German association of the Chemical Industry, all metals with a density above 4.5 g/cm^3 are considered heavy metals, including all kinds of metals as well as the precious metals.

The same situation exists in other countries, where no clear definition of the term *heavy metal* can be found. This lack of a clear definition is astonishing because nearly everything else in industry is well defined and standard methods are published by the different associations in all countries. In our own experience, the interpretation of the term heavy metal varies from customer to customer. Some customers require only “free of lead and cadmium pigments,” while others exclude all heavy metals listed, for example, in the European Resolution AP (89)1 or in the German *BgVV-Empfehlung*, Chapter IX and – as an extreme case – a few customers exclude all heavy metals. In practice many discussions between the supplier of the color preparation and the customer were the logical consequence.

The description of heavy metals only says something about the density of the metal but nothing about toxicological and/or environmental aspects. Heavy metals are widespread in our environment, even in our food, because plants absorb them. In addition, several heavy metals are essential trace elements in our bodies, such as iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), chromium (Cr), molybdenum (Mo), and cobalt (Co). The daily requirement is in the range of 0.1–20 mg, depending on the heavy metal. If our bodies are not sufficiently supplied with those heavy metals then deficiency diseases occur.

The most important inorganic pigments were examined very carefully with regard to both toxicological and ecological effects. Summarizing the results, the most important inorganic pigments, with the exception of the harmful and banned lead chromates and cadmium pigments, are harmless toxicologically as well as ecologically [28, 29]. This results from, among other factors, the insolubility of inorganic pigments; they are not bioavailable in our stomachs (accidental swallowing) or in the environment. The toxicological effects of the lead chromates and cadmium pigments are based on their solubility in acids, for example, in gastric acid, and because of this these pigments are bioavailable.

The consequence of this situation is a further customer requirement that “the color preparation must be free of lead and cadmium.” Lead and cadmium are widespread in nature and minerals. Minerals are the raw material for most of the inorganic pigments, and it is therefore unavoidable that inorganic pigments are

contaminated with traces of lead and cadmium, in the range of a few milligrams per kilogram of pigment, a quantity that is concurrent with all national and international regulations regarding the purity of colorants. The customer requirement can specify only “free of lead and cadmium pigments,” because the requirement “free of lead and cadmium” would exclude even traces of these two heavy metals. An absolute absence of lead and cadmium in inorganic pigments is neither technically feasible nor required by any legal regulation.

Based on the description of heavy metals by the German Association of the Chemical Industry all inorganic pigments except aluminum flakes, carbon black, and ultramarine blue and violet contain heavy metals.

5.1.1 White Pigments

White pigments are used for pure white coloring, for shading (brightening) of colors, and for covering shades. For opaque shades titanium dioxide is preferred because of its very good hiding power. Covering shades are requested whenever a showthrough of the content of a package and/or of the underground is to be avoided. In those opaque colors the white pigment must be covered by color first before the color matching can begin. The result is a rather large need for colorant, which has a negative effect on the costs of the color preparation. It is therefore advisable to check first the efficiency of different additions of the color preparation with regard to its hiding power in the planned plastic article. Sometimes it may be more economical to increase slightly the amount of color preparation during the coloring process and/or to increase slightly the wall thickness instead of increasing the concentration of the white pigment in the color preparation. The result of these considerations should be a balance between costs and hiding power.

By definition, all substances with a refractive index higher than 1.7 are classified as white pigments. If the refractive index is lower than 1.7 they are classified as fillers (Table 5.2).

Strictly considered, the limiting value of 1.7 is not a constant but depends on the matrix of the pigments, because every matrix has its own specific refractive index. Polymers are no exception; therefore the refractive indices of pigments vary from polymer to polymer, and are consequently different for materials such as plastics, alkyd resins, cellulose, poly(ethylene terephthalate) (PET) fibers, and so forth.

Good optical properties are expected from white pigments, for example, high scattering power, a high degree of hiding power, good lightening power, a high degree of lightness, only an insignificant undertone (preferably none), and a high degree of whiteness. The most important property is the scattering power, which depends on the refractive index, particle size, and distribution and degree of dispersion.

Because of these dependencies the scattering power is a relative value and not an absolute value. The other parameters, such as hiding power, lightness, undertone and whiteness depend more or less on the scattering power of the white pigment.

Table 5.2: *Refractive Indices of Several White Pigments and Fillers*

Pigment	Color index number	Refractive index
Antimony oxide (Sb_2O_3)	Pigment white 11	2.19
Barium sulfate (BaSO_4)	Pigment white 21	1.64
Basic lead carbonate [$(\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3]$	–	2.01
Silica (SiO_2)	Pigment white 27	1.55
Chalk (CaCO_3)	Pigment white 18	1.58
Titanium dioxide – anatase (TiO_2)	Pigment white 6	2.55
Titanium dioxide – rutile (TiO_2)	Pigment white 6	2.70
Zinc oxide (ZnO)	Pigment white 4	2.00
Zinc sulfide (ZnS)	Pigment white 7	2.37
Zirconium oxide (ZrO_2)	Pigment white 12	2.40

Inorganic pigments are relatively easy to disperse in a polymer melt, much easier than organic pigments. They nevertheless undergo an aftertreatment. The treatment consists of coating the individual pigment particles with colorless inorganic and/or organic substances. The purpose of such an aftertreatment is to improve the dispersibility in a polymer matrix, the light fastness, and weather resistance. A complete dispersion of any pigment in the polymer matrix is important because only then can the optimum of tinting strength be exploited, which affects the economics of a color preparation.

The following description of the white pigments and fillers and/or processing aids is in alphabetic order for systematic reasons.

Aluminum silicate ($\text{Al}_2\text{Si}_2\text{H}_4\text{O}_9$) – Pigment white 19 / 77005

Filler and raw material for the synthesis of ultramarine blue and violet.

Antimony (III) oxide (Sb_2O_3) – Pigment white 11 / 77052

This white pigment is no longer used for coloring of plastics because of its toxicological effects. In technical plastic parts it is still used as a co-flame retardant.

Barium sulfate (BaSO₄) – Pigment white 21 / 77120 / CAS 7727.43.7

Properties: The mineral barite (barium sulfate) is very common in nature. Its density is in the range of 4.3–4.6 g/cm³. Owing to its low Mohs hardness of 3.5 it is not very abrasive in comparison to other inorganic pigments, which is favorable in regard to abrasion of plastic processing machines. Barium sulfate is practically inert toward acids, alkalis, and organic solvents; in addition, the light fastness and weather resistance are very good. The heat stability is high (above 300 °C [572 °F]). Because of its low tendency to form agglomerates it is easy to disperse.

Application: Owing to its low refractive index of 1.64 it is not considered a white pigment. The main use is as a filler and/or processing aid in color preparations. Barium sulfate is used, for example, in lamp covers made of plastic. In this case its low opacity is advantageous – on the one hand it is transparent enough for the light, and on the other hand a certain amount of light is scattered. The result of this combined effect is the required diffuse light scattering of lamp covers.

Two types of barium sulfate are marketed. One type is a very fine milled, natural barite and the other is a precipitated, synthetic barium sulfate. The synthetic type, available in different particle sizes, is preferred as a component of color preparations. Barium sulfate improves the flowing properties of the premixed colorants, especially in the case of a high concentration of organic pigments, and in addition it helps to disperse the pigments in the polymer melt during production of a color preparation.

Another very specific application of barium sulfate is in toys, a use that is not very obvious at first glance. In the past barium sulfate was the classic X-ray contrast medium. There are currently better ones in use. Still, barium sulfate can help to locate a toy swallowed accidentally by a child.

Pure barium sulfate is harmless toxicologically, and its use in plastics in contact with food is therefore permitted in many countries, including the United States (according to the FDA) and in most European countries.

In addition, barium sulfate is a component of Lithopone, Pigment white 5.

Basic lead carbonate [Pb(OH)₂·2PbCO₃] / – / CAS 1319.46.6

This pigment is no longer in use for coloring of plastics owing to its toxicological problems.

Chalk (CaCO₃) – Pigment white 18 / 77220 / CAS 1317.65.3

Properties: Calcium carbonate is besides quartz the most common mineral on earth. There are several types according to its formation and appearance.

- Calcite – colorless, transparent, translucent or opaque, dense crystals with perfect rhombohedral cleavage. Some varieties are fluorescent in UV light. Soluble in acids.
- Chalk – Chalk is a very pure limestone formed during the cretaceous period of fine calcite crystals consisting mainly of shells and skeleton of microscopic small fossils. There are many deposits that are exploited commercially.
- Limestone – Limestone is a compact form of chalk, formed also from the accumulation of calcareous skeletons of marine organisms.
- Marble – Marbles are produced by the metamorphism of limestone around igneous intrusions. Marble is essentially calcite but may contain greater or lesser amounts of dolomite and other minerals. It is a very coarse compacted mineral.

A chalk deposit can be commercially exploited if the purity of the calcium carbonate is higher than 99%. The lightness of chalk increases with decreasing amount of impurities. The most common impurities are iron oxides and carbonates of magnesium, strontium, and barium.

Besides the natural deposits, calcium carbonate is produced synthetically by precipitation. These grades, however, are much more expensive than the natural types.

Calcium carbonate is semihard and not very abrasive. The Mohs hardness is 3, and the density is between 2.6 and 2.8 g/cm³. Calcium carbonate is soluble in weak acids and insoluble in alkali. The properties can be adjusted by aftertreatment.

Application: Calcium carbonate is not a white pigment because of its low refractive index of 1.58. The main application is to reinforce plastics, and another use is as a processing aid. Similarly to barium sulfate, it improves the flowing properties of premixed colorants, especially at high concentrations of organic pigments, and the dispersing of the pigments in the polymer melt during the production of a masterbatch. Other applications are as a diluent in powdery color preparations and in the form of specially treated grades as antisedimentation agent in liquid color preparations.

Lithopone (ZnS/BaSO₄) – Pigment white 5 / – / CAS 1345.05.7

Properties: Lithopone is produced by coprecipitation and subsequent calcination of a mixture of zinc sulfate and barium sulfate. The ratio between both components varies, for example, a type with 60% ZnS and 40% BaSO₄ is marketed. The use of zinc sulfide and barium sulfate in contact with foods is permitted by the US FDA and in most European countries. Soluble zinc is toxic in large amounts, but the human body requires small quantities for metabolism. Owing to its low

solubility it is harmless in the human. Studies showed that there was no case of poisoning or chronic damage to health in the manufacture of this pigment despite exposure to dust during handling of the very finely ground pigment.

Application: Lithopones are used in many plastics, especially in glass fiber reinforced plastics, because the soft texture of lithopone prevents mechanical fiber damage during the coloring of the reinforced polymer. This is the main advantage in comparison to titanium dioxide, which damages the glass fiber of reinforced plastics during the coloring process.

Mica {K/Na/Al₂[(OH,F)₂Si₃O₁₀]} – Pigment white 20 / 77019 / CAS 12001.26.2

A raw material for the production of pearlescent pigments. Mica is the collective term for a whole series of minerals chemically known as hydrous alkaline aluminum silicates. The most important members of this group of silicates are muscovite, phlogopite, biotite, and paragonite. They differ in their content of potassium, sodium, and fluorine, and their characteristic feature is an appearance as very thin sheets.

Mainly muscovite and phlogopite are coated with a thin layer of metal oxides. The silvery pearlescent pigments result from a coat of titanium dioxide, colored pearlescent pigments result from iron and/or chromium oxide as a coat.

Silica or Silicon dioxide (SiO₂) – Pigment white 27 / 77811 / CAS 7631.86.9 respectively 112945.52.5

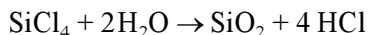
(Remark: The term Pigment white 27 is valid only for the naturally occurring silica, not for the synthetic grade, which is normally used in coloring of plastics.)

Owing to its low refractive index of 1.55, silica is not used as a white pigment but is a very important processing aid. The main functions of silica are:

- Improvement of the flow properties of organic pigments in a premix prior to the extrusion of color preparations (masterbatch production)
- Improvement of the flow properties of a powdery color preparation, including a stabilizing effect on storage
- Use as a thickening or antisedimentation agent in a liquid color preparation and to adjust the viscosity
- Grades of silica with an extremely high specific surface applied as carriers for liquid additives, for example, antistatic agents
- Filler in rubber and sealing compounds based on plastic
- Matting agent in plastic films
- Antiblocking agent in plastic films

Synthetic amorphous silica is produced either by precipitation or by a thermal process. Precipitated silica is manufactured by hydrolysis of an aqueous sodium silicate solution with an acid.

There are two variations of the thermal process, either silicon tetrachloride is combusted with steam according to the formula



or by reaction of quartz and coke in an electric furnace at high temperature.

The properties of silica are usually adjusted by aftertreatments to fulfill all requirements and to fit all applications. There are hydrophobic and hydrophilic grades, and grades with a broad variation of specific surface and/or particle size distribution.

Silica is chemically inert, soluble only in hydrogen fluoride (HF). The fastness properties are excellent.

Synthetic silica is amorphous, a very important fact. Naturally occurring silica is crystalline and toxicologically harmful. Crystalline silica causes silicosis through inhalation. The MAK value (Maximale Arbeitsplatz Konzentration = maximal allowed concentration of a harmful substance on the workplace; list of harmful products and substances in Germany) of silica dust is limited to 6 mg/m³ of air. The LD₅₀ is > 5000 mg/kg body weight, rat, oral application, and not irritating to skin and mucous membrane.

Talc [$\text{Mg}_6(\text{Si}_8\text{O}_{20})(\text{OH})_4$] – Pigment white 26 / – / CAS 14807.96.6

Properties: This magnesium silicate is chemically inert, very soft, no white pigment, excellent heat stability.

Application: Talc is used mainly to reinforce plastics, similar to glass fiber and chalk. Specially treated types are applied as nucleating agents in polyolefins.

Tin dioxide (SnO_2) – Pigment white 15 / 77861 / CAS 18282.10.5

Tin dioxide occurs in nature as cassiterite (tinstone), which is a very dense (density 6.8–7.1 g/cm³) and hard substance (Mohs hardness 6–7). It is not used as a white pigment, but it plays an important role in the production of the silvery pearlescent pigments. The pearlescent pigments are manufactured by precipitation of titanium dioxide on thin mica platelets. Anatase is formed during the subsequent calcination. This grade of pearlescent pigments shows an insufficient light fastness and weather resistance. If the mica platelets, however, are treated with tin dioxide prior to the precipitation of titanium dioxide, rutile is formed during the calcination. This grade of pearlescent pigments shows a good light fastness and weather resistance. They contain approx. 1–2% tin dioxide.

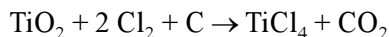
Titanium dioxide (TiO₂) – Pigment white 6 / 77891 / CAS 13463.67.7

Properties: Titanium dioxide dominates the market of white pigments and is the most important inorganic pigment in terms of quantity. Titanium dioxide occurs in nature in the crystal modifications rutile (tetragonal), anatase (tetragonal), and brookite (rhombohedral). Rutile and anatase are produced industrially in large quantities. Brookite is difficult to produce and therefore it plays no role in the pigment industry. Rutile is the most thermodynamically stable modification and has the most compact atomic structure and therefore the highest density. The density of anatase is approx. 3.9 g/cm³ and that of rutile approx. 4.2 g/cm³. Rutile is the hardest modification with a Mohs hardness of 6.5–7. Anatase is softer, with a Mohs hardness of 5.5–6. Not only are the optical properties of rutile superior to those of anatase (refractive index of rutile is 2.70, of anatase 2.55), but also the light fastness and weather resistance of the rutile modification are superior to those of anatase.

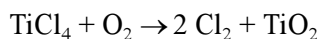
Titanium dioxide pigments are produced by two different processes, the sulfate process and the chloride process. The anatase modification can be produced only by the sulfate process, while the rutile modification is produced by both processes.

Sulfate process is the older of the two processes. Titanium containing raw materials such as the mineral ilmenite (FeTiO₃) or titanium slag is broken down with concentrated sulfuric acid at higher temperatures. In the resulting solution the dissolved Fe³⁺ (of the ilmenite or the titanium slag) must be reduced to Fe²⁺; the solution is then cooled to crystallize the FeSO₄, which is separated by filtration or centrifugation. The reduction of the iron is important, because a trivalent iron sulfate is too soluble in sulfuric acid. The next step is the precipitation of titanium oxide hydrate by hydrolysis, which is filtered off the solution and the filter cake washed several times with water or dilute acid to remove further impurities. To produce specific pigment grades the hydrate must be treated prior to calcination. Depending on the kind and substances of treatment either rutile or anatase is formed during the subsequent calcination.

The *chloride process* requires a concentrated titanium slag. The titanium of the raw material is converted to titanium tetrachloride in a reducing atmosphere at high temperature. The following reaction takes place:



The titanium tetrachloride is first purified by fractional distillation and then combusted with oxygen at high temperature to form titanium dioxide and chlorine.



Because of the high temperature of 900–1400 °C (1652–2552 °F) during the combustion of titanium tetrachloride only the thermodynamically stable rutile modification is formed.

An aftertreatment of the titanium dioxide is essential for its fastness properties. Titanium dioxide absorbs water, and accordingly its surface is saturated by coordinately bonded water, which forms hydroxyl ions. The presence of hydroxyl groups makes photochemical induced reactions possible. The treatment consists of coating each individual pigment particle with colorless inorganic compounds by precipitating them onto the surface. Zirconium (Zr), tin (Sn), aluminum (Al), and silicon (Si) compounds are used as coating, sometimes followed by an additional coating with specific organic compounds [30]. By choosing the right organic compound the final surface can be made either hydrophobic or hydrophilic [31, 32].

The coat prevents direct contact between the plastic matrix and the reactive surface of the titanium dioxide, consequently the light fastness and weather resistance are improved.

Titanium dioxide is inert, insoluble (except in concentrated sulfuric acid and hydrogen fluoride), and very stable. It is regarded as completely nontoxic, which is underlined by its application in tooth paste and in the coat of medical pills.

Application: Rutile, the preferred type, is applied to color nearly all types of plastics, either for pure white shades or for the lightening of colored shades including colors with a good hiding power. There is, however, one restriction. The high hardness of the rutile is disadvantageous in glass fiber reinforced plastics, because the rutile can damage the glass fiber during the coloring process combined with a severe loss of mechanical strength of the final plastic part. In spite of the inferior optical properties the much softer lithopone or zinc sulfide is the white pigment of choice to color glass fiber reinforced plastics.

Another application is for matting of plastic fibers, in this case the anatase modification is preferred because its lower abrasion.

Zinc oxide (Zinc white – ZnO) – Pigment white 4 / – / CAS 1314.13.2

Properties: Zinc oxide is a very fine white powder. The chemical stability is not very good because zinc oxide is amphoteric; it reacts with acids and is soluble in alkaline solutions. This is an disadvantageous in the field of packaging material. The density is approx. 5.67 g/cm³; the Mohs hardness is 4–4.5. The optical properties are inferior to those of titanium dioxide. Zinc oxide is easy to disperse and the light fastness is good.

Zinc oxide is manufactured by two different processes, either by the direct or American process or by the indirect or French process.

The *direct or American process* is a very simple one at low cost. A mixture of coal as reducing agent and zinc oxide containing raw materials or zinc ores are heated up to 1000–1200 °C (1832–2192 °F). Under this condition the zinc oxide (of the raw material) is reduced to metal, which evaporates. The zinc vapor is then oxidized to zinc oxide. The purity of the zinc oxide is determined by the composition of the raw materials used.

The *indirect or French process* starts from metallic zinc, which is boiled and the resulting vapor oxidized to zinc oxide.

Zinc ores are contaminated usually with several other metal oxides, mainly cadmium, lead, iron, and aluminum oxides. Various separation techniques are therefore necessary to purify the zinc vapor before oxidation.

Zinc oxides with different degrees of purity are commercially available; some types still contain a few percent of lead. Before use the colorist should check the quality of the zinc oxide to enable him to fulfill all customer requirements regarding impurities of heavy metals.

Zinc is an essential trace element for humans, animals, and plants. Lack of sufficient zinc causes deficiency diseases, for example, it affects the growth of hair and reproduction.

Zinc oxide is not considered to be toxic or dangerous, although a few early studies showed some toxic effects. These toxic effects were probably the result of impurities, especially of lead, in the zinc oxide used for the studies.

Zinc oxide is insoluble in water and can be separated from waste water rather easily. Because of the toxicity of zinc ions in water to fish and other aquatic living things the concentration of zinc ions in waste water is limited.

Application: The most important use is in the rubber industry and in molding compounds. It plays no important role in coloring of thermoplastic resins.

Zinc sulfide (ZnS) – Pigment white 7 / 77975 / CAS 1314.98.3

Properties: Zinc sulfide is the second most important white pigment after titanium dioxide. The refractive index is 2.37. It is a soft pigment, and the Mohs hardness is 3; therefore the pigment is not very abrasive, which makes it especially suitable for coloring of glass fiber reinforced plastics. The light fastness of zinc sulfide is good but the weather resistance is insufficient. UV radiation in combination with humidity oxidizes zinc sulfide to the colorless zinc sulfate (ZnSO_4) in several plastics. In contrast, however, zinc sulfide improves the light fastness and weather resistance of polyolefins. The use of zinc sulfide in poly(vinyl chloride) (PVC) is restricted depending on the system of stabilization. In lead containing systems zinc sulfide reacts with lead forming the dark lead sulfide.

Because of its low solubility it is harmless in human. Studies have shown there was no case of poisoning or chronic damage to health in the manufacture of this pigment despite exposure to dust during handling of the very finely ground pigment. Zinc sulfide is permitted in contact with food by the US FDA and in most European countries. Soluble zinc, however, is toxic in large amounts, although as the human body requires small quantities for metabolism, zinc belongs to the essential trace elements.

Zinc sulfide is the main component of lithopone, Pigment white 5, and the base of some luminescent pigments. One form of luminescent pigments consists of zinc sulfide doped with silver (Ag) or copper (Cu). This type of effect pigment is described in the chapter on additional inorganic effect pigments.

Application: The optical properties of zinc sulfide are obviously inferior to those of titanium dioxide and therefore its use is restricted. Similar to the use of lithopone, zinc sulfide is applied especially in systems that require a low abrasion of the pigment, and in glass fiber reinforced plastics, because the soft texture of zinc sulfide prevents a mechanical fiber damage during the coloring process. This is the main advantage in comparison to titanium dioxide, which damages the glass fiber of reinforced plastics during extrusion.

Zirconium dioxide (ZrO_2) – Pigment white 12 / 77990

Zirconium dioxide is completely substituted by the superior titanium dioxide. It is used, together with other substances, during the aftertreatment of titanium dioxide to improve the fastness properties of rutile.

5.1.2 Black Pigments

Similar to the role of titanium dioxide for white shades, carbon black dominates the market for black shades. Black pigments are used either for pure black shades or for darkening of colored shades. Strictly considered there are only three basic formulas of black inorganic pigments: carbon black (Pigment black 7), iron oxide black (Pigment black 11) and iron titanium brown (Pigment black 12). The other black pigments, Pigment black 22, and Pigment black 26 through 30, are variations of iron oxide black, Fe_3O_4 , (Pigment black 11). In these pigments the iron is partly substituted by other metals such as copper (Cu), manganese (Mn), chromium (Cr), cobalt (Co), and nickel (Ni), either alone or in combination (Table 5.3).

Carbon black (C) – Pigment black 7 / 77266 / CAS 1333.86.4

Properties: Carbon black, pure carbon, is a very fine pigment with a very high tinting strength. Carbon black is classified as an inorganic pigment, for example,

in the German standard DIN 55944, in spite of the fact that carbon is one of the main components in the whole of organic chemistry [23].

Table 5.3: List of Black Pigments for Coloring of Plastics

Product	Formula	Color Index Number
Carbon black	C	Pigment black 7
Iron oxide black	Fe_3O_4	Pigment black 11
Iron titanium brown spinel	Fe_2TiO_4	Pigment black 12
Copper iron chromite black	$\text{Cu}(\text{Cr},\text{Fe})_2\text{O}_4$	Pigment black 22
Manganese ferrite black spinel	$(\text{Fe},\text{Mn})_2\text{O}_4$	Pigment black 26
Iron cobalt chromite black spinel	$(\text{Co},\text{Fe})(\text{Fe},\text{Cr})_2\text{O}_4$	Pigment black 27
Copper chromite black spinel	$\text{Cu}(\text{Cr},\text{Fe})_2\text{O}_4$	Pigment black 28
Iron cobalt black spinel	$(\text{Fe},\text{Co})\text{Fe}_2\text{O}_4$	Pigment black 29
Chrome iron nickel black spinel	$(\text{Ni},\text{Fe})(\text{Cr},\text{Fe})_2\text{O}_4$	Pigment black 30

Carbon black is manufactured by several production processes. The most important are the furnace black process and the channel black process; other processes of less importance are the lamp black process, the thermal black process, and the acetylene black process. They differ in technical details and the raw materials used. Most common are gaseous (natural gas) or liquid hydrocarbons (oil). The basis of all processes is a partial combustion of hydrocarbons.

The properties of carbon black are determined by the particle size distribution, the structure (coalescence of primary particle into aggregates), the specific surface area and the chemical composition of the pigment surface [34, 35].

The *primary particle size* of carbon black is in the range of 10–300 nm, it is a very fine grained pigment.

The *specific surface area* varies widely. A coarse grade of carbon black has a specific surface area as small as $10\text{m}^2/\text{g}$, while the finest grades can have a specific surface area as large as $1200\text{m}^2/\text{g}$. During the handling of very fine grades of carbon black it is necessary to take precautions. One aspect is to avoid a heavy soiling of the workers, machines, and the surroundings by the fine dust, and another involves wetting problems during incorporation in a polymer melt. Very fine carbon black is difficult to wet with the polymer melt, as this requires not only very effective dispersing agents but also a high shear during incorporation. Only in the case of a complete dispersal is it possible to make the most of the full color depth of carbon black, which is an important feature when carbon black is

used to darken a colored shade in addition to maintaining consistency of the exact shade from production to production. The color depth of carbon black increases with decreasing particle size. On the other hand, a coarser carbon black is easier to disperse in a polymer melt than a very fine grade. In the case of dispersal problems it may be advisable to use a coarser carbon black. Although the color depth of a coarser carbon is lower the visual impression is a higher color depth because of the more complete dispersion. The dependencies of typical properties of carbon black on the particle size are shown in Fig. 5.1.

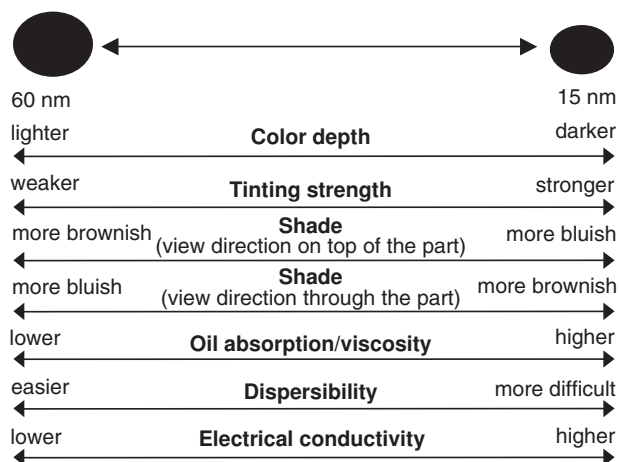


Figure 5.1: Dependencies of typical properties of carbon black on the particle size

As mentioned previously the color depth of carbon black increases with decreasing particle size. At constant concentration the number of pigment particles increases at the same time, which results in a higher light absorption and less scattering. The absorption rate of very fine grades of carbon black can reach nearly 99.5%, which is a very “deep” black. Consequently a coarser carbon black absorbs less light and is scattered more; the visual impression is that of a “lighter” black. The bluish or brownish tone of carbon black is the result of this interaction between light absorption and light scattering, which depends on the particle size. Whether a bluish or brownish tone is noticeable depends on the angle of vision. A bluish tone appears when looking through a transparent part, colored with a coarse carbon black, and the brownish tone appears when looking on top of the surface of the same part. In case of a very fine grade of carbon black it is the reverse.

The exact shade depends not only on the particle size but also on its *structure*. During the production process the primary particles of carbon black, almost

spherically shaped, coalesce into aggregates in the form of chains or clusters. The type of aggregates is called the structure of carbon black.

The dependence of some typical properties of carbon black on the structure is shown in Fig. 5.2.

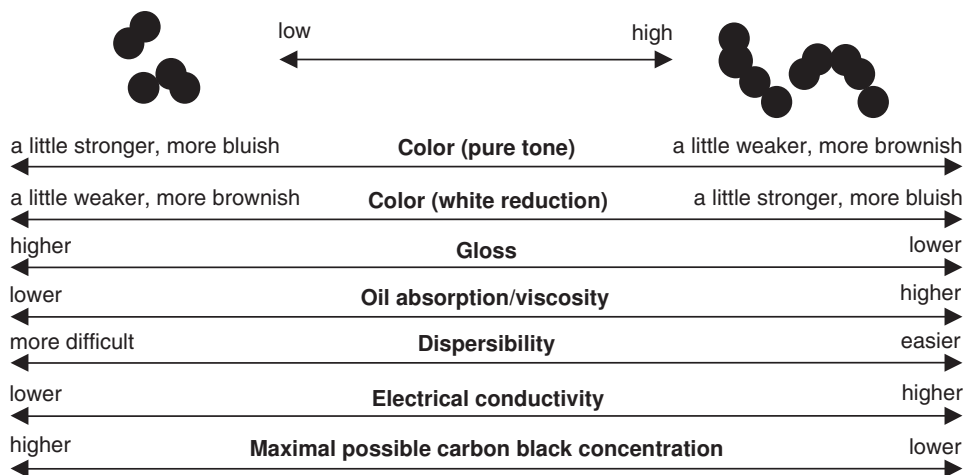


Figure 5.2: Dependence of some typical properties of carbon black on its structure

Carbon black is manufactured by a partial combustion of hydrocarbons; therefore the surface of the particles contains oxygen, bound to the surface in the form of acidic or basic functional groups. The amount of surface oxides and their composition depends on the production process and the raw material. The amount of surface oxides can be increased by an oxidative aftertreatment. The structure and number of oxygen-containing functional groups on the surface of carbon blacks influence the application properties. The chemical composition of the carbon black surface is called *surface chemistry*.

Many polymers are degraded by UV radiation under atmospheric conditions. In those plastics, especially in polyolefins, carbon black acts as a stabilizer by absorbing the UV radiation. The stabilizing action of carbon black increases with decreasing particle size and with increasing concentration up to approx. 2–3%. A medium-fine and highly structured grade of carbon black is the preferred grade for such an application.

Another property of carbon black is its electrical conductivity. Depending on the requirements the plastic part has to fulfill, this electrical conductivity is either dis-

ruptive or required. The electrical conductivity depends on the type of production process, as well as on the specific surface area and structure, and of course on the concentration of carbon black in the finished part. If required, special grades of carbon black are marketed to lend polymers antistatic or electrically conductive properties. The necessary concentrations, however, are much higher than usually applied for the coloring of polymers.

Every substance with a very high specific surface area adsorbs larger amounts of gaseous or liquid components. Grades of carbon black with a large specific surface area have a remarkable adsorption capacity for solvents, binders, polymers, and additives; therefore interactions cannot be excluded. The adsorption of stabilizer or antioxidants can cause problems in polymer systems, such as a reduced light fastness or weather resistance. The adsorption of dispersing agents leads to problems regarding wetting and dispersing of carbon black, and an adsorption of the polymer melt increases its viscosity. In rubber carbon black can influence the speed of vulcanization.

In Fig. 5.3 is shown how a combination of particle size and structure influences the properties of a finished part.

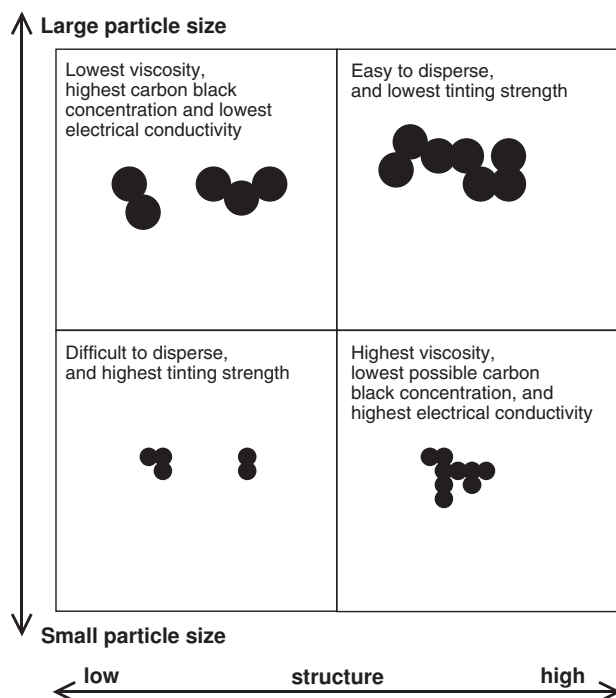


Figure 5.3: Dependence of properties on the combination of particle size and structure of carbon black

The LD₅₀ of carbon black is > 5 000 mg/kg body weight, rat, oral application, it is not irritating to the skin or mucous membranes. Carbon black is used to color household article, toys, packaging material, and so forth. The legal requirements regarding purity of the carbon black differ from country to country. The main aspect is the content of polycyclic aromatic hydrocarbons as impurities, evaluated by an extraction with toluene. A special grade of carbon black has been approved by the US FDA for plastic articles in contact with food.

Application: More than 90% of the total amount of the carbon black produced is used as reinforcing filler in rubber for tires and other technical rubber goods. The use as colorant is approx. 2–4% of the produced quantity, nevertheless this is a large quantity considering that the yearly production is about 6 million tons of carbon black.

In comparison to carbon black the *other black pigments* play no important role in coloring of plastics. Their main disadvantage is the low tinting strength. They are used if carbon black cannot be used for any reason or for tinted shades. Generally considered, for the tinting of a color only very small amounts of a colorant are necessary, and on the other hand a very even distribution of a small quantity in a larger mixture is difficult to achieve. In such a case a low tinting strength can even be an advantage. If such a pigment is used for tinting, the necessary quantity increases and mixing problems decrease. In addition, these other black pigments, based on metal oxides, are much easier to disperse in a polymer melt than carbon black.

The heat stability of these pigments is very good with the exception of iron oxide black, which is oxidized (to red iron oxide) at temperatures above 250 °C (482 °F). The light fastness and weather resistance are good. They are insoluble and chemically inert.

Iron oxide black (Fe₃O₄) – Pigment black 11 / – / CAS 1317.61.9

Iron oxide black occurs in nature in the form of the mineral magnetite. At present, the natural material cannot be used as a colorant because of impurities. In prehistoric times it was used, together with other minerals, for rock and cave paintings.

Iron oxide black is synthesized by oxidation of iron and is a mixture of Fe²⁺ and Fe³⁺ oxide. The divalent iron (Fe²⁺) is sensitive to oxygen, and is easily oxidized to the trivalent iron (Fe³⁺). The heat stability of iron oxide black is therefore limited to about 250 °C (482 °F).

Iron titanium brown spinel (Fe_2TiO_4) – Pigment black 12 / 77543 /
CAS 68187.02.0

This pigment is produced by high-temperature calcination of iron oxide (FeO) and titanium dioxide (TiO_2). As a modifier it may contain one or a combination of the following oxides: Al_2O_3 , CoO, Cr_2O_3 , Fe_2O_3 , MnO, or ZnO [33]. The color varies between brown, dark brown, and brownish black, depending on the kind and quantity of the modifier. Crystal modification: spinel.

Copper iron chromite black [$\text{Cu}(\text{Cr,Fe})_2\text{O}_4$] – Pigment black 22 / 77429 /
CAS 55353.02.1

This pigment is produced by high-temperature calcination. The metals copper and chromium are ionically interdiffused in the crystalline matrix of spinel, therefore copper and chromium lose their own typical chemical, physical, and physiological properties.

Manganese ferrite black spinel [$(\text{Fe,Mn})(\text{Fe,Mn})_2\text{O}_4$] – Pigment black 26 /
77494 / CAS 68186.94.7

This pigment is the reaction product of high-temperature calcination of manganese (II) oxide (MnO), manganese (III) oxide (Mn_2O_3), iron (II) oxide (FeO), and iron (III) oxide (Fe_2O_3). As a modifier it may contain one or a combination of the following oxides: Al_2O_3 , CoO, CuO, NiO, SiO_2 , or TiO_2 [33]. Crystal modification: spinel.

Iron cobalt chromite black spinel [$(\text{Co,Fe})(\text{Fe,Cr})_2\text{O}_4$] – Pigment black 27 /
77502 / CAS 68186.97.0

Produced by high-temperature calcination of iron (II) oxide (FeO), cobalt (II) oxide (CoO), iron (III) oxide (Fe_2O_3), and chromium (III) oxide (Cr_2O_3). As a modifier it may contain one or a combination of the following oxides: Al_2O_3 , B_2O_3 , CuO, MnO, NiO, or SiO_2 [33]. Crystal modification: spinel.

Copper chromite black spinel [$\text{Cu}(\text{Cr,Fe})_2\text{O}_4$] – Pigment black 28 / 77428 /
CAS 68186.91.4

This pigment is the reaction product of high-temperature calcination of copper (II) oxide (CuO) and chromium (III) oxide (Cr_2O_3). Many grades contain iron (III) oxide (Fe_2O_3) as a modifier.

Iron cobalt black spinel [$(\text{Fe,Co})\text{Fe}_2\text{O}_4$] – Pigment black 29 / 77498 /
CAS 68187.50.8

Produced by high-temperature calcination of iron (II) oxide (FeO), cobalt (II) oxide (CoO), and iron (III) oxide (Fe_2O_3). As a modifier it may contain one or a

combination of the following oxides: Al_2O_3 , B_2O_3 , MnO , NiO , or SiO_2 [33]. Crystal modification: spinel.

Chrome iron nickel black spinel $[(\text{Ni},\text{Fe})(\text{Cr},\text{Fe})_2\text{O}_4]$ – Pigment black 30 / 77504 / CAS 71631.15.7

This pigment is the reaction product of high-temperature calcination of chromium (III) oxide (Cr_2O_3), iron (II) oxide, iron (III) oxide, and nickel (II) oxide in varying amounts. Several grades are marketed. As a modifier it may contain CuO , MnO , or Mn_2O_3 [33]. Crystal modification: spinel.

5.1.3 Colored Pigments

The most colored inorganic pigments are complex mixed metal oxides. They can be classified according to various aspects, based on either coloristic or on chemical considerations. In contrast to the organic pigments, the properties of which depend on their chemistry to a large extent, this is not noticeable in the case of inorganic pigments. The classification scheme for inorganic colored pigments therefore follows coloristic considerations.

5.1.3.1 Blue Pigments

Chemically considered there are only three inorganic blue pigments: ultramarine blue (Pigment blue 29), cobalt tin blue-gray spinel (Pigment blue 35), and cobalt aluminate blue spinel (Pigment blue 28). The other three pigments (Pigment blue 36:1, blue 36, and blue 72) are modification of Pigment blue 28, in which parts of the cobalt are substituted either alone or in combination with chromium and zinc. These variations differ in their tinting strength and color shade (Table 5.4).

Table 5.4: List of Inorganic Blue Pigments

Product	Formula	Color index number
Cobalt aluminate blue spinel	CoAl_2O_4	Pigment blue 28
Ultramarine blue	$\text{Na}_{6-8}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_n$ ($n = 2-4$)	Pigment blue 29
Cobalt tin blue-gray spinel	Co_2SnO_4	Pigment blue 35
Cobalt chromite blue-green spinel	$\text{Co}(\text{Al},\text{Cr})_2\text{O}_4$	Pigment blue 36
Zinc chrome cobalt aluminum spinel	$(\text{Zn},\text{Co})(\text{Cr},\text{Al})_2\text{O}_4$	Pigment blue 36:1
Cobalt zinc aluminate blue spinel	$(\text{Co},\text{Zn})\text{Al}_2\text{O}_4$	Pigment blue 72

Cobalt aluminate blue spinel (CoAl_2O_4) – Pigment blue 28 / 77346 / CAS 68186.86.7

Cobalt chromite blue-green spinel [$\text{Co}(\text{Al},\text{Cr})_2\text{O}_4$] – Pigment blue 36 / 77343 / CAS 68187.11.1

Zinc chrome cobalt aluminum spinel [$(\text{Zn},\text{Co})(\text{Cr},\text{Al})_2\text{O}_4$] – Pigment blue 36:1 / 77343:1 / CAS 74665.01.3

Cobalt zinc aluminate blue spinel [$(\text{Co},\text{Zn})\text{Al}_2\text{O}_4$] – Pigment blue 72 / 77347 / CAS 68186.87.8

Properties: These four pigments can be summarized because they have the same chemical basis. The basic product, Pigment blue 28, is produced by high-temperature calcination of cobalt (II) oxid (CoO) and aluminum oxide (Al_2O_3). The other variations are produced by a partial substitution of the cobalt by chromium and zinc, either alone or in combination. According to the literature [33] each single pigment can be modified additionally by other metal oxides. The result is a large variety of marketed products. These blue pigments differ in their tinting strength and shades (reddish or greenish blue) depending on the exact chemical composition.

All of them form the crystalline modification of spinel during calcination. They are chemically inert, absolutely insoluble, have a good hiding power and an excellent heat stability, show very good light fastness and weather resistance, and they do not cause warpage in partially crystalline polymers. All toxicological studies showed no signs of toxicity to humans or the environment [5, 29].

In this connection something else should be mentioned. In Germany as well as in some other countries *cobalt as metal, as cobalt oxide or cobalt sulfide* are classified as carcinogenic, for example, in Germany by the “Gefahrstoffverordnung” (dangerous goods ordinance) dated August 16, 1986. The cobalt, however, is incorporated into the crystal lattice of spinel so tightly that it completely loses its typical chemical, physical, and physiological properties. Several toxicological studies proved this [29], and there are no signs of any toxicological or carcinogenic effects. These cobalt-containing blue pigments are consequently not considered as *hardly soluble cobalt compounds* in the sense of this ordinance. This statement is important because many customer requirements prohibit any colorants containing cobalt.

Application: The main use is for light blue colors or pastel shades.

Ultramarine blue ($\text{Na}_{6-8}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_n$) – Pigment blue 29 / 77007 / CAS 57455.37.5

Properties: Ultramarine blue is the most frequently used blue inorganic pigment. The mineral lazurite is chemically very closely related to ultramarine blue, a rock rich in lazurite called lapis lazuli, a semiprecious stone. Powdered lazurite was once the source for the pigment ultramarine. Today it is synthesized by a multistage process. The raw materials are china clay, feldspar, anhydrous sodium carbonate, sulfur, and a reducing agent (oil or coal). The first step is the activation of the clay by heating up to about 700 °C (1292 °F). Then the activated clay is blended with the other raw materials and heated to about 750 °C (1382 °F) under reducing conditions. At this stage the sodium carbonate reacts with the sulfur and in combination with the reducing agent sodium polysulfides are formed. Finally the “raw” ultramarine is purified from byproducts and refined. The refinement is of special importance because the content of free sulfur should be below 5 ppm, otherwise the typical “sulfur smell” occurs during the processing of plastics colored with ultramarine.

The forming of the two sulfur groups S_3^- and S_2^- is responsible for the color. Both groups show the character of a radical, stabilized by lattice entrapment.

Violet ultramarine is produced by heating the blue grade with ammonium chloride at approx. 240 °C (464 °F) in the presence of air. Treating the violet grade with hydrogen chloride (HCl) gas at 140 °C (284 °F) gives the *pink* ultramarine.

