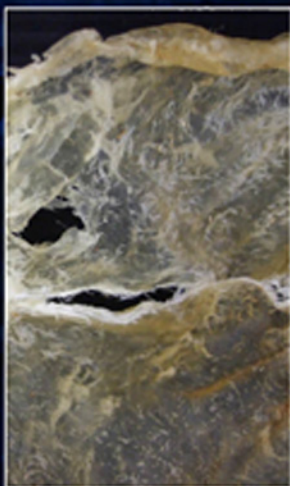
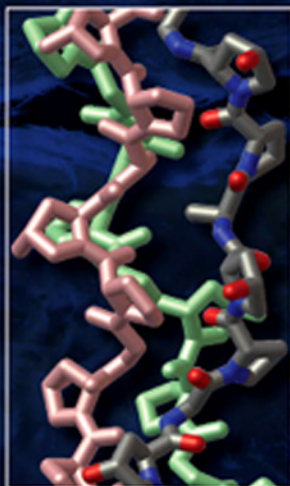


SECOND EDITION

Materials for Conservation

*Organic consolidants,
adhesives and coatings*



Velson Horie



Materials for Conservation

To Neill and Velson
The continuing reason

Materials for Conservation

Organic consolidants, adhesives and coatings

Second edition

Velson Horie



AMSTERDAM • BOSTON • HEIDELBERG • LONDON
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Preface

The conservation of historic materials requires the application of a wide range of knowledge and skills. The aim of this book is to provide background information on one aspect of conservation treatments: the properties of organic consolidants, adhesives and coatings as they affect the treatment of objects. The variety of film-forming and binding materials, together with associated materials such as oils, is not covered by a single descriptive term. The inadequate word ‘polymer’ or ‘resin’ will often be used to encompass these materials. The vast number of commercial polymers and formulations creates considerable scope for harmful as well as beneficial changes in the practice and philosophy of conservation. Polymer science has increased our insight into polymer properties, offering the potential for valuable improvements in treatments and the materials used. It is my hope that the reader will assess the use of both new and old materials on objects more rigorously.

The last decade has seen a revolution in materials. Many new materials have been invented. The highly complex properties of polymers are being increasingly understood in terms of their chemical structure and nano-scale assemblages. Quality control and specification of polymer production and supply, both natural and synthetic, have improved enormously. Many of the commercial products used by past conservators are being changed or discontinued as both production and research facilities of the chemical industry are radically reorganized, resulting from global acquisitions of chemical firms. The consequence of this increase in choice across the consumer and industrial fields is that the user is now expected to be able to make informed choices, ranking the various qualities and consequent compromises. ‘Brands’ are no longer (if they ever were) a reliable indicator of properties. Conservators must therefore understand and specify their materials using explicit, measurable, physical properties. The limited technical resources available to the relatively small field of conservation must be used economically to provide these specifications. As in all fields, there needs to be continual quality assurance that the specifications are both appropriate and achieved. This is not cheap nor easy to organize across a diverse, international, field.

Conservators must know about the added material and its effects on objects before making a decision on whether, and how best, to incorporate a material into a treatment for the object. Current good practice is to develop a treatment incorporating materials with appropriately specified properties, designed to fulfil a defined conservation need. It is not appropriate to apply a material designed for one purpose to another.

Part I outlines the properties of polymers that are important in the interaction of polymers with objects. **Chapters 1 and 5** provide a qualitative introduction

and summary of the scientific basis for defining and assessing those properties, which are covered in the intervening chapters. Part II provides a detailed consideration of individual polymers, their properties and uses in conservation. Most polymer types that have been used in the conservation of objects are included. At the end of the book are appendices that summarize data referred to in the text.

Various introductory texts in this field have been prepared for conservators in the past decades (Torraca, 1968; Feller et al., 1971; Conservation Unit, 1992). Many more books are now available for schools and the general public that outline the concepts and properties of polymers. More detailed reference books that assume some knowledge of chemistry include Painter and Coleman (1997), Brydson (1999), and Cowie and Arrighi (2008). The reader is assumed to have access to publications of the International Institute for Conservation. Polymers that have been adequately described in those publications have been given a slighter treatment here to avoid duplication.

This text both looks forward, with advances in application of new ideas and materials to objects, and backwards to past treatments. It is based primarily on published information that can be verified, so is limited to sources available to the author. Suggestions from readers of significant omissions or errors have been valuable in expanding the sources used. Further suggestions and comments are welcome and can be sent through www.horie.co.uk/

CONCLUSIONS

1. The interactions between objects and polymers, etc. are ill-understood. Assuming that the object is the primary concern of the conservator, consolidants, adhesives and coatings should be applied only when necessary to the survival of the object. They should not be used as an alternative to proper packaging, environmental control, etc. Given the difficulties of removing polymers, they should be applied sparingly.
2. One of the most difficult tasks of a conservator is reversing the conservation treatment of an object before starting new stabilization treatments, etc. Publication of past treatments, assessments of their effects and reversal methods is rare but most welcome to the conservator who must treat objects with comparable problems. Conservation is dependent on the material history that survives. The history of conservation, which is rarely written, is an integral part of conservation studies.
3. Most commercial polymers are produced for industrial applications that are ephemeral by conservation standards. Conservators both past and present have used products whose suitability is untested. The understanding, and limits of understanding, of a material's properties should be made explicit in any specification of a material for conservation use. The composition (both major and minor components) and properties for an applied material should be declared. Withholding of information about composition, properties etc must be viewed with suspicion. There is sufficient information available to

enable formulations to be developed to conservation standards and revealed in the public domain. These recipes would reduce the need for commercial products of unknown composition and variability.

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SECOND EDITION

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Cover images: The photograph of raw isinglass was kindly provided by Juanita Navarro; the model of a stretch of a collagen molecule is based on 1 cag data in the Protein Data Bank www.pdb.org/ rendered by David Goodsell using the Python Molecular Viewer.

FIRST EDITION

The impetus for the writing of this book was given to me by the late Professor R. G. Newton and I am grateful to him and Mrs J. Newton for their support in the early stages of its formation. The need for a conservation text on polymers, etc. was made clear to me by students of conservation at various institutions who, by their interest and questions during lecture courses, have prompted me to look more closely at the problems of objects and their treatment. Miss L. Bacon, Professor S. Rees-Jones, Dr D. Kenyon and Professor W. J. Feast have kindly read through portions of the text and suggested valuable improvements both in style and content.

The data on individual products were collated from information supplied by their manufacturers. I was pleasantly surprised by how many manufacturers provided advice and unpublished data on their products, so increasing insight into their application for conservation.

I wish to thank the following for advice and data that helped to clarify specific points or wider issues: Dr R. L. Feller, Dr S. G. Croll, Mr G. Berger, Dr E. P. Mel'nikova, Professor Dr K. Ueberreiter, Dr J. Winter, Professor W. C. Wake, Professor J. D. Ferry and Dr N. Tennent.

Disclaimer

Many of the materials mentioned in this book are hazardous to the operator or other people and property. Although some hazard information has been provided, the responsibility for ensuring the completeness or accuracy of the appropriate hazard information is the responsibility of the person undertaking the process.

The mention of a material or process does not constitute a recommendation for its use on objects – usually the reverse.

The author and publisher accept no responsibility for the consequences of the application of information or opinion expressed in this book.

About the Author

Velson Horie BSC, FMA, FHC, ACR, MAPM, Collection Care and Conservation Consultant (www.horie.co.uk). After training in chemistry and archaeological conservation, Velson Horie was the archaeological conservator for the north of England for 3 years. As Keeper of Conservation at the Manchester Museum for 28 years, he carried out: managing conservation and storage improvements; research into natural history, archaeological and polymer conservation; curatorial advice to a local heritage centre; major museum capital developments; as well as external change management. Having project managed a major research project into paper deterioration at the British Library, he is now a consultant for libraries and museums. He has written approximately 80 published works. He initiated professional standards for conservators now adopted for the UK profession and is currently Treasurer of the International Institute for Conservation.

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Introduction

1.1 USE OF RESINS IN CONSERVATION

Resins are used for many purposes in the conservation of objects:

- Consolidants
- Adhesives
- Coatings
- Moulding
- Casting
- Support stands
- Display and storage materials.

This list is ranked according to the intimacy of contact with the object. The closer the contact, the more likely the object is to be affected by the polymer properties. In the first four categories the resin is applied to the object rather than the other way around. These are therefore of greater concern.

In conservation it is an important discipline to study an object before one works on it. One should:

1. Find out what is wrong with the object.
2. Discover the cause of the defect.
3. Decide on the type of action.
4. Choose the appropriate method and materials.

Neither (1) nor (2) are discussed in this work, but both (3) and (4) are determined by the potential and limitations of the available materials. The possible roles that the resin will play in the conserved object must be examined closely. Resins frequently serve two purposes at once. When sticking friable pottery, the adhesive may also consolidate and strengthen the edges. When coating loose paint, the varnish will both cover the paint flakes and stick them to the substrate. These dual roles may be of great importance when the time comes to reverse the treatment.

Now the role(s) of the material have been stated, the required properties may be specified. In the real world one can never satisfy all the ideal specifications, and value judgements must therefore be made about the relative importance of the various properties required. Normally the choice is restricted to the products available commercially, though increasingly materials are being designed

and made for conservation. These can present a bewildering range of different materials that claim to do the same job, and one must choose between them in an educated way.

The detailed specifications will vary from one application to another but some general guidelines can be given:

1. On setting, the product must not change the object physically or chemically.
2. The product should remain totally removable at any time in the future without harm to the object.
3. The product must not alter so as to affect the object physically or chemically.
4. The product should have a long service life.
5. The product should be easily worked or removed without harm to the operator.

The general term ‘product’ has been used rather than a specific description such as polymer, as it is rare for a pure polymer to be applied. Much more frequently, the product is applied as a mixture, e.g. in a solvent, or as a precursor to the polymer.

The last three requirements are largely determined by the exact details of the product. However, the first two merit a separate discussion.

1.2 SETTING PROCESSES

In all cases where a product is applied to an object, it must be applied in a fluid state in order to achieve a coverage of the interstices of the object. One cannot achieve a good coating by applying beads of solid polymer. This basic requirement usually restricts the range of materials to those that can be put into liquid form in conditions that do not harm the object. In any application of a coating, adhesive or consolidant, adhesion between the polymer and the object must be ensured. Lack of adhesion can lead to the separation of parts of an object or to the penetration of water and pollutants along the object’s surface. These requirements for good adhesion are of course reversed when using moulding materials or temporary supports for the object. To be in a liquid form when applied, the polymer or its precursor may be in a mobile carrier or itself be liquid. Methods of applying the polymer are various:

1. One can use a liquid as a non-setting adhesive. Some adhesives remain as liquids. These are the contact adhesives used in pressure-sensitive tapes and labels.
2. A product can be applied as a molten liquid which cools, so forming a solid. Heat-activated adhesives in laminating systems are of this type.
3. Some materials such as oil paint and epoxy resin are applied as liquid pre-polymers, which set by chemical reaction to form a polymer.

4. A solution of polymer sets by evaporation of the solvents. This is the most common method of applying polymers in conservation, but it is of declining importance in industry. An example of a conservation use is picture varnish.
5. The polymer can be applied in a hot solution, which sets by cooling. The swollen solid will then lose its solvent by evaporation, e.g. bone glue.
6. Some polymers are applied in emulsions or dispersions. An emulsion sets to a film, first by loss of the dispersant, usually water, and then by coalescence of the small polymer particles. In order for this to happen the particles must be soft enough to flow into one another. Poly(vinyl acetate) emulsion 'white glues' and wax polishes are examples of this type.
7. Pre-polymers may be applied in gaseous form and reacted directly in contact with the object.

Similar polymers can be prepared and applied in different forms. Acrylic polymers can be applied in solution, as emulsions, as pressure-sensitive adhesives or as pre-polymers. The method of application depends on the role of the polymer and on the circumstances of application. A polymer can be applied using a combination of these methods. For example, a polyurethane lacquer used on stained glass (Bettembourg, 1976) is made from two components, mixed and applied in solution. The solvent evaporates and the two components react to form the polymer.

In passing from a liquid to a solid, shrinkage occurs. This can be large (a 20% solution of a polymer must reduce to one-fifth of its volume on setting) or small (less than 0.5% for some silicone rubbers).

1.3 REVERSIBILITY (ODDY AND CARROLL, 1999)

The decision to add or remove later materials when working with inadequate original objects has had a long and controversial history. Thorensen's proposed restoration of the Parthenon sculpture and the Cleaned Pictures Exhibition (Hendy, 1947) were highly publicized examples of alterations normally carried out routinely by conservators. These changes must of course be recorded in a detailed way to help future conservators decide what may be removed. Equally the changes must not cause harm to the original, however this is defined. Harm can be assessed in many ways. Aesthetic alterations were the first to receive condemnation. With increasing and changing awareness of the significance of alterations to the materials of the object, 'harm' has been extended to include physical deterioration of the object. The use of salt-contaminated mortars for mounting porous stone has been shown, many years after use, to cause damage to the original object. Techniques of examination have now progressed sufficiently that contamination with materials added by conservators may invalidate analytical investigations. An obvious example is the use of carbon-14 dating: a sample contaminated with paraffin wax (derived from oil) will appear millions of years old, whereas a sample contaminated with modern beeswax will appear recent.

Ideally a treatment used on an object should not cause any changes following the complete cycle of application, ageing and removal. Changes to an object can result from chemical or physical effects of the added material, or indeed the change may be in the spiritual value (Clavir, 1999). The liquid product that is applied may have solvent effects on the object. These may be immediate as in the cockling of paper by water-based adhesives. Alternatively the object may dissolve slowly in the polymer – some inks on maps migrate slowly into laminating adhesives (Baynes-Cope, 1975). The product itself may react with the object, thus ensuring the impossibility of removal without disruption of the object's surface. For example, poly(vinyl alcohol) (PVAL) is sufficiently stable, when considered by itself, to be used in some fields of conservation (De Witte, 1976), but it will permanently fix to textiles and paper immediately on application (Thomson, 1963; Boersma, 1998). During setting, the product may shrink, causing physical damage to the object that may not be revealed until the supporting polymer is removed – many pieces of friable pottery have been damaged in this way by glue. Resins used for consolidating paint films can change the optical environment of the particle, and this usually results in a significantly altered appearance of the object.

Changes also occur as the polymer ages under the influence of time, air, light and heat. Cross-linking or oxidation of the chains may cause a polymer to become insoluble in solvents that can be safely used on an object (Sease, 1981). The polymer may also cause the object to degrade more rapidly than it otherwise would have done (Berger and Zeliger, 1975; Baer et al., 1976). The cause of these deleterious effects is probably a combination of chemical reactions induced by the polymer and the physical restraint imposed by the polymer on a very different type of material.

Removal of a polymer usually involves the use of solvents, all of which cause swelling of the polymers and perhaps the object. This is likely to cause disruption of those parts of the object that are embedded in the polymer. Solvents necessary to remove polymers frequently threaten or cause damage to an object. This continues to be a cause of concern in the conservation of paintings (Phenix, 2003) and in many other fields.

The effect of a treatment cycle is thus determined by the properties of the polymer, those of the object and how they interact. A polymer may be applied to one object and be completely removable, e.g. a lacquer on metal. However, when it is applied to a porous material or one with which the polymer reacts, it may be impossible to remove more than a small proportion of the same polymer. New techniques, such as plasma (Rutledge et al., 1995) or laser cleaning (Pan et al., 2009), may enable the removal of otherwise intractable polymers.

The concept and use of reversibility are contentious, with arguments that the term embeds sloppy thinking and unprofessional expectations (Barclay, 1999) and that removability or measurable change are more useful concepts. The concept is premised on an 'original state' that is superior to a changed one. However, change is an inevitable consequence of ageing and of a conservator's actions, and

most actions are a combination of beneficial and harmful effects. Reversibility may therefore be considered as the lightness of touch of a conservator, the net change created by a treatment cycle of treatment, ageing and reversal.

Four categories of reversibility may be defined:

1. Many treatments have no known method of reversal. There is no method of removing a cross-linked polymer from a porous object, e.g. silanes in stone.
2. A treatment that allows an object to be taken back to a state that approximates to the pretreatment state is the most basic level of reversibility. An example is the dismantling of a restored pot into its component sherds.
3. A higher standard of reversibility was that demanded by picture restorers in Berlin in the 1840s; that the treatment when reversed should not affect subsequent treatments (Mure, 1853). This is one of the necessary requirements for a facing technique on paintings.
4. Techniques for examination are increasingly sensitive and require uncontaminated samples. It is unlikely that many treatments can be reversed to remove every trace of the polymer applied yet make no alteration to the object. The extent of reversal of many treatments has not been tested. From the limited evidence available there appears to be little hope of complete reversibility being achieved. It has been shown that only 50% of soluble consolidants applied in solution to porous objects such as stone and pottery (Horie, 1983) can be removed by extracting with solvents. In most cases where a consolidant is necessary, the object will be too weak to withstand the processes of removal. Even in the case of an acrylic lacquer on new glass, complete removal is not certain. With more delicate surfaces, such as paintings or friable wood, a choice has frequently to be made between leaving some of the unwanted material, such as a varnish, and removing some of the original object with the coating.

Reversibility is a test against which a treatment can be assessed. Change in materials or interactions with time is inevitable, so a statement of expected change is part of the conservation planning process.

Most objects that have been in care for a length of time have undergone repeated preservation treatments. Frequently one of the more difficult tasks for a conservator is reversing past treatments to allow better techniques to be applied. Embedding friable pottery sherds in cement or repairing paper with rubber-based self-adhesive tape can prove difficult to reverse without damaging the object. For this reason a treatment must always be designed as a complete cycle of application, ageing and removal. The extent of reversibility of the proposed treatment must be assessed against other possibilities and their relative merits.

The responsibility for choosing the correct materials and methods of application lies with the conservator carrying out the treatment. There are few bad materials as such but there are many examples of inappropriate applications. The conservator must have sufficient understanding of the processes involved

to enable evaluation of the possible irreversible effects on a particular object. Limits of knowledge and the risks involved can be made explicit in justifying the chosen treatment method.

1.4 HISTORY

Objects are made for use, however that use is defined and redefined, and must undergo repair and maintenance to retain their usefulness. The methods used for repair of objects were usually similar to those used originally to make them. Objects were often more or less remade without much regard for the original state. This is exemplified by the treatment of Egyptian mummies by their contemporaries (Harris and Wente, 1980) and the mediaeval reworking of wall paintings (Marijnissen, 1967) when they became damaged. Where an object was not amenable to reworking, familiar methods and materials were adapted to restore its usefulness. Repair of materials such as pottery might have been achieved by riveting (Williams, 1983). The concept of conservation, that the original object is intrinsically interesting and worth preserving, has been widespread only in the past few hundred years. Some examples from the more distant past include the consolidation of St Cuthbert's coffin in 1104 (Cronyn and Horie, 1985) and the restoration of historic ceramics by the Japanese.

The techniques that could be applied were limited by the materials available. The basic range that most societies possessed included starch pastes, plant gums and resins, protein binders of glue or albumin, beeswax and fats. As technology and trade developed, a wider range of resins became available and drying oils were introduced. These natural products were the only materials available for the repair of objects until the late nineteenth century (Masschelein-Kleiner, 1985). They were, and still are, widely used.

None of these natural products lend themselves to easy analysis, especially after ageing. It may thus be difficult to distinguish materials of the original object from the later additions. This may account for the fact that there are few studies detailing the conservation history of individual objects.

From the point of view of Europe, the available resins included colophony, mastic and sandarac, depending on the area (Gettens and Stout, 1942). These would originally have been applied in liquid form, perhaps as heated balsam or dissolved in drying oils. Trade in other resins later enlarged the range available. Only from the seventeenth century were solvents (spirits of turpentine and spirits of wine) used for dissolving and applying resins. Dammar was first recommended as a picture varnish in the early nineteenth century (Feller, 1966). Paraffin wax (Salzer, 1887) and natural rubber (Rathgen, 1905) were applied in the late nineteenth century.

During this period, when the wealth of natural products was being introduced, the first synthetic polymer, cellulose nitrate, was being developed for conservation (Posse, 1899). By the early 1920s other cellulose derivatives (Scott,

1923; Jenkinson, 1924) and silicone compounds (Grissom and Weiss, 1981) had been introduced. There is hardly a polymer that has not been suggested and used for a conservation application. The unrecorded work of an adventurous conservator in the past may cause complications during the inevitable retreatment of the object. The materials used in the past may be significantly different from modern materials of nominally the same composition. In reviewing the solubility of dammar, Mantell et al. (1942) found that the solubility range they determined was very different from that found by previous workers who had studied dammar. An early study of poly(vinyl acetate) (PVAC) in 1929 obviously used a material that was less pure and less stable to light ageing than the modern products (Gamble and Stutz, 1929). This is a good reason for retaining in the conservation record samples of polymers that come from the same batch as was used on an object.

1.5 INFORMATION SOURCES

Conservators draw their data about materials from many sources, from fellow practitioners, from suppliers and from the science community. This information must be evaluated for its relevance, its rigour and its application. Producing data requires an investigation of properties, assessing the observations then reporting on the important aspects. Because there is an infinity of possible properties, each person provides limited information necessary to answer the question addressed. A conservator will focus on the treatment, or object, frequently thinking less clearly about the material itself, usually reporting in subjective terms about the outcome. The supplier will focus on the properties important to its major users, usually reporting in terms of industry standard tests. The scientific researcher will concentrate on a narrow range of properties, usually reporting results that extend current experimental techniques so the data may have few direct comparators. The data sources may therefore be incompatible and probably do not directly address the aspect important to the application in hand. It takes considerable experience and care to extrapolate from incomplete data, without making unwarranted assumptions.

The unique contribution of conservation to research, both for and outside the heritage field, is the extended time period of the samples and associated data. However, conservators have not been rigorous at recording this information, and rarely make it available. Recorded information about a treatment should be expected to contribute not only to the subsequent study or conservation of the object, but also add to increasing insights into the effects (positive and negative) of the treatment method applied to many objects by many conservators. Tools for recording and sharing data have developed in other fields that acknowledge the importance of analysing mass data, particularly time sequences. Exchanging data and voucher specimens has enabled significant advances in natural history for centuries. Astronomy and high-energy physics place their data fairly promptly on accessible electronic databases.

When conservators make their data, obtained by practical experience or by research, available for wider examination and analysis, the field will have the tools to advance more efficiently.

The pioneering conservation scientists published in *Technical Studies in the Field of the Fine Arts*, 1932–1941. From the 1950s, an increasing amount of research was published in conference proceedings and low circulation newsletters that were available to few people at the time and are now very difficult to find. Some of Dr Robert Feller's seminal works have become available only because they have been republished (Whitmore, 2002). This pattern continues with the result that many studies do not receive peer review and evaluation, even from within the conservation community, necessary to critique and build upon the results. Some of the investigations are of poor standard and should be ignored. Unfortunately, publication of studies of conservation practice have declined even within the established conservation journals and is retreating to proceedings of seminars, etc. The ability of practitioners and researchers to use data from practical experience is therefore reduced by its inaccessibility.

The specialized materials and their associated data for conservation gradually developed from the early nineteenth century, coming from commercial sources (Spon, 1888). Confusion about a material, its name and its source are apparent from the earliest records. St Cuthbert's coffin was reported (1104) to have been consolidated with wax, but analysis showed it to be rosin (Cronyn and Horie, 1985). The nature, name and source of dammar continued in doubt from its introduction in the 1820s (Feller, 2002) through the 1940s (Mantell et al., 1942), and many recent research papers on dammar still give scant regard to the original source or nature of their experimental materials (Polikreti et al., 2005). From the early twentieth century with the rise of the chemical industries, synthetic materials and data could be more closely identified, building upon the manufacturer's released information. Although some of this information survives, few samples of the materials have done so, except where they can be identified on objects. From the 1950s until the 1990s, many manufacturers made materials whose name was consistent, but whose nature was poorly defined in the detail desired by conservators. A good example is Paraloid B-72, which was analysed and shown to be a poly(methyl acrylate/ethyl methacrylate) (De Witte et al., 1978), a composition shown to have useful properties in the early 1930s (Salkind et al., 1959). However, the conservation research community had previously assumed (after testing) that the polymer was poly(ethyl acrylate/methyl methacrylate) (Feller, 1963, 1975). The manufacturer (Rohm & Haas) has always refused to comment on the composition. Since the 1990s, many manufacturers have changed hands, with materials and names well known in conservation being abandoned or their nature changed. For instance, Hoechst with its range of poly(vinyl acetate) polymers and derivatives has been split and materials such as Mowilith PVAC resins no longer manufactured, even though some suppliers are still relabelling other PVAC resins as Mowilith. Because the industry and their products can change in months, their addresses and materials

are not listed here. Current details can be obtained by searching their websites. Where historic materials are referenced, the relevant manufacturers' details are given. The lack of stability in supplier and materials makes it even less likely that a literature reference to a material will be valid in the future. The applicable data sheet and sample with identifying details, such as supplier, date and batch number, should therefore be kept as part of the treatment or research record.

The number of materials made especially for conservation is still limited, but similar caveats apply. The composition of BEVA 371 was declared publicly but inadequately copied until a court case restricted its manufacture and supply to one authorized company (Berger et al., 2004). However, the composition of the dispersion BEVA D-8, supposedly an EVA dispersion, has not been revealed. Lack of knowledge is similar for other materials made for conservation and must be acknowledged in any decision-making process. As with many other technologies, the care in choosing ingredients and the process of manufacture is a significant factor in the consistency and long-term properties of materials, which is difficult to monitor without transparent standards of test.

The mode of publication is changing radically. Any study that aims for widespread acceptance is now almost exclusively published in peer-reviewed journals, with conference proceedings being relegated to informal presentation of work in process. Journal publications are increasingly, and sometimes exclusively, being placed on the internet, frequently accessible only by members of academic institutions and therefore closed to most conservators. The web-based search tools enable the publications to be found, and include ISI World of Knowledge, which enables tracing developments in a topic through links to citations, and the Art and Archaeology Technical Abstracts, which provides far less flexibility in searching but includes much literature exclusive to conservation. A digital divide is opening up that conservation organizations have not addressed. The increasing complexity of scientific techniques has also changed how information is gathered. Whereas in the early days of conservation research, a single person perhaps with an assistant could make significant advances, most research now relies on a range of expertise and resources. In order to take part in quality research, conservators need to understand and participate in these groups.

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Polymer Science

2.1 FILM-FORMING MATERIALS

The guidelines in [Chapter 1](#) are very general and do not help much when materials must be chosen from the many available products. The products can be described by many properties, such as clarity, strength and stability, which will be determined by the chemical structure, the physical state of the material and how it is applied. Many materials form films when spread out properly. In general, the longer the molecule, the stronger the material. Where great strength is required, long molecules are used: cellulose for wood, collagen for sinew and polyethene for plastic bags. When wood and sinew are converted into cellophane and glue, the long molecules are released from their fibrous state and reduced in size. Films prepared from these derived materials have less strength than the original source materials but more than films prepared from small molecules.

Most natural film-forming materials – resins, gums and waxes – are made up of molecules that are large by comparison with solvent molecules but small by comparison with synthetic polymers. Because of this, only those natural materials that are composed of very large molecules, such as natural rubber or cellulose, find a continuing industrial demand. From the beginning of the twentieth century, conservation followed trends in wider society with natural materials being replaced by more versatile synthetic alternatives. Many of the synthetics had considerable advantages but with disadvantages that became apparent after extended experience – one of the characteristics of conservation. During the latter decades of the twentieth century, this learning from experience has increased insights into the criteria and properties that must be considered. As a consequence, there has been a move back towards natural materials and their synthetic analogues. The increased size, strength and stability of synthetic polymers are now often seen as potential disadvantages in comparison with the natural comparators.

Film-forming materials that are useful as coatings, consolidants or adhesives all have large molecular size as a common factor. Most film-forming materials, both natural and synthetic, are based on polymers ([Grosberg and Khoklov, 1997](#)). A polymer is a large molecule built up from many small identical units, called monomers. In order for a polymer to be formed from monomer molecules,

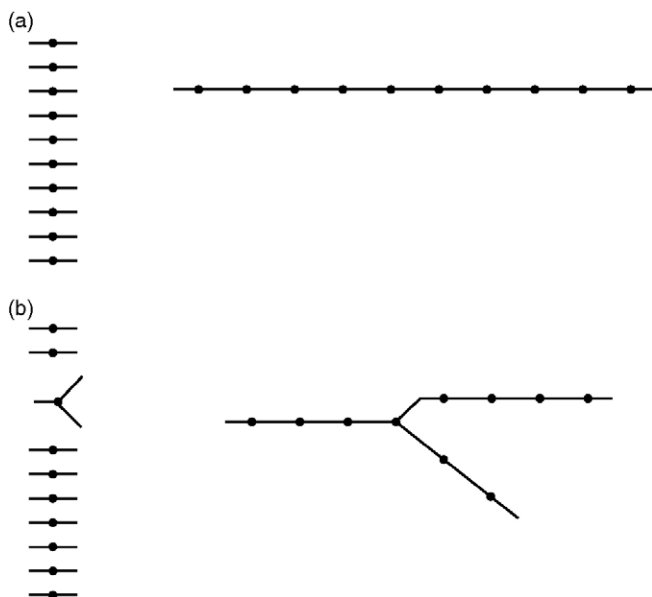


FIGURE 2.1 (a) Straight-chain polymers are formed from difunctional monomers. (b) Branched polymers are formed from difunctional and trifunctional monomers.

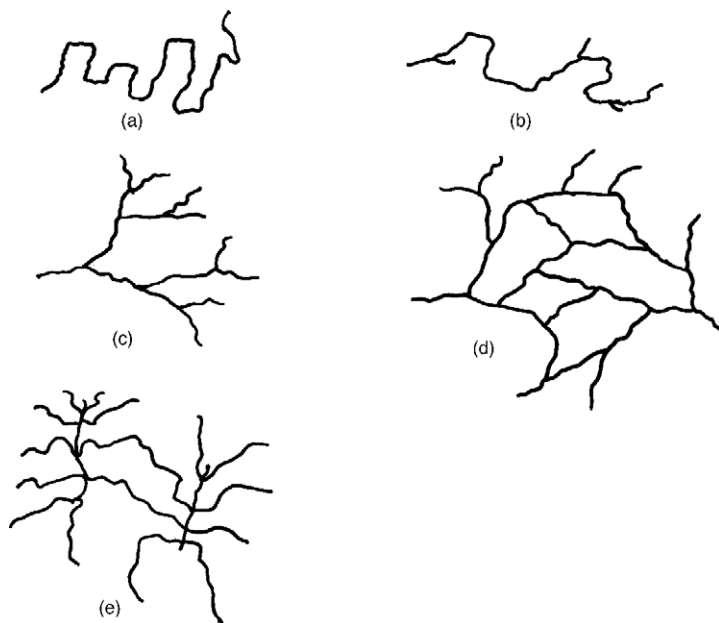
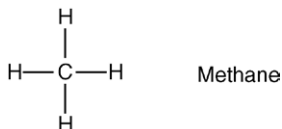


FIGURE 2.2 Monomers can form different shapes of polymer. (a) Randomly coiled linear thermoplastics, e.g. PMMA. (b) Slightly branched thermoplastics, e.g. PVAC. (c) Highly branched thermoplastics, e.g. polyurethane foam pre-polymer. (d) Cross-linked polymers with trifunctional junctions, perhaps formed by reaction of (c), e.g. epoxy resin. (e) Cross-linked polymer with tetrafunctional junctions, e.g. polyester casting resin. **Source:** *Brydson (1982)*.

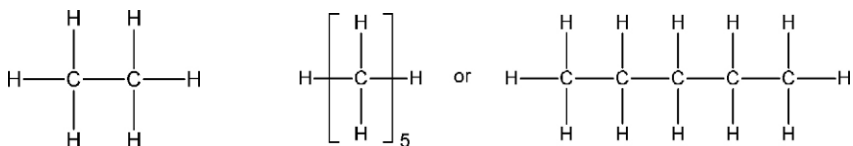
each monomer molecule must be able to join up with two other molecules. Continued reaction of these difunctional monomers produces a straight-chain polymer (Figure 2.1a). If some of the monomers can react with three others, a branched chain results (Figure 2.1b).

At this stage, each of these polymers is composed of discrete molecules that can be separated from one another. As there are no formal chemical bonds attaching one polymer molecule to another, the molecules can flow past one another. They can be dissolved in solvents and will melt when heated; because of this latter property they are called thermoplastics. If there are sufficient trifunctional monomers, the chains join with one another, as shown in Figure 2.2. It will then be impossible to separate one chain from another without breaking a chemical bond. The many molecules are joined up into a cross-linked immobile mass. This will not melt with heating, but will only soften; nor will it dissolve in solvents, but will only swell, although it may be broken down by some solvents.

The change in properties with increasing size of the molecules is well illustrated by the alkanes. This family of materials is composed only of carbon and hydrogen, and makes up the bulk of petroleum. The first member of the series is methane, with one carbon atom and four hydrogen atoms. It is a gas at room temperature. The formula for a molecule of methane is CH_4 :



Other members of the series are ethane, with two carbon atoms, and pentane with five:



As the number of carbon atoms in the chain increases, the molecules become progressively larger and their boiling and melting points rise (Table 2.1). All these materials have similar chemical properties. The larger members of the homologous series can be considered to be successive members formed from the methylene unit, i.e.

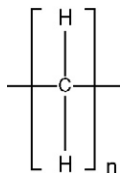


TABLE 2.1 Properties of Hydrocarbons (with the composition C_nH_{2n+2}) as They Vary in Molecular Weight

Number of Carbon Atoms	Name of Compound	M.p. (°C)	B.p. (°C)	Usual Form Encountered
1	Methane		−162	Fuel gas
2	Ethane		−88	Fuel gas
4	Butane		0	Fuel gas
5	Pentane		36	Liquid fuel (gasoline)
16	Hexadecane	18	292	Liquid fuel (kerosene)
20	Eicosane	36		Grease (weak solid)
16–30	Paraffin wax	45–60		Wax (weak solid)
350–1500	Low-molecular-weight polyethylene	80–100		Tough solid
>30,000	High-molecular-weight polyethylene	≈130		Stiff strong solid

In practice, ethene is used to make the polymer. A commercial polymer is commonly named after the monomer from which it is made, so the polymer is called polyethene in this instance. An alternative method of nomenclature is based on the chemical structure of the polymer; under this system the above polymer would be called polymethylene, following IUPAC (International Union of Pure and Applied Chemistry) rules (Jones et al., 2009). The use of structure-based rules implies that the structure of the polymer is known in detail. However, the structures of commercial polymers are frequently not well defined. For this reason, the internationally recognized trivial names and abbreviations (BS EN ISO 1043-1, 2002; Elias, 1999) will be used here, with the structure-based names being listed in [Appendix 1](#) when appropriate. The naming of simpler molecules should be more straightforward. But the use of traditional ‘trivial’ names is widespread and accepted (with structure-based names also being acceptable), for instance acetone (propanone or dimethyl ketone) and toluene (methyl benzene). The increasing use of computers for data searching and manipulation has promoted the use of unique ‘codes’ for chemicals. The CAS Chemical Abstract Service registry numbers (CAS Registry, 2009) are arbitrary numbers, e.g. acetone (106-36-5) and polyethene (9002-88-4), widely used in paper and online

reference works and in this volume. Novel systems are being introduced that provide structural information that can be manipulated by computer, e.g. SMILES – Simplified Molecular Input Line Entry Specification (Weininger 1988)–acetone (O=C(C)C); or InChI – IUPAC International Chemical Identifier (Heller and McNaught, 2009)–acetone (1/C3H6O/c1-3(2)4/h1-2H3), but polymers are yet to be included in the systems.

Polymers are distinguished by two properties that set them apart from materials made up of smaller molecules – the variability of molecular weight and the glass transition temperature.

2.2 MOLECULAR WEIGHT AND SIZE (STEVENS, 1999)

A molecule is a chemical combination of atoms. For many molecules, this grouping of atoms can be expressed as a chemical formula, e.g. $C_6H_{12}O_6$ (glucose) (Figure 2.3). The molecular weight (MW) can be found by adding up all the component atomic weights:

$$12 \text{ (atomic weight of carbon)} \times 6 = 72$$

$$1 \text{ (atomic weight of hydrogen)} \times 12 = 12$$

$$16 \text{ (atomic weight of oxygen)} \times 6 = 96$$

$$\text{Molecular weight of glucose} = 180$$

The natural resins used for picture varnishes are made up of mixtures of larger molecules, many of which have now been separated and identified. The molecular formula of the major component of dammar, oleanonic acid (Boon and van der Doelen, 1999), is $C_{30}H_{46}O_3$, MW 454. There are many terms that are used for this concept (Table 2.2), but this book will use molecular weight for simplicity.

The molecular weight of a polymer molecule is worked out in a similar manner to that of a smaller molecule. The molecular weight of a single molecule can be determined by multiplying the weight of the repeating unit by the degree

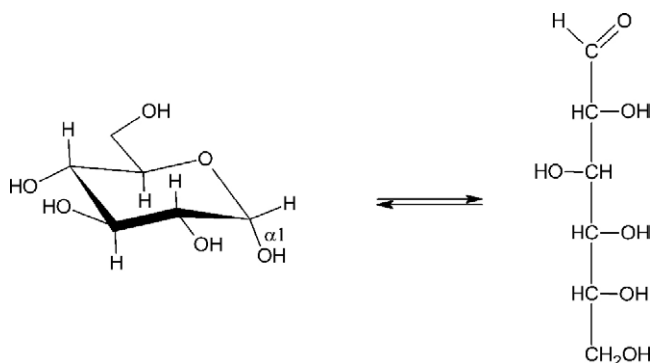


FIGURE 2.3 A glucose molecule, $C_6H_{12}O_6$, normally exists as a ring, glucopyranose as shown on the left with the chain form also occurring in solution.

of polymerization (DP). For instance, for polyethene, the weight of the repeating unit (ethene, C_2H_4) is 28. A high-molecular-weight polythene, with a DP of 1150, therefore has a molecular weight of $1150 \times 28 = 32,200$, neglecting the very small contribution that the end groups make. However, in any sample of polymer, one has a mixture of molecules with different molecular formulae. The molecules are very similar as they differ only in the number of monomer units

TABLE 2.2 Different Terms for Molecular Weight

Term	Abbreviation	Definition	Gloss
Molecular weight	MW	Weight of an individual molecule or the weight of a molar quantity of the molecules	Because weight is dependent on the gravity when being measured, mass is the important concept. MW is so engrained in the field that it is largely used and understood. Care is sometimes required in its use
Molecular mass	Da (dalton)	Mass of one molecule of that substance, relative to 1/12 the mass of one isotope of carbon-12 (u)	
Molar mass	M	Mass of one mole of a substance	Usually given in g/mol
Relative molecular mass	M_r	Ratio of the mass of a molecule to the mass of a ^{12}C atom	As a ratio, this is a dimensionless quantity
Number-average molecular weight	M_n	$\sum N_i M_i / \sum N_i$	Useful to compare properties where the number of molecules is important
Weight-average molecular weight	M_w	$\sum N_i M_i^2 / \sum N_i M_i$	Useful to compare properties where the mass of molecules is important
Viscosity-average molecular weight	M_v		The MW measured using viscosity usually lies between M_n and M_w depending on the interaction between the solvent and polymer
Polydispersity index	PDI	M_w / M_n	Measures how uniform the molecules are

incorporated. When the DP is small, less than about 10, the polymer molecules are sufficiently different to be separated. These molecules are called oligomers. For many polymers, the degree of polymerization can be thousands or even millions. It is then impossible to separate molecules into their different sizes.

What is the molecular weight of a mixture of molecules? The weight, length, etc. of a molecule determines its size. Polymers increase the viscosity of a solution because the larger molecules increase resistance to flow. A typical molecule in solution might look like Figure 2.4, if captured in a snapshot. In a good solvent the molecule is more spread out, and in a poor solvent it contracts, with corresponding changes in viscosity. There is no hard edge between a polymer molecule and the solvent as there is for a droplet of oil in water. A better analogy is strands of spaghetti floating in a pan of water. Different molecular weights can be calculated for the same sample to give emphasis to different ways of considering the molecules.

The molecular weight of different polymer samples was traditionally determined by a relatively simple viscosity measurement (BS EN ISO 1628-1, 2009),

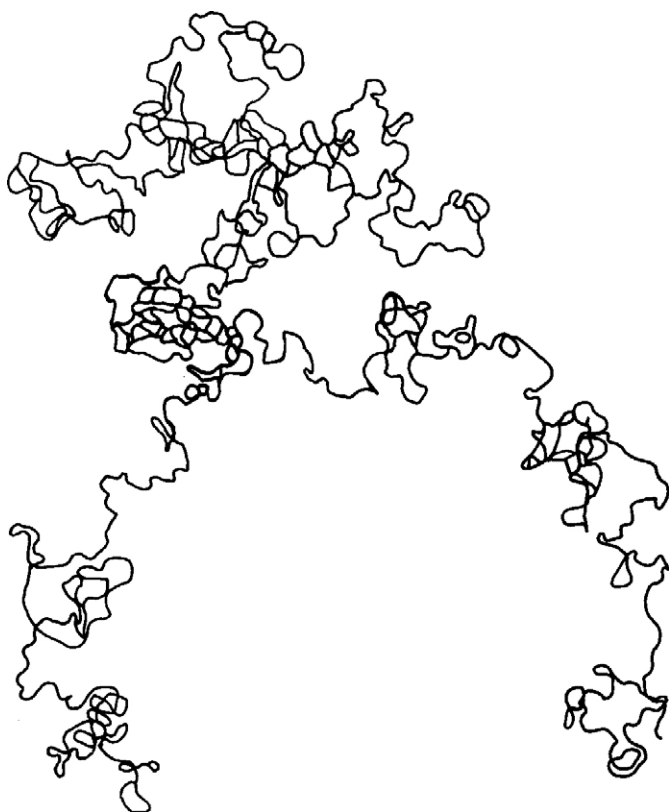


FIGURE 2.4 A polymer molecule, in solution or in its relaxed state as a solid, is coiled and contorted in three dimensions. This diagram is a theoretical model of a polyethylene chain with 500 monomer units. **Source:** *Treloar (1975). Reproduced with the permission of Clarendon Press.*

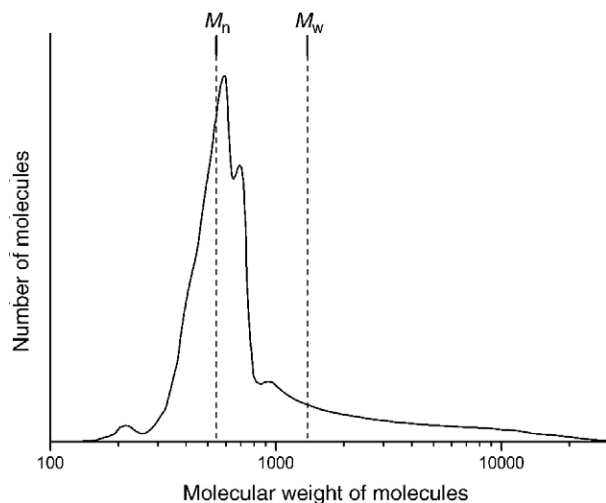


FIGURE 2.5 Molecular weight distribution of a sample of dammar. Size exclusion chromatography (also called gel permeation chromatography) separates the molecules by sorting them by size in a chromatography column then measuring the number of molecules emerging. By calibrating the system, one can plot the distribution of molecular sizes in a sample. The values for the different molecular weight averages can be calculated from the curves. The various peaks result from different molecules being eluted. The major peak is made up of the triterpenoids and the long tail is made up of polymerized material, which increases with ageing. For this sample, $M_n=543$, $M_w=1327$, $PDI=2.44$. **Source:** *de la Rie (1988)*.

providing the viscosity average molecular weight M_v , for checking batches or for following the changes of a polymer with ageing. However, polymers, particularly mixtures of polymers, can have an interesting and thus informative distribution of molecular weights, so this information is lost when compressed to a single number. Two averages, number-average molecular weight (M_n) and weight-average molecular weight (M_w), are commonly used. M_n is used when the number of molecules in a sample is being considered, e.g. chemical reactivity of end groups in epoxy resins. M_w is important when contributions of the weight of each molecule determine the property, e.g. strength. Newer (expensive) techniques, especially size exclusion chromatography (SEC) (Malawer, 1995), are routinely used to quantify the composition, and thus other properties, of the polymer (Figure 2.5). In conservation, changes in the molecular weight distribution provide early signs of significant reactions and changes in properties.

2.3 GLASS TRANSITION TEMPERATURE (SCHILLING, 1989; HIEMENZ AND LODGE, 2007)

The glass transition temperature (T_g) of a polymer is important in choosing a consolidant, adhesive or coating, and is an accurate indication of the softness of

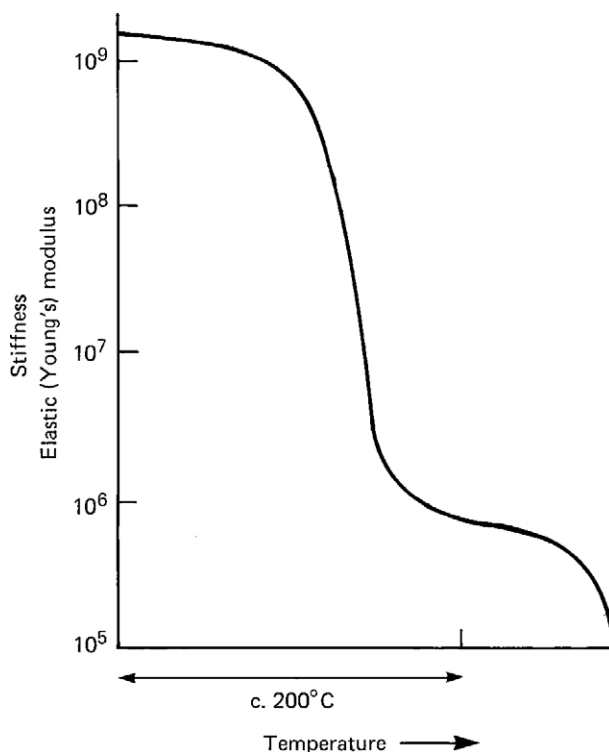


FIGURE 2.6 A glassy material changes from a stiff to a flaccid material as it is heated. The shape of the curve is similar for most thermoplastics, although the temperature at which the change occurs can range from -123 to 250°C (for polymers).

the polymer. This has two aspects. A polymer that is too soft will lead to cold flow in an adhesive or dirt pick-up in a coating. A polymer that is too stiff may crack when stressed or may not be able to respond to movements in the object. Most polymers applied to objects have T_g around room temperature.

Polymers go through various stages as they are heated from a very low temperature. All polymers can be cooled to form brittle solids; rubber, for example, can be broken like glass when cooled in liquid nitrogen. As the temperature is raised, the polymer changes from a glassy state to a liquid one. This change is not sharp but occurs over a range of temperature (Figure 2.6). The temperature of this transition is called the glass transition temperature, conventionally when the viscosity is $10^{12.3}$ Pa.s. T_g determines many of the mechanical and some of the chemical properties of a polymer (Appendix 1). Below T_g , the material will not flow but will stretch only slightly before breaking. Thermoplastics and cross-linked materials both undergo changes when heated through T_g . Thermoplastics above T_g can be considered as liquids and will therefore flow, however slowly, when forces are exerted on them. They thus become plastic and can be shaped by heating. Cross-linked materials cannot flow but become

rubbery above T_g . Mechanical properties of a polymer therefore change around T_g . This is indicated by the change in stiffness (modulus of elasticity) on raising the temperature of a polymer. Similar examples of change around T_g are apparent in many different types of property: refractive index, specific gravity, impact resistance, etc.

Above T_g , large sections of the polymer chains are able to move cooperatively in adjusting to stresses. Below T_g , the chain segments are frozen into place. Three effects can act against the internal movements: the stiffness of the polymer chain, intermolecular forces such as hydrogen bonds, and the interlocking of bulky side groups. For instance, poly(ethylene oxide) (PEO) has low stiffness of the chain, no side groups to interlock and therefore a low T_g , -55°C . Polystyrene chains are stiffened by the presence of the phenyl groups on the chain and T_g is correspondingly higher, 95°C .

The ability of the polymer chains to move past one another and adjust to a changed situation depends not only on how mobile the chains are, i.e. how much above T_g the polymer is, but also on how fast the change is made. The value of T_g can be lowered by increasing the time scale of the force. When an object is stuck together for display, the time scale is long – perhaps many decades. There is an approximate relationship between T_g and the time of measurement. Most T_g measurements are made over time scales of around 1 minute. If the measurement time is increased to 10 minutes, T_g will drop by 3°C . If the time is decreased to 6 seconds, T_g will rise by about 3°C . An extreme example is the T_g of PVAC, the measured value of which is 68°C at 67 MHz and 36°C at $2.5^\circ\text{C}/\text{minute}$ (Nambia and Blum, 2005). This change of T_g for every 10-fold change in time has important implications for polymers with T_g around room temperature. A material with T_g of 30°C (measured over 1 minute) will have an effective T_g of 12°C when used on an object for 1.2 years. It is obvious that the T_g of a polymer is lowered considerably over time, with unfortunate results for the attached object (Figure 2.7). This flow occurs not only with adhesives but also with coatings. When a dust particle lands on a soft surface, the polymer will gradually flow around it. This results in dirt pick-up where the dirt has become part of the polymer film. The dirt cannot be removed without removing the polymer film. If an adhesive is used to attach a book binding, the stresses of opening or closing a book will be applied in a fraction of a second. An effective adhesive must be able to adjust within this time span, e.g. wax/polyethylene mixtures. The effective T_g of a polymer used in this situation will be considerably higher than that used for sticking an object.

The glass transition is proving (scientifically) difficult to understand (Donth, 2001) because it is the result of movements at all levels of molecular structure, from internal vibration of side chains to long-range adjustment involving many large molecules. T_g is measured using different physical properties, e.g. heat capacity (by differential scanning calorimetry, DSC; Figure 2.8) (ISO 11357-2:1999, 1999), or mechanical properties (by thermomechanical analysis TMA (ISO 11359-2:1999, 1999)) or refractive index change. Different properties result from different parts of the structure, resulting in measured T_g differences up to 25°C (Riesen and



FIGURE 2.7 The slumping, after 30 years, of a piece of wood stuck in place with poly(vinyl acetate). **Source:** *Cronyn and Horie (1985).*

Schawe, 2003). The transition being measured depends critically on the current state and thus history of the material, both thermal and chemical (Doumenc et al., 2008). Current measurement specifications therefore specify a heating pretreatment in order to reduce the effects of the previous history and provide a standard, reproducible, value. As a result, many of the past T_g values of bulk polymers given in the literature cannot be directly compared with currently measured values. For instance, the T_g of PVAC has apparently risen from ≈ 24 to $\approx 32^\circ\text{C}$ in recent years without any chemical change. The importance of the history of the sample has implications for objects treated with polymers, whose properties are determined by the history and may not be comparable to the bulk properties as measured by the standard methods. This may account for the unexpected T_g values of PVAC and Paraloid B-72 cast from solvent (Hansen, 1995) and an observed T_g of $\approx 60^\circ\text{C}$ for a 40-year-old PVAC picture varnish (Hansen, 1996).

The T_g of a polymer increases slightly with increased molecular weight because the chains have less freedom of movement (Table 7.1). Their freedom of movement can be increased by separating the chains. Low-molecular-weight additives will lower the effective T_g . Non-volatile liquids, plasticizers, are

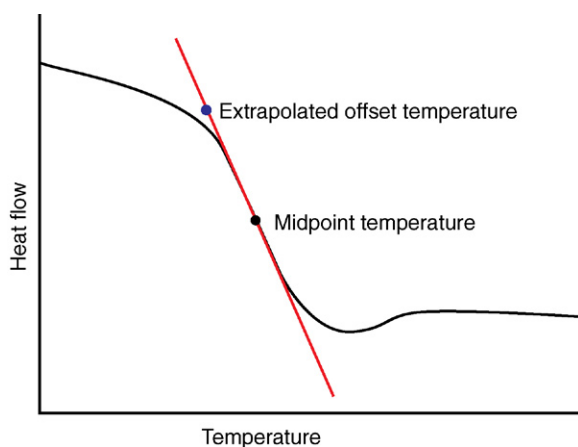


FIGURE 2.8 The glass transition temperature (T_g) indicates the temperature at which a glassy material starts to change to a flaccid material, with the curve indicating that the properties change gradually with change (increase or decrease) in temperature. Differential scanning calorimetry (DSC) is the most convenient and quick method, though T_g changes significantly with the speed of testing. The midpoint temperature is normally reported as the T_g , but in the past the offset temperature was used to specify T_g (Nielsen, 1974). As a result, it can be unwise to compare published T_g values unless one is certain that the methods of measurement are identical. The property measured by DSC is heat flow. However, a number of different properties can be measured to assess the transition, e.g. stiffness, volume, electrical, optical, each of which probes a different scale of the polymer structure and therefore gives a different value of T_g . Redrawn from ASTM E1356-08 (2008).

commonly added to plastics in order to make them flexible. Poly(vinyl chloride) (PVC) is frequently modified in this way. The same effect occurs with solvents (Figure 3.11). A film of poly(methyl methacrylate) (PMMA) is above its T_g at room temperature if it holds less than 18% toluene. As the film dries, it will therefore cease to flow while still containing up to a fifth of its volume as solvent. As this solvent evaporates, the polymer film will shrink. A good solvent for the polymer has a greater effect in reducing T_g than a poor solvent. There will thus be less volatile material remaining when flow in the polymer film stops, and less consequent shrinkage will occur. This has important implications for both reversibility and adhesion.

The T_g of a cross-linked polymer is complicated by the inability of the molecules to flow past one another (Figure 2.9). These materials change at T_g from a glass to a rubber, which can be stretched by force but which will revert back to the original shape when the force is removed. Cross-linked resins will reduce to a limiting stiffness, which is not much reduced by increasing temperature. As the density of the cross-links rises, T_g also rises. When the chain length between the cross-links drops below a critical length, the lack of freedom of movement eliminates the T_g phenomenon, e.g. with formaldehyde resins.

T_g is not the only transition that occurs on changing the temperature of a solid polymer. Other minor transitions contribute to the toughness of the polymer by absorbing energy on impact. The effect of heating a polymer above

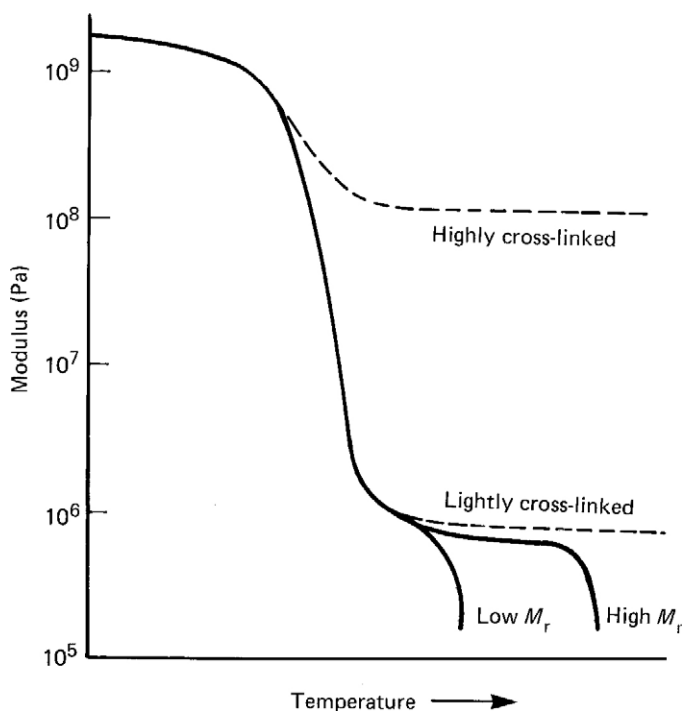


FIGURE 2.9 Effect on its stiffness (elastic modulus) of heating a polymer. Although T_g is only slightly affected by the molecular weight of the polymer, physical properties above T_g are more affected. A low-molecular-weight polymer will quickly become fluid, whereas a high-molecular-weight polymer will require a higher temperature. Cross-linking prevents flow and thus imparts a stiffness that is increased as the cross-linking density increases.

T_g is determined by the structure of the polymer. Most of the polymers used on objects are amorphous thermoplastics, and only show T_g before liquefying. Some polymers (polyethene and wax are the best examples) are partly made up of crystals. The crystals melt at a higher temperature (T_m) than T_g , causing a second transition in properties on heating or cooling.

2.4 MECHANICAL PROPERTIES (WARD AND SWEENEY, 2004; SHAH, 2007; COWIE AND ARRIGHI, 2008)

A polymer responds to a pulling force (tensile stress) by being stretched (tensile strain). The mechanical properties of a polymer can be described partly by the values derived from the tensile stress–strain curve (Figure 2.10). Polymers are viscoelastic materials – that is, they can behave simultaneously as liquids with viscous flow and as elastic solids. When a polymer is stretched, the sample goes through various stages. The first part of the curve describes the elastic properties of the polymer, when the sample can be stretched without permanent distortion.

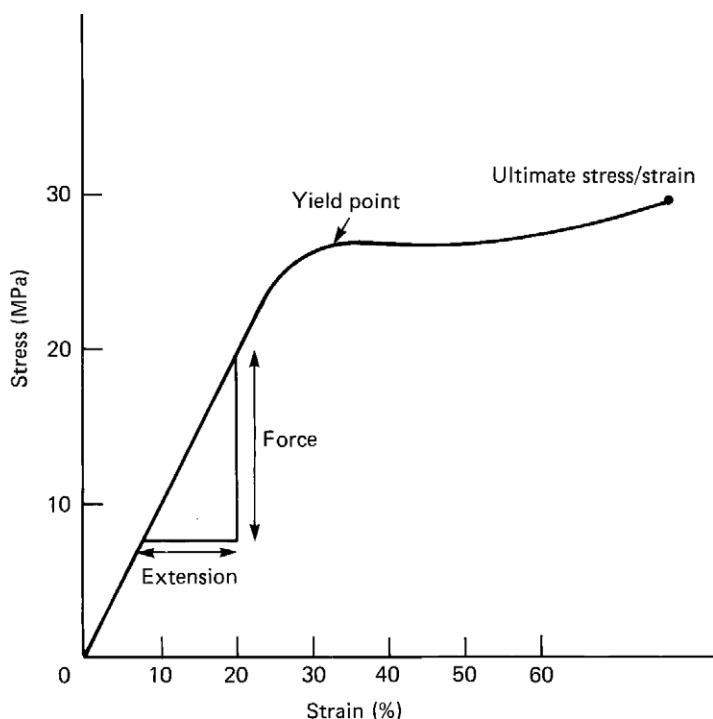


FIGURE 2.10 Generalized tensile stress–strain curve of a polymer.

$$\text{Elastic (Young's) modulus} = \frac{\text{Stress } (\sigma)}{\text{Strain } (\epsilon)} = \frac{\text{Force (per unit area of sample cross-section)}}{\text{Extension (per unit length of original sample)}}$$

Source: *Ward and Sweeney (2004).*

This elastic region is described by the modulus of elasticity (E , Young's modulus). If a rubber band is pulled or an acrylic sheet is bent, they will snap back into their original shapes when the force is released. Stiffer materials have high values of Young's modulus, i.e. more force is required to stretch them. These are usually well below their glass transition temperatures. Some thermoplastics above their glass transition temperatures will start flowing immediately force is applied. They will therefore have few elastic properties. As the stretching is continued, many polymers will suddenly distort irreversibly at the yield point; polyethylene is an example. The distortion will continue with further stretching until the material finally breaks, at the ultimate strength. Little distortion will take place if the polymer is well below its glass transition temperature or if it is highly cross-linked.

The mechanical properties of a polymer sample are determined by many factors. Resins vary from extremely flexible but strong rubbers to brittle weak materials such as the natural resins (Figure 2.11). Contrasts can be made in the ability to be stretched without permanent distortion (elasticity of cross-linked rubber), in the distortion caused by stretching (polyethene distorts if stretched

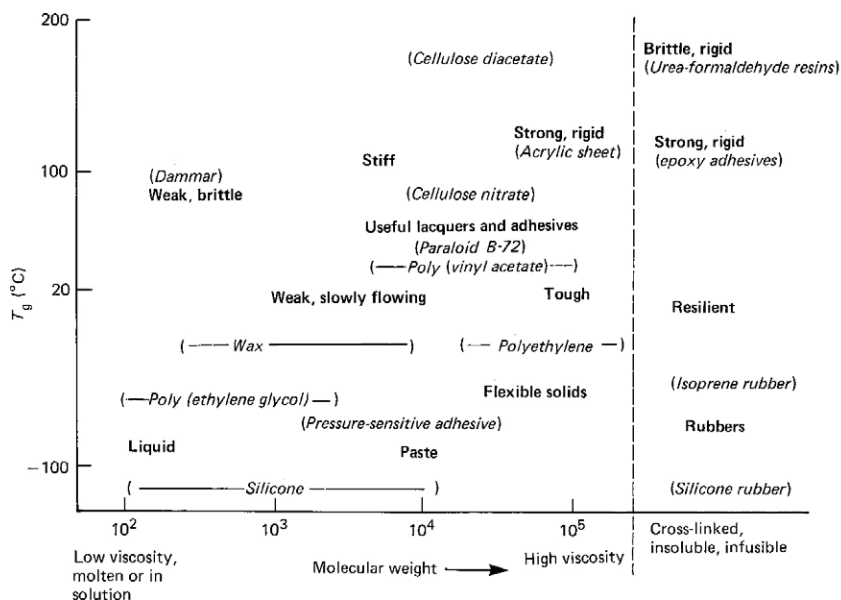


FIGURE 2.11 Physical properties of polymers related to their molecular weight (MW) and glass transition temperature (T_g). Polymers that can form crystals, e.g. wax and polyethylene (Chapter 6), are more rigid than the molecular weight and T_g would suggest. **Source:** Nielsen (1974).

too much), or in the force required to cause fracturing (dammar films break if little force is applied) (Figure 2.12).

Increasing molecular weight increases strength only up to a limiting value (Figure 2.13), though the distribution of molecular weight also has considerable effect on flow properties. The glass transition temperature, allied with the speed and temperature of testing and the way in which a sample is prepared, are important. For example, a polymer film cast from solution will be weaker than a heat-moulded film. Also, polymers change on ageing as internal stresses relax or chemical reactions take place.

These polymer properties have considerable effects on the object. A polymer with a high Young's modulus requires a high force to achieve small stretching. If it is applied to wood which then expands with rising humidity, a tension is set up between the object and polymer. The strong polymer will resist stretching and will tend to pull off, probably with part of the wood surface attached. If the polymer is relatively weak, i.e. it has low ultimate strength, movement in the wood will cause the polymer to crack. Craquelure of paint varnishes is probably caused by this effect. If the polymer stretches irreversibly with the expansion, subsequent contraction of the wood will lead to bubbling or wrinkling of the film (Berger and Russell, 1990). The area under the stress-strain curve is a measure of the amount of energy put into the system. This energy will have to be released, frequently by the failure of the weakest component. When designing

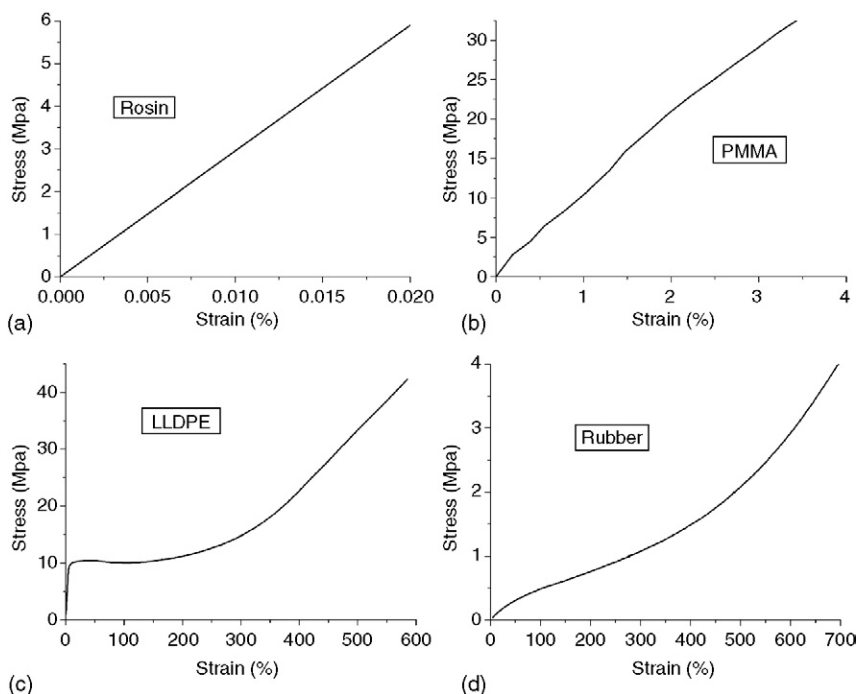


FIGURE 2.12 Typical stress–strain curves of rosin, poly(methyl methacrylate) (PMMA), linear low-density polyethylene (LLDPE), and lightly vulcanized rubber. Note the very different scales of both stress and strain. (a) Rosin, Young’s modulus 2550 MPa, ultimate stress 5.9 MPa, ultimate strain 0.2% (Houwink, 1954). (b) PMMA, Young’s modulus 1500 MPa, ultimate stress 72.8 MPa, ultimate strain 11.5% (Cheng and Chen, 2004). (c) LLDPE, Young’s modulus 1010 MPa, ultimate stress 15 MPa, ultimate strain 550% (Watson, 1992). (d) Rubber, Young’s modulus 50 MPa, ultimate stress 12 MPa, ultimate strain 67% (Treloar, 1975).

an intervention, one must take account of the relative strengths of the materials and their bonds.

The mechanical properties are usually important in choosing a polymer. Highly specified standard tests (e.g. BS EN ISO 527-1, 1996) are widely used for industrial evaluation, but these are rarely of direct relevance to conservation applications (Berger and Zeliger, 1984). The tensile test is useful for polymers applied as adhesives (Vestergaard and Horie, 1996), films or fibres. Other applications require the assessment of different properties. Values analogous to tensile elasticity, yield and ultimate stress/strain can be obtained from bending and compression tests, used for evaluating mounting and reinforcement methods (Bradley, 1984). Other types of mechanical test can also provide valuable information, e.g. tearing strengths (for silicone rubbers) and resistance to peeling (for textile and paper adhesion techniques). For most conservation purposes, the strength of applied polymers is greater than needed, sometimes dangerously so.

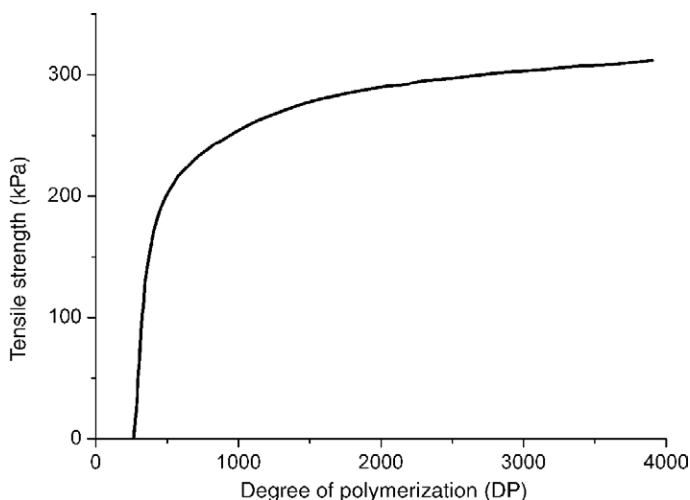


FIGURE 2.13 Effect of degree of polymerization of PVAC (molecular weight = $DP \times 86$) on tensile strength (Scherer and Chinai, 1955). This is typical behaviour of polymers, both thermoplastics and thermosetting polymers. The strength rapidly rises towards a limiting value, above which using a higher MW adds little strength. However, in the 200–700 DP region, small amounts of chain scission or cross-linking can make a considerable difference to the mechanical properties.

2.4.1 Hardness (Guévin, 1995)

The term ‘hardness’ encompasses a range of properties. Four main measures of hardness are widespread: resistance to indentation, scratch resistance, damping of a pendulum, and flexibility. Indentation hardness is commonly used to indicate the hardness of rubbers. A soft, flabby, silicone rubber would have a Shore A hardness of 20, and a hard, stiff, rubber a hardness of 70.

Scratch resistance, or resistance to physical marring, is frequently measured by rubbing abrasives over a surface and assessing the damage at the end of the test. Pencil hardness is used to assess the hardness of a coating, though it may not be reliable. A pencil is sharpened and drawn at 45° across the polymer surface (ISO 15184, 1998). The hardness of the hardest pencil that does not mar the surface is assigned to the polymer. This method is probably more repeatable than ‘fingernail hardness’, which is often used as a rule of thumb.

The hardness or resilience of a coating may be described by Sward rocker hardness (ASTM D2134-93, 2007). Plate glass has a hardness of 100, and a thin film of poly(vinyl acetate) has a hardness of 63 (Feller, 1971b). Sward hardness is partly correlated with the glass transition temperature, but it cannot be used reliably to compare coatings of widely differing types (Sato, 1984).

A common method of measuring the flexibility of a polymer coating is to take a film of standard thickness and bend it around a series of cylinders, or a conical mandrel (BS EN ISO 6860, 2006). The diameter of the smallest mandrel that the film can be bent around without cracking demonstrates the flexibility of the polymer.

2.5 OPTICAL PROPERTIES (WICKS ET AL., 2007)

2.5.1 Refractive Index

The refractive index determines properties such as reflection and transmission when the polymer is in combination with other substances, e.g. pigments, the object or air (Figure 2.14). These reflections can prove important, for example, when choosing an adhesive for glass (Tennent and Townsend, 1984a; Koob, 2006). Reflections occur on the microscopic scale when pigments are surrounded by medium. As linseed oil ages over centuries, the refractive index of the linseed oil rises, from ≈ 1.48 to 1.59 (Laurie, 1937), approaching the values of mineral pigments, though doubt has been expressed about the higher values (Townsend, 1993). Oil paint therefore becomes more transparent with time. A polymer applied from solution retains solvent for a considerable time and can take years to reach its final value (Tennent and Townsend, 1984a). Loss of plasticizer or variation of moisture content with humidity changes will have an effect on the

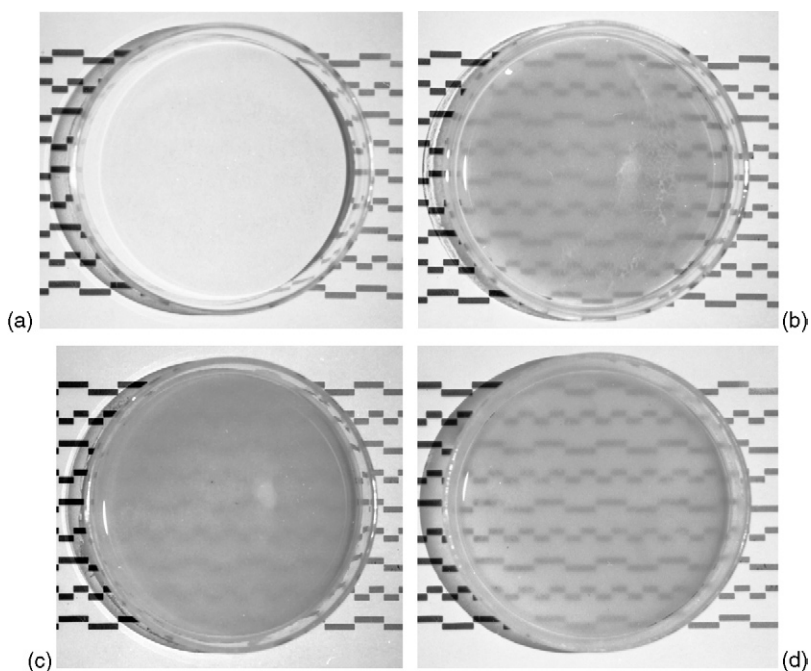


FIGURE 2.14 Glass beads, refractive index (nD) = 1.529, have been immersed in fluids (media) of different nD . When the difference is great, e.g. air (nD = 1) (a), most of the incident light is reflected from the bead's surfaces. As the match between the medium and substrate improves, the reflection from the interface decreases, so improving the transparency of the mixture – pyridine (nD = 1.507) (b) and carbon disulphide (nD = 1.628) (c). A good match of refractive indices (nD = 1.529) (d) allows the light to penetrate through deep layers of the mixture and enables the inherent colour of the beads (grey) to be seen in a mixture of chlorobenzene and benzyl benzoate.

refractive index. Although the refractive index was thought to have a significant effect on the appearance of a varnished oil painting, this has been shown to be at most a minor influence (Feller, 1957; Berns and de la Rie, 2003).

2.5.2 Colour (Berns, 2000)

The colour of most polymers is restricted to a yellow tinge. This is usually reported in terms of the yellowness index (ASTM E313-05, 2005; ISO 4582, 2007), which is calculated from reflection or transmission measurements. In comparing two materials, a difference of about two points in the index is just visible under good conditions of viewing (Tennent and Townsend, 1984b).

2.5.3 Gloss (Hammond and Kigle-Boeckler, 1995)

Gloss is the description of a shiny surface, opposite to matt. Various methods are available for measuring different types of gloss. The gloss of varnishes is usually assessed by measuring the specular reflection using 60° incident and 60° reflected light, with additional standard angles of 20° (for high gloss surfaces) and 85° (for low gloss surfaces) (BS EN ISO 2813:2000, 2000; ASTM D523-08, 2004). The degree of gloss can prove useful in reporting the changes in the properties of coatings and to assess the type and level of gloss of acceptable treatments (Delaney et al., 2008).

2.6 POLYMERIZATION (PAINTER AND COLEMAN, 1997; COWIE AND ARRIGHI, 2008)

Polymers are built up by reacting monomers together, each monomer molecule being able to react with at least two other molecules. Two main mechanisms are used commercially, vinyl polymerization and condensation polymerization, with addition polymerization normally being used for cross-linking resins. Other mechanisms are employed that are frequently specific to the polymer being formed. Polymers may be applied as finished molecules or as pre-polymers, which are reacted in situ. Vinyl polymerization is used to produce poly(vinyl acetate) and to cure polyester casting resins. Vinyl polymerization results from the ability of a carbon–carbon double bond to open (Figure 2.15). This occurs under the influence of an initiator. Free radicals are the usual and most convenient initiators. The radical is not destroyed in the process but is transferred on to the end of the chain, creating a chain reaction. Free radicals are extremely reactive and may incorporate impurities into the chain, e.g. oxygen. Free radicals are generated from unstable chemicals, e.g. benzoyl peroxide, by heat, for instance during the laboratory or commercial preparation of polymers, or by catalysts, as during the curing of polyester casting resins. Alternatively, high-energy radiation, ultraviolet or gamma rays may be used. The length of the polymer chains can be controlled by adding chain transfer agents. Where a single monomer has been used, a homopolymer is produced. Copolymers can be made in a similar

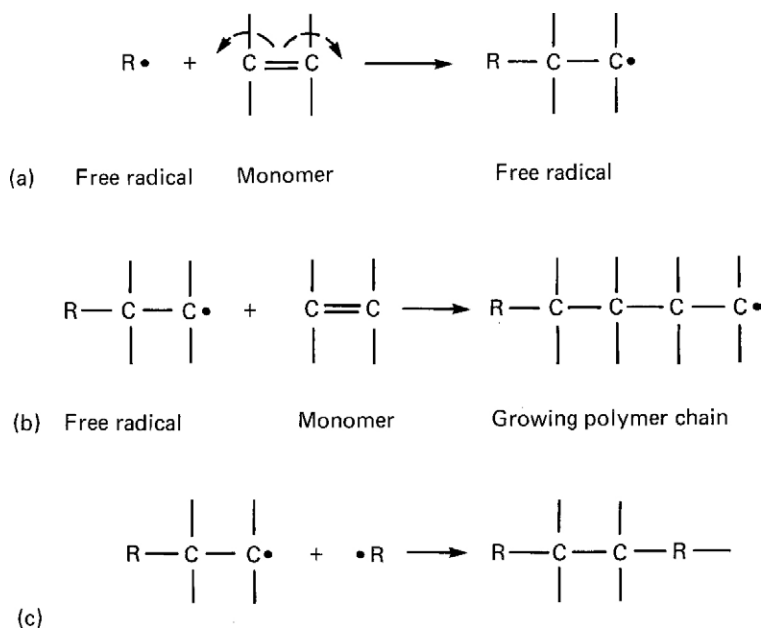


FIGURE 2.15 Vinyl free-radical polymerization process. (a) First stage of polymerization. (b) The chain grows step by step without interruption by the addition of monomer molecules. (c) Combination of two growing chains, which stops the polymerization process for these chains.

fashion by mixing two or more monomers. Four conditions of polymerization are used (Table 2.3).

Dispersion polymers (incorrectly but commonly termed emulsions) are heavily contaminated, when dried, by the emulsifiers. The polymer, frequently a copolymer, is usually of high molecular weight and may be deliberately cross-linked. The polymeric emulsifiers used may be neutral, e.g. poly(vinyl alcohol) and cellulose ethers, or ionic, e.g. sodium carboxymethyl cellulose or poly(acrylic acid). These emulsifiers can take part in the reactions, being degraded or incorporated into polymer, causing cross-linking (Donescu, 1981). Sensitive materials can be damaged by these dispersions, which may have an inappropriate pH (acidity/alkalinity), corrosive salts or volatile additives, e.g. ammonia. The viscosity of a dispersion is completely independent of the molecular weight of polymer in the droplets. High percentages of polymer, up to 70%, can be held in a stable dispersion at very low viscosities compared with equivalent polymer solutions. The viscosity can be increased by adding water-soluble polymers, which increase the viscosity of the medium, or by adding solvents that swell the particles. Polymers in dispersion have many advantages during handling and application. However, since they are complex mixtures, the effects on objects are more difficult to predict.

The process of film formation is being worked out (Winnik, 1997; Ludwig et al., 2007). As the dispersing water evaporates, the particles are forced together.