Consequently synthetic ultramarine is commercially available in three colors:

- Reddish blue ultramarine – Pigment blue 29 / 77007 / CAS 57455.37.5
- Violet ultramarine – Pigment violet 15 / 77007 / CAS 12769.96.9
- Pink ultramarine – Pigment red 259 / 77007 / CAS 12769.96.9

The color of ultramarine blue is a reddish blue with high tinting strength. Ultramarine blue is insoluble, most grades are easy to disperse in polymer melts, it has a good heat stability, shows a good light fastness and weather resistance, and causes no warpage in partially crystalline polymers [36]. The normal grades of ultramarine blue are sensitive to acids. Acid-resistant grades are coated by silica and are commercially available. The density is 2.35 g/cm³. The ultramarine particles are hard and can cause abrasion.

Ultramarine is safe, and the only known hazard is the evolution of the (poisonous) hydrogen sulfide in contact with acid. The LD₅₀ is > 10,000 mg/kg body weight, rat, oral application; it is nonmutagenic, nonirritant, and nonsensitizing to skin. Because of its insolubility it is not toxic to fish.

Application: Ultramarine blue can be used to color any polymer. In the case of packaging material it is recommended to check the storage stability, because

interactions between the pigment and the filling good cannot be excluded always. This depends on the composition of the filling good.

Cobalt tin blue-gray spinel (Co_2SnO_4) – Pigment blue 35 / 77368 / CAS 68187.05.3

This pigment is produced by high-temperature calcination of cobalt (II) oxide and tin (IV) oxide. It may contain as modifier for the shade Al_2O_3 , Fe_2O_3 , or NiO [33]. Crystal modification: spinel. Its main use is for coloring of ceramic glazes, and is very seldom used in plastics.

5.1.3.2 Brown Pigments

There are numerous brown inorganic pigments on the market. The large number of brown pigments, however, can be synthesized by three processes:

- The rutile crystal lattice (TiO_2) is modified by incorporation of color giving metals such as chromium, nickel, or manganese and to maintain the valence of four the colorless antimony, niobium, or tungsten. The results are yellowish or brownish color shades. Depending on the exact chemical composition they are listed in the color index either as yellow or brown pigment. Figure 5.4 contains the pigments produced according to this principle, and for the purpose of completeness the yellow and brown pigments are listed together.
- The brownish red shade of iron (III) oxide (Fe_2O_3) can be shifted into a dark brown by a partial substitution of the iron by other metals, for example, chromium, manganese, or zinc.
- The result of a partial replacement of chromium by iron, zinc, or manganese (either alone or in combination) in chromium (III) oxide (Cr_2O_3) is a color shift from a dull green to a dark brown.

All these pigments differ in color, color shade, and tinting strength. They are absolutely insoluble, chemically inert, have excellent heat stability, show good light fastness and weather resistance, and do not cause any warpage in partially crystalline polymers. By the incorporation in the host crystal lattice the metals lose their typical chemical, physical, and physiological properties. This is important in the case of the metal oxides of antimony and nickel, which are harmful. The chromium is in the trivalent stage, which is – in contrast to chromium-VI – harmless.

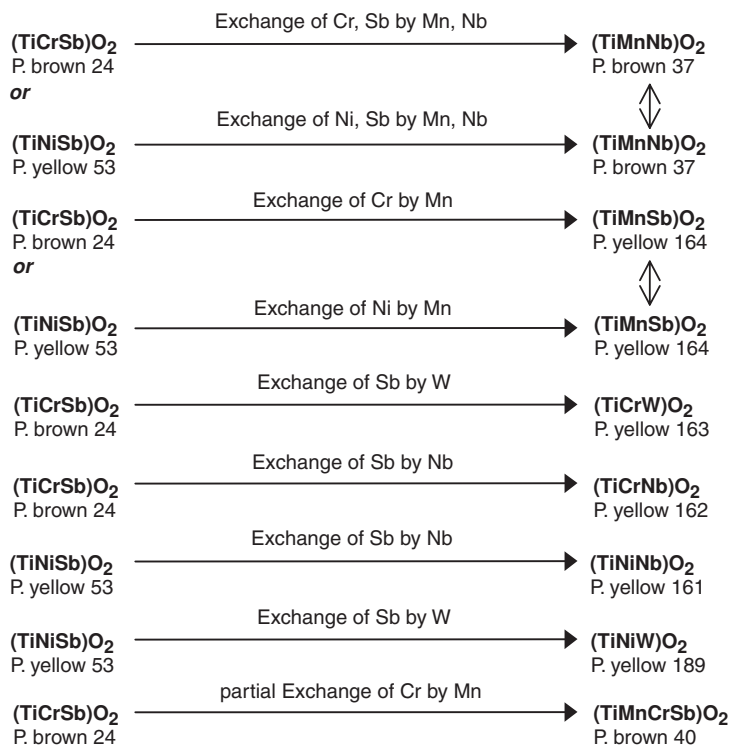


Figure 5.4: Principle of synthesis of inorganic yellow and brown mixed metal oxide pigments

In the past this type of pigment was called a *mixed metal oxide pigment*. This term is misleading, because it is not a mixture in the true sense of the word but is a homogeneous incorporation of colored cations in the crystal lattice. The American Dry Color Manufacturers' Association denotes these colorants now as *complex inorganic color pigments* [33], a term that describes this type of pigment more accurately.

On the other hand intensive brown colors can be achieved by mixing of red and black colorants. Whether it is more favorable to use a brown pigment or a mixture of red and black colorants depends on the shade to be matched. In practice both methods are common.

The commercially available brown pigments for coloring of plastics are listed in Table 5.5.

Table 5.5: List of Inorganic Brown Pigments

Product	Formula	Color index number
Chrome antimony titanium buff rutile	$(\text{Ti,Cr,Sb})\text{O}_2$	Pigment brown 24
Iron chrome oxide	$(\text{Fe,Cr})_2\text{O}_3$	Pigment brown 29
Zinc iron chromite brown spinel	$(\text{Zn,Fe})(\text{Fe,Cr})_2\text{O}_4$	Pigment brown 33
Iron chromite brown spinel	$\text{Fe}(\text{Fe,Cr})_2\text{O}_4$	Pigment brown 35
Manganese niobium titanium brown rutile	$(\text{Ti,Mn,Nb})\text{O}_2$	Pigment brown 37
Chrome manganese zinc brown spinel	$(\text{Zn,Mn})\text{Cr}_2\text{O}_4$	Pigment brown 39
Manganese chrome antimony titanium brown rutile	$(\text{Ti,Mn,Cr,Sb})\text{O}_2$	Pigment brown 40
Iron manganese oxide	$(\text{Fe,Mn})_2\text{O}_3$	Pigment brown 43

Chrome antimony titanium buff rutile $[(\text{Ti,Cr,Sb})\text{O}_2]$ – Pigment brown 24 / 77310 / CAS 68186.90.3

Properties: This pigment is produced by a high-temperature calcination of titanium dioxide (TiO_2), chromium (III) oxide (Cr_2O_3), and antimony (V) oxide (Sb_2O_5) in varying amounts. The chromium cation is responsible for the color shift from the white of the titanium dioxide to this yellow-brown, and the colorless antimony is used to maintain the valence of four. Both metals are incorporated in the crystal matrix of rutile, and at the same time they lose their own typical properties [28, 38]. This is important for antimony because antimony oxide is classified as carcinogenic. This pigment is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are excellent.

All studies showed no toxicological effects [38], and it is considered to be safe in handling and use. Nevertheless the usual precautionary methods for handling of fine powders should be applied to avoid a drying out of the skin, which may open the way for other skin diseases.

Application: Can be used in any type of polymer.

Iron chrome oxide $[(\text{Fe,Cr})_2\text{O}_3]$ – Pigment brown 29 / 77500 / CAS 12737.27.8

Properties: This pigment is produced by a high temperature calcination of chromium (III) oxide (Cr_2O_3) and iron (III) oxide (Fe_2O_3) in varying amounts. It is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are excellent.

Application: Can be used in any type of polymer.

Zinc iron chromite brown spinel $[(\text{Zn,Fe})(\text{Fe,Cr})_2\text{O}_4]$ – Pigment brown 33 / 77503 / CAS 68186.88.9

Properties: This spinel is produced by a high-temperature calcination of zinc oxide (ZnO), iron (II) oxide (FeO), iron (III) oxide (Fe_2O_3), and chromium (III) oxide (Cr_2O_3) in varying amounts [33]. Numerous grades of this pigment are the result of this variation in composition, differing in shade.

This pigment is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

Application: Can be used in any type of polymer.

Iron chromite brown spinel $[\text{Fe}(\text{Fe,Cr})_2\text{O}_4]$ – Pigment brown 35 / 77501 / CAS 38187.09.7

Properties: This pigment is produced by a high-temperature calcination of iron (II) oxide (FeO), iron (III) oxide (Fe_2O_3), and chromium (III) oxide (Cr_2O_3) in varying amounts. It forms the crystal matrix of a spinel. Chemically it could be considered as Pigment brown 33 without zinc.

This pigment is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

Application: Can be used in any type of polymer.

Manganese niobium titanium brown rutile $[(\text{Ti,Mn,Nb})\text{O}_2]$ – Pigment brown 37 / 77890 / CAS 70248.09.8

Properties: This pigment is one of the variations of Pigment brown 24 or yellow 53 (refer to Fig. 5.4). Chromium or nickel are substituted by manganese and antimony by niobium. Crystal matrix: Rutil.

This pigment is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

Application: Can be used in any type of polymer.

Chrome manganese zinc brown spinel $[(\text{Zn,Mn})\text{Cr}_2\text{O}_4]$ – Pigment brown 39 / 77312 / CAS 71750.83.9

Properties: It is produced by high-temperature calcination of chromium (III) oxide (Cr_2O_3), manganese (II) oxide (MnO), and zinc (II) oxide (ZnO) by varying amounts. Spinel. Chemically it may be considered as a kind of variation of Pigment brown 33.

This pigment is absolutely insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

Application: Can be used in any type of polymer.

Manganese chrome antimony titanium brown rutile $[(\text{Ti}, \text{Mn}, \text{Cr}, \text{Sb})\text{O}_2]$ –
Pigment brown 40 / 77891 / CAS 69991.68.0

This pigment is closely related to Pigment brown 24 and is the result of a partial substitution of chromium by manganese (refer to Fig. 5.4). The properties and use are similar to those of Pigment brown 24.

Iron manganese oxide $[(\text{Fe}, \text{Mn})_2\text{O}_3]$ – *Pigment brown 43* / 77536 /
 CAS 12062.81.6

Properties: This pigment can be considered as a variation of Pigment red 101, Fe_2O_3 . By a partial substitution of iron by manganese the color is shifted from a brownish red to brown. This pigment is insoluble, chemically inert, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good. The LD_{50} is > 5000 mg/kg body weight, rat, oral application, and it is not irritating the skin or mucous membrane.

Application: Can be used in any type of polymer. It is recommended, however, to check the grade for soluble manganese ions, because soluble manganese may accelerate the aging of polypropylene.

5.1.3.3 Yellow Pigments

In the past the color yellow was dominated by lead chromate (Pigment yellow 34) and the cadmium pigments (Pigment yellow 35 and yellow 37). Because of toxicological considerations the use of these pigments was banned by several regulations.

Lead chromate is chronically toxic; therefore in the European community it is classified as *category one substance*, which means any part containing more than 0.5% lead must be labeled with the death's head indicating a poison [21].

Guideline EU 91/338 of the European Community bans the use of cadmium pigments in many plastic materials, which are listed in detail. The list includes most of the plastics usually used for packaging material or household goods [39]. For safety reasons, cadmium pigments can be used only if absolutely required.

The use of cadmium, without naming these pigments, is in fact banned by the CONEG-regulation (USA) and the European guideline EU 94/62 in any packaging material in contact with food. These two guidelines limit the total amount of cadmium, lead, chromium (VI), and mercury to 100 ppm in 1 kg (2.2 lb) of the plastic packaging material. This limiting value is far below the concentration required for tinting of plastics. The origin of traces of these elements consequently can be only as impurities of (mainly inorganic) pigments.

As a result of this ban many colors had to be matched anew. The alternative color preparations no longer showed the same properties, such as hiding power and/or fastness properties. In addition the colorist was forced to use organic pigments, which are significantly more expensive than the previously used cadmium and lead pigments. All this caused much work and many discussions with the customer, but finally all problems were solved.

The greenish yellow bismuth vanadate molybdate (Pigment yellow 184) can be considered as a kind of replacement because its coloristic properties resemble those of the cadmium and lead pigments.

The inorganic yellow pigments for coloring of plastics are listed in Table 5.6. For the purpose of completeness the banned cadmium and lead pigments are mentioned also, and in addition it is noticeable that several pigments are variations of Pigment brown 24 or Pigment yellow 53 (refer to Fig. 5.4).

Table 5.6: List of Inorganic Yellow Pigments for Coloring of Plastics

Product	Formula	Color index number
Lead chromate	$\text{Pb}(\text{Cr,S})\text{O}_4$	Pigment yellow 34
Cadmium yellow	CdS	Pigment yellow 35
Cadmium yellow	$(\text{Cd,Zn})\text{S}$	Pigment yellow 37
Iron oxide yellow	$\alpha\text{- or } \gamma\text{-FeO}(\text{OH})$	Pigment yellow 42
Nickel antimony titanium yellow rutile	$(\text{Ti,Ni,Sb})\text{O}_2$	Pigment yellow 53
Zinc ferrite brown spinel	ZnFe_2O_4	Pigment yellow 119
Nickel barium titanium primrose priderite	$2\text{NiO} \cdot 3\text{BaO} \cdot 17\text{TiO}_2$	Pigment yellow 157
Nickel niobium titanium yellow rutile	$(\text{Ti,Ni,Nb})\text{O}_2$	Pigment yellow 161
Chrome niobium titanium buff rutile	$(\text{Ti,Cr,Nb})\text{O}_2$	Pigment yellow 162
Chrome tungsten titanium buff rutile	$(\text{Ti,Cr,W})\text{O}_2$	Pigment yellow 163
Manganese antimony titanium buff rutile	$(\text{Ti,Mn,Sb})\text{O}_2$	Pigment yellow 164
Bismuth vanadate molybdate	$\text{BiVO}_4 / \text{Bi}_2\text{MoO}_6$	Pigment yellow 184
Nickel tungsten yellow rutile	$(\text{Ti,Ni,W})\text{O}_2$	Pigment yellow 189

Lead chromate [$\text{Pb}(\text{Cr,S})\text{O}_4$] – Pigment yellow 34 / 77603 / CAS 1344.37.2

No longer used.

Cadmium yellow [CdS respectively $(\text{Cd,Zn})\text{S}$] – Pigment yellow 35 respectively yellow 37

No longer used.

Iron oxide yellow [α - or γ -FeO(OH)] – Pigment yellow 42 / 77492 / CAS 20344.49.4

Properties: α -FeO(OH) occurs in nature in the form of the mineral goethite and γ -FeO(OH) as lepidocrocite. They differ in their crystal lattices. These iron oxides are synthesized by precipitation and oxidation. The starting material is iron (II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), a byproduct of the titanium dioxide production (sulfate process) or from other sources. The solution of the iron salt is first mixed with alkali and then oxidized, usually with air. The total amount of alkali, reaction time, and temperature are controlled very carefully. This method is one of several processes that yield the yellow pigment α -FeO(OH).

This pigment has limited heat stability, because at higher temperatures it loses water forming the red iron (III) oxide Fe_2O_3 . To improve heat stability, the pigment is coated by a mixture of aluminum and silicon oxides. Such a coated, stabilized pigment shows a heat stability of approx. 260 °C (500 °F), while the heat stability of the unstabilized grade is only approx. 200 °C (392 °F).

Application: The use of this pigment for coloring of plastics is very limited because of the unusual low heat stability of an inorganic pigment. It can be used to color PE-LD or other polymers with similar low processing temperatures.

Nickel antimony titanium yellow rutile [(Ti,Ni,Sb)O₂] – Pigment yellow 53 / 77788 / CAS 71077.18.4

Properties: This pigment is produced by high temperature calcination of titanium dioxide (TiO_2), nickel (II) oxide (NiO), and antimony (V) oxide (Sb_2O_5). It can be considered as base material for other yellow pigments, which are produced by substitution of nickel and/or antimony by other metals (refer to Fig. 5.4).

This pigment is absolutely insoluble and chemically inert, shows a good hiding power, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

The LD_{50} is higher than 5000 mg/kg body weight, rat, oral application, and it does not irritate the skin or mucous membrane [38].

In this connection something else should be mentioned. In Germany but also in some other countries *nickel as metal, as nickel oxide, or as nickel sulfide* is classified as carcinogenic, for example, in Germany by the “Gefahrstoffverordnung” (dangerous goods ordinance) dated August 16, 1986. In addition, nickel is known to be allergenic. The nickel, however, is incorporated into the crystal lattice of rutile so tightly that it completely loses its typical chemical, physical, and physiological properties. Several toxicological studies proved this [28, 29, 38], there are no sign of any toxicological or carcinogenic effects. These nickel-containing

pigments are consequently not considered as *hardly soluble nickel compound* in the sense of this ordinance. This statement is important because many customer requirements prohibit any colorants containing nickel.

Application: Can be used in any type of polymer.

Zinc ferrite brown spinel [(Zn,Fe)Fe₂O₄] – Pigment yellow 119 / 77496 / CAS 68187.51.9

Properties: This pigment is produced by high-temperature calcination of zinc oxide (ZnO), iron (II) oxide (FeO), and iron (III) oxide (Fe₂O₃) in varying amounts. As modifier it may contain in addition Al₂O₃, In₂O₃, NiO, SiO₂, or TiO₂ [33]. Crystal matrix: Spinel.

This pigment is absolutely insoluble and chemically inert, shows a good hiding power, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

The LD₅₀ is higher than 2000 mg/kg body weight, rat, oral application, and it does not irritate the skin or mucous membrane [5].

Nickel barium titanium primrose priderite (2NiO·3BaO·17TiO₂) – Pigment yellow 157 / 77900 / CAS 68610.24.2

Properties: This pigment is produced by high-temperature calcination of nickel oxide (NiO), barium oxide (BaO), and titanium oxide (TiO₂) in varying amounts. Crystal matrix: Priderite.

This pigment is absolutely insoluble and chemically inert, shows a good hiding power, and does not cause any warpage in partially crystalline polymers. The fastness properties are very good.

Application: Can be used in any type of polymer.

The following five yellow pigments can be considered as variations of Pigment brown 24 and/or Pigment yellow 53. They are the result of a partial or complete substitution of the coloring metals chromium, nickel, or antimony, which is necessary to maintain the valence of four, by other metals (refer to Fig. 5.4). These pigments differ in their shades and tinting strength. All pigments form the crystal matrix of rutile. All other properties are very similar and comparable to Pigment brown 24 and Pigment yellow 53.

Nickel niobium titanium yellow rutile [(Ti,Ni,Nb)O₂] – Pigment yellow 161 / 77895 / CAS 68611.43.8

In this pigment the antimony of Pigment yellow 53 is substituted by niobium. Its tinting strength is slightly higher than those of Pigment yellow 53.

Chrome niobium titanium buff rutile $[(\text{Ti,Cr,Nb})\text{O}_2]$ – Pigment yellow 162 / 77896 / CAS 68611.42.7

In this pigment the antimony of Pigment brown 24 is substituted by niobium.

Chrome tungsten titanium buff rutile $[(\text{Ti,Cr,W})\text{O}_2]$ – Pigment yellow 163 / 77897 / CAS 68186.92.5

In this pigment the antimony of Pigment brown 24 is substituted by tungsten.

Manganese antimony titanium buff rutile $[(\text{Ti,Mn,Sb})\text{O}_2]$ – Pigment yellow 164 / 77899 / CAS 68412.38.4

The substitution of the coloring metal chromium (Pigment brown 24) or nickel (Pigment yellow 53) by manganese leads to this pigment.

Nickel tungsten yellow rutile $[(\text{Ti,Ni,W})\text{O}_2]$ – Pigment yellow 189 / 77902 / CAS 69011.05.8

In this pigment the antimony of Pigment yellow 53 is substituted by tungsten.

Bismuth vanadate molybdate $(\text{BiVO}_4/\text{Bi}_2\text{MoO}_6)$ – Pigment yellow 184 / – / CAS 14059.33.7

Properties: Two types of pigments are marketed commercially. The composition varies between a modified BiVO_4 and a two-phase pigment bismuth vanadate molybdate, $4\text{BiVO}_4 \cdot 3\text{Bi}_2\text{MoO}_6$, depending on the supplier. The grades for coloring of plastics are stabilized by coating mainly with silicates but also in combination with other inorganic oxides (boron, aluminum, and zinc oxides). These oxides form a glasslike coat, which improves the heat stability. During the production of a color preparations but also later during the coloring of plastics it is important to avoid excessive shear, otherwise the heat stability decreases. The data for heat stability varies between 280 °C (536 °F) and 300 °C (572 °F) depending on the supplier and type of stabilization. Bismuth vanadate is a pigment with a brilliant greenish yellow color, and shows a high tinting strength and good hiding power. The light fastness and weather resistance (4–5 on the gray scale, 2 years Florida) is good both in pure tone and in white reduction with titanium dioxide. The density is approx. 7.7 g/cm³; it is a rather heavy pigment. The refractive index is approx. 2.45. Bismuth vanadates are insoluble and resistant to acids and alkalis. This pigment does not cause warpage in partially crystalline polymers.

The LD₅₀ value is higher than 5000 mg/kg body weight, rat, oral application; it does not irritate the skin or mucous membrane, and it is not sensitizing (test animal guinea pigs). Long-term inhalation studies (3 months) showed some toxic effects in the lungs of rats, probably caused by the content of Vanadium (V) oxide

[5, 7]. Minimizing any risk, it is delivered in a relative coarse, dust-free form; in addition the usual precaution methods for handling of dusts are recommended. The pigment is insoluble and therefore it can be easily separated from waste water.

Application: It can be used in many plastics but not in the engineering plastics because of the limited heat stability of this pigment. In case of doubt it is recommended that a heat stability test be run in the intended plastic material prior to color matching.

5.1.3.4 Green Pigments

Green colorants for coloring of plastics are rare, regardless of their chemistry. There are only three inorganic pigments and one organic green pigment (phthalocyanine green, two different shades). The most important inorganic green pigment is chromium (III) oxide (Table 5.7).

Table 5.7: List of Inorganic Green Pigments

Product	Formula	Color index number
Chromium green-black hematite	Cr_2O_3	Pigment green 17
Cobalt chromite green spinel	CoCr_2O_4	Pigment green 26
Cobalt titanate green spinel	$(\text{Co,Ni,Zn})_2\text{TiO}_4$	Pigment green 50

Green shades can be achieved also by a subtractive color mixing, which means by mixing of a yellow and blue pigment.

Chromium oxide green (DCMA designation: Chromium green-black hematite)
 $[\text{Cr}_2\text{O}_3]$ – Pigment green 17 / 77288 / CAS 68909.79.5

Properties: This pigment is produced by reduction of alkali dichromate or by thermal decomposition of ammonium dichromate and subsequent calcination. If potassium dichromate is used as the starting material instead of sodium dichromate, a green pigment with a more bluish tint is obtained. In addition the pigment can be modified by precipitation of hydroxides of, for example, titanium or aluminum before the calcination. The result is a green pigment with a more yellowish shade. Regardless of the production method used, the resulting chromium (III) oxide pigment must be free of chromium (VI), which is harmful. The grades of chromium (III) oxide for coloring of plastics contain usually < 5 ppm of chromium (VI).

In this connection it is very important to accentuate that the chromium of this green chromium oxide is trivalent. Trivalent chromium oxide is considered harmless. No toxicological or carcinogenic effects were detected in rats receiving up to 5% chromium (III) oxide in their feed [54]. The LD₅₀ value of chromium (III) oxide is > 5 000 mg/kg body weight, rat, oral application, and it does not irritate the skin or mucous membrane. Trivalent chromium belongs to the essential trace elements for humans and animals. Animal experiments proved that a shortage of chromium leads to deficiency symptoms and even deficiency diseases.

Sixvalent chromium compounds, the so-called chromates (e.g., lead chromates) are classified as toxicological and carcinogenic.

The toxicity of chromium compounds depends on the valence of the chromium; therefore it is of great importance to differentiate always between the safe chromium (III) and the harmful chromium (VI) valence.

Chromium (III) oxide is insoluble and chemically inert. The green shade is rather dull, and therefore it cannot be used for brilliant green color shades. The pigment has a high tinting strength and good hiding power. The heat stability, light fastness, and weather resistance are very good. It does not cause any warpage in partially crystalline polymers.

Chromium (III) oxide crystallizes in the rhombohedral structure of the corundum type. This type of crystal lattice is known for its hardness, consequently chromium (III) oxide is a very hard (Mohs hardness ca. 9) and abrasive pigment. This must be taken into account in its use as a colorant, especially at higher concentrations in a color preparation. Wear and tear take place not only during the production of the color preparation but also during the coloring process of plastics.

Application: Can be used in any type of polymer.

Cobalt chromite green spinel (Co₂Cr₂O₄) – Pigment green 26 / 77344 / CAS 68187.49.5

Properties: This pigment is produced by high-temperature calcination of cobalt (II) oxide (CoO) and chromium (III) oxide (Cr₂O₃) in varying amounts. To modify the color shade, this pigment may contain also aluminum oxide (Al₂O₃), magnesium oxide (MgO), silica (SiO₂), zinc oxide (ZnO), or zirconium dioxide (ZrO₂), either alone or in combination. These variations are included in the designation Pigment green 26. Depending on the exact composition the commercially available pigments differ in tinting strength and shade.

These pigments are insoluble and chemically inert. Their tinting strength is low, but their hiding power is good. The heat stability, light fastness, and weather resistance are very good. They do not cause any warpage in partially crystalline polymers.

Application: Can be used in any type of polymer for light green colors or pastel shades.

Cobalt titanate green spinel $[(\text{Co}, \text{Ni}, \text{Zn})_2\text{TiO}_4]$ – Pigment green 50 / 77377 / CAS 68186.85.6

Properties: The basic formula is Co_2TiO_4 , but in the commercially available pigments for the coloring of plastics, parts of the cobalt are substituted by other metals, mainly nickel and zinc, but also by iron and other oxides. The marketed grades differ by their shades.

These pigments are insoluble and chemically inert. Their tinting strength is low, but their hiding power is good. The heat stability, light fastness, and weather resistance are very good. They do not cause any warpage in partially crystalline polymers.

Application: Can be used in any type of polymer for light green colors or pastel shades.

5.1.3.5 Red/Orange Pigments

For many years these two colors were dominated by cadmium pigments and lead chromates, which have been banned because of toxicological and ecological considerations. The reasons for this ban were explained in section 5.1.3.3.

Today the red iron (III) oxides and the newly developed cerium sulfide pigments are the only commercially available inorganic red and orange pigments for coloring of plastics (Table 5.8).

Table 5.8: List of Inorganic Red/Orange Pigments

Product	Formula	Color index number
Cadmium red	$\text{Cd}(\text{S}, \text{Se})$	Pigment orange 20
Cerium sulfide	*	Pigment orange 75
Cerium sulfide	*	Pigment orange 78
Iron brown hematite	$\alpha\text{-Fe}_2\text{O}_3$	Pigment red 101
Lead chromate molybdate	$\text{Pb}(\text{Cr}, \text{Mo}, \text{S})\text{O}_4$	Pigment red 104
Cadmium red	$\text{Cd}(\text{S}, \text{Se})$	Pigment red 108
Cerium sulfide	*	Pigment red 265
Cerium sulfide	*	Pigment red 275

* The exact chemical composition is not yet published.

Cadmium red [Cd(S,Se)] – Pigment orange 20 and Pigment red 108

No longer used.

Lead chromate molybdate [Pb(Cr,Mo,S)O₄] – Pigment red 104 / 77605 / CAS 12656.85.8

No longer used.

Iron brown hematite (Fe₂O₃) – Pigment red 101 / 77491 / CAS 1309.37.1

Properties: Iron oxide is widespread in nature; whole regions are colored red by iron oxide in the soil. In prehistoric times naturally occurring iron oxides were used, together with other oxides, for rock and cave paintings. Today the natural iron oxide cannot be used as a colorant because of its impurities, for example, crystalline silicon dioxide and other heavy metals. The synthesized iron oxide is produced by two different processes:

- Precipitation and hydrolysis of solutions of iron salts
- Laux process involving reduction of nitrobenzene

The starting material for the *precipitation process* is very often an aqueous solution of FeSO₄, which is a byproduct of the titanium dioxide sulfate process. The bivalent iron is oxidized first, then hydrolyzed, and the yellow FeO(OH) precipitated. A subsequent high-temperature calcination transforms the FeO(OH) into the red iron oxide by separation of water [40].

In the *Laux process* nitrobenzene is reduced by metallic iron. It was used to produce aniline and the iron oxide had more the character of a (valuable) byproduct. Aniline has lost much of its former importance because of its classification as a carcinogenic substance.

The shade of the iron oxide depends on the purity of the iron, the process parameter, and particle size. It varies between red and red-brown.

Iron oxide is insoluble. It does not cause any warpage in partially crystalline polymers. It has an excellent heat stability, a high tinting strength and a good hiding power, and very good light fastness and weather resistance. Iron oxide is considered to be safe for humans, and belongs to the essential trace elements for the body, as proved by many toxicological studies.

Application: Iron oxide can be used in almost every polymer. One exception is poly(vinyl chloride) (PVC), especially in outdoor applications. Iron oxide in combination with traces of HCl, always present in PVC, and humidity causes a decomposition of PVC.

Cerium sulfide – Pigment red 265 / 77283-2 / CAS 12014.93.6

Pigment red 275 / 77283-0 / CAS 12014.93.6

Pigment orange 75 / 77283-1 / CAS 12014.93.6

Pigment orange 78 / 772850 / CAS 12014.93.6 + 12031.49.1

Properties: Cerium sulfide pigments are a very new development and have been commercially available for about 2 years. Their exact chemical structure is not yet published. The different color index numbers and CAS numbers indicate chemical differences, but the exact types of differences are not quite clear.

The thermal stability of *pure* cerium sulfide is not sufficient for coloring of plastics, but the supplier found a possibility to stabilize them. According to their data sheets the heat stability of those stabilized grades is about 290–310 °C (554–560 °F), which is sufficient for several plastics [41]. Cerium sulfide has a good tinting strength and hiding power, shows good light fastness and weather resistance, and does not cause warpage in partially crystalline polymers. It is a relatively hard pigment, with a Mohs hardness of 4–5.

Cerium sulfide is not stable in (strong) acids; one reaction product is the gaseous, poisonous hydrogen sulfide (H_2S). This sensitivity to acids should be taken into consideration during storage, handling, and processing, and also when cerium sulfide is used as a colorant in packaging material. It is recommended to check the packaging material in combination with the filling good prior to use.

Application: It can be used in several polymers but not in all types because of the limited heat stability. In case of doubt preliminary tests are recommended.

5.1.3.6 Violet Pigments

The most important violet pigment is ultramarine violet, the other pigments can be used only for light violet colors or pastel shades owing to their lack of a high tinting strength. Some of the violet pigments are used as *decolorizers* of plastics. Owing to the synthesis of polymers, they very often have a very weak, mainly yellowish tint as their own color, which can be covered by these violet pigments. The result is a “colorless polymer” (Table 5.9).

Table 5.9: List of Inorganic Violet Pigments

Product	Formula	Color index number
Cobalt violet phosphate	$\text{Co}_3(\text{PO}_4)_2$	Pigment violet 14
Ultramarine violet	$\text{Na}_{6-8}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_n$ ($n = 2-4$)	Pigment violet 15
Manganese ammonium polyphosphate	$\text{NH}_4\text{MnP}_2\text{O}_7$	Pigment violet 16
Cobalt lithium violet phosphate	CoLiPO_4	Pigment violet 47
Cobalt manganese red-blue borate	$(\text{Co,Mg})_2\text{B}_2\text{O}_5$	Pigment violet 48

Cobalt violet phosphate [$\text{Co}_3(\text{PO}_4)_2$] – Pigment violet 14 / 77360 / CAS 13455.36.2

Properties: It is produced by a high-temperature calcination of cobalt (II) oxide (CoO) and phosphorus (V) oxide (P_2O_5). The pigment is stable in acids and alkalis, but unstable in water (hydrolysis). It possesses a very low tinting strength.

Application: Can be used only for light violet shades and/or pastel shades in various polymers, and is used as decolorizer.

Ultramarine violet ($\text{Na}_{6-8}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_n$) – Pigment violet 15 / 77007 / CAS 12769.96.9

Properties: Ultramarine pigments were described in the section on blue pigments (compare Pigment blue 29). It is the most important violet pigment. It has a good tinting strength and good light fastness and weather resistance.

Violet ultramarine is produced by heating the blue grade with ammonium chloride at approx. 240 °C (464 °F) in the presence of air. The heat stability of the violet ultramarine is, however, slightly lower in comparison to the blue grade, but still high enough for various polymers.

Application: Analogous to the blue grade, it can be used for coloring of many polymers.

Manganese ammonium polyphosphate ($\text{NH}_4\text{MnP}_2\text{O}_7$) – Pigment violet 16 / 77742 / CAS 10101.66.3

Properties: This pigment was used already about 1900. It is produced by heating a suspension of manganese salts, manganese oxide, phosphorus acid, and ammonium salts of phosphorus acids and a subsequent calcination.

It is insoluble in water and organic solvents. It is stable in acids but not very stable in alkali. The sensitivity to alkali should be taken into consideration when it is

used as a colorant in packaging materials. The heat stability is good ($> 300^{\circ}\text{C}$), it shows a good light fastness. The tinting strength is on the weak side. It is considered to be safe for humans, which is underlined by its use as colorant in cosmetics, for example, in lipsticks.

Application: The use is limited owing to its low tinting strength, it is used for light violet shades and/or pastel shades, and can be applied in various polymers.

Cobalt lithium violet phosphate (CoLiPO_4) – Pigment violet 47 / 77363 / CAS 68610.13.9

Properties: It is produced by a high-temperature calcination of cobalt (II) oxide (CoO), lithium oxide (LiO), and phosphorus (V) oxide (P_2O_5). It can be considered as a variation of Pigment violet 14. The tinting strength is very low.

Application: Can be used in very light violet shades, and predominantly as a decolorizer.

Cobalt magnesium red-blue borate $[(\text{Co,Mg})_2\text{B}_2\text{O}_5]$ – Pigment violet 48 / 77352 / CAS 68608.93.5

Properties: It is produced by a high-temperature calcination of cobalt (II) oxide (CoO), magnesium oxide (MgO), and boron (III) oxide (B_2O_3). Its tinting strength is very low.

Application: Can be used in very light violet shades, and predominantly as a decolorizer.

5.1.4 Pearlescent Pigments

Pearlescent pigments are produced by coating of mica with titanium dioxide (silvery shiny pearlescent pigments) or other metal oxides, for example, iron oxide, either alone or in combination with titanium dioxide. The results of the second method are the colored pearlescent pigments.

The idea behind the pearlescent pigments is to imitate the natural pearl luster. A pearl is formed when a grain of sand enters a mussel. The grain of sand is a foreign body in the mussel, and as a kind of resistance, the mussel coats the grain of sand with alternating layers of calcium carbonate and protein. These layers differ in their refractive indices. Parts of the light are reflected, and other parts pass on to the next layer, and this is repeated on each following layer. The visual effect of pearl luster is produced by this multiple reflection and transmittance of the (sun) light on these thin layers (Fig. 5.5) [42].

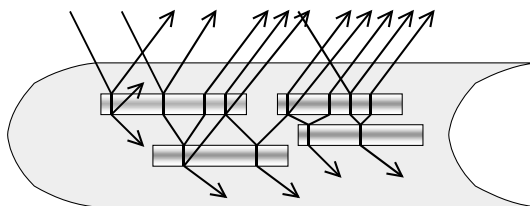


Figure 5.5: Schematic drawing of the process of multiple reflection and transmittance

The pearlescent pigments are produced by coating of thin mica platelets with an exactly defined and controlled layer of titanium dioxide. During the subsequent calcination the titanium dioxide forms the anatase modification. The light fastness of this grade of pearlescent pigments is not sufficient for several applications, for example, for a nonfading coloring of polymers. Pearlescent pigments with a good light fastness are produced when the mica is first coated by a thin layer of tin dioxide (SnO_2), which catalyzes the formation of the rutile modification. This grade of pearlescent pigments contains between 1 % and 2 % of tin dioxide.

The effect of pearlescent pigments depends on the particle size distribution of the mica used as carrier. The optical impression varies from a silvery pearl luster to a bright sparkling.

The commercially available pearlescent pigments for coloring of polymers usually have the following particle size distribution:

- 5–25 μm $\Rightarrow$ silvery shining with a distinct pearl luster
- 10–50 μm $\Rightarrow$ brilliant shining
- 30–150 μm $\Rightarrow$ bright sparkling

The thickness of the titanium dioxide layer is between 40 and 60 nm in these silvery pearlescent pigments.

An increase of the TiO_2 layer thickness leads to *interference pearlescent pigments*. In this case the color effects depend on the angle of vision. This kind of pigment plays no role in the coloring of plastics, and is used mainly in cosmetics.

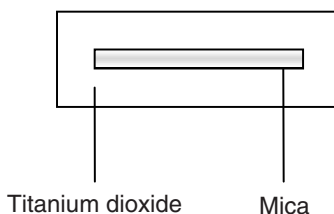
Colored pearlescent pigments are produced by exchange of the titanium dioxide by another metal oxide, for example, iron oxide. Depending on the layer thickness of the iron oxide the color varies with increasing layer thickness from bronze, over copper-red, red, red-violet to a red-green. The color effect is the result of a combination of light absorption and interference.

Besides these monolayer pearlescent pigments, there are multilayer pigments, which are called *combination pearlescent pigments*. They are produced by a stepwise process. First the mica is coated with titanium dioxide, and on top of it a

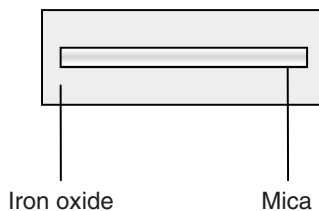
second layer is applied. Iron oxide as a second coat gives gold-colored pigments, while chromium (III) oxide gives green-colored pigments with varying shades of green. The intensity of the golden shade increases with increasing layer thickness of the iron oxide (Fig. 5.6).

Monolayer pearlescent pigments

Silvery pearlescent pigments



Colored pearlescent pigments



Combination pigments

Golden colored pigments

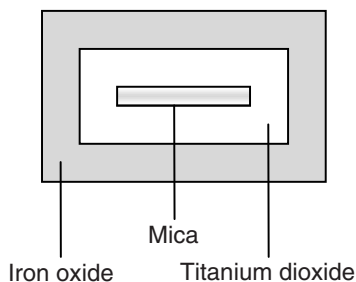


Figure 5.6: Principles of composition for different pearlescent pigments

All three types of pigments, the silvery, the colored monolayer, and the colored combination pearlescent pigments are applied for coloring of plastics, either alone or in combination. Very interesting color effects can be achieved by mixing them with organic colorants, with metal effect pigments, and/or with traces of carbon black. There are really no limits to the creativity of the colorist.

The intensity of luster and sparkling effect are greater the better the transparency of the polymer is. In opaque or reinforced plastics it is very hard to achieve a really satisfying effect. As a kind of compromise a very opaque polymer can be painted with a lacquer-containing pearlescent pigment, but this is very seldom done because of the cost.

The mica platelets are fragile, and therefore a few precautions methods are unavoidable. A critical point is the production of a masterbatch. For a good dispersing of any pigment in a polymer melt a certain amount of shear is absolutely necessary. On the other hand any excessive shear will damage the original particle size distribution of the pearlescent pigment. For the manufacture of a masterbatch containing pearlescent pigments the use of a corotating extruder is recommended, because the shear in such an extruder is less than in a counterrotating extruder. In addition the processing parameter of the extruder must be adjusted to avoid unintentional damage. The danger of unintentional damage increases with increasing particle size of such an effect pigment.

The damage of pearlescent pigments in a extruder is noticed very easily. The silvery pigments lose their silvery luster, which turns to a more or less dull gray, and a colored pearlescent pigment changes its shade, which can be noticed in comparison to the original pigment. The practice shows that the damage of pearlescent pigments can be minimized but not completely avoided during the production of a masterbatch.

The next critical point is the addition of such a masterbatch during the coloring of the final product, especially when a pin gate and/or a hot runner is used. The diameter of the pin gate and/or the channel of the hot runner must be large enough to avoid excessive shear, otherwise a damage of the pigments is unavoidable. If needed the diameters should be adjusted to the particle size of the pearlescent pigment.

An incomplete dispersion of pearlescent pigments in a masterbatch causes specks of agglomerated pigments later on during the manufacture of the final product. This is not only a visual defect, but also can cause holes in a thin-walled packaging material, and liquid filling goods may leak out.

The pearlescent pigments are tiny platelets. To reach an optimum of optical effect, special care has to be given to ensure a parallel alignment of the platelets during application. This can be influenced by the mold construction. One important point

is the position of the gate, and another is the design of the part as such. In practice, however, the normal procedure is to use an already existing mold. Many colors of plastic articles, especially for household and personal use, depend on the fashionable colors, which change on a yearly basis. In the worst case the use of an existing mold can exclude the application of pearlescent pigments because the effect is not satisfying enough.

All effective pigments, pearlescent pigments are no exception, possess an unpleasant property, the occurrence of flow lines. Parallel alignment of the pigment is hindered in the front area of a polymer melt, and a disorientation of the platelets takes place. The result is flow lines. All shapes, except the spherical, show this physical phenomenon.

Experience shows that plastic articles with functional gaps are usually not colored with pearlescent pigments. The polymer melt is divided at the gap, and both parts join again behind it. In this area of confluence the flow lines are too clearly visible.

Flow lines are a disturbing visual effect. Their appearance can be minimized but not completely avoided. Several methods are described, and the most important one are:

- Use of a polymer with a higher melt viscosity
- Increase of pigment concentration
- Change the position of the feed point in such a way that the flow line moves toward an invisible part
- Increase the injection rate in combination with a larger gate
- Change processing parameters (temperature, time, etc.)

In many cases first a combination of these actions is successful in minimizing the visually disturbing flow lines.

5.1.5 Metal Effect Pigments

More and more, plastics are replacing metals as constructing materials. The reasons are manifold, but the result is always an improvement. Possible reasons are:

- Saving of weight – plastic parts are much lighter than metallic parts, they are easier to handle and to manufacture; in addition they save energy because of the weight reduction (e.g., car industry).
- Fulfilling of specific mechanical, physical and/or chemical requirements of the part – an important fact within many industries.
- Question of design – many items of our daily life, household appliances, entertainment equipment, today are made of plastics.

In connection with colors the last reason is of special importance. The thermoplastic processing of plastics allows well designed items that please our senses in addition to other advantages, for example, lighter weight, easier to handle, more convenient, and so forth. Now shapes are possible that previously had been impossible in metal as constructing materials because of the comparable difficult processing of metal. On the other hand the new plastic goods should resemble the earlier metal parts. This goal is reached by a coloring of plastics with metal effect pigments. There are two chemical different types, pure aluminum and copper alloys, mainly bronze (copper/tin alloy) and brass (copper/zinc alloy).

Aluminum (Al) – Pigment metal 1 / 77000 / CAS 7429.90.5

Aluminum is marketed in two different shapes, as a powder and as tiny platelets. The particle size of the powder ranges from approx. 15 μm up to approx. 200 μm . The platelets are produced by stamping out different shapes, and their thickness depends how thin the original aluminum foil is rolled out. The shape chosen can be a polygon, rectangle, or square, in varying sizes.

Very fine aluminum is sensitive to oxygen, and on the surface a thin layer of aluminum oxide is formed by oxidation. In this way the aluminum loses its rich luster, and it becomes matte. To protect the surface for oxidation, the aluminum is coated by a thin layer of a transparent lacquer, and it keeps its rich luster.

Another type of effect pigment is based on this technique. The aluminum platelets can be coated also with a colored lacquer instead of a transparent type. The result is a colored *speckled effect pigment*. This type of effect pigments is available in all primary colors, including black. These platelets are sensitive to shear and temperature; therefore precautionary methods have to be implemented to avoid any damage. Analogous to pearlescent pigments one method is to avoid excessive shear, therefore the use of a corotating extruder is recommended during the manufacture of a masterbatch containing this type of pigment. Excessive shear can cause a separation of the colored layer from the aluminum platelets, and the shiny aluminum appears again. This can be noticed very easily under a microscope. Another kind of damage is caused by (excessive) temperature.

The heat stability of the lacquer is not always sufficient, especially in plastics that require higher processing temperatures. The colored lacquer layer weakens, separates from the aluminum platelets, and is dispersed in the polymer melt. The result is a discoloration of the basic color of the plastic part, for example, a white as basic color turns into a gray.

Very fine, pure aluminum powder is explosive. To reduce the risk of explosion during handling, the grades for the coloring of plastics are delivered in a harmless form. There are several possibilities to reach this goal. One possibility of stabili-

zation is to mix the aluminum powder with solvents such as paraffin oil. These pastes contain between 60% and 80% aluminum. Another method, specially developed for the coloring of plastics, is the incorporation of the aluminum powder in a plastic matrix at the site of the supplier. Such concentrates contain 70–80% aluminum in different types of polymer matrix, and corresponding to the production method the results are longish, cylindrical pellets. The type of polymer matrix has to be considered when such a concentrate is applied in a masterbatch. In addition to these stabilized grades of aluminum, unstabilized, pure, dust-free grades of aluminum powder are marketed.

There is no general guideline for the selection of the most suitable grade of aluminum effect pigment for a masterbatch. The grade depends on the intended effect. For the manufacture of a highly concentrated masterbatch an aluminum paste and/or the concentrate is advantageous. For specific effects sometimes only a small amount of aluminum effect pigment is required in combination with an organic colorant. In such a case the pure aluminum powder may be advantageous. The coarse concentrate (the pellets) can cause problems in regard to a homogeneous distribution of the aluminum in a masterbatch, and the paraffin oil of a paste may hinder a complete dispersing of the organic colorant.

The intensity of luster and sparkling effect is greater the better the transparency of the polymer is. In opaque or reinforced plastics it is very difficult to achieve a really satisfying effect. As a kind of compromise a very opaque polymer may be painted with a lacquer containing these aluminum pigments, but this is very seldom done because of the costs.

All effect pigments, including aluminum pigments, possess an unpleasant property, the occurrence of flow lines (compare pearlescent pigments).

The heat stability, hiding power, and fastness properties of aluminum pigments are very good.

Copper alloys (bronze / brass) – Pigment metal 2 / 77400

The two copper alloys, bronze (copper/tin alloy) and brass (copper/zinc alloy), are applied as metallic effect pigments. Similar to aluminum they are sensitive to oxygen and in addition to gaseous contamination of the environment. By attack of oxygen and other gases, oxides and sulfides are formed on the surface of these pigments, which cause a discoloration and loss of luster. But there is also another reason for discoloration. These pigments may react with other components of a color preparation.

In theory this sensitivity can be eliminated by a change of the composition of these alloys. In practice, however, this is not possible. One reason is the color shade of those alternative alloys would move from the wanted “warm” copper

shade to an unpleasant “cold” white shade. The other reason is a technical one. The hardness of those alternative alloys increases considerably, and they are too hard for milling or other ways of cutting into a powdery form.

The bronze and brass pigments are coated with a thin layer of a transparent lacquer or are incorporated in a polymer matrix [43], the same methods of protection that are applied to stabilize the aluminum pigments. The behaviors of these bronze and brass pigments are consequently the same regarding handling, concentration, and application in a masterbatch.

Bronze and brass pigments are marketed in different particle sizes, which varies between very fine (approx. 5–10 μm) and very coarse (approx. 200–300 μm).

Their shades differ depending on the composition. Their heat stability, hiding power, and fastness properties are very good. The intensity of luster and sparkling effect is greater the better the transparency of the polymer is. In opaque or reinforced plastics it is very difficult to achieve a really satisfying effect. As a kind of compromise a very opaque polymer may be painted with a lacquer containing these pigments, but this is very seldom done because of the costs.

All effect pigments, including copper alloys, possess an unpleasant property, the occurrence of flow lines (compare pearlescent pigments).

The intensity of the metallic effect depends on the particle size, and therefore it can be adjusted. Very fine metal effect pigments create a very homogeneous optical impression, combined with a very good hiding power, while coarse metal effect pigments give a lighter color with a clear sparkling effect.

5.1.6 Conductive Pigments

In many fields of technology electrostatic electricity is a large security risk. Plastics are known as very poor conductors of electricity, including of course also the electrostatic electricity. To avoid any risk, the plastic parts must be equipped with antistatic and/or conductive substances. This includes plastic objects such as floors, floor coverings, cases, instruments, packaging material, container, pipes, and so forth, to name only a few. Whether an antistatic or conductive supplementation of the object is necessary depends on the classification of the area of use and the legal conductivity requirements, for example, any part in an ex area has to be conductive equipped. One way of course is to replace plastics as constructing material with metal. This is seldom possible, and therefore the plastics have to be supplemented with either an antistatic or conductive substance. Several inorganic substances, including inorganic pigments, can be used for this purpose:

- *Metal effect pigments* – their application as conductive pigment requires concentrations in plastics that are considerably higher in comparison to a use

as colorant. The concentration must be in a range in which the pigments touch each other; the part is then conductive.

- *Carbon black* – various conductive grades of carbon black are marketed. Such objects have a visual disadvantage, as they are always black.
- *Coated mica platelets* – using the technology of pearlescent pigment manufacture, mica can be coated principally with any metal oxides. Two types of conductive pigments are marketed, a gray and a transparent type. Gray conductive types are made by coating the mica with titanium dioxide and silicon dioxide and on top a layer of tin dioxide doped with antimony oxide. In the case of transparent conductive types the mica platelets are coated directly with tin dioxide doped with antimony oxide. Pure tin dioxide is an isolator, but becomes a semiconductor by doping with antimony oxide. These pigments do not have the disadvantage of the black color, and can be used in objects with light colors. At a minimal concentration of 3% there are already effects of conductivity, but higher concentrations are recommended [52]. Mica platelets are sensitive to shear. As described previously in the section on pearlescent pigments, the same precautionary methods should be used during the incorporation in a polymer melt.
- *Metal fibers* – glass fibers are very common to reinforce plastics. Using the same technology of incorporation, the glass fibers can be replaced by metal fibers. This replacement leads to a conductive object provided that the concentration is high enough for the fibers to touch each other.

The best way to achieve the required conductivity cannot be predicted, as too many applications and specific requirements are involved.

5.1.7 Pigments for Laser Marking

There are several reasons why technical components have to be marked, and the question of product liability is certainly one of them. The use of a laser for labeling and marking has gained much acceptance, especially if the traditional printing process cannot be applied because of the surface shape, size, and/or construction of the part. At first glance the marking, labeling, and decorating of plastic products with a laser seems to be rather easy. The laser beam is focused by an optics, which through computer control directs the beam toward the component to be marked. Under the influence of the heat, generated by the impact of the laser beam, the surface of the plastic component is changed, and the result is a marking in this area. In practice, however, it is more complicated. For a successful application of a laser several preconditions must be fulfilled, and in addition all parameters must be coordinated with each other.

The most important parameters are:

- Type of plastic to be marked
- Colorants in the plastic
- Additives in the plastic
- Construction and operating mode of the laser
- Size and shape of the component to be marked
- Type and size of the required marking

The surface of the plastic component is changed by the impact of the laser beam. The following three alterations of the surface can occur:

- A thin layer of foam is formed by the heat, developed during the impact of the laser beam.
- A thin layer is cleared away; the result is an engraving.
- The absorbed energy of the laser beam damages the surface of the plastic component. This process is called carbonization.

These three alterations are shown schematically in Fig. 5.7.

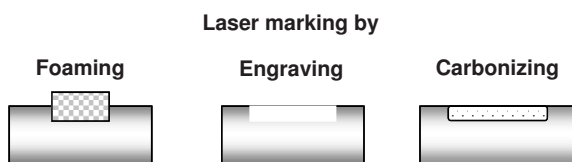


Figure 5.7: Alterations of the plastic surface by a laser beam

Carbonization is not only the simplest method of marking but also the most frequently used one. By carbonizing a dark writing is created on a preferably light colored plastic component. The maximal contrast appears on a white background. Suitable plastics for this method are polymers containing aromatic groups, for example, polycarbonate (PC) and polyester (PET, PBT). The intensity of the writing can be increased by special additives, and the marking then appears nearly black. One additive frequently used for laser marking is modified pearlescent pigments. In the presence of a modified pearlescent pigment other polymers such as polyolefins (PO) and acrylonitrile-butadiene-styrene (ABS) can be marked by carbonization. The marking of these polymers requires a concentration of at least 0.1% of these modified pearlescent pigments. Higher concentrations are preferred because the legibility of the marking then increases.

Besides these modified pearlescent pigments there are still other additives in use, for example, modified aluminum flakes.

A colored marking is possible when the polymer contains two colorants with different sensitivities to laser light. One possibility is to color the plastic component with a combination of a colorant that is not sensitive to laser light and a special grade of carbon black that is sensitive to laser light. The carbon black is cleared away completely by the impact of the laser beam, and the colored background appears. This process, however, requires that no carbonization occurs, which would cover the colored mark. This method is applied preferably to mark polyacetal (POM), in the case of polyolefins the marking is not very clear.

Another possibility to achieve a white writing on a black background is to apply a thin layer of a black foil on top of a white colored component. By a complete clearing away of the black foil by the laser the white writing appears.

A multicolored marking is not possible at the present state of technology.

Different laser types and processes are available for laser marking (Table 5.10).

Table 5.10: *Laser Types and Processes of Marking*

Properties	Nd:YAG laser	Excimer laser
Wavelength	1064 nm or 532 nm	351 nm
Operating mode	Pulsed	Pulsed
Energy	50–80 Watt	50–200 Watt
Mode of marking	Vector mode	Mask mode
Speed of marking	Up to 1000 mm/s	Up to 100 symbols/s
Size of the field to be marked	150 mm diameter	200 mm ²

The *Nd:YAG laser* operates in the vector mode. With the help of two deflecting mirrors the beam of laser light is diverted by computer control, and a special optics focuses the beam on the surface of the component to be marked. The laser “writes” symbol by symbol. This method produces the best flexibility, and the writing can be changed any time with the use of a computer. This flexibility is significant when serial numbers, date of production, and/or other important dates are to be integrated in the marking.

The *excimer laser* operates in the mask mode. Between the laser and the component to be marked, a mask is positioned, and only those parts of the laser light that

pass the mask, containing gaps in form of symbols and/or a complex decoration, can mark the component. This technology produces a complex decoration with extensive proportions within a very short time. One disadvantage is that any change in the marking requires a change of the mask, and another disadvantage is the high price of an excimer laser.

Laser marking is a process without any contact; therefore inaccessible surfaces and/or bend components can be marked without any difficulty. This is the decisive advantage of laser technology, because every printing technology fails in these cases.

Further advantages of laser technology in comparison to the traditional printing technology are:

- No printing colors necessary
- No preparation of the plastic surface prior to printing
- No equipment for the drying of the print necessary and/or other typical precautions
- The marking is forgery-proof

For laser marking, polyolefins should contain at least 0.1% of the modified pearlescent pigments; a higher concentration is advisable to achieve a clearer marking. For the handling and incorporation of these pigments the same precautionary methods should be implemented as described in the section on pearlescent pigments.

5.1.8 Additional Inorganic Effect Pigments

Two different types of pigments are marketed for very specific effects:

- Luminescent pigments
- So-called “color flop pigments”

5.1.8.1 Luminescent Pigments

Inorganic luminescent pigments are synthetically produced substances absorbing energy (light), which is emitted subsequently as light, either immediately or over a longer period of time. These pigments shine for a certain time even in complete darkness. This phenomenon is also called phosphorescence. Chemically they belong to the following groups:

- Zinc sulfide doped with metals, for example, silver (Ag) or copper (Cu). The results are pigments with the following formula: $\text{ZnS} \cdot \text{Ag}$ or $\text{ZnS} \cdot \text{Cu}$.
- Aluminates doped with lanthanides, for example, $\text{Al}_2\text{O}_3 \cdot \text{Sr} \cdot \text{Eu}$.

- Alkaline earth metal sulfides, doped with lanthanides or other metals, for example, SrS·Eu or SrCaS·Bi.

The emitted color and the intensity and duration of luminescence depend on the chemistry of these pigments. The doped zinc sulfide and the aluminates emit a yellowish green light, while the alkaline earth metal sulfides shine in a orange (SrS·Eu) or blue (SrCaS·Bi) [44].

The heat stability of these pigments is good ($> 400\text{ }^{\circ}\text{C}$ [$752\text{ }^{\circ}\text{F}$]). Sulfides are generally sensitive to strong acids. For a distinct effect the particle size of these pigments has to be between 20 and 60 μm , which means they are very coarse in comparison to a typical colorant and therefore not suitable for thin-walled plastic components.

No problems are reported during production and handling of a masterbatch, and luminescent pigments can be processed like any other inorganic pigment.

Many uses are imaginable and practiced, for example, in toys and to mark emergency exits or other safety related items.

5.1.8.2 Color Flop Pigments

This is as yet not an official designation of this very new group of pigments; it describes only the effect. The characteristic of these pigments is that they change color depending on the angle of vision – basically the appearance of interference. One type of pearlescent pigments shows this effect too, but it is very weak. The goal of further development was to achieve pigments with a strong effect of interference, and it took a long time before the first pigments appeared on the market.

The first two colors, a golden and a red shade, are now available. They are produced by the BASF corporation in Ludwigshafen, Germany, and their trade name is Variochrome. Chemically it is a multilayer pigment, and the bases are aluminum platelets coated with silicon dioxide and iron oxide in varying thickness. The color varies between golden and red depending on the thickness of the iron oxide. This is just the beginning, and it can be expected that in the near future further colors will follow. The fastness properties are very good.

Similar pigments produced by other companies are available at least as experimental pigments, for example, by E. Merck in Darmstadt, Germany.

5.2 Organic Pigments

In comparison to the inorganic pigments there is a large variety of organic colorants. This diversity is the consequence of their chemistry, because within organic chemistry there are not only much more fundamental components but in addition

they can be varied by replacement of their substituents, which are nearly unlimited. The results are many colorants with slightly different shades. In practice the number of commercially marketed colorants is limited. Limitations are present in terms of economic, technical, toxicological concerns, and/or other disadvantageous properties.

The organic pigments can be subdivided either according to the chemical structure or the color. Both systems are practiced in the literature, and both have advantages and disadvantages besides the tendency to overlap. Overlapping occurs especially in the colors red, yellow, and violet. For the purpose of this book it may be useful to list the organic pigments according to the chemical constitution. One reason is the fact that several properties, for example, light fastness, weather resistance, and heat stability, are very similar within a group of pigments with the same basic chemical structure. The organic pigments are therefore subdivided according to the basic formula, which predicts to a certain extent the expected, typical properties. New pigments without published formulas can be classified only when at least their assignment is known.

Not all marketed colorants can be used for the coloring of plastics. One reason that excludes their use for the coloring of plastics is insufficient heat stability. The main fields of application then are printing paints and lacquers. These pigments are not described in this book. Analogous to inorganic pigments those pigments, which are no longer in use because of, for example, toxicological concerns, are just mentioned but not described in detail.

Each organic pigment that is suitable for the coloring of plastics is described with its characteristic properties. In this context it should be emphasized that several data can be used only as guidelines and not as exact data for any color preparation. Data such as heat stability, light fastness, and weather resistance are based on standardized test methods in standard plastics. In practice, however, the composition of an actual color preparation and/or the final product is much more complex.

Several colorants are marketed by more than one supplier. Those pigments differ usually in their optical and physical properties, and consequently the shades are not absolutely identical. The main reasons for those differences are different particle size distribution and different aftertreatments to improve the stability of the crystal and the dispersing in the polymer melt. As a result the data regarding heat stability and/or light fastness may differ also.

All marketed organic pigments, including those that are applied only in printing paints or lacquers, are described in detail in the publication *Industrial Organic Pigments* by W. Herbst and K. Hunger [45].

In view of the many types of plastics and their manifold applications in combination with all the specific requirements for the final product, it would be far beyond

the scope of this book to describe every plastic in detail, including all suitable colorants. An additional restriction is given by the fact that the manufacturer of colorants checks the performance of his colorants usually only in the most important types of plastics. This alone is very laborious and time consuming. The supplied data sheets contain this information together with a sample of the color shade.

Another reason for this restriction is the variety of requirements for the final product based on the intended application. A technical part has to fulfill many specific requirements, while those of a disposable item are relatively limited. The colorist recognizes which properties are required of the new color preparation on the basis of the customer supplied requirements specification. In case of doubt it is recommended to check with the manufacturer whether the colorant is suitable for the intended use.

The organic pigments can be divided into two main groups, azo pigments and nonazo pigments, which are also known as polycyclic pigments. Both main groups can be subdivided further according to structural characteristics, for example, by the number of azo groups or the type of disazo component, and the type of rings that constitute the aromatic structure of the polycyclic pigments (Fig. 5.8). In addition to these two main groups single organic pigments are marketed that cannot be classified in one of these main groups, for example, the metal complex pigments and the isoindolinone or isoindoline pigments.

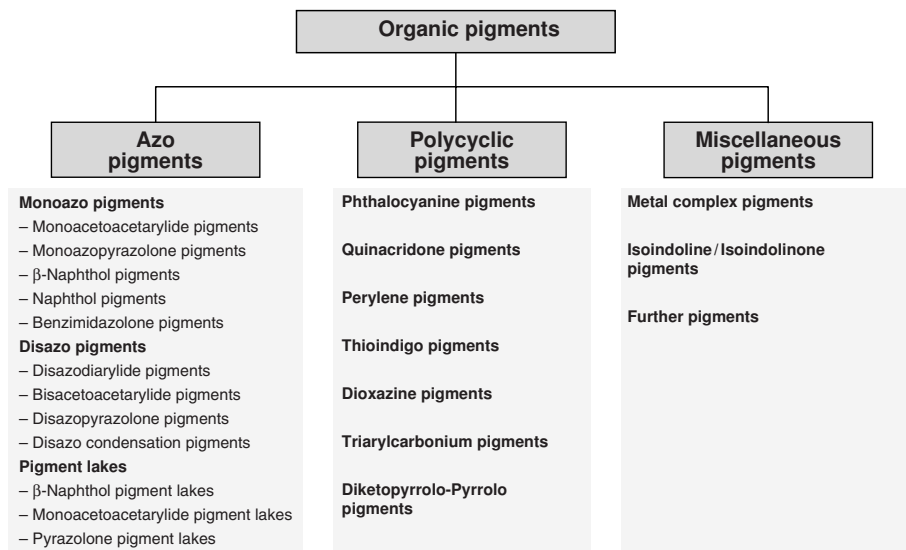


Figure 5.8: Classification of organic pigments based on the chemical structure

The characteristic of organic colorants is the presence of chromophores, a system of conjugated double bonds (π -electron system). The appearance of color is associated with electronic excitation caused by an absorption of selected wavelengths of the incident visible light, thereby giving the molecule the shade of the resulting complementary color.

5.2.1 Azo Pigments

The characteristic of all azo pigments is the azo group $[-N=N-]$. Monoazo pigments contain one azo group, the disazo pigments contain two azo groups, and there are no products on the market with more than two azo groups.

The basic formula of a monoazo pigment is $[R'-N=N-R'']$ and of a disazo pigments it is $[R'-N=N-R'''-N=N-R'']$. R' , R'' , and R''' are different components with varying substituents. The chemical constitution of the components can be used for a further subdivision of azo pigments. When an azo pigment contains as a substituent an acidic group, for example, a sulfo or carboxy group, then it forms by precipitation azo pigment lakes. Metal cations such as calcium, strontium, barium, magnesium, or manganese are used usually for precipitation. This leads to a further subdivision of azo pigments, in nonlaked azo pigments and laked azo pigments.

The azo pigments can be subdivided the following way:

- Monoazo pigments
 - Monoacetoacetarylide pigments
 - Monoazopyrazolone pigments
 - β -Naphthol pigments
 - Naphthol pigments
 - Benzimidazolone pigments
- Disazo pigments
 - Disazodiarylide pigments
 - Bisacetoacetarylide pigments
 - Disazopyrazolone pigments
 - Disazo condensation pigments
- Pigment lakes
 - β -Naphthol pigment lakes
 - Monoacetoacetarylide pigment lakes
 - Pyrazolone pigment lakes

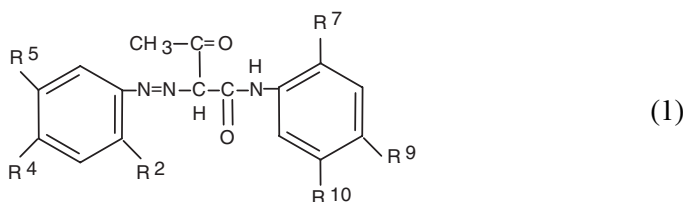
Numerous combinations of the different components are possible, including varying substituents, which result in a large number of azo pigments. The color of azo pigments is usually in the range of yellow, orange, red, and brown with many

different shades. No green or blue azo pigments are marketed; these two colors are covered by polycyclic pigments.

5.2.1.1 Monoazo Pigments

Monoacetoacetarylides Pigments

This group of azo pigments has a certain historical importance, because the very first marketed azo pigment belongs to this group with basic formula 1. Many other pigments followed, and consequently this is numerically the largest group of azo pigments.



In spite of the large number of pigments only a few can be used for the coloring of plastics (Table 5.11). Most of them cannot be applied because of a too low heat stability and/or other disadvantageous properties, for example, migration.

Pigment yellow 49 / 11 765 / CAS 2904.04.3

Properties: Greenish yellow, good light fastness.

Application: For viscose spin dyeing and for the mass coloration of viscose foils [45].

Pigment yellow 97 / 11 767 / CAS 12225.18.2

Properties: Medium yellow, average tinting strength, tendency to migrate in plasticized PVC at low concentrations, pigment does not affect shrinkage.

Average heat stability: 240 °C (464 °F) in PE-HD. At commonly used concentrations the pigment dissolves almost completely at temperatures about 200 °C (392 °F) in PS, combined with a color shift.

Good light fastness: 6–7 (pure tone) / 8 (white reduction) in rigid PVC, 7/7 in PE, and 7–8 / 5 in PS.

Application: It can be used in several polymers, for example, rigid poly(vinyl chloride) (PVC-U), polyolefins (PO), polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), poly(methyl methacrylate) (PMMA), and epoxy resins, unsaturated

polyester resin. In the case of plasticized polyvinyl chloride (PVC-P), it is recommended to consider the possibility of migration.

Pigment yellow 116 / 11790 / CAS 30191.02.7

Properties: Reddish yellow, a slight tendency to migrate in plasticized PVC.

Low heat stability: approx. 180 °C (356 °F).

Good light fastness: 7–8 (pure tone) / 6 (white reduction) in PVC.

Application: Its use is restricted to PVC; the insufficient heat stability limits the application in other polymers, for example, PO, PS.

Table 5.11: List of Substituents of Azo Pigments According to Basic Formula 1

Color index number	Substituent					
	R ²	R ⁴	R ⁵	R ⁷	R ⁹	R ¹⁰
P. yellow 49	CH ₃	Cl	H	OCH ₃	Cl	OCH ₃
P. yellow 97	OCH ₃	SO ₂ NH-C ₆ H ₅	OCH ₃	OCH ₃	Cl	OCH ₃
P. yellow 116	Cl	CONH ₂	H	H	NHCOCH ₃	H

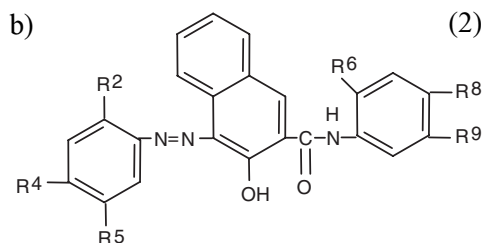
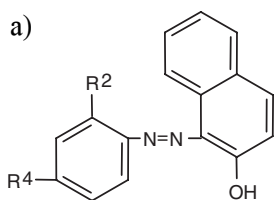
Monoazopyrazolone Pigments

The nonlaked monoazopyrazolone pigments play no role in the coloring of plastics.

β-Naphthol Pigments/Naphthol Pigments

These two groups can be summarized because their chemical structures are very closely related. The β-naphthol pigments show no further substituents on the β-naphthol group, and their chemical structure is relatively simple (basic formula 2a). The naphthol pigments are much more complex (basic formula 2b). They show substituents on the β-naphthol group in the *m*-position to the azo group, and an additional substituent on the coupling component (R⁵).

From the β-naphthol pigments (basic formula 2a) only two pigments can be applied to some extent (Table 5.12). All the other pigments of this group are not suitable for the coloring of plastics because of their disadvantageous properties, for example, insufficient heat stability, tendency to migrate, and others disadvantages.



Pigment orange 5 / 12075 / CAS 3468.63.1

Properties: Insufficient heat stability, strong tendency to migrate because of its solubility in many solvents.

Good light fastness: 8 (pure tone) / 6 (white reduction) in rigid PVC.

Application: Its use is limited to rigid PVC.

Pigment red 3 / 12120 / CAS 2425.85.6

Properties: Insufficient heat stability, strong tendency to migrate because of its solubility in many solvents, but fair light fastness.

Application: Its use is limited to rigid PVC.

Table 5.12: List of Substituents of β -Naphthol Pigments According to Basic Formula 2a

Color index number	Substituent	
	R ²	R ⁴
P. orange 5	NO ₂	NO ₂
P. red 3	NO ₂	CH ₃

The naphthol pigments with their more complex chemical structure (basic formula 2b) possess a much better profile of properties in comparison to the relatively simple β -naphthol pigments. Consequently many pigments of this group are applied for the coloring of plastics, among them some widely used pigments (Table 5.13).

Pigment red 5 / 12490 / CAS 6410.41.9

Properties: bluish red (carmine), insufficient heat stability, strong tendency to migrate, therefore cannot be applied in plasticized PVC.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in rigid PVC.

Application: Its use is limited to rigid PVC, and it is used for spin dyeing of viscose rayon.

Pigment red 31 / 12360 / CAS 6448.96.0

Properties: Bluish red (bordeaux).

Good heat stability: 280 °C (536 °F) in PS and PMMA.

Good light fastness: 7 (pure tone) in PMMA.

Application: It can be applied in several polymers, for example, rubber, PS, PMMA, unsaturated polyester resin, and so forth. This pigment is used primarily in the United States and Japan, and is not very common in Europe.

Pigment red 112 / 12370 / CAS 6535.46.2

Properties: Brilliant red shade, not completely fast to migration, insufficient heat stability.

Good light fastness: 8 (pure tone) in rigid PVC, but only 5–6 in white reduction.

Application: Its use is limited to rigid PVC, and it is used for spin dyeing of viscose rayon.

Pigment red 146 / 12485 / CAS 5280.68.2

Properties: Bluish red, not completely fast to migration.

Insufficient heat stability: Below 200 °C (392 °F).

Good light fastness: 8 (pure tone) in rigid PVC, but only 6 in white reduction.

Application: Its use is limited to rigid PVC.

Pigment red 150 / 12290 / CAS 56396.10.2

In the past this pigment was used to color PVC, but it has now more or less been completely replaced by other pigments with better properties.

Pigment red 164 / – / 12216.95.4

Properties: Yellowish red, little tinting strength, not completely fast to migration. The chemical constitution has not yet been published.

Heat stability: The heat stability varies and depends on the polymer to be colored. The heat stability is about 270 °C (518 °F) (pure tone) and 250 °C (482 °F) (white reduction) in PS, but only 220–200 °C (428–392 °F) in polyolefins.

Average light fastness.

Application: This pigment can be used in several polymers, for example, polyurethanes, PS, rigid PVC, and PE with low processing temperature (PE-LD).

Pigment red 170 / 12475 / CAS 2786.76.7

Properties: Bluish red, good tinting strength, not completely fast to migration. Pigment red 170 is polymorphous, there are two crystal modification, which differ slightly in terms of opacity and color shade.

Average heat stability which in addition depends on the concentration in the polymer: 240 °C (464 °F) in PE at a concentration of 0.1%, but only 220 °C (428 °F) in PE at a concentration of 0.05%.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE

Application: The use of this pigment is limited to polyolefins, rigid PVC, and spin dyeing of viscose rayon. Because of its solubility in several solvents, including plasticizer, it should not be applied in polymers containing plasticizer, for example, plasticized PVC and polyurethane. It is not recommended for the coloring of polystyrene and acrylonitrile butadiene styrene copolymers.

Pigment red 187 / 12486 / CAS 59487.23.9

Properties: Pigment red 187 is polymorphous, and two crystal modifications are known, which differ considerably in fastness properties and color shade. Only the bluish red modification is commercially available. The pigment does not migrate in plasticized PVC. The shrinkage of PE is only slightly affected by this pigment.

Good heat stability: 300 °C (572 °F) in PS and PC; 290 °C (554 °F) in ABS; 260 °C (500 °F) in PE. The heat stability is independent of the concentration within a wide range, therefore it can be used to nuance shades.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE; 7 / 7 in PVC.

Application: It can be used in many polymers, for example, PVC, PO, PS, ABS, and for spin dyeing of PP and PAN.

Pigment red 188 / 12467 / CAS 61487.48.1

Properties: Yellowish red, it tends to bloom in plasticized PVC at low concentrations.

Heat stability: Approx. 220 °C (428 °F) in PE.

Application: Its use is limited to rigid PVC and grades of PE with a low processing temperature, mainly PE-LD.

Pigment red 222 / – / CAS 71872.63.4

Properties: Bluish red, average tinting strength, tends to migrate in plasticized PVC. The chemical constitution is not yet published, but it is classified as member of this pigment group.

Average heat stability: 240 °C (464 °F) in PE, at higher temperatures the color shifts toward the bluish side.

Application: Its use is more or less limited to rigid PVC, POs, and PU.

Pigment orange 22 / 12470 / CAS 6358.48.1

Properties: Reddish orange, good fastness properties.

Application: Its use is limited to spin dyeing.

Pigment orange 38 / 12367 / CAS 12236.64.5

Properties: Yellowish red, fast to migration, only a slight effect on the shrinkage of polyethylene.

Good heat stability: 260–280 °C (500–536 °F) in PE, which decreases at concentrations below 0.05%, and is only 240 °C (464 °F) at 0.005%.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC, similar fastness in PE.

Application: It is used primarily in PVC, PO, PS, and for spin dyeing.

Pigment brown 1 / 12480 / CAS 6410.40.8

Properties: Neutral brown, not stable in many organic solvents, which limits its use considerably.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in rigid PVC.

Application: This pigment has lost much of its importance, but it is still used for brown transparent PVC bottles. The pigment dissolves in PS at the processing temperature, giving an orange shade.

Table 5.13: List of Substituents of Naphthol Pigments According to Basic Formula 2b

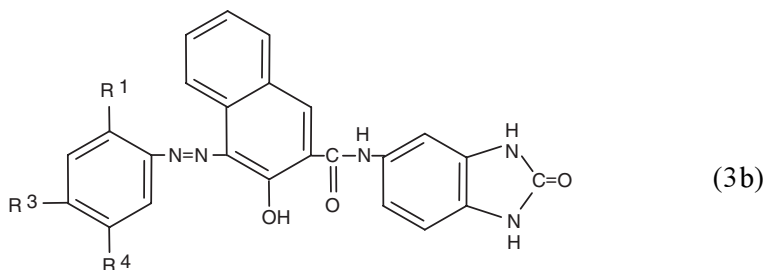
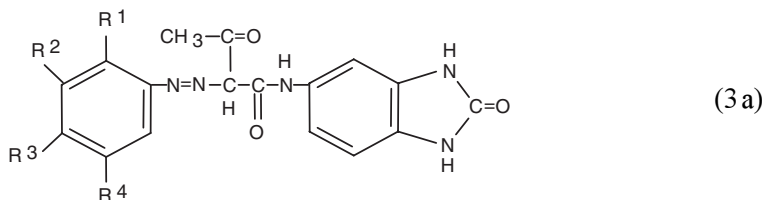
Color index number	Substituents					
	R ²	R ⁴	R ⁵	R ⁶	R ⁸	R ⁹
P. red 5	OCH ₃	H	SO ₂ N(C ₂ H ₅) ₂	OCH ₃	OCH ₃	Cl
P. red 31	OCH ₃	H	CONHC ₆ H ₅	H	H	NO ₂
P. red 112	Cl	Cl	Cl	CH ₃	H	H
P. red 146	OCH ₃	H	CONHC ₆ H ₅	OCH ₃	Cl	OCH ₃
P. red 150	OCH ₃	H	CONHC ₆ H ₅	*		
P. red 164	**					
P. red 170	H	CONH ₂	H	OC ₂ H ₅	H	H
P. red 187	OCH ₃	H	CONHC ₆ H ₄ - (p)CONH ₂	OCH ₃	OCH ₃	Cl
P. red 188	COOCH ₃	H	CONHC ₆ H ₃ - Cl ₂ (2,5)	OCH ₃	H	H
P. red 222	**					
P. orange 22	Cl	H	Cl	OC ₂ H ₅	H	H
P. orange 38	Cl	H	CONH ₂	H	NHCOCH ₃	H
P. brown 1	Cl	H	Cl	OCH ₃	H	OCH ₃

* The substituent is only CONH₂, no additional benzene ring.

** Chemical constitution not yet published.

Benzimidazolone Pigments

The shades of benzimidazolone pigments are either yellow and orange or red and brown. All pigments contain the 5-aminocarbonyl benzimidazolone group, but there are differences in detail. In the case of the yellow and orange shades the coupling component is 5-acetoacetylaminobenzimidazolone, and this leads to basic formula 3a, which parallels the acetoacetarylides of the monoazo pigments (the benzene ring is replaced by the benzimidazolone group; refer to basic formula 1). The red and brown pigments can be considered as a variation of the naphthol pigments (refer to basic formula 2b), where the benzene ring is replaced by the benzimidazolone group, which leads to the basic formula 3b.



The following benzimidazolone pigments are based on basic formula 3a (Table 5.14):

Pigment yellow 120 / 11783 / CAS 29920.31.8

Properties: Greenish yellow, no tendency to migrate, no effect on the shrinkage of PE-HD.

Good heat stability: 270 °C (518 °F) in PS; 260 °C (500 °F) in PO; and 250 °C (482 °F) in ABS. In PE the heat stability decreases only at a concentration below 0.01%.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC, PE, and PS.

Good weather resistance: 4–5 in PE.

Application: It can be used in many polymers.

Pigment yellow 151 / 13980 / CAS 61036.28.0

Properties: Greenish yellow, no tendency to migrate, only a slight effect on the shrinkage of PE-HD.

Good heat stability: 280 °C (536 °F) in ABS; 260 °C (500 °F) in PS and PO. The heat stability decreases only slightly with decreasing concentration in PE.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC, similar data in PS and PE.

Application: It can be used in many polymers.

Pigment yellow 154 / 11 781 / CAS 63 661.02.9

Properties: Greenish yellow, no tendency to migrate.

Low heat stability: 210 °C (410 °F) in PE

Good light fastness and weather resistance in PVC, which makes it suitable for exterior use in this polymer.

Application: The low heat stability limits the use of this pigment to PVC and grades of polyethylene with a low processing temperature (PE-LD).

Pigment yellow 175 / 11 784 / CAS 35 636.63.6

Properties: Greenish yellow, low tinting strength, no effect on the shrinkage of PE-HD; although insoluble in most solvents it may be advisable to check the migration in plasticized PVC.

Good heat stability: 270 °C (518 °F) in PE.

Good light fastness and weather resistance in PVC-U.

Application: It can be used in several polymers.

Pigment yellow 180 / 21 290 / CAS 77 804.81.0

Properties: Greenish yellow, no tendency to migrate, no effect on the shrinkage of PE-HD. In contrast with the other pigments of this group it is a disazobenzimidazolone pigment.

Good heat stability: 300 °C (572 °F) in PS and PC; 290 °C (554 °F) in PO; 280 °C (536 °F) in PMMA and PET; 260 °C (500 °F) in PA 6. The heat stability in PE is independent of the concentration within a wide range, and decreases only below 0.005%, which means this pigment can be used to nuance color shades.

Good light fastness: 6–7 (pure tone) / 6–7 (white reduction) in PVC; 6–7 / 6 in PE, 7–8 / 6 in PA 6; 6–7 / 7–8 in PET; 5–6 / 3–4 in PMMA.

Application: It can be used in many polymers, including POM (minimum concentration > 0.1%).

Pigment yellow 181 / 11 777 / CAS 74 441.05.7

Properties: Reddish yellow, low tinting strength, no tendency to migrate, no effect on the shrinkage of PE-HD.

Good heat stability: 300 °C (572 °F) in PO and PS, 280 °C (536 °F) in ABS. In PE there is only a slight decrease in heat stability at a concentration between 0.1% and 0.005%.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC, PE, and PS.

Good weather resistance: 4 in PE.

Application: It can be used in many polymers, including POM (minimum concentration > 0.1%). It is not recommended for the coloring of PA and PC.

Pigment yellow 194 / – / CAS 82199.12.0

Properties: Medium yellow, good tinting strength, tendency to migrate in plasticized PVC.

Medium heat stability: 250 °C (482 °F) in PS; 230 °C (446 °F) in PE. It is noticeable that the heat stability decreases in PE rather fast at a concentration < 0.1%.

Medium to good light fastness: 6 (pure tone) / 5–6 (white reduction) in PVC; 7 / 7 in PE and PS.

Application: The relative low heat stability limits its use to polymers with a low processing temperature, for example, PVC, PE-LD, PS. It is not recommended for the coloring of ABS.

Pigment orange 36 / 11780 / CAS 12236.62.3

Properties: Reddish orange, no tendency to migrate in plasticized PVC, no effect on the shrinkage of PE-HD.

Low heat stability: 220 °C (428 °F) in PE.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC.

Application: The low heat stability limits its use to polymers with a low processing temperature, for example, PVC, PE-LD.

Pigment orange 62 / 11775 / CAS 75601.68.2

Properties: Yellowish orange.

Low heat stability: 200–220 °C (392–428 °F) in PE.

Good light fastness in rigid PVC.

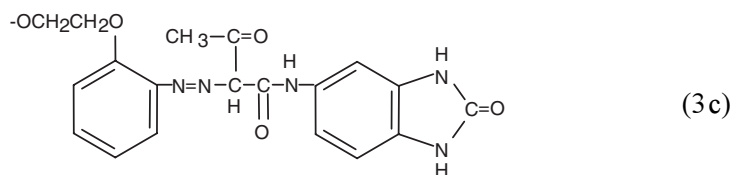
Application: The low heat stability limits its use to polymers with a low processing temperature, for example, PVC, PE-LD; in addition it is used for spin dyeing of PP grades with good flow behavior.

Table 5.14: List of Substituents of Benzimidazolone Pigments According to Basic Formula 3a

Color index number	Substituent			
	R ¹	R ²	R ³	R ⁴
P. yellow 120	H	COOCH ₃	H	COOCH ₃
P. yellow 151	COOH	H	H	H
P. yellow 154	CF ₃	H	H	H
P. yellow 175	COOCH ₃	H	H	COOCH ₃
P. yellow 180	*	H	H	H
P. yellow 181	H	H	-OCNH-C ₆ H ₄ -CONH ₂	H
P. yellow 194	OCH ₃	H	H	H
P. orange 36	NO ₂	H	Cl	H
P. orange 62	H	H	NO ₂	H

* This substituent has the following chemical constitution:

Substituent R¹ of P. yellow 180:



The following benzimidazolone pigments are based on basic formula 3b (Table 5.15):

Pigment red 171 / 12512 / CAS 6985.95.1

Properties: Bluish red, high tinting strength, no migration in plasticized PVC.

Medium heat stability: 240 °C (464 °F) in PE.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PVC; 6–7 / 6 in PE.

Application: The low heat stability limits its use to polymers with a low processing temperature, for example, PVC, PE-LD; in addition it is used in unsaturated polyester and for spin dyeing of PAN.

Pigment red 175 / 12513 / CAS 6985.92.8

Properties: Dull red, no migration in plasticized PVC, only a very slight effect on the shrinkage of PE-HD.

Good heat stability: 300 °C (572 °F) in PS; 290 °C (554 °F) in ABS; 270 °C (518 °F) in PE. The heat stability decreases with decreasing concentration in PE.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC; 8 / 8 in PE and PS.

Good weather resistance: It is used in combination with carbon black for brown PVC window frames.

Application: It can be used in many polymers, for example, PVC, PO, PET, PUR, and for spin dyeing of PP. It is not recommended for the coloring of PC.

Pigment red 176 / 12515 / CAS 12225.06.8

Properties: Bluish red, no migration in plasticized PVC.

Good heat stability: 300 °C (572 °F) in PS; 270 °C (518 °F) in PO; 260 °C (500 °F) in PMMA. It should be taken into consideration that the heat stability decreases in some polymers with increasing amounts of titanium dioxide.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in PVC; 7 / 7 in PO; 7 / 4 in PMMA.

Application: It can be used in many polymers, for example, PVC, PO, PS, and for spin dyeing of PP and PAN. It is not recommended for the coloring of ABS.

Pigment red 185 / 12516 / CAS 61951.98.2

Properties: Bluish red, nearly no migration in plasticized PVC.

Medium heat stability: 270 °C (518 °F) in PS; 250 °C (482 °F) in PE. The heat stability is more or less independent of the concentration within a range between 0.1 and 0.005% (pure tone) in PE, but the heat stability decreases with increasing amounts of titanium dioxide (white reduction).

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC; 6 / 5–6 in PE; 7 / 6–7 in PS.

Application: Its use is limited to polymers with low processing temperatures, for example, PVC, PUR, PVCD, PE-LD, and PP.

Pigment red 208 / 12514 / CAS 31778.10.6

Properties: High tinting strength, no migration in plasticized PVC.

Low heat stability: Approx. 220–200 °C (428–392 °F). The heat stability is higher in a transparent specimen (pure tone) than in a white reduction.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in PVC.

Application: Because of the insufficient heat stability it can be used only in PVC and for spin dyeing of PP and PAN, provided that the processing temperature is < 200 °C (< 392 °F). It cannot be used in polyolefins.

Pigment violet 32 / 12517 / CAS 12225.08.0

Properties: Bluish red, high tinting strength, no migration in plasticized PVC.

Low heat stability: < 210 °C (< 410 °F) in PE.

Good light fastness: 7–8 (pure tone) / 6–7 (white reduction) in PVC.

Application: Because of insufficient heat stability it can be used only in PVC and for spin dyeing of viscose rayon. It may be used in some light-flowing PE-LD grades, provided that the processing temperature is < 210 °C (< 410 °F). A preliminary examination is recommended.

Pigment brown 25 / 12510 / CAS 6992.11.6

Properties: Reddish brown, high tinting strength, nearly no migration in plasticized PVC (depending on the concentration), only a slight effect on the shrinkage of PE-HD.

Good heat stability: 280 °C (536 °F) in PET and PS. The heat stability depends clearly on the concentration in PE; it is 290 °C (554 °F) at a concentration of 0.1%, but only 240 °C (464 °F) at a concentration of 0.005%.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 8 in PE; 7 / 6–7 in PET.