TABLE 2.3 Vinyl Polymerization Methods

Method	Ingredients Used	Form of Polymer Produced	Relative Advantages (Relative Parts)
Bulk	Monomer (100) Initiator (0.5)	Solidified melt, in lumps	Purest chemically but may contain chain irregularities, e.g. branching
Suspension	Water (350) Monomer (100) Initiator (0.5) Suspending agent (1)	Small beads	Slightly contaminated with suspending agent, e.g. gelatine/talc. Convenient for handling and dissolving
Solution	Solvent (100) Monomer (100) Initiator (0.5)	Solution	Solvent may be incorporated into polymer. Can be used directly as solution
Emulsion	Water (180) Monomer (100) Emulsifying agent (5) Initiator (1)	Dispersion (emulsion)	Emulsifying agents are incorporated into solid polymer, leading to reduction in properties, e.g. clarity, stability to yellowing. Can be used directly as dispersion

If they are soft enough to deform, they will form a transparent film. The lowest temperature at which this takes place is the minimum film-formation temperature (MFFT). If the temperature of drying is below this, the particles are too stiff to adapt to the shape of their neighbours and the film is weak and translucent or opaque (Figure 2.16). If drying near the MFFT, the particles are soft enough to distort, but they largely retain their identity, i.e. a core of polymer surrounded by a layer of surfactants and emulsifiers. This creates a porous hydrophilic network that is sensitive to water and mechanical forces. Only if the temperature is well above the MFFT will the polymer chains have sufficient mobility to flow across the particle boundaries, so forming a coherent film. This flow takes place hours or days after the water has evaporated. The polymer must therefore be soft enough to flow, i.e. be above its glass transition temperature. The polymer itself may have a low glass transition temperature. Alternatively, the glass transition temperature may be lowered by additives. Plasticizers soften the polymer but would not now be used in a polymer for conservation. Solvents are used widely to permit film formation at low temperature, and the formation of an ultimately

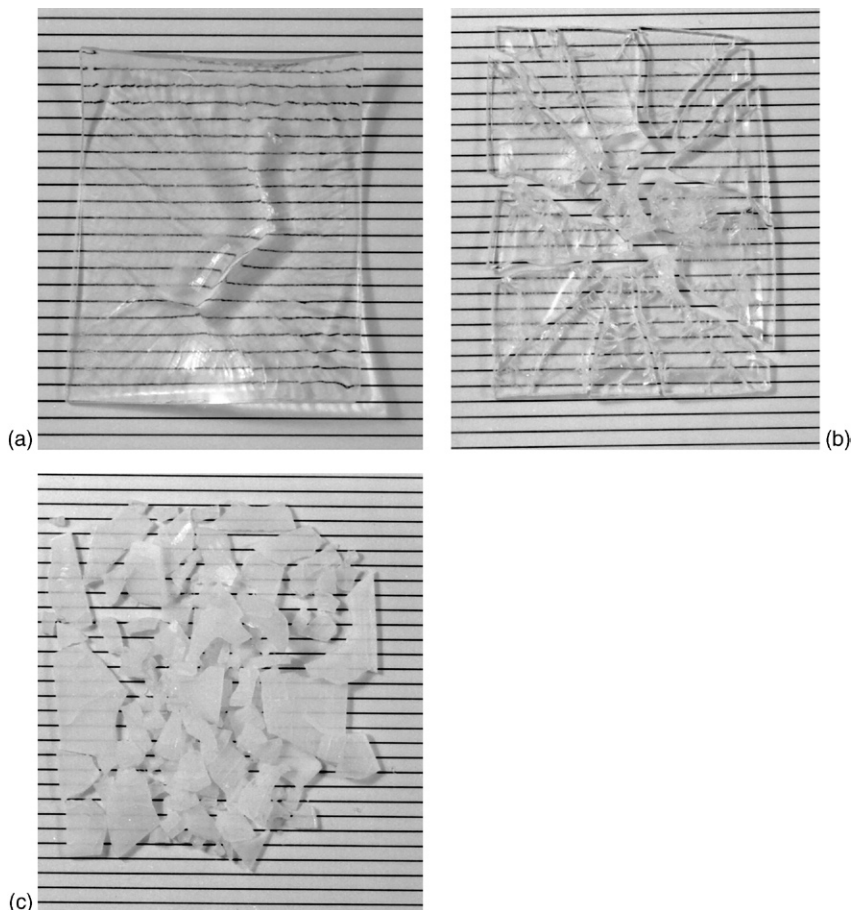


FIGURE 2.16 The effect of minimum film-formation temperature (MFFT) of a dispersion on its drying behaviour. Primal (Rohm & Haas) dispersions were allowed to dry at room temperature, $\approx 21^\circ\text{C}$, in a silicone rubber mould. An MFFT above room temperature results in incomplete coalescence of particles and poor film formation. The cracks and distortion that occur in the films result from the movement of water and shrinkage during drying. (a) AC-34 MFFT, 12°C . (b) AC-73 MFFT, 37°C . (c) B-85 MFFT, 90°C .

hard film as the solvent evaporates. Only small amounts of solvent are tolerated before the dispersion is destabilized. Both the MFFT of the dispersion and the glass transition temperature of the final film are important properties. If the polymer is very soft, coalescence will occur readily, but the film will be soft, weak and absorb dirt more easily. If the polymer is hard, the film may not form at all or be too stiff. Mixing dispersions of polymers of different T_g values enables the creation of a good, coherent, film that is stronger and has reduced dirt pick-up. In order to improve mechanical properties, e.g. cold flow,

commercial products frequently incorporate up to 50% cross-linked polymer. All these variables increase the sensitivity and unpredictability of dispersion applied films as part of objects or as added materials (Zumbühl et al., 2007).

Although vinyl polymerization is used to make by far the largest bulk of (man-made) polymers, condensation polymerization is widely used. Condensation polymerization proceeds differently from vinyl polymerization. Two molecules react together to eliminate a small molecule, usually water, hence the name condensation. Chains are built up by isolated reactions to form the polymers. Copolymers can be produced by a variety of compatible monomers. Condensation polymers are used, both as thermoplastics, e.g. nylon, and cross-linking resins, e.g. phenol–formaldehyde resins. Biological systems make the huge masses of polymer by condensation polymerization, e.g. cellulose (monomer uridine 5'-diphosphate-glucose), collagen (amino acid monomers) and even rubber (monomer isopentenyl pyrophosphate).

Many other reactions are used for preparing synthetic polymers, both by modification of existing polymers and by the cross-linking of existing pre-polymers. These methods are discussed under the entries for individual polymers.

2.7 DETERIORATION OF POLYMERS

Polymers used in conservation must not change and cause harm to the objects. Most polymers are applied to objects in the hope, if not the expectation, that the process need not be repeated for 20 years as a minimum and 100 years in most circumstances. However, this lifetime is long by comparison with commercial uses: ‘... copolymers [of polyacetals] have lasted in a creep test for up to two years, a longer period than the operational life of a typical car’ (Barker and Price, 1970).

The useful life of a polymer has to be defined for conservation. Feller developed a rule of thumb for classifying materials by their photochemical stability, a useful tool that should inform all stages in the conservation process, from planning to use (Table 2.4). In most fields, it is expected that a conservation treatment will have to be reversed in the future. For instance, picture varnishes have traditionally been replaced every 80–120 years and stained glass window installations every 2–300 years. It is likely that a material used for temporary fixing may never be entirely removed (Section 1.3). It is therefore necessary that even these have long-term stability.

Deterioration is any change in the polymer that makes it unfit for use in its context. Many changes may be undergone by polymer films; they can yellow, become brittle, weaker or insoluble, shrink, flow, become dirty and, when applied to objects, react with them over short or long periods, chemically or physically.

The primary causes for these changes are usually chemical reactions in the film, though physical properties cause dirt pick-up and flow or production of stresses. The agents of deterioration – light, heat and oxygen – act on the weak-

TABLE 2.4 Classification of Useful Life for Conservation Materials and Processes

Class	Classification	Proposed Lifetime	Examples
T	Temporary	<6 months	Cyclododecane consolidant
C	Unstable or fugitive	<20 years	Pressure-sensitive adhesive
B	Intermediate	20–100 years	Poly(vinyl butyral) adhesive
A2	Excellent	>100 years	Acid-free board boxing Paraloid B-72 picture varnish
A1	Excellent	>500 years	Parchment infill

The useful life is dependent on the material's properties, the interaction with the object, the environment and the criteria of properties used to define the term 'useful'. The classification is thus specific to each application, which should be evaluated separately.

Adapted from Feller (1978).

nesses inherent in the polymer film. All these influences interact in a complex and often uncertain manner.

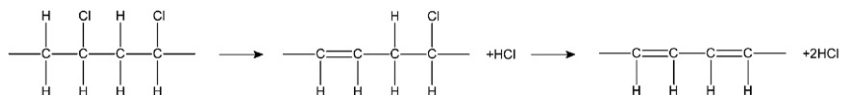
2.7.1 Degradation Studies (Allen and Edge, 1992)

Vinyl polymers are the most intensively studied group because of their nominal uniformity of structure. The less uniform thermoplastic and cross-linking resins have not been investigated in such detail and have only recently attracted concerted efforts at understanding their degradation. A chain is only as strong as its weakest link – in no field is this more true than in polymer chemistry. The study of polymer deterioration is largely the location and study of these weak links. Parallel to the deterioration studies are efforts put into the industrial development of stabilizers to prevent the deterioration. The major chemical changes that can occur are: cross-linking between chains; chain scissioning; and oxidation of the main chains or side groups. These chemical changes in the polymer structure may reveal themselves as increasing insolubility, reduction in strength, increasing polarity and change in colour.

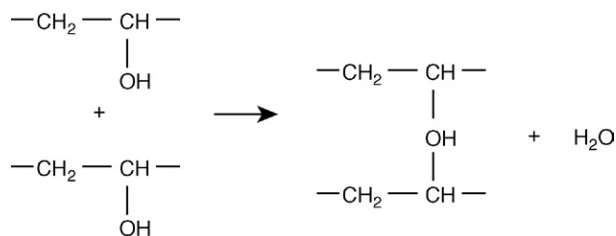
Thermal Deterioration

Purely thermal degradation is probably unknown at room temperature or even in direct sunlight, though it will occur during the processing of polymers. However, thermal degradation studies reveal the forms of degradation that occur in more complex situations. They also provide a quick test for the effects on degradation of minor modifications to the polymer or its formulation.

Poly(vinyl chloride) (PVC) undergoes reaction along the main chain. Theoretically the structure should not break down below $\approx 300^\circ\text{C}$ (David, 1975), but even good grades of PVC degrade below 100°C , producing hydrochloric acid:



Long sequences of conjugated double bonds are created, leading to light absorption and a yellow discoloration of the polymer. The process is prompted by imperfections in the chain and by impurities such as solvents or metal ions. Discoloration can occur early in the life of a polymer, long before physical properties are affected. Pendant groups on a polymer chain can react without affecting the main chain structure. For example, poly(vinyl alcohol) can dehydrate to form ether cross-links:



Various structures in a polymer molecule cause it to become more reactive and thus unstable (Figure 2.17). When they form part of the main chain of the molecule, they cause particular instability. Many natural resins contain these groups and are thus less stable.

Photolytic Deterioration (Rabek, 1996)

Many polymers used in conservation are exposed to light. Light can be visualized as being a stream of small packets of energy, called quanta. No material is totally transparent. Absorbed energy will cause heating but a small proportion may initiate chemical change. Light of different colours is composed of quanta of different energies, red being least energetic and blue most energetic. Ultraviolet radiation is yet more energetic.

Each chemical reaction requires a minimum amount of energy to activate the breaking of the first chemical bond. The energy of a quantum of ultraviolet radiation is sufficient to break many of the chemical bonds in polymers. Impurities, e.g. metal ions, and imperfections, e.g. oxygen incorporated into the polymer, are affected by visible light. Visible light causes slow changes in polymer properties (Feller et al., 1981). Ultraviolet absorbers and stabilizers are used to increase the

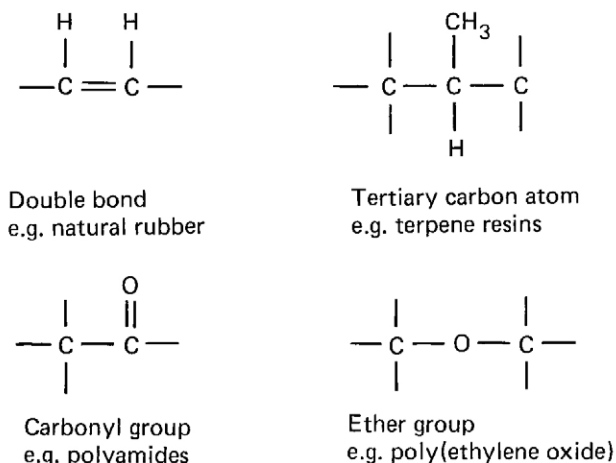


FIGURE 2.17 Destabilizing groups in a polymer molecule. These may be part of the formal structure of the polymer, or may have been introduced during polymerization, processing or ageing.

life of unstable polymers such as PVC and PE. Although polymers used in conservation are more stable than these, the proposed lifetime is also much greater. Efforts have therefore been made towards incorporating ultraviolet stabilizers into coatings (de la Rie et al., 2002). As most conservators would be suspicious of a material that might migrate into the object, the preference is to use an inherently stable material. Stabilizers of all sorts must be chosen with care and tailored to individual polymers. The wrong stabilizer may increase the rate of oxidation or discoloration.

Oxidation

Although heat and light provide the activation energy, reactions with oxygen usually cause the greatest damage. Oxidation occurs with all organic materials but the resistance of different materials varies greatly. Polyethene oxidizes at an appreciable rate in the dark at 60 °C, whereas poly(methyl methacrylate) is stable at 170 °C (Hawkins and Winslow, 1964). Polymers that contain oxygen in their backbone, such as cellulose derivatives, are far less stable.

Oxidation is essentially the reaction of oxygen with radicals formed in the polymer. The first process is initiation, the production of free radicals at imperfections and reactive points in the molecules. Once the radical has been created, it can react with oxygen to form peroxides and hydroperoxides, $-\text{OOH}$. Hydroperoxides are moderately stable but can be broken down under the influence of light, heat or catalysts to continue a self-initiating process of oxidation. The radicals and peroxides formed can cause oxidation of the main or side chains – chain scission or cross-linking respectively. The chain reaction will be terminated by reactions of the radicals with molecules, which lead to stable, non-reactive products. Many

other reactions occur during the oxidation that result in the production of small, volatile fragments. The oxidation process may therefore result in an increase in weight by incorporation of oxygen, e.g. during the oxidative cross-linking of drying oils, or a loss in weight by degradation of polymers, e.g. during the photo-oxidation of poly(vinyl butyral). Four stages of oxidation can be identified (Feller, 1977): inception (adjustment of the polymer to the conditions of exposure); induction (build-up of peroxide groups in the polymer); steady oxidation (reaction of the reactive groups in the polymer); and finally decline (the reactive groups used up). For many purposes, the induction period is the maximum usable life of a polymer. This may be extended by adding antioxidants or ultraviolet absorbers. It can be shortened by exposure to ultraviolet radiation or catalysts.

This outline has followed changes in the oxygen adsorption of the polymer. However, other changes result from the oxidation. The polymer may become unacceptably deteriorated at relatively early stages in the oxidation process. Yellowing, chain scission or cross-linking are all effects that occur after low levels of reaction. Unfortunately these subtle effects, together with increase in polarity, may remain undetected until the conservator comes to remove the polymer. All polymers must be expected to oxidize, either quickly or slowly, with time. The photo-oxidation of natural varnish resins results in increased polarity and in increased weight as oxygen is absorbed (Scalarone et al., 2003). This is also observable with Paraloid B-72, an extremely stable polymer (Toniolo et al., 2004). Many polymers applied to objects are mixtures, e.g. dispersions, wax/resins. The deterioration of each component may take place separately or synergistically.

Pigments

The influence of pigments on the ageing of synthetic resins has been studied for commercial reasons (Allen, 1993). The choice of pigments is unexpectedly important (Spathis et al., 2003). For example, the oxidation of propan-2-ol in the presence of various white pigments showed a wide range of reaction rates with different pigments. The relative rates were titanium dioxide (anatase) 10, zinc oxide 4, titanium dioxide (rutile) 4, barium sulphate 2 and barium tungstenate 0.3 (Irick, 1972). Because of the other useful properties of titanium dioxide, pigments are now surface-treated to reduce the catalytic activity. Many pigments, organic and inorganic, can increase the oxidation of polymers (Hagadorn, 2004). One should choose pigments for conservation purposes that will have the least harmful effects on the polymeric medium.

Substrate

Polymers have been shown to affect the deterioration of objects where they have been studied, e.g. paper (Baer et al., 1976), canvas (Berger and Zeliger, 1975) and metals (Williston, 1982). The object can in principle make an enormous difference to the ageing behaviour of the applied polymer. However, this seems to have been noticed in only a few cases. Most objects in conservation are old ones and have themselves started to degrade to some extent. Cellulose rapidly

oxidizes, forming peroxide complexes (Daniels, 1984), which will start the main process of oxidation immediately.

Other effects are possible. Poly(vinyl alcohol) becomes insoluble and fixed to textiles on drying at room temperature (Thomson, 1963; Marten, 2002). The reason is uncertain, but is probably a combination of oxidation and reaction between the alcohol groups on the polymer and the acid oxidation fragments on the object. Decaying glass has an alkaline surface that can cause hydrolytic degradation of adhesives and lacquers. Degradation and other reactions can occur rapidly along a metal/polymer interface (Chan and Allara, 1974). It may be possible to pretreat the object or include stabilizers in the polymer to reduce the extent of reaction. Some polymers react together to form insoluble products. This happens particularly with water-soluble polymers (Table 3.3).

Gaseous Pollution

Pollutants affect polymers to varying extents, though they are usually of less importance than oxygen or water (Kamal, 1970). Both sulphur dioxide and nitrogen oxides increase the rates of oxidation under ultraviolet, causing chain scissioning (Dulog, 1997). It has been known for many years that ozone reacts with double bonds, a particular problem of rubber, causing chain scission (Datta et al., 2007). Double bonds occur as impurities in many commercial polymers. The effects are similar to, and contribute to, oxidation processes.

Hydrolysis

Those polymers that were originally prepared by condensation reactions may undergo hydrolysis. Polyamides and cellulose derivatives are at risk of chain breaking at the susceptible points. This has led to severe degradation of polyurethane foams, prepared from polyester pre-polymers, used in wet storage of objects. Cured polyester resins can be broken down by hydrolysis, leading to leaching and cracking (Boinard et al., 2000).

Cross-Linking and Chain Scissioning (Feller, 1994)

The thermoplastic resins are commonly used in the expectation that, in theory, they can be removed by solvents. It is therefore important that they do not become insoluble for any reason. One reason for insolubility in a solvent is cross-linking between the polymer chains to form an intractable three-dimensional network. This is the same process, but occurring over a longer period, as a resin being deliberately cross-linked. A considerable effort by the conservation world has been put into the search for thermoplastic polymers resistant to cross-linking (Feller et al., 2007). The alternative reaction to cross-linking is chain scissioning. The molecular weight is halved for each break and the polymer is considerably weakened. This can happen to both thermoplastic and thermosetting resins, whose strength and ability to be stretched without breaking are reduced.

In industry the effects of cross-linking are viewed in two ways. If a thermoplastic cross-links slightly after processing, it will acquire thermal and mechanical

stability. Polyethene has been extensively modified in this way to improve stability. Cross-linking and scissioning reactions during ageing obviously affect the usable life of a polymer. Too much, especially of scissioning, can make the polymer rapidly useless. Cross-linked polymers also undergo further cross-linking and chain scissioning reactions, resulting in changes in properties.

Relationship Between Cross-Linking and Chain Scissioning

Of considerable importance to conservators is the distinction between those thermoplastics that remain permanently soluble and those that become more or less insoluble with age. The two reactions of cross-linking and scissioning occur relatively independently and their rates respond differently to changes in the deteriorating environment. When a polymer only reacts by chain scissioning it will remain permanently soluble, become weaker and may eventually liquefy. The opposite to a scissioning polymer is a purely cross-linking polymer. Each time a cross-link occurs a molecule increases in size. Only the most inappropriate polymers for conservation, e.g. poly(butyl methacrylate), undergo cross-linking alone (Feller, 1977). The continual breakage and formation of new bonds will change the physical and chemical properties of the polymer, particularly if oxygen is incorporated into the chain during the process. A polymer might become so changed that the cross-linking or scissioning behaviour is also changed. The ratios are altered considerably by changing the test temperature, particularly around the glass transition temperature. Cross-linking reactions are less likely to occur below the glass transition temperature when the chains cannot move towards each other. These methods and results have proved a powerful tool in preparing a polymer to order and as an important criterion in deciding between potential polymers to use on objects (Favaro et al., 2007).

Physical Deterioration

A polymer can deteriorate physically in various ways: it may shrink, expand, flow, crack or absorb dirt. These changes may result from the inherent properties of the polymer, from a change in these properties or from outside influences. Polymers applied to objects are normally around their glass transition temperatures. They can thus adjust, by flowing, to the movements in the object. A polymer that is well below its glass transition temperature and is weak may crack if the object moves. If the polymer is above its glass transition temperature it will tend to flow, particularly when placed under stress. Liquid adhesives in self-adhesive tapes can be sucked by capillary action into porous substrates. Traces of low- T_g polymer left on the surface after incomplete removal may hold dirt, causing disfigurement of the surface.

There is always some shrinkage of a polymer in going from the liquid state to the solid state. Shrinkage of polymers after they have set is usually due to loss of some of the film-forming material. Plasticizers are frequently added to glassy polymers to reduce their rigidity, e.g. flexible PVC coatings and celluloid. Over time, the additive can diffuse out of the film. This process of removal is helped by washing

or by absorption into an adjacent porous material. The shrinkage that results can cause damage if it distorts the attached object. Other results are brittleness and cracking of the polymer. For these reasons the use of plasticized polymers should be avoided. Small molecules formed as fragments during oxidation may be lost by evaporation, washing or absorption. An example is the shrinkage and cracking of linseed oil putty, which degrades severely towards the end of its life.

2.8 TESTING OF POLYMERS

The ideal way to test a polymer for conservation purposes is to apply the polymer to a likely range of objects, of little value, using various application methods, leave them for a time, say 100 years, then reverse the treatment and assess the results. This is, in practice, how many conservation treatments have traditionally been developed and assessed. However, it is not a realistic way to test slightly or even grossly unsuitable methods that are newly proposed.

The first part of any test procedure is to decide on the role of the polymer and the general characteristics it must have. Many requirements are specific to the task in hand and may not be discovered until full-scale experiments are attempted. Usually a small range of polymers will then be shown to be apparently suitable. The reversibility of the treatments must also be assessed before continuing to the next stage of intensive study.

Evaluating treatments for conservation has to be undertaken with rigour if the results are to be useful. Too many studies have produced results, after considerable work, that have little validity but are applied to objects anyway (Reedy and Reedy, 1992), often with damaging effects. Unlike materials for science research, objects are rarely well characterized or their history understood. This adds uncertainty to the results of the experiment and doubts about the implications to the wider population of objects. This inevitable uncertainty must be part of any design for an experiment. Indeed the treatment of an object is a unique experiment from which lessons can be learned and added to a growing body of conservation knowledge. Fortunately, techniques for dealing with complexities and uncertainties have been well developed in other fields, such as medicine and natural history.

In the past, much conservation research has been carried out on model objects. These sample objects have the advantage of being (reasonably) well characterized, uniform and available in quantity. However, they have the disadvantage of representing only one small set of object properties. The results will therefore have limited, or no, relevance to the wide variety of real objects to be preserved. For years, this approach has held up advances in stone conservation research (Price, 1995). A symptom of the limited input (intellectually and in resources) into development of treatments is the uncritical use of a tried and tested method in one area applied to another. An example is the extensive evaluation of Paraloid B-72 as a picture varnish, which was tested for exposure on a painted surface to limited (visible) light exposure in a room with good climatic conditions. Its application

without a comparable evaluation to other uses is inappropriate. More serious was the application of soluble nylon without the necessary follow-up tests.

A proposed treatment with poor results can usually be discovered in preliminary trials. Although the development of a more successful treatment can frequently be carried out in reasonably short periods, 3–10 years, using model objects and then real objects, the success of a treatment can be judged only in the long term. The testing of treatments relies upon the monitoring of objects in the long term, requiring excellent documentation at all stages of the investigation. An example is the 60-year trial of book-binding leathers with different tannages (Larsen, 1996). The development and refining of treatments builds upon well-documented and evaluated treatments of real objects from the past (Shashoua et al., 1992).

Evaluation methods for polymer properties may be divided into two groups. First are those designed by researchers into polymer properties. Most industries have introduced a battery of tests to validate the properties of the starting materials, the intermediate products, to the final output. These tests have been increasingly standardized at national level, e.g. American ASTM International and British Standards Institute, and international level, e.g. International Organization for Standardization. Increasingly, conservation institutions are ensuring that they have access to these techniques, either internally or through external research bodies. These industrial standard tests are usually carried out by people for reasons unconnected with conservation and their results should not be applied uncritically to conservation. Methods leading to tests with wide acceptance and application in the field are being developed slowly, e.g. on ageing (Bilz and Grattan, 1993) or cellulose molecular weight (Stol et al., 2002). All require the outlay of considerable expense and time from the community before consistent results are achieved. Polymers and other materials used on objects should be subjected to the same rigorous specification and routine scrutiny demanded for industrial materials. Tests should be carried out on both newly acquired products and products that have been stored. Many products such as dispersions and epoxy resins deteriorate while in the liquid form (Christensen and Pedersen, 1982).

The second group of tests are those examining the interaction between the object (or model object) and the added material. With more materials involved, the number of variables to be understood increases so the investigations have to be designed with greater care. Conservators have considerable understanding of the objects and their variability so are essential participants in object-based research. Tests carried out by the working conservator necessarily use simpler equipment than is available in a research laboratory. They can, however, be equally or more informative concerning their application to conservation practice (e.g. Karsten and Down, 2005). The conservator should if possible carry out simple investigations on every batch of material to be used on objects. If the samples and results of tests are retained on file, they will become a valuable resource (by natural ageing) when the treatment must later be assessed and reversed.

The samples and tests are more valuable if they are prepared in the same way over many years. During ageing tests on polymers, sufficient samples should be

prepared to answer all the likely questions that might be asked of the polymer. Samples made using reproducible and well-documented methods become more valuable with ageing, especially those that are decades old. For instance, ageing paint samples have proved invaluable in studying the effect of solvents on films of different ages (Stolow, 1971). If possible, sufficient test samples should be made so that subsequent generations of conservators can build upon and compare the results of the fresh samples. Conservation has a very long time scale for the use of its materials so it should ensure that the research results with their voucher materials are documented and preserved to allow real long-term tests. There was a tendency of conservators and other researchers not to publish the raw data, but to report on the results (usually fairly positive) that confirmed the hypothesis under examination. This frequently prevents future workers building upon the results to formulate or test a new hypothesis resulting from advances in knowledge. The previous work is thus wasted because it cannot be reused or tested. Tools are becoming available to archive and make available the underpinning data to papers (Kleppner and Sharp, 2009).

2.8.1 Setting Properties

It is enlightening to be able to handle a sample of the solid polymer. A useful method for forming a sheet of polymer is to cast the liquid into a silicone rubber mould, say $75 \times 75 \times 1$ mm deep. A silicone mould can only be used with materials that do not seriously swell the rubber, e.g. dispersions, epoxies and wax. Preparing a hand sample for a liquid that reacts with the mould material, e.g. solutions in organic solvents, is more difficult. One can allow a puddle on polyethene to dry or cast in a well made by waxed microscope slides (Bradley and Wilthew, 1984), but it is difficult to achieve uniformity between samples in this way. Equipment is commercially available for the purpose from polymer and paint test instrument manufacturers, and is usually more cost-effective and the results more transferable than trying to make one's own equipment.

The shrinkage of a setting polymer occurs in two stages: while it is still mobile and later when the chains can no longer flow past one another – the gel state. The gel can be caused by chemical cross-linking or by increasing entanglement of the chains, preventing movement. Shrinkage before the gel point is only of concern if one has to fill a volume completely, e.g. taking a cast from a mould or ensuring that an object is completely consolidated. Shrinkage after the gel point can be more serious. Damaging shrinkage is a combination of two properties, the post-gel shrinkage and the elastic modulus (the force necessary to stretch the set polymer). Total shrinkage must be measured by taking a known volume of liquid polymer and measuring the volume after setting.

Post-gel shrinkage of a thermosetting resin is relatively easy to assess. A simple method is to take an impression from a steel rule, using a release agent if necessary. Gross changes in length can be measured in the mould of the engraved scale, using the rule itself or a travelling microscope. An alternative method is to cast a cylinder

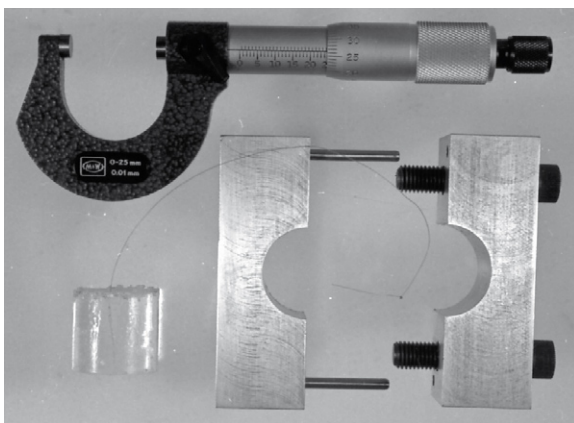


FIGURE 2.18 A stainless-steel cylindrical mould (internal diameter 25 mm×25 mm high) with a micrometer for measuring the diameter. A sample of polyester has a piece of thread cast in to aid specific gravity measurement.

of the polymer in a steel mould (Figure 2.18). Shrinkage occurs mostly during the initial setting but can continue for a considerable time afterwards. Samples must therefore be measured initially and at increasing intervals until a stable value is achieved. The method introduced by Werner (1962) of casting a film into plywood (or cardboard) frames appears inconsistent (De Witte, 1975). Thermoplastics cast from emulsions or solutions also reduce in volume during drying but the post-gel shrinkage is not measured easily (Moran and Whitmore, 1994; Parker, 2005). Shrinkage of coatings is important industrially so there has been considerable research into methods of quantifying and measuring shrinkage and stress development (Lei et al., 2002), though no agreed method has yet been developed.

2.8.2 Solubility

There are three aspects to solubility that are important: what liquids dissolve the material (or do not), what is the viscosity of the solution formed, and to what extent the material dissolves. For cross-linked polymers, the swelling effect of solvents is also important. The viscosity of polymers either in solution or as pre-polymers is usually derived from manufacturers' data.

Manufacturers' information for polymer/liquid combinations is often insufficient for conservation purposes and tests must therefore be carried out. A known weight of the solid polymer is placed in the test liquid to form a 20–40% solution, which only half fills the container; 10 ml is adequate. The closed container is agitated for 24 hours. At the end of the 24 hours, the container is inspected and the liquid placed in one of three classes: solvent, borderline and non-solvent. A totally clear solution implies that the liquid is a solvent. A turbid liquid implies that the liquid is borderline. If the liquid is in two phases, e.g. has solid particles apparent or has separated into two layers, the liquid is classed as a non-solvent.

Only liquids of interest need be tested, though 33 solvents plus mixtures are suggested in the standard test (ASTM D3132-84, 1996) (now discontinued but still a good guide to methodology) and Hansen (2007) used a set of 65 solvents.

If the polymer is only partly soluble, the degree of solubility can be assessed. The liquid is decanted or filtered off after the 24-hour mixing. Both the soluble and insoluble portions can be dried in pre-weighed containers to constant weight in a vacuum desiccator or by gently warming (40 °C) in the oven. The percentage solubility can be established from either or both of the determinations.

The swelling behaviour of a cross-linked resin is usually determined on a volume basis. A known weight of polymer, whose density has been determined, is placed in a pre-weighed container. The solvent is added. After swelling has stopped, usually within 48 hours, the polymer is quickly freed of liquid and weighed in its container to prevent premature evaporation of the liquid. The volume increase of the polymer is derived from the following:

$$\text{Volume increase (\%)} = \frac{(W_s - W_p)D_p}{D_p \times W_p} \times 100$$

where W_s = weight of swollen polymer (g), W_p = original weight of polymer (g), D_p = density of polymer (g/cm³) and D_s = density of solvent (g/cm³).

The effects of chain scissioning or cross-linking can be assessed by the solubility measurements or by chromatographic techniques. Ideally, gel permeation chromatography (also known as size exclusion chromatography) can be used to follow the changes in molecular weight (Malawer, 1995; Maines and de la Rie, 2005). Simpler paper chromatographic techniques were originally used to follow these changes (Feller, 1971a) and can be sensitive diagnostic tools.

Feller has proposed a series of solvent mixtures that may be used to assess the removability of a picture varnish (Feller, 1976, 1978) (Table 2.5, Figure 2.19). Because the technique and the solvents closely match the practical application of the results, this method has proved useful in following changes in solubility and swelling of low-polarity coatings that have been aged, both artificially and naturally (de la Rie et al., 2002), allowing meaningful comparison over decades and between practitioners and researchers. The mixtures can be used in two ways. A simple test of the proportion of an ageing polymer that dissolves in each solvent mixture may indicate that the polymer requires increasingly polar solvents for dissolution, or that the polymer becomes insoluble in any solvent, or possibly both effects. Picture varnishes are normally removed by rolling solvent-laden swabs over the surface. The use of these solvent mixtures may indicate the least polar solvent required to remove the coating in a reasonable time. For a more accurate estimate of solution properties over a critical solvent range, the composition of the mixtures used can be adjusted in smaller steps. A considerable amount of information can be obtained by an experienced observer during this test, though methods of documenting the sensations are still idiosyncratic.

TABLE 2.5 Feller's Series of Solvents for Assessing Changes in Picture Varnishes, Having a Steadily Increasing Polarity

Solvent	Volume (%)			Teas Parameters		
Number	Cyclohexane	Toluene	Acetone	f_d	f_p	f_h
1	100	0		99	0	1
2	75	25		95	2	3
3	50	50		91	3	5
4	25	75		87	5	7
5		100		84	7	9
6		87.5	12.5	79	10	11
7		75	25	75	13	12
8		62.5	37.5	70	16	14
9		50	50	66	19	15
10		25	75	56	25	18
11			100	47	32	21

Data recalculated using recent Hansen Solubility Parameters (Hansen, 2007).

2.8.3 Dirt Pick-Up (Wagner and Baumstark, 2002)

A film may be applied to a white tile or a glass sheet and placed in a suitably dusty environment. Two effects can be noted – the amount of dust adhering to the surface and the amount of dirt held by the polymer after washing. The attraction exerted by a polymer on dust particles depends partly on the static charges that build up on the surface. In many cases the likelihood of incorporation of dirt into a polymer will be related with the glass transition temperature of the polymer.

2.8.4 Effect of Polymer on Mechanical Properties (Anderson, 1977)

The adhesion of a polymer film to a substrate is the major reason to apply a polymer to a substrate. However, each application has its own criteria of success and failure, resulting in a large number of specific industrial tests, e.g. for coatings (Nelson, 1995). Conservation can use some of the industry standard tests but frequently needs to create new tests reflecting the relevant properties, particularly the long time scales and low strain rates experienced by heritage items. Creating a new test protocol is time consuming because many potential variables, e.g. substrate properties, humidity, strain rate, adhesive type, must be explored in order to define the limits of validity, experimental error within and between research

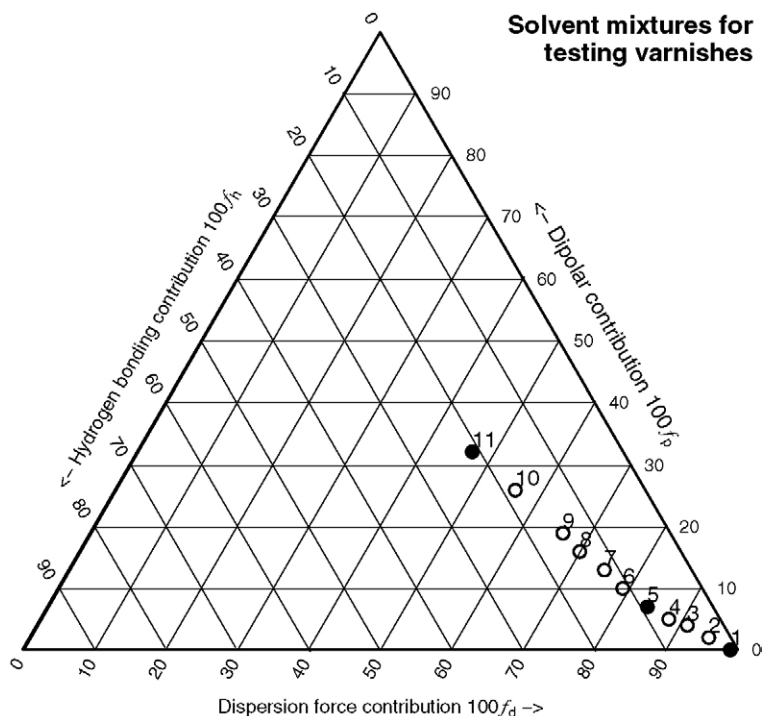


FIGURE 2.19 Teas plot of solvent mixtures of cyclohexane (1), toluene (5) and acetone (11) for assessing the solubility of picture varnishes (see Table 2.5 and Section 3.2). **Sources:** *Feller (1976, 1978).*

laboratories, and usefulness. As in many areas of investigation, a lot of effort is expended finding out what question would provide the most insightful answer.

Tensile testing of the adhesive bond has been carried out on leather (Belaya, 1970; Kronthal et al., 2003), painting canvases (Berger, 1970; O'Malley, 1990; Young et al., 2002), textiles (Leene, 1972; Pretzel, 1997; Karsten and Down, 2005), fossil bone (Vestergaard and Horie, 1996) and paper (McGlinchey and Yuan, 2004). The consolidation of weak materials is more difficult to assess, both theoretically and practically, reflected in the relatively few studies in this area, e.g. on textiles (Hedley, 1975; Halvorson and Kerr, 1994) and paper (Burgess and Grattan, 1991), but more commonly on stone (Wheeler, 2005) and wood (Schniewind and Kronkright, 1984).

2.8.5 Accelerated Ageing (Feller, 1994)

Predicting the changes in properties that will occur over an extended period of natural ageing is a problem that occupies many industrial scientists. Even though techniques have been refined, accelerated ageing processes have been

shown to be only crude approximations to the natural situation. The conclusions of accelerated ageing tests will always need to be verified by comparison with naturally aged materials (Horie, 2009). With increasing sensitivity of analytical tools, one can discern the effects of natural ageing in shorter times and thus enable correlation with accelerated ageing tests. These are powerful experimental tools but must be used with care and understanding of their defects.

There are two main methods of accelerating the ageing process:

1. by concentrating on the effects of only one environmental influence, e.g. light, while keeping other influences constant; or
2. subjecting the sample to extremes of all the influences expected, e.g. in weatherometers.

The former method is a sharp tool to clarify and study single effects that are combined in the latter experiments. If one is studying beefsteak and using a scalpel to divide it up, one may never discover how tough it is.

The usual technique is to choose the apparently important influences and subject the material to extreme conditions of these. It is important that the extreme conditions employed are the same conditions, but magnified, as will be experienced in normal existence. As with all experiments, it is important to ensure that the measurements of conditions of exposure are calibrated against traceable standards, e.g. temperature, humidity, spectral distribution, etc. No instrument is perfect so a measurement of its error must be made. For instance, before an ageing chamber is used, the uniformity of relative humidity (RH) in the volume used for samples must be assessed. Thorough testing frequently involves using three replicates of each sample being placed at random in different parts of the chamber to assess the error caused by the variability of exposure. Similarly, reports of light exposure testing should include, explicitly, the variability of the light exposure across the samples.

The following paragraphs indicate the methods by which ageing might be accelerated. Relevant properties of the polymer and polymer/substrate may then be reassessed to follow the changes.