Good weather resistance: The pigment meets the requirements for long-term exposure, for example, in window frames composed of PVC.

Application: It can be used in many plastics, for example, PVC, PO, PS, PET, and for spin dyeing of PP and PAN.

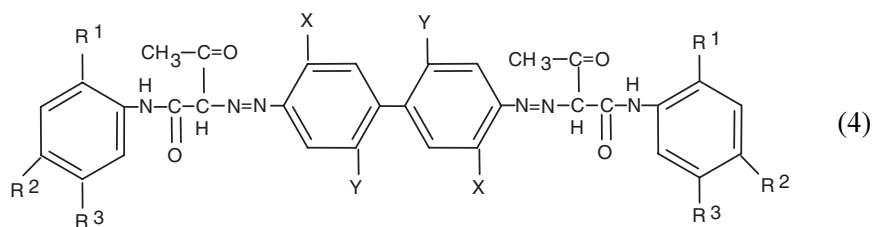
Table 5.15: List of Substituents of Benzimidazolone Pigments According to Basic Formula 3b

Color index number	Substituent		
	R ¹	R ³	R ⁴
P. red 171	OCH ₃	NO ₂	H
P. red 175	COOCH ₃	H	H
P. red 176	OCH ₃	CONHC ₆ H ₅	H
P. red 185	OCH ₃	SO ₂ NHCH ₃	CH ₃
P. red 208	COOC ₄ H ₉ (n)	H	H
P. violet 32	OCH ₃	SO ₂ NHCH ₃	OCH ₃
P. brown 25	Cl	H	Cl

5.2.1.2 Disazo Pigments

Disazodiarylide Pigments

The chemical constitution of the disazodiarylide pigments follows basic formula 4. In the past most members of this group were very important and very often used pigments, for example, Pigment yellow 12, yellow 13, yellow 14, yellow 17, and yellow 83. The characteristic of this pigment group is the content of dichlorobenzidine as component.



The substituent X consists mainly of chlorine, and the substituent Y of hydrogen. A further variation of the substituent X is either a CH₃ or OCH₃ group. Studies done in 1989 and 1990 showed that these pigments may decompose during

processing in polymers at temperatures above 200 °C (392 °F). The first decomposition products are a monoazo substance and an aromatic amine, and the decomposition of the monoazo substance continues at temperatures > 240 °C (464 °F), especially after a prolonged exposure to this temperature, and dichlorobenzidine is formed. The result of analytical investigations proved that only traces of dichlorobenzidine (a few ppm) were formed. Dichlorobenzidine and some other benzidine derivatives are classified as carcinogenic according to toxicological studies (in Germany dichlorobenzidine is listed as a group III A2 compound = proved carcinogenic effects in animals). As consequence of these studies the processing temperature of these pigments was limited to 200 °C (392 °F). The processing temperature of polymers is usually higher; therefore these pigments cannot be used any longer for the coloring of polymers, except PVC, which is normally processed below 200 °C (392 °F).

In Amendment 2 of the German *Bedarfsgegenständeverordnung* [46], dated 1994, all azo colorants were banned that decompose under specified test methods forming a listed amine. The list contains 20 amines that are classified as carcinogenic, including dichlorobenzidine and other benzidine derivatives. Many dyes and pigments cannot be used any longer for coloring of polymers. Numerous colors had to be matched anew which caused some problems because the properties of alternative colorants were quite different, for example, with respect to their hiding power and price.

Bisacetoacetarylide Pigments

From this group of pigments only Pigment yellow 155 is of commercial interest for coloring of plastics.

Pigment yellow 155 / – / CAS 68516.73.4

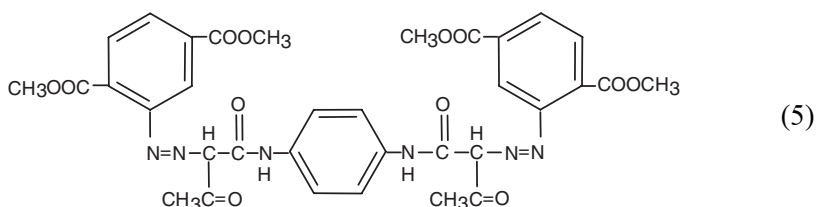
Properties: Greenish yellow, good tinting strength, not completely fast to migration in plasticized PVC.

Good heat stability: 260 °C (500 °F) in PE.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE, similar fastness in PVC and PS.

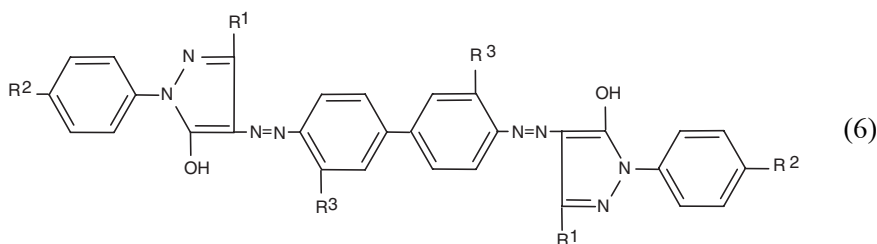
Application: It can be used in many polymers, for example, PVC, PO, PMMA, and PS. It is not recommended for the coloring of ABS and SAN.

Pigment yellow 155 has the following chemical constitution:



Disazopyrazolone Pigments

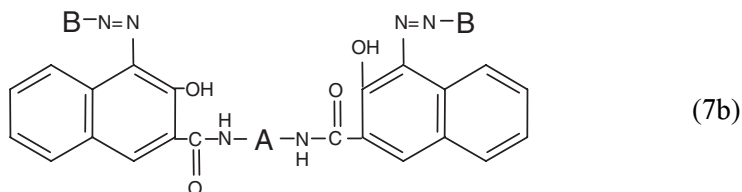
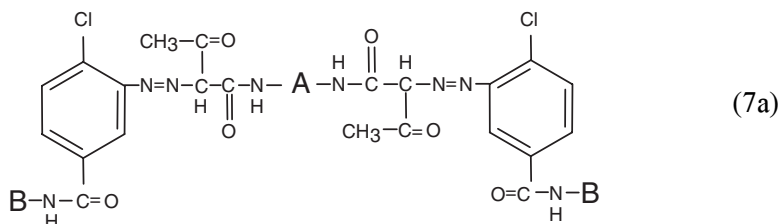
The disazopyrazolone pigments are based on basic formula 6.



Basic formula 6 indicates that this type of pigments also contains benzidine derivatives as a central component. The substituent R^3 is either chlorine or the methoxy group. These two benzidine derivatives are banned accordingly to Amendment 2 of the German Bedarfsgegenständeverordnung (refer to the chapter on disazodiarylide pigments). In the past Pigment orange 13, orange 34, and Pigment red 37, red 38, and red 41 played an important role in the coloring of plastics, but today they are insignificant.

Disazo Condensation Pigments

The pigments of this group are either yellow or red, as a consequence of their different chemical constitutions, which however is very close related to each other. The pigments based on formula 7a are yellow, whereas pigments with the basic formula 7b are red. A general characteristic of these pigments is a good heat stability and high light fastness in several polymers; they therefore play an important role in the coloring of plastics.



The following disazo condensation pigments are based on the formula 7a (Table 5.16):

Pigment yellow 93 / 20710 / CAS 5580.57.4

Properties: Greenish yellow, good tinting strength, no migration in plasticized PVC, only a slight effect on the shrinkage of PE-HD.

Good heat stability: 250–280 °C (482–536 °F) in PE, depending on the concentration.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC; 7–8 / 6–7 in PE; providing the processing time is short. The light fastness decreases when the processing time is up to 5 minutes.

Medium weather resistance: 3–4 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, and for spin dyeing of PP.

Pigment yellow 94 / 20038 / CAS 5580.58.5

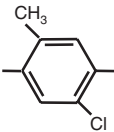
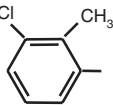
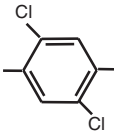
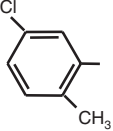
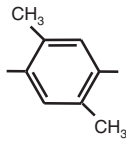
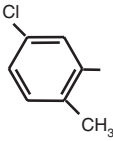
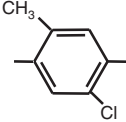
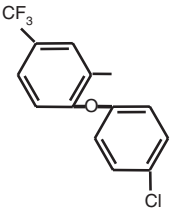
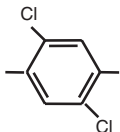
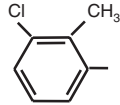
Properties: Greenish yellow, medium tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Good heat stability: 290 °C (554 °F) in PE; it should be mentioned that the heat stability depends on the amount of titanium dioxide in the color preparation. In pure tone the heat stability decreases at a concentration < 0.1%, but is constant in white reduction down to 0.001%.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, and for spin dying of PP and PAN.

Table 5.16: List of Substituents of Disazo Condensation Pigments Based on Formula 7a

Colour Index Number	Substituent	
	A	B
P. yellow 93		
P. yellow 94		
P. yellow 95		
P. yellow 128		
P. yellow 166		

Pigment yellow 95 / 20034 / CAS 5280.80.8

Properties: Reddish yellow, high tinting strength, no migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good heat stability: 260–280 °C in PE, depending on the concentration.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC; 7 / 6–7 in PE.

Medium weather resistance: Only 2–3 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, PUR, and for spin dyeing of PP.

Pigment yellow 128 / 20037 / CAS 57971.97.8

Properties: Greenish yellow, medium tinting strength, no migration in plasticized PVC, only a slight effect on the shrinkage of PE-HD.

Medium heat stability: 240 °C (464 °F) in PE.

Good light fastness: 7–8 (pure tone) / 8 (white reduction) in PVC, 8 / 7–8 in PE.

Application: The use of this pigment is limited to polymers with a low processing temperature, for example, PVC, PE-LD, and for spin dyeing of PP and PAN, provided the required processing temperature is low enough.

Pigment yellow 166 / 20035 / CAS 76233.82.4

The pigment is available only in Japan [45].

The following disazo condensation pigments are based on formula 7b (Table 5.17):

Pigment orange 31 / 20050 / CAS 12286.58.7

Properties: Reddish orange, good to medium tinting strength, not completely fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD. It is used very often in combination with carbon black for brown shades.

Good heat stability: 300 °C (572 °F) in PE.

Medium light fastness: Approx. 6 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, and for spin dyeing of PP.

Pigment red 144 / 20735 / CAS 5280.78.4

Properties: Bluish red, high tinting strength, not completely fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD. This pigment is marketed by several manufacturers, and differs mainly in its crystal size. This is probably the reason why the data regarding fastness properties differ.

Good heat stability: 280–290 °C (536–554 °F) in PE.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PE.

Good weather resistance: 4 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, PS, PUR, and for spin dyeing of PP and PAN.

Pigment red 166 / 20730 / CAS 12225.04.6

Properties: Yellowish red, high tinting strength, not completely fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Good heat stability: 280–290 °C (536–554 °F) in PE, depending on the concentration.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 7 in PE; 7 / 6–7 in PP.

Good weather resistance: 4 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, PS, PUR, and for spin dyeing of PP and PAN.

Pigment red 214 / – / CAS 40618.31.3

Properties: Bluish red, high tinting strength, not completely fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Good heat stability: 300 °C (572 °F) in PE, PS, acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC).

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 7–8 in PE; 6 / 7 in ABS; 6–7 / 6–7 in PS; 7–8 / 7 in PC.

Application: It can be used in many polymers, but is not recommended for the coloring of polyamide (PA).

Pigment red 220 / 20055 / CAS 57971.99.0

Properties: Yellowish red, medium tinting strength, only slight effect on the shrinkage of PE-HD (> 260°C [>500 °F]).

Good heat stability: 280–290 °C (536–554 °F) in PE, depending on the concentration.

Good light fastness: 7 (pure tone) / 7 (white reduction) in PVC; 7 / 6–7 in PE.

Medium weather resistance: Approx. 3 in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, and for spin dyeing of PP and PAN.

Pigment red 221 / 20065 / CAS 61815.09.6

Properties: Bluish red, high tinting strength, not completely fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD (warpage).

Good heat stability: Approx. 280–290 °C (536–554 °F) in PE.

Good light fastness: 7–8 (pure tone) / 6–7 (white reduction) in PVC.

Application: It is recommended especially for the coloring of PVC and PUR. An application in PE may be problematic because of the strong effect on the shrinkage (warpage).

Pigment red 242 / 20067 / CAS 118440.67.8 (CAS 52238.92.3)

Properties: Yellowish red, medium tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD (warpage).

Good heat stability: 290–300 °C (554–572 °F) in PE, PS, PC.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 7–8 in PE; 7–8 / 7 in PS; 7 / 7 in ABS; 7–8 / 7–8 in PC.

Application: It can be used in many polymers.

Pigment red 248

Properties: Bluish red, high tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD depending on the processing temperature (warpage). The chemical constitution is not yet published, but it is classified as a disazo condensation pigment.

Good heat stability: 290 °C (554 °F) in PE

Good light fastness: 8 (pure tone) / 7 (white reduction) in PVC, similar data for PE.

Application: It can be used in many polymers, for example, PVC, PE, PS.

Pigment red 262

Properties: Bluish red. The chemical constitution is not yet published, but it is classified as disazo condensation pigment.

Good heat stability: 290–300 °C (554–572 °F) in PE, PS, PC.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 7–8 in PE; 5–6 / 5 in PS; 6 / 6 in ABS; 7–8 / 7 in PC.

Application: It can be used in many polymers, for example, PVC, PE, PS, ABS, PC. It is not recommended for PA.

Pigment brown 23 / 20060 / CAS 57972.00.6

Properties: Reddish brown, medium to good tinting strength, not completely fast to migration in plasticized PVC (depending on the plasticizer), medium effect on the shrinkage of PE-HD. Because of its good weather resistance this pigment is used in combination with carbon black in PVC window frames.

Good heat stability: 280 °C (536 °F) in PE and PS.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC.

Application: It can be used in many polymers, for example, PVC, PE, PS, and for spin dyeing of PP and PAN.

Pigment brown 41

Properties: Yellowish brown, medium tinting strength, not completely fast to migration in plasticized PVC. The chemical constitution is not yet published, but it is classified as a disazo condensation pigment.

Good heat stability: 300 °C (572 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE.

Application: It can be used in many polymers, for example, PVC, PE, PS, PMMA, ABS, and SAN. It is not recommended for the coloring of PA.

Pigment brown 42

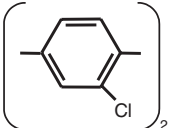
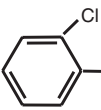
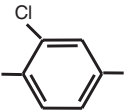
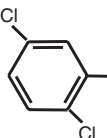
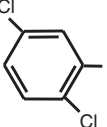
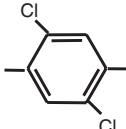
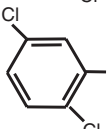
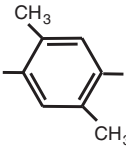
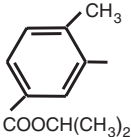
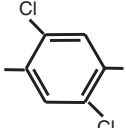
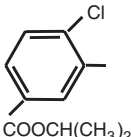
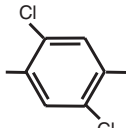
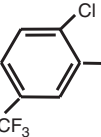
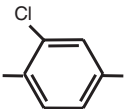
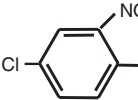
Properties: Yellowish brown, medium tinting strength, not completely fast to migration in plasticized PVC. The chemical constitution is not yet published, but it is classified as disazo condensation pigment.

Good heat stability: 280 °C (536 °F) in PE.

Good light fastness and weather resistance in PVC.

Application: This rather new pigment is recommended especially for the coloring of PVC, but it can be used also in other polymers.

Table 5.17: List of Substituents of Disazo Condensation Pigments Based on Formula 7b

Colour Index Number	Substituent	
	A	B
P. orange 31		
P. red 144		
P. red 166		
P. red 214		
P. red 220		
P. red 221		
P. red 242		
P. brown 23		

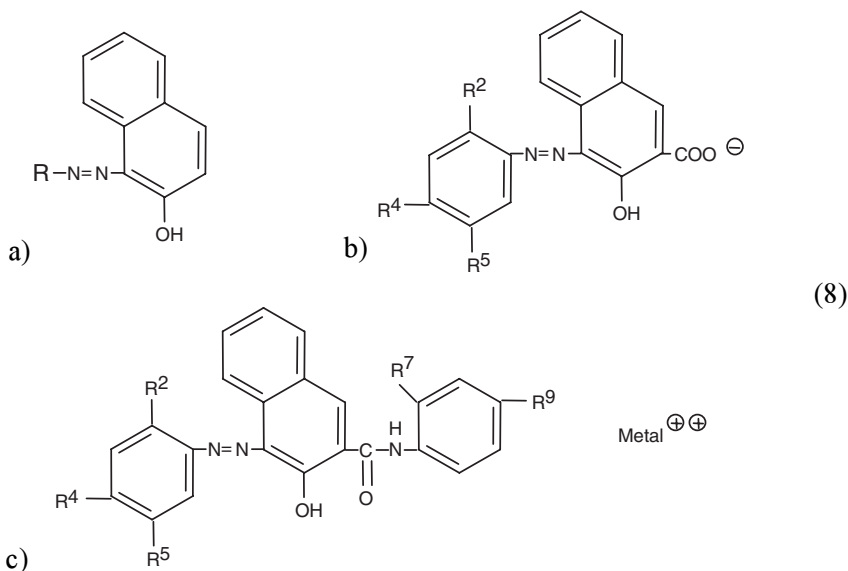
5.2.1.3 Azo Pigment Lakes

β -Naphthol Pigment Lakes

Analogous to the nonlaked naphthol pigments there are several variations. The defining characteristic is the presence of at least one acidic group (sulfonic acid and/or carboxylic acid) as a substituent. The simplest molecule is a diazo component and β -naphthol as coupling component; the disazo component contains the acid group (basic formula 8a).

The replacement of the β -naphthol component by **beta-oxynaphthoic acid (BONA)** as coupling component leads to basic formula 8b. The coupling component contains an additional acid group ($-\text{COO}^-$).

This acidic group can be used to add a further benzene ring with substituents, which gives basic formula 8c.



The following naphthol pigment lakes are based on formula 8a (Table 5.18):

Pigment red 53 / 15585 / CAS 2092.56.0

Pigment red 53:1 / 15585:1 / CAS 5160.02.1

Properties: Medium to good tinting strength, nearly completely fast to migration in plasticized PVC, no effect on the shrinkage of PE-HD. The pigment is today marketed mainly as barium salt (Pigment red 53:1), in the past also as sodium salt

(Pigment red 53) and as strontium salt (Pigment red 53:–), but both disappeared more or less completely from the market. There are only slight differences between these salts.

Soluble barium as an impurity in colorants is limited in many countries, for example, in Germany according to the BgVV-Recommendations, chapter IX, and in the European community according to the EU-Resolution AP (89) 1. The *normal* quality of Pigment red 53:1 does not fulfill these requirements regarding the content of soluble barium impurities. *Special* qualities of this pigment are, however, marketed that fulfill these requirements. This goal was reached by modifying the synthesis process of this pigment in combination with special cleaning steps. In using this pigment for color matching it is important to choose the right quality depending on the customer requirements. This pigment is marketed by many manufacturers, and therefore it is not surprising that the supplied data vary more or less, but basically they are the same.

Good heat stability: 250–280 °C (482–536 °F) in PE; 290 °C (554 °F) in PS; 270 °C (518 °F) in ABS. The heat stability decreases considerably below a pigment concentration of 0.05–0.1%.

Medium to insufficient light fastness: 6 (pure tone) / 2 (white reduction) in PVC; 3–4 / 2–3 in PE; 4 / 3–4 in PS; 3 / 2–3 in ABS.

Application: This pigment can be used only when there are no special requirements regarding light fastness.

Pigment red 68 / 15525 / CAS 5850.80.6

Properties: Yellowish red (scarlet), medium tinting strength, not completely fast to migration in plasticized PVC, no effect on the shrinkage of PE-HD, calcium salt.

Good heat stability: 290–300 °C (554–572 °F) in PE

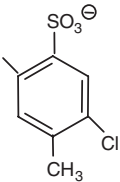
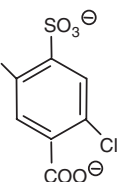
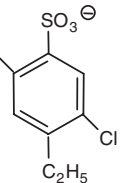
Medium light fastness: 4–5 (pure tone) / 3–4 (white reduction) in PE.

Application: This pigment can be used only when there are no special requirements regarding light fastness; it no longer plays any role in the coloring of plastics.

Pigment orange 46 / 15602 / CAS 67801.01.8

This pigment no longer plays any role in the coloring of plastics owing to its insufficient light fastness.

Table 5.18: List of the Substituents of the Pigments According to Basic Formula 8a

Color Index Number	R	Metal
P. red 53 P. red 53:1 P. red 53:-		$\text{Na}^{\oplus}$ $\text{Ba}^{\oplus\oplus}$ $\text{Sr}^{\oplus\oplus}$
P. red 68		$\text{Ca}^{\oplus\oplus}$
P. orange 46		$\text{Ba}^{\oplus\oplus}$

The following naphthol pigment lakes (BONA) are based on formula 8b (Table 5.19):

Pigment red 48

This pigment is marketed as barium, calcium, strontium, manganese, and magnesium salt. The properties of the different salts differ only slightly. Their application is limited to PVC and PE-LD owing to the low heat stability. In addition the light fastness is not good; consequently these pigments can be used only when there are no high requirements regarding the light fastness for the final product.

Pigment red 48:1 / 15865:1 / CAS 7585.41.3

Properties: Barium salt, medium tinting strength, no migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Low heat stability: 200–240 °C (392–464 °F) in PE.

Low light fastness.

Application: As a barium salt this pigment does not fulfill the requirements regarding soluble barium as an impurity in colorants, therefore and in connection with the insufficient light fastness, it does not play any role in the coloring of plastics.

Pigment red 48:2 / 15865:2 / CAS 7023.61.2

Properties: Calcium salt, good tinting strength, no effect on the shrinkage of PE-HD. The heat stability and the light fastness are slightly better than those of the barium salt.

Medium heat stability: 220–250 °C (428–482 °F) in PE, 250 °C (482 °F) in PS.

Medium light fastness: 7 (pure tone) / 4 (white reduction) in PVC, 6 / 4–5 in PE.

Application: This pigment can be used only when there are no special requirements regarding light fastness of the final product, especially in white reduction.

Pigment red 48:3 / 15865:3 / CAS 15782.05.5

Properties: Strontium salt, no migration in plasticized PVC, no effect on the shrinkage of PE-HD. Within the Pigment red 48 group it is the most stable salt and consequently used most frequently.

Medium heat stability: 240 °C (464 °F) in PE, 250 °C (482 °F) in PS, 260 °C (500 °F) in ABS.

Medium light fastness: 6–7 (pure tone) / 5–6 (white reduction) in PVC; 6–7 / 6 in PE; 6 / 4–5 in PS; 4–5 / 4–5 in ABS.

Application: This pigment can be used only when there are no strict requirements regarding light fastness for the final product.

Pigment red 48:4 / 15865:4 / CAS 5280.66.0

Properties: Manganese salt, high tinting strength, no effect on the shrinkage of PE-HD.

The manganese salt should not be used for the coloring of PP, because manganese ions accelerate the aging of this polymer (depending on the type), and the PP becomes brittle very fast.

The heat stability and the light fastness are inferior to those of Pigment red 48:3, therefore this manganese salt more or less disappeared from the market.

Pigment red 48:5 / 15865:5

Properties: Magnesium salt. According to the literature the properties of this salt are similar to those of Pigment red 48:2.

Pigment red 57:1 / 15850:1 / CAS 5281.04.9

Properties: Calcium salt, bluish red, good tinting strength, slight effect on the shrinkage of PE-HD.

Low heat stability: 220–240 °C (428–464 °F) in PE. The heat stability decreases considerably at a pigment concentration below 0.1%, therefore this pigment can be used only for intensive colors.

Medium light fastness: 6–7 (pure tone) / 5–6 or 3–4 (white reduction) in PVC; 4 / 5 or 6 / 3 in PE. The supplied data vary in detail between the different manufacturers, but they show basically the same tendency.

Application: The use of this pigment for the coloring of plastics is limited owing to its low heat stability. In addition, it can be used only if there are no strict requirements regarding the light fastness of the final product.

Pigment red 200 / 15867 / CAS 58067.05.3

Properties: Calcium salt.

Application: The use of this rather new bluish red pigment is limited to plastic parts without special requirements regarding light fastness.

Table 5.19: List of the Substituents of the Pigments According to Basic Formula 8b

Color index number	Substituent			
	R ²	R ⁴	R ⁵	Metal ion
P. red 48:1	SO ₃ [−]	CH ₃	Cl	Ba ⁺⁺
P. red 48:2	Same substituents			Ca ⁺⁺
P. red 48:3	Same substituents			Sr ⁺⁺
P. red 48:4	Same substituents			Mn ⁺⁺
P. red 48:5	Same substituents			Mg ⁺⁺
P. red 57:1	SO ₃ [−]	CH ₃	H	Ca ⁺⁺
P. red 200	SO ₃ [−]	Cl	C ₂ H ₅	Ca ⁺⁺

The following naphthol pigment lakes are based on formula 8c (Table 5.22):

Pigment red 151 / 15890 / CAS 61013.97.6

Properties: Barium salt, bluish red, medium tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Good heat stability: 260 °C (500 °F) in PE. The pigment can dissolve partially in PS and ABS at temperatures above 260 °C (500 °F), combined with a slight color change.

Medium to good light fastness: 7 (pure tone) / 6 (white reduction) in PVC; 6–7 / 5–6 in PE.

Application: It is used in several polymers, for example, PVC, PE, PP, PS, ABS. Another use is the coloring of cast resins such as methylmethacrylate and unsaturated polyesters because of its good resistance to peroxide catalysts, which are usually used for the polymerization.

Pigment red 237

Properties: Yellowish red, medium tinting strength, no migration in plasticized PVC. The exact chemical structure has not yet been published.

Application: This rather new pigment is recommended especially for coloring of PVC.

Pigment red 239

Properties: Bluish red, medium tinting strength, no migration in plasticized PVC. The exact chemical structure has not yet been published.

Good heat stability: 270 °C (518 °F) in PE.

Application: It can be used in several polymers, for example, PVC, PE, PP, and others.

Pigment red 240

Properties: Bluish red, low tinting strength. The exact chemical constitution has not yet been published.

Good heat stability: 300 °C (572 °F) in PE.

Application: It can be used in several polymers. At this time it is only of regional importance (Japan) [45].

Pigment red 243 / 15910 / CAS 50326.33.5

Properties: Barium salt, yellowish red, nearly completely resistant to migration in plasticized PVC, affects the shrinkage of PE-HD.

Low light fastness: 4 (pure tone) / 3 (white reduction) in PVC.

Application: It is recommended for PVC and PE-LD, but owing to its low light fastness this pigment can be used only if there are no strict requirements regarding the light fastness of the final product.

Pigment red 247 / 15915 and Pigment red 247:1 / 15915:1 / CAS 43035.18.3

Properties: Both pigments have the same chemical composition but a different crystal modification; consequently their properties differ slightly. Calcium salt, bluish red, medium tinting strength, not completely resistant to migration in plasticized PVC, only a very slight effect on the shrinkage of PE-HD.

Both grades of this pigment are marketed.

Good heat stability (independent of the pigment concentration) (Table 5.20):

Table 5.20: Heat Stability of Pigment Red 247 and 247:1

Pigment	Polymer				
	PE	PS	ABS	PET	PC
P. red 247	300 ° (572 °F)	300 °C (572 °F)	300 °C (572 °F)		310 °C (590 °F)
P. red 247:1	280–300 °C (536–572 °F)	300 °C (572 °F)	300 °C (572 °F)	280 °C (536 °F)	310 °C (590 °F)

Medium to good light fastness (Table 5.21):

Table 5.21: Light Fastness of Pigment Red 247 and 247:1

Pigment	Polymer				
	PE	PS	ABS	PET	PC
P. red 247	6–7/6	6–7/6	6/5–6		5/4–5
P. red 247:1	6–7/5–6	6/6	6/6–7	7/4–5	5/5–6

Application: Both crystal modifications can be used in many polymers, but they are not recommended for the coloring of PA.

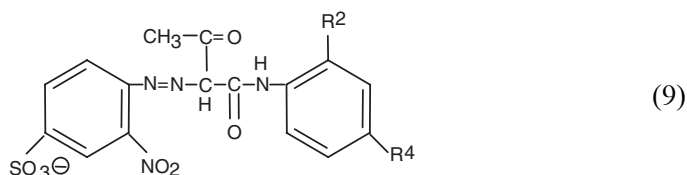
Table 5.22: List of the Substituents of the Pigments According to Basic Formula 8c

Color index number	Substituents					
	R ²	R ⁴	R ⁵	R ⁷	R ⁹	Metal ion
P. red 151	SO ₃ ⁻	H	H	H	SO ₃ ⁻	Ba ⁺⁺
P. red 237	*	*	*	*	*	*
P. red 239	*	*	*	*	*	*
P. red 240	*	*	*	*	*	*
P. red 243	SO ₃ ⁻	CH ₃	Cl	OCH ₃	H	Ba ⁺⁺
P. red 247	CH ₃	H	CONHC ₆ H ₄ SO ₃ ⁻ (p)	H	OCH ₃	Ca ⁺⁺

* chemical constitution not yet published

Monoacetoacetarylide Pigment Lakes

The chemical constitution of these pigments is analogous to that of the nonlaked pigments; the only difference is that the lakes contain an additional SO₃ group as a substituent. This leads to the basic chemical formula 9.



A further consequence of the analogous chemical constitution is the color of these monoacetoacetarylide pigment lakes, which are also yellow pigments (Table 5.23).

Pigment yellow 61 / 13880 / CAS 12286.65.6

Properties: Calcium salt, greenish yellow, low tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Medium heat stability: 250 °C (482 °F) in PE.

Medium light fastness: 5–6 (pure tone) / 5–6 (white reduction) in PE.

Application: Owing to its medium heat stability the use of this pigment is limited to polymers with a rather low processing temperature, for example, PVC, PE, and PP.

Pigment yellow 62:1 / 13940:1 / CAS 12286.66.7

Properties: Calcium salt, reddish yellow, low tinting strength, nearly completely resistant to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Medium heat stability: 240–260 °C (464–500 °F) in PE

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC and PE.

Application: Owing to its medium heat stability the use of this pigment is limited to polymers with a relative low processing temperature, for example, PVC, PE, PP, PS, PUR.

Pigment yellow 133 / – / CAS 132821.92.2

Properties: Strontium salt, greenish yellow, low tinting strength. The exact chemical constitution has not yet been published.

Medium heat stability: 260 °C (500 °F) in PE

Application: This pigment is only of regional importance (Asia) [45].

Pigment yellow 168 / 13960 / CAS 71832.85.4

Properties: Calcium salt, greenish yellow, low tinting strength, no migration in plasticized PVC, affects the shrinkage of PE-HD.

Low heat stability: 240 °C (464 °F) in PE.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC and PE

Application: Owing to its low heat stability the use of this pigment is limited to polymers with a low processing temperature, for example, PVC, and light-flowing grades of PE and PP.

Pigment yellow 169 / 13955 / CAS 73385.03.2

Properties: Calcium salt, reddish yellow.

Properties and applications very similar to Pigment yellow 168.

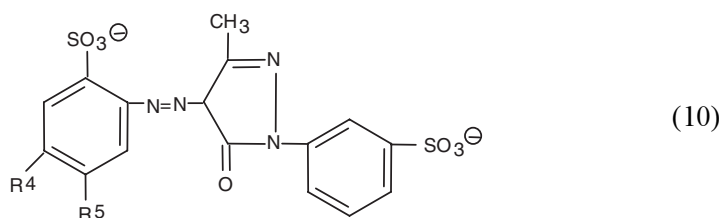
Table 5.23: List of the Substituents of Pigments According to Basic Formula 9

Color index number	Substituents		
	R ² ,	R ⁴	Metal ion
P. yellow 61	H	H	Ca ⁺⁺
P. yellow 62:1	CH ₃	H	Ca ⁺⁺
P. yellow 133	*	*	Sr ⁺⁺
P. yellow 168	Cl	H	Ca ⁺⁺
P. yellow 169	H	OCH ₃	Ca ⁺⁺

* chemical constitution not yet published

Pyrazolone Pigment Lakes

The nonlaked monoazopyrazolone pigments play no role in the coloring of plastics, but the situation is completely different in case of the laked pyrazolone pigments. They are very important and often used pigments (Table 5.24). The chemical constitution of this group of pigments is according to basic formula 10.



Pigment yellow 183 / 18792 / CAS 65212.77.3

Properties: Calcium salt, reddish yellow, low tinting strength, no migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good heat stability: 300 °C (572 °F) in PE.

Medium to good light fastness: 6 (pure tone) / 6–7 (white reduction) in PVC, 8 / 5 in PE. The light fastness decreases in PE depending on the degree of white reduction.

Application: This pigment can be used in many polymers, for example, PVC, PE, PP, PS, ABS, SAN, PMMA. It is not recommended in PA and PC.

Pigment yellow 190 / – / CAS 141 489.68.1

Properties: Calcium salt, low tinting strength. Owing to a very slight solubility in water there might be a slight coloring of the water bath during the manufacture of a masterbatch (granulation step). The exact chemical constitution has not yet been published.

Good heat stability: 300 °C (572 °F) in PE, 270 °C (518 °F) in PA.

Application: This pigment can be used in many polymers, for example, PVC, PE, PP, PS, ABS, and others, including PA.

Pigment yellow 191 / 18795 / CAS 129423.54.7

Properties: Calcium salt, reddish yellow, medium tinting strength, no migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good heat stability: 260–280 °C (500–536 °F) in PE, PS, ABS; 280 °C (536 °F) in PET, PMMA; 260 °C (500 °F) in PA; 320 °C (608 °F) in PC. The heat stability is independent of pigment concentration within a wide range in PE.

Good light fastness: 7 (pure tone) / 6 (white reduction) in PVC; 7–8 / 6–7 in PE; 7–8 / 7–8 in PET; 7 / 6–7 in PA; 7 / 7 in PS and ABS; 4–5 / 3–4 in PMMA; 6 / 4–5 in PC.

Medium weather fastness: 4/3 in PE.

Application: The pigment can be used to color a wide range of polymers.

Table 5.24: List of the Substituents of the Pigments According to Basic Formula 10

Color index number	Substituents		
	R ⁴	R ⁵	Metal ion
P. yellow 183	Cl	Cl	Ca ⁺⁺
P. yellow 190	*	*	Ca ⁺⁺
P. yellow 191	CH ₃	Cl	Ca ⁺⁺

* chemical constitution not yet published

5.2.2 Polycyclic Pigments

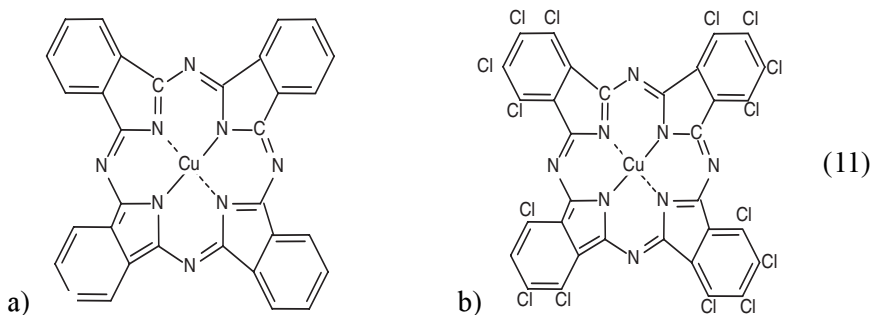
The name of this pigment group indicates the basic chemistry. Polycyclic pigments are made of several condensed aromatic and/or heterocyclic ring systems. The

many different colors are the result of variations of the ring system in combination with a large variety of possible substituents. The exact color and several properties depend on the crystal modification and/or isomerism (*cis*, *trans*). Generally speaking their main characteristics are good fastness properties and good resistance to solvents. On the other hand they are more costly than azo pigments, apart from the phthalocyanine pigments.

5.2.2.1 Phthalocyanine Pigments

The unsubstituted copper phthalocyanine pigments are blue (basic formula 11 a), while a nearly complete halogenation produces the green copper phthalocyanine pigments (basic formula 11 b). The commercially available green copper phthalocyanine pigments contain either (approximately) 15 chlorine atoms per molecule (Pigment green 7) or a mixture of chlorine and bromine (Pigment green 36). The ratio of the mixture of chlorine and bromine varies between the different manufacturers of green phthalocyanine pigments. The most yellowish green pigment contains (approximately) 11–12 bromine and 4–5 chlorine atoms as substituents. Pigments with only a partial halogenation gained no commercial interest.

The unsubstituted blue copper phthalocyanine pigment is polymorphous and five crystal modifications are known, whereas the green pigment shows only one crystal modification.



Copper can be exchanged by other metals, for example, zinc, iron, cobalt, but those products play no role in the coloring of plastics.

A detailed description of the blue and green phthalocyanine pigments, history, and production methods and properties is available in form of a company leaflet [47].

The copper phthalocyanine pigments are difficult to disperse in a polymer melt; therefore the use of an effective dispersing agent and sufficient shear during the

manufacture of a masterbatch are essential. Otherwise insufficiently dispersed pigments produce the visual disturbing color specks in the final product.

The coloring of plastics with a powdery color preparation, containing a higher concentration of phthalocyanine pigment, is very problematic because the single screw extruder, normally used for the injection molding of plastic parts, does not develop enough shear. The result can be that intensive blue or green colors without color specks are more or less impossible.

The unsubstituted blue copper phthalocyanine pigment (Pigment blue 15) is polymorphous. There are five crystal modifications (α , β , γ , δ , ϵ). The thermodynamic stability depends on the crystal modification; the β -modification shows the highest and the α -modification the lowest thermodynamic stability. The thermodynamic stability of these crystal modifications decreases in the following order: $\beta > \epsilon > \delta > \alpha \approx \gamma$.

The β - and the stabilized α -modifications are commonly used in the coloring of plastics. Special steps during the manufacture of this pigment produce the desired crystal modification. Each modification differs slightly in the exact shade.

The α -modification is thermodynamically not stable enough at the processing temperatures of polymers and would be converted into the stable β -modification. To avoid this the α -modification is stabilized by adding 0.5–1 atom chlorine; another method of stabilization is to treat the crystal surface with special substances.

Pigment blue 15 / 74160 / 147.14.8

Properties: α -modification, unstabilized, reddish blue. It plays no role in the coloring of plastics because at temperatures above 200 °C (392 °F) it is converted to the thermodynamic stable β -modification.

Pigment blue 15:1 / 74160 / 147.14.8

Properties: α -modification, stabilized with 0.5–1 atom chlorine, reddish blue, high tinting strength, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD, hard to disperse in a polymer melt.

Good heat stability: 300 °C (572 °F) in PE, ABS, and PC; 280 °C (536 °F) in PET; 270 °C (500 °F) in PS; 260 °C (500 °F) in PA 6.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC, PE, PP; and PA-6; 7 / 8 in PET.

Application: Nearly every polymer can be colored with this blue pigment. Some problems were reported while coloring some grades of ABS and PC; in this case preliminary trials are recommended. For the coloring of natural rubber, special available grades of this pigment should be used, because the *normal* qualities may

show detrimental effects on the vulcanization and/or aging of this polymer. These detrimental effects are caused by impurities of “free” copper ions. Applied in unsaturated polyester resins the speed of curing may be reduced considerably.

Pigment blue 15:2 / 74160 / 147.14.8

Properties: α -modification, stabilized with 0.5–1 atom chlorine, reddish blue. This grade is stabilized in addition against flocculation in lacquers and printing inks. The properties and applications correspond closely to those of Pigment blue 15:1.

Pigment blue 15:3 / 74160 / 147.14.8

Properties: β -modification, no stabilization necessarily, because this modification is thermodynamically the most stable form. Greenish blue, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD, hard to disperse in a polymer melt.

Good heat stability: 320 °C (608 °F) in PC; 300 °C (572 °F) in PE, PP, and PS; 280 °C (536 °F) in ABS and PET; 240–280 °C (464–536 °F) in PMMA; 260 °C (500 °F) in PA-6. Applied in PE, the heat stability decreases only at pigment concentrations below 0.01% (pure tone) and 0.05% (white reduction).

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC, and PA-6; 7–8 / 7–8 in PE, PP, PET, PS, and PC.

Good weather resistance: 5 in PE.

Application: Nearly every polymer can be colored with this blue pigment. For the coloring of natural rubber special, available grades of this pigment should be used, because the *normal* qualities may show detrimental effects on the vulcanization and/or aging of this polymer. These detrimental effects are caused by impurities of “free” copper ions. Applied in unsaturated polyester resins the speed of curing may be reduced considerably.

Pigment blue 15:4 / 74160 / 147.14.8

Properties: β -modification. This grade is stabilized in addition against flocculation in lacquers and printing inks. The properties and applications correspond closely to those of Pigment blue 15:3.

Pigment blue 15:6 / 74160 / 147.14.8

Properties: ϵ -modification, stabilized, strong reddish blue. In comparison to Pigment blue 15:1 and blue 15:3 this grade plays no role in the coloring of plastics. This is partly due to the fact that a strong reddish tint can be matched by mixing of a blue and a red pigment.

Pigment blue 16 / 74100 / CAS 574.93.6

This pigment is the metal-free variation of the blue copper phthalocyanine pigment (Pigment blue 15). It plays no role in the coloring of plastics, but is mentioned here because of the reason of completeness.

Pigment green 7 / 74260 / CAS 1328.53.6

Properties: Bluish green, contains typically (approximately) 14–15 atoms chlorine, no migration in plasticized PVC, strong effect on the shrinkage of PE-HD, hard to disperse in a polymer melt. It occurs in only one crystal modification.

Good heat stability: 300 °C (572 °F) in PE; 260–300 °C (500–572 °F) in PMMA; 290 °C (554 °F) in PS; 280 °C (536 °F) in PET; 260 °C (500 °F) in PA-6. The heat stability is independent of the pigment concentration within a wide range.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC; 7–8 / 7–8 in PE, PP, PS, ABS, and PC.

Good weather resistance: 5 in PE.

Application: Nearly every polymer can be colored with this green pigment, however preliminary tests are recommended when applying color to PA, PET, and PC.

Pigment green 36 / 74265 / CAS 14302.13.7

Properties: Yellowish green. This pigment contains a mixture of chlorine and bromine; the ratio is variable, depending on the manufacturer. Typically it contains two to eight atoms chlorine and nine to four atoms bromine. The yellowish tint increases with increasing number of bromine atoms. It occurs only in one crystal modification. It is hard to disperse in a polymer melt, and affects strongly the shrinkage of PE-HD. No migration in plasticized PVC.

Good heat stability: 300 °C (572 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE and other polymers.

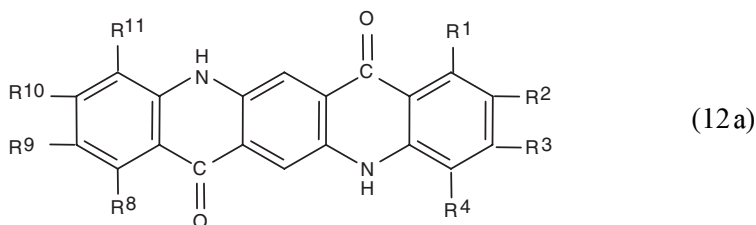
Good weather resistance: 5 in PE.

Application: Nearly every polymer can be colored with this green pigment, however, preliminary tests are recommended when applying color to ABS, PA, and PC.