Light

Materials absorb radiation in a number of ways. Chemical changes induced in a polymer on heritage items are usually caused by ultraviolet (UV) or light (visible radiation), which are absorbed by the material causing activation of the chemical bonds. The changes depend on two principal factors: the quality and quantity of radiation. An alteration in the quality of the radiation, e.g. by changing the higher energy ultraviolet content, can change the type of reaction. In most cases, radiation will produce the same effect whether provided at a high intensity for a short time or at a low intensity for a longer time. This 'reciprocity law' is the basis of accelerated ageing but there are exceptions, e.g. some oil paints are bleached by strong light; many coloured materials apparently contain a small proportion of an extremely fugitive component, which results in a very fast initial change in colour on exposure (Crews and Crews,

1987; Horie, 1990). High-intensity light will cause heating, which may lead to drying of the specimen or raising of the temperature above the glass transition temperature of the polymer. A specialist light-ageing apparatus is available (BS EN ISO 105-B02:1999, 1999; ASTM G155-05a, 2005), though a somewhat slower but more easily managed light source is a bank of fluorescent lamps (Bilz and Grattan, 1993). These radiate little heat, have closely controlled and specified spectral output, can match closely gallery conditions and, as important, are relatively inexpensive to install. It is of course important to check and allow for the variability of exposure across the apparatus. Running 24 hours a day with greater exposure to radiation, they cause ageing faster than would be experienced on a moderately lit gallery. However, these conditions have not yet been standardized between research groups so it can be difficult, if not impossible, to make direct comparison between their results (Saunders and Kirby, 2001).

The monitoring of total exposure to radiation is a necessary part of testing. A widely used method of monitoring light exposure is the use of blue wool fading standards (BS EN ISO 105-B01:1999, 1999). The eight standards have been chosen to fade at different rates. Standard 1 is very fugitive, fading visibly in an hour of sunlight. The dye of Standard 8 is so light-fast that the wool disintegrates when fading occurs. Unfortunately the assessment and interpretation of the results requires care. It is important that the spectral output of the source and relative humidity during exposure be determined if realistic comparisons are to be made between different experimental conditions.

If the material becomes unserviceable before blue wool Standard 3 starts to fade visibly, it is placed in Feller's class C (Section 2.7) (Feller, 1978). If the material is more stable than Standard 3 but deteriorates before Standard 6 starts to fade, it is placed in class B. Those materials that survive as well or better than Standard 6 are placed in class A. Feller has suggested some standard polymer materials that can be compared to the material under test when light-ageing; these are Paraloid B-72 for class A and poly(n-butyl methacrylate) (Elvacite 2044) for class B.

Heat

At absolute zero (-273°C , 0 K), there is no movement or reaction. In order to increase the temperature, one has to supply energy. This energy goes into making the atoms move and collide violently. A small proportion of the collisions will result in chemical reactions. The higher the temperature, the more energy is available and the more likely are the chemical reactions to occur. Reactions that require low energy to activate them will occur at low temperatures. The rate of a chemical reaction is thus determined by the activation energy of the reaction and the temperature. This relationship is shown mathematically by the Arrhenius equation (see Mills and White (1994) and Feller (1994) for further discussion):

$$k = Ae^{-E_a/RT}$$

where k =rate constant for the reaction, A =a constant, E_a =activation energy (kJ/mol), R =gas constant (8.31 J/K/mol) and T =temperature (kelvin).

According to this equation, increasing the temperature increases the reaction rate. However, reactions with different activation energies are affected to different extents. On increasing the temperature, all the reactions will speed up but the relative importance of the reactions will change as well. The rate of a reaction can be assessed from simple observations of a change in the property of the material, e.g. yellowing, or by more complex analyses of the reaction processes. Figure 2.20 shows two possible results. The solid straight line demonstrates the normal situation – a single reaction with an activation energy of 100 kJ/mol. From a knowledge of this straight line, the change occurring at any given combination of temperature and time can be confidently predicted. However, the curved line is an example of a more complex situation, two reactions occurring together. One has an activation energy of 100 kJ/mol, the other an activation energy of 250 kJ/mol. Without some knowledge of the shape and slope of the

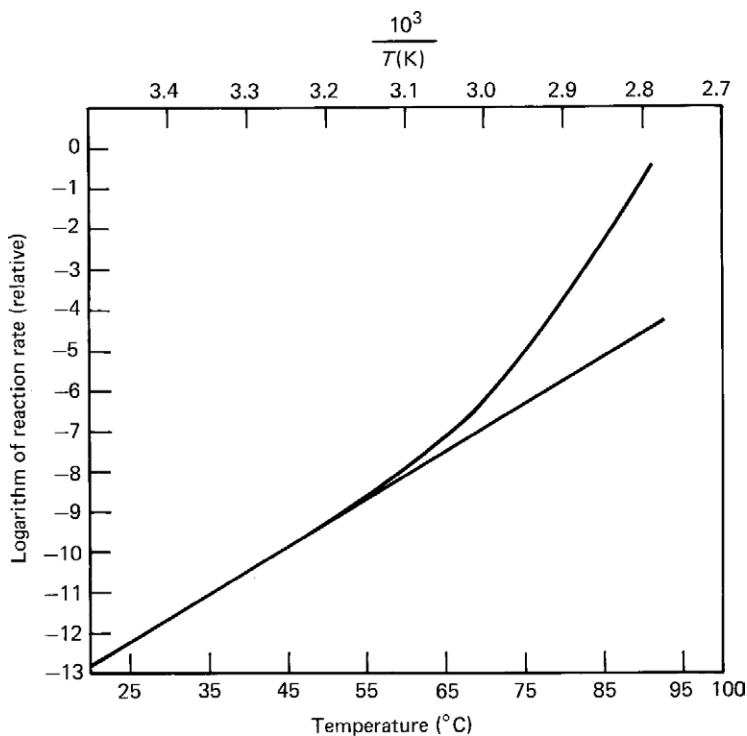


FIGURE 2.20 Comparison between the rates of deterioration at different temperatures of two different (hypothetical) materials. The straight line is for a material with a single deterioration reaction with an activation energy of 100 kJ/mol. The curved line is for a material with two simultaneous reactions with activation energies 100 and 250 kJ/mol. The reaction rate is on a logarithmic scale.

curve, predicting properties from single measurements can be misleading. One has to be careful to test the reaction which occurs at elevated temperatures is the same as occurs at room temperature.

Failure to do this can result in seriously wrong conclusions. One example of this occurred when assessing Parylene, poly(*p*-xylylene). The initial experiments carried out between 200 and 125 °C provided estimated useful lifetimes at room temperature of this interesting material at 3880 (Parylene N, activation energy 141 kJ/mol) and 132,000 (Parylene C) years, prompting the statement that these materials were stable conservation materials (Grattan and Bilz, 1991). Extending the experiment to lower temperatures takes longer. When the experiment was later carried out down to 68 °C, the useful lifetimes at room temperature were re-estimated and reduced to 11 (Parylene N, activation energy 67 kJ/mol) and 15 (Parylene C) years (Bilz and Grattan, 1996), with shorter periods (0.3–2.3 years) seen with photolytic ageing. The use of unstable Parylene in conservation can be justified only in extreme cases.

The importance of ensuring that the conditions used for accelerated ageing match those of actual use is demonstrated by cellulose triacetate cinema film, used to make archival copies from degrading cellulose nitrate film. Cellulose acetate (CA) film was tested by ageing strips hanging in glass vials at various temperatures, resulting in an estimated useful life of 100–300 years (Adelstein and McCrea, 1981; Ram and McCrea, 1988), thus validating the wholesale copying (and destruction) of the original films on cellulose nitrate (CN). However, after only a couple of decades, film archives were coping with a major problem of CA degradation, the vinegar syndrome, while the remaining CN films were in relatively better condition. Carrying out accelerated ageing of film reels stored in the normal steel tins produced an estimated life for CA films of 35 years (Allen et al., 1992). The hydrolysis reaction was complicated by auto-acceleration of film degradation by acetic acid trapped within the film and the acid corrosion and migration of the iron into the film, where it acted as a potent oxidation catalyst. Similar questions have been raised about past research on paper deterioration (Calvini and Gorassini, 2006).

One would not expect a conservation material to have a degradation reaction with an activation energy below that of good-quality paper, about 95 kJ/mol, or indeed cellulose, around 120 kJ/mol (Strlic and Kolar, 2004). Recent research has confirmed that cellulose seems to deteriorate in an uncomplicated way, and heating samples can be a valid method for predicting the lifetime of paper, though there is no widely applicable methodology. The differences in ageing reactions and thus measurable properties caused by variables such as humidity, temperature, bulk and single sheet, impurities, etc. have yet to be teased out before an accelerating regime with wide validity can be proposed.

The situation is complicated with synthetic polymers. On raising the temperature above the glass transition temperature, many properties change, including the rates of the deterioration reactions. It is usual to have a disconti-

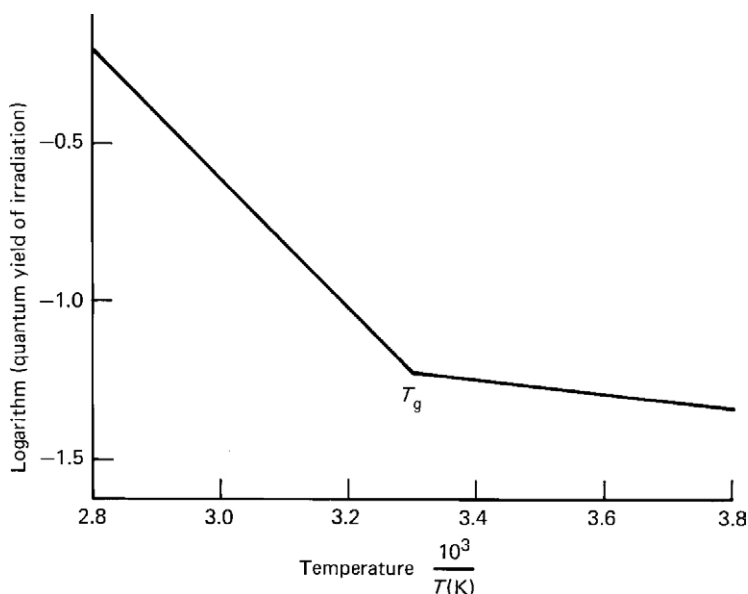


FIGURE 2.21 The rate of chain scissioning of poly(vinyl acetate) (Mowilith 70) (Hoechst) under the influence of ultraviolet light (253 nm) at different temperatures. This Arrhenius plot has been drawn conventionally with temperature increasing to the left. The rate of reaction increases markedly around the T_g (30 °C) on increasing the temperature. **Source:** *Geuskens et al. (1972)*.

nuity in the line at T_g as the material changes. One must ensure that raising the temperature of the test does not change the polymer from its glassy to the plastic state (Figure 2.21), or vice versa for polymers plasticized by water. Where a polymer is to be applied or used at high temperatures, e.g. poly(ethylene oxide) and wax, it should also be tested in that condition.

Water

Many polymers are used in contact with water. The conditions may be made more extreme by heating the water (but see above), by changing the pH or dissolved salts, or by using alternating wet/dry periods. Polymers that react with water, often by hydrolysis, will be sensitive to changes in pH. A notable example reported in conservation is the cross-linking of soluble nylon in even mildly acidic conditions (Bockhoff et al., 1984).

Impurities

Reactions between the added material and the materials of the object can cause changes in both the polymer and object. It would be useful for screening tests to be carried out using model objects. This procedure is routinely used in paper conservation research, where the chemical variation between objects is relatively minor. Unfortunately, it is carried out infrequently.

TABLE 2.6 Polymers Affected by Water

Polymer	Effect of Cold Water	Effect of Hot Water After Soaking in Cold	Colour Reaction with Iodine Solution ¹	Effect of Organic Solvents
Methyl cellulose	Soluble	Gels at >54 °C	None	No effect (with current products)
Ethyl hydroxyethyl cellulose	Soluble	Precipitates >40 °C	None	No effect
Hydroxyethyl cellulose	Soluble	Soluble	No effect	
Hydroxypropyl cellulose	Soluble	Precipitates <40 °C	None	See Appendix 3, Figure A3.20
Sodium carboxymethyl cellulose	Soluble	Soluble	None	No effect
Starch	Swells (translucent)	Soluble >80 °C	Deep blue	No effect
Dextrin	Soluble	Soluble	No effect	
Agar	Swells (translucent)	Soluble >85 °C	Crimson	No effect
Gum arabic	Soluble	Soluble	None	No effect
Glue	Swells (transparent)	Soluble >40 °C	No effect	
Casein	Swells (translucent)	Swells	None	No effect
Poly(vinyl pyrrolidone)	Soluble	Soluble	None	See Appendix 3, Figure A3.17

TABLE 2.6 Polymers Affected by Water continued

Polymer	Effect of Cold Water	Effect of Hot Water After Soaking in Cold	Colour Reaction with Iodine Solution ¹	Effect of Organic Solvents
Poly(vinyl alcohol)	Swells (transparent) (degree of hydrolysis <92% soluble)	Soluble	Green	Few (Section 7.2)
Poly(ethylene glycol)	Soluble	Soluble	Brown precipitate	See Appendix 3, Figure A3.19
Poly(vinyl acetate)	Swells (white) may disperse	Swells		See Appendix 3, Figure A3.6

¹Test solution: dissolve 3.3 g potassium iodide in 40 ml water, dissolve 2.54 g iodine in solution, dilute to 200 ml with water, add to a dilute solution of the polymer.

2.9 IDENTIFICATION OF POLYMERS

Many different polymers have been used on objects. The choice of treatment or reversal methods frequently depends on knowledge of the polymers used in the past on the object. The unambiguous identification of a polymer may require the sacrifice of large samples, though increasingly the availability of spectrometers (e.g. Macdonald et al., 2005; Tennent et al., 2009) is enabling the provisional identification of materials without sampling, non-destructively. Differentiating between similar copolymers may require the synthesis of samples of known composition to enable detailed comparison with the unknown (De Witte et al., 1978). The use of simpler methods (Braun, 1982) is a compromise between ease of use and rigorous identification.

In some fields of conservation, relatively few polymers have been used. Identification is then simplified to distinguishing between a handful of alternatives. Unfortunately, most polymers have been altered by natural ageing and may give different results from those found with modern equivalents. In addition, mixtures of polymers or additives can complicate the identification process by giving positive results in a confusing manner. The first stage is to remove the polymer (safely) from the object, by scraping some off or by dissolving it. Frequently the physical properties provide valuable pointers to the likely polymer. A preliminary evaluation of a polymer can be made by the solubility in organic solvents (Table 2.6) and in water (Table 2.7). Reaction with iodine solutions can provide additional clues for water-soluble materials (Table 2.6) and water-insoluble materials (Howie, 1995). Further investigations need resources beyond those found in most conservation laboratories.

TABLE 2.7 Solvents for Recent Samples of Thermoplastics, 10% Solution

Ethanol	Acetone	1,1,1-Trichloro-ethane	Toluene	Cyclohexane
Shellac	PMMA	Dammar	Dammar	Dammar
PVB	PEMA	Mastic	Mastic	PBMA
Mastic	PBMA	PEMA	PMMA	PS
Ketone resin	PVAC	PBMA	PEMA	Natural
	CA	PVAC	PBMA	EVA
	CN	PS	PS	
		Chlorinated rubber	PVAC	
		Ketone resin	Chlorinated	
		Beeswax	Natural rubber	
		EVA		
		Natural rubber		
Soluble nylon >40 °C		PE >82 °C	PE >66 °C	PE (hot)

Other polymers: PVC and PVDC dissolve in only a few ketones. PTFE dissolves in nothing.

Abbreviations: CA, cellulose diacetate; CN, cellulose nitrate; EVA, ethene/vinyl acetate copolymer; PBMA, poly(butyl methacrylate); PE, polyethylene; PEMA, poly(ethyl methacrylate); PMMA, poly(methyl methacrylate); PS, polystyrene; PTFE, polytetrafluoroethylene; PVAC, poly(vinyl acetate); PVB, poly(vinyl butyral); PVC, poly(vinyl chloride); PVDC, poly(vinylidene chloride).

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Solvents

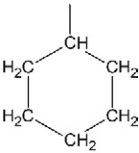
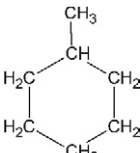
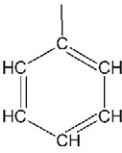
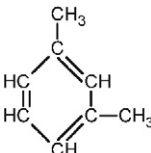
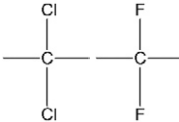
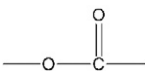
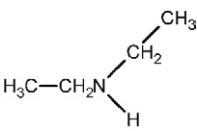
A solution may be obtained by a reversible chemical interaction, e.g. dissolving sugar in coffee, or by an irreversible reaction, e.g. dilute nitric acid on limestone. The solvents discussed below are primarily the mobile organic liquids (and water) that undergo reversible interactions with their solutes (the solids, liquids or gases that are dissolved). Occasionally the more reactive solvents, particularly the amines, are used to alter a polymer, perhaps by hydrolysis, to ease its dissolution. Some mobile liquids modify an object's properties. For instance, water makes organic materials such as cellulose more flexible by reacting (reversibly) with the polymer. In this case, water partly swells the polymer, so plasticizing it. Because of the increasing need to control emissions harmful to the environment and people, new solvent classes are being introduced. Liquefied gases, particularly carbon dioxide, are being introduced as solvents, but will not be considered here.

3.1 CHEMICAL TYPE AND PURITY

Solvents are used for three main purposes in conservation – for cleaning off contaminants (Durkee 2006), for applying polymers, or for removing polymers. When choosing a solvent there are many properties that must be considered: chemical type and purity, solubility parameters, evaporation rate, toxicity and flammability. These properties are dealt with below and listed in [Appendix 2.1](#). Many other properties such as density, optical properties and diffusion rate can be important, and details may be found in standard texts (Wypych, 2001; Marcus, 2002; Ash, 2003; Reichardt, 2003; Stoye, 2005).

Solvents are usually classified by the functional groups of the molecule. The most used classes are listed in [Table 3.1](#) and in [Appendix 2.1](#). Each solvent of a class has properties similar to other members of the class. Solvents transformed the ability of technology, and conservators, to manipulate materials. However, widespread use has been shown to have many deleterious side-effects such as toxicity, flammability, damage to water and air quality, effect on the ozone layer, cost, etc. New solvents are being introduced to reduce these effects, e.g. the use of siloxane-based fluids (Cull and Swanson, 2001) or propylene glycol-derived solvents replacing ethylene glycol-derived ones.

TABLE 3.1 Functional Groups in Solvents

Class	Characteristic Group	Example	Cas No.
Aliphatic (paraffinic)	$\text{H}-(\text{CH}_2)_n-\text{H}$	$\text{H}-(\text{CH}_2)_7-\text{H}$	n-Heptane 110-54-3
Cycloparaffinic (naphthenic)	 Cyclohexyl	 Methylcyclohexane	108-87-2
Aromatic	 Phenyl	 m-Xylene or 1,3-dimethylbenzene	108-38-3
Halogenated		$\text{Cl}_3\text{C}-\text{CH}_3$	1,1,1-Trichloroethane 71-55-6
Ether	$-\text{O}-$	$\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5$	Diethyl ether 60-29-7
Ester		$\text{C}_2\text{H}_5-\text{O}-\text{C}(=\text{O})-\text{CH}_3$	Ethyl acetate or ethyl ethanoate 141-78-6
Ketone		$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{CH}_3$	Acetone or propan-2-one 67-64-1
Alcohol	$-\text{OH}$	$\text{H}_5\text{C}_2-\text{OH}$	Ethanol 64-17-5
Amine	 	Diethylamine	109-89-7

Most solvent molecules are made up of two or more functional groups, e.g. diacetone alcohol (aliphatic, ketone and alcohol) or benzylamine (aromatic and amine).

3.2 SOLUBILITY PARAMETERS (BARTON, 1991; PHENIX, 1998b; SILLA ET AL., 2001)

Subjectively, it is appreciated that ‘like dissolves like’, but this aphorism is insufficient to predict the effect of a solvent on a polymer. No one has yet managed to tie down ‘like’ (Özdemir and Güner, 2007). Ethanol is a solvent for shellac but is very weak for wax. Hydrocarbon solvents have no effect on shellac yet are solvents for wax. Early attempts to quantify the strength of a solvent used empirical methods. The kauri gum–butanol number (ASTM D1133-09, 2009) is obtained by adding a test hydrocarbon (non-solvent) to a solution of the gum in butanol. The number of millilitres of the non-solvent required to induce precipitation of the gum is the K-B number. This is widely used for specifying the solvent power of hydrocarbons. A series of three solvents – cyclohexane, toluene and acetone – were developed by Feller (1976) for testing the ageing (increasing polarity) of picture varnishes (Table 2.5). Although these schemes work well within the discipline for which they were developed, they are of little general applicability.

‘Like dissolves like’ is the intuitive realization that the forces between the molecules of a good solvent must be about the same as those between the molecules of polymer (Figure 3.1). The kauri–butanol experiment starts with a solution and, by changing the composition of the solvent (A), reduces the interaction of the solvent with the gum (B). The solute molecules bind closer to each other than to the solvent and insolubility develops.

If one mixes pure A with pure B, the forces between the molecules of A and B, F_{AA} and F_{BB} respectively, will be broken. Overcoming these forces requires energy, which can be provided by the energy released when the new interactions between A and B develop. This energy is quantified as the cohesive energy density of the two components, δ_A^2 and δ_B^2 , from which are derived the solubility

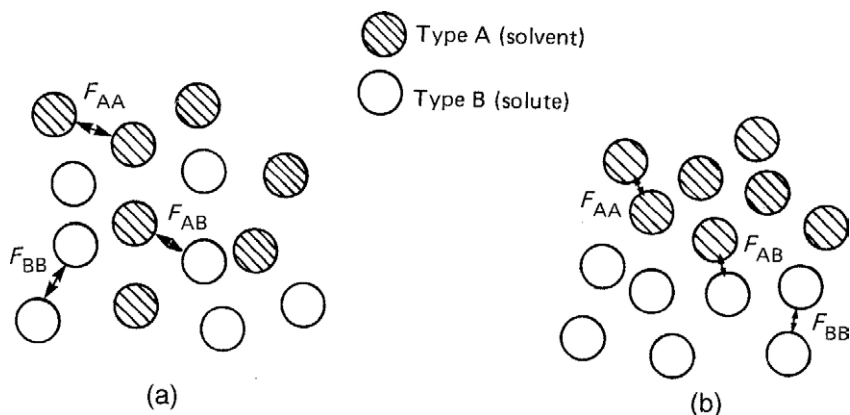


FIGURE 3.1 Schematic representation of the forces between solvent and solute. F_{AB} = forces between molecules of A and B. (a) If $F_{AB} \geq F_{AA}$ and $F_{AB} \geq F_{BB}$, the mixture is compatible and a solution forms. (b) If F_{AA} or $F_{BB} > F_{AB}$, the solution does not form and the molecule types separate out. **Source:** Brydson (1999).

parameters, δ_A and δ_B . The change from the neatly ordered A and B to a random mixture increases disorder (entropy), which increases with temperature. The increase in disorder increases the likelihood of a solution. One implication is that low-molecular-weight polymers will dissolve more readily than high-molecular-weight polymers. Conversely, solvent molecules are likely to be held strongly at high polymer concentrations.

The simple description of solubility behaviour using a single solubility parameter, δ , works only in the absence of strong polar and hydrogen bonding forces, which impose a structure on the liquid. Many descriptions using multiple components (up to eight) have been developed. The most widely used approximation is that of Hansen (2007), who proposed that the forces be considered additively, i.e.

$$\delta^2(\text{cohesive energy density}) = \delta_d^2 + \delta_p^2 + \delta_h^2$$

where δ_d^2 = contribution of dispersion forces, δ_p^2 = contribution of polar forces and δ_h^2 = contribution of hydrogen bonds.

The inadequate one-dimensional ranking of solvents is thus replaced by three partial solubility parameters.

To understand the interactions of solvents, one can start from the intermolecular forces. The forces acting between solvent and polymer molecules may be divided into three types (Figure 3.2):

- a. Dispersion force arises from the movement of electrons around molecules. This is a very weak force and is the only force that holds symmetrical molecules, e.g. methane, together. Very little energy is necessary to separate the molecules, and this accounts for the low boiling point of methane (-164°C). This force is present in all substances.
- b. Polar forces arise from non-symmetrical molecules that have an unbalanced distribution of electrons (dipole moment). This imbalance causes further attraction between the molecules, e.g. chloromethane has a higher boiling point (-24°C) than methane.
- c. Hydrogen bonds are an extreme form of polar attraction and occur when the hydrogen is directly attached to oxygen and nitrogen atoms. The subsequent attraction takes place between, for instance, an oxygen atom of one molecule and the hydrogen atom of another. Methanol has a much higher boiling point (65°C) than methane or chloromethane.

Methanol would therefore have three components of attraction, dispersion, polar and hydrogen bond forces; chloromethane would have two main components, dispersion and polar; and methane would only have dispersion forces.

The interactions of small solvent molecules are short range. However, the polymer molecules are much larger and they do not have sharply defined solubility parameters. The region of solubility can be drawn as a rough sphere in the three-dimensional space of partial solubility parameters. The description of a polymer's solubility characteristics by Hansen has four components – three partial

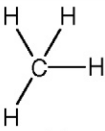
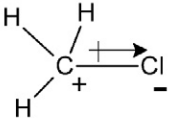
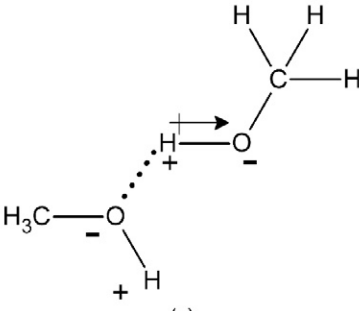
Formula	Compound	Boiling point °C	δd (MPa) ^{1/2}	δp (MPa) ^{1/2}	δh (MPa) ^{1/2}
 (a)	Methane CH ₄	-196	9.2	0	0
 (b)	Chloromethane CH ₃ Cl	-24	15.3	6.1	3.9
 (c)	Methanol CH ₃ OH	65	15.1	12.3	22.3

FIGURE 3.2 The forces between molecules. (a) Methane – a symmetrical molecule attracted only by dispersion forces. (b) Chloromethane – an asymmetric molecule with a permanent dipole. (c) Methanol – hydroxyl groups enable attraction between the oxygen and hydrogen atoms to create a hydrogen bond. The amount of force between molecules is indicated by the boiling point. Methane requires very little energy to break the forces between molecules, so the boiling point is low. As the forces between the molecules increase, so does the boiling point and the contributions from the different types of forces.

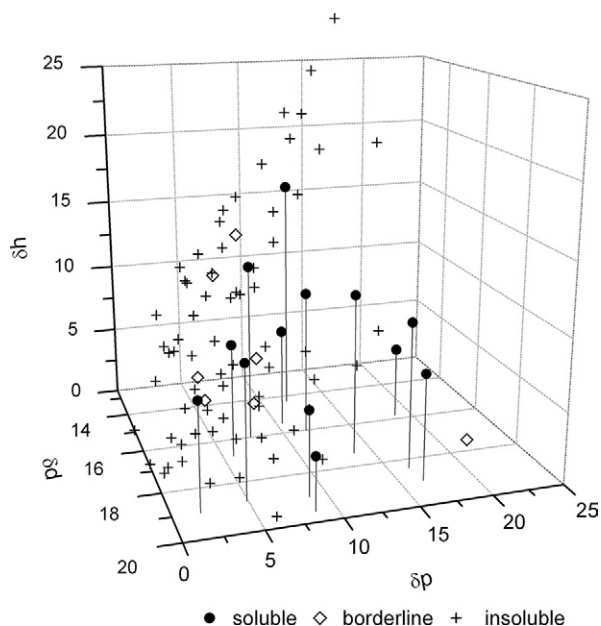


FIGURE 3.3 Hansen solubility plot (three-dimensional) for cellulose acetate (Hansen, 2007), with Hansen partial solubility parameters, δ_d , δ_p and δ_h , in $\text{MPa}^{1/2}$. See [Figure A3.28](#) for the same data plotted in a ternary Teas chart.

parameters defining the centre and the radius of the sphere (see [Appendix 2.1](#)). To display these values graphically on a sheet of paper presents difficulties ([Figure 3.3](#)). Interpolations are even more difficult to visualize. The solubility parameters of a mixture of solvents can be worked out as an arithmetic average of the components' parameters and compared with the resultant position on the 3D plot. An accessible computer program is available to help the calculations of solubility parameters for proposed mixtures ([Stavroudis and Doherty, 2007](#)).

The cohesive energy density is defined as the energy per unit volume, and the solubility parameter is the square root of that. In the cgs system of units, the cohesive energy density was measured as cal/cm^3 , so the solubility parameter was $(\text{cal}/\text{cm}^3)^{1/2}$. In the current SI system used in this text, cohesive energy density is given in MPa, so the solubility parameter is $\text{MPa}^{1/2}$. Multiply the old $(\text{cal}/\text{cm}^3)^{1/2}$ value by 2.046 to convert to $\text{MPa}^{1/2}$.

A way of providing the description in two dimensions is to rank solvents by both solubility parameter and hydrogen bonding ability ([ASTM D3132-84, 1996](#)). Unfortunately the values of the hydrogen bonding index were based on obsolete data, and this reduces the value of this description.

In an effort to retain the three components in a two-dimensional description, Teas ([Gardon and Teas, 1976](#)) proposed a triangular graph ([Appendix 3](#)), using reduced solubility parameters, derived from Hansen's partial solubility

parameters. The three components, f_d , f_p and f_h , add up to 1 but are usually expressed as a proportion of 100:

$$100f_d = 100 \times \frac{\delta_d}{\delta_d \times \delta_p \times \delta_h}$$

where f_d = fractional cohesion parameter (dispersion component), δ_d = Hansen's solubility parameter (dispersion component) and $\delta_d + \delta_p + \delta_h$ = solubility parameter (total).

f_p and f_h are derived similarly from δ_p and δ_h .

Solubility parameters for mixtures of solvents are derived from the weighted average by volume of the various components. The fractional parameters for a mixture of two solvents would be derived thus:

$$f_d = \frac{v_1 f_{d1} + v_2 f_{d2}}{v_1 + v_2}$$

where f_d = dispersion partial solubility parameter of mixture, v_1 , v_2 = volumes of the two components, and f_{d1} , f_{d2} = dispersion partial solubility parameters of the components.

f_p and f_h are derived similarly.

The outer perimeter of solubility on the solubility chart of a polymer can be indicated by drawing a line outside all those solvents that dissolve the polymer. As the dispersion forces are much the weakest, this plot squeezes the less polar solvents into the bottom right corner and distorts the solubility curve out of the circular shape, which is intuitively more likely. Because the solubility parameters are additive, it is possible to mix two non-solvents of a polymer, at opposite sides of the soluble area, to create a combined solvent that will dissolve the polymer. This is reflected in Figure 2.19, where the solubility parameters of mixtures do not fall on a straight line.

Insights into the complexity of solvent interactions are increasing and being reflected in the descriptions of solution behaviour. For instance, smaller solvent molecules such as methanol are more likely to dissolve a polymer than their position on a chart would indicate (Miller-Chou and Koenig, 2003) and smaller polymer molecules are also more likely to have a large region of solubility. Most solubility parameters assume that solvent is a homogeneous material and are derived from measurements of bulk properties. However, the actual interactions are largely on a molecular basis. Much of the re-evaluation of solution behaviour incorporates these molecular interactions into theoretical models that have useful predictive power, greater than the existing ones such as Hansen. For instance, 'like dissolves like' is complicated by the mutual attraction of opposites, producing interactions specific to the pair of compounds.

Polar forces result from two types of molecular interaction. Two dipolar molecules will naturally orientate themselves positive to negative, producing a force between them depending on the strength of the dipoles. In addition, a dipolar molecule will induce a dipole in a neighbouring molecule, depending on the strength of the dipole and the polarizability of the neighbour. So each molecule should be characterized by the two factors, its dipole and its polarizability.

Hydrogen bonding occurs as the result of a molecule having a partly charged hydrogen atom giving a hydrogen bond (e.g. trichloromethane), or a partner molecule accepting the hydrogen bond (e.g. acetone), or both (e.g. ethanol). Again, a molecule can be characterized by the two factors, hydrogen bond donation and acceptance.

These interactions, particularly the hydrogen bond, create structures within a pure solvent, notably water but also self-associating molecules such as formamide and acetic acid. The strength of the structure can cause other structures to form in the solute. When dissolved in water, surfactants self-organize into micelles as the hydrophobic tails are excluded from the hydrogen-bonded water to form stable non-polar regions. Smaller but similar effects are observed in the interactions with alcohols and acetone (Song and Peng, 2008).

The situation becomes more complex with mixtures of solvents (Marcus, 2002). A simple example of specific interactions between solvents is seen in azeotropes, where the boiling point of a mixture is not predictable by extrapolating from a knowledge of the boiling points of the components. These interactions are reflected in the uncertainty in making predictions about evaporation at room temperatures (Figure 3.4), and will also affect the properties of polymer solutions.

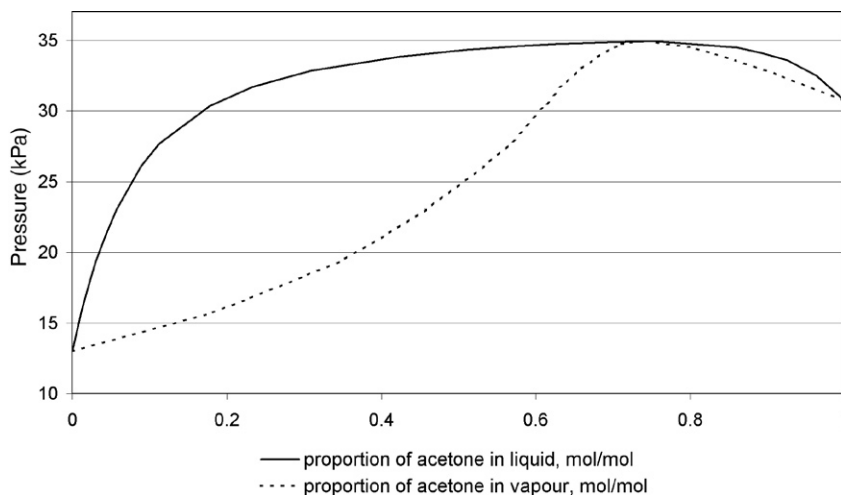


FIGURE 3.4 Evaporation of a mixture of acetone and cyclohexane at 25°C. If a mixture of acetone–cyclohexane (50:50) is allowed to evaporate, the vapour that comes off will have a composition of $\approx 69:31$, i.e. acetone will evaporate preferentially. This progressively changes the composition of the mixture until, at 74% acetone, the vapour that comes off is also 74% acetone. This constant evaporation mixture will then evaporate until dry. Similarly if one starts with a mixture of acetone–cyclohexane (90:10), the vapour that comes off will have a composition of $\approx 83:17$, i.e. cyclohexane will evaporate preferentially until the azeotropic composition of 74% acetone is reached. The change of solubility parameters of the solvent will affect the stability, viscosity, etc. of a polymer solution. Azeotropes are usually described as constant boiling mixtures, but their behaviour at room temperature is more important for conservators. There are fewer published details of the mixtures at room temperature. The effect of the dissolved polymer on the relative evaporation rates has yet to be elucidated.

Source: Tasic *et al.* (1978).

Hansen's system is being developed to be the most widely accessible method of predicting solubility with improvements to the underlying theoretical basis and methodologies for determining (and predicting) the partial parameters (e.g. Stefanis and Panayiotou, 2008). The value of parameters (for solvents and polymers) change as more data are gathered and methods of estimation improve. One should be careful in comparing values to make sure that they are consistent. Hansen's system cannot account for a number of factors such as highly hydrogen-bonded polymers and molar volume (McGlinchey, 2002), so a range of other approaches are being developed (e.g. Phenix, 1998a; Senichev and Tereshatov, 2001). Unfortunately, it has been suggested that describing solvent behaviour may take nine separate parameters (Katritzky et al., 2004), which would need to be manipulated by computer modelling. Changes of temperature have greater effect on solvents than polymers (except either side of the T_g), so predicting solution properties over a range of temperatures must allow for this.

3.2.1 Use of Solubility Charts

On the simplest level, Teas charts (see Appendix 3), derived from manufacturers' or conservators' data, can provide a visual summary of the solubility of the polymer of great use when the properties of a number of polymers or solvents are being compared. However, they should be used with caution and only for narrowly defined comparisons. The concepts and data used in these charts are known to be incomplete and compress multidimensional properties on to a flat sheet of paper. There is much overlapping of the solvents and non-solvents on the charts. The conclusions must be checked when dealing with unfamiliar materials. The Teas fractional parameters used in this book are derived from recent Hansen solubility parameters (Hansen, 2007).

Solubility parameters are useful in predicting the effects of mixed solvents and in situations where two polymers having overlapping solubility areas are present. The charts have been found particularly useful when looking at trends working with mixed solvents (Smith and Johnson, 2008). Dissolved polymers will affect the solubility parameter of the solution. For instance, addition of the relatively polar MS2A to a non-polar solvent caused dissolution of underlying polymers that were unaffected by the solvent alone (Sutherland, 2000; Smith and Johnson, 2008). These problems are often encountered in painting conservation, where the object is itself affected by solvents and affects the solvents. The experimental data of past investigators have been evaluated using developing descriptions of solvent parameters (Phenix and Sutherland, 2001). However, new data are being gathered and interpreted with changing knowledge of solvent interactions (Phenix, 2002; Zumbühl, 2005).

3.3 EVAPORATION RATE

The boiling point of a solvent gives only an approximate indication of its volatility. The rate at which a solvent evaporates at room temperature is dependent on

many factors, such as the vapour pressure, the heat of vaporization, the presence of solute and the rate of heat supply. Because of the many variables, one should therefore compare evaporation rates only where the technique of measurement is identical (Yuh, 1995). Different methods measure rates. For instance, xylene has an evaporation rate of 0.7 (relative to butyl acetate = 1 (ASTM D3539-87, 2004) – low number has low volatility) and 15 (relative to diethyl ether = 1 (DIN 53170, 2009) – low number has high volatility). Solvents are divided into three groups according to the evaporation rate (relative to butyl acetate, Appendix 2.1):

1. High-volatility solvents, >1.5
2. Medium-volatility solvents, 1.5–0.4
3. Low-volatility solvents, <0.4.

High-volatility solvents are used to reduce the time for film formation, and so convert the mobile solution into a non-slumping film as soon as possible. Heat is removed by the evaporating vapour, and this cools the solution. The cooling can lower the temperature of the surrounding air below the dew point, causing precipitation of water from the atmosphere. If the condensed water dissolves in the solution, the polymer is likely to precipitate. This results in a white bloom or blush in the film. If the water is insoluble, it will lie on the surface, cause unevenness and create a matt finish, which may be desired. These effects can be countered by incorporating in the formulation medium- or low-volatility solvents that will evaporate after the water has gone. The better of these solvents form azeotropes with water, and this ensures the removal of the water before the film becomes immobile. These solvents include butanol, butan-2-ol, methyl, ethyl and butyl acetates, and 1,2-dichloroethane (Speight et al., 2005). Mixtures of solvents themselves form azeotropes and their suitability must be tested before use.

The selection of solvents for applying a polymer will depend on the method of application. An adhesive or brushing lacquer will have a high proportion of high-volatility solvents. For spraying, such a formulation would give rise to stringing or cobwebbing caused by the premature evaporation of the solvent in flight. A greater proportion of medium-volatility solvents is therefore used. The low-volatility solvents are rarely used as they result in delayed shrinkage of the film.

3.4 HAZARDS (LEWIS, 2004; URBEN, 2007)

Care is required whenever chemicals are stored, used or discarded. Fume-extraction facilities should be used whenever necessary. These should be tested and maintained. Sometimes one is able to exchange a dangerous solvent for a less hazardous one that has similar solvent properties. The hazards of solvents fall into three main categories: flammability, toxicity and environmental. For a more complete listing of the hazards and test methods, standard texts should be

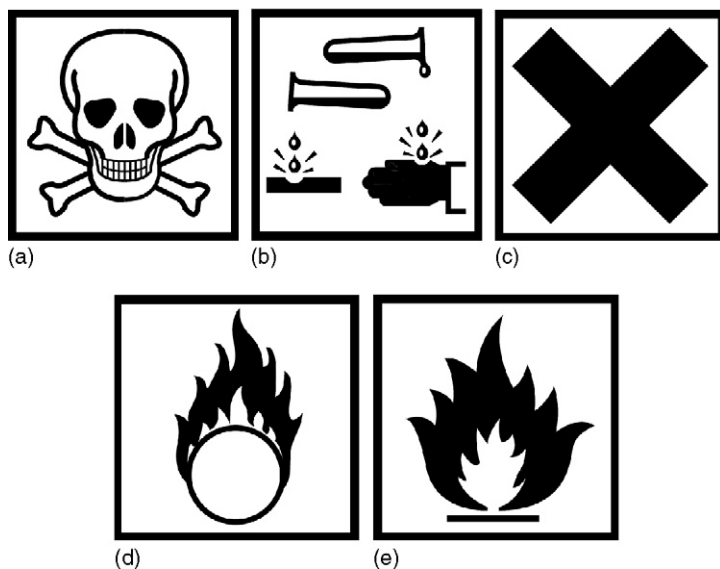


FIGURE 3.5 Typical hazard warning labels for containers of chemicals, mandatory within the European Economic Community (to 2015). The label will usually be accompanied by a phrase defining more accurately the particular hazard. The absence of a hazard label on a container does not necessarily mean that no hazard exists – just that no hazard has been legally identified. See [Appendix 2.4](#) for further details and for the replacement Globally Harmonized System labels.

consulted. The following is no more than an indication of the possible dangers. Advice should be sought periodically from a local expert as a check against the unconscious introduction or continuation of unsafe practices (NRC, 1995). Ensuring the safe use of potentially dangerous materials is normally the responsibility both of the person using the material and of the supervisor of the laboratory. The transport, storage and use of solvents is closely regulated in each country (e.g. NFPA 704, 2007; EAC, 2009; HSE, 2009), and local regulations should be consulted and complied with before use. Every container should have the name of its contents clearly and indelibly attached with a label displaying the symbols of the hazards associated with the contents (Figure 3.5 and [Appendix 2.3](#)). Each country has had its own labelling system until recently. A Globally Harmonized System of Classification and Labelling of Chemicals (GHS) has been developed, providing for standardized hazard ratings and appropriate labels (UNECE, 2009).

3.4.1 Flammability (NFPA 325, 2001)

All organic solvents, except the highly halogenated ones, are flammable. As a solvent fire must start in the air/vapour mixture, the more volatile solvents are

more readily ignited. The flash point is the lowest temperature at which a flame above the liquid will cause the vapour to ignite ([Appendix 2.1](#)). Obviously, the lower the flash point, the more likely is the vapour to ignite at room temperature. Any large containers of solvent, over 1 litre, should be housed in closed steel cabinets. Cabinets should be constructed to prevent leakage of solvent vapour or liquid if a container releases its contents. Only small containers of solvents, less than 500 ml, should be kept on open shelves, which should be away from sources of heat or direct sunlight. Decanting large volumes of solvents generates static electricity with the possibility of sparks and ignition of the vapour. Whenever more than 5 litres of a solvent are likely to be stored and transferred, expert advice should be sought. Many specially designed containers for solvents and other flammable materials are now available. Vapours of solvents are heavier than air and can flow along bench tops, into ducting or on to the floor. The vapours can travel some distance from an open vessel containing solvent and hence naked flames, cigarettes, electric switches, static electricity and other sources of sparks must be removed when solvents are used. In general those solvents with a flash point below 21 °C are considered most dangerous, while any solvents with a flash point below 32 °C are still dangerously flammable. Chlorinated solvents form dangerous by-products, e.g. phosgene, when heated or exposed to flames.

Solvents do not lose their hazard when work with them has finished. Objects and cleaning materials may be placed in a fume cupboard or well-ventilated area until the solvents have evaporated. Some solvents and oils contain sufficient peroxides to cause wiping rags to ignite while drying. These wastes should therefore be held in fireproof bins until disposal. Solvents should not be washed into the sewage system except with the explicit approval of the water authorities and in a very dilute form – the solvents can cause explosion in sewers and damage water treatment works. Waste solvents should be collected separately in fireproof containers for speedy disposal by specialists who will usually require a list of the contents. It is especially important that chlorinated solvents are collected separately as they can react with other solvents, e.g. acetone, to create explosive mixtures. Waste and impure solvents must be compatible with the containers – waste containing small amounts of water could cause disastrous corrosion of steel cans. Ethane-1,2-diol derivatives can react with aluminium to produce hydrogen.

3.4.2 Toxicity

All solvents should be approached with care, and their dangers to health must be assessed before use ([EC IHCP, 2009](#)). Liquid solvents will be absorbed through the skin, will dissolve protective chemicals from the skin, allowing access to infection, and will cause irritation to sensitive membranes, especially in the eyes. These dangers can be reduced by taking commonsense precautions and wearing protective clothing. Perhaps the most insidious damage is caused by

breathing the solvent vapours over extended periods. For this reason the effects and relative dangers of solvent vapours have been extensively investigated.

There are two different kinds of vapour toxicity and these may occur with the same solvent. Narcotic effects are those of drunkenness or poisoning, which wear off as the solvent is eliminated from the body, e.g. ethanol. Long-term effects may occur after the solvent has been absorbed, either as poisoning, e.g. methanol, or carcinogenic, e.g. benzene. With wider use of solvents, it is being found that chronic effects are much more common than had been realized.

The danger of a solvent is indicated by the concentration of vapour in air that can be tolerated by the average worker without undue risk ([Appendix 2.1](#)). The concentration of vapour is measured in mg/m^3 or parts per million (ppm) by volume of the air. Two values are commonly listed: one for exposure during the whole of the working week, the time-weighted average (TWA); and the other for short-term exposure, up to 15 minutes (STEL). Different countries use different procedures and measures for indicating risk. Most have been developed from the American threshold limit value (TLV) ([ACGIH, 2009](#)). National recommendations should be consulted for further details of values and methods of evaluation, e.g. Arbeitsplatzgrenzwerte (AGW; previously Maximale Arbeitsplatz-Konzentration, MAK) ([TRGS 900, 2009](#)) and workplace exposure limit (WEL; previously occupational exposure limit, OEL) ([HSE, 2005](#)). It is wise to pull solvent vapours away from people, even when working at levels well below the recommended TLV. It becomes increasingly difficult to achieve very low levels so any solvent with a TLV less than 200 ppm should be treated with considerable caution.

Suppliers of chemicals should be able to provide information on the toxicity of any product they supply. It is practically impossible to discover the concentration or toxicity of a material whose chemical composition is not known. The use of such materials presents unknown hazards to the conservator and, incidentally, to the objects. Individuals can vary in their sensitivities to chemicals. When one has been sensitized, irritation can occur at much lower concentrations than the average. To counter the possible dangers, periodic checks on the atmosphere breathed by a conservator are desirable. These should be made in the same conditions as normally found around the face of the worker, with solvent swabs, containers of solvents and solvent-covered objects in their normal positions.

The measurement of the concentration of a solvent has been made much easier in recent years by the development of simple and relatively inexpensive instruments ([ESIG, 2008](#)). The Draeger, and similar, system uses a hand pump to draw a known amount of air through a tube of chemicals that indicates the concentration of vapour in the air. Tags containing absorbents accumulate the solvent, which is analysed by the supplier of the tag. Electronic detectors are available for an increasing number of chemicals, providing instantaneous concentration values. One cannot rely on the sense of smell for warning, as many of the solvents have very mild smells. More importantly, the nose rapidly becomes accustomed to a solvent vapour, which may not be smelt at all without considerable

effort. The anaesthetic effect of many solvents will ensure a happy ignorance of the increasing danger.

Environmental

There has been increasing realization about the ill effects of solvents and other chemicals on the environment (Warnon, 2004). These may be poisoning the water courses (and sewage works), causing air pollution or creating damage to the ozone layer. Various familiar chemicals have therefore been withdrawn from use: nonylphenol ethoxylate surfactants (e.g. Synperonic N) build up in water courses and cause oestrogenic effects in aquatic animals; ethyl benzene promotes the production of photochemical smog; 1,1,1-trichloroethane and similar solvents are ozone layer depleters. Chlorofluorocarbons, such as 1,1,2-trichloro-1,2,2-trifluoroethane, are potent ozone depleters and are being replaced by hydrofluorocarbons such as carbon trifluoride, which are greenhouse gases contributing to global warming. It is likely that further solvents will be restricted with increasing knowledge of long-term effects.

Commercial Solvents

The range and purity of solvents have improved considerably over recent centuries. At the beginning of the twentieth century, it was difficult (and expensive) to obtain acetone without water or toluene without sulphur contamination (Thorpe, 1913). These contaminants would have short- and long-term effects on objects and would create different behaviours to that expected now of nominally the same materials. All solvents contain impurities. Solvents bought as chemicals can be obtained at very high purity, up to 99.999% for critical applications such as pesticide analysis. For many industrial purposes, high purity (>95%) is not necessary. However, the purity of solvents used on objects should be at least 99%, and there should not be any non-volatile impurities or any that might react with or remain in the object (Khanjian et al., 2004). Many solvents are not sold as pure chemicals but to conform with performance specifications, particularly ethanol and hydrocarbon solvents. For instance, specifications for Xylene S do not explicitly state that xylene is present (Shell, 2007) and commercial 'xylene' often contains ethyl benzene as part of the mixture.

Ethanol solvents are usually compounded with 'denaturing' additives, such as colouring agent, bittering agent, pyridine, methanol, hexane, t-butanol, etc., to make the liquid poisonous or unpalatable, with up to 10% water. The USA (CFC 27, ch. 1, pt 21, 2009) and UK (Denatured Alcohol Regulations, 2005) regulations provide for many different grades, providing designations for denatured alcohols (e.g. industrial denatured alcohol, previously industrial methylated spirits). Absolute alcohol (usually containing $\approx 5\%$ methanol, $<1\%$ water) normally also contains small amounts of benzene as an impurity of distillation.

Hydrocarbon solvents (Appendix 2.2) are made by distillation and modification of petroleum fractions. Many grades are available, varying in chemical composition, molecular weight, evaporation rate, toxicity, flammability,

colour and impurities. The early (1920s) designations of hydrocarbon, mineral, solvents were concerned primarily with flammability specified by their flash point: white spirit, 32 °C (BS 245, 1976); Stoddard solvent 38–61 °C (Harris and Bittner, 1993; ASTM D235-02, 2007). In practice, these and similar mineral spirits usually are largely paraffins and naphthenic ingredients, with undeclared aromatic content up to 50%, made up of C₇–C₁₂ molecules. A wide range of more highly specified and consistent hydrocarbon solvents are used in conservation. These are chosen to have a composition, evaporation and contaminants appropriate to the purpose (Pocobene, 2004).

The composition and commercial designation of solvents should be checked as far as possible before use by obtaining manufacturers' data sheets. Many solvents, e.g. ethers, propan-2-ol and turpentine and unsaturated components, absorb oxygen from the air to form reactive, sometimes explosive, peroxides. Solvents should be kept in full, dark-coloured, glass bottles to reduce their deterioration.

3.5 SOLVENT–SOLUTE INTERACTION

There are two aspects to the interaction: the degree of interaction and the speed of interaction. The degree of interaction is best described by the use of the solubility parameters, which reflect the underlying thermodynamic drivers, and the speed of interaction, the kinetics, by the size and shape of the molecules.

3.5.1 Solutions (Barnes, 2000; van Krevelen and Nijenhuis, 2009)

Polymers form viscous solutions. Intuitively, it is more difficult, i.e. takes more force and energy, to move a large, long, polymer molecule than a small solvent one.

Viscosity values may be quoted using two different scales. Dynamic viscosity is a measure of the energy needed to maintain flow. The SI unit is the Pa.s, in practice the mPa.s, which replaced the poise, P and cP (= 1 mPa.s). A less used measure is the kinematic viscosity, m²/s and 10^{−6} m²/s (obsolete – centistoke, cSt). The two scales are related by the density of the liquid:

$$\text{Kinematic viscosity} = \frac{\text{Dynamic viscosity}}{\text{Density of liquid}}$$

Table 3.2 shows a comparison of typical values of viscosity. At the molecular level, in order to move part of a polymer molecule, there has to be a hole available to accommodate it. The viscosity of a solution is therefore increased when the required holes can form with difficulty. Viscosity is increased by increasing the viscosity of the solvent, or by increasing the polymer concentration or the molecular weight of the polymer (Figure 3.6). Solvents vary considerably in viscosity, and their viscosity is reduced considerably with increased temperature.

In a 'good' solvent (one with a close match of solubility parameters), a polymer molecule is stabilized and expanded. This has different effects as the solution concentration increases. A polymer in a good solvent occupies more volume and therefore in a dilute solution has a higher viscosity relative to one of

TABLE 3.2 Typical Viscosities of Common Liquids

	Dynamic viscosity (mPa.s)	Kinematic viscosity (10^{-6} m ² /s)	Temperature
Acetone	0.33	0.41	20°C
Dichloromethane	0.44	0.33	
Toluene	0.59	0.68	
Water	1.03	1.03	
Ethanol	1.16	1.52	25°C
Ethane-1,2-diol	20	18	
Olive oil	83	91	
Glycerol	1490	1183	
Elvacite 2043 20% solution in toluene	15		
Elvacite 2043 30% solution in toluene	50		
Elvacite 2043 40% solution in toluene	300		

a poor solvent. However, at concentrations greater than 15–30%, poor solvents result in higher viscosity solutions (Hoernschemeyer, 1974). This is because the polymer molecules interact more strongly with each other than with the solvent, effectively causing larger clusters, which flow less easily (Wicks et al., 2007). Good solvents therefore allow the polymer to flow more readily at high concentrations, e.g. during the last stages of drying. An optimum combination of solvents for applying a polymer film might seem to be a mixture of a volatile poor solvent with a small amount of good, slower evaporating, solvent. The same consideration may apply to adhesive formulations. However, it appears that the requirements for consolidation are different. The diffusion constant of a polymer in a good solvent is higher than that in a poor solvent.

Simple liquids such as solvents have the same viscosity no matter how fast they are stirred (Barnes, 2000). These are Newtonian liquids. Polymer solutions differ from simple liquids in the way they react to stirring (Wicks et al., 2007). Polymer molecules impart a structure to the liquid. The structure is disturbed while the solution is stirred vigorously. There are a number of different behaviours on stirring. Viscosity can reduce on stirring (shear thinning) as the molecules line up in the direction of flow, so reducing the viscosity

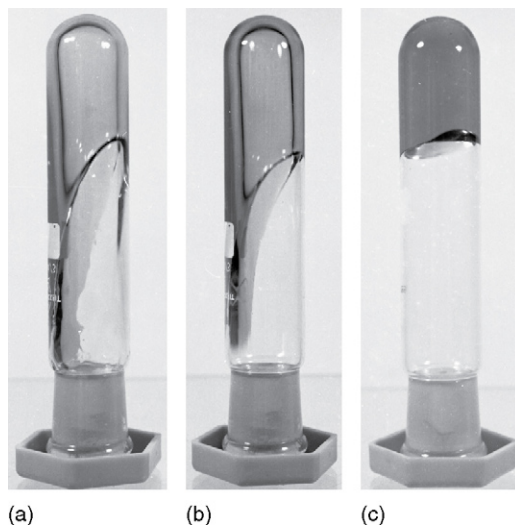


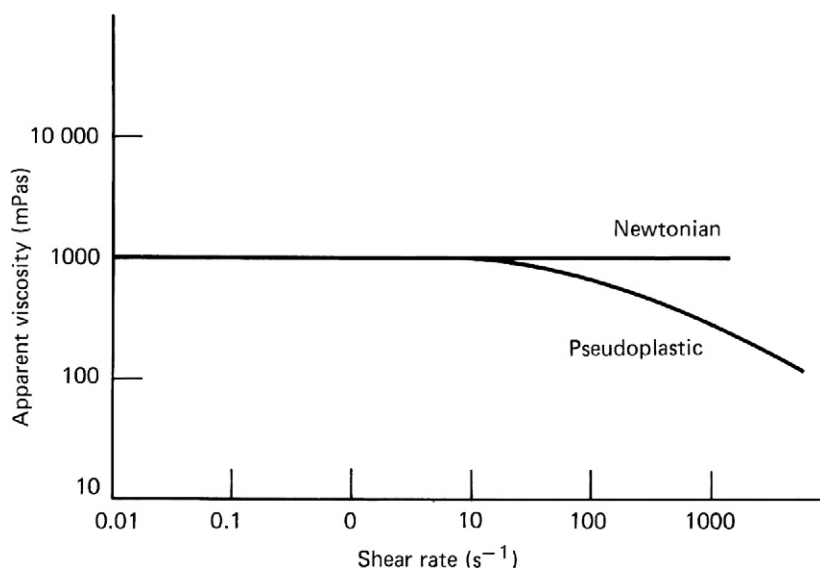
FIGURE 3.6 Effect of molecular weight on the viscosity of PVAC solutions. PVAC polymers (Cairn) (Table 7.1) were dissolved in cyclohexanone to form 40% solutions (by weight). These were dyed to aid visibility. The test tubes were tipped over and photographed after 2 seconds. The low-molecular-weight polymer solutions flowed faster: (a) S2 $\frac{1}{2}$. (b) S7. (c) S27.

(Figure 3.7). Viscosity can increase on stirring (shear thickening) when dispersions or particles clog up the flow. Solutions of water-soluble polymers exhibit more extreme properties because of the very strong interactions and structures that are developed by hydrogen bonding. Structuring can cause thixotropy, where the viscosity depends on the stirring history. This is usually not noticeable with polymer solutions in organic solvents. Thixotropy is a reduction in viscosity that persists even after stirring has stopped, because the structure that is broken takes some time to re-establish itself (Figure 3.8). A number of water-soluble polymers form structures in solution, a gel, that will not flow until a critical force is reached. The reversible gel in water can be broken into a liquid by stirring but will gel again on standing. The use of these gels allows the placing of a polymer solution that will not flow.

Polymers frequently do not form stable mixtures. When solutions of incompatible polymers are mixed, they separate (Tables 3.3 and 3.4). On drying, the solutions dry in patches. Although this would be disfiguring if it occurred on objects, no problems seem to have been noticed. Mixtures of incompatible water-soluble polymers can cross-link by hydrogen bonding to form gels or precipitates.

3.5.2 The Dissolution Process (Miller-Chou and Koenig, 2003)

The reaction of a solvent with a polymer to produce a solution goes through four stages (Figures 3.9 and 3.10):



10^{-4}	10^{-2}	10	10^2	10^3	10^6
Pigment settling	Levelling, sagging	Paint brush pick up	Mixing	Brushing	Spraying

FIGURE 3.7 The viscosities of simple liquids do not change on increasing the rate of stirring (shear rate), i.e. Newtonian. The viscosities of some polymer solutions decrease when stirred rapidly (pseudoplastic). The pseudoplastic curve is typical of carboxymethyl cellulose solutions (Blanose; Hercules) in water. The shear rate is a measure of how fast a force is applied.

Source: Reynolds (2004).

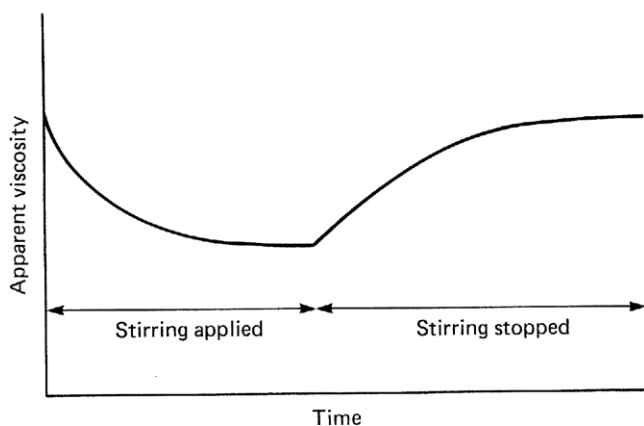


FIGURE 3.8 The viscosity of a thixotropic solution depends on the rate of stirring and the past history. Stirring will tend to break the polymer/solvent (usually water) structure and so reduce the viscosity. Once the stirring has stopped, the structure reforms slowly with consequent increase in viscosity.

TABLE 3.3 Compatibility of Water-Soluble Polymers Used in Aqueous Solution and of the Films Formed from Mixed Solutions

	PEG	PVAL	MC	HPC	HEC	CMC	Gelatine	Gums	Starch
PVAL	IC								
MC	IC	IC							
HPC	C	C	C						
HEC	–	IC	C	C					
CMC	X	?C	–	C	–				
Gelatine	IC	IC	C	C	–	–			
Gums	IC	?C	C	C	C	C	IC		
Starch	?IC	IC	C	–	–	–	–	–	
PVP	C	C	C	–	–	C	IC	C	–

Key: C, forms compatible solutions and deposits clear films; IC, solutions separate and deposit cloudy or patchy films; X, forms a water-insoluble film when dried; ?, conflicting information.

Abbreviations: CMC, sodium carboxymethyl cellulose; HEC, hydroxyethyl cellulose; HPC, hydroxypropyl cellulose; MC, methyl cellulose; PEG, poly(ethylene glycol); PVAL, poly(vinyl alcohol).

TABLE 3.4 Compatibility of Polymers in Organic Solvents and of Films Applied from Mixed Solutions

	PVAC	PVbutyral	PRA	PRMA	CA	CN	Shellac	HPC	PVP	Dammar
PVbutyral	IC									
PRA	–	–								
PRMA	C (PMMA)	IC	IC	IC (for different R)						
	IC (rest)									
CA	IC	IC	IC	IC						
CN	C	IC	C	C	–					
Shellac	IC	C	IC	C	–					
HPC	–	–	–	–	–	C				
PVP	IC	C	–	–	C	–	C	–		
Dammar	C	C	–	IC	–	C	–	–	–	
Ketone resin	IC	IC	IC	IC	IC	C	IC	–	–	C

Key: –, no information; C, compatible solutions and deposits clear films; IC, solutions separate and deposit cloudy or patchy films. Compatibility depends on the solvent used to deposit films of the mixed polymers.

Abbreviations: CA, cellulose acetate; CN, cellulose nitrate; HPC, hydroxypropyl cellulose; PMMA, poly(methyl methacrylate); PRA, polyacrylate polymer; PRMA, polymethacrylate polymer; PVAC, poly(vinyl acetate); PVbutyral, poly(vinyl butyral); PVP, poly(vinyl pyrrolidone).

Sources: Krause (1978), Krause and Goh (1999), and manufacturers' information.

Pore polymer	Infiltration layer	Solid swollen layer	Gel layer	Solution layer	Pure solvent
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FIGURE 3.9 Schematic composition of a polymer dissolving in a solvent.

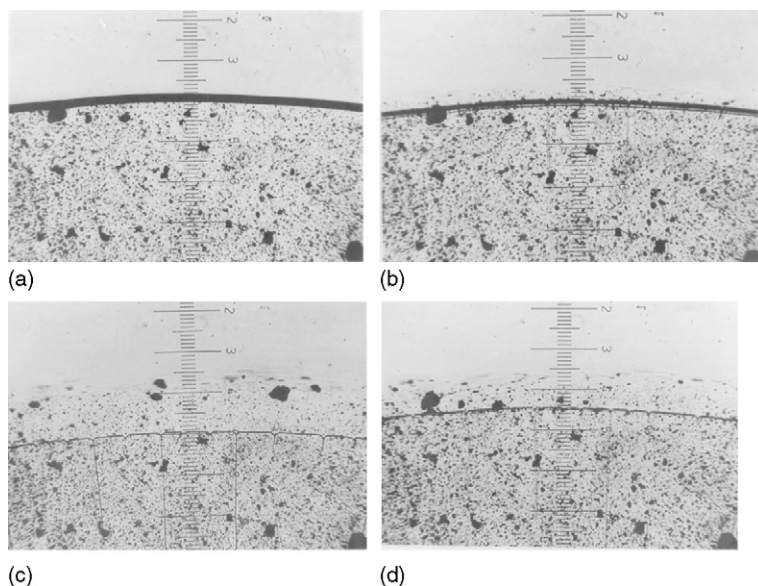


FIGURE 3.10 The process of dissolving polystyrene in a solvent, toluene, flowing left to right. The polystyrene is made visible by graphite particles in the film (Ueberreiter, 1968). (a) After a few seconds of contact, toluene penetration between chains causes the light to be refracted along the black line. (b) Swelling of the polymer occurs before dissolution. The interface between the swollen polymer and solvent has moved into the solvent. (c) Dissolution starts. Polymer, with graphite, flows away. Cracks penetrate deep into the polymer from the surface. The polymer mass is still swelling into the solvent. (d) Depth of swollen layer reaches an equilibrium thickness. Solvent penetrates at the same rate as the polymer dissolves. The photographs were kindly provided by Prof. Dr K. Ueberreiter. Reproduced by permission of Academic Press.

1. The solvent molecules infiltrate between the polymer chains by diffusion.
2. The outer layer of the polymer interacts with the solvent and swells.
3. The outer layer of the swollen polymer absorbs more solvent and becomes a rubbery gel.
4. The polymer molecules are lost from the surface at a rate depending on the flow of solvent over the surface.

The swelling is a necessary precondition of dissolution. All parts of the polymer molecule must be released from the solid mass before it can escape into solution, i.e. the polymer/solvent mixture must be above the effective T_g . The rate of loss of polymer decreases with increasing molecular weight until it practically comes to a halt. The gel thickness increases over time, expanding the object that

is embedded in the polymer (Uuano et al., 1977). Polymers chosen for conservation treatments should have the lowest molecular weight that provides sufficient mechanical properties in order to reduce any subsequent strains during removal. Increasing the temperature increases the loss of polymer but increases the rate of solvent diffusion even more. While this is useful in preparing solutions, one should reduce the temperature when dissolving polymers off objects. If the temperature of dissolution is much below the glass transition temperature of the polymer, very little gel layer will be formed. The swelling at the surface can cause the underlying polymer to crack. The polymer (with any attached object) cracks because it is too stiff to stretch. The hard-edge phenomenon noticed during removal of some picture varnishes (Feller, 1981) may result from the high glass transition temperature of the resins used. Polymers with plasticizers, retained solvent or low T_g will swell more but dissolve more quickly.

When removing a polymer from an object, solvents should be chosen to cause the minimum swelling necessary to enable the polymer to be dissolved or scraped off. In many situations where polymers must be removed from objects, a large amount of swelling is undesirable. For instance, a paint film varnished with poly(butyl methacrylate) was disrupted by the swelling of the varnish with toluene (Thomson, 1963). Small non-solvent molecules penetrate rapidly into the polymer, swelling the polymer up to three times its original volume (Manjkow et al., 1987), and these small molecules make dissolution by a solvent much faster (Gonzalez-Benito and Koenig, 2006). The swelling and dissolution by a solvent are affected by molecular size of the solvent as well as its solubility parameter. The depth of swelling is reduced by using large solvent molecules at low temperature and by removing the polymer from the surface as quickly as possible by agitating the solvent vigorously. To reduce swelling during dissolution, the solvent used should have a good match of solubility parameters so that the polymer molecules diffuse away from the surface rapidly so reducing the depth of gel, are stabilized in solution, and form a low-viscosity solution. The conclusions arising from comparisons of diffusion rate are therefore different from those arising from comparisons of solubility parameter; there may be no optimum solvent.

When the polymer is cross-linked, it is impossible to pass from the gel state into solution. The swelling action can be so fast that severe stresses build up and parts of the polymer are thrown off violently. A corroded metal object that had been coated with a polyester resin for support was disintegrated by the solvent swelling action necessary to remove it. This effect is worst with rapidly penetrating solvents (Alfrey et al., 1966). Cross-linked polymers cannot be dissolved using solvents. These polymers may be removed from surfaces by swelling with solvents then mechanically scraping off. They cannot be removed from porous objects. Many proprietary paint strippers or resin disintegrators (Wollbrinck, 1993) have been based on penetrating solvents such as dichloromethane combined with undisclosed acid or alkaline additives, though dichloromethane has been withdrawn in the European Community because it is carcinogenic. It has been shown that home-made mixtures, based on dichloromethane and of known composition, are quite adequate for conservation purposes (Daniels, 1981). A cross-linked polymer

may contain low-molecular-weight portions, plasticizers and degradation products, which will be extracted with solvents. If the solvent evaporates before the polymer is totally removed, the remaining polymer can shrink to a smaller volume than it had originally and may cause further stress on the object.

When dissolving a polymer for use in solution, mixtures of solvents are often used to prepare a solution in a shorter time. A low-molecular-weight solvent is chosen to penetrate and swell the polymer. The other component is chosen to have a good match of solubility parameters with the polymer. Heating, stirring and making sure that no lumps form speed up the process. Of course, the solvents chosen must be compatible with the object to which they are to be applied.

Removing varnishes and overpaint from paintings (cleaning) was traditionally carried out before the introduction of solvents by mechanical methods, scraping with a knife. Solvents interact on a chemical basis, but penetrate deeply into the underlying paint film, frequently removing components of the original object. The technique has recently been modified by the introduction of gels containing water, solvents, surfactants, etc. (Wolbers, 2000; Stavroudis et al., 2005). The penetration of solvent into the surface is considerably reduced by applying it in a gelled form (Khanjian et al., 2004).

Cleaning technologists have found that the best solvent for a cleaning task is one in which there is a strong interaction between the soil and the solvent (Durkee, 2007). Solvents are frequently used with special surfactants, which must be rinsed off after use (Landi, 1981).

3.5.3 Film Formation From Solution (Wicks, 2002)

When a polymer solution loses its solvent by evaporation, it evolves from a freely flowing liquid, becomes an immobile but tacky film, which becomes ‘touch-dry’ (viscosity $\approx 10^6$ mPa.s, $T_g \approx -29^\circ\text{C}$, $\approx 15\%$ solvent), resistant to ‘blocking’ (viscosity $\approx 10^{10}$ mPa.s, $T_g \approx 4^\circ\text{C}$), then passes through its room temperature glass transition temperature (viscosity $\approx 10^{12}$ mPa.s). The solid film may still contain $>2\%$ solvent that will continue to evaporate, sometimes for many years.

The bulk of a solvent usually evaporates quickly from a wet film according to the evaporation rates given in Appendix 2.1. During this stage, when the viscosity is rising, the surface tension differences across the surface tend to flatten imperfections, e.g. brush marks (Overdiep, 1986). Solvent is lost from the surface, which leads to a crust or gel layer, further slowing evaporation of the solvent. Counter-intuitively, evaporation from a polymer film can be increased by maintaining a solvent-rich atmosphere above the drying film to delay the formation of the gel layer. Also during this stage, bubbles can form in the film. These are caused by the oxygen and nitrogen dissolved in the solvent becoming insoluble in the concentrated polymer solution (Pourdarvish et al., 2009). This effect can be reduced by lowering the temperature and by choosing a solvent/polymer combination where the gas can preferentially dissolve in the polymer. By keeping the surface of the film mobile, the polymer can flatten to a very smooth, glossy surface, either during the initial drying or by later exposing it to

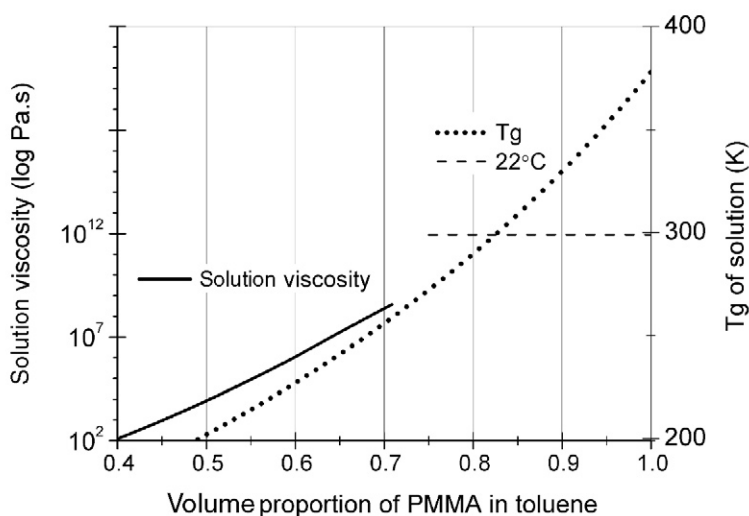


FIGURE 3.11 PMMA/toluene solutions: dependence of viscosity (left axis) (Dreval et al., 1973) and glass transition temperature (right axis) (Kelley and Bueche, 1961) of the solution on the polymer concentration; With increasing polymer concentration, the viscosity rises rapidly (notice the log scale on the left). The T_g of toluene is -158°C (115 K) and of PMMA is 105°C (378 K). As the solvent evaporates from the liquid, the glass transition temperature of the solution rises (temperature scale on the right), becoming a glass (viscosity $\approx 10^{12}$ Pa.s) at room temperature (22°C , 295 K) with only 82% polymer content, i.e. 18% of the volume is solvent that is still to evaporate. By using a polymer with a lower T_g , the polymer solution reaches T_g at room temperature with a much lower solvent content.

the atmosphere of a good solvent (Anthamatten et al., 2004). Alternatively, the surface can be roughened and made matt by blowing (Yamamura et al., 2009), as an alternative to using matting agents. Once the freely moving solvent has gone and the surface of drying film has become rubbery, the rate of loss of solvent drops off markedly (Peter et al., 2009) as the solvent molecules have to negotiate the holes between the polymer molecules.

If the solvent is evaporating from a glassy polymer, the glass transition temperature of the mixture gradually rises and passes through room temperature (Figure 3.11). At this point, the solution can no longer flow and subsequent solvent loss results in shrinkage of the solidified film. If this shrinkage is restrained, for example by attaching the coating to a surface, stresses build up in the film, at the interface with, and within, the substrate (Whitmore et al., 1999; Francis et al., 2002). These stresses can result in distortion in the object, e.g. curling. The stresses built up increase with the amount of shrinkage occurring after solidification, i.e. greater with a high- T_g polymer but possibly reduced by a good solvent, and the elastic modulus of the polymer.

The changes with time, concentration and temperature of a polymer/solvent film as it dries and the consequent effects on strength, T_g , etc. are still poorly understood (Doumenc et al., 2006), with apparently contradictory results seen with

different polymer/solvent pairs (Hansen, 1995). Films cast from good solvents have a greater strength than those cast from poor solvents (Briscoe et al., 2002).

The last few percent of solvent from a dry film are adsorbed on to the polymer structure (Errede et al., 1994). It is the solvents with the greatest affinity with the polymer that are held preferentially (Wang et al., 2001), even if in very small proportion in the original solvent mix. These become trapped in the polymer structure, especially if it is in its glassy state. Linear, unbranched, solvent molecules have less difficulty in passing between polymer molecules, i.e. less steric hindrance (Table 3.5) so, considered from this

TABLE 3.5 Solvent Retention

1	Methanol
2	Acetone
3	2-Methoxyethanol
4	Butanone
5	Ethyl acetate
6	2-Ethoxyethanol
7	n-Heptane
8	2-Butoxyethanol
9	n-Butyl acetate
10	Benzene
11	2-Ethoxyethyl acetate
12	Dioxane
13	Toluene
14	Chlorobenzene
15	<i>m</i> -Xylene
16	2,4-Dimethylpentane
17	Cyclohexane
18	Methyl cyclohexane
19	Cyclohexanone
20	Methyl cyclohexanone

List of solvents in approximate order of increasing retention in polymer films. Solvents that interact strongly with the polymer will be retained relatively longer.

Source: Newman and Nunn (1975).

aspect, branched solvents should be avoided. Solvent left in the film will cause a gradual shrinkage and change in properties over a period, perhaps many years, of evaporation. Remaining solvents may also cause chemical instability in the film.

The conclusions arising from comparisons of dry-stage evaporation rate are therefore different from those arising from comparisons of solubility parameter; there may be no optimum solvent. In order to reduce the solvent to low levels quickly, one must use a solvent that has a relatively poor match of solubility parameters and that has no side chains. Conversely, to relax the polymer chains into stable conditions, one must ensure that the last solvent to leave the film is closely matched to the solubility parameter of the polymer. Even a very small proportion of good solvent will be held tenaciously.

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Adhesion

4.1 INTRODUCTION (GORDON, 1978; NELSON, 1995; POCIUS, 2002)

Joints between different objects can be made in many ways. Carpentry joints are held by mechanical keying, hot-welded iron is held by the merging of the metal from the separate pieces, and dust is held on to the surface of plastics by the electrostatic attraction of dust particles for the surface. These phenomena depend on the physical properties of the objects themselves to create the joint. In conservation, an adhesive is employed to bridge and fill the gap between two objects. The adhesive is applied as a liquid, which forms a strong bond to the object's surface. The principles of adhesion between a polymer and object surface are relevant to coatings, consolidants and adhesives – and dirt.

Ordinary water can be used as an adhesive, and water pressed between two sheets of glass will prevent the sheets being pulled apart. However, the sheets can be slid past one another to break the joint. This use of water illustrates the first essential requirements for adhesion:

1. The liquid must cover the surface and have a strong attraction for the surface, i.e. it must wet the surface.
2. The liquid must then set to prevent the relative movement of the objects.
3. A further requirement is that it must be able to adjust to the stresses that develop during and after the setting of the adhesive.

4.2 WETTING THE SURFACE

The best joint between a liquid and a surface is made when the liquid covers the entire surface, i.e. liquid has wetted the surface completely. The extent to which this is achieved depends on the forces within the liquid and between the liquid and the surface. These forces are illustrated by the concept of surface tension. The surface tension of a liquid is the result of unbalanced forces of attraction between its molecules and those in the vapour above it (Figure 4.1), creating a 'skin' that resists expansion to create more surface area.

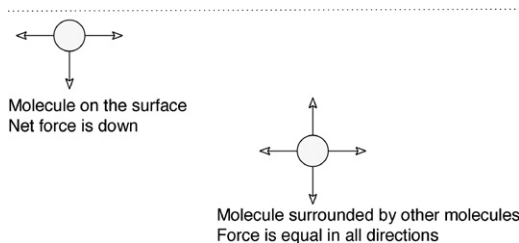


FIGURE 4.1 Surface tension.

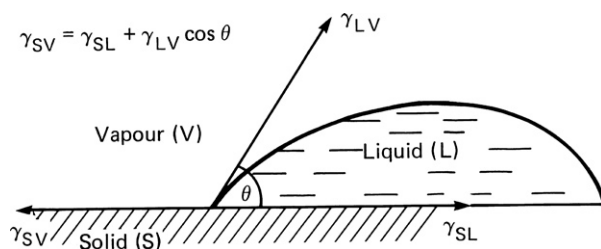


FIGURE 4.2 The forces in a stable drop of liquid on a surface. γ_{SV} is the surface tension of the solid in the presence of the liquid vapour. γ_{SL} is the surface attraction between the solid and the liquid. γ_{LV} is the surface tension of the liquid in the presence of its own vapour.