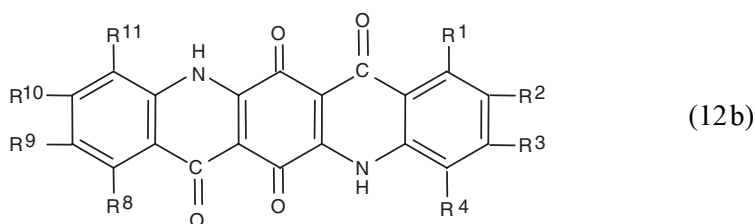
5.2.2.2 Quinacridone Pigments

The typical quinacridone structure is a five-ring polycyclic system, consisting of three benzene and two pyridone rings (as bridge between the benzene rings). The combination of the five rings can be either in an angular or linear form, and the arrangement of the heterocyclic pyridone rings can be either in *trans*- or *cis*-position. This gives four possible constitutions of quinacridone pigments, but only the

linear, *trans*-quinacridone pigment is of commercial interest for the coloring of plastics (basic formula 12a).



The central benzene ring can be oxidized, which gives the quinacridone quinone pigments (basic formula 12b).



The linear, *trans*-quinacridone exhibits several crystal modifications; the known ones are the α -, β -, δ -, and γ -modifications. Most synthetic methods produce the α -modification, which, however, shows insufficient fastness properties. This is the reason why the α -modification must be converted to the more stable β - or γ -modifications.

The exact shade of quinacridone pigments depends not only on the crystal modification but also on the substitution pattern. Experience shows that the substituents lighten the shade; therefore commercially available substituted quinacridone pigments contain no more than two substituents, either chlorine or the CH_3 group, on the peripheral benzene rings (Table 5.25).

Another method to change the shade is the formation of mixed crystal phases, containing a mixture of an unsubstituted and a substituted quinacridone pigment or a mixture of an unsubstituted quinacridone with a quinacridone quinone pigment. Several variations are commercially available.

The quinacridone pigments are difficult to disperse in a polymer melt; therefore the use of an effective dispersing agent and sufficient shear during the manufacture of a masterbatch are essential. Otherwise incomplete dispersed pigments produce visually disturbing color specks in the final product.

The coloring of plastics with a powdery color preparation, containing a higher concentration of quinacridone pigment, is very problematic, because the single screw extruder, normally used for the injection molding of plastic parts, does not develop enough shear. The result can be that intensive colors without any color specks are more or less impossible.

Pigment violet 19 – β -modification / 73900 / CAS 1047.16.1

Properties: Reddish violet, medium tinting strength, no migration in plasticized PVC, medium effect on the shrinkage of PE-HD.

Good heat stability: 290–300 °C (554–572 °F) in PE, PS, and ABS; 290 °C (554 °F) in PC; 280 °C (536 °F) in PET; 260 °C (500 °F) in PA-6. The heat stability is independent from the pigment concentration within a wide range.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE, PET, and PS; 7–8 / 7 in PVC, 7 / 6 in PA 6; 8 / 6–7 in PC.

Good weather resistance: 5 or 4–5 in PE.

Application: A wide range of polymers can be colored with this pigment. When applied to color POM the formation of a deposit on the surface of the mold is possible at concentrations below 0.1%.

Pigment violet 19 – γ -modification / 73900 / CAS 1047.16.1

Properties: Bluish red, medium tinting strength, no migration in plasticized PVC, medium effect on the shrinkage of PE-HD.

Good heat stability and light fastness, which are not completely independent of the particle size.

Application: A wide range of polymers can be colored with this pigment, including PA. When applied to color PET the pigment might dissolve at very low concentrations.

Pigment red 122 / 73915 / CAS 980.26.7

Properties: Bluish red, medium tinting strength, no migration in plasticized PVC, affects the shrinkage of PE-HD.

Good heat stability: 310 °C (560 °F) in PC; 300 °C (572 °F) in PE, PS, and ABS; 280 °C (536 °F) in PET; 260 °C (500 °F) in PA-6. The heat stability is independent of the pigment concentration within a wide range.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE, PS, PC, and PET; 8 / 7–8 in ABS, 7–8 / 7 in PVC; 7–8 / 6 in PA-6.

Good weather resistance: 5 in PE.

Application: A wide range of polymers can be colored with this pigment. When applied to color POM the formation of a deposit on the surface of the mold is possible at concentrations below 0.1%.

Pigment red 202 / 73907 / CAS 68859.50.7

Properties: Bluish red, strong effect on the shrinkage of PE-HD.

Good heat stability: 290–300 °C (554–572 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC; 7–8 / 8 in PE.

Good weather resistance: 5 in PE.

Application: A wide range of polymers can be colored with this pigment.

Pigment red 207 / 73900 + 73908 / CAS 1047.16.1 + 3089.16.5

Properties: Yellowish red. Mixed phase pigment of an unsubstituted quinacridone and 4,11-dichloroquinacridone.

The fastness properties correspond to the individual components.

Application: A wide range of polymers can be colored with this pigment.

Pigment red 209 / 73905 / CAS 3089.17.6

Properties: Yellowish red, low tinting strength, no migration in plasticized PVC, medium effect on the shrinkage of PE-HD. Mixed phase pigment of chlorinated quinacridone pigments (3,10-, 1,8-, and 1,10-dichloroquinacridone).

Good heat stability: 320 °C (608 °F) in PC; 300 °C (572 °F) in PE. The heat stability is independent of the pigment concentration within a wide range.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE, PC, and PS; 7–8 / 7–8 in PVC.

Application: A wide range of polymers can be colored with this pigment.

The following three pigments are mixed phase pigments of an unsubstituted quinacridone and a quinacridone quinone. The exact ratio between the single components is not yet published.

Pigment red 206 / 73900 + 73920 / CAS 1047.16.1 + 1503.48.6

Properties: Yellowish red.

Application: It is seldom applied for the coloring of plastics.

Pigment orange 48 / 73900 + 73920 / CAS 1047.16.1 + 1503.48.6

This pigment plays no role in the coloring of plastics because it may dissolve in PA and some other polymers. It is used to some extent in spin dying.

Pigment orange 49 / 73900 + 73920 / CAS 1047.16.1 + 1503.48.6

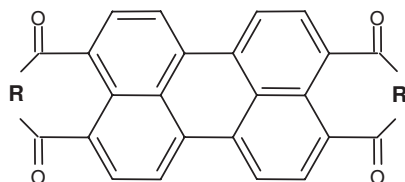
This pigment plays no role in the coloring of plastics.

Table 5.25: List of Substituents of Pigments According to Basic Formulas 12a and 12b

Color index number	Substituent							
	R ¹	R ²	R ³	R ⁴	R ⁸	R ⁹	R ¹⁰	R ¹¹
P. violet 19	H	H	H	H	H	H	H	H
P. red 122	H	CH ₃	H	H	H	CH ₃	H	H
P. red 202	H	Cl	H	H	H	Cl	H	H
P. red 207	H	H	H	Cl	H	H	H	Cl
<i>Mixed phase pigment with an unsubstituted quinacridone</i>								
P. red 209	H	H	Cl	H	H	H	Cl	H
<i>Mixed phase pigment with 1,8- and 1,10-dichloroquinacridone</i>								
P. red 206	Mixed phase pigment of unsubstituted quinacridone and quinacridone quinone							
P. orange 48	Mixed phase pigment of unsubstituted quinacridone and quinacridone quinone							
P. orange 49	Mixed phase pigment of unsubstituted quinacridone and quinacridone quinone							

5.2.2.3 Perylene Pigments

Perylene pigments are derivatives of basic formula 13; the component R is rather variable.



(13)

Depending on the chemical constitution of R, the perylene pigments exist in a wide range of colors, providing red, bordeaux, violet, brown, and black shades. Although the brown and black shades are chemically interesting pigments, they do not play a role in the coloring of plastics; only the red and violet pigments are of special commercial interest.

The application of perylene pigments in HALS (**H**indered **A**mine **L**ight **S**tabilizer) stabilized polyolefins, e.g., PE, is problematic. Depending on the perylene pigment concentration the HALS stabilizer might be inactivated or even destroyed; consequently the plastic part would fail to fulfill its requirements. If the use of perylene pigments in stabilized PE cannot be avoided, it is recommended to run preliminary tests to evaluate a possible interaction.

Perylene pigments offer a high tinting strength and provide very good fastness properties, not only in plastics but also in automobile paints, the other important field of application (Table 5.26).

Pigment red 123 / 71145 / CAS 24108.89.2

Properties: Medium red shade (scarlet-red), not entirely fast to bleeding in plasticized PVC (dependent on the plasticizer system), affects the shrinkage of PE-HD considerably.

Good heat stability: 300 °C (572 °F) in PE.

Application: This pigment is seldom used because of its inferior properties in comparison to Pigment red 149.

Pigment red 149 / 71137 / CAS 4948.15.6

Properties: Bluish red, high tinting strength, no migration in plasticized PVC, affects the shrinkage of PE, however, this influence decreases with increasing temperature.

Good heat stability: 310 °C (560 °F) in PC; 300 °C (572 °F) in PE; 280 °C (536 °F) in PS, PMMA and PET; 250 °C (482 °F) in ABS. The heat stability is independent of the pigment concentration within a wide range.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PVC; 8 / 7 in PE and PS; 8 / 6–7 in PMMA; 6–7 / 7–8 in PET.

Application: A wide range of polymers can be colored with this pigment, including cast resins such as methacrylic acid methylester or unsaturated polyesters, which are polymerized with peroxide catalysts. In polymers, stabilized with HALS, a possible interaction between the pigment and the stabilizer should be considered.

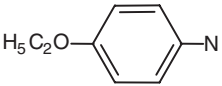
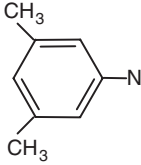
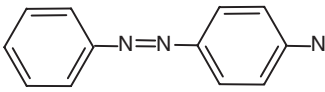
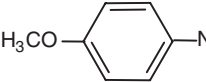
Pigment red 178 / 71155 / CAS 3049.71.6

Properties: The pigment crystallizes in two modifications, but only one is commercially available. The pigment is fast to migration in plasticized PVC, affects the shrinkage of HD-PE.

Good heat stability: 300 °C (572 °F) in PE.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PE.

Table 5.26: List of the Substituents of Pigments According to Basic Formula 13

Color Index Number	Substituent R
P. red 123	
P. red 149	
P. red 178	
P. red 179	$\text{CH}_3\text{—N}$
P. red 190	
P. red 224	O
P. violet 29	HN

Application: A wide range of polymers can be colored with this pigment. In polymers, stabilized with HALS, a possible interaction between the pigment and the stabilizer should be considered.

Pigment red 179 / 71130 / CAS 5521.31.3

Properties: In comparison to the other pigments of this class, the heat stability of Pigment red 179 is rather low.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE.

Good weather resistance: 5 (pure tone) / 4 (white reduction) in PE.

Application: Owing to its low heat stability the use is limited to polymers with a low processing temperatures, for example, PVC and PE-LD.

Pigment red 190 / 71140 / CAS 6424.77.7

The use of this bluish red pigment is preferably in automobile paints. In spite of its good heat stability it is seldom used as colorant for polymers.

Pigment red 224 / 71127 / CAS 128.69.8

Owing to its low heat stability the use of this bluish red pigment as colorant for polymers is very limited. One application is, for example, in spin dyeing of polyacrylonitrile.

Pigment violet 29 / 71129 / CAS 12236.71.4

Properties: A rather dull, dark violet, no migration in plasticized PVC.

Good heat stability: 300 °C (572 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE.

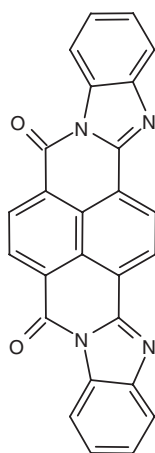
Medium weather fastness: 4 (pure tone) / 3 (white reduction) in PE.

Application: A wide range of polymers can be colored with this pigment. It is recommended to run preliminary tests in ABS, PA, PC, and PET.

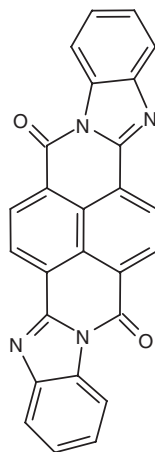
5.2.2.4 Perinone Pigments

The chemical constitution of perinone pigments (basic formula 14) indicates the existence of two isomeric forms, a *cis*- and a *trans*-isomer.

At present, only unsubstituted perinone pigments are commercially available as colorants for polymers. There are three products, a pure *cis*- and *trans*-isomer and a mixture of both. These isomers differ in color and properties.



cis-Form



trans-Form

(14)

Pigment orange 43 – trans-isomer / 71105 / CAS 4424.06.0

Properties: Reddish orange, high tinting strength, no migration in plasticized PVC, affects strongly the shrinkage of PE-HD.

Good heat stability: 280 °C (536 °F) in PE and PET. The heat stability in PE decreases considerably at concentrations < 0.1 %. The pigment dissolves in PET at very low pigment concentrations accompanied by a change of its shade to yellow.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE; 8 / 7–8 in PVC; 6 / 5–6 in PET.

Good weather resistance: 5 in PE.

Application: A wide range of polymers can be colored with this pigment.

Pigment red 194 – cis-isomer / 71100 / CAS 4216.02.8

Properties: Bluish red. At higher temperatures this *cis*-isomer dissolves in several polymers, for example, PVC, and PS, combined with a color shift.

Good heat stability: 270 °C (518 °F) in PE.

Application: The pigment is seldom used to color plastics.

Vat red 74 – mixed phase of both isomers / 73305

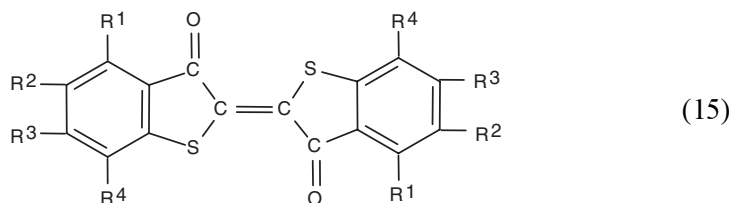
Properties: Scarlet.

Good heat stability: 300 °C (572 °F).

Application: Mainly used in spin dyeing of PP.

5.2.2.5 Thioindigo Pigments

The chemical structure of thioindigo (basic formula 15) indicates the possibility of several derivatives, which were marketed in the past. Today only two pigments (Pigment red 88 and red 181) and one dye (Vat red 41) are still commercially available (Table 5.27).



A characteristic feature of thioindigo pigments is the tendency to dissolve, depending on the polymer and processing temperature.

Pigment red 88 / 73312 / CAS 14295.43.3

Properties: Red-violet, affects considerably the shrinkage of PE-HD. Several grades of this pigment are marketed, differing in their tendency to migrate in plasticized PVC and in their fastness properties as result of different aftertreatments.

Good heat stability: 260–280 °C (500–536 °F) in PE. The pigment dissolves in PS depending on the processing temperature, combined with a color shift.

Good to medium light fastness: 8 (pure tone) / 6 (white reduction) in PVC; 8 / 5 in PE.

Insufficient weather resistance: 3 (pure tone) / 2 (white reduction) in PE.

Application: It is mainly used to color PVC, PUR, PE, PP, and for spin dyeing.

Pigment red 181 / 73360 / CAS 2379.74.0

Properties: Bluish red, good light fastness, dissolves in PS and similar polymers. It is a special purpose product for PS. In other polymers it is not applied.

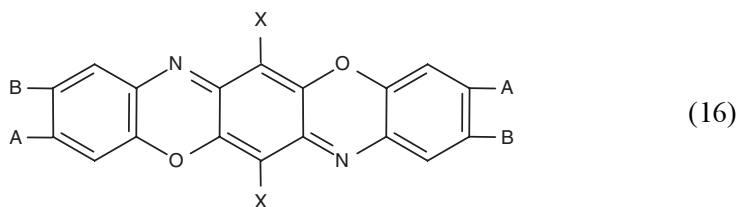
Vat red 41 – unsubstituted thioindigo. It is a dye.

Table 5.27: List of Substituents of Colorants According to Basic Formula 15

Color index number	Substituent			
	R ¹	R ²	R ³	R ⁴
P. red 88	Cl	H	H	Cl
P. red 181	CH ₃	H	Cl	H
Vat red 41	H	H	H	H

5.2.2.6 Dioxazine Pigments

In the past this group of pigments were important dyes to color textiles, but they have lost their former importance. This is partly due to certain deficiencies in their properties. Regarding the coloring of plastics, only two violet products of commercial importance are left. The general chemical constitution shows the basic formula 16.



Pigment violet 23 / 51319 / CAS 6358.30.1

Properties: Bluish violet, high tinting strength, not completely fast to migration in plasticized PVC, affects the shrinkage of PE-HD. The supplied data vary partly considerably among manufacturers, probably due to different particle sizes and/or aftertreatments.

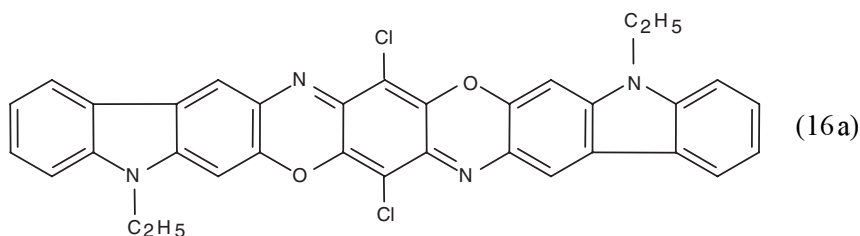
Good to medium heat stability: 280 °C (536 °F) in PE. It is remarkable that the heat stability depends strongly on the degree of white reduction. The heat stability drops in PE to 240 °C (464 °F) at a 1/25 standard pigment concentration; in addition a concentration below 0.5% should be avoided in PE. The pigment dissolves in PS and PET at processing temperatures above 250 °C (482 °F). The heat stability in PA-6 is 260 °C (500 °F).

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC; 6–7 / 4–5 and 8 / 7–8 in PE (depending on the manufacturer); 8 / 7–8 in PA-6; 7 / 7 in PS.

Good weather resistance: 4–5 in PE.

Application: The pigment can be used in many polymers, including spin dying.

Chemistry: In case of Pigment violet 23 the substituents A and B (basic formula 16) are not single components but are used to add a further ring system. The result is formula 16a, the chemical constitution of Pigment violet 23.



Pigment violet 37 / 51 345 / CAS 57971.98.9

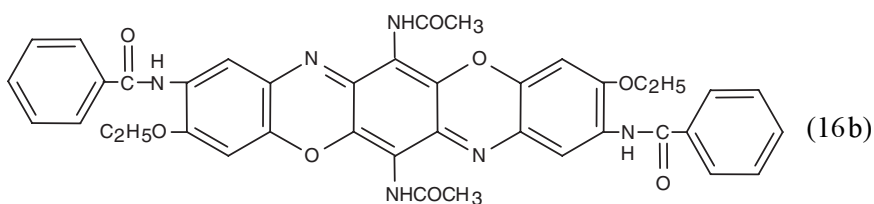
Properties: Reddish violet, high tinting strength, not completely fast to migration in plasticized PVC, affects considerably the shrinkage of PE-HD.

Good heat stability: 280–300 °C (536–572 °F) in PE, which decreases clearly with increasing white reduction.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE, which decreases clearly with increasing white reduction (1/25 standard pigment concentration).

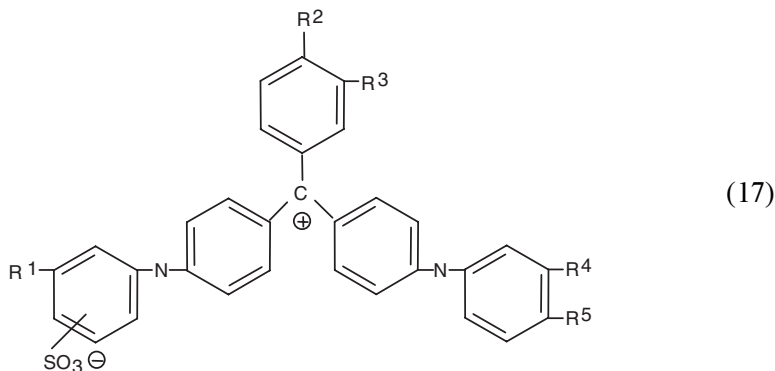
Application: The pigment can be used in many polymers, including spin dying.

Chemistry: The chemical constitution of Pigment violet 37 shows formula 16b.



5.2.2.7 Triarylcarbonium Pigments

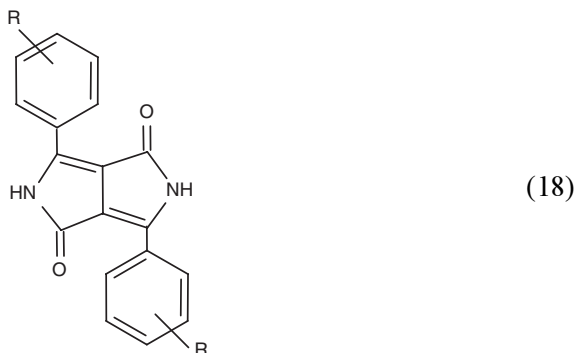
The chemical constitution of triarylcarbonium pigments is based on the general formula 17.



Miscellaneous triarylcation pigments are commercially available, which are applied exclusively in printing inks. They play no role in the coloring of plastics, but are mentioned here for the purpose of completeness.

5.2.2.8 Diketopyrrolo-Pyrrolo (DPP) Pigments

Although the constitution of this molecule has been known for a long time, industrial production started only in the last decade. The first member of this group was the Pigment red 254, and several other derivatives have since become available. The general chemical constitution of DPP pigments shows formula 18. The chemistry and number of the substituent R have not yet been published. In the case of Pigment red 254 the substituent R is chlorine (because of the chlorine content) and probably in the *p*-position.



Pigment red 254 / 56110 / CAS 122390.98.1

Properties: Red, high tinting strength, no migration in plasticized PVC, affects more or less the shrinkage of PE-HD (depending on the PE grade).

Good heat stability: 280–300 °C (536–572 °F) in PE; 290 °C (554 °F) in PS; 260 °C (500 °F) in PMMA. The pigment dissolves in PC at temperatures above 320 °C (608 °F), giving a bright fluorescent yellow.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC, PE, and ABS.

Good weather resistance: 5 in PE.

Application: The pigment can be used in many polymers.

Pigment red 255 / – / CAS 120500.90.5

Properties: Scarlet, nearly completely fast to migration in plasticized PVC.

Medium heat stability: 240 °C (464 °F) in PE.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PE.

Application: The use of this pigment is limited because of its low heat stability.

Pigment red 264 / – / –

Properties: Ruby, no effect on the shrinkage of PE-HD.

Good heat stability: 280–300 °C (536–572 °F) in PE. The heat stability decreases clearly in PE with increasing white reduction.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE.

Good weather resistance: 5 in PE.

Application: The pigment can be used in many polymers.

Pigment red 272 / – / –

Properties: Flame-red, no migration in plasticized PVC, slight effect on the shrinkage of PE-HD.

Good heat stability: 300 °C (572 °F) in PE.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PE.

Medium weather resistance: 2–3 in PE.

Application: The pigment can be used in many polymers.

Pigment orange 71 / – / –

Properties: Orange, slight effect on the shrinkage of PE-HD.

Good heat stability: 280–300 °C (536–572 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PE; 7–8 / 7–8 in PVC.

Good weather resistance: 4–5 in PE.

Application: The pigment can be used in many polymers.

Pigment orange 73 / - / -

Properties: Orange, not completely fast to migration in plasticized PVC.

Good heat stability: 280–300 °C (536–572 °F) in PE.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PE; 7–8 / 6–7 in PVC.

Application: The pigment can be used in many polymers.

5.2.3 Miscellaneous Pigments

In this section all the pigments are described that can not be categorized in one of the other pigment groups. Some pigments have a chemical composition that resembles one of the previously described pigment groups but nevertheless they are single pigments. Here, too, the chemical structure is shown (if published).

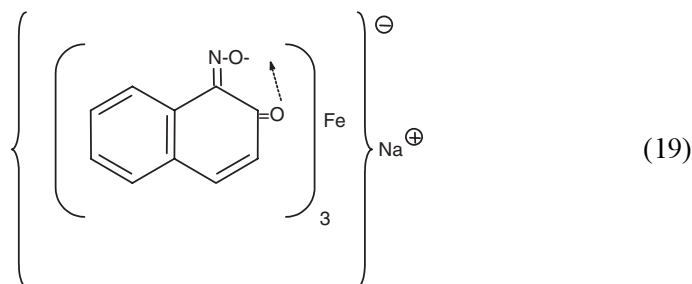
5.2.3.1 Metal Complex Pigments

A main feature of these pigments is the possibility of an interaction between the metal of the pigment and metal containing additives in the polymer, for example, metal containing stabilizer in PVC. The result of an interaction might be a darkening and/or color shift in the plastic part.

Pigment green 8 / 10006 / CAS 16143.80.9

Properties: Yellowish green.

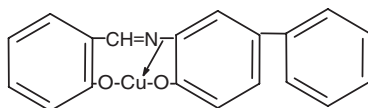
Application: This pigment is mainly used to color rubber. Owing to its low heat stability (220 °C [428 °F]) it can be applied only in polymers with a low processing temperature, for example, PVC and PE-LD. Another disadvantage that limits its use is the low light fastness of approx. 2–3. The pigment lost much of its former importance in comparison to the superior Pigment green 7.



Pigment yellow 117 / 48043 / CAS 21405.81.2

Properties: Greenish yellow, high tinting strength.

Application: In case of use in PVC, stabilized, for example, with tin compounds, the possibility of an interaction should be considered. The pigment is used mainly to color thermosets, where it shows a good light fastness and weather resistance.

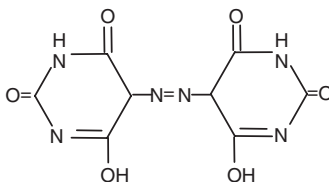


(20)

Pigment yellow 150 / 12764 / CAS 68511.62.6

Properties: Good fastness properties. When the color matching requires a white pigment to brighten the shade, the use of zinc sulfide (Pigment white 7) should be avoided because of a possible interaction that would result in a darkening of the shade (formation of dark nickel sulfide).

Application: The main use of this pigment is the spin dyeing of PP and PA, but also at the injection molding of PA and other polymers.

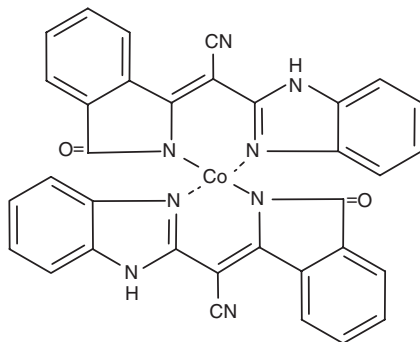


Ni-complex

(21)

Pigment yellow 177 / 48120 / CAS 60109.88.8

Application: This pigment was developed especially for spin dyeing of PP and PA. In other fields of coloring of plastics it is not applied.

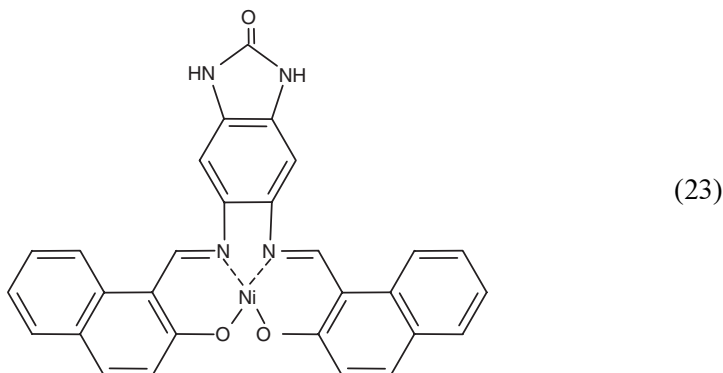


(22)

Pigment orange 68 / – / CAS 42844.93.9

Properties: The pigment is marketed in different particle sizes, which differ in the shades.

Good heat stability: 320 °C (608 °F) in PC; 300 °C (572 °F) in PE, PS, and ABS. The heat stability is independent of the pigment concentration within a wide range.



Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PE; 8 / 7 in PC; 7 / 7 in PS, PMMA, and PA-6; 6–7 / 6–7 in ABS and SAN.

Application: The pigment can be used in many polymers, including PA and PC.

5.2.3.2 Isoindoline / Isoindolinone Pigments

Pigment yellow 109 / 56284 / CAS 12769.01.6

Properties: Greenish yellow, low tinting strength, fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

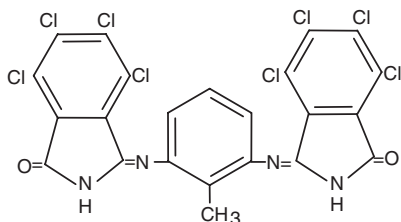
The two pigments Pigment yellow 109 and yellow 110 differ only by one substituent, a CH₃ group on the central benzene ring. This is a good example of the importance and effect of a substituent on the shade of a pigment.

Good heat stability: 280 °C (536 °F) in PE. The heat stability depends clearly on the pigment concentration. At a concentration of 0.1% the heat stability is 280 °C (536 °F), but only 240 °C (464 °F) at a concentration of 0.01% (in PE).

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE; 7–8 / 7–8 in PVC.

Good weather resistance: 4–5 in PE.

Application: The pigment can be used in many polymers, including for the spin dyeing.



(24)

Pigment yellow 110 / 56280 / CAS 5590.18.1

Properties: Reddish yellow, medium tinting strength, fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

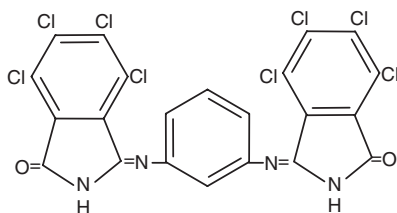
The two pigments Pigment yellow 110 and yellow 109 differ only by one substituent, a CH₃ group on the central benzene ring. This is a good example of the importance and effect of a substituent on the shade of a pigment.

Good heat stability: 270–280 °C (518–536 °F) in PE, depending on the pigment concentration.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC and PE.

Good weather resistance: 4–5 in PE.

Application: The pigment can be used in many polymers, including for the spin dyeing.



(25)

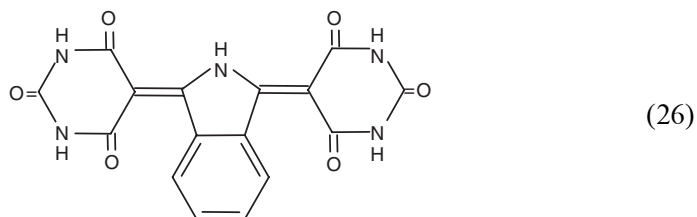
Pigment yellow 139 / 56298 / CAS 36888.99.0

Properties: Reddish yellow, medium tinting strength, fast to migration in plasticized PVC.

Medium heat stability: 250–260 °C (482–500 °F) in PE.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PE.

Application: The main fields of use are the coloring of PVC, PO, and PUR.



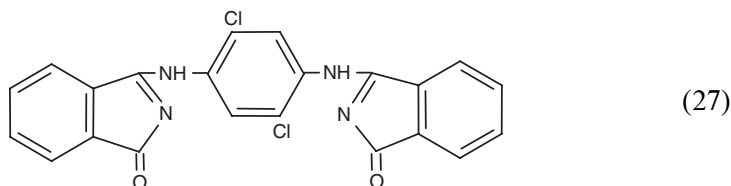
Pigment yellow 173 / – / CAS 51016.63.8

Properties: Greenish yellow, low tinting strength, nearly completely fast to migration in plasticized PVC (depending on the plasticizer).

Good heat stability: 290–300 °C (554–572 °F) in PE.

Good light fastness: 7–8 in PVC.

Application: The pigment can be used in many polymers.



Pigment orange 61 / 11265 / CAS 76168.74.6

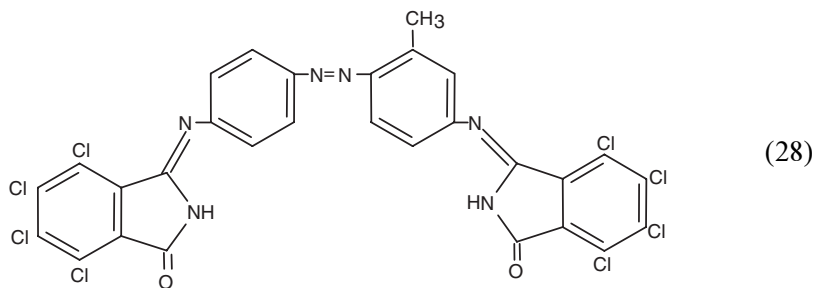
Properties: Orange, low tinting strength, fast to migration in plasticized PVC, strong effect on the shrinkage of PE-HD.

Good heat stability: 270–290 °C (518–554 °F) in PE. The heat stability decreases clearly at a pigment concentration of < 0.01% (pure tone) and < 0.05% (white reduction).

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PE.

Good weather resistance: 4–5 in PE.

Application: The pigment can be used in many polymers, including for the spin dyeing.



Pigment brown 38 / – / CAS 126338.72.5

Properties: Yellowish brown, low tinting strength, not completely fast to migration in plasticised PVC. It is classified as an isoindoline pigment, although its exact chemical constitution has not yet been published.

Medium heat stability: 240 °C (464 °F) in PE.

Good light fastness: 8 (pure tone) / 8 (white reduction) in PVC.

Application: Due to its low heat stability the use of this pigment is limited to polymers with a rather low processing temperature, for example, PVC and PE-LD.

5.2.3.3 Aminoanthraquinone Pigments

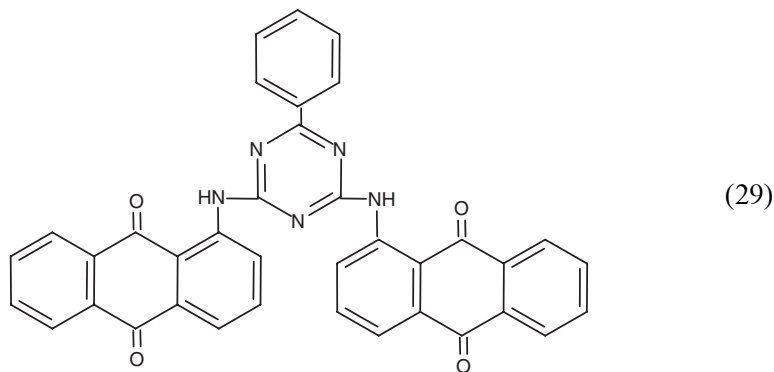
Pigment yellow 147 / 60645 / CAS 76168.75.7

Properties: Reddish yellow, low tinting strength, fast to migration in plasticized PVC.

Good heat stability: 300 °C (572 °F) in PE, PS, PET, and PC.

Good light fastness: 7 (pure tone) / 7 (white reduction) in PC.

Application: The pigment can be used in many polymers, including for the spin dyeing of PP.



Pigment red 177 / 48120 / CAS 60109.88.8

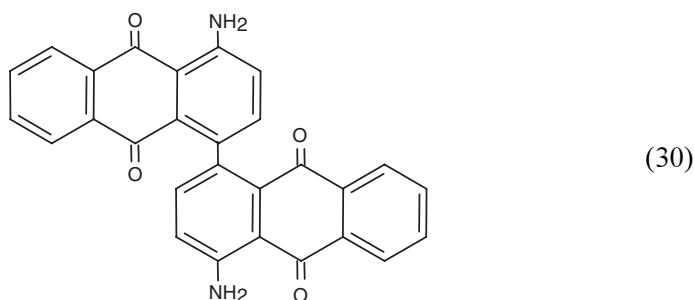
Properties: Red, low tinting strength, not completely fast to migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good heat stability: 270–280 °C (518–536 °F) in PE, the heat stability decreases clearly at pigment concentration < 0.1%.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC, 8 / 7 in PE.

Medium weather resistance: 3–4 in PE.

Application: The pigment can be used in many polymers, including for the spin dyeing of PP, PAN, and PA.

**5.2.3.4 Indanthrone Pigments***Pigment blue 60 / 69800 / CAS 81.77.6*

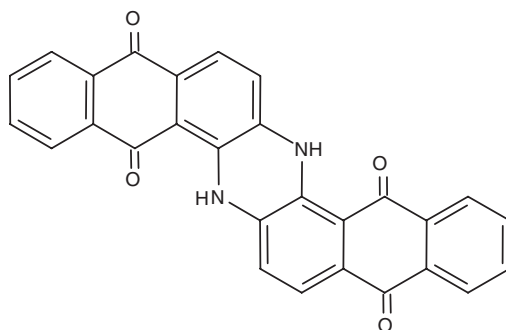
Properties: Blue, medium tinting strength, not completely fast to migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good heat stability: 270 °C (518 °F) in PE, depending on the pigment concentration.

Good light fastness: 7–8 (pure tone) / 7 (white reduction) in PVC, 7–8 / 7–8 in PE.

Good weather resistance: 5 in PE.

Application: The pigment can be used in many polymers, including rubber and for the spin dyeing, but it is not recommended for the coloring of PA, PC, and PET.



(31)

5.2.3.5 Flavanthrone Pigments

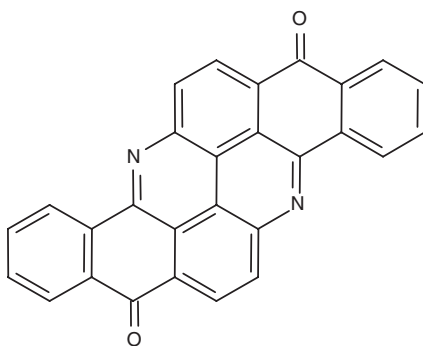
Pigment yellow 24 / 70600 / CAS 475.71.8

Properties: Reddish yellow, medium tinting strength.

Good heat stability: 270 °C (518 °F) in PE. The heat stability decreases clearly with increasing white reduction.

Good light fastness:

Application: The pigment can be used in several polymers, including for the spin dyeing (PAN). It should be noted that the pigment may dissolve partially in some polymers at higher processing temperatures combined with a color shift to a more greenish yellow.



(32)

5.2.3.6 Pyranthrone Pigments

Pigment red 216 / 59710 / CAS 1324.33.0

Properties: A tribromopyranthrone derivative, bluish red, low tinting strength, not completely fast to migration in plasticized PVC.

Medium heat stability: 250 °C (482 °F) in PE.

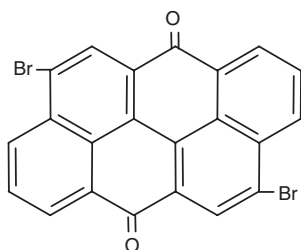
Good light fastness: 8 (pure tone) / 6 (white reduction) in PE; 8 / 8 in PVC.

Application: Owing to its medium heat stability the use of this pigment is limited to polymers with a rather low processing temperature, for example, PVC and PE-LD.

5.2.3.7 Anthanthrone Pigments

Pigment red 168 / 59300 / CAS 4378.61.4

Application: Owing to its low heat stability (approx. 180 °C [356 °F]) it can be used only to color PVC. The main fields of use are coatings and paints, where the pigment shows very good fastness properties.



(33)

5.2.3.8 Quinophthalone Pigments

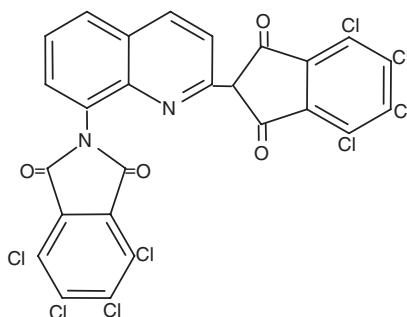
Pigment yellow 138 / 56300 / CAS 56731.19.2

Properties: Greenish yellow, medium to good tinting strength, affects the shrinkage of PE-HD (depending on the processing temperature).

Good heat stability: 290 °C (554 °F) in PE.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE. The light fastness decreases with increasing white reduction.

Application: The pigment can be used in many polymers.



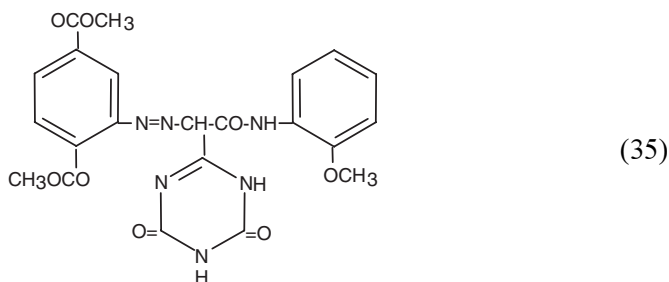
(34)

5.2.3.9 Additional Pigments with Known Chemical Structure

Pigment yellow 182 / – / CAS 67906.31.4

Properties: Reddish yellow, high tinting strength, not completely fast to migration in plasticised PVC, no effect on the shrinkage of PE-HD.

Good to medium heat stability: 280–250 °C (536–482 °F). The heat stability depends on the degree of white reduction and drops with increasing white reduction. The pigment dissolves in PS at temperatures > 200 °C (392 °F) combined with a significant color shift. The same behavior can be observed in ABS.



Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PE.

Application: The use of this pigment is more or less limited to PVC-U and polyolefins.

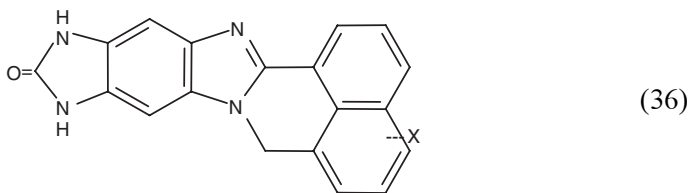
Pigment yellow 192

Properties: The chemistry of the substituents has not yet been published, only the general constitution is known. The pigment dissolves in PA, PC, and PMMA at a pigment concentration < 0.3%; at concentrations > 0.3% the dissolution is incomplete, which causes differences in the shade.

Good heat stability: 300 °C (572 °F) in PA.

Good light fastness: 8 in PA.

Application: The pigment was developed especially for the spin dyeing of PA, but because of the good fastness properties it is used also in other polymers.



Pigment orange 64 / 12760 / CAS 72102.84.2

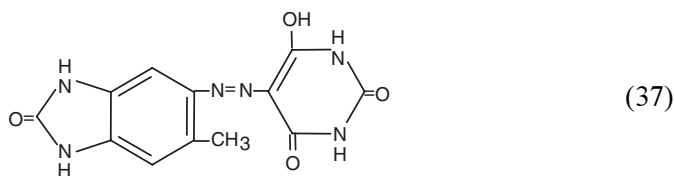
Properties: Orange, medium tinting strength, fast to migration in plasticized PVC, no effect on the shrinkage of PE-HD.

Good to medium heat stability: 280–240 °C (536–482 °F) in PE, depending on the pigment concentration.

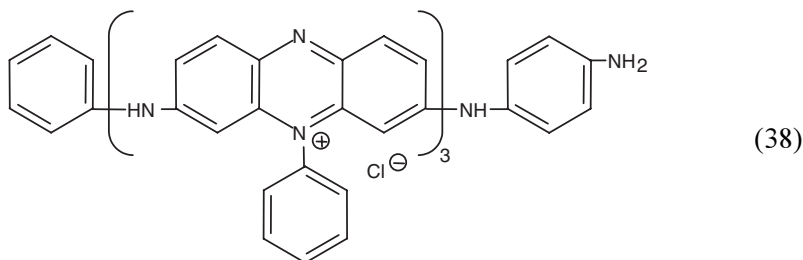
Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PVC, 7 / 7 in PE.

Good weather resistance: 4 in PE.

Application: The pigment can be used in many polymers.

*Pigment black 1 / 50440 / CAS 13007.86.8*

Pigment black 1 is also known as aniline black, its use is discontinued to color polymers because of the content of aniline, which is classified as carcinogenic.

**5.2.3.10 Additional Pigments with Unknown Chemical Structure***Pigment yellow 99 / – / 12225.20.6*

Properties: Reddish yellow, low tinting strength, good heat stability. It is described as anthraquinone pigment, but without chemical details.

Application: The pigment is recommended for textile printing and to color plastics. At present the pigment has only regional importance (Japan) [45].

Pigment yellow 187

Properties: Greenish yellow.

Good heat stability: 320 °C (608 °F) in PA.

Medium light fastness: Approx. 4 in PA.

Application: The pigment was developed especially to color PA.

5.3 Dyes

Dyes are defined as colorants that are (completely) soluble in a polymer at the processing temperature. The result is a solution of the dye, a molecular distribution of the dye in the polymer, and a crystalline structure is no longer noticeable. Contrary to dyes, pigments are defined as (completely) insoluble in a polymer at the processing temperature. The practice, however, shows that this differentiation between dyes and organic pigments is not always clear. It is known that some organic pigments dissolve at least partially in a polymer melt, depending on the polymer and the processing temperatures. A typical example is the DPP-Red, Pigment red 254. In most of the polymers it acts as pigment, giving a brilliant red shade. In PC, however, Pigment red 254 dissolves completely at a temperature above 320 °C (608 °F), giving a brilliant fluorescent yellow. In PC Pigment red 254 shows the typical behavior of a dye.

Analogous to pigments, dyes are subdivided into inorganic and organic substances, but in contrast to the inorganic pigments inorganic dyes do not exist for the coloring of plastics for systematic reasons. Consequently only organic dyes can be used to color plastics.

The dye must be soluble in a polymer melt, but should be insoluble in water. The insolubility in water is a very important requirement for dyes; otherwise it may migrate in contact with humidity. Any migration of color is not only a detrimental effect, for example, in the case of toys and/or packaging material, but generally banned by legal requirements (“non-migration principle”, followed by FDA and the European countries).

Dyes may be soluble, at least partially, in several solvents, fats, and oils. This property demands caution depending on the intended use of the colored plastic article. In case of packaging material it is recommended to run preliminary storage tests to evaluate a possible migration of the color into the filling good. Colored textiles should be fast during dry cleaning. There are many other occasions in which a colored plastic article may come in contact with solvents, for example, during decoration with printing inks and/or household goods and cleaner.

The general product profile of colorants, including dyes, was described in section 4.4, but there are still some other features specific for dyes. In a plastic article colored with pigments, the impression of color is due to an interplay of absorption and reflection in combination with a scattering of light on the surface of the pigment particles (crystals), the so-called Tyndall effect, whereas transparent plastic articles colored with dyes show only the interplay between absorption and reflection (Fig. 5.9).

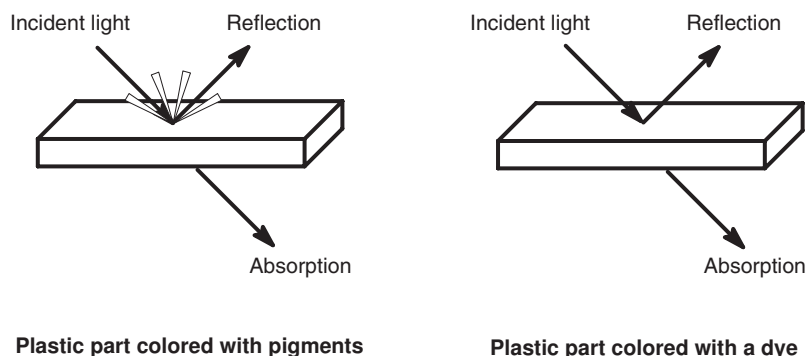


Figure 5.9: Differences in the optical behavior of pigments and dyes

The use of dyes is limited to amorphous polymers, which are polymers with a high glass transition temperature (Table 5.28). Dyes, applied in partial crystalline polymers, for example, polyolefins, would migrate directly.

Table 5.28: Glass Transition Temperature of Several Polymers

Polymer	Glass transition temperature
Glass	500–700 °C (932–1292 °F)
PS	98–100 °C (208–212 °F)
SB / ABS / SAN	80–105 °C (176–221 °F)
PMMA	105 °C (221 °F)
PC	143–150 °C (289–302 °F)
PVC-U	80 °C (176 °F)
PA 6	60–70 °C (140–158 °F)
PE (amorphous)	–80 °C (–112 °F)
PP (isotactic, 55% crystalline texture)	+3 °C (–37 °F)
PP (atactic, 5% crystalline texture)	–5 °C (–23 °F)

Dyes do not migrate from amorphous polymers under normal conditions of use, for example, at room temperature. This temperature is well below the glass transition temperature, and in a range in which the polymer chains as well the dye molecules are totally restricted in their molecular motion. In this solid dye solution in an amorphous polymer, there is no recrystallization or moving of the dye to the surface of the plastic possible. This behavior is proven by the following experiment: A plastic part, colored with a dye, was kept for a longer time clearly above its glass transition temperature. At temperatures above the glass transition temperature the polymer chain as well the dye molecules are no longer restricted in their molecular motion; consequently a migration of the dye was observed.

Originally the use of dyes was limited to transparent polymers, for example, PS, SAN, PMMA, PC, and PET. The necessary dye concentration for a transparent coloration is usually in the range of 0.01–0.1%, depending on the required intensity of the coloration. At those low concentrations migration does not occur. Dyes are applied also in opaque systems, systems containing an inorganic pigment with a good hiding power (e.g., titanium dioxide) and a dye as colorant. Analogous to the colored pigments the white component must be colored first before the color can be matched according to the customer supplied specimen. In opaque systems the necessary dye concentration is consequently clearly higher than in the case of a transparent coloration. At the same time the possibility of migration increases. When a dye is applied in an opaque system it is recommended to check beforehand the migration to ensure that the plastic article fulfills the “non-migration requirements.”

The real reason for the increasing use of dyes in opaque systems is their comparatively higher heat stability, which is very often in the range of 300 °C (572 °F). Analogous to pigments, the heat stability of dyes depends on the concentration in the plastic, on the type of polymer, and on the processing temperature and residence time during the processing of the amorphous polymer. The heat stability of dyes is very often higher than of chemically similar pigments. Only the dissolved dye molecule must be thermal stable in the polymer melt, while pigments must have not only a thermostable molecule but also a thermostable crystal modification.

The chemical structure of dyes is very similar to those of organic pigments; therefore it would be possible to subdivide the dyes analogously. However, the dyes are described according to their color because of the limited number of still usable products for the coloring of plastics. In the last few years many frequently used dyes were banned because of toxicological considerations.

A closer examination of the chemical constitution of dyes proves that their molecular structure is much simpler in comparison to pigments of the same chemical group. Two examples may demonstrate this (Fig. 5.10 and 5.11).

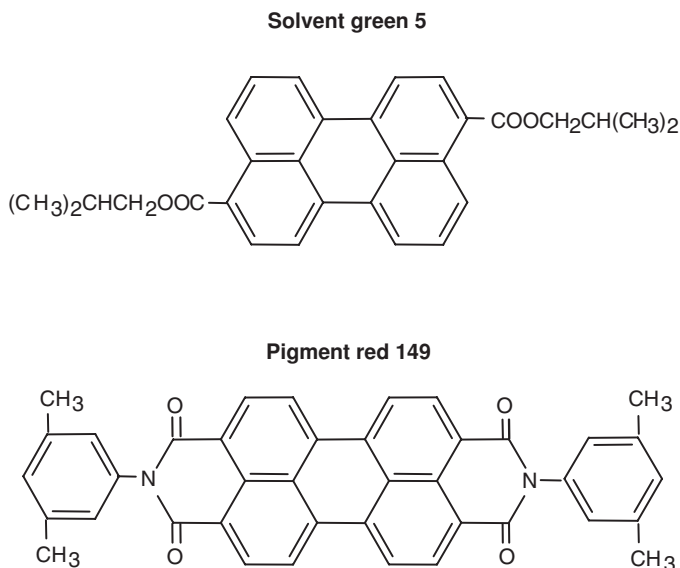


Figure 5.10: Comparison of the chemistry of perylene colorants

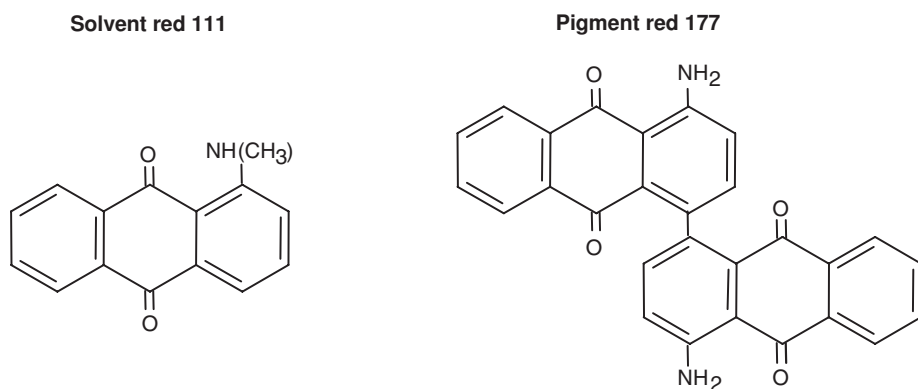


Figure 5.11: Comparison of the chemistry of anthraquinone colorants

At the same time these two examples show clearly the importance of chromophores, a system of conjugated double bonds that are responsible for the

absorption of light and finally responsible for the color. The first example is characterized by a color shift from green to red. The additional ring system of the Pigment red 149 causes another orientation of the conjugated double bonds (in comparison to Solvent green 5), associated with a different need of energy to excite the π -electrons. Different energies mean different wavelengths of the absorbed light, and consequently different colors. The second example does not show a color shift. Simplified expressed the molecule of Solvent red 111 is doubled in Pigment red 177; therefore the orientation of the conjugated double bonds is more or less the same in both colorants, and consequently there is no color shift. The Color Index differentiates between *solvent* and *disperse dyestuffs*. These two different terms do not express any differences in the chemical structure of a colorant but indicate the field of application – a nontextile and a textile application. This is one of the reasons why several chemical identical colorants are listed both as solvent and disperse dyestuff (Fig. 5.12).

Solvent yellow 114

Disperse yellow 54

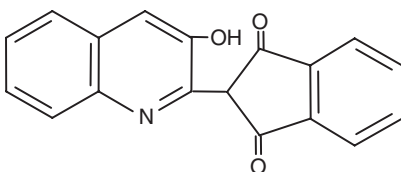


Figure 5.12: *Identical chemistry but different terms of dyes*

At the very beginning the only field of application of dyes was the coloring of textiles. Decades later, other fields of application for colorants were discovered, the nontextile applications. New colorants, synthesized by different manufacturers, were listed according to the intended field of application. At this stage the exact chemical structure was not always known and/or was not published for reasons of competition. This is probably another reason for the double term of “older” dyes.

Detailed data regarding the solubility of dyes in a polymer melt are not available. A certain assessment, however, is possible because the solubilities of several dyes in monomers, for example, methyl methacryl acid ester and styrene, were deter-

mined and additionally, as comparison in the rather polar solvent ethanol. The solubilities vary considerably, and a general idea is given in Table 5.29 [48].

Table 5.29: *Solubility of Dyes in the Monomers of PMMA and PS*

Dye	Solubility (in g/L)		
	Methyl metacryl acid ester	Styrene	Ethanol
Solvent yellow 160:1	2.4	4.7	0.3
Disperse yellow 201	110	400	1.3
Disperse yellow 54	1.8	3.1	0.7
Solvent yellow 130	0.1	0.2	< 0.1
Solvent orange 86	8.5	13	1
Disperse orange 47	4	6	21
Solvent red 111	7.5	13	0.7
Solvent red 179	1.6	4.5	0.1
Disperse violet 31	35	25	1
Solvent blue 97	18	55	< 0.1
Solvent green 3	4	11	< 0.1
Solvent green 28	10	25	< 0.1

In this context another physical phenomenon, sublimation, should be mentioned. Sublimation takes place when at increasing temperature a substance changes from the solid state directly into the gaseous one, leaving out the liquid state. Several dyes show this phenomenon. At high processing temperatures parts of the dye dissolved in the polymer melt go over into the gaseous state at the moment the colored polymer melt leaves the die to fill the mold. The gaseous dye deposits directly on the comparatively cool surface of the mold, slowly forming an increasing deposit. This deposit can cause flaws on the surface of the injection molded plastic part if it is not removed in time. In theory sublimation can be avoided by a decrease of the processing temperature, but in practice this is impossible, because each polymer requires for this type a typical (high) processing

temperature. The only possibility to avoid those deposits is therefore to exchange the dye applied for the color matching.

Sublimation takes place not only during the injection molding of plastics but also already during the drying of a masterbatch in a recirculating air dryer, for example, which is essential for PA or PET prior to their processing

A typical example of such a disturbing sublimation is Solvent red 111, which sublimates at the normal processing temperatures of amorphous polymers. On the other hand sublimation does not disturb the processing of a polymer if the dye sublimates at a temperature well above its processing temperature. A typical example for such a dye is Solvent red 135 (Fig. 5.13).

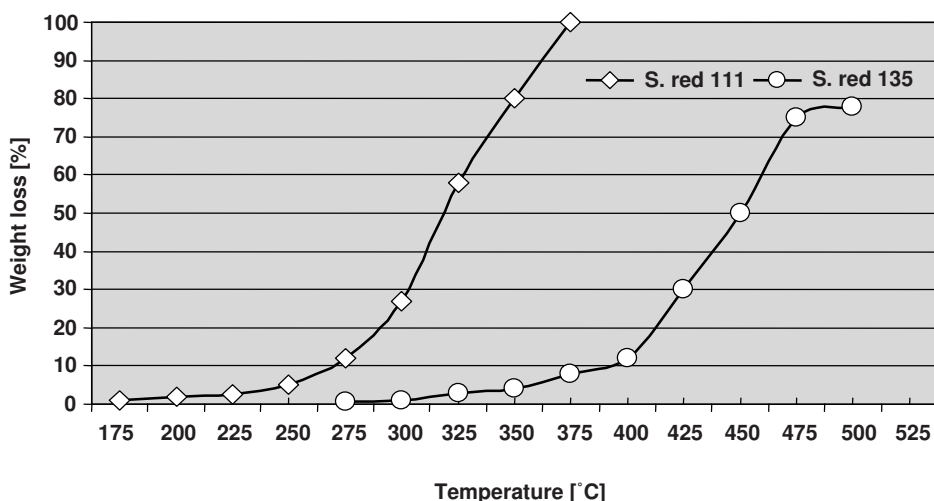


Figure 5.13: Sublimation temperatures of two dyes

The phenomenon sublimation is exploited in smoke signal rockets for military and/or civil purposes, which is another important field of application of Solvent red 111. The importance of the criterion *sublimation fastness* increased steadily in the past, because of:

- The necessary concentration of dyes increased clearly in opaque colors.
- The processing of plastics takes place at higher temperatures (faster cycles, pin gate, hot runner).
- Higher degree of automation (cleaning of the mold is no longer possible because of the construction of the mold and/or economic reasons).

The processing of dyes differs only slightly from those of pigments. There are of course no dispersing problems, because the dyes dissolve in the polymer melt. Dyes reach their maximum color intensity when they are completely dissolved. The completeness of the solution and in addition a homogeneous distribution of the molten dye in the polymer melt are essential to avoid any flaws in the final product. An incomplete solution of a dye would cause color specks and/or color streaks during the coloring of plastics. The result of an inhomogeneous distribution of the dissolved dye in the polymer melt would be color streaks. Both flaws are visually very disturbing and must be avoided.

The manufacture of a dye containing granular color preparation (masterbatch) requires relatively high processing temperatures to accelerate the dissolving, an increase of residence time to allow a complete dissolving, and a good mixing screw profile to reach a homogeneous distribution of the molten and/or dissolved dye in the polymer matrix. A fast distribution of the molten dye in the polymer melt is very important, not only because of the large differences in viscosity between the low-viscous dye melt and the high- viscous polymer melt but also to avoid a local oversaturation, which would negatively influence the speed of dissolving of the dye. The last point requires special attention at a higher dye concentration, which occurs in color preparations with a good covering property.

The melting point of several dyes is listed in Table 5.30.

Table 5.30: *Melting Points of Several Dyes*

Dye	Melting point
Solvent yellow 160:1	209 °C (408 °F)
Disperse yellow 201	115 °C (239 °F)
Solvent yellow 93	181 °C (359 °F)
Disperse yellow 54	264 °C (507 °F)
Solvent yellow 130	300 °C (572 °F)
Solvent orange 60	230 °C (446 °F)
Solvent orange 86	180 °C (356 °F)
Solvent red 179	255 °C (491 °F)
Solvent red 135	318 °C (604 °F)
Solvent red 52	280 °C (536 °F)
Disperse violet 31	186 °C (367 °F)

Table 5.30: Continuation

Dye	Melting point
Solvent violet 13	189 °C (372 °F)
Solvent violet 36	213 °C (415 °F)
Solvent blue 97	200 °C (392 °F)
Solvent green 3	213 °C (415 °F)
Solvent green 28	245 °C (473 °F)

The melting point of some dyes is higher or within the range of the processing temperature of polymers. In such a case the dissolving speed of the dye in the polymer melt is the time-determined process. To ensure a complete dissolving of the dye, the residence time during the manufacture of a masterbatch demands special attention. An incomplete solution of the dye would cause the visually very disturbing color specks and/or color streaks in the final product.

The available palette of dyes for the coloring of plastics diminished considerably in the last few years. In Amendment 2 of the German *Bedarfsgegenständeverordnung* [46], dated July 15, 1994, all azo colorants were banned that decompose under defined specific test conditions forming a listed amine. The list contains 20 amines that are classified as carcinogenic. The reason for this ban was originally the dying of textile, but later on it was extended to the whole field of coloring of plastics.

The shade of chemically identical pigments depends, besides other criteria, on the crystal size and crystal modification; therefore pigments produced by different manufacturers, show differences in their shades. They cannot be exchanged with each other without a new color matching. In contrast to the pigments, the shade of a dye depends only on the chemical structure. Assuming the same purity, chemically identical dyes, synthesized by different manufacturers, can be exchanged without any problems.

Considering the limited number of dyes, they are subdivided according to their color and not their chemistry, which was the subdivision of the organic pigments. Most of the dyes consist of a polycyclic ring system, and are mainly anthraquinone derivatives.

The exact chemical constitution of the dye is added, when this is known. Practice has proven that knowledge of the structure composition can be very helpful in answering all customer questions, for example, content of chlorine in a colorant.

5.3.1 Blue

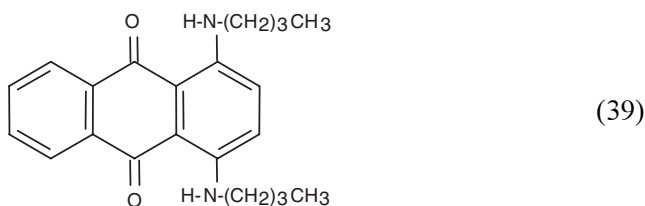
Solvent blue 35 / 61554 / CAS 17354.14.2 – Anthraquinone derivative

Properties: Blue, melting point 127 °C (260 °F), no migration at concentrations < 0.1%.

Good heat stability: 280–300 °C (536–572 °F) in PS; 280 °C (536 °F) in PET; 250 °C (482 °F) in PMMA and ABS.

Good to medium light fastness: 7 (pure tone) / 4–5 (white reduction) in PMMA and PET, 7 / 4 in PC, 6 / 4 in PS. The light fastness decreases with increasing degree of white reduction.

Application: The dye can be used in many amorphous polymers.



Solvent blue 67 – a copper phthalocyanine sulfamid

Properties: Blue, exact chemical constitution has not yet been published

Good heat stability: 280 °C (536 °F) in PET.

Medium light fastness: 6 in PET.

Application: The product was developed specially for the coloring of PET.

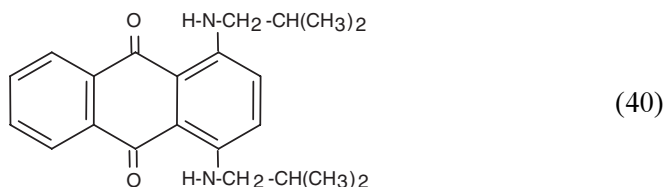
Solvent blue 78 – Anthraquinone derivative

Properties: Blue, melting point 160 °C (320 °F).

Good heat stability: 280–300 °C (536–572 °F) in PS.

Medium to low light fastness: 6 (pure tone) / 3–4 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers.



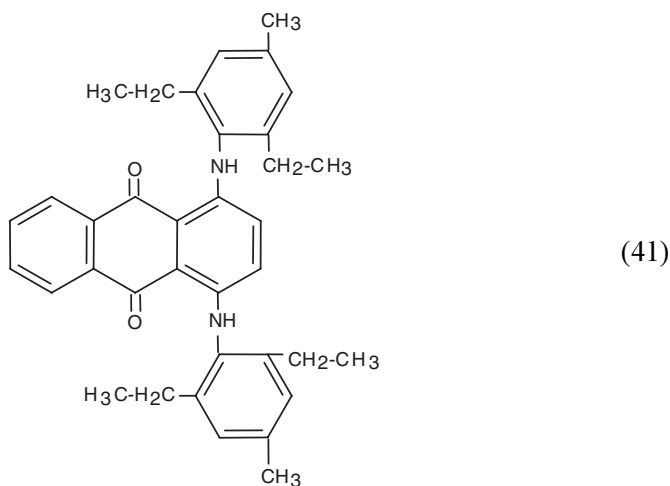
Solvent blue 97 / – / CAS 32724.62.2 – Anthraquinone derivative

Properties: Blue, melting point 200 °C (392 °F), no migration at concentrations < 0.1%.

Good heat stability: 340 °C (644 °F) in PC; 300 °C (572 °F) in PS, PMMA, and PA-6; 290 °C (554 °F) in PET; 260–280 °C (500–536 °F) in ABS.

Good light fastness: 7 (pure tone) / 6 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.

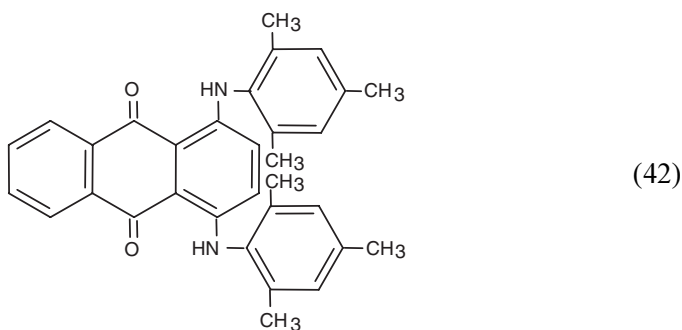
*Solvent blue 104 – Anthraquinone derivative*

Properties: Blue, melting point 240 °C (464 °F).

Good heat stability: 300 °C (572 °F) in PS.

Good light fastness: 7–8 (pure tone) in PS, SAN, PC, and PMMA.

Application: The dye can be used in many amorphous polymers.



Solvent blue 132 – Anthraquinone derivative

Properties: Blue, exact chemical constitution has not yet been published.

Good heat stability: 300 °C (572 °F) in PA-6.

Good light fastness: 7 in PA-6.

Application: This dye was developed especially to color PA-6.

5.3.2 Brown

At present no brown dyes are commercially available. The previously marketed dyes were banned according to Amendment 2 of the German *Bedarfsgegenständeverordnung*. This lack of brown dyes is no real problem, because brown shades can be matched easily by a combination of a red and a black colorant.

5.3.3 Yellow

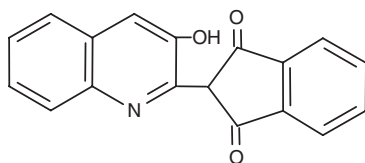
Disperse yellow 54 = Solvent yellow 114 / 47020 / CAS 17772.51.9 – Quinophthalone derivative.

Properties: Yellow, melting point 264 °C (507 °F), no migration at concentrations < 0.1%.

Good heat stability: 340 °C (646 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–280 °C (572–536 °F) in SAN; 290 °C (554 °F) in PET.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of PA-6.



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Disperse yellow 201 = Solvent yellow 179 / – / CAS 54079.53.7 – Methine derivative

Properties: Yellow, melting point 115 °C (239 °F), no migration at concentrations < 0.1%. The exact chemical constitution has not yet been published.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS, SAN, and PMMA; 290 °C (554 °F) in PET; 240–260 °C (464–500 °F) in ABS.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of PA-6.

Disperse yellow 241 – Azo dye

Properties: Yellow, melting point 254 °C (489 °F), no migration at concentrations < 0.1%. The exact chemical constitution has not yet been published.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS; 290 °C (554 °F) in PET; 300–260 °C (572–500 °F) in PMMA; 260 °C (500 °F) in SAN.

Good light fastness: 7 (pure tone) / 5–6 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of ABS and PA-6.

Solvent yellow 93 / 48160 / CAS 4174.09.8 – Pyrazolone derivative

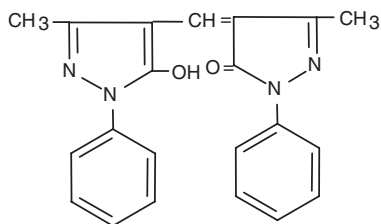
Properties: Yellow, melting point 181 °C (358 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–270 °C (572–518 °F) in SAN; 280 °C (536 °F) in PET.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PS.

Medium weather resistance: 4 (pure tone) / 3 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of ABS and PA-6.



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Solvent yellow 98 / 56238 / CAS 27870.92.4 – Amino ketone derivative

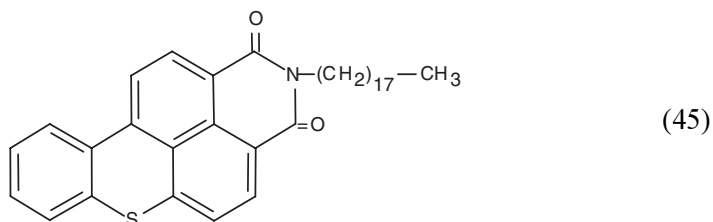
Properties: Yellow, fluorescent, melting point 98 °C (208 °F).

Good heat stability: 300 °C (572 °F) in PS, PMMA, PC, and PET.

Good to medium light fastness: 7 (pure tone) / 4–5 (white reduction) in PMMA.

The light fastness decreases with increasing degree of white reduction.

Application: The dye can be used in many amorphous polymers.



Solvent yellow 135 – Coumarin derivative

Properties: Greenish yellow, fluorescent, melting point 289 °C (552 °F).

Good heat stability: 300 °C (572 °F) in PS and PMMA; 280–300 °C (536–572 °F) in SAN; 240–260 °C (464–500 °F) in ABS.

Medium light fastness: 6 (pure tone) / 3–4 (white reduction) in PS. The light fastness decreases with increasing degree of white reduction.

Application: The dye can be used in many amorphous polymers, including the coloring of PA-6.

Solvent yellow 145 – Methine derivative

Properties: Yellow, melting point 240 °C (464 °F), at processing temperatures > 280 °C (536 °F) there is the tendency to sublime.

Heat stability: 300 °C (572 °F) in PC; 260 °C (500 °F) in PA-6. The heat stability varies considerably depending on the type of polymer to be colored.

Light fastness: 7 (pure tone) in PC, 3 (pure tone) in PA-6. The light fastness varies considerably depending on the polymer to be colored.

Application: The use of this dye is clearly limited due to its dependencies of fastness properties on the type of polymer.

Solvent yellow 160:1 / – / CAS 35773.43.4 – Coumarin derivative

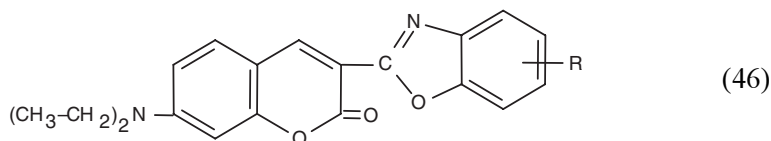
Properties: Greenish yellow, fluorescent, melting point 209 °C (408 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS, PMMA, and PA-6; 300–280 °C (572–536 °F) in SAN; 280 °C (536 °F) in PET; 240–260 °C (464–500 °F) in ABS.

Medium light fastness: 6 (pure tone) / 3–4 (white reduction) in PS. The light fastness decreases with increasing degree of white reduction.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.

Remark: Only the basic formula of this dye is known; the exact chemical constitution of the substituent is not (yet) published.



Solvent yellow 163 / 58840 – Anthraquinone derivative

Properties: Yellow, melting point 180 °C (356 °F).

Good heat stability: 340–360 °C (644–680 °F) in PC; 300 °C (572 °F) in PS.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in PS; 7 / 7 in PET.

Application: The dye can be used in many amorphous polymers, it is not recommended for the coloring of PA-6.

5.3.4 Green

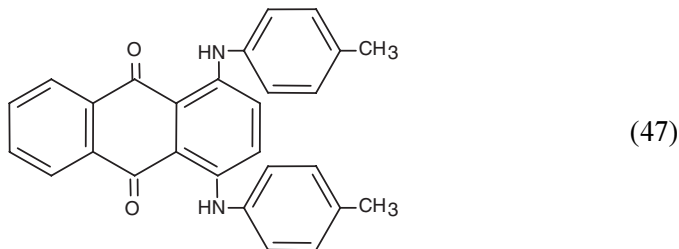
Solvent green 3 / 61585 / CAS 128.80.3 – Anthraquinone derivative

Properties: Bluish green, melting point 213 °C (415 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–280 °C (572–536 °F) in SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in PA-6 and ABS.

Good to medium light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PS; 7 / 6–7 in PC; 7 / 5 in PET; 6 / 5 in PA-6.

Application: The dye can be used in many amorphous polymers.



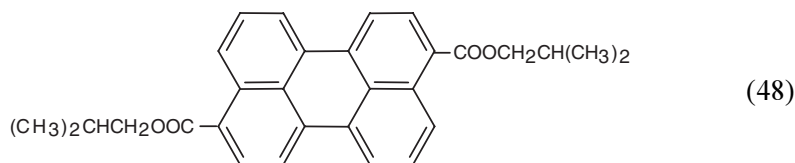
Solvent green 5 / 59075 / CAS 2744.50.5 – Perylene derivative

Properties: Greenish yellow, fluorescent, melting point 210 °C (410 °F).

Good heat stability: > 300 °C (572 °F) in PS.

Light fastness: 7 (pure tone) / 3 (white reduction) in PS. The light fastness decreases strongly with increasing white reduction, while a transparent shade (pure tone) shows a good light fastness.

Application: This dye is recommended especially for the coloring of PS, SAN, PMMA, and PC; preliminary tests are recommended for the coloring of SB, ABS, ASA, and PET. It is not recommended for the coloring of PA-6.

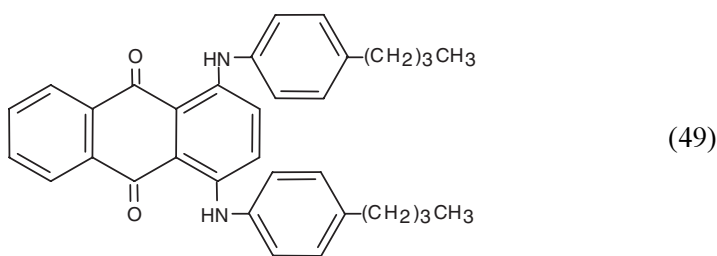
*Solvent green 20 – Anthraquinone derivative*

Properties: Green.

Good heat stability: 300 °C (572 °F) in PS and PC, 280 °C (536 °F) in PET.

Good light fastness: 7 (pure tone) / 7 (white reduction) in PET; 7 / 6–7 in PS; 7 / 6 in PC.

Application: The dye can be used in many amorphous polymers; it is not recommended for the coloring of PA-6.

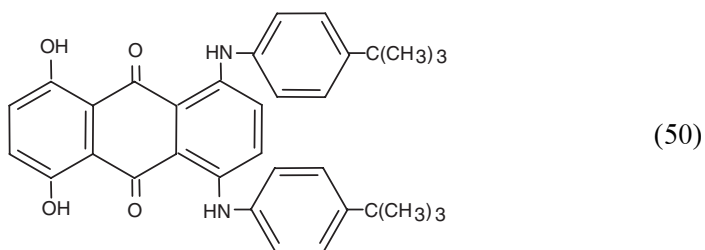
*Solvent green 28 / – / CAS 4851.50.7 – Anthraquinone derivative*

Properties: Yellowish green, melting point 245 °C (473 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–280 °C (572–536 °F) in SAN; 290 °C (554 °F) in PET; 260–280 °C (500–536 °F) in ABS.

Good light fastness: 7–8 (pure tone) / 7–8 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers; it is not recommended for the coloring of PA-6.



5.3.5 Orange

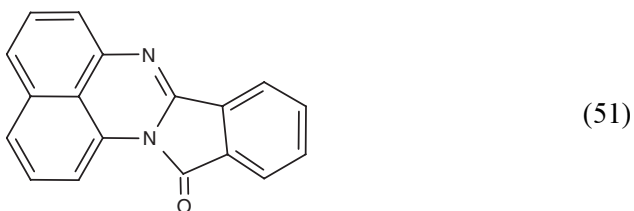
Disperse orange 24 = Solvent orange 60 / – / CAS 6925.69.5 – Perinone derivative

Properties: Yellowish orange, melting point 230 °C (446 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 280–300 °C (536–572 °F) in SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in ABS and PA-6.

Good light fastness: 8 (pure tone) / 7–8 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.



*Disperse orange 47 = Solvent orange 107 / – / CAS 5718.26.3 –
Methine derivative*

Properties: Reddish orange, melting point 225 °C (437 °F), no migration at concentrations < 0.1%.

Good heat stability: 320 °C (608 °F) in PC; 300 °C (572 °F) in PS and SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in ABS and PMMA.

Good light fastness: 7–8 (pure tone) / 5–6 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of PA-6.

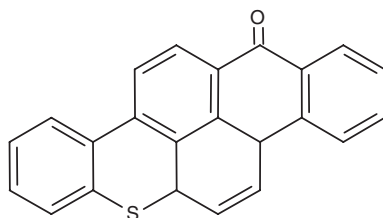
Solvent orange 63 / 68550 / CAS 16294.75.0 – Modified anthraquinone derivative

Properties: Red, fluorescent, melting point 260 °C (500 °F).

Good heat stability: 320 °C (608 °F) in PC; 300 °C (572 °F) in PS, PMMA, and PET.

Good to medium light fastness: 7–8 (pure tone) / 4 (white reduction) in PMMA; 5–6 / 6–7 in PC.

Application: The dye can be used in many amorphous polymers. A dye concentration < 0.3% is recommended.



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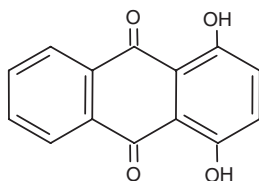
Solvent orange 86 / 58050 – Anthraquinone derivative

Properties: Orange, melting point 180 °C (356 °F).

Good heat stability: 300 °C (572 °F) in PS, PMMA, and SAN.

Good light fastness: 7 (pure tone) in PS.

Application: This dye no longer plays a role in coloring of plastics, because it can be used only for transparent colors.



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5.3.6 Red

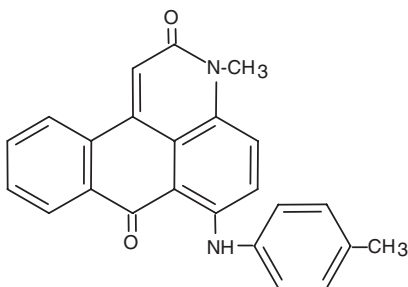
Solvent red 52 / 68210 / CAS 81.39.0 – Anthraquinone derivative

Properties: Bluish red, melting point 280 °C (536 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PMMA and PA-6; 280–300 °C (536–572 °F) in SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in PS and ABS.

Good to medium light fastness: 7 (pure tone) / 3–4 (white reduction) in PS. The light fastness decreases strongly with increasing degree of white reduction.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.



(54)

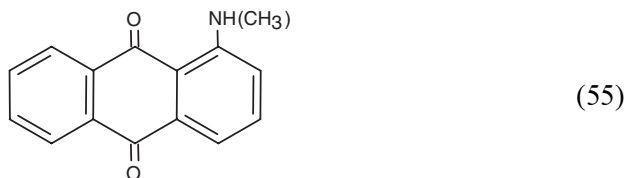
Solvent red 111 / 60505 / CAS 82.38.2 – Anthraquinone derivative

Properties: Red, melting point 170 °C (338 °F), no migration at concentrations < 0.1%. Strong tendency to sublime at the usual processing temperatures of amorphous polymers.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PMMA; 300–280 °C (572–536 °F) in PS and SAN; 270–280 °C (518–536 °F) in PA-6; 260–280 °C (500–536 °F) in ABS.

Good light fastness: 7 (pure tone) / 6 (white reduction) in PS, 7 / 4–5 in PC.

Application: In spite of its good fastness properties the use of this dye is limited because of its strong tendency to sublime.



Solvent red 135 / – / CAS 20749.68.2 – Perinone derivatives

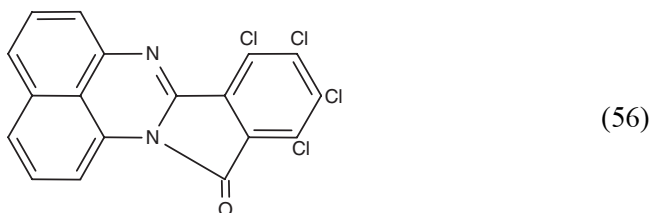
Properties: Yellowish red, melting point 318 °C (604 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PMMA; 280–300 °C (536–572 °F) in PS and SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in PA 6, 260–280 °C (500–536 °F) in ABS.

Good light fastness: 8 (pure tone) / 6 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.

Remark: This dye tends to sublime but only at temperatures well above the processing temperatures of amorphous polymers.



Solvent red 179 / – / CAS 6829.22.7 – Perinone derivative

Properties: Yellowish red, melting point 255 °C (491 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS, PA-6, and PMMA; 300–260 °C (572–500 °F) in SAN; 280 °C (536 °F) in PS.

Good light fastness: 8 (pure tone) / 6 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.

Solvent red 195 – Monoazo derivative

Properties: Red.

Good heat stability: > 300 °C (572 °F) in PS.

Good light fastness: 8 (pure tone) / 7 (white reduction) in PS.

Weather resistance: 4 (pure tone) / 2 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers.

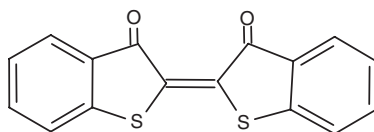
Vat red 41 / 73300 / CAS 522.75.8 – (unsubstituted) Thioindigo

Properties: Red, fluorescent, melting point > 300 °C (572 °F).

Good heat stability: 300 °C (572 °F) in PC and PMMA; 280 °C (536 °F) in PS.

Medium light fastness: 5–6 (pure tone) / 5–6 (white reduction) in PC; 4 / 3 in PMMA.

Application: The dye can be used in many amorphous polymers, but only when there are no strict requirements regarding the light fastness of the final product.



(57)

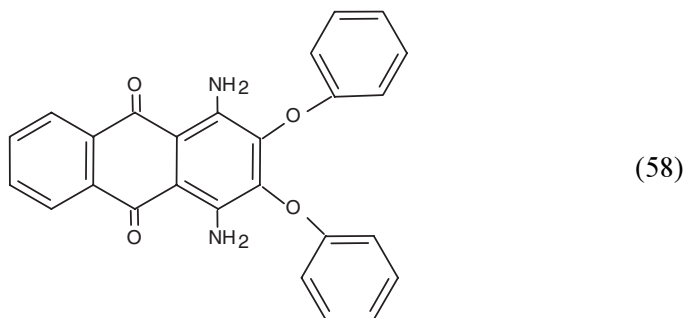
5.3.7 Violet*Disperse violet 26 = Disperse violet 31 / 62025 / CAS 6408.72.6 – Anthraquinone derivative*

Properties: Bluish violet, melting point 186 °C (366 °F), no migration at concentrations < 0.1%.

Good heat stability: 300 °C (572 °F) in PC and PS; 300–280 °C (572–536 °F) in SAN; 280 °C (536 °F) in ABS; 270–260 °C (518–500 °F) in PET.

Good light fastness: 7–8 (pure tone) / 6–7 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of PA-6 and PMMA.



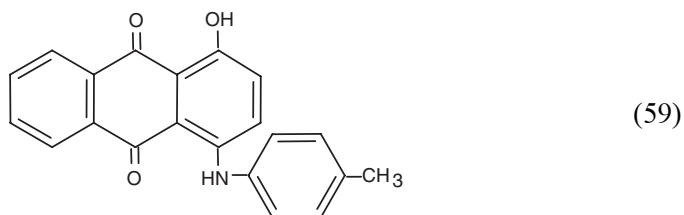
Solvent violet 13 / 60725 / CAS 81.48.1 – Anthraquinone derivative

Properties: Bluish violet, melting point 190 °C (374 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–280 °C (572–536 °F) in SAN; 290 °C (554 °F) in PET; 280–260 °C (536–500 °F) in ABS.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) and 8 / 5 in PS, depending on the supplier of this dye.

Application: The dye can be used in many amorphous polymers, but it is not recommended for the coloring of PA-6.



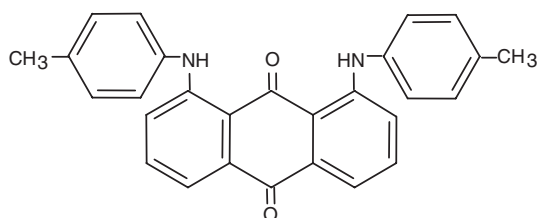
Solvent violet 36 / – / CAS 82.16.6 – Anthraquinone derivative

Properties: Reddish violet, melting point 213 °C (415 °F), no migration at concentrations < 0.1%.

Good heat stability: 350 °C (662 °F) in PC; 300 °C (572 °F) in PS and PMMA; 300–280 °C (572–536 °F) in SAN; 290 °C (554 °F) in PET; 280 °C (536 °F) in PA-6; 280–260 °C (536–500 °F) in ABS.

Good light fastness: 7 (pure tone) / 6–7 (white reduction) in PS.

Application: The dye can be used in many amorphous polymers, including for the coloring of PA-6.



Solvent violet 37 – Anthraquinone derivative

Properties: Violet.

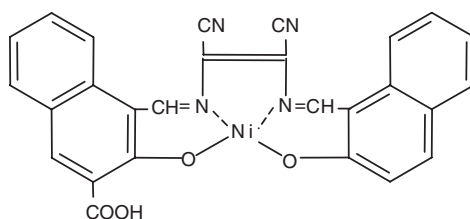
Good heat stability: 300 °C (572 °F) in PS.

Good light fastness: 7–8 (pure tone) in PS.

Application: The dye can be used in many amorphous polymers.

Solvent violet 49 / 48520 – Nickel complex

Application: This dye was developed especially for the spin dyeing.



5.3.8 Black

The commercially available black dyes are always a mixture of several (colored) dyes; a single black substance is not marketed at present.

5.4 Effect Colorants

One of the main functions of colors is their use as design elements; therefore designers look for new effects all the time. Analogous to the inorganic pigments, there are also organic effect pigments. The organic effect pigments can be subdivided into:

- Daylight fluorescent pigments
- Optical brighteners

- Speckled effect pigments
- Thermal colors
- Marble batches

5.4.1 Daylight Fluorescent Colors

This type of colorant consists of fluorescent dyes dissolved in a polymer matrix. A modified polyamide is used mainly as polymer matrix, but other polymers as carriers for the daylight fluorescent dyes are also quite common. The daylight fluorescent dyes are dissolved in a polymer matrix, and the product obtained is milled to a fine powder. These colorants therefore show the typical behavior of a pigment, and can be applied consequently also in partially crystalline polymers. Polyolefins (PO) are the main field of application of daylight fluorescent pigments.