The molecules in a drop of liquid at the junction with the surface of a solid will be subjected to three forces along the interface (Figure 4.2):

1. The attractive forces acting from within the liquid itself
2. The attractive forces acting from the surface of the solid with the vapour above it
3. The attractive force between the liquid and the solid.

If the liquid molecules are much more attracted to each other than they are to the solid – such as water on polyethylene – they will ball up to form droplets sitting on the surface. This preference can be measured by the angle, $\theta > 90^\circ$. If the liquid molecules are much more attracted to the solid than they are to each other, the liquid will spread out completely and wet the surface spontaneously, e.g. acetone on clean glass, and θ is 0° . At intermediate values of θ , i.e. between 90° and 0° , the liquid will spread and wet the surface if force is used to expand the drops. It takes energy to stretch the skin and make more surface.

This description of a spreading drop applies only when the surface is absolutely smooth. However, most surfaces contain pores and crevices into which the liquid must flow if complete wetting is to be achieved (Figures 4.3 and 4.4). Air trapped in a pore will oppose the penetration of the liquid. If the air has time to diffuse out of the hole before the adhesive sets, the penetration will be deeper. This is one cause for the increasing adhesion of self-adhesive tapes with time, since the adhesives used remain liquid. A consolidant or adhesive used in conservation should be given time to penetrate before it hardens. A low-viscosity liquid is obviously more likely to flow readily into the pores.

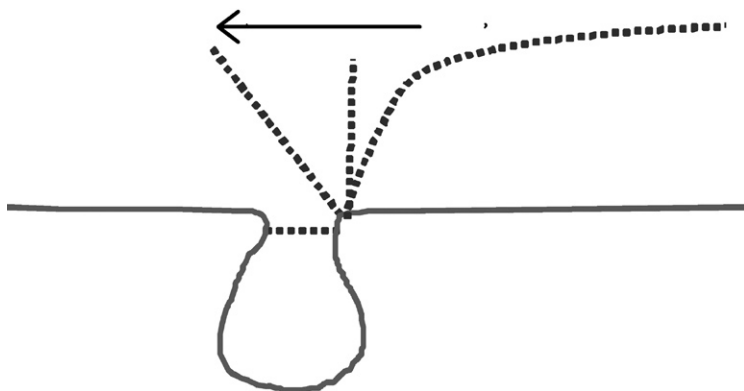


FIGURE 4.3 The flow of a liquid over a surface impeded by a hole. When the liquid (flowing from right to left) reaches the hole, the contact angle with the surface increases rapidly. In order for the liquid to flow and wet the surface, it has to accommodate the increased contact angle, which takes time and energy. The liquid may not flow into the crevice but bridge to the other side, so creating an area of no adhesion – a weak point. The trapped air can also prevent the liquid flowing into the crevice.



FIGURE 4.4 Time, choice of a suitable viscosity and curing time enable the flow of a liquid adhesive into the interstices of a substrate and the flow of air away from the pores in the interface. This increases mechanical interlocking of the adhesive with the adherend, the difficulty of reversing the joint and removing the adhesive. Adapted from *Pocius (2002)*.

The liquid adhesives used in conservation have low surface energies, below 10^{-5} N/m. Hard solids such as dry glass or metals have much higher energies, 5×10^{-5} to 10^{-3} N/m, and are termed high-energy surfaces (Zisman, 1977). A low-energy liquid will spread and wet a high-energy solid. Therefore, initial wetting and adhesion is rarely a problem with these materials, provided the surface is free of contaminants. It is likely that the adhesive force in the majority of instances is derived from the physical attractive forces of dispersion, dipolar and hydrogen bonding described in Section 3.2.

The wetting description above implies that a polymer in solution should spread easily over a flat surface, although it may need mechanical assistance and/or time to achieve good coverage over a real object surface. There are two types of situation where this does not occur. The first is when the object surface has been contaminated by a layer of detergent, fatty acid or alcohol. The polar part of the molecules stick to the polar surface, leaving the hydrocarbon ends of the molecules sticking up. These act like a layer of wax on the surface and so repel most solvents. This is the reason that strong alkalis are used to clean glass milk bottles, in order to strip these organic molecules off the surface.

The other problem situation is the application of a polymer coating to an organic surface, e.g. a picture varnish over oil paint (Hulmer, 1976; Zisman, 1977; Feller, 1983). To ensure good wetting behaviour on these organic surfaces, the surface tension of the liquid must be slightly but not much higher than that of the substrate. Applying low-polarity solvents to oxidized paint films with relatively high polarity will not produce an even coverage.

4.3 EFFECTS OF SETTING PROPERTIES ON ADHESION

The greatest change in property on setting is the transformation from a mobile liquid to a static solid. At some point in the setting process, the material is transformed into a gel, a solid swollen with liquid.

A cross-linking resin will form a gel part way through the reaction process. A material that sets by cooling can either precipitate crystals, e.g. wax, or form relatively stable intermolecular bonds, e.g. gelatine. A solution sets when the glass transition temperature rises through ambient temperature as the solvent evaporates (Section 2.3). An emulsion sets when the coalescence of the particles is initiated. All these processes involve a reduction in volume, which is initially accommodated by liquid flow (Francis et al., 2002). At the gel point, the shape of the gel is fixed. Further shrinkage of the polymer mass cannot be accommodated by flow. Anything embedded in the polymer will be drawn in by the contracting mass. If the shrinkage is restrained by being attached to a substrate, the polymer will, in effect, be stretched by the amount it would otherwise have shrunk. This stretching will be achieved by the substrate applying a tensile force to the polymer. The inbuilt stresses reduce the strength and durability of the adhesive bond. The shrinkage and stress can be reduced by ensuring that the glass transition temperature of the polymer is around ambient temperature. Polystyrene films ($T_g = 95^\circ\text{C}$) applied from solution may generate stresses up to 10.9 MPa, whereas poly(isobutyl methacrylate) ($T_g = 55^\circ\text{C}$) will produce only 3.4 MPa (Croll, 1980). Shrinkage stresses appear to be the reason for the pulling off of poly(methyl methacrylate) (PMMA) coatings from degraded glass (Hedvall et al., 1951). The stresses may be eliminated entirely in a thermoplastic with a glass transition temperature at ambient temperature. When applying cross-linking resins, solvents or plasticizers should not be lost after gelation, otherwise large stresses will be generated (Croll, 1981; Lange et al., 1997). Damage to an object caused by shrinkage may not be noticed until the polymer is removed.

Polymers that set by chemical reaction may react not only within the components of pre-polymer mixtures, but also with the substrate. This occurs principally with pre-polymers that are sensitive to water, such as isocyanates in polyurethanes and silanes. The chemical links can be deliberately created by using a reactive primer, e.g. a silane coupling agent. Many water-soluble polymers, e.g. poly(vinyl alcohol) and cellulose derivatives, may be expected to adhere more strongly and irreversibly because of the presence of reactive groups on degraded objects.

4.3.1 Surface Preparation

The previous discussion has assumed that the polymer has been applied to a clean, dry surface. However, a clean surface is achieved with difficulty even in the most advanced industries of medicine and electronics. Common contaminants are oils, air pollutants and greases from the skin. Once a surface has been cleaned it should not be touched. Some contaminants, such as detergents, can form stable chemical bonds with the surface. Industrial methods of cleaning frequently involve removing the surface layer mechanically or with acid or alkaline solutions (Pocius, 2002). A less destructive method of cleaning inorganic objects is to use an oxygen plasma (Daniels et al., 1979). Washing with solvents is a more widely used method of cleaning. Solvents or water used for final rinsing must of course be free of oily impurities.

Water is a ubiquitous surface contaminant. Its presence can be reduced by working in warm and appropriately dry conditions. Water may be removed by employing solvents in the adhesive formulation that will dissolve water from the surface as the liquid front advances.

An improvement to the adhesive bond can be made using coupling agents, e.g. silanes. These react both with the substrate and with the applied adhesive. They are usually used to reduce (but will not eliminate) sensitivity to water of the adhesive bond.

4.4 STRENGTH OF ADHESION BONDS

There is no one theory on what causes adhesion or how it works, probably because there are a number of separate, collaborating, causes of adhesive properties:

- **Mechanical theory.** A simple explanation is mechanical interlocking. The liquid adhesive penetrates the pores or between fibres then sets. In order to separate the adherends, the adhesive needs to be stretched and maybe broken.
- **Electrostatic theory.** When the adhesive and adherend come into very close contact, they exchange charges, which cause the attraction and adhesion. The discharge can be seen when stripping self-adhesive tape from a substrate.
- **Adsorption theory.** The surface-active parts of the adhesive interact with the substrate, forming close secondary bonds and thus creating the adhesion.
- **Diffusion theory.** The adhesive molecules and the substrate molecules (typically polymeric substrates) dissolve and diffuse slightly into each other, so it becomes difficult to pull out the molecules from each other on separation.

However, the forces that are involved in making a bond, the interaction between the liquid with the substrate then transformation from liquid to solid are very different from those occurring when breaking a bond. When an adhesive joint is put under stress, it is not only the adhesive that distorts, the substrate does too. For example, a lap joint between two moderately flexible materials such as metals

or fabric will stretch at various places, so concentrating strain (Figure 4.5). The strength of joint is therefore dependent on the combination of all three properties: the adhesive bond strength, the cohesive strength of the adhesive and the cohesive strength of the adherend. Testing the adhesive properties of adhesives, coatings and consolidants is therefore carried out on the complete assembly and is best evaluated using an analysis of the forces at the various interfaces. Test methods for the simplest adhesive joints have been given serious health warnings by the standards organizations (ASTM D4896-01(2008)e1, 2008). The traditional simple methods for assessing adhesion of coatings, such as the

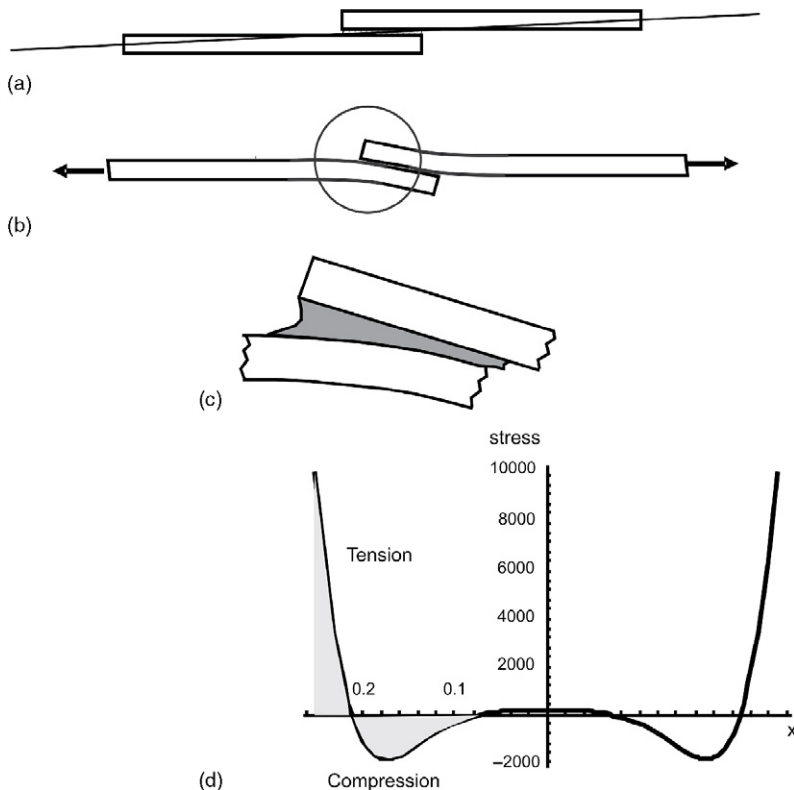


FIGURE 4.5 Illustration of the stresses that develop in a joint under stress. (a) Two pieces of thin metal sheet were adhered. (b) The sheets were pulled from either end with the adhesive put under shear, distorting both the metal and the adhesive. (c) The detail shows that, at the open edge of the joint, the adhesive is put under tension perpendicular to the applied stress, tending to peel the adhesive off the metal. (d) Calculations show that not only is the adhesive under tension at the end, but it is squeezed under compression because of the distortion of the metal. Similar non-intuitive effects have to be calculated and accommodated in the design of adhesive joints. *Illustration courtesy of David Dillard, Adhesive and Sealant Science Professor, Virginia Tech, Blacksburg, Virginia, USA.*

cross-hatch or adhesive tape tests, have been shown to be poor indicators of adhesion, and more reliable tests are difficult and problematic (Wicks et al., 2007). No standard tests appear to have been developed to assess the effect of consolidants on materials.

4.5 FAILURE OF JOINTS

A join can fail in any or all of three distinct ways (Figure 4.6):

- a. The bond between the adhesive and the object may fail along the interface; this is termed ‘adhesion failure’. Many initially good bonds between object and polymer, e.g. glass/epoxy, are affected by water. Adsorption of water from the environment results in the formation of a layer of water at the interface, which displaces the adhesive (Lefebvre et al., 2000).
- b. The adhesive material itself may fail because of a weakness in the polymer mass, termed ‘cohesive failure in the adhesive’. A brittle coating will tend to crack when applied to a surface that cannot respond to the stresses in the polymer. If the polymer has a low glass transition temperature, e.g. poly (vinyl acetate), flow will gradually allow a joint to stretch and distort.
- c. The object may break, leaving a portion of the surface attached to the adhesive; this is termed ‘cohesive failure in the substrate’. This is to be avoided

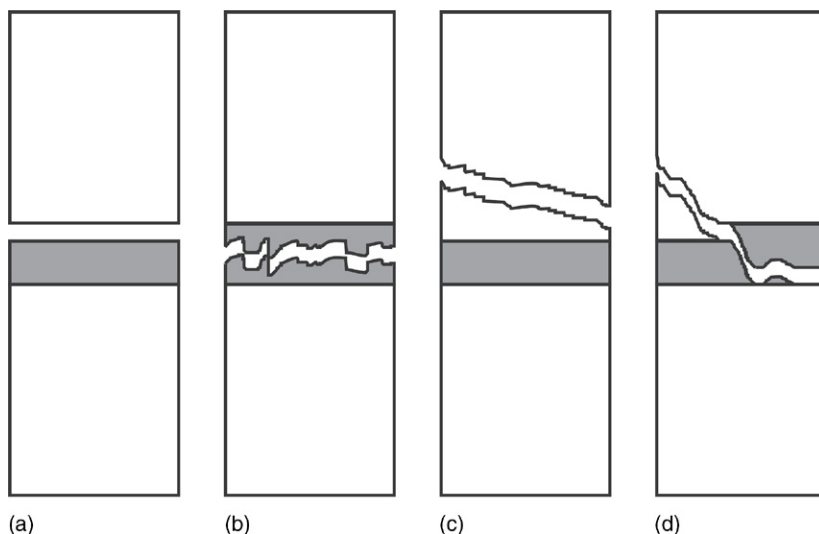


FIGURE 4.6 The failure of a joint can be in any or all of three sites. (a) Adhesive failure, where there is a clean separation between the adhesive and adherend. (b) Cohesive failure in the adhesive, where the adhesive breaks or flows (see Figure 2.7). (c) Cohesive failure in the adherend (object), where the substrate breaks. The most common mode of failure in conservation is (d), where the adhesive bond, the object and the adhesive all fail. *Figure redrawn from an original of Jane Down (Canadian Conservation Institute).*

but frequently occurs due to the inherent weakness of conserved objects. The failure of a joint is usually caused by stresses in the adhesive and/or object. These may be generated during setting, by deterioration of the adhesive or substrate, or by movement in the joint.

Reversibility of a joint requires that the adhesion failure should be complete, but only when required. If a polymer is chemically bound to an object it is most unlikely that it will be removed without causing physical damage to the surface. A bond that is durable to weathering is probably irreversible.

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Uses and Requirements of Applied Polymers – A Summary

The specific requirements of materials for conservation must be determined for each object. There are a number of general requirements that can be listed about the products and their usage. These requirements should be set aside only for good, explicit, reasons.

5.1 STABILITY

The following should not be used:

- Products that contain plasticizers, e.g. cellulose nitrate adhesives.
- Polymers that deteriorate rapidly on ageing by yellowing or oxidation, e.g. poly(vinyl chloride), rubber.
- Thermoplastics that cross-link on ageing, e.g. poly(butyl methacrylate).

5.2 REVERSIBILITY

- The techniques for reversal should be made explicit during the initial conservation procedures.
- The application of thermoplastics is more likely to be reversible than that of cross-linking resins.
- The lowest practicable molecular weight (MW) polymer should be used.

5.3 GLASS TRANSITION TEMPERATURE

- Thermoplastics that are above or near their glass transition temperature at ambient temperatures, e.g. poly(vinyl acetate), should not be exposed to stress or dirt over the long term.
- Polymers with a glass transition temperature above $\approx 65^{\circ}\text{C}$ should not be used.

5.4 SETTING

- Maximum adhesion is obtained by using a low-viscosity liquid on a clean surface.

- Products that react with the object's surface should not be used, e.g. poly(vinyl alcohol), silicone rubbers.
- Products that set with a large amount of shrinkage should not be used, e.g. gelatine, methyl methacrylate polymerization.

5.5 STRENGTH

- A product should be slightly weaker than the object to which it is applied.

5.6 APPLICATION

Many treatments are envisaged to carry out only one function: consolidation, coating or adhesion. However, because objects are usually weak and porous, most treatments result in two or all three of these roles acting on the object. It is therefore wise to think through the likely movement of the product applied and what role(s) it will involve in practice. A rule of thumb is:

- Consolidants act on parts or particles of the object that are not or cannot be individually identified, such as the interior of degraded wood or pigment particles.
- Adhesives are applied to and act on parts that are individually identified, such as shards or paint flakes.
- Coatings are applied to and act on surfaces that are visible at the time of application, such as picture varnishes or sealants of porous edges before applying adhesives.

5.7 CONSOLIDATION

Most consolidation is irreversible, so only materials of proven stability should be used. The minimum amount of consolidant necessary should be incorporated in an object. It is wise to assume that an object weak enough to warrant consolidation is too weak to withstand attempts to remove the consolidant. Objects consolidated with products whose glass transition temperature is below ambient temperature are unlikely to be self-supporting.

Consolidation acts at many levels, from the microscopic to the monumental. Consolidation has mechanical, chemical and optical effects, as the consolidant interacts with the adherend. Frequently the primary purpose is to increase the cohesive strength of the substrate, on a large or small scale. The chemical reaction between the consolidant and the adherend may be through formal chemical bonds, intermolecular bonds or very little. The consolidant may react to form part of the object, such as in the use of poly(vinyl alcohol) sizes on paper. The consolidant may join the particles together but be removable (in theory, if not in practice). Or the consolidant may just act primarily as a bulking material as in the consolidation of waterlogged wood. The optical properties of a porous layer are changed as the air/particle interfaces are replaced by consolidant/particle interfaces. The diffuse reflection from the particles is reduced by the consolidant as the saturation (physical and optical) tends towards the critical pigment volume concentration. This is a desirable outcome for, say, varnished wood, but not for a matt ethnographical paint.

Consolidation of pigments and similar thin layers of friable material can be achieved by applying the consolidating material as a dilute solution of a polymer in the form of a fine aerosol (Michalski, 2008), which does not saturate or mobilize particles but which deposits sufficient binding material to increase the strength (Figure 5.1). The consolidation of porous matt materials appears to require creating minimal optical connection with maximum mechanical connection between the particles. The most appropriate consolidants appear to form gels (e.g. gelatine) or be marginal solutions (e.g. funori). Multiple applications of very small quantities of solution added at any one time are used and allowed to dry so there is insufficient liquid to promote the mass flow of the particles or the drying shrinkage by surface tension of the liquid. The polymer concentrations are kept low to so that coherent films do not form. The multiple applications encourage subsequent deposition of the polymer to occur on top of existing deposits, so strengthening spot adhesion between particles and not encouraging a widespread deposition with less strength and greater optical contact. Temporary consolidation, which used too be carried out using wax or easily re-soluble resins, can now be achieved using subliming consolidants, especially cyclododecane (Jägers and Jägers, 1999).

Structural consolidation depends on placing the consolidant where strengthening is required. Distribution of the solid consolidant in the object should be as uniform as possible to reduce stresses at interfaces. However, uniformity of distribution is not easily achieved and seems possible only if the consolidant can be immobilized where it is needed. This can be achieved using consolidants, which react by cross-linking with themselves or the object, for example silane consolidation of fossils but not the matrix (Davidson and Alderson, 2009). The consolidant can be immobilized by freezing it in situ, as in the poly(ethylene glycol) consolidation of waterlogged wood (Jensen and Jensen, 2006). The penetration of the consolidant into the smaller pores or molecular structure is

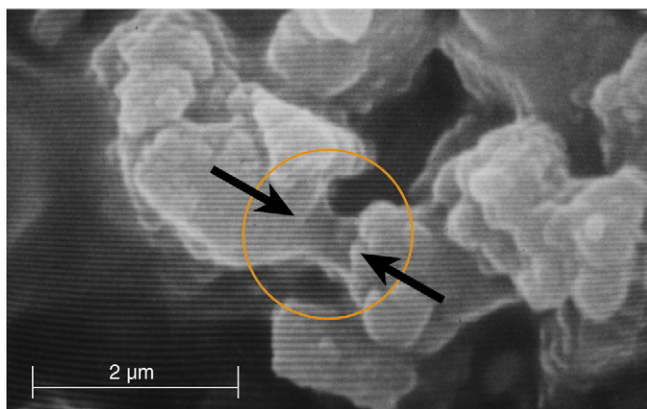
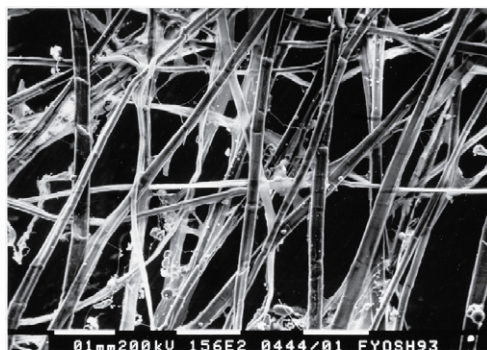


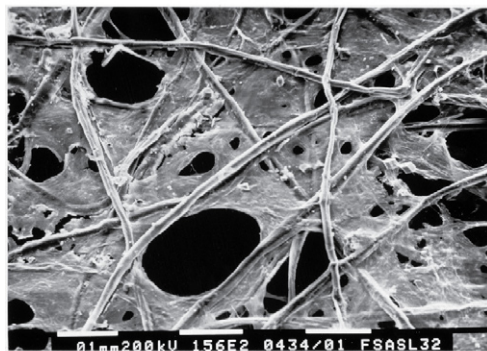
FIGURE 5.1 Consolidation of pigment particles using funori applied in four applications of dilute 0.5% solution in water as an aerosol produced by an ultrasonic mister (Kessler et al., 1998). The funori can be seen bridging between pigment particles. SEM image courtesy of Prof. G. Banik.

dependent on the size of the pores and the size of the molecules in solution (Jensen, 1997). Sizing (consolidation) of paper is achieved by allowing the consolidant to deposit in the fibre structure, frequently using a consolidant such as starch or hemicellulose that is in suspension or barely soluble, so reducing the effect of liquid flow during water evaporation (Figure 5.2). Strengthening of paper has frequently been achieved by adding dispersions to individual sheets, which were then rebound. The early products used had low T_g values with the result that sheets blocked under long-term pressure (Cains, 1992).

Consolidating with thermoplastic polymers applied in solution is more problematic. Domaslowski and Lehmann (1972) showed, in the majority of trials, that the polymer was deposited in the outer 3–5 mm of a limestone block. The best consolidation of 5 cm × 5 cm × 5 cm blocks of limestone was achieved using a poor solvent for the polymer, then reducing the rate of evaporation by wrapping the object or drying in an atmosphere of the solvent. In later experiments, this was shown to be the result of reverse migration of the polymer as the solvent



(a)



(b)

FIGURE 5.2 Tissue papers made from kozo fibres (Rischel, 1992). (a) From Japan with very little amorphous binder. (b) From Thailand, incorporating binder between the fibres. SEM photographs courtesy of Anna-Grethe Rischel.

evaporated (Domaslowski, 1988) (Figure 5.3). Similar effects also occur even on the small scale of 3 mm × 3 mm × 50 mm wooden specimens (Schniewind and Eastman, 1994). The distribution of consolidant was surprisingly non-uniform on the microscopic scale with plugs of polymer next to completely polymer-free vessels (Figure 5.4). This may be due to the development of Taylor flow (Eastman, 2005) caused by the evaporation of the solvent pulling bubbles of air and liquid through the pores, then solidification in plugs along the vessels. The consolidation of substantial porous objects appears to be largely caused by the bulking of the added material, rather than the adhesion to and reinforcement of the degraded material.

The consolidation process appears to take place because of the combination of various factors, discussed below for a standard consolidation of a porous object using a polymer dissolved in solvent:

- There does not appear to be a sieving effect or reduced polymer penetration during the solution transport.
- There seems relatively little adsorption/adhesion between the polymer and the substrate, resulting in little chromatographic effect during the solution transport.
- Evaporation must occur at the surface, fastest where there is greatest area with access to a flow of air to carry away the solvent vapour.
- This results in volume loss, which is filled by drawing in air at other points in the object.
- The flow of air will set up a Taylor flow (Liu et al., 2005) of bubbles of air and solution being drawn through the porous structure.
- The bubbles wipe the solution from the walls of the pores.
- The flow will draw the solution toward the evaporation area, where the polymer will be concentrated.
- The viscosity of solution will rise primarily near the surface where the evaporation takes place, with little increase in concentration in the other parts of the object.
- The flow will continue as the viscosity rises until the force required to pull the column of solution is exceeded by the vapour pressure of the solution.
- The bubbles of polymer solution will then stay more or less intact unless at that stage the viscosity stays low enough for the solution to spread and wet the surrounding pores, e.g because there is a high solvent concentration in the pores, or the T_g of the polymer is low.
- The viscosity is increased by the following factors:
 - the polymer concentration increases;
 - the polymer has a high MW;
 - the polymer has a high T_g ;
 - the viscosity of the solvent is high;
 - the solvent has a high T_g ;
 - the solubility parameters of the solvent and polymer are mismatched;
 - the temperature is lower.

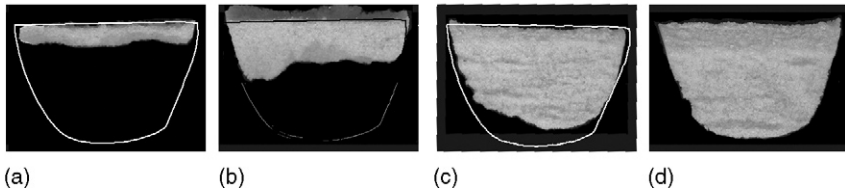
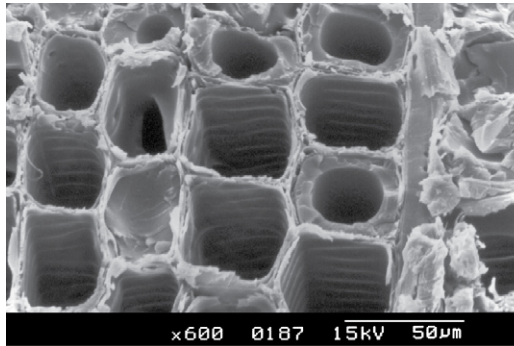
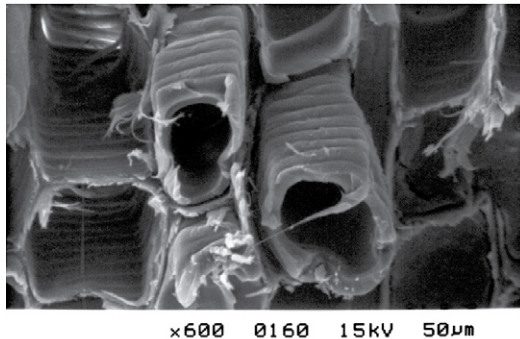


FIGURE 5.3 Reverse migration during consolidation (Brown, 2002). Paraloid B-72 dissolved in acetone was mixed with sand. The slurry was placed in small containers (outline indicated), then allowed to evaporate from the top exposed surface. Once dry, the contents were dumped out and the consolidated plug cut in half. The loose sand showed no sign of any polymer present. (a) 12.5 g/l. (b) 25 g/l. (c) 50 g/l. (d) 100 g/l. *Images courtesy of Gregory Brown, University of Nebraska State Museum.*



(a)



(b)

FIGURE 5.4 Distribution of polymer consolidant in wood vessels deposited from consolidating solution applied to 3 mm × 3 mm × 50 mm specimens of degraded Douglas fir, seen on SEM pictures of fracture sections (Schniewind and Eastman, 1994). (a) Plugs of Paraloid B-72 (applied as a 20% solution in toluene) partly or completely filling the wood vessels next to vessels with no sign of even a thin film deposited. (b) Plugs of Butvar B98 (applied as a 5% solution in toluene–ethanol) pulled out of the fracture surface, appearing not to have adhered to the wood surface. *SEM images courtesy of Peter Y. Eastman, Senior Scientist, Rohm & Haas Company, obtained while studying at University of California, Berkeley.*

The following factors indicate the methods, application and properties of a consolidant solution that should best provide polymer retention in the pores:

- Assuming the higher viscosity method is chosen, the internal surfaces of the object should first be wetted with solvent vapour to reduce the contact angle with the solution and thus increase the wetting rate.
- Evaporation should take place over the whole surface.
- Evaporation should take place slowly to reduce the suction effect and flow of the solution.
- Evaporation should take place in a high solvent atmosphere to encourage the spreading out of the polymer within the pores.
- The viscosity raising factors should be implemented.
- A poor solvent/polymer mix appears desirable.
- Cooling the object impregnated with the consolidating solution during the evaporation stage may encourage early deposition of the polymer.

However, there are a number of competing factors:

- A high initial polymer MW and concentration can increase the viscosity, so reducing wetting and flow into the pores.
- A higher MW polymer would create difficulties with reversing the consolidation.
- A high- T_g polymer will cause long-term shrinkage, not have good long-term adhesion nor be able to adjust to strains in the object, creating brittleness.
- Because of the higher viscosity and lower flow rate, the time to carry out the consolidation will be greater.

To achieve maximum penetration of the consolidation material, it should replace all the air and wet the internal surfaces. A consolidating liquid poured on to a friable surface will be absorbed very rapidly by capillary action, frequently so quickly that the fragile material is displaced by the escaping air. The surface tension difference and shock can be reduced by placing the object in an atmosphere saturated with the solvent used to apply the consolidating material. This is best achieved by removing the air, then applying the consolidant. Removing the air reduces the potential for and size of air pockets trapped by the advancing liquid (Figure 5.5).

The reversibility of consolidation treatments has been shown to be incomplete (Figure 5.6) or nearly complete (Schniewind, 1988).

5.8 ADHESION

An adhesive system should enable the parts of the object to be separated without damage. The adhesive should be strong enough to hold the object together when subjected to the predicted stresses in its application. Ideally, the joint should fail, either in service or during reversal, by cohesive failure within the adhesive or at the adhesive interface. For many applications, this is best achieved using a thermoplastic material that can be dissolved in solvents or melted by

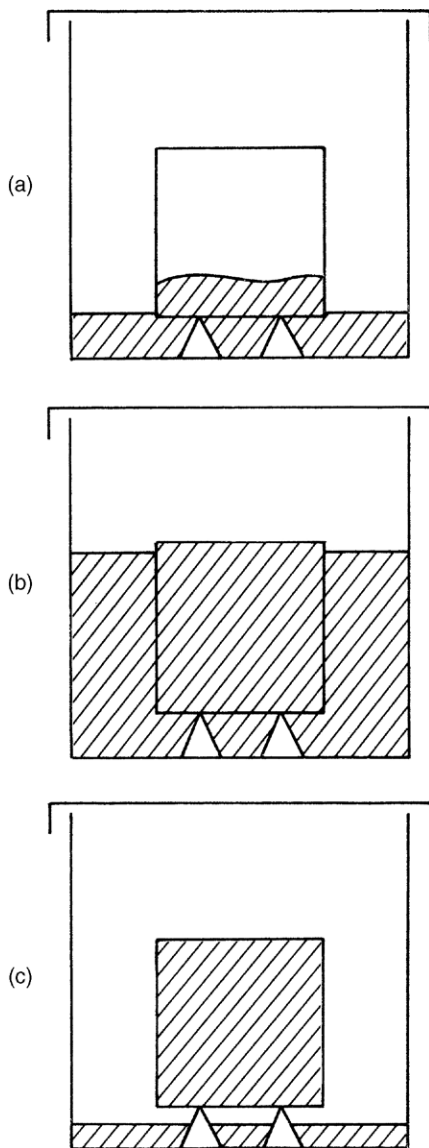


FIGURE 5.5 A guide to the application of consolidant to an object. If the application is carried out under vacuum, the container should be evacuated before the addition of the liquid consolidating material. A cover should be placed over the container to prevent premature evaporation or reaction with atmospheric moisture. The object is lifted off the bottom of the container to reduce the possibility of air pockets (a). A small amount of polymer in liquid form is added to start the penetration process. This liquid is drawn up into the porous material by capillary absorption (b). The object is soaked in consolidant allowing time for trapped air to dissolve and the diffusion of the various components in the liquid to approach equilibrium. Any vacuum that has been applied is broken slowly and carefully to prevent sudden stresses being applied to the object (c). Excess consolidant is allowed to drain out before the drying or setting takes place. This reduces excess consolidant and reduces the formation of a surface skin with solvent-applied polymers.

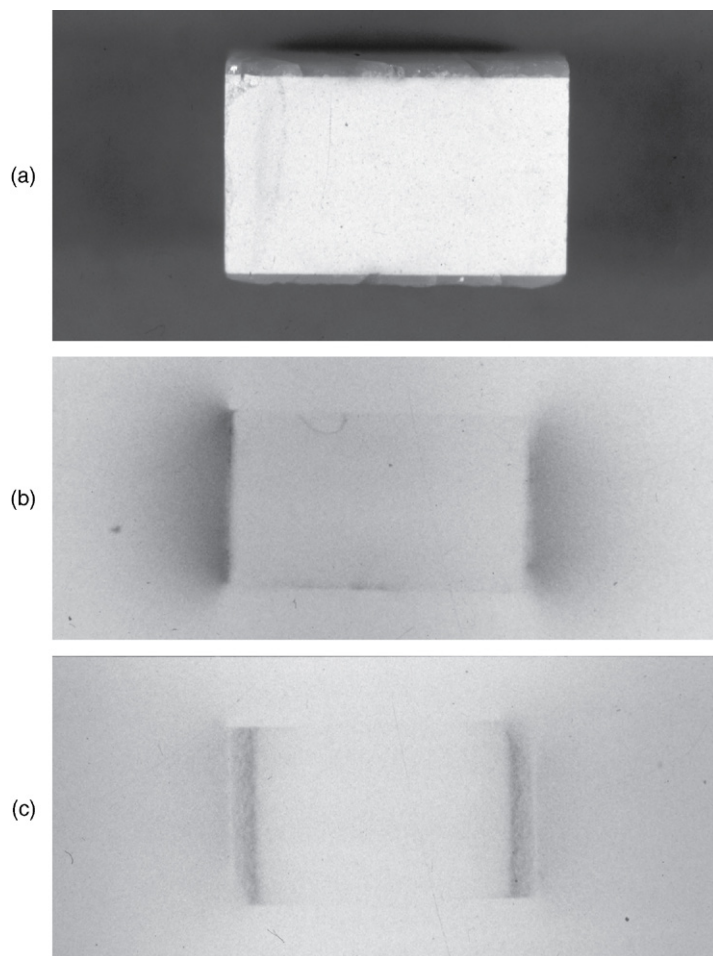


FIGURE 5.6 Reversibility of consolidation. (a) A terracotta bar ($0.9\text{ cm} \times 1.2\text{ cm} \times 1.5\text{ cm}$ long) glazed along the length and open at the ends was consolidated with ^{14}C -tagged PMMA, 50 g/l in chloroform, and allowed to dry. (b) One cylinder was sectioned and placed on photographic film to create this autoradiograph. The PMMA is concentrated at each open end where evaporation took place. (c) One cylinder was washed in recycled acetone in a Soxhlet extractor for 8 hours, dried and sectioned, then an autoradiograph taken. About 50% of the polymer had been extracted, concentrated at the open ends. **Source:** *Horie (1983)*.

heating. Design of adhesive joints is increasingly integrating all aspects by employing recent developments in stress analysis and materials: object properties, stresses applied, mechanical components, adhesive properties, method for reversal (McGlinchey and Yuan, 2004). This may involve complete rethinking and reconfiguring previous methods. A greater understanding of the mechanical properties of canvas paintings is informing the design of lining adhesives.

In the past, a single material might have been expected to fulfil multiple roles, adhesion, structural support and gap filler. However, these requirements

can be provided by combining different solutions. For instance, two parts of a stone statue can be properly located in space using an external armature, which provides the structural strength by taking the gravitational weight, while the physical adhesion and aesthetic filling roles are achieved using a non-structural adhesive (Figure 5.7). Choosing a joining system therefore starts with the



FIGURE 5.7 The upper section of an ancient monumental marble sculpture is being lowered on to its lower section. The lower contact surface was first coated with Paraloid B-72 (to assure reversibility) then with a cast in place epoxy resin. This distributes the compressive load evenly, avoiding point loading at unevenness caused by weathering or previous damage. The two large fragments, weighing well over 500 lb each, are handled by compressive clamp bars. The bars contact strategic points of the sculpture through conformal cast areas of epoxy paste along the length of the clamp bars. Image courtesy of Jerry Podany, J. Paul Getty Museum. Sculpture: *Skulpturensammlung, Staatliche Kunstsammlungen Dresden*.

properties of the object and the expected stresses. The range of potential support and joining techniques is explored. If an adhesive is to be part of the overall solution, the interaction between the two materials will be specified, in application, ageing and reversal. This in turn will guide the choice in the type then composition of the adhesive.

There are relatively few investigations into the physical and chemical nature of the interaction. A solution-applied polymer adhesive will lose its solvent on setting, so the bond line will be mostly air filled, while a dispersion will fill more of the bond line, and a reaction-type adhesive will completely fill the bond line, but with some shrinkage (Figure 5.8).

A thermoplastic adhesive should normally have a glass transition temperature above 40 °C if it is to resist creep. Flexible thermoplastic adhesives (T_g below 15 °C) should be used only where there is no long-term stress or risk of diffusion into porous materials. Cross-linked materials might be used in

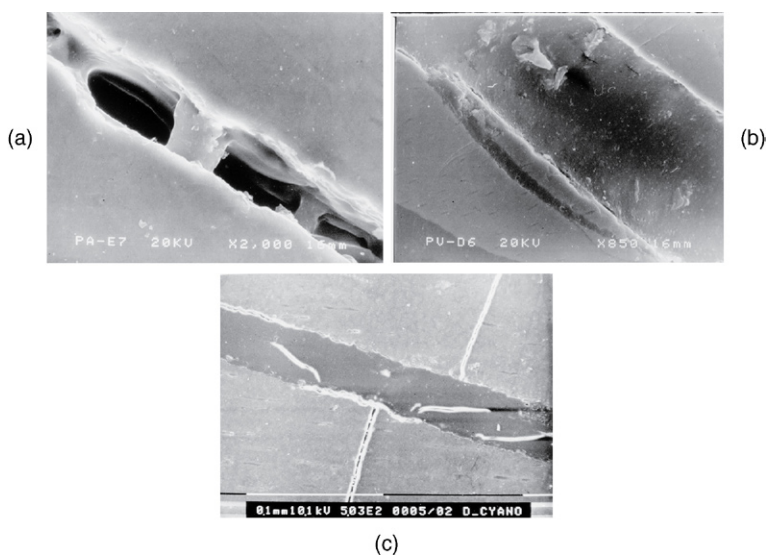


FIGURE 5.8 The effect of polymer setting style on the adhesive joint. Stubs of mammoth tooth were adhered with a number of adhesive materials, allowed to dry, then sections through the joints were examined by SEM. (a) 20% Paraloid B-72 in acetone. Only a small proportion of the joint is filled because of the loss of solvent. The formation of the B-72 pillar is probably due to the same causes as the uneven deposition of a consolidant. Any force placed on the joint will be transmitted and concentrated through a small area of adherend. One would expect these areas to pull away with the adhesive or be the starting point of a more serious cohesion failure of the substrate. (b) Vinamul 9910 (≈53% PVAC and 10% dibutyl phthalate dispersion in water). This image shows the bond nearly full but drying shrinkage has caused cohesive failure in the tooth enamel. (c) Super 7431 (80–100% ethyl cyanoacrylate). Shrinkage during polymerization has caused adhesive failure, and internal shrinkage stress caused cohesive failure in the adhesive. **Source:** Vestergaard and Horie (1996).

these circumstances. Temporary adhesives should conform to high standards of reversibility.