Chemically the two principal classes of fluorescent dyes are the rhodamines, which reinforce the red region, and the greenish yellow aminonaphthalimide derivatives.

The concentration of these dyes in the polymer matrix is said to be in the range of 5%. The data sheets of the different manufacturers/suppliers of daylight fluorescent pigments do not contain details regarding the type of fluorescent dye involved or the effective concentration of the dye in the polymer matrix. Only the type of the polymeric carrier is mentioned.

The daylight fluorescent colors absorb not only visible light but also the ultraviolet (UV) fraction of daylight. The absorption of daylight is responsible for the basic color, while the absorbed UV light is transformed and emitted in the visible range. The result is a very high degree of reflectance, and the colored material appears to glow.

The daylight fluorescent dyes are sensitive to heat and duration of the heat impact. This requires special attention during manufacture of a masterbatch, but also later on during the production of the colored final product. The processing temperature should be as low as possible in combination with a short residence time. In practice there are limits, because every processing of a polymer requires a typical temperature range defined for the polymer to achieve a proper polymer melt. In addition the melting of a polymer takes a certain time, depending on the temperature. At a too low temperature and/or too short residence time a plasticizing screw has enough power to force an incomplete molten polymer through the extruder; at the same time an unknown amount of frictional heat is developed. The result might be thermal damage of the daylight fluorescent dye. A thermal damage of

the fluorescent dye is easily discernible, as the color loses more or less its high degree of brightness.

Owing to the limited heat stability of daylight fluorescent pigments, their application is limited to polymers with a rather low processing temperature, for example, PE-LD and light flowing grades of PP.

It is quite common during the injection molding to recycle directly flawed parts and/or the sprue parts. In the case of daylight fluorescent pigments this might be problematic because every additional impact of heat can increase the degree of thermal damage.

The concentration of a daylight fluorescent dye in the polymer matrix is rather low, which amounts to a high concentration of the daylight fluorescent pigment in the final product. The recommendations vary between 1% and 2% of the pigment. In practice such a high concentration causes slowly growing deposits on the mold and/or screw during injection molding. An addition of chalk during the processing of daylight fluorescent pigments may reduce the deposition but cannot prevent it completely. The reason for the formation of a deposit is an incompatibility between the polymer matrix of the daylight fluorescent pigment, for example, modified polyamide, and the polymer to be colored, mainly polyolefins.

Another disadvantage of daylight fluorescent pigments is the low degree of light fastness; the UV part of daylight is especially harmful. To improve gradually their light fastness, some suppliers recommend the addition of an UV absorber during the production of the colored final product and/or the application of a transparent UV absorber containing protective coat. The lacquering of colored plastic parts is practiced in case of safety related products, but this is too expensive for consumer goods. On the other hand the high brightness of a daylight fluorescent dye is the result of the transformation of absorbed UV light into visible light. The use of an UV absorber to improve light fastness would consequently reduce the high brightness. This is a typical example of the mutual exclusion of requirements.

Daylight fluorescent pigments are marketed in the colors yellow, green, red, blue, and violet. The yellow pigments are quantitatively the main product, certainly because yellow is used worldwide as a warning color.

5.4.2 Optical Brighteners

The optical brighteners are closely related to the daylight fluorescent dyes. They are colorless substances, emitting a bluish visible light after the transformation of absorbed UV light. Optical brighteners are applied as pure substances. The application concentration in the final part is in the range of 25–250 ppm.

Optical brighteners must behave like dyes, and dissolve in the polymer to show their effect. Contrary to organic dyes, optical brighteners can be used also in partially crystalline polymers. This is possible because of the extremely low application concentration. In this range of concentration they are fast to migration.

There are two fields of application of these substances. One is use as a decolorizer in polymers. Naturally colored polymers very often possess a very slight yellowish tint, which can be eliminated by the incorporation of an optical brightener. For this use the necessary concentration is in the range of 10–50 ppm. In this context it should be mentioned that the manufacturers of polymers do not release any information regarding the type and concentration of the incorporated optical brightener. The lack of such information considerably complicates the work of a colorist.

The other field of application is the coloring of polymers. The addition of an optical brightener to any color creates the impression of a higher brightness and cleanness of the color. Experience shows that colored plastic articles do not infrequently contain an optical brightener, but it is difficult to determine its source. There are two principal possibilities – the source is either the color preparation or the polymer.

A typical example of the use of an optical brightener is the color white. The addition of a small amount of an optical brightener to a white colored plastic part enhances the impression of white; the part is “whiter than white.” Depending on the type and grade of polymer the necessary concentration is in the range of 50–250 ppm.

We come across this application nearly daily. It is quite common that white colored textiles contain an optical brightener. To create special effects, the light in a disco changes in short intervals to all possible colors, including a pure UV light. In this case the white shirts and blouses glow with a bluish tint.

The absorption of UV light is the common method to detect the presence of an optical brightener in polymers. A light cabinet, used for the exact assessment of colors during the process of color matching and/or of colored specimen, contains in addition an UV lamp.

The work of a colorist is complicated by the presence of an optical brightener, for example, if the supplied color specimen does not contain an optical brightener but is present in the supplied polymer sample. A 100% matching of the color is impossible in such a case, and only a dialogue between the colorist and the customer can solve the problem.

The other possibility is that the supplied color specimen contains an optical brightener. This case, too, is very complicated. The basic color can be matched but an identical brightness and cleanness of the color is impossible to achieve as

long as the colorist does not know the colorants and the type of optical brightener used in the color specimen.

Generally speaking color can be matched by using quite different colorants, but on the other hand each colorant reacts differently to the presence of an optical brightener. Differences in brightness and cleanness are therefore quite normal. Another reason for differences in brightness and cleanness of a color is of course the type of optical brightener applied, because its efficiency to brighten a color varies from type to type. Several types of optical brightener are marketed for application in polymers.

Considering the large number of colorants and optical brighteners it is impossible to check all possible combinations to receive an identical color match.

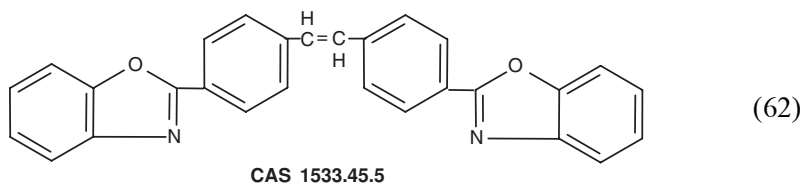
Here, too, only a dialogue between the colorist and the customer can solve the problem.

The incorporation of an optical brightener into a color preparation does not require special precaution methods, just a generally valid one. If blending a small quantity into a large one, it is advisable to check the homogeneity of the mixture.

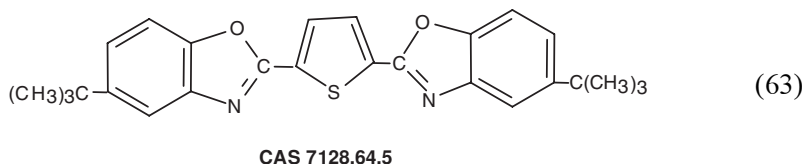
The chemical structures of optical brighteners for use in polymers resemble those of organic polycyclic colorants, but not exclusively. The chemical structure of some often applied optical brighteners are shown below.

They have the following structures:

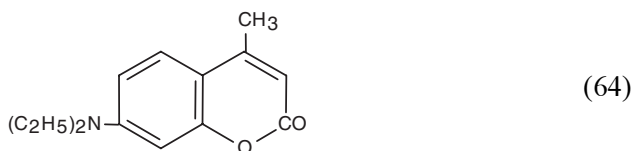
a) Benzoxazolyl derivatives



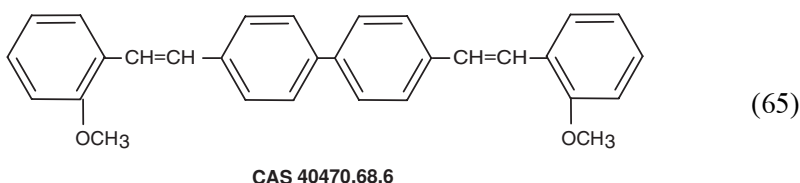
and



b) Coumarin derivatives



c) Ethylenediarylide derivatives



Additional products with similar or different chemical structures are known and commercially available.

5.4.3 Speckled Effect Pigments

There are many possibilities to create a speckled effect. Some of these possibilities are described in the section on *inorganic pigments*, for example, the different types of aluminum flakes. Organic speckled effect pigments are also known. They consist of textile fibers, available in the colors black, white, and colorful. The speckled effect increases with increasing size of the fibers, but the diameter and length of those fibers is limited for technical reasons. On one hand, the production methods of fibers limit the sizes, and on the other hand the fibers should not be so coarse and long that they may cause weak spots and/or defects in the final product, especially in thin-walled plastic articles.

Different types of polymers are used as fiber matrices. The requirements for the fiber matrix are a good heat stability, and no softening or melting at the processing temperature of the polymer to be colored. For the coloring of the fiber, colorants with a good heat stability and light fastness are usually applied. One example of often used speckled effect pigments are fibers based on a modified and cross-linked cellulose as matrix, and commercially available in the colors white, black, and colorful, mainly in blue, green, and red.

Considering the large number of polymers it may be necessary to check if the fiber can be applied in the selected type of polymer. A rather fast method is to add

the fiber to a homogeneous white or black colored plastic specimen (the choice depends on the color of the fiber). An insufficient heat stability of the fiber at the processing temperature of the selected polymer can be recognized by a visual comparison of the shape of the processed fiber with the raw fiber. A melting or softening of the fiber causes a visible color shift. Black, insufficient stable fibers will tint a white specimen gray, while white fibers will lighten a black specimen. Colorful fibers will tint a white specimen in the color of the fiber.

The concentration of those fibers in the final part depends on the desired intensity of the speckled effect; consequently the effective concentration can vary considerably.

5.4.4 Thermal Colors

A colored cup becomes colorless as a hot liquid is poured in, a straw takes on a new color when a cold beverage is sipped, a baby spoon becomes red when the food is still too hot. These are but a few examples of the process of thermochromism, the generic name for temperature-sensitive colors. Thermal colors are colorants that change their color if exposed to a higher temperature. This process is *reversible*, for example, such a colorant can be colorless at room temperature (20 °C [68 °F]) and colored at 40 °C (104 °F). After cooling down to room temperature the product will be colorless again. This process can be repeated many times.

Another group of substances shows an *irreversible* color change. They are used, for example, for the calibration of temperatures. These chemicals are not used in polymers, because there is no demand (not yet) for an irreversible color change in plastic parts; therefore they are not described in this context.

Thermal colors are a two-component system, consisting of an electron acceptor and an electron donor. Both substances are together microencapsulated in a polymer shell. At increasing temperatures at least one of the two substances melts, which causes a change in the force of attraction between the electron acceptor and electron donor. At the same time a change in the force of attraction means different energies (wavelengths of the light) to excite the electrons. The appearance of color depends on the wavelength of the absorbed light; consequently differences in the absorbed wavelength produces different colors. A similarity to organic pigments is very obvious. An organic pigment shows also a color shift in the case of a partial solubility at a too high processing temperature. An extreme case is the Pigment red 254, which dissolves in PC completely at a temperature of 320 °C (608 °F), giving a bright fluorescent yellow color, while the pigment colors other polymers a brilliant red.

Different colors can be produced by selection of appropriate dyestuff intermediates with different definite melting points. This second point is important for the predetermined temperature range of the color change. The commercially available thermal colors cover a temperature range of -25°C (-77°F) up to $+55^{\circ}\text{C}$ (131°F), in increments of approx. 5°C (41°F). The difference in temperature between a “cold” and a “hot” color is approx. 10°C (50°F).

The color change is a relatively slow process, because plastics are known as poor heat conductors. Thermal colors are available in the colors yellow, orange, red, green, brown, and black. The heat stability of the thermal colors marketed today is in the range of $180\text{--}200^{\circ}\text{C}$ ($356\text{--}392^{\circ}\text{F}$); therefore they can be applied only in polymers with a low processing temperature, for example, PE-LD, and light-flowing grades of PP or PS. The light fastness of thermal colors is not very good. The shell of the microcapsules is made of PE, PP, or PS.

The tinting strength of thermal colors is low; therefore high pigment concentrations, approx. 5–20%, are necessary. Interesting effects can be created when a very small amount of a “normal” colorant is added as basic color.

The incorporation of thermal colors in a color preparation, for example, masterbatch, causes no specific problems; they behave like normal pigments. Attention must be paid only to the low heat stability.

5.4.5 *Marble Batches*

Designers look for new effects all the time. The imitation of the natural marble effect in plastics was one of their objectives. In contrast to the other effects the imitation of the marble effect cannot be produced by a single substance, but requires a mixture of (mostly) two differently designed masterbatches.

An appropriate designed masterbatch does not cause any color streaks during the coloring of plastics. This goal is achieved by a good choice of the carrier, preferably of the same type of polymer that is to be colored, and selection of additional components, for example, waxes to influence the melt flow properties of the masterbatch. A well designed masterbatch possesses a processing temperature and melt viscosity comparable to those of the polymer to be colored. On the other hand color streaks occur when the melt viscosity of the masterbatch is much higher than those of the polymer and/or the masterbatch requires a clearly higher processing temperature. A masterbatch with such properties is rejected for the “normal” coloring of plastics, but this is the basis for the marble effect.

A marble batch consequently contains two different designed masterbatches, a normal, appropriately designed masterbatch for the basic color of the plastic article, and a second one for the marble effect. The second masterbatch is

designed in such a way that its use causes purposely color streaks. One possibility is that the second masterbatch contains a carrier that requires a higher processing temperature in comparison to the polymer to be colored; another possibility is to increase the melt viscosity of the second masterbatch.

In theory the designing of a marble batch seems easy, but in practice it requires a good balance between the processing parameters of the second masterbatch and the polymer to be colored. A too large difference in their properties can lead to the problem of incompatibility of both components, and the result would be faulty parts. A too small difference gives an insufficient marble effect.

The normal procedure is to run preliminary tests with differently designed marble batches on the production machine, the only way to check the marble effect and the quality of the colored final product. The small plastic specimens, used during the color matching are worthless in this context.

The principle of a marble batch is well defined. But in consideration of the numerous polymers in combination with the varieties of design it is difficult to create at once a sufficient marble effect. Usually it takes several test runs before the desired result is achieved. In addition it should be mentioned that a marble effect is not always possible, for example, when the mold contains gaps and/or is very rugged. In such a case the marble effect can be unsightly and therefore impossible.

6 Additives for Polymers

During the processing of polymers several selected substances are added to optimize specific properties of a polymer, because only after the incorporation of an additive can the polymer in question fulfill those specific requirements. Supplementation of polymers with additives is quite common.

The additives can be:

- Antimicrobiological substances
- Antistatic agents
- Flame retardants
- Fillers
- Lubricants / dispersing agents / release agents
- Nucleating agents
- Stabilizers
- Blowing agents
- Plasticizers

There are principally two methods of adding the additives either as a component of a color batch or as a separate additive batch.

Some additives must be incorporated by the manufacturer of the polymer because of the large concentration necessary. One example of such a case are fillers; some specific grades of polymers contain up to 55–60% filler, e. g., the glass fiber reinforced grades. On the other hand it is quite common that the customer requests the incorporation of an additive in the color preparation, for example, the use of stabilizer to improve the light fastness of the plastic article.

A combination of color plus additive in *one* batch can be problematic. There are several reasons for this. Any additive needs space in the recipe of the color preparation. As a result, the concentration of the colorant in the batch must be reduced, especially in the case of very intensive colors. The result is a higher coloring concentration for the final product. Another reason is the fact that some additives are not colorless, and consequently they also must be colored, which further increases the amount of colorant in the recipe.

Some additives are marketed as batches. In these cases it is certainly worthwhile to check if using two separate batches, a color batch and an additive batch, or a combination batch, color plus additive, is more economical.

Additives can be inorganic as well as organic substances. An interaction between additive and colorant cannot be excluded right away, and such an interaction can be negative or positive.

The function of an additive is the optimization of a specific property of a polymer. This requires tailor-made substances for each polymer depending on its chemical structure. The consequence is a large number of additives. The following sections contain only a general description of the additives. It would be beyond the scope of this book to go into too much detail.

6.1 Antimicrobiological Substances

Tests proved that bacteria and/or fungi can settle on plastics and even penetrate into the surface of the polymer. A mechanical cleaning of the surface is therefore not sufficient to remove them. A harmful contamination of the surface with bacteria and/or fungi can be avoided by adding an antimicrobiological substance to the polymer. The supplementation of polymers with an antimicrobiological substance is an additional precautionary measure, and it shall not and cannot replace the usual rules of hygiene.

Examples for fields of application are:

- Hospitals – floors, walls, appliances / equipment, protective gloves, bed linens, mattress, packaging material for medical equipment, and so forth.
- Household – kitchen, bathroom, bedroom
- Textile – work clothes of some occupational groups

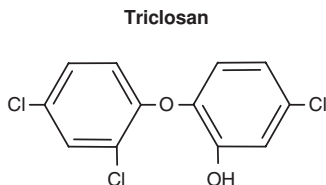
Antimicrobiological substances for application in polymers are not new substances, but well known substances, previously applied successfully in disinfectants for many years.

An antimicrobiological substance is suited to application in polymers, when several requirements are fulfilled.

The main requirements are:

- Good activity in polymers
- Good heat stability to withstand the processing temperatures of polymers
- Insoluble in water to avoid removal during cleaning or washing

An example of such a substance is 2,4,4'-trichloro-2'-hydroxydiphenylether, a phenol derivative with the generic name Triclosan.



(66)

2,4,4'-Trichloro-2'-hydroxydiphenylether

A concentration of 0.1–1.0% Triclosan is recommended for use in polymers. Additional substances are known.

6.2 Antistatic Agents

Many polymers possess good electrical insulating properties, and this makes them susceptible to the accumulation of static electricity. Static electricity is generated when two materials with different susceptibilities to electron loss are rubbed against each other; these can be two different polymers or two different materials. The friction from rubbing causes the natural balance of electrons to shift; one material loses electrons and becomes positively charged, and the other material gains electrons and, with them, a negative charge. In contact with a conductive material a discharge (spark) occurs. Dryness is an important factor for the buildup of static electricity; therefore especially in wintertime any static electricity can cause serious problems. The buildup of static electricity can be reduced considerably by adding antistatic agents to the polymer. The effect of an antistatic agent is the formation of a very thin layer of humidity on the surface of the polymer, which is to a certain extent conductive.

The fields of application of antistatic agents include:

- Packaging – reducing the collection of dust on consumer goods, causing poor customer appeal
- Electronics – safety at work, avoidance of faulty circuits or short circuits
- Industry – general precaution method (safety) to avoid problems associated with the presence of static electricity, for example, danger of dust explosions, during handling of inflammable liquids, and so forth
- Processing of plastics – processing aid to avoid bridging of resins during conveying and feeding operations

Practice shows that especially the last point causes problems during the processing of polymers without being discernible right away. For the feeding of a color batch

it is quite common to use a volumetric metering unit. Each cavity of this unit is filled and emptied in a rhythm defined by calibration. The cavity and the color batch normally consist of different polymers. Rotation during the feeding can cause a buildup of static electricity, and an incomplete emptying of the cavity is the result. This is clearly visible at an inhomogeneous and/or weak coloring of the polymer.

It is quite common that polymers and additives, for example, color batch, are not fed directly on the plasticizing screw but first in a hopper with a small window to control the flow of the materials. The window is often made of a transparent polymer. The rotation in the hopper, necessary for a good premix of the polymer pellets and the color batch, can also cause static electricity, and the color batch sticks to the window. The results are faulty colored parts. Another reason for a static electricity is the severe drying of polymers, which is required for the processing of polymers such as polycarbonate (PC) and poly(ethylene terephthalate) (PET).

Problems during the coloring of polymers related to static electricity can be solved by adding an antistatic agent to the color preparation. For this purpose the addition of 0.1–0.3% antistatic agent is sufficient.

In this context it should be mentioned that several dispersing agents show a side effect of antistatic activity.

The primary compounds used as antistatic agents are:

- Fatty acid esters
- Ethoxylated fatty acid esters
- Alkylamine derivatives
- Ethoxylated alkylamine derivatives
- Alkylsulfonates

The effect of an antistatic agent is the formation of a very thin layer of humidity, but this requires that the antistatic agent migrate to the surface of the polymer. The application concentration depends on the chemistry of the antistatic agent and the type of polymer.

The necessary concentration in a partial crystalline polymer is in the range of 0.1–0.5%, while amorphous polymers require a higher concentration, in range of 1.0–1.5%. The direction of migration is of course not only to the outer surface of the polymer but also to the inner surface, which could cause a harmful contamination of the filling good.

The use of an antistatic agent in a consumer good in contact with food and/or packaging of other sensitive products, for example, cosmetics, requires the observance of legal regulations. Restrictions exist in many countries for the purpose of preventing any harm to the consumer.

All listed types of consumer goods must fulfill several legal requirements. Which plastic part is listed as a consumer good varies from country to country, but generally it includes everything in contact with food, beverages, products for the household, and other sensitive products such as cosmetics and toys. In Germany, for example, all plastic articles in contact with food, packaging material for food, smoking materials, products for the household, cosmetics, and everything in contact with the skin for a longer time are listed. In those items the use of an antistatic agent is limited, and only approved and listed antistatic agents are allowed within a defined concentration; for example, ethoxylated alkylamine derivatives are allowed only up to a concentration of 0.15% in the final product. In the United States, only FDA-approved antistatic agents are allowed to be used in consumer goods.

Many antistatic agents are either liquid at room temperature or have a melting point well below any processing temperature of polymers, for example, the ethoxylated alkylamine derivatives and the ethoxylated fatty acids. The incorporation of a liquid substance in a solid color preparation requires special precaution methods, especially at higher concentrations. On the other hand, often used liquid antistatic agents are commercially available as solid concentrates, either absorbed on a high absorptive carrier such as silica or as a highly concentrated batch. Addition of these concentrates causes no problems during the production of a solid color preparation and they are therefore the preferred types.

6.3 Flame Retardants

The majority of polymers are more or less combustible. High standards in fire protection are responsible for the use of flame retardants. To comply with rules/laws polymers must be equipped with a flame retardant.

The main fields of application are:

- Electrical/electronic appliances, for example, TV compounds, fuse boxes, switches, plugs, and so forth
- Interior decor of public transport systems, such as busses, railways, and airplanes
- Protection of buildings (inside/outside), for example, airport buildings, railway stations, and so forth

In the past chlorinated/brominated substances were preferred because of their effectiveness at relatively low concentrations. But they showed a very significant disadvantage. In case of fire they release gaseous halogen hydrides, which in combination with water are highly corrosive. Even if the fire is small, the smoke fumes

can destroy entire installations by attacking the sensitive electronic components. The consequential damage was very often higher than the damage of the fire as such. The importance of this group of flame retardants diminished considerably in the last decade, and today they no longer play a role as flame retardants in polymers. A modern flame retardant is halogen-free. Their disadvantage is the high concentration necessary to reach the commonly used standard in industry, UL 94V-0. The addition can reach then 25–30%, and in extreme cases even higher.

Supplementation of the polymer with a flame retardant is done by the manufacturer of the polymer, for several reasons:

- The necessary concentration of a modern halogen-free flame retardant is too high as a component of a color preparation.
- Question of guarantee. The different fields of application are governed by several statutory regulations, and include the type of allowed flame retardant, its concentration, test methods, approval procedures for the final part, and so forth. The manufacturer of the plastic part has to document this to his customer in the industry.

The last point is clearly beyond the scope of a manufacturer of color preparations. Flame-resistant types of polymers usually are available only in standard colors. But there is an increasing demand for colors specific for the manufacturer of a flame-resistant plastic part (e.g., for color as trademark). The design of a color preparation for the coloring of a flame-resistant polymer is difficult because:

- No loss of the flame retardancy is permitted.
- Several flame retardants are not colorless; they first must be colored, which can increase the demand of color preparation considerably.
- A high concentration of color preparation can cause problems in highly filled polymers (filled with flame retardant) during the processing.
- Negative interactions between flame retardant and colorant cannot be excluded.

Because of these problems it is recommended to develop any color preparation for the coloring of flame-resistant polymers only in cooperation with the manufacturer of this type to be colored.

In the electrical/electronic industry an international standard for the classification of flame-resistant plastic parts is UL 94. The following practical experience may demonstrate how tricky the coloring of a flame-resistant polymer can be. Pure, powdery titanium dioxide (Pigment white 6), absolutely not flammable, was added as a colorant during the injection molding of a flame-resistant polymer. The result was a loss of the flame resistance of the part. At first this seemed a very

astonishing result. But a detailed examination of the UL 94 method explained this result. One very important criterion for the classification is the behavior of the ignited specimen. The hot melt should not form droplets, which when falling down ignite the wad of cotton wool. When this happens the plastic part does not fulfill the strict UL 94 requirements. Titanium dioxide is a “heavy” substance, which increased the weight of the polymer melt, and droplets were formed.

Substances of the following groups are applied as flame retardants:

- Aluminum hydroxide
- Zinc borates
- Red phosphorus
- Melamine derivatives (borates, cyanurates, phosphates)
- Phosphate derivatives (ammonium polyphosphates, aryl phosphates)
- Phosphorous acid ester (chlorinated and chlorine-free grades)
- Antimony pentoxide
- Chlorinated aliphatic hydrocarbons

The concentration depends on the chemistry of the flame retardant, the type of polymer, and the classification group (UL 94V-0, V-1, and so forth).

6.4 Fillers

Many technical plastic parts must have a high mechanical strength, sometimes in combination with a good durability at higher temperatures of use. This goal is achieved by the addition of fillers. The supplementation of polymers with fillers is usually done by the manufacturer of polymers. The concentration varies between 5% and 60%. Which filler is added depends on the type of filler, the type of polymer, and the specific requirements the final product has to fulfill during its entire life span. For many applications there are grades available that have been developed especially for this purpose.

The following fillers are usually applied to reinforce polymers:

- Glass fibers and glass spheres
- Carbon fibers
- Calcium carbonate (chalk)
- Talcum (silicates)
- Barium sulfate

During the color matching for the coloring of reinforced polymers some characteristic properties must be considered. The most important points probably are:

- Possible damage of the glass fibers. In accordance with their crystal modification several inorganic pigments are very hard and can break the glass fiber during the coloring procedure; these pigments should therefore be avoided, at least when a decrease of the mechanical strength is not acceptable. A typical example of such damage is titanium dioxide (Pigment white 6, rutile modification). When applied in a glass fiber reinforced polyamide, for example, a breakage of the glass fiber was observed, combined with a significant, unacceptable decrease of the mechanical strength of the final product. In this case there was no other possibility than to substitute the titanium dioxide by the optically inferior, but “softer” Pigment white 7 (Zinc sulfide) or Pigment white 5 (Lithopone). This danger of breakage should be considered not only in case of a pure white coloring but also when the pigment is used in white reduction. Another example is the very hard, abrasive chromium green hematite (Pigment green 17). In comparison to the titanium dioxide this pigment is seldom used, and can be substituted relatively easy by an organic pigment.
- Heat stability. A high concentration of filler causes a clear increase of the processing temperature of the polymer and a higher melt viscosity. A higher melt viscosity means a longer cycle time and residence time. The result of such a combined effect can be that the heat stability of an organic colorant, still applicable in the naturally colored polymer, is no longer sufficient for the coloring of the same, but reinforced polymer.
- Pigment concentration in the color preparation. Most fillers are not colorless. They first must be colored, which increases the necessary amount of colorant in the color preparation. The additional amount of colorant can be considerable, especially in the case of very intensive, brilliant colors. Several organic pigments are difficult to disperse, and a higher concentration of these increases the risk of an incomplete dispersion. Color specks in the final product are the logical consequence of an incomplete dispersion, and therefore precautionary methods are a necessity to avoid them.
- Melt viscosity of the color preparation. The melt viscosity of a reinforced polymer is higher in comparison to the naturally colored grade of the same polymer. This must be taken in consideration. The melt viscosity of the color preparation must be adjusted to those of the reinforced polymer; otherwise color streaks and/or other problems during the coloring process may occur.
- Intensive, brilliant colors. Not *every* intensive, brilliant color is possible in a reinforced polymer, especially in the case of highly filled grades of polymer. The fillers show the side effect of lightening colors. In an extreme case the necessary amount of color preparation can exceed the capacity of the reinforced polymer for an additional, large amount of color preparation.

- Use of dyes as colorants. Dyes can be used to color reinforced polymers. In a reinforced polymer, the proportion of the polymer in the product is lower (in comparison to the naturally colored grade). This may cause a migration of the dye at a very low but otherwise safe concentration.
- Interactions. Interactions between the filler and the colorants cannot be excluded. Interactions were reported in the case of glass fibers.

The design of a color preparation for the coloring of a reinforced polymer is not especially difficult when the specific properties and behavior of a reinforced polymer are taken into consideration.

6.5 Dispersing Agents/Lubricants/Release Agents

During the processing of polymers various difficulties can arise, ranging from problems in demolding a part during the injection molding to a sticking together of films during film blowing. Another difficulty may be the reproduction of a structured surface of the mold on the plastic part. In many cases a fast remedy is possible by adding a lubricant and/or release agent.

A strict differentiation between a lubricant and a release agent is impossible because the physical phenomena of adherence and glide merge into one another. The substances usually applied show both effects, and the effect that predominates depends on the polymer and the concentration. An application as release agent normally requires a higher concentration than for use as a lubricant. The concentration varies between 0.1 and 2.0%, depending on the efficiency of the substance, the intended effect, and the type of polymer. Specific grades of polymers are already equipped with those additives by the manufacturers of the polymer, but sometimes it may be advantageous to add it later.

The following substances are recommended as lubricants/release agents:

- Fatty acids, for example, stearic acid, palmitic acid.
- Fatty acid ester, for example, sorbitan tristearate, pentaerythritol fatty acid ester
- Fatty acid amides, for example, oleic acid amide, stearic acid amide, erucic acid amide
- Fatty alcohol, linear and branched grades
- Paraffin oil
- Waxes and their derivatives

A comparison of the chemical structures of these substances with dispersing agents shows that several of these substances are chemically identical. Every

color preparation contains dispersing agents in a variable concentration, and quite often their concentration is high enough to show positive side effects as lubricants and/or release agents. If the side effect is not yet sufficient it is not a problem to increase their concentration.

A substance is effective as a lubricant/release agent when it migrates at least partially to the surface of the polymer. This must be considered when the plastic part is used “in contact with food.” In many countries there are limits for global migration, which of course includes also lubricants, release agents, and dispersing agents. When the extent of the global migration exceeds the allowed limit, it is recommended to determine the chemical structure of each migrated substance, as only in this way is it possible to differentiate between the sources, the polymer, or the color preparation.

6.6 Nucleating Agents

Before an injection molded plastic part can be demolded, it must be cooled down. During this step of injection molding, partial crystalline polymers, for example, polyethylene (PE) and polypropylene (PP), start to crystallize, to form the so-called crystallites. The crystallization is a two-stage process. The first step is the formation of a stable nucleus, which occurs by local ordering of polymer chains. This is followed by the growth stage, which is governed by the rate of addition of other chains to the nucleus. Dust, impurities, remainders of catalysts, and so forth influence the first stage, because they can function as nuclei. The crystal growth takes several days before it is completed. The results are relative large crystals, known as spherulites that are visible in polarized light.

The presence of dust and other impurities is a coincidence, varying from batch to batch. The result would be a variable amount of shrinkage, which is influenced, among other factors, by the size and number of the spherulites. This effect would make it more difficult to reproduce the exact measurements in each injection molded plastic part; therefore nucleating substances are added to avoid this source of irregularities. If a nucleating agent is added to the system, crystallization can be induced at higher temperatures. With more nuclei available and the growth rate unaffected, crystallization is completed sooner. The availability of many nuclei also leads to more and smaller spherulites.

As described in section 3.3 *Shrinkage/Warpage*, several organic pigments act as nucleating agents, and cause the known problems regarding shrinkage and warpage in partially crystalline polymers, preferably in PE-HD and PP.

Experience shows that even in these cases the addition of a nucleating agent to the color preparation helps to reduce these problems. The nucleating agent seems to

be “faster.” The reason for this behavior is not clear, but the key is probably the first step of crystallization, the formation of a stable nucleus.

Although special grades of polymers, equipped with a nucleating agent, are commercially available, it is quite common to add a nucleating agent to the color preparation. In contrast with other additives, only a very small number of nucleating agents are known, and in addition their effectiveness is strictly related to the type of polymer.

The known nucleating agents have the following chemical structures:

- DBS (dibenzylidensorbitol) – in PP
- Aluminum benzoate – in polyolefins
- Calcium and lithium salts of higher aliphatic carbon acids – in PA
- Talcum (special grades) – in polyolefins

The necessary concentrations are in the range of 0.1–0.2% in the final product. Incorporation in color preparations causes no problems at all.

6.7 Stabilizers

Like every other organic substance, polymers age. The addition of a stabilizer to polymers can slow down the aging process, but a complete prevention is impossible. Any aging of polymers is combined with a significant loss of mechanical and physical properties, including change of color. Aged polymers are often very brittle, and the surface is no longer shiny.

Aging occurs for various reasons. Among these are thermodynamically unstable conditions in the material (internal factors), but the majority of causes are environmental effects on the material (external factors). Some typical examples of the influence of the environment on aging are:

- Impact of ionized rays – for example, medical technology, the sterilization of medical appliances by γ -rays
- Impact of weather – for example, outdoor use of polymers
- Biological impacts – for example, by bacteria and fungi. The basis for the decomposition of biodegradable polymers is this impact, and therefore in this special case a positive effect
- Chemical impacts – for example, interactions between the content and the packaging material, in chemical plants, industrial exhaust
- Mechanical impact – for example, rotation/movement of plastic parts, pressure (conveyor belts)

- Thermal impacts – for example, high temperatures during the processing of polymers and during the use (in chemical plants, in cars under the hood, etc.).

Analytical investigations very often showed that a combination of different impacts caused the aging. In Section 3.6 *Light Fastness / Weather Resistance* it was discussed that these fastness properties depend on the whole system, consisting of colorants and polymer. It is impossible to differentiate between the light fastness of an organic colorant and the polymer. The addition of stabilizers to the whole system is necessary if there are strict demands with respect to fastness. Fastness properties are essential requirements; therefore the stabilization of polymers is described in more detailed.

Model tests showed that a PE, consisting of a perfect chain $[-CH_2-CH_2-CH_2-]$, does not need any stabilization, as such an ideal PE is stable and withstands the damaging effects of the environment [49]. The chain of technical grades of PE is by far not perfect, and contains defective spots of a different nature and even double bonds. These defective spots are the real reason for the need of stabilization with a light stabilizer.

The aging of PE caused by the influence of weather is a photooxidative degradation. The first step, the formation of a polymer radical, is initiated by the absorption of energy, for example, intensive UV light. This radical reacts at once with atmospheric oxygen to create a peroxide radical, which starts a chain reaction. The most important steps of reaction are shown in Fig. 6.1.

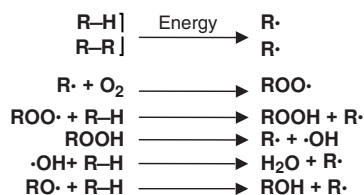


Figure 6.1: Chain reactions of peroxide radicals

The peroxide radical reacts with another molecule of the polymer, and the result is a peroxide hydroxide and a new polymer radical. The polymer radical can react either with itself, with a resulting breaking off of the chain reaction, or with atmospheric oxygen, in which case the chain reaction starts again. By the impact of energy the peroxide hydroxide disintegrates into a hydroxide radical and a polymer oxide radical, which react with further molecules of the polymer, and the chain reaction starts again.

These are only the most important steps of reaction, but further reactions are possible, for example, a reaction with double bonds and/or other defective spots in the polymer chain.

The reaction mechanism indicates that any impact of energy should be avoided: without energy no formation of radicals can be initiated, and without radicals the chain reaction cannot start. In practice, however, this is impossible. Energy in the form of heat is essential for the processing of polymers, and the absorption of light is unavoidable during the use of plastic parts. Consequently an effective stabilization against heat, light, and atmospheric oxygen is necessary for polymers to withstand prolonged exposure to the damaging effects of the environment.

The damaging effect of sunlight can be reduced, but not completely avoided, by the addition of an ultraviolet (UV) absorber to the polymer. Tests showed that the surface of a polymer cannot be protected by the addition of UV absorber, as they are effective first in deeper layers. The primary goal therefore must be the deactivation of the radicals before they can start a chain reaction.

During development of stabilizers it was recognized very early that the different reactions of decomposition require very specific substances for an optimized protection of the polymer during the entire life span. The results of all these efforts are the following groups of stabilizers:

- Processing stabilizers
- Long-term thermal stabilizers
- Light stabilizers

The *processing stabilizers* are added directly after the synthesis of the polymer by the manufacturer. Their function is the stabilization of a polymer during the processing. A minimum temperature of $> 130\text{ }^{\circ}\text{C}$ ($266\text{ }^{\circ}\text{F}$) is required to be effective. The optimal effectiveness of processing stabilizers is within the usual range of the processing temperatures of polymers. They protect the polymer against a heat-initiated decomposition.

Processing stabilizers are derivatives of the following chemical groups:

- Phosphites
- Hindered phenols
- Hydroxylamines
- Lactones

At temperatures below $130\text{ }^{\circ}\text{C}$ ($266\text{ }^{\circ}\text{F}$) the processing stabilizers are not effective (with the exception of the hindered phenols). Technical applications of plastic parts require a good thermal stability for a long time. These parts have to withstand the attack of elevated temperatures during the intended use. These tempera-

tures are clearly lower than the processing temperatures. But nevertheless the polymer must be stabilized, otherwise it is damaged before the expected time. This temperature range requires another type of stabilizer, the long-term thermal stabilizer.

Long-term thermal stabilizers are also added by the manufacturer of the polymer. They reach their optimal effectiveness at temperatures below 130 °C (266 °F).

Long-term thermal stabilizers belong to the following chemical groups:

- Hindered phenoles
- Hindered amines stabilizer (HAS)
- Thiosynergist (in combination with hindered phenoles)

The long-term thermal stabilizers are not effective at the processing temperatures of polymers (with the exception of the hindered phenoles).

The processing stabilizers and the long-term thermal stabilizers protect the polymer against the damaging attack of heat, while the third group, the light stabilizers, reduces the damaging effect of light and atmospheric oxygen.

The *light stabilizers* are the stabilizers that are applied to improve the light fastness and weather resistance of colored and natural polymers. Although there are special grades of polymers on the market that already contain light stabilizers, added by the manufacturer, it is a common practice to add light stabilizers to color preparations.

There are two types of light stabilizers according to the different function they have to fulfill. The *UV absorber* absorbs those wavelengths of the light that are responsible for the initial step of the formation of radicals in a polymer, while the *HALS* (**H**indered **A**mine **L**ight **S**tabilizer) deactivate any radical before it can start a chain reaction. A combination of UV absorber and HALS shows the chemical phenomenon of synergy, in which interaction of two active components of a mixture is such that the total effect is greater than the sum of the individual effects.

Chemically the UV absorbers belong to the following groups:

- Benzotriazoles
- Benzophenones
- Cyanoacrylates
- Oxanilides
- Phenylsalicylic acid esters

Besides the different chemical structures they differ in the wavelength of maximal absorption and consequently in the area of activity.

UV light is commonly subdivided according to the wavelengths:

- UV-A range – 315 to $\leq$ 400 nm
- UV-B range – 280 to $\leq$ 315 nm
- UV-C range – 100 to $\leq$ 280 nm

Consequently the UV absorbers can be assigned to one of these ranges depending on the wavelength of maximal absorption.

The term HALS already indicates the primary chemical principle. They consist of a heterocyclic, nitrogen-containing ring system, containing bulky substituents neighboring to the nitrogen. The diversity of commercially available products proves the variability of this principle.

The stabilization of a polymer against the damaging attack of light always requires the addition of a HALS. The type depends on the polymer to be stabilized. The concentration should be adjusted to the intensity of irradiation at the area of use and demanded light fastness; consequently the concentration is variable. The addition of a UV absorber as costabilizer is recommended because of the synergistic effect. Typical concentrations for the stabilization of a polyolefin are approx. 0.2–0.4% in the final product.

The majority of light stabilizers are solid substances, and an incorporation into a solid color preparation is uncomplicated. In the case of a liquid color preparation liquid light stabilizers are preferred, however, this is not always possible depending on the polymer to be colored. The liquid stabilizer is not necessarily the first choice for the stabilization of this polymer.

All stabilizers, including the light stabilizers, are naturally not inert substances, and therefore negative interactions with other components of the recipe, for example, filler, colorant, flame retardant, cannot be excluded. Several interactions are well known:

- The use of perylene pigments for the coloring of polymers stabilized with HALS should be avoided, as the perylene pigments can deactivate the HALS.
- HALS are alkaline and may interact with other alkali-sensitive components in the polymer, for example, colorants, flame retardants.
- HALS are alkaline and may interact with acidic substances, for example, thiosynergists and colorants.
- HALS may be absorbed on the surface of components with a high absorptive capacity, for example, carbon black and special grades of silica.
- HALS can be deactivated by environmental influences. The deactivation of HALS in agricultural films is known, caused by the contact with certain insecticides.

These and other possible negative interactions should always be taken into consideration during the process of color matching.

The stabilization of consumer goods “in contact with food” requires the consideration of legal aspects. Not all commercially available stabilizers are approved in every country; there are considerable differences, sometimes only in the allowed concentration. This aspect gains importance because of the increasing export of plastic items. The manufacturers of stabilizers are very helpful, and supply all necessary data for each country.

Finally, specific problems a colorist encounters should be mentioned. One problem is that usually the manufacturer of polymers does not release the type of processing stabilizer and long-term thermal stabilizer added. The colorist is therefore not able to estimate the possibility of negative interactions with components of his color preparation. There are grades of polymers available that are already equipped with light stabilizers. Here, too, the manufacturer of this grade does not release the type and concentration of the added stabilizer. On the other hand the customer of the colorist demands a statement regarding the light fastness to be expected from the colored plastic item. Without the knowledge of the type and concentration of the light stabilizer in this grade of polymer the colorist is not able to calculate if a further addition of light stabilizer is necessary, and if so, the additional quantity needed. These problems can be solved only in cooperation with the customer and a series of experiments to determine the light fastness. Another possibility is an analytical determination of the stabilizers, but this is not only time consuming but also rather costly.

6.8 Blowing Agents

The production of a foam requires the addition of a blowing agent to the polymer melt. In the past fluorinated hydrocarbons were used, but these substances were banned after their ozone layer depleting effect became known. Substances can be used as blowing agents when they are either light volatile or release a large quantity of gaseous products as a result of a thermal decomposition at the processing temperature. Examples of the second type of blowing agents are azodicarbonamide and toluene sulfohydrazide. Blowing agents are very seldom added to a color preparation, and possible only in the case of a powdery or liquid color preparation. The addition to a masterbatch is excluded because of the thermal instability of the blowing agents.

The coloring of a foam is not more difficult than the coloring of a solid polymer, if some specific properties of a foam are taken into consideration, for example:

- A homogeneous coloring of a foam demands a homogeneous cellular structure of the foam, which includes the size and wall thickness of each cell.
- The coloring of a foam demands a much higher concentration of color preparation, comparable to the coloring of a film.
- Colorants may influence the cellular structure of the foam.
- The color of a foam may slightly differ from the shade in a solid polymer. The cells are hollow, variable in size and wall thickness. All this may lead to differences in light absorption and reflection (comparatively to the solid polymer).