Adhesives frequently penetrate into a porous substrate and act as consolidants (Figure 5.9) so can be very difficult to remove (Bonet et al., 2007). These materials require higher standards of stability than most adhesives. It is often wise to use separate processes for consolidation and adhesion. Similarly, it may be wise to separate the functions of adhesive and gap filler.

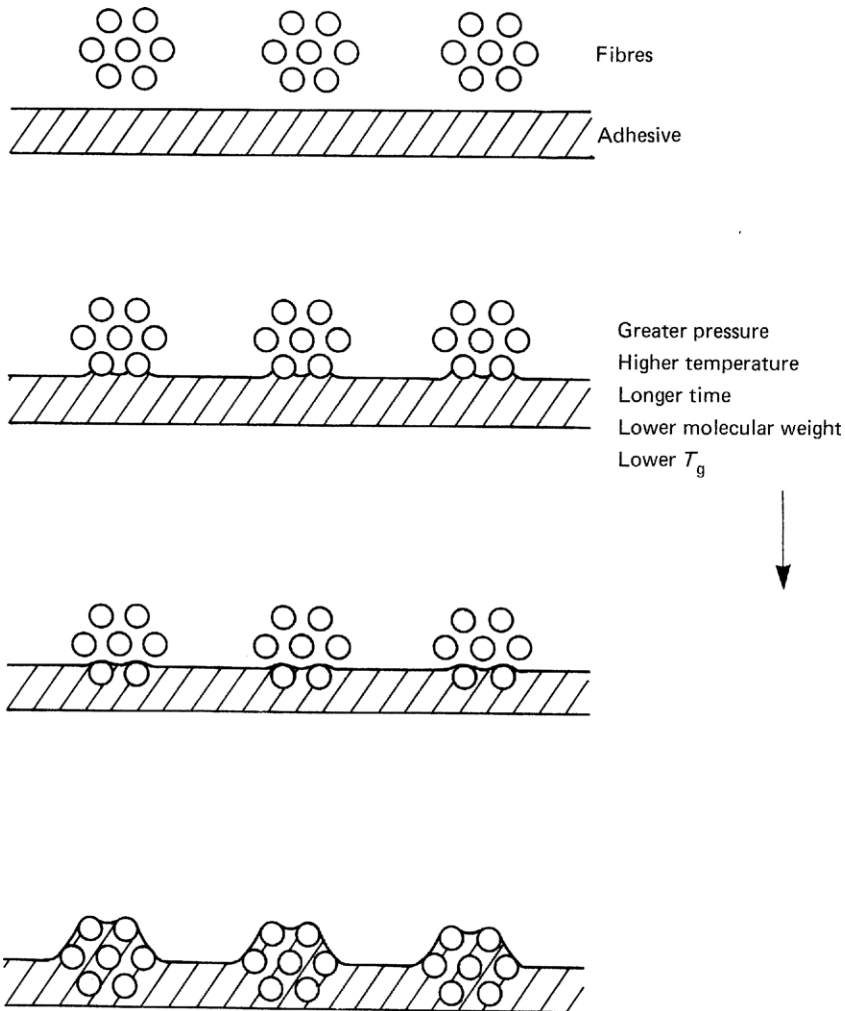


FIGURE 5.9 Development of an adhesive bond between a textile substrate and a high-viscosity liquid adhesive.

A two-stage process of a permanently soluble primer with a cross-linking adhesive may ensure reversibility for the process (Podany et al., 2001). The use of adhesion promoters such as coupling agents should be considered only in extreme conditions of use, e.g. on externally exposed glass, as the chemical bonds with the adherend can be broken only by dissolving away a bit of its surface.

5.9 COATINGS

Because coatings are so exposed to the elements causing deterioration, they are usually designed as temporary additions to an object, although the actual service period may extend to many decades. It should be expected that all coatings will be damaged and replaced periodically. Coatings are therefore designed to have as complete a reversibility as possible.

No semi-permanent coating should have a glass transition temperature below 40°C. Most complete coverage is ensured by multiple thin coats, preferably sprayed on. No polymeric coating can prevent diffusion of water vapour and other contaminants, though it may slow the rate considerably (Comyn, 1985).

The shortest-term coatings are fixatives protecting a fragile element of an object during a potentially damaging treatment, for instance the use of a cyclododecane/Paraloid B-72 coating protecting water-soluble ink on paper being washed (Muñoz-Viñas, 2007).

Liquid coatings require repeated reapplication to ensure that the coating is maintained, as the coating flows, is absorbed by a porous substrate or is rubbed off. Iron swords (Hallam et al., 2004) and machinery (BS ISO/TS 12928:1999, 2000) have been traditionally protected with oils and then with modified oils intended to be reapplied regularly. However, these treatments can be unnecessary if the environmental conditions are adequate (Argyropoulos et al., 2005). Liquid fluorinated polymers have been applied to building stones to increase water repellency while maintaining water vapour transmission (Chiavarini et al., 1993). Oil and wax coatings must be renewed as they drain off or become dirty.

Wax is a traditional water-repellent renewable coating for furniture (Rivers and Umney, 2003) but has been applied with bad consequences to stone (Pan et al., 2009) and iron (Johnson, 1984), from which it has proved difficult to remove.

Considerable research over centuries has been devoted to improving picture varnishes. However, some of these materials tested for use in indoor galleries are being applied in far more extreme environmental conditions without the same rigour in testing for the new conditions.

Coatings may be used as carriers for chemicals that stabilize objects, e.g. corrosion inhibitors and ultraviolet absorbers.

5.10 MOULDING

Moulding materials should not react with the object nor should any oils be left on the object after removal of the mould (Figure 5.10). Any separating layers used during moulding should be treated as a temporary coating and be completely removable. Moulding materials should normally be weaker than the object to reduce the risk of damage during demoulding. Materials with minimal shrinkage should be used.

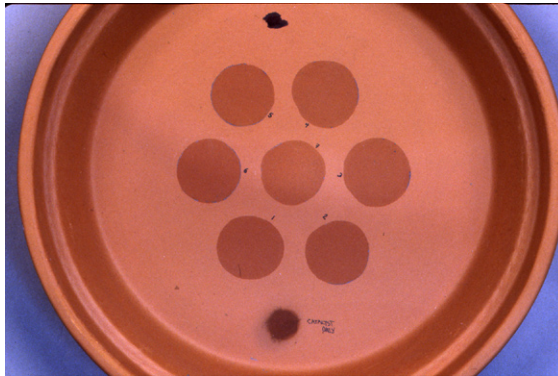


FIGURE 5.10 Staining of surfaces by moulding rubbers. A number of silicone moulding rubbers were poured on to an unglazed terracotta plate and allowed to set. All caused staining (Maish, 1994). Image courtesy of Jeff Maish, J. Paul Getty Museum.

5.11 SPECIFYING A PRODUCT FOR CONSERVATION

A product has many aspects, each of which may be relevant to its proposed use. The headings in Table 5.1 should be considered when choosing or recommending a product. Although the use of standard methods of reporting properties are most useful, even qualitative descriptions of the properties are more valuable than none at all. When a material has been specified as part of a conservation plan, the rationale for the choice should be recorded along with any manufacturer's and internal test data, accompanied by voucher samples. This will enable reconsideration of the material and method by conservators or researchers in the future.

TABLE 5.1 Specifying a Product for Conservation

Necessary Information	Desirable Information	Reasons	Example
<i>Product Information</i>			
Name of product/ declared composition	Batch number, date of supply, data sheet, independent evaluation, previous references	Product name should be used for referring to the materials. Products can change and no untested assumptions should be made about composition	Paraloid B-72 changed its formula without notice
Address of supplier/ manufacturer		A product may be manufactured in a number of sites, perhaps by different manufacturers. Product names can differ across frontiers	Blanose (Europe) and Cellulose Gum (USA) were synonymous
	Pack sizes, price, shipping hazards	Some materials cannot be purchased in the small quantities used by conservators	
<i>Properties of Product</i>			
Properties of product as supplied	Solid/solution/liquid pre-polymers, viscosity	These properties, derived from the manufacturer's literature, indicate the limits of usefulness of the material	Epoxy resins are available in many grades, from pastes to thin liquids
Method of setting	How activated (UV, heat, mixing), proportions of components, setting time, shrinkage	Ditto	Silicone rubbers are available as 1 or 2 parts, set in 5 minutes to 48 hours and shrink 3% to 0.5%, depending on grade
Modification of product by conservator	Solvents used, changing viscosity, pigmentation, de-airing	A material can frequently be adapted to suit its use better	Only a limited range of pigments is compatible with polyester resins

continued

TABLE 5.1 Specifying a Product for Conservation continued

Necessary Information	Desirable Information	Reasons	Example
Special requirements	Shelf life, pretreatment of objects	The material may deteriorate before use or may require an unacceptable change to an object	Many PVAC emulsions have a shelf life of only 6 months
Hazards: toxicity, flammability, disposal	Precautions necessary	These data will alert the conservator to dangers, in working, for users and the environment	Lacquering objects may produce toxic vapours
<i>Properties of Materials That Have Set</i>			
Role of polymer	Adhesive/coating/consolidant/moulding material	A brief description of the tested conservation application is valuable	Cellulose acetate was rejected as a picture varnish
Physical properties	Tensile strength, hardness, extensibility, glass transition temperature	These data (derived from manufacturer's literature or practical experience) indicate the limits of use	PVAL coatings form strong films but have little adhesion to picture varnish
Optical properties	Colour, clarity, refractive index	The appearance of the object can be improved by educated choice of conservation material	Epoxy adhesives can be chosen to have a matching refractive index to the substrate
Modification when set	Polishing, coating, adhering	The use of a material may prejudice the next stage of treatment	A silicone release agent may prevent any further adhesion to the surface
Reversibility of treatments		All treatments involving added materials should be tested for reversibility before use and the test recorded	Wax impregnation of stone has been found to prevent further treatment

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Survey of Polymers

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Hydrocarbons

6.1 POLYETHENE (PE) AND PARAFFIN WAX

6.1.1 Background

Polyethene (Figure 6.1) is made by polymerizing ethene gas. Two main forms are made: a highly branched, low-density polyethene (LDPE) and a more uniform, high-density polyethene (HDPE) (Peacock, 2000). When the chains in PE are highly regular, they can pack closely together to form crystals. These crystals form within the amorphous polymer mass. LDPE forms fewer and smaller crystals than HDPE. The latter is usually opaque because of light scattering by the crystals. The waxes can be considered as low molecular weight versions of PE, with two main forms available, 'paraffin' and 'microcrystalline' (Wolfmeier et al., 2000). Most waxes are derived from fractions of crude oil, though some very low molecular weight PEs are manufactured to fill the gap between petroleum waxes and LDPE. Waxes are also found as minerals in rocks, either pure (ozokerite) or impure (montan, ceresin). The straight-chain alkanes make up the bulk (>90%) of the paraffin waxes, defined here as being the straight-chain variety of wax, C_{16} – C_{40} . Microcrystalline wax is composed of mainly highly branched and naphthenic molecules, C_{23} – C_{85} , with larger molecules than paraffin waxes. Paraffin waxes form large crystals when solid and are more brittle than the tougher microcrystalline waxes. A mixture of the two ($\approx$ 20–40% microcrystalline wax) is stronger than either separately (Mozes, 1982). Waxes are frequently used as moisture vapour barriers. Microcrystalline wax films are less likely to fracture than macrocrystalline waxes and therefore retain their barrier properties over time.

The physical properties of the polyethenes depend on both the molecular weight and the crystallinity (Figure 6.2, Table 6.1). On solidification, the paraffin waxes shrink to a greater extent (13–14% by volume) than do the microcrystalline waxes (9–10%) (Mozes, 1982). PE undergoes about 15% shrinkage on cooling from the molten state (Roff and Scott, 1971). PE will not dissolve in solvents at room temperature but must be heated in order to melt the crystalline areas. The better solvents (tetrachloroethene, trichloroethene, methyl cyclohexane, tetrachloromethane) also cause significant swelling at room temperature, up to 40%. Wax is slightly soluble (up to 20%, decreasing with

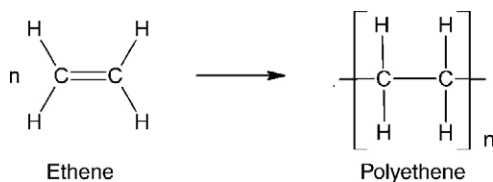


FIGURE 6.1 Polymerization of ethene monomer to polyethene.

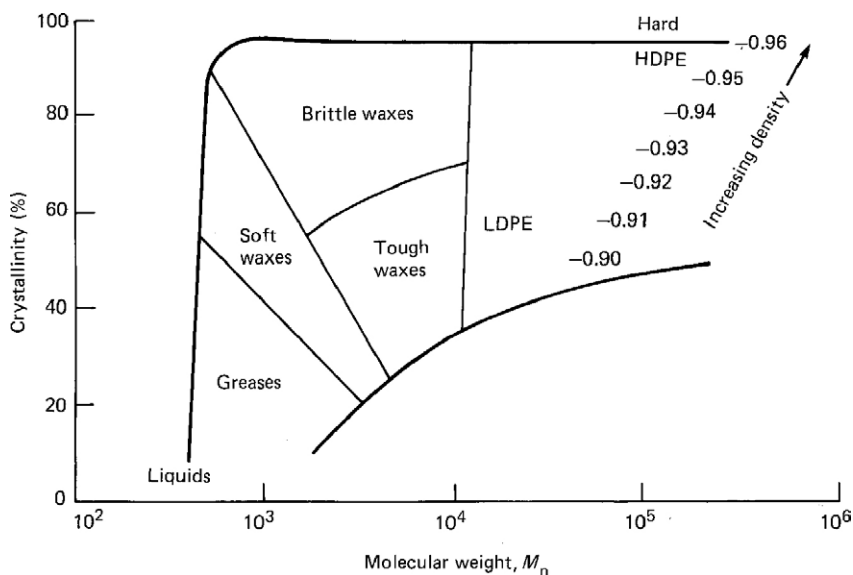


FIGURE 6.2 Correlation of properties of polyethene with crystallinity and molecular weight. Adapted from Richards (1951).

molecular weight) at room temperature. Petroleum jelly, microcrystalline wax swollen with oil, is a pasty grease at room temperature. PE and waxes are inert to aqueous chemicals and to many organic solvents. PE and waxes are subject to photo-oxidation, undergoing degradation, cross-linking, embrittlement and discoloration, with microcrystalline wax being slightly more susceptible than paraffin wax. PE (and wax) has a low glass transition temperature and is subject to dirt pick-up.

Ethene is frequently copolymerized with other monomers to modify its properties. Propene, alone (PP) or copolymerized with ethene, creates a more rigid polymer that can be heated to higher temperatures. It is therefore widely

TABLE 6.1 Hydrocarbon Polymer Properties (see also Table 2.1)

Material	CAS No.	Molecular Weight ¹	Melt Flow Index ²	Branching	n_D ³	Softening Point (°C)	Typical Products
Petroleum jelly		450		High	1.43	45–60	Petrolatum
Paraffin wax	8002-74-2	300	2000	Very low	1.53	40–65	
Microcrystalline wax	63231-60-7	600		Very high	1.45	55–85	Cosmolloid (Astor)
Polyethene wax	9002-88-4	2000		Variable		106	Lumax A (was Wax A) (BASF)
LDPE	9002-88-4	24,000	20	Moderate	1.51	108	
HDPE		200,000	0.02	Very low	1.52	130	
Rubber	9006-04-6	500,000		Low	1.52	–77 (T_g)	
Gutta-percha	9000-32-2	70,000		Low	1.51	33 (T_g)	
Chlorinated rubber	9006-03-5					50 (T_g)	Alloprene (was ICI)

¹Approximate molecular weight (M_n).²A measure of the ability to flow at 190 °C; lower molecular weights have higher values.³Approximate refractive index at room temperature.

used for boxing materials, though it is less stable to photo-oxidation and stress cracking than PE.

Ethene is the principal co-monomer ($\approx 60\text{--}80\%$) in poly(ethene/vinyl acetate) (EVA) copolymers (Zutty et al., 1967). The vinyl acetate (VAC) component reduces crystallinity and increases flexibility (T_g below 0°C). It also increases adhesion and solubility (Appendix 3). The presence of VAC in the copolymer reduces the cross-linking tendency under ultraviolet ageing until at 25% VAC this reaction is negligible (Feller and Curran, 1970).

6.1.2 Conservation

Petroleum jelly has been added to organic materials (e.g. leather) to impart flexibility (Leechman, 1931; Yusupova, 1979). The more fluid portions of the jelly are likely to migrate out of the object. Petroleum jelly is very tacky and will hold dirt readily.

Paraffin wax has been used for over 100 years as a consolidant for corroded iron (Salzer, 1887; Plenderleith, 1956), later modified with microcrystalline wax (Organ and Shorer, 1962) and graphite (Western, 1972). Wax is not an efficient water vapour barrier (Stevens and Johnson, 1950) for corrosion protection (Keene, 1984). Wax has been used as a consolidant for ivory (Petrie, 1904; Lowe, 1910; Packard, 1971), textiles (Newell, 1933), zoological specimens (Noble and Jaekle, 1926), corroded copper alloy (Fink, 1933), and frescoes and stonework (Heaton, 1921). Unfortunately the impregnated wax has frequently caused damage, e.g. terracotta (Tomba, 2007), wall paintings (Ballantyne and Hulbert, 1993) and polychromy on wood (Froysaker, 2006), cannot be completely removed (Berger and Zeliger, 1975; Hatchfield and Koestler, 1987) and prevents the application of other materials for conservation (Ashley-Smith, 1978; Johnson, 1984). This use has been largely abandoned except on lead (Green, 1990) and wood (Jensen et al., 1994).

Paraffin wax was widely used in the nineteenth and twentieth centuries as a lifting material on archaeological sites (Petrie, 1904; Greene, 2003) by pouring the molten liquid over objects. Wax has been used for temporary protection for fugitive pigments on paper during aqueous treatments. Advantage is taken of the inertness of wax in moulding. Wax polish provides a very good release agent for most resins.

A mixture of microcrystalline and paraffin waxes made up as a paste in hydrocarbon solvent has been recommended (Plenderleith and Werner, 1971) to replace beeswax polish on objects such as furniture and metals: 100 g Cosmolloid 80H (microcrystalline wax) and 25 g Wax A (a PE wax; BASF), melted together and poured into 300 ml of a high-flash-point hydrocarbon solvent, stirred constantly until cool (Renaissance Wax).

A harder coating (Larson, 1979) can be made by heating together: 90 g Cosmolloid 80H, 30 g Ketone Resin N (BASF), 200 ml of a high-flash-point

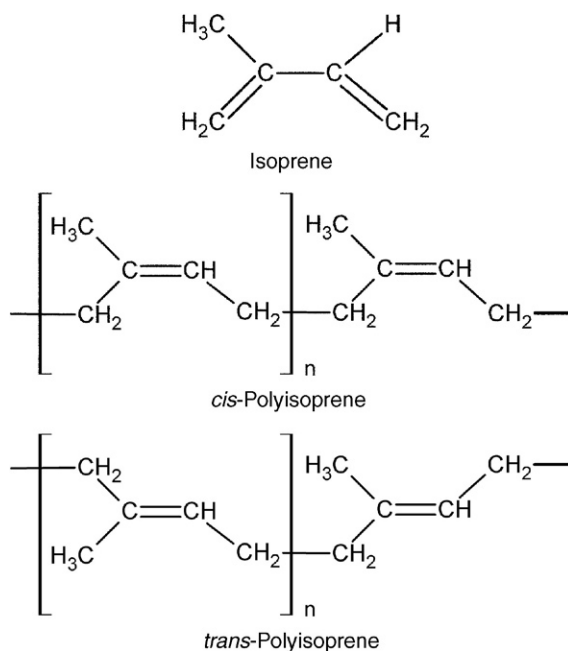


FIGURE 6.3 Monomer, isoprene, and the unit of its polymers, *cis*-polyisoprene (rubber) and *trans*-polyisoprene (gutta-percha).

hydrocarbon solvent, stirred while cooling with further additions of white spirit to produce a suitable brushing consistency.

Reversal of these wax coatings requires the use of hot solvents (Moffett, 1996). The insolubility of microcrystalline wax in cool solvents enables its use as a matting agent in varnishes (Curran, 1975; De Witte, 1975). The wax, 1–4%, must be dispersed in the varnish by heating the solution. If the varnish has to be removed later, the wax may remain in the object.

Polyethylene was introduced in the 1950s as a moisture vapour barrier for panel paintings (Werner, 1952). PE film was later used for laminating paper by heating and melting the polymer under pressure (Belen'kaya and Strel'tsova, 1964). A relatively low-molecular-weight LDPE would be required to ensure good flow and adhesion at moderate temperature (120 °C). The polymer may be dissolved in hot (70 °C) hydrocarbon or chlorinated solvent (Dadic and Ribkin, 1970). A small amount of surface pigment is lost, presumably due to the shrinkage from the molten state during application and the swelling of the polymer by the solvent.

The major use of EVA polymers in conservation is as additives to hot seal adhesives. Elvax 150 (Du Pont; VAC ≈ 33%) and A-C Copolymer 400 (Allied; VAC ≈ 15%) form the bulk of solids of BEVA 371 picture lining adhesive and consolidant (Berger, 1976) (Figure A3.4), and has been widely applied for other types of objects (Kronthal et al., 2003; Karsten and Kerr, 2004). BEVA products

(Conservator's Products) were made (unlicensed) by a number of suppliers, so past products may be variable (Berger et al., 2004). Although BEVA 371 is usually applied in a solvent swollen paste, the components are not soluble at room temperature and must be removed by swelling and rubbing off (Caley, 1998). BEVA D-8 is a poly(ethene/vinyl acetate) emulsion with solvent that is dried to a film then used as a hot melt adhesive (Figure A3.5) (Berger, 1975; Wolfe and Nagy, 2001). Elvax 40 (VAC $\approx$ 40%) has been suggested as a matting agent for varnishes (Hulmer, 1976).

Cross-linked and foamed EVA polymers, e.g. Evazote, are widely used as soft sheet for cushioning during packaging.

6.2 RUBBER

6.2.1 Background

The term 'rubber' can have a number of different meanings. The word 'rubber' was first applied to the solid natural polymer that was found to erase pencil marks. Rubber may also mean the cross-linked material that is made by vulcanizing natural rubber, usually with sulphur. By extension, the term has come to mean any material that exhibits rubbery properties. This section will deal only with the polyisoprene polymers (e.g. natural rubber), cross-linked derivatives (vulcanized rubber) and analogous synthetic polymers (Greve, 2005). Natural rubber is contained in the latex obtained by tapping the bark of *Hevea brasiliensis*. The rubber is predominantly *cis*-1,4-polyisoprene (Figures 6.3 and A3.6). Polyisoprene has a very low glass transition temperature, enabling it to flow at room temperature. The molecular weight can be reduced sufficiently to create the viscous liquids used in pressure-sensitive tapes (Karmann and Kummer, 2002). Polyisoprene is also produced by polymerizing isoprene catalytically.

Solid natural rubber has some elasticity, i.e. it will snap back if stretched and released. This rubbery property is highly developed when the chains are cross-linked. The amount of cross-linking is slight for a soft solid such as erasers. Use of larger quantities of sulphur increases the strength and rigidity. The vulcanized rubbers are insoluble in solvents but are swelled by many hydrocarbons.

Commercial rubber latex is produced by concentrating the latex drawn from the tree, to 60% rubber, with ammonia added to prevent deterioration. The rubber is vulcanized while in the latex form. This will then dry to form an elastic and strong film.

The double bonds in the polymer create potential sites for rapid oxidation at room temperature. The molecular weight of an unvulcanized rubber will therefore fall rapidly. Vulcanized rubbers may become tacky or even pasty. Antioxidants are widely used to reduce the short-term susceptibility to oxidation. Rubber is especially sensitive to attack by ozone and to the catalytic effects of metal ions (Datta et al., 2007).

A material chemically similar to rubber is gutta-percha, *trans*-1,4-polyisoprene, also obtained as a latex from a tree, particularly *Palauquium gutta*.

However, the configuration of the molecule is different, leading to plastic, not elastic, properties. Although rigid at room temperature, it becomes pliable at around 30 °C and melts at 55–80 °C, depending on its composition (Kolokuris et al., 1992). The molecules tend to crystallize within a few months of storage, producing a higher tensile strength and lower extension at break. Its T_g decreases from 38 °C to 5 °C as its moisture content (equilibrium RH) increases (Arvanitoyannis et al., 1993).

Chlorinated rubber, e.g. Duroprene (ICI; Figure A3.7), is a saturated polymer. Although more stable than rubber, it is sensitive to light and ultraviolet, probably in a similar fashion to PVC, resulting in oxidation and discoloration. Chlorinated rubber can react with various pigments such as zinc oxide, copper salts, Prussian blue (ferric ferrocyanide) and ultramarine to form cross-links.

6.2.2 Conservation

Solutions of natural rubber were used during the nineteenth century as consolidants for iron corrosion products and textiles (Rathgen, 1905). They have been used as adhesives for paper (Weidner, 1967), textiles (Rice, 1972), facings on paintings (Cursiter and De Wild, 1939), pottery (Gedye, 1968) and as an isolator during the development of fossil bone (Toombs, 1948). Pressure-sensitive adhesives, based on degraded rubber and rosin derivatives, have been available since the 1920s. The low-molecular-weight resins migrate into porous substrates. These polymers are not stable and are not designed for long-term use. When a tape is pulled off an object, a small amount of adhesive remains on the object surface. These remnants can result in dirt pick-up or discoloration. Removal of old pressure-sensitive adhesives (Book and Paper Group, 1992) can be difficult, starting with mechanical methods then trying a succession of solvents, whose success depends on the formulation of the adhesive, its ageing and substrate: denatured ethanol, acetone, 1,1,1-trichloroethane, toluene and aliphatic hydrocarbon solvent. If these fail, a mixture of 5 ml 1,1,1-trichloroethane, 5 ml of acetone, 1 ml of 0.88 ammonia solution and 10 ml of ethanol may be successful (Collings, 1983). Rubber is too unstable for application to objects in conservation.

The sulphur and other vapours given off by vulcanized rubber can cause severe staining (Cooper, 1939) and corrosion of nearby objects (Oddy, 1975).

Vulcanized rubber is used during cleaning to remove dirt particles from objects. It may be used either as a solid block or as a powder. The soiled powder is removed by brushing or lightly applied compressed air. Being tacky, the very small particles are held in fibrous material. Over time and exposure to light, the powder adheres to itself, forming a film, yellowing slightly at the same time. The rubber is almost totally insoluble in solvents. The sulphur components will discolour brass.

Rubber latex has been widely used since the 1930s as a moulding material (von Fuehrer, 1938; Watkinson, 1982). The pre-vulcanized latex is applied to

the object, allowed to dry to a film and peeled off the surface. The latex will shrink by $\approx 8\%$ on drying unhindered. The latex, stabilized with ammonia, will react with many metals and alkali-sensitive objects. Rubber latex sheet, when dry, will stick to itself and requires a separator of talc or similar to prevent this. Rubber moulds deteriorate very quickly in light and air, becoming weak and brittle within a couple of months. Gutta-percha has been used to make moulds as an impression material by heating the material in hot water then allowing to cool in situ (Nimmo and Prescott, 1968).

Chlorinated rubber was introduced as a general consolidant for organic materials (Carter, 1926; Leechman, 1931) and as a lacquer for iron, sometimes with graphite added (Scott, 1933). Although its susceptibility to deterioration was pointed out in 1931 (Anon, 1931), it continued in use into the 1950s on geological material (Tornesite) (Ewing, 1950).

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Vinyl Acetate-Derived Polymers

7.1 POLY(VINYL ACETATE) (PVAC)

7.1.1 PVAC Homopolymers

Background

PVAC (Figure 7.1) is prepared by all of the free-radical polymerization methods: bulk, solution, suspension or emulsion (Lindemann, 1971a; Cordeiro and Petrocelli, 2003). The polymer is usually slightly branched. PVAC homopolymers are available with a wide range of molecular weights (Table 7.1). The glass transition temperature of PVAC is around room temperature, contributing to its toughness and adhesiveness but also to dirt pick-up and cold flow over long periods (Section 2.2). Although pure alcohols are non-solvents, the addition of small amounts of water may convert them to solvents (Figure A3.8). PVAC is swollen by water, becoming opaque white but reverting to a clear film on drying. The properties of PVAC films cast from solvents depend on the solvent and time of drying (Hansen et al., 1991) – for instance, 4% toluene is retained for months, with effects on the physical properties. Of all the polymers available to conservators, PVAC has been shown to be one of the most stable to light ageing (Thomson, 1963; de la Rie et al., 2000), although when exposed to UV in air at 257 nm PVAC suffers oxidation and cross-linking (Vaidergorin et al., 1987). Down et al. (1996) surveyed a number of PVAC resins used as adhesives, showing that the AYA* range and Vinac B-15 yellowed both in dark and light ageing, but others, such as UHU All-Purpose Clear, were much more stable. PVAC has been shown to be dissolvable from objects and paintings after more than 30–40 years (Cronyn and Horie, 1985; Lomax and Fisher, 1990). PVAC is incompatible with methacrylates in solution (Table 3.4).

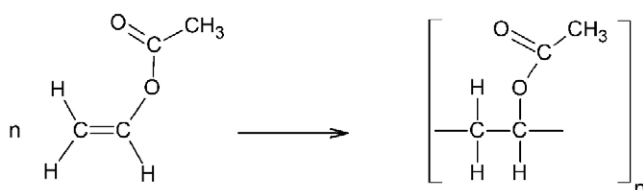


FIGURE 7.1 Polymerization of vinyl acetate monomer to poly(vinyl acetate).

TABLE 7.1 Commercial Poly(Vinyl Acetate) Grades

Trade name	Manufacturer ¹	Grade Designations ²									Notes
Mowilith ³	Hoechst ⁴		20	25	30	40	50	60	70		⁵
PVAC resins	Cairn ⁶	S1 $\frac{1}{2}$	S2 $\frac{1}{2}$			S7		S27		S88	
Rhodopas ³	Rhone-Poulenc ⁷	BB	B		30			H	HH	HV1	
Vinac ³	Air Products					B-7	B-15	B-25		B-100	B-800 ⁸
Vinylite ³	Union Carbide ⁹	AYAC					AYAA	AYAF	AYAT		⁸
PVAC beads	McGean				B-9	B-15	B-25			B-100	
Vinapas	Wacker	B1.5	B17		B60	B100		UW4			
$10^{-3} M_w$ ¹⁰		15	40		63	90	113	290		226	
Viscosity grade ¹¹		1.3	2.8		4.3	5.8	15	27	60	100	800
T_g (°C) ¹²		33	39		42	47		44			

Recent decades have seen major amalgamations and restructuring of the PVAC industry. Many firms have merged with losses of trade names traditionally used in conservation. As part of the general improvements in quality control, the standard of many PVACs has risen, as demonstrated by the increasing water whiteness of the products. However, few of these new products (even if still traded under old names) will have been tested for conservation purposes.

¹Other ex-manufacturers of PVAC include Wacker (Vinnapas) and Montedison (Vinavil).

²Approximately equivalent grades.

³Name is no longer current for PVAC resins.

⁴The Hoechst business was sold to Clariant c. 1999, then the European Mowilith business was later transferred to Celanese.

⁵Mowilith 35/73, a copolymer of VAC and dibutyl maleate, was a softer polymer used in solution.

⁶Cairn is no longer extant.

⁷Rhone-Poulenc chemical products were transferred to Rhodia in 1998, who no longer supply Rhodopas.

⁸Down et al. (1996).

⁹Union Carbide was bought by Dow, who in c. 2005 passed the PVAC range to Ashland, who discontinued all grades but AYAF. For some time in the 1990s and 2000s, Talas sold PVACs of unnamed origin as AYA* products.

¹⁰Weight-average molecular weight (approximate).

¹¹Viscosity of 10% solution of the polymer in ethyl acetate.

¹²Approximate glass transition temperature.

TABLE 7.2 Some Poly(Vinyl Acetate) Dispersions Used in Conservation

Product	Declared composition ¹	Solids content	Particle size (μm)	Viscosity (mPa.s)	pH	MFFT ² (°C)	T _g (Brittle point) ³ (°C)	% Soluble in solvents	Stabilizing emulsifier	Note
Vinamul 3250	Ethene	55	1–2	14,000	4.5–5	3	(5)	90	PVAL	⁴
Vinamul 3252	Ethene	57		2000	4.5–5		3		PVAL	Still manufactured by Celanese Emulsions
Vinamul 6515	15% Vcaprate	56	1–2	100	4–4.5	9	(10)	>95		
Vinamul 6525	25% Vcaprate	56	1–2	200	4–4.5	4	(5)		PVAL	
Vinamul 6815	15% 2-EHA	55	0.5	300	4.5–5.0	10	(10)	>95	PVAL	
Vinamul 8100	None	55		40	6.2	0				
Vinamul 9146	20% DBP	55	1–2	2000	4–4.5	1				
Vinamul 9910	10% DBP	53	1–2	6000	4.5–5.0	4				
Hoechst										
Mowilith DMC2	35% dibutyl maleate	55		8000	4.5	10	10		Cellulose ether	⁵
Mowilith DM427	35% dibutyl maleate	55		20,000	4.5	4			PVAL	⁵
Mowilith DM5	35% BA	53	0.2	3500	4–5	3	2			
Mowilith DM22	⁶	50	0.1–1.5	8000	4–5	0	–5			

continued

TABLE 7.2 Some Poly(Vinyl Acetate) Dispersions Used in Conservation continued

Product	Declared composition ¹	Solids content	Particle size (μm)	Viscosity (mPa.s)	pH	MFFT ² (°C)	T _g (Brittle point) ³ (°C)	% Soluble in solvents	Stabilizing emulsifier	Note
Mowilith DM155	Ethene	55	1.3	6000	5	0	10			
Mowilith D50	None	50	0.5–5	25,000	3.5	16	29		PVAL	
<i>Air Products</i>										
Flexbond 800 ⁷	Dibutyl maleate	53	0.7	70	5–6					7
<i>Reichhold</i>										
Elvace 40-704	Ethene	55	0.2–11	400	5					8
<i>Aabbitt</i>										
Jade 834-403N	Ethene	50	6–7							Was no. 403

Most of these products are no longer made. The caveats given in the table apply to dispersion products to an even greater extent than to homopolymers.

¹Balance of monomer VAC. Co-monomers: BA, butyl acrylate; 2-EHA, 2-ethyl hexyl acrylate; Vcaprate, vinyl caprate. Plasticizers: DBP, dibutyl phthalate; dibutyl maleate.

²Minimum film-formation temperature.

³T_g, glass transition temperature. Brittle point is the highest temperature the film will crack on bending.

⁴Originally Vinyl Products, then as Vinamul Products became part of the National Starch and Chemical Company (part of ICI), then taken over by Celanese (2004). Most of the products have been discontinued.

⁵DMC2 discontinued 1995, replaced by DM427, replaced by Appretan MB extra (Clariant).

⁶Co-monomers are vinyl fatty acid ester and acrylate ester.

⁷Discontinued c. 1973 (Anon, 1983).

⁸Was Elvace 1874 (Du Pont), until the mid-1980s (Kaplan, 1988).

Conservation

The first report of PVAC in conservation was in 1932 as a facing and attaching adhesive for the transfer of a fresco (Stout and Gettens, 1932). The grade of PVAC used was Vinylite A, precursor to AYAF (Union Carbide) (Feller, 1971). PVAC was soon used on frescoes, on wallpaper, on pottery as a glaze, and as lining adhesive for painting (Gettens, 1935) and bone (Woodbury, 1936). Use of PVAC has been extended to most aspects of conservation (Plenderleith, 1956) and was proposed as a picture varnish (Stout and Cross, 1937). PVAC is used as the medium in conservation-grade paints for restoration (de la Rie et al., 2000; Szmit-Naud, 2003). PVAC, either as a varnish or as a medium for restoration in paintings, should be overcoated by varnishes of methacrylate polymers (Feller, 1983). There is constant change in manufacturers and their products, faster than the testing and trialling of materials for conservation. A number of suppliers of PVAC materials to conservators have retained obsolete designations while substituting different but similar products. Examples are the discontinued ranges of Union Carbide PVAC resins, and the Mowilith PVAC resins and dispersions.

7.1.2 Dispersions (Erbil, 2000)

Background

Dispersions of PVAC homopolymer require relatively high temperatures for good film formation; minimum film-formation temperature (MFFT) is $\approx 20^{\circ}\text{C}$. Vinyl acetate monomer lends itself to copolymerization and most current formulations are therefore copolymers with a glass transition temperature and MFFT below 5°C (Table 7.2). Products once used in conservation had plasticizers incorporated. These plasticizers are likely to be lost within a few decades (Barrow Research Laboratory, 1965). PVAC dispersions are particularly unstable in storage, releasing acetic acid, which can react with objects (Oddy, 1975). Stocks should be kept in cool conditions and be discarded when too old, typically 6 months after production. The film cast from the dispersion will not be soluble in water, though some formulations will disintegrate on soaking in water (Bradley et al., 1983). The molecular weight and cross-linking can be varied considerably during manufacture, but details are rarely available from the manufacturer. Because the protective colloids such as poly(vinyl alcohol) (PVAL) and ethyl cellulose become incorporated during the polymerization reaction, the resultant polymer has these water-soluble materials attached. As a result, some portions of the dried film are solvent soluble, some parts water soluble and some not soluble in either. Although previous generations of dispersion-applied films yellowed considerably faster than solvent-applied resins, because of the relatively unstable emulsifiers and stabilizers used (Howells et al., 1984), recent studies have shown that the most stable PVAC films are based on poly(vinyl acetate/ethene) (VAE) copolymer dispersions (Down et al., 1996). An exhaustive investigation into the effect of additives in VAE dispersions for conservation purposes has been carried out at the Canadian Conservation Institute (Down, 2000), providing a set

of guidelines for choosing products for conservation. However, even the chosen model dispersion was not completely soluble, giving rise to concerns about reversibility of treatments where VAE dispersions are used.