6.9 Plasticizers

The classical field of application of plasticizers is PVC, but this is not exclusive. Plasticizers are also added to other polymers, for example, PUR and several grades of rubber, to increase the flexibility of a polymer. Numerous plasticizers are marketed. Chemically they belong to the following groups:

- Phthalic acid ester
- Trimellitic acid ester
- Adipic acid ester
- Sebacic acid ester
- Fatty acid polyglycolester
- Chlorinated paraffin

Toxicological animal experiments point to a certain carcinogenic potential, if a high dosage of diethylhexylphthalic acid ester (DEHP) is repeatedly given in the animal food [50]. Other studies, however, showed that this effect is not applicable to humans. Nevertheless in many European countries the use of this specific phthalic acid ester is banned in those plastic items that may come in contact with food and similar applications. Although only this single substance is banned, many customers require polymers and/or color preparations to be “free of *any* phthalic acid ester.” This is not justified at all.

The design of a color preparation for the coloring of a plasticized polymer is not difficult if some specific properties of a plasticizer are taken into consideration.

Migration. The choice of organic colorants is restricted because many organic colorants are not completely fast to migration. In this case it is recommended to check the migration under the condition of the intended use of the colored plastic article. In the worst case the exact desired shade is impossible.

Influence on the hardness (Shore hardness). It is not uncommon that colorants and/or the carrier of the color preparation influence the shore hardness. In such a case it

is not always possible to adjust the shore hardness by varying the quantity of the plasticizer. The choice of the colorant and/or carrier requires special attention.

Plasticizers as carriers in liquid color preparations. The simplest way to color a plasticized polymer is the use of a liquid color preparation based on the plasticizer of the polymer. This is common practice in the case of plasticized PVC. The concentration of the color preparations depends on the quantity of the plasticizer in the final product.

Interactions. The possibility of interactions between the stabilizers of PVC and colorants should be considered.

Experience shows that every problem encountered so far could be solved in cooperation with the customer.

7 Processing Errors and Their Elimination

Everywhere where people work, errors are made, and the coloring of polymers is no exception. Each type of polymer processing of, for example, injection molding, blow molding, film blowing, and transfer molding, has typical technical problems. These problems are not considered in this chapter, but only those that are related more or less directly to the coloring of polymers. The spectrum of errors starts with problems during the production of a color preparation and ends with problems during the coloring of polymers. In the event of problems during the processing of polymers, very often the first thing is to blame the color for it, “*Without the color there was no problem, it started after adding the color...*”. There are many examples in which as a result of a successful error analysis the implicated color was proved “innocent.” This remark should not give the impression that color preparations do not cause any problems, because they do. On the other hand, the fact is that several processing problems first become apparent after addition of the color, which leads to citing the color as the cause.

Table 7.1 contains the most frequent errors related directly or indirectly to colors, the possible reasons and corresponding possible methods of elimination.

Table 7.1: List of Possible Processing Errors, Reasons, and Possible Methods of Elimination

Error	Possible reason	Possible method of elimination
Color specks in the color preparation	• <i>Masterbatch</i> – No optimal dispersion of the pigments	• <i>Masterbatch</i> – Increase the quantity of dispersing agent. – Increase the shear in the extruder. – Add processing aids.
	– Inhomogeneous premix	– More intensive mixing of the premix
	– Humidity in the polymer and/or other components of the recipe	– Use of dry products and/or drying of the humid component
	– Worn out plasticizing screw	– Replace the screw.
	– Incompletely dissolved dyes	– Change the processing parameter of the masterbatch.

Table 7.1: Continuation

Error	Possible reason	Possible method of elimination
Color specks in the color preparation	• <i>Liquid color preparation</i> – No optimal milling	• <i>Liquid color preparation</i> – Check the milling parameters. – Check the milling device; replace worn parts.
	– Humidity in the binder and/or other components of the recipe	– Use of dry products and/or drying of the humid component
Color specks in the final product	• <i>Masterbatch</i> – Incomplete dispersion of pigments – Incomplete dissolving of dyes	• <i>Masterbatch</i> – Use another batch. – Use another batch.
	• <i>Liquid color preparation</i> – Incomplete dispersion of pigments	• <i>Liquid color preparation.</i> – Use another batch
	• <i>Powdery color preparation</i> – Not enough or wrong coupling agent	• <i>Powdery color preparation</i> – Add more or another coupling agent.
	– No or not enough dispersing agent	– Add a dispersing agent or increase the quantity.
	– Not enough shear during the manufacture of the final part	– Increase the shear or use a mixing head or a similar device.
Color streaks in the final product	– Incomplete mixing of polymer melt and color preparation melt – a) Mechanical – b) Thermal – c) Too large difference in the melt viscosity of both components (masterbatch) – d) Too low coloring concentration (masterbatch)	– Use a mixing head or similar devices. – Check the function of each heating band of the extruder. – Check/adjust the temperature settings of the barrel heating zones. – Check/adjust the residence time. – Use a batch with a better adjusted melt viscosity. – Increase the coloring concentration.

Table 7.1: Continuation

Error	Possible reason	Possible method of elimination
Color streaks in the final product	– Contaminated with other colors – a) Contaminated color preparation – b) Later contamination by handling errors (drying, cleaning of hopper, contaminated recycled material, etc.)	– use another batch of color preparation. – Check the source of contamination (improve the handling, more care, better cleaning at color change, avoid contamination of recycled material, etc.).
Black spots	– Thermally damaged colorants	– Change/reduce the processing temperature. – Reduce the residence time. – Avoid dead spots in nozzle or hot runner. – Avoid the production of small parts in a too large extruder (too high screw volume = too long residence time).
	– Thermally damaged polymer	– Change/reduce the processing temperature. – Reduce the residence time. – Avoid dead spots in nozzle or hot runner. – Reduce the sticking of the melt on barrel, screw, etc. (add lubricant or use another alloy).
	– Contaminated colorants and/or polymer (dirt, impurities, foreign bodies, etc.)	– Use clean material. – Check the source for the contamination.
	– Worn screw, barrel, etc.	– Replace the worn parts.
	– Oxidation through compressed air (Diesel effect)	– Provide/improve venting. – Inject more slowly.
	– Contaminated recycled material	– Use clean material.

Table 7.1: Continuation

Bubbles/ streaks in flow direction (color- less)	– Humidity in the raw material	– Check moisture content of all components. – Check drying (increase the drying time or temperature). – Check the function of the dryer.
	– Later contamination with humidity (during storage, condensed water, leakage, etc.)	– Store all raw materials at room temperature and in a dry place. – Check cooling system on leakage.
Bubbles/ streaks (brownish)	– Too high processing temperature or too long residence time (begin of damage) – Too high shear (frictional heat because of too small feeding system)	– Reduce the processing temperature. – Reduce the residence time. – Check the temperature of the hot runner. – Check the hot runner diameter, if necessary enlarge it. – Reduce the injection rate.
Flow lines (pearlescent pigments and other effect pigments)	– Disorientation of effect pigments in the melt	No complete elimination possible, improvement by: – Adjusting the processing parameter – Changing the gate position

To summarize Table 7.1 the most common processing errors are:

- Color specks
- Color streaks
- Thermal damage
- Impurities
- Humidity streaks

Color specks in the final product are caused by incompletely dispersed pigments and sometimes by incompletely dissolved dyes. The source of these is absolutely clear if a masterbatch or a liquid color preparation was used for the coloring of the polymer. Color specks may occur preferably when these two types of color prepa-

ration contain a high concentration of organic, “hard to disperse” pigments, for example, the blue and green phthalocyanine pigments. It requires a great deal of shear to break up their agglomerates in a polymer melt as well as in a liquid color preparation during milling. The possibilities of elimination were described in an earlier chapter. Another reason for color specks in a color preparation is humidity. Humid pigments are very hard to disperse in a polymer melt; a typical example are the pearlescent pigments. In the case of a liquid color preparation a later contamination with humidity may cause a partial flocculation of the formerly well dispersed pigments, and the results are also color specks.

A very detailed error analysis, however, is necessary if a powdery color preparation was used for the coloring of the polymer. The pigments are not dispersed, determined by the system, and can be dispersed first during the coloring process. The reason for color specks can be not enough shear in the single-screw extruder, not enough coupling agent, and/or not enough dispersing agent. It is quite common that a combination of these reasons is responsible for the color specks.

Color streaks in the final part are caused mainly by an incomplete mixture of the molten polymer with the masterbatch melt. The reasons are manifold, for example, a too short mixing zone of the screw, too low processing temperature, too short residence time, too large difference in the viscosity of both melts, and a too small coloring concentration of the masterbatch. In addition color streaks in amorphous polymers can be caused by dyes that are not completely dissolved in the masterbatch. The elimination of color streaks usually requires a detailed error analysis.

An error analysis should not immediately exclude “impossible” causes, as the following example shows. Color streaks occurred during the coloring of PC on an injection molding machine, and without color there were no visible problems. The same problem arose in a new batch, and of course the color was blamed. After a while the real reason was found. A defective heating band in the middle of the barrel caused an incomplete plasticizing (this heating zone was too cold), which was not visible in the natural polymer but became visible when the color was added. After replacement of the defective heating band there were no further coloring problems, not even with the rejected batch. The customer was very fair and did send a letter of apology.

The consequences of *thermal damage* are mainly either brownish color streaks or black (dark) spots.

Brownish color streaks are the sign of a (beginning) thermal damage of the molten polymer. Hot runners and their construction (dead spots, too small dimensions etc.) are very often the source of this problem, but not exclusively. Thermal damage can also be caused by incorrect processing parameters, for example, too

long residence time, too fast injection, and/or faulty construction regarding the position and dimension of the gate.

If the thermally damaged part of the polymer melt is not replaced with every shot, the thermal damage continues, and black spots (carbonized polymer) are the final result.

This process takes more or less a longer time, therefore the appearance of black spots after a longer processing time indicates thermal damage. Black spots, directly visible at the beginning of a processing, are impurities in the polymer and/or other components.

In this context something else should be mentioned. In the case of very intensive dark colors it is possible to confuse dark spots with color specks. Even a colorist sometimes has difficulties in differentiating between both possibilities. As an example, the crystals of the blue phthalocyanine pigment are nearly black.

A (too) long residence time cannot be avoided all the time. One example of this is the production of tiny technical parts. The construction of every injection molding machine requires a minimum size and screw volume, but this can still be too large for those parts. Another reason for a prolonged residence time is the fact that some polymers tend to stick to the wall of the barrel; consequently this thin layer is not replaced with every shot, and a slow damage of this layer is unavoidable. The addition of lubricants and/or the use of other alloys as linings for the barrel may reduce those problems.

The sources of *impurities* are also manifold. Impurities can be present in the raw materials, and those can be detected rather quickly. It is more difficult to detect the source of impurities caused by a later contamination. They are quite often caused by “bad” handling habits and/or not enough care, for example, during the cleaning of peripheral devices during a color change. Contamination with other colors may cause color streaks.

Impurities can also be caused by abrasion. Every barrel and screw of an extruder should be replaced in time. Any worn barrel and/or screw can cause not only impurities, including a gray tinting of the color, but also problems during the processing, either during the production of a masterbatch or during the coloring of the polymer on the injection molding machine.

Humidity streaks are typical for technical polymers. Technical polymers, for example, PC and PET, must be dried very thoroughly prior to their processing. Another reason for humidity streaks is condensation, mainly in the winter. Warehouses are usually cold, while production halls are warm, with the heat developed by the many extruders alone contributing to this in large part. A contamination with condensation occurs if the “cold” raw materials (polymer and color preparation) are processed directly without the possibility of taking the temperature of the

production hall. To avoid this problem, it is recommended to store some quantities of the raw materials prior to processing in the production hall to allow an adjustment of the temperatures. Another, less frequent source of condensation are the pipes of the cooling system (dripping water) and/or a leakage of this system.

Another point must be mentioned in this context, the *accuracy of the color* from batch to batch. Differences are not necessarily a processing error. Every technical product varies in its properties from batch to batch, and a certain difference must be tolerated within limits. During color matching a certain color batch and polymer was used for the specimen. On the other hand the approval of the colored plastic item by the final customer takes time, usually several months. In the meantime other batches are in use. It is quite common that the shade of the specimen and that of the first production differs slightly; a *slight* difference cannot be avoided. It is therefore important to fix the tolerance limits right away with the customer. Only if the shade of the color preparation is outside of the agreed tolerance limit is it a production error. (For further details refer to Chapter 8 Quality Assurance)

8 Quality Assurance

Any new product can be marketed successfully only if the quality is good. To reach this goal it is necessary to run numerous tests during the development of the new product, to define its specifications, and to establish a quality assurance for the investigation of the quality [51].

All these tasks can be subdivided into three closely related fields of work:

- Determination of specifications, including the (agreed) tolerance limits
- Inspection of incoming products
- Inspection of finished products

A new product goes through several stages. It starts with the design and ends with the production of the new product. Intermediate stages are mold construction, prototype production, a check as to whether all requirements are fulfilled, and of course an early fixing of the color. Production will be repeated from time to time depending on the sales. In practice, however, the situation differs somewhat from this ideal, especially in regard to the color. An early fixing of the color, preferably before the production of the prototype starts, is infrequent. Typically all test runs of a new mold are done with natural polymer, including the check of all properties of the new product, and before production starts the color is fixed. While this is done there is failure to notice that any additive to a natural polymer influences several properties of the finished part. Colorants can affect shrinkage considerably, especially in partially crystalline polymers. In the worst case the size of the part or parts is no longer within the tolerance, a serious problem if parts are assembled to the final product. The result may be an expensive reworking of the mold.

The color of basic consumer items is a question of design, while the color of technical parts is determined by national or international agreements. The manufacturer of a color preparation asks his customer for approval of the supplied colored specimen. At the same time that the approval is given, this specimen acquires the status *specimen of origin*. The same procedure is also valid for each type and grade of polymer to be used in the new product, and may be repeated if there is more than one supplier of the polymer. This situation is quite usual for economic reasons.

For later purposes all relevant processing parameters of the colored specimen must be well documented, as well as, on the customer side, its processing parameters of the prototype production. The specimen of origin should be stored very

carefully. Special attention needs to be paid to the conditions of storage. The specimen should be stored in a dark, lightproof, and well sealed container. The packaging material should not contain any plasticizer, optical brightener, or other additives that may migrate. The condition “well sealed” excludes the influence of gaseous pollutants in the industrial environment and of dust. These requirements are important to avoid an adulteration of the specimen during storage.

As all polymers age, the storage time is limited even under these strict conditions of storage. The recommendation is therefore to replace the specimen approximately every 2 years; otherwise a misinterpretation of a new delivery may occur. It has proven successful to store a larger quantity of the color preparation and the polymer (1–5 kg [2.2–12 lb]), which guarantees the periodical replacement of the specimen.

The next step is the agreement of tolerances between supplier and customer. The tolerance limits should allow on one hand an economic production of the color preparation and on the other hand a constant color for each production of the final product. These contrary interests may cause a clash of interests.

Supplier = large tolerance $\Leftrightarrow$ customer = small (no) tolerance

Experience shows that a direct comprehensive dialogue between both parties can avoid such a clash of interests.

Before the tolerance can be fixed several parameters must be defined:

- Product properties
 - Color
 - Field of application
 - Material (polymer)
 - Surface structure
 - Further specific requirements
- Conditions of visual inspection
 - Source of light
 - Geometry of light reflection
 - Viewing geometry
- Conditions of inspection with a color measuring instrument
 - Type of color measuring instrument
 - Measuring geometry
 - Source of light
 - Color system (usually CIELAB)
 - Preparation of the specimen

Usually suppliers and customers have different color measuring devices. The common practice in such a case is to measure the *same* colored specimen on both

color measuring instruments. By comparison of the data, a tolerance can be determined separately for each instrument. The results are two tolerances, one for each color measuring instrument of the same colored specimen, and each party must agree to the tolerance of the other color measuring instrument. This procedure should cause no problems, because ultimately it is the same color, only measured on two different instruments. This procedure is recommended even if both parties have the same color measuring instrument. Color measuring instruments are a technical product with certain tolerances in spite of all efforts of the manufacturer to minimize them as far as possible.

The tolerance should be smaller than $\Delta E = 0.8-1.0$. Such a difference is just still visible depending on the shade, especially if the entire difference lies on one coordinate. This indicates it is usually not enough to fix only a ΔE , but fixing a tolerance limit for each coordinate is recommended. The sensitivity of our eyes to a specific color varies according to the shade. In accordance with the different sensitivities the tolerance can vary on each coordinate, therefore it is not necessary to ask for the same tolerance on each coordinate.

During the *inspection of the incoming products* each delivery must be checked carefully, and the data compared with the specification. This procedure helps to avoid the use of faulty raw material. It is recommended to check during the inspection of the incoming products only those properties that are relevant for the quality of the product. The costs of inspection can thereby be limited. A complete check of all data would be too cost intensive.

Quality-relevant points of a specification are, for example:

- Polymer – natural color, melt flow index, visual check (impurities, etc.)
- Colorant – colorimetric examination, humidity, visual check (impurities, etc.)
- Color preparation – color (colorimetric examination), melt flow index, humidity, visual check (impurities, contamination with other colors, etc.)

A specimen mold is usually used for this purpose. The production of each specimen must be in accordance with the processing parameter, fixed and documented in the specification. This is necessary to avoid misinterpretations, because slight differences in the processing parameter may cause slightly different shades. The data for each batch can be drawn in a diagram. With increasing amounts of data the diagram shows very well the variation within the tolerance field. In a data sheet or diagram something else is very discernible. The distribution of the data within the tolerance field can occur just by pure chance or the data may move more or less in one direction. An example of such a data sheet is given in Fig. 8.1.

Data sheet (Inspection of incoming goods and/or of finished products)

Article:

Article-No.:

Color:

Colorimetric Data

Date	Target	Standard	Tolerance/Difference
		L* a* b*	ΔL^* Δa^* Δb^* ΔE^*

Batch-No. _____

Figure 8.1: Example of a data sheet for color preparations

The tolerance can be enlarged if a batch just outside of the tolerance limit did not show any negative influence on the quality. On the other hand the tolerance must be reduced if a batch just inside of the tolerance limit influenced the quality of the final product.

The same basic principle is valid for the *inspection of the final product*. The quality assurance of a final product requires not only specifications of the raw materials and the final product but also a specification of the processing parameters. The last point is very important, because a change in a processing parameter can cause a difference in color or quality. A specification of processing parameter should therefore contain all parameters that are relevant to the color or quality. To

work out such a specification or in other words to define the processing “window,” it is necessary to change each processing parameter and to check its influence on the quality. The result is a list of those parameters that are relevant to the quality. It is quite normal if the list of the manufacturer of a color preparation differs in detail from the list of the producer of the final product. Such a difference is the consequence of a different significance of a single processing parameter in the quality. But the importance of a processing specification is in principle the same for both manufacturers. Analogous to the inspection of incoming products the data of the inspection of the final product must be compared with the specification. The same or a very similar data sheet can be used for the documentation of those results (Fig. 8.1).

The manufacturer of the color preparation checks the quality of his product by injection molding of a specimen and a colorimetric examination. These data together with the specimen are supplied to the customer.

The producer of the final product checks its quality, for example, the color, by comparison with the specimen and his own former productions, and this includes visual as well a colorimetric examination. Depending on the design of the product it is possible to measure the color direct on the product, which, however, requires an even part on it, or a separate specimen is produced, using a bypass on its extruder.

These basic features of quality assurance do not indicate the practical problem. It starts with the production of the specimen. The mold and laboratory injection molding extruder for the production of the specimen differ from the mold of the final product and the production extruder; consequently both parts are produced with different processing parameters. The color preparation is in both cases the same, but not the batch of the polymer. In addition the (small) samples for the approval of a color and color preparation are produced on a laboratory scale extruder, while the production is done on a production extruder. These different quantities of a color preparation are produced necessarily under different processing parameter. These facts may underline the importance of specifications and agreed tolerances. It is common practice to establish besides the specimen of origin a second one, a *specimen of (the first) production*, including all specifications.

The influence of processing parameters on the color (and other properties) is very often underestimated in spite of many publications that prove their importance. A technical college in Germany (KIMW – **K**unststoff**i**nstitut der **m**ittelst**ä**ndischen **W**irtschaft) is very active in this respect. Several theses proved the influence of processing parameters on the color and quality. These studies showed that the change of one processing parameter causes directly or indirectly a different strain on the molten polymer by temperature and time. On the other hand these two pa-

rameters are very important factors with regard to the heat stability of polymers and colorants and the fastness properties of the final product. These studies proved that the following processing parameters are relevant for the color and quality:

- Melting temperature
- Residence time
- Temperature of the mold
- Injection rate
- Revolutions of the screw
- Back pressure

In practice a change of processing parameter is quite common, usually caused by the production process. If the number of pieces is reached, production stops and the mold is dismantled. It would be ideal to use the same extruder for all further production runs, but this is not always possible. Often a similar injection molding extruder must be used for the next production of the same article, which causes at least slightly different processing parameters. This requires a special careful investigation of the first produced parts to avoid production flaws.

Finally a practical example may demonstrate the importance of processing parameters in combination with the construction of the mold. If a manufacturer of technical devices needs a very large number of pieces, usually two independent processors of polymers will produce them. They use different injection molding machines and differently constructed molds. At the beginning one processor had problems with the exact shade of his parts, while the other processor, using the same batch of color preparation, had no color problems. This problem was solved by a slight adjustment of the recipe of the color preparation for the processor with problems.

9 Mold Construction

Polymers and colorants are subject to the impact of temperature during processing. This thermal strain is not only the result of the processing parameter, but also a consequence of the construction of the mold. A suboptimally constructed mold may cause such an additional thermal strain that the sum of all thermal strains is already in the range of a beginning thermal damage. To avoid this, several points should be considered for the construction of the mold.

Special attention should be paid to the following points:

- Gate system. The diameter of the gate should not be too small, or a too high frictional heat may be the consequence. Another important point is the right position of the gate.
- Mold cooling system. Polymers are poor heat conductors. The cooling system must be not only efficient but also should ensure that the surface temperature of the mold is correct everywhere, because uneven heat dissipation in the mold can lead to differential shrinkage with all the detrimental effects on the quality of the molded part; in addition a poor heat dissipation in some regions of the mold can cause a substantial lengthening of the cycle time, leading to increased costs of the injection molding. A correct surface temperature of the mold is also important for a perfect surface finish of the molded part, for example, gloss, reproduction of surface structures.
- Surface finish of the mold. All parts of the mold should have the same surface finish, including the same alloy for the lining of all (at least visible) parts of the mould. Different alloys, for example, may cause a differential reproduction of the surface structure.
- Good venting of the mold. This is important to avoid black spots caused by the Diesel effect.
- Sharp edges. Generally sharp edges should be avoided, as they may cause a too high shear with a detrimental effect on the quality of the molded part.
- “Dead” spots. They must be avoided principally to prevent a thermal damage of polymer and/or colorant

The choice of the right hot runner system determines the function of the mold and the quality of the molded parts. Unsuitable hot runner systems usually cause high pressure losses, and they should be operated, if used at all, only at a very high temperature. But this high temperature usually will cause the polymer and/or col-

orant to degrade, and therefore their use should be avoided. The construction of a hot runner should avoid sharp edges, “dead” spots, too small dimensions, and should allow a good temperature control.

Problems related to the construction of a mold and/or hot runner are usually recognized during the test program. Whether a complete elimination of the problem is possible depends on the kind of problem, and of course on the expenditure of time and costs of elimination.

Most problems can be excluded if the above described critical points of construction are taken into consideration during the planning phase of the new mold and hot runner.

10 Legislation

Our everyday life is governed by laws and regulations, and new ones or at least amendments are added constantly. In recent years, the number of laws providing protection during the manufacture, use, storage, and transport of chemicals has risen worldwide. The same is true for regulations concerning waste removal. It is therefore no wonder that the processing of polymers is also subject to many laws and regulations. They vary from country to country, sometimes in substance, and sometimes only in detail. Today it is no longer sufficient to know the laws and regulations of one's own country. The increasing export of goods requires in addition the knowledge of the laws of the receiving country or even countries. Without exceeding the scope of this book, only an outline of the most important laws and regulations related to the coloring of polymers can be given. Generally considered all laws pursue the same aim, namely the protection of the consumer against any harm during the intended use of plastic items and the protection of workers during transportation, storage, handling, and processing. The way to reach this aim varies from country to country. In case of doubt it is recommended that one always check the latest status of the original text of the law or regulation. The most important laws and regulations are:

Unites States

- Toxic Substances Control Act (TSCA) (1976)
- Occupational Safety and Health Act (OSHA) (1970)
- Superfund Amendments and Reauthorization ACT (SARA) (1986)
- FDA, Code of Federal Regulations

CFR 21 § 178.3297 – Colorants for polymers

CFR 21 § 170.39 – Threshold of regulation for substances used in food-contact articles

CFR § 176.170 – contains the methods for the evaluation of migration

CFR 16 § 1501-1518 – Federal hazardous substances act regulations (toy safety)

- Standard Consumer Safety Specification on Toy Safety – ASTM F 963 – 92, 96a
- CONEG Regulation

European Community (EC)

- Guidelines for the Classification, Packaging, and Labeling of Dangerous Substances with Several Amendments (1967), (67/548 EC, 91/325 EC, etc.)
- General Preparations Directive (88/379 EC, amendment 93/18 EC)
- Safety of Toys (87/C343/EC), EN 71 part 3: chemical properties)
- Directive for Materials and Articles Intended to Come into Contact with Foodstuff (89/109 EC)
- Directive for Plastic Material Intended to Come into Contact with Foodstuff (90/128 EC, amendments 92/39 EC, 95/3 EC, 96/11 EC)
- Safety Data Sheets (93/112 EC, in combination with 88/379 EC and 91/115 EC)
- Packaging Regulation 94/62 EC (the European version of the CONEG regulation)
- EC Resolution AP (89) 1 – Impurities in colorants

Germany

- Chemical Law (1980), several amendments
- Hazardous Substances Ordinance (1986)
- 178th Communication of the BGA
- “Lebensmittel- und Bedarfsgegenständegesetz” (Consumer good ordinance)
- DIN EN 71, part 3 – Safety of toys

Other Countries

Every other country has its own laws and regulations, which sometimes correspond to those of the European Community, sometimes to US FDA regulations, and sometimes they are very specific for the country.

At the first glance this number of different laws is confusing. In reality, however, it is not as overwhelming as it looks. To describe important details of all the different laws and regulations, a completely different kind of description is chosen instead. In this way it is easier to work out similarities but also differences of the numerous regulations. The “guideline” will be on one hand the consumer goods and their requirements, and on the other hand the requirements all components of a colored plastic article are required to fulfill.

10.1 Consumer Goods: Definition and Requirements

The general idea of all regulations is to protect the consumer against any harm during the intended use of a specific item. All the different regulations vary therefore more or less only in detail.

First, the question of what is a consumer good must be answered. In Germany [Consumer good ordinance § 5 (1), dated 10.4.1992] a consumer good is defined in the following way:

- All articles, that are intended to be used in the production, processing, trading and consumption of foodstuffs and thereby come into contact with foodstuffs or have an effect on these
- All container and packaging material for cosmetics and smoking materials
- Devices for dental and oral hygiene, except medical instruments
- Devices (and products) for personal hygiene
- Toys and joke articles
- All articles that come in contact with the body (skin) for a longer time, for example, wigs, glasses, bed linen, clothes, jewelry, artificial eyelashes, and so forth
- Cleansing agents, including impregnating agents, and others products for consumer goods

In principle, these statements are valid for all other countries.

The US FDA defines consumer goods very similarly, but they differentiate in addition between household goods (“Housewares Exemption,” CFR 39 § 13285, dated 12.04.1974) that come in contact with food only for a *short time* and packaging material for food that stays in contact with food for a *long time*.

The *universal* requirement is that consumer goods must be free of any toxicological substance, must be odorless and tasteless, and must be free of impurities except those that are technically unavoidable [e.g., German consumer good ordinance § 31 (1), similar statement by the US FDA]. This goal can be reached only if every component of the plastic article fulfills specific requirements, and this is the original reason for all the requirements and regulations. For the production of consumer goods only approved components are allowed to be used; only then can it be expected there will be no harmful effects.

The condition “free of any toxicological harmful substance” is obviously the reason for several regulations, for example, the CONEG regulation, the European version 94/62 EC, and the Amendment 2 of the German consumer good ordinance.

CONEG Regulation (Coalition of Northeastern Governors): This regulation bans de facto the use of the toxicological cadmium pigments and lead chromates, but without naming them. Any packaging material for consumer goods is not allowed to contain totally more than 100 ppm of cadmium, lead, mercury, and chromium VI in 1 kg (2.2 lb) of packaging material. This low limit was chosen because on one hand at such a low concentration the pigments in question cannot yet develop any tinting strength, and on the other hand the amount is in the range of a permissible content of these substances as technical unavoidable impurities.

The *European packaging regulation 94/62 EC* is absolutely identical with the CONEG regulation; in other words it is the European version of it.

The *Amendment 2 (and 3) of the German Consumer Good Ordinance*, dated 15.7.1994, bans the use of those azo colorants that can separate one of 20 listed carcinogenic amines under certain test conditions. These conditions, including the analytical method for the evaluation, are defined. The list of these amines contains, for example, dichlorobenzidine, which is a component of the formerly very often used disazodiarylide and disazopyrazolone pigments (refer also to the chapter on azo pigments). Originally only the use of these azo pigments in textiles was banned, the ban has been broadened for all consumer goods.

10.2 Safety of Toys

Generally speaking, toys are defined as consumer goods, and consequently all the requirements applying to consumer goods must be fulfilled. There are, however, further regulations regarding the safety of toys. The requirements for a consumer good are just one part of the safety of toys. The term “intended use” varies considerably between a consumer good and a toy. A toy has to withstand very rough treatment, and in case of breakage the broken parts cannot cause any harm to children. To achieve this goal, all the different potential dangers must be considered in the construction and properties of toys. This is the reason for the regulations “safety of toys,” which consist of several parts. In this context only the part dealing with chemical properties, migration of impurities, is relevant.

The European Toys Standard EN 71 (1988) consists of three parts. The first two parts deal with the construction and handling properties of a toy, while the third part (EN 71-3), relevant in this context, defines the limits of regulated, soluble, technically unavoidable impurities in colorants or other components. In Table 10.1 the limits for plasticine and modeling clays and fingerpaints are added, which play no role in this regard.

Table 10.1: Limits of Regulated Impurities in Toys

Element	Limit – EN 71-3	Plasticine/fingerpaints
Antimony	60	10
Arsenic	25	5
Barium	1000	350
Lead	90	25
Cadmium	75	15
Chromium	60	25
Mercury	60	5
Selenium	500	50
Amount in ppm, soluble in 0.07 N hydrochloric acid (HCl), based on 1 kg (2.2-lb) toy.		

This strength of the hydrochloric acid, 0.07 N HCl, corresponds more or less with the strength of the gastric acid, and is chosen to calculate possible risks when a toy is accidentally swallowed. The impurities must be *soluble*, a very important condition. In this way inorganic pigments, consisting of insoluble oxides containing antimony, barium, or chromium, are not banned. The pigments in question are approved and considered to be nontoxic (refer also to the chapter on inorganic pigments).

The safety of toys includes still another condition, the *fastness to saliva and sweat*. Contact with saliva and/or sweat is another, very common potential risk for children.

The different regulations therefore contain standard test methods to investigate this route of a possible contamination, for example, the German standard DIN 53 160 “Prüfung von bunten Kinderspielwaren auf Speichel- und Schweißsechtheit” (test method to check the fastness to saliva and sweat) [19]. The test liquids are simulated saliva and sweat. The test method contains a detailed description of the composition of these test liquids and all other test parameters. This test, too, must be done on the final toy.

In other countries the rules and regulations are basically the same, but differ in detail. It is recommended to check in every case the original text, and always the latest status, for the country in question.

10.3 Requirements for Components of Consumer Goods

Worldwide any component of each consumer good must be approved for its specific application. The differences are just the list of the approved substances, their limits of concentration, and methods/conditions for their approval. This starts with polymers and colorants and ends with any additive.

10.3.1 Polymers

Any polymer for such an application must comply with the specific regulations of each country. These regulations usually contain a list of allowed monomers, the catalysts for the polymerization, including their maximal concentration as impurities in a polymer, any production-based impurity, and any additive necessary for the production of a polymer. Additional test methods, any restriction regarding the concentration of a substance or impurity, and migration limits are described. The application for approval requires a long list of physical, chemical, and toxicological data. Approved additives are sometimes only listed, because their approval is done by separate regulations. The basic requirements are more or less the same in each country, varying mainly only in details.

The relevant requirements for polymers are published in the following regulations:

USA: Published by FDA in the Code of Federal Register (CFR). Several paragraphs deal with the specific requirements for polymers.

European Community: 90/128 EC with the amendments 92/39 EC, 95/3 EC, and 96/11.

Germany: There are two independent regulations, the consumer good ordinance and the 178th recommendations of BGA; the latter is updated periodically.

Consumer good ordinance (dated 10.4.1992), including several amendments. This ordinance is partly a carryover of several EC regulations into a German regulation, and contains a general list of monomers and other substances allowed in polymers, including the ban of some substances.

The 178th *Recommendation of the German Health Authority* (formerly BGA, now BgVV) contains (besides other chapters) for each type of polymer a separate chapter, in which the requirements for this specific polymer are described in detail, including a list of approved substances.

10.3.2 Colorants

In comparison to the regulations for polymers and additives, the regulations for colorants differ considerably in some aspects. Common for all regulations is the “non-migration principle,” in which any migration of a colorant is not permitted. The differences are a consequence of a different way of looking at things. In the United States only those colorants may be used for the coloring of consumer goods that are approved and listed by their chemical constitution; it is a positive list. In contrast, the European Community allows generally all colorants that fulfill specific requirements regarding purity, and that are toxicological harmless. It is consequently not a positive list. The basic idea is, the authorities do not want to hinder the development of new colorants and their (fast) application. At the same time the responsibility for the safety of a new colorant clearly rests with the manufacturer.

The situation in France is confusing. A positive list exists (still) in France (the only positive list in Europe); on the other hand France agreed to the European Resolution AP (89) 1, which allows generally all colorants that fulfill specific requirements regarding purity, and that are toxicological harmless.

The relevant requirements for colorants are published in the following regulations:

USA: Published by FDA in the Code of Federal Register (CFR), *CFR 21 § 178.3297 – Colorants for Polymers*, which contains the positive list of approved colorants [part (e) – list of substances]. The colorants are listed with their chemical terms, color index number, and CAS number, except in the case of commodities such as chalk or iron oxide. In addition the list contains limitations in spite of the general definition given in § 178.3297. Paragraph 178.3297 defines the colorants and use in the following way: “*The substances, listed in paragraph (e) of this section may be safely used as colorants in the manufacture of articles or components of articles intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding food, subject to the provisions and definitions set forth in this section: ...*” Paragraph 178.3297 (c) says: “*Colorants in this section must conform to the description and specifications indicated...*”

Strictly speaking, the approval is valid only for the quality of the registered colorant and within the published limitations. This does not mean that all chemically identical colorants, manufactured by a company different from the company that asked for the approval, are automatically also approved. This is given only if the quality corresponds closely to the quality of the listed colorant.

Table 10.2 contains a list of approved colorants, but it must be emphasized that the list can be only incomplete, because several colorants are registered for approval. New approvals of colorants are published in the regular revision of CFR.

Table 10.2: *List of Colorants Approved by § 178.3.297 (Status 2001)*

Color index number	Color index formula	CAS number	Limitations
P. blue 15:1, 15:2, 15:3, 15:4	74160	147.14.8	
P. blue 28	77346	68186.86.7	Yes (see original text)
P. blue 29	77007	57455.37.5	Yes
P. black 7	77266	1333.86.4	Yes
P. black 28	77428	68186.91.4	Yes
P. green 7	74260	1328.53.6	
P. green 17	77288	68909.79.5	Yes
P. orange 64	12760	72102.84.2	
P. red 101 (approved as iron oxide)	77491	1309.37.1	
P. red 177	65300	4051.63.2	
P. red 187	12486	59487.23.9	Yes
P. red 220	20055	57971.99.0	
P. red 254	56110	122390.98.1	Yes
P. violet 15	77007	12769.95.9	Yes
P. violet 19	73900	1047.16.1	
P. white 4	—	1314.13.2	Yes
P. white 6	77891	13463.67.7	
P. white 7	77975	1314.98.3	Yes

Table 10.2: Continuation

Color index number	Color index formula	CAS number	Limitations
P. white 18 (approved as calcium carbonate)	77 220	1317.65.3	
P. white 20 (approved as aluminum and potassium silicate)	—	—	
P. white 21 (approved as barium sulfate)	77 120	7727.43.7	
P. white 26 (approved as magnesium silicate)	—	14807.96.6	
P. yellow 95	20034	5280.80.8	
P. yellow 110	56280	5590.18.1	
P. yellow 138	56300	56731.19.2	Yes
P. yellow 147	60645	76168.75.7	Yes
P. yellow 151	13980	61036.28.0	Yes
P. yellow 180	21290	77804.81.0	
P. yellow 181	1177	74441.05.7	
P. yellow 191	—	129423.54.7	Yes
P. Metal 1 (approves as aluminum)	—	7429.90.5	

The original list also contains some optical brighteners, but the list does not contain dyes. This is probably the consequence of a very strict application of the “non-migration principle,” because tiny traces of dyes may be detectable under the required test conditions.

There is another possibility for the approval of colorants, *CFR 21§ 170.39 – Threshold of Regulation for Substances Used in Food-Contact Articles*. This paragraph states: “Exemptions to regulation as a food additive are granted under this regulation, if the use of the substance in a food-contact article results in a dietary concentration at or below 0.5 ppb, or if the use of a regulated direct food additive is at or below 1% of the acceptable dietary intake.” In other words, the migration limit is 0.5 ppb. It is obvious that under these conditions only very pure inorganic pigments have a chance of approval.

The following inorganic pigments are approved at levels up to 2% in all types of food contact polymers according to this paragraph:

- Pigment brown 24
- Pigment green 50
- Pigment yellow 53

In this context another paragraph is important, *CFR 21 § 176.170*. This paragraph describes the method for an evaluation of any migration for consumer goods in food contact.

In view of the large number of available colorants only a few colorants can be used for the coloring of consumer goods, if “FDA conformity” is requested. This limits the number of possible shades.

European Community: Within the EC any colorant can be used if it fulfills the specific requirements regarding purity, if it does not migrate under the condition of the intended use, and if it is toxicologically safe. The colorants must fulfill the conditions described in: *Resolution AP (89) 1 – On the use of colorants in plastic materials coming in contact with food*. This resolution is accepted from the majority of the European countries in the meantime. The resolution contains the following sections:

- Field of application
- General principles
 - Migration
 - Specification
 - Soluble metals as impurities
 - Aromatic amines as impurities
 - Carbon black – extractable fraction in toluene
 - Polychlorinated biphenyls as impurities
 - Toxicological tests
- Description of the analytical method, including definition of the test liquids

The importance of each section varies depending on the type of colorant, for example, soluble metals as impurities are relevant in the case of inorganic pigments but not a problem in the case of organic pigments (except barium lakes) and dyes, while aromatic amines and polychlorinated biphenyls cannot be present in a calcinated inorganic pigment. A special case is carbon black with the extractable fraction, a consequence of the specific production method.

Table 10.3 contains the limits of regulated metals and aromatic amines. For the purpose of a better comparison with still existing national regulations, the valid limits of other countries are included in the table. The comparison clearly shows the similarity of all national regulations, which differ only in a few details.

Table 10.3: *Limits of Impurities by (Regulated) Metals and Aromatic Amines (Status 2/1999)*

Metal	Resolution AP (89) 1	Germany	Belgium	England	Netherlands	Spain
Lead	100	100	100	100	100	100
Arsenic	100	100	50	100	100	50
Mercury	50	50	50	50	50	50
Cadmium	100	100	2000	100	1000	2000
Zinc	—	—	—	2000	—	2000
Selenium	100	100	100	100	100	100
Barium	100	100	100	100	100	100
Antimony	500	500	2000	500	2000	2000
Chromium	1000	1000	1000	1000	1000	1000
Aromatic amines – all countries 500 mg/kg (0,1 n HCl)						

Amount in ppm, soluble in 0.1N hydrochloric acid (HCl), based on 1 kg (2.2 lb) of colorant

The impurities must be *soluble*, a very important condition. In this way inorganic pigments consisting of insoluble oxides containing antimony, barium, or chromium are not banned. These pigments in question are approved and considered to be toxicologically safe (refer also to the chapter on inorganic pigments).

The list of regulated metals is the same for toys (Table 10.1) and consumer goods, but the limits differ. A first glance may create the impression that the require-

ments for toys are stricter, but this is not the case. The explanation lies in the different points of reference. The limits of impurities in toys are based on 1 kg (2.2-lb) toy, while the limits of impurities for consumer goods are based on 1 kg of colorant. The usual concentration of a colorant in plastics, including toys, is in the range of a few percent, and because of this dilution effect it is no problem to fulfill the requirements of toys with these qualities.

The section on *test methods* describes the procedure for checking the migration. The test liquids to be used are defined and should simulate different types of food. Which test liquid should be used depends on the type of food.

There are the following test liquids:

- Distilled water
- Acetic acid, 2% by weight
- Ethanol, 10% by volume
- Coconut fat or oil or peanut oil

Germany: The German regulations are published in the 178th Recommendations of the health authorities. Chapter A IX describes the requirements of colorants for polymers and chapter B II/IX the test methods. The German regulation corresponds de facto to Resolution AP (89) 1.

10.3.3 Additives

Similar to polymers and colorants every additive must be approved for use in consumer goods. The conditions for approval are very similar to those for polymers and colorants. The approved additives can be found in different regulations depending on the characteristic of the additive, for example, optical brighteners and some fillers are considered as colorants, while antistatic agents, dispersing agents, lubricants, and so forth are usually listed in regulations regarding polymers.

A special case are the *flame retardants*. The risk of a fire is ubiquitous, and this is the reason for many specific regulations [53]. These regulations cover the potential risks in the different fields of application, for example:

- Electrical appliances / electronics – in Germany the VDE (Association of the German electrical engineers) – regulations, for example, VDE 0304, VDE 0471, VDE 0472, and so forth
- Building industry – in Germany the DIN standards, for example, DIN 4102 part 1–7, DIN 66081, DIN 66082, and so forth
- Automobile industry – for example, in the United States regulation MVSS 302 (Federal Motor Vehicle Safety Standards) and in Germany the standard DIN 75200.

- Aircraft industry – for example, in the United States regulation FAR 25853 (Federal Aviation Regulations) and in Germany regulation LTV 1500-850 (Luft-Tauglichkeits-Vorschrift)
- Plastics – the standard is UL 94

All these regulations differ in detail, but all regulations pursue the same goal: the prevention of a fire. The basic principle of all regulations is the test of fire behavior of any piece of equipment. The different test methods describe in detail the way to set light to the piece of equipment, and it is classified on the basis of its fire behavior.

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The successful coloring of plastic parts, beginning with the formulation of the color preparation and ending with the manufacture of the final product, is the result of the interaction of chemical, physical, and technological factors. In-depth knowledge of these factors and their interrelation and the consideration of national and international regulations are prerequisite for anyone working in this field.

This book describes the various aspects of coloring plastics. The reader is enabled to identify the color preparation that meets given product requirements. Only if color preparation, polymer material, and final product design and requirements are well coordinated will the customer be pleased with the colored plastic product.

Contents

- Methods for Coloring of Plastics
- Requirements for Color Preparations
- Composition of Color Preparations
- Colorants and Additives
- Processing Errors and Troubleshooting
- Quality Assurance
- National / International Regulations

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