Conservation

Dispersions of PVAC became widely available in the late 1940s (Corey et al., 1977). By the early 1950s, they were proposed as adhesives, plasticized by dibutyl phthalate, for relining paintings (Werner, 1952) and modern varieties are still in use occasionally (Ackroyd et al., 2002). Dispersions became widely used for textile and paper conservation. Vinamul 6525 was proposed as a heat-set adhesive for attaching fragile textiles to supports (Beecher, 1959, 1963). These early PVAC dispersions were probably too widely used, judging by the difficulties encountered during the re-conservation of objects made necessary by severe changes in flexibility, colour and dirt pick-up (Karsten and Kerr, 2002). The polymer may be removable, if it remains soluble, by soaking in an ethanol/water mixture (Blum, 1996). PVAC dispersions were investigated for use in paper (Barrow Research Laboratory, 1965), but better materials were needed for long-term use in conservation (Baer et al., 1976). This is confirmed by the regret expressed for the use of PVAC dispersions on globes (Baynes-Cope, 1975).

An emulsion of PVAC formed by mixing a toluene solution of PVAC with a water detergent solution was suggested for consolidating waterlogged archaeological materials (Unwin, 1951). Commercial dispersions have been used to consolidate wet and dry bones from both archaeological (Werner, 1968) and geological contexts (Rixon, 1976).

PVAC dispersions continue to be used for paper as consolidants (Wächter, 1987) and adhesives, especially the VAE copolymers (Maynor and van der Reyden, 1989; Scheper, 2005).

7.2 POLY(VINYL ALCOHOL) (PVAL)

7.2.1 Background (Lindemann, 1971a; Molyneux, 1983; Marten, 2002)

PVAL (Figure 7.2) cannot be made from its nominal monomer, vinyl alcohol, which is not stable. Instead the acetate groups are removed from PVAC and replaced by hydroxyl groups by a process of alcoholysis, similar to hydrolysis but using alcohol instead of water. The reaction need not go to completion. There is thus a choice in the amount of acetate groups left on the molecule, creating what may be thought of as a copolymer of vinyl alcohol and vinyl acetate monomer units. The proportion of alcohol groups in commercial polymers can be nearly 100% – ‘fully hydrolysed’ grades – or down to 70%. Various methods are used to describe the alcohol content (Table 7.3). The molar degree of hydrolysis will be used here for identification of the polymer type (Figure 7.3). PVAL chains

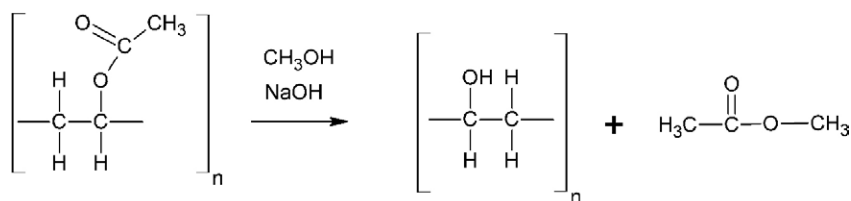


FIGURE 7.2 Monomer unit of poly(vinyl alcohol) homopolymer.

align closely together through the attraction of the hydroxyl groups along the chain. As a result, PVAL with a degree of hydrolysis >93% will dissolve only in hot water and, on cooling and standing, will form either a gel or a precipitate. Between 90% and 85% hydrolysis, the polymer forms stable solutions in cold and hot water. With less than 80% hydrolysis, the polymer will dissolve in cold water only. PVAL has few organic solvents at room temperature, though addition of small amounts of alcohols (<10%) reduces the viscosity of solutions. In aqueous solutions, PVAL has a pH of 4.5–7 and lowers the surface tension. The tensile strength is greatest with fully hydrolysed material (12 kg/mm², extension at break $\approx$ 150%). PVAL is hygroscopic and will absorb water vapour, particularly above 75% relative humidity (RH). The physical and mechanical properties are affected considerably by water content, for instance the T_g varies from 85 °C

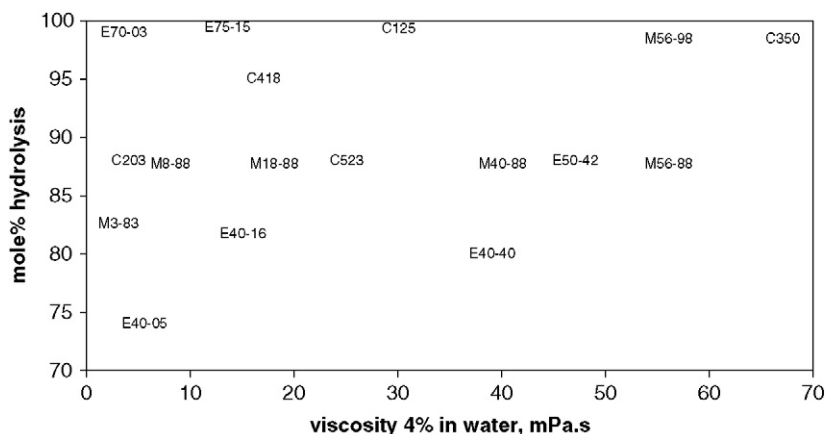
TABLE 7.3 Different Measures of –OH Content in Poly(Vinyl Alcohol)

Hydrolysis (mole %) ¹	Ester index ²	Residual acetate weight (% PVAC) ³
100	0	0
98	13	1.9
92	95	14.5
86	157	24.1
81	205	31.4
78	232	35.5
72	281	43.2

¹Number percentage of hydroxyl groups formed in the molecule.

²The weight, in mg, of potassium hydroxide necessary for complete saponification of 1 g of polymer.

³The weight percentage of the vinyl acetate component of the molecule.



Notes:

Gelvatol (Monsanto) discontinued by 2000

Kuraray supplies Mowiol in Europe (from 2001 had been supplied by Hoechst, then by Clariant) and Povidol in Asia.

Rhodoviol (Rhône-Poulenc) discontinued

Polyviol (Wacker) range restricted to speciality solutions

FIGURE 7.3 Some commercial poly(vinyl alcohols). E, Elvanol (DuPont); C, Celvol (Celanese); M, Mowiol (Kuraray). From manufacturers' information; other grades available. After Toyoshima (1973).

(dry) to $\approx 65^\circ\text{C}$ (100% RH). Oxygen, nitrogen and carbon dioxide permeate at a low rate through PVAL films. Although this property is valuable in commercial barrier films, the lack of adhesion of a PVAL solution when applied to most organic coatings has prevented practical applications in conservation (Feller, 1983). Films formed when drying from a solution will shrink if the PVAL is a grade that forms a gel at room temperature.

Pure PVAL has been shown to be very stable to ultraviolet/oxygen ageing, undergoing fairly slow chain scission (Ciabach, 1983). It may become insoluble by the formation of ether cross-links on light ageing (Thomson, 1963) or heating. The hydroxyl groups are extremely reactive. In slightly acid or alkaline conditions the chains will cross-link and become insoluble (Billmeyer, 1984). It will react with polyaldehydes or polyacids to form insoluble complexes. It will also react with many inorganic salts and some dyes becoming insoluble, especially on exposure to light (Corey et al., 1977). These cross-linking habits probably account for the insolubility of films formed from PVAL-stabilized poly(vinyl acetate) dispersions.

7.2.2 Conservation

The first reports of PVAL use in conservation were in the early 1950s for adhering textiles to backings (Mueller-Christensen, 1957), as a size (Takakage, 1951), as an adhesive for parchment (Gairola, 1958) and as a heat-seal adhesive for

paper (Griebenow et al., 1982) commercialized as Lamatec. By the early 1960s doubts were expressed about the solubility of PVAL that had been applied, particularly to textiles (Geijer, 1961a; Thomson, 1963), but it continued to be used as mass treatment (Anon, 1969). It is wise to assume that these treatments are irreversible. Many of the PVALs that have been used in conservation were fully hydrolysed. Redissolving these polymers will involve washing in changes of hot ($\approx 93^{\circ}\text{C}$) water (Modi, 1980). Advantage has been taken of the chemical cross-linking. PVAL has been shown to increase the strength of paper considerably when added to the paper as a size (Blank, 1978), even more so when a cross-linking agent (borax) is added (Basta, 2004). The conditions of accelerated ageing lead to cross-linking. PVAL fibres mixed with cellulose fibres have been used in a pulp for strengthening degraded paper (Nyuksha et al., 1975). Neither the cellulose nor PVAL fibres would be removable.

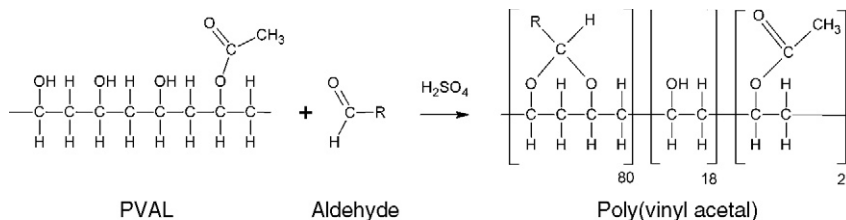
PVAL has been widely used for the fixing of pigments (Savko, 1971; Bicchieri and Mucci, 1996) and for inpainting (Falvey, 1981). Shrinkage of the drying film on paintings on paper resulted in the curling up and exfoliation of the pigments to which a PVAL/agar-agar consolidant had been applied (Chemical Research Section and Research Section for Repairing Techniques, 1968). Reversal of the treatment involved removal of the bulk of the surface coating, facing and re-adhering the flakes. PVAL will cross-link with many metallic salts, some of which are used as pigments.

PVAL has been used as an adhesive for ivory (Makin, 1997) and a consolidant for wall paintings (Hu, 1989). PVAL is used in glass restoration as a release agent during casting, moulding and adding new materials for reintegration (Hartleitner, 1990; Davison, 2003).

7.3 POLY(VINYL ACETALS)

7.3.1 Background (Hallensleben, 2005)

Poly(vinyl acetals) (Figure 7.4) are manufactured by reacting PVAL with an aldehyde. The resultant poly(vinyl acetal) is essentially a terpolymer of ‘vinyl acetal’, ‘vinyl alcohol’ and ‘vinyl acetate’ monomers. Poly(vinyl acetals) have been available, and used in conservation, since the early 1930s. Poly(vinyl butyral) (PVB) is the most widely used of these polymers (largely for laminating safety glass and cross-linked metal primers), and poly(vinyl formal) still has commercial uses (cross-linking insulator for wires), though poly(vinyl acetal) itself has been discontinued. PVB is available at various molecular weights and proportions of the $-\text{OH}$ groups remaining (Table 7.4). PVB with a high proportion of hydroxyl groups (17–21% molar) is soluble in solvents only with a considerable hydrogen bonding capability (Appendix 3). Low-hydroxyl PVB (9–13%) is soluble in a wider range of solvents and has a lower glass transition temperature. Viscosity of PVB solutions is reduced by using mixed solvents, e.g. 60% ethanol–40% toluene. Difficulties have been found with adhesion of



R = -H, i.e. poly(vinyl formal)

R = -CH₃, i.e. poly(vinyl acetal)

R = -CH₂CH₂CH₃, i.e. poly(vinyl butyral)

Figure 7.4 Structure of poly(vinyl acetals) with typical proportions of components that are more or less randomly distributed along the chain.

the higher hydroxyl PVB (Howie, 1984), perhaps due to the high glass transition temperature.

A major application of poly(vinyl acetals) is as a cross-linking polymer by traces of acids and heat and other chemicals such as dialdehydes. Unfortunately few conservation studies have been carried out on objects in order to demonstrate (or not) the reversibility of the application of poly(vinyl acetals). A thorough study of PVB by both UV/light and heat ageing demonstrated that it is fairly stable, oxidizes, yellows little, degrades slowly to become brittle, and does not cross-link significantly below its glass transition temperature (Feller et al., 2007). Of two types tested, Mowital B30H and Rhovinal B10-20, the Rhovinal appeared less suitable as it yellowed, became slightly brittle and lost solubility (Blackshaw and Ward, 1983). Extreme UV conditions cause considerable cross-linking with some degradation, leading to an insoluble network (Ciabach, 1983).

7.3.2 Conservation

Poly(vinyl formal) was tried as a consolidant for textiles (Geijer, 1961b; Leene, 1963) but could not be redissolved, presumably because of cross-linking with acid and aldehyde groups on the degraded textile.

Poly(vinyl acetal) itself was used from the 1930s (Woodbury, 1936) to the 1960s (Howie, 1984) for the conservation of geological bone and ivory (Gyermek, 1964) and wood (Spirydowicz et al., 2001). It was replaced in the 1960s by PVB. PVB has been widely used as a consolidant for textiles (Mowital B60HH) (Leene, 1972), (Mowital BH10) (Lodewijks and Leene, 1972), fossils (Butvar B98 and B76) (Howie, 1984), wood (Butvar B90) (Barclay, 1981), (Butvar B98) (Spirydowicz et al., 2001) and paper (Belen'kaya, 1964), and as an adhesive for wood (Mowital B20H) (Cronyn and Horie, 1985), glass (Mowital B60HH) (Vos-Davidse, 1969) and paint films (Kostrov, 1956; Higuchi, 1980). A modelling material (AJK dough) was based originally on poly(vinyl acetal)

TABLE 7.4 Commercial Poly(Vinyl Butyrals) (Manufacturers' Data)

Product	Manufac- turer	Weight propor- tions of			Molecular weight, $10^{-3} M_w$	Solution T_g (°C) viscosity ² (mPa.s)
		Vbutyral	VAL ¹			
Butvar B-73	Solutia ³	80	19	50–80	87	62–68
Butvar B-74		80	19	100–150	140	62–68
Butvar B-76		88	11	45–55	45	48–55
Butvar B-79		88	11	34–38	25	48–55
Butvar B-90		80	19	38–45	59	62–68
Butvar B-98		80	19	30–34	25	62–68
Mowital B20H	Hoechst	76	20		14	
Mowital B30H		76	20		25	
Mowital B30T		70	26		25	
Mowital B60H		77	20		65	
Mowital B60HH		83	14		60	
Rhovinal B 7/20	Rhone- Poulenc	77	19		16	
Rhovinal B 10/20		77	19	30–35	29	
Rhovinal B 20/20		77	19	≈55	54	
Rhovinal B 50/20		77	19	150	140	

¹VAL, vinyl alcohol component, vinyl acetate content about 0.5–2.5%. Balance made up in volatiles.

²Viscosity of a 5% solution of the polymer in *n*-butanol.

³Solutia took over the Butvar range from Monsanto in 1997.

(Alvar) (Gedye, 1968), later replaced by PVB (Butvar B98) (Patterson, 1978). This kneadable paste is prepared from an emulsion of water in a resin solution to which was added kaolin and jute flock. This models well and produces a strong, lightweight material widely used for infilling pottery losses. Unfortunately the dough undergoes short- and long-term shrinkage on drying, presumably through the slow loss of solvent and water.

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Acrylic Polymers

8.1 BACKGROUND

The majority of acrylic polymers used in conservation are made from two families of monomers (Figure 8.1): the acrylates, derived from acrylic acid, and the methacrylates, derived from methacrylic acid, which are used in acrylate (Slone, 2003a) and methacrylate (Slone, 2003b) polymers. Other monomer groups appear in conservation materials, acrylonitrile (the comonomer in vinylidene chloride polymers) and cyanoacrylates. There has also been an increasing interest in the stability of fluorinated acrylic polymers. Abbreviations are widely used in discussion of the various polymers (Table 8.1). The glass transition temperatures (T_g) of the homopolymers are highest when the side chain is shortest and the T_g of a methacrylate polymer is higher than its acrylate counterpart. It is relatively easy to make copolymers with a chosen T_g by using two or more acrylic monomers. The polymerization of acrylic monomers results in considerable shrinkage, $\approx 21\%$ by volume in the case of MMA. Heat is also generated, ≈ 60 kJ/mole for methacrylate and 79 kJ/mole for acrylate polymerizations.

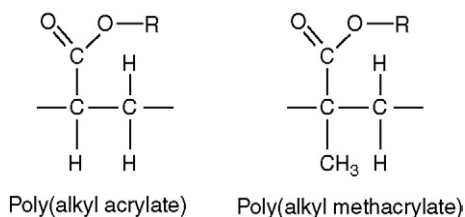


FIGURE 8.1 Acrylic polymers, monomer units. The alkyl ($-R$) group can be chosen to produce a range of polymers (Table 8.1).

PMMA is extremely stable to degradation by heat and oxygen/ultraviolet ageing but, when exposed to simulated sunlight, its toughness reduces considerably (Colom et al., 2001). However, the higher methacrylate polymers (PEMA and above) cross-link under ultraviolet (Chiantore and Lazzari, 2001) and visible light exposure (Feller et al., 1981). The cross-linking under light appears to occur through reactions on the side chains by an oxidation mechanism. The methacrylates are more likely to cross-link if they are exposed above or near their glass

TABLE 8.1 Acrylic Homopolymer Properties and Abbreviations¹

Side Chain Radical	Acrylate Polymer				Methacrylate Polymer			
	Abbreviation	T _g (°C)	n _D (25 °C)	CAS no.	Abbreviation	T _g (°C)	n _D (25 °C)	CAS no.
–CH ₃ (methyl)	PMA	6	1.479	9003-21-8	PMMA	105	1.490	9011-14-7
–C ₂ H ₅ (ethyl)	PEA	–24	1.464	9003-32-1	PEMA	65	1.484	9003-42-3
–(CH ₂) ₃ CH ₃ (n-butyl)	PnBA	–50	1.474	9003-49-0	PnBMA	20	1.483	9003-63-8
–CH(CH ₃)C ₂ H ₅ (isobutyl)	PiBA	–43		26335-74-0	PiBMA	50	1.477	9011-15-8
–CH ₂ (CH ₂) ₂ (CH ₃) ₂ (isoamyl)					PiAMA	26 ²		
–CH ₂ CH(C ₂ H ₅) (CH ₂) ₃ CH ₃ (2-ethylhexyl)	P2EHA	–55		9003-77-4	P2EHMA	–10		25719-51-1
–C ₆ H ₆ (phenyl)	PPhA				PPhMA	110	1.571	25189-01-9
–H (acid)	PAA	162		9003-01-4	PMAA	220		25087-26-7

Sources: Penzel (2005), Stickler and Rhein (2005).

¹Abbreviations for copolymers are expressed as in *P(MMA/EA)* for a copolymer of methyl methacrylate (major component) and ethyl acrylate.

²Feller (1972).

transition temperatures. In PEMA, the chain scissioning reactions predominate at room temperature but higher methacrylates form insoluble gels. The lower acrylates do not cross-link in simulated sunlight (including ultraviolet) exposure (Chiantore and Lazzari, 2001). In copolymers of acrylates with methacrylates, the formation of a gel depends on the proportion of the monomer groups and the temperature of exposure with respect to the glass transition temperatures of the polymer (Grassie, 1982). It is possible to construct copolymers with the required physical properties and with the desired balance of scissioning/cross-linking behaviour. Oxygen is incorporated into the polymer leading to an increase in the polarity of the solvents required for dissolution (Feller, 1963).

In the 1950s, Feller (1972) showed that fluorinated acrylics had even higher stability than those currently available. These have been extensively researched for use on external stone surfaces (see Table 8.2 for typical examples). They cannot be used as homopolymers, because they have relatively high T_g values and dissolve in few solvents. As has been similarly shown with the parent polymers, the distribution of the fluorine substituents appears to be important in determining the photo-oxidative stability of the polymer (Signori et al., 2006). However, suitable polymers have yet to be developed that meet the other requirements of this usage (Toniolo et al., 2002).

Acrylic lacquers have poor solvent release from touch-dry films (Gaynes, 1967) and retain solvents for considerable times. Toluene has been shown to be held very strongly – for much longer than 2 months in films of Paraloid B-72. By contrast, *p*-xylene evaporates more slowly during the initial wet stage of drying but leaves freely during the later stages (Dauchot, 1976). This was ascribed to the difference in polarity of the solvents.

8.1.1 Commercial Reaction Adhesives

Cyanoacrylate polymers (Figure 8.2, Table 8.3; also see Figure A3.41) are polymerized in situ from monomers (Schoenberg, 1990). The reaction is initiated in the film of moisture on the surface. It is thus dependent on the nature of the surface and the relative humidity of the air. Alkaline surfaces such as glass promote rapid adhesion, whereas acid surfaces such as wood require polymerization activators.

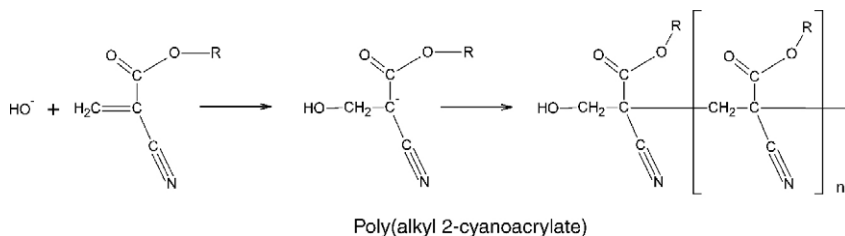


FIGURE 8.2 Cyanoacrylate monomer units polymerize in a join by an anionic mechanism, typically initiated by hydroxyl groups in adsorbed water. The alkyl (–R) group can be varied to modify the polymer properties. R may be methyl, ethyl or butyl, or contain an unsaturated group allowing cross-linking between chains and thus greater stability.

TABLE 8.2 Typical Fluoroacrylics Being Investigated for the Protection of Externally Exposed Stone

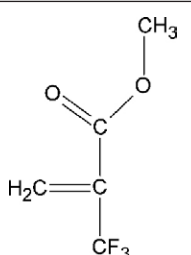
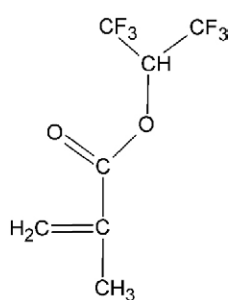
Monomer Structure	Monomer Name	Abbreviation	Polymer T _g (°C)	CAS No.	Reference
	Methyl α -trifluoromethyl acrylate	MTFMA	89	382-90-1	Ciardelli et al. (2000)
	1,1,1,3,3,3-Hexafluoro-2- propyl methacrylate	HFIMA	81	3063-94-3	Signori et al. (2006)

TABLE 8.2 Typical Fluoroacrylics Being Investigated for the Protection of Externally Exposed Stone continued

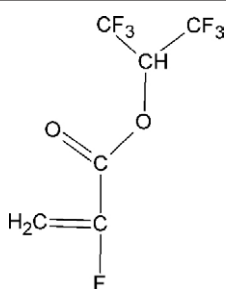
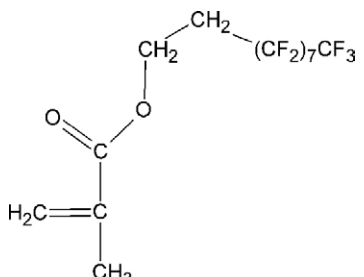
Monomer Structure	Monomer Name	Abbreviation	Polymer T _g (°C)	CAS No.	Reference
	1,1,1,3,3,3-Hexafluoro-2-propyl fluoroacrylate	HFIFA	108	74359-06-1	Signori et al. (2006)
	1H,1H,2H,2H-Perfluorodecyl methacrylate	XFDMA	47	1996-88-9	Lazzari et al. (2001)

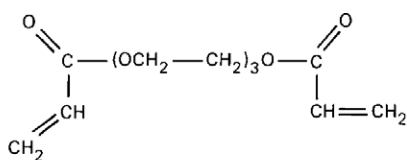
TABLE 8.3 Properties of Poly(2-Cyanoacrylates)

Polymer	Monomer	T_g^1 (°C)	Solubility Parameter	CAS No.
PMCA	Methyl	100	14.7	25067-29-2
PECA	Ethyl	56	11.2	25067-30-5
PBCA	n-Butyl	115	10.7	25154-80-7

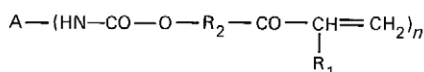
¹Kulkarni et al. (1973).

Very-high-molecular-weight polymers ($\approx 10^9$) are formed with high T_g values during setting. The monomers are very mobile liquids (2–3 mPa), which can drain out of a joint before setting and cannot fill gaps. Commercial products contain plasticizers or soft polymers, stabilizers to prevent premature polymerization and thickeners to stop the liquid draining out of the joint before setting. PMCA can be dissolved with difficulty in methylene chloride, γ -butyrolactone or nitromethane, whereas the higher analogues can dissolve in acetone, tetrahydrofuran, etc. Prolonged soaking (>5 weeks) in acetone causes degradation of PECA (Han et al., 2008) and will often break down the joint (Davison, 1978). Cyanoacrylate adhesives appear to lose strength on prolonged light exposure (A. Moncrieff, personal communication). Cyanoacrylates degrade severely in alkaline conditions by hydrolysis (Donnelly and Pepper, 1981), and less rapidly in alkaline conditions on fossils (Down and Kaminska, 2006).

Many acrylic derivatives are used as pre-polymers in thermo-setting adhesives (Damico, 1990). Typical pre-polymers are formed by reaction with glycols or isocyanates (Figure 8.3). These materials polymerize to form highly



Triethylene glycol dimethacrylate (Martin, 1977)



Urethane methacrylate (Murray et al., 1977)

A = polyisocyanate, e.g. diphenylmethane-4, 4'-diisocyanate

$\text{R}_1 = \text{H}_1\text{CH}_3$

$\text{R}_2 = \text{---C}_2\text{H}_4\text{---}, \text{---C}_2\text{H}_4(\text{CH}_3)\text{---}$

FIGURE 8.3 Examples of monomers used in acrylic reaction adhesives, e.g. anaerobic and ultra-violet curing types.

cross-linked structures that will not swell appreciably in solvents. The products can be formulated to set when initiated in the absence of oxygen (anaerobic adhesives), by an activator applied to one surface or by ultraviolet radiation. The few ultraviolet curing adhesives that have been tested for light stability have yellowed and lost adhesion (A. Moncrieff, personal communication).

8.2 CONSERVATION

Acrylic polymers have been available in solid or in solution (Table 8.4) and it is apparent that the commercial product is variable. During the early 1930s acrylic polymers, Lucite 44 and 45 (now Elvacite 2044 and 2045 (Feller, 1959)) started to be used as picture varnishes (Feller, 1971a). These PBMA polymers were increasingly used for varnishes but about 20 years' experience was gained before this use was published (Rawlins and Werner, 1949; Werner, 1952; Feller, 1971b). PBMA has the advantages of resistance to yellowing, solubility in hydrocarbon solvents and sufficient flexibility, yet (in the case of PiBMA) a glass transition temperature that will prevent dirt pick-up, and it is commercially available at relatively low molecular weights. Unfortunately PBMA was shown to be unsuitable for long-term use because of the unexpected cross-linking of the polymer under the influence of light (Feller, 1971b). After 22 years' exposure on a laboratory wall, it became about 50% insoluble (Feller, 1971a) and required more polar solvents for removal. PiAMA was made available as an experimental varnish in the early 1950s. After c. 40 years ageing, it and PBMA varnishes proved difficult to remove using low-polarity solvents (Lomax and Fisher, 1990).

The failure of an apparently excellent material prompted a search for more stable polymers. Paraloid B-72 does not become insoluble or degrade significantly on internal exposure in a gallery (Feller, 1978) or accelerated solar exposure (Chiantore and Lazzari, 2001), although oxidation and other changes do occur slowly (Ciabach, 1983). It has therefore become a standard of stability, a Feller Class A material. Paraloid B-72 has been reported as P(MMA/EA) (Feller, 1967) on the authority of Rohm & Haas, P(EMA/MA) with a molar ratio of 68:32 (early less polar version) and 70:30 (De Witte et al., 1978), and then as P(EMA/MA/BMA), 66:32:2 (Chiantore and Lazzari, 1996). In a direct photodegradation comparison between B-72 and a P(EMA/MA) analogue, B-72 showed slightly greater tendency to cross-link, probably as a result of the difference in composition (Bracci and Melo, 2003).

Formulations of Paraloid B-72 with various solvents and matting agents have been suggested (Figure A3.15). Toluene or xylene are usually the major components (Hulmer, 1976), *p*-xylene probably being the best choice (Dauchot-Dehon and De Witte, 1978). Solutions for picture varnishes are around 20% solids for brushing and 10% for spraying. Matting agents include microcrystalline wax (up to 47% of total solids), aerosol silica (up to 18% of total solids) or ethylene/vinyl acetate polymers, e.g. Elvax 40 W (Du Pont; up to 10% of total solids)

TABLE 8.4 Reported Acrylate Polymer Composition and Properties

Name	Monomer Composition (%)	M_n (10^{-3})	M_w (10^{-3})	M_w/M_n	T_g^1 (°C)	n_D	Elongation at Break (%)	Solubility Chart	Note ²
Rohm & Haas									
<i>Paraloid</i> ³									
B-44	MMA/EA/nBMA 70:28:1	23	105	4.56		1.4790		A3.11	Used in Incralac ⁴
B-44S	MMA/EA >>50:50						20–300		5
B-48N	MMA/BMA 75:25	48	184	3.83		1.4807			4
B-48S	MMA/BA 70:30						40–70		5
B-67	iBMA	24	48	2.00	50				4
B-67	iBMA	11	45	4.08				A3.12	6
B-67					64				7
B-72	MMA/EA 50:50								8
B-72	EMA/MA 68:32					1.479			‘Old’ lumpy version ⁹
B-72	EMA/MA 70:30					1.481			‘New’ more polar, lower MW ⁹

TABLE 8.4 Reported Acrylate Polymer Composition and Properties continued

Name	Monomer Composition (%)	M _n (10 ⁻³)	M _w (10 ⁻³)	M _w /M _n	T _g ¹ (°C)	n _D	Elongation at Break (%)	Solubility Chart	Note ²
B-72	EMA?	11	65	5.72		1.487			⁶
B-72	EMA/MA/nBMA 66:32:2	41	88	2.15	40	1.4756			Might be a mixture of two polymers ⁴
B-72		44.8	104.9	2.34			110–350 ⁵	A3.13	¹⁰
B-82	MMA/EA 50:50				41 ⁷		200–330		⁵
B-82	MMA/EA/BMA 56:43:1	96	38	2.53	35	1.4766			Might be a mixture of two polymers ⁴
Lucite previously Dupont									
<i>Elvacite</i>									
2042	EMA		220		63		25		
2043	EMA		50		65		0.6	A3.9	
2044	nBMA		142		15		300	A3.10	Once known as Lucite 44 ¹¹
2045	iBMA		195		55		1	A3.10	Once known as Lucite 45 ¹¹

Continued

TABLE 8.4 Reported Acrylate Polymer Composition and Properties continued

Name	Monomer Composition (%)	M_n (10^{-3})	M_w (10^{-3})	M_w/M_n	T_g^1 (°C)	n_D	Elongation at Break (%)	Solubility Chart	Note ²
Degussa									
<i>DEGALAN</i>									
P550	nBMA		65		25				Was Plexisol P550 (Rohm until 1996)
P675	iBMA		180		48				Was Plexigum 675 (Rohm until 1996)
N742	EMA		60		64				Was Plexigum 742 (Rohm until 1996)
Cray Valley									
<i>Synocryl</i>									
9122X	nBMA								Was Bedacryl 122X (ICI)
Lascaux									
P550	BMA								8

TABLE 8.4 Reported Acrylate Polymer Composition and Properties continued

Name	Monomer Composition (%)	M_n (10^{-3})	M_w (10^{-3})	M_w/M_n	T_g ¹ (°C)	n_D	Elongation at Break (%)	Solubility Chart	Note ²
Pliantex EA									Discontinued 1996 ¹²
Pliantex EA/MMA >66							140–220		5

¹Manufacturer's information.

²It is apparent that commercial products are variable. It is therefore unfortunate that these authors do not provide the batch number or date of production of the materials under test.

³Paraloid resins were designated Acryloid in the North American market. They were manufactured at various sites around the world.

⁴Chiantore and Lazzari (1996).

⁵Down et al. (1996).

⁶de la Rie (1987).

⁷Schilling (1989).

⁸Feller (1972).

⁹De Witte et al. (1978).

¹⁰Bracci and Melo (2003).

¹¹Feller (1971a).

¹²Waterer (1972).

(Hulmer, 1976). The mattness of a sprayed coating can of course be varied by adjusting the conditions of spraying. There is a gradual loss of gloss over the months of solvent evaporation (De Witte, 1975).

Paraloid B-67, a PiBMA (Chiantore and Lazzari, 1996), is used as a picture varnish (Figure A3.14). Although it cross-links (Feller, 1976), especially under severe UV exposure (Chiantore and Lazzari, 2001), it appears to be peculiarly stable and of Class A standard (Feller, 1983). However, this stability appears to derive from an unknown composition, which creates an extended induction period before cross-linking starts. It is soluble in less polar solvents than B-72. When applied to marble, $\approx 15\%$ rapidly becomes insoluble, which increases on accelerated ageing to 70% (Favaro et al., 2006).

In an attempt to deal with the perceived inadequacies as a picture varnish of the then available acrylics, De Witte et al. (1981) designed a P(MMA/PhA) (ratio 70:30) with a high refractive index (1.547), slightly higher than that of dammar (1.53), and a relatively low molecular weight to improve penetration. Accelerated light ageing showed that it degraded slightly, but fell within Feller's Class A.

Acrylic polymers have been applied in solution to many other types of object. PMMA, the most widely available of the acrylics (Figure A3.10), has too high a glass transition temperature to be applied successfully. It is likely to separate from the substrate. It was recommended as a coating for glass (Hedvall et al., 1951), to consolidate pigments (Takakage, 1951), as an adhesive for paper (Gairola, 1958) and as a lacquer for silver (Bhowmik, 1967). Incralac, a clear coating based on Paraloid B-44 (Figure A3.13), developed by INCRA (International Cooper Research Org.) has been widely used on copper and silver alloy objects, because of its resistance to weathering and incorporation of the corrosion inhibitor benzotriazole (Moncrieff, 1966). After 10 years of external exposure on sculpture, it has been shown to become insoluble, but not significantly oxidized, presumably by cross-linking (Erhardt et al., 1984).

PEMA (Figure A3.11) has been used for the consolidation of wood (Cronyn and Horie, 1985) and PiBMA as a lacquer for mosaic (Stout, 1969). The two PBMA's became increasingly used from the 1930s to the 1960s. Typical uses were for laminating plants (PiBMA) (Wheatley, 1941), coating silver (Biek, 1952), consolidating fossils (PnBMA) (Rixon, 1965), pigments (Kostrov, 1956), leather (Waterer, 1973), plaster (Gerassimova and Mel'Nikova, 1978), stone (Ageeva et al., 1978) and earth (Shorer, 1964; Natchinkina and Cheinina, 1981), and as adhesive for textiles (PnBMA) (Beecher, 1968) and wood (Angst, 1979). PBMA has been largely displaced by more stable polymers such as Paraloid B-72 and PVAC. It continues in use for those purposes requiring a low glass transition temperature, low molecular weight and solubility in petroleum solvents, which tend to be cheaper. There are no stable materials that duplicate the useful qualities of PBMA,

though stable low-molecular-weight resins (Chapter 11) have been developed for picture varnishes.

Paraloid B-72 was used initially as a silver lacquer in 1947 (Anon, 1950; Olson and Thordeman, 1951) and is still used for this purpose (Jett, 1993), then for textile consolidation (Geyer and Franzen, 1956). Although polymers with more appropriate physical properties could be designed, B-72 remains one of the few polymers that has been intensively tested and cleared for conservation use, albeit primarily as a picture varnish in low light levels with minimal UV exposure. The uses suggested for Paraloid B-72 include: hot melt adhesive for paper (Zappalà and La Mendola, 1978); consolidant for matt pigments (Welsh, 1980), lacquerwork (Sawada, 1981) and wood (Serck-Dewaide, 1978); facing for marquetry (von Reventlow, 1978); and coatings for iron (Evers, 1968). The location and penetration of acrylic resins used for the consolidation of wood can be identified using Raman spectroscopy (Ohlidalova et al., 2006). Although Paraloid B-72 has been shown to have poor penetration for stone consolidation (Accardo et al., 1981), it, or something similar, appears to be used in the acrylic/silane consolidant, Raccanello 55.050 (once E0057; Raccanello) (A. Moncrieff, personal communication) and is an ingredient with a polymethylsiloxane in the Bologna Cocktail (Haake et al., 2004). Although it appears that B-72 as a pure material does not cross-link when exposed to accelerated ageing, it cross-links severely when aged on marble surfaces, so becoming very difficult to remove by solvent action (Favaro et al., 2006).

The solvents providing the best penetration for consolidating solutions have been found to be petroleum solvent for PnBMA (Domaslowski and Lehmann, 1972) and dichloromethane for PMMA (Lewin and Papadimitriou, 1981). A limited range of solvents was surveyed. PEA in solution is used as a consolidant for leather (Waterer, 1973).

8.2.1 Acrylic Monomers

Natural history (and other) specimens were encapsulated in PMMA (Hibben, 1937; Organ, 1963) or PEMA (Puckett, 1940) blocks by both ultraviolet and chemically initiated polymerization. PMMA/MMA slurries have been used for restoration of glass (Technovit 4004a; Kulzer) (Jackson, 1983), Plastogen G (Schmidt) and other materials. The two parts are a PMMA powder that contains an initiator and MMA liquid. The slurry sets to a translucent solid. The initial viscosity of the slurry, rate of setting and total shrinkage depend on the proportion of powder added.

Consolidation of wood and stone by impregnation and radiation polymerization of MMA was developed for conservation in the 1960s (Munnikendam, 1967; Moncrieff, 1968). Other monomers such as nBMA (Munnikendam, 1971) and ethylene glycol dimethacrylate (1,2-dimethacryloxyethane) (Munnikendam,

1973) were suggested. This method was extensively used for the consolidation of stone (Wihr, 1995). The specimen is liable to crack, particularly if radiation or low-temperature methods are used (De Witte et al., 1977; Kotlík et al., 1980; Vassallo and Lewin, 1981). The use of higher temperatures and an N₂ blanket reduces the problem. Monomer impregnation and polymerization has been used for consolidating polychrome sculpture. Acrylic monomers are good solvents and could easily damage paint films (Mitanov and Kanaivanov, 1975). The polymer that is formed during the polymerization cannot be dissolved out as it appears to be of high molecular weight and is perhaps chemically attached to the substrate.

Gaseous impregnation of paper and books with an EA/MMA mixture followed by gamma-irradiation was proposed for the strengthening of paper in bulk (Burstall et al., 1986) but the idea has not been developed.

Cyanoacrylates have been reviewed for conservation (Down, 2001). They have been suggested for use as consolidants and adhesives for glass (André, 1976; Ferranzinni, 1976). However, cyanoacrylates break down in the alkaline conditions on most glass surfaces. Cyanoacrylates have been suggested as temporary holding adhesives for glass before the application of epoxy resins (Kühn, 1981; Terwen, 1983). Cyanoacrylate adhesives have been found to react with a brass substrate (Williston, 1982) and with minerals in fossils (Howie, 1984). PBCA is more stable than PECA and more stable in contact with acid rather than alkaline fossils (Down and Kaminska, 2006). A cyanoacrylate product (Paleobond) has been prepared specially for palaeological conservation and is widely used. Joins made with cyanoacrylates break down more reluctantly than those of epoxy resins (Moncrieff, 1975), possibly because the joins are much tighter.

8.2.2 Dispersions (Table 8.5)

The manufacture of dispersions requires relatively low investment, and lends itself to easy variation (deliberate or not) of the product. A large number of similar competing products have therefore been available. The differences between nominally identical and similar products make an informed choice uncertain. Acrylic dispersions slowly increased in popularity during the 1950s because of the films' greater resistance to yellowing as compared with PVAC dispersion applied films, e.g. PMA (paper) (Yabrova, 1964), PBMA (frescoes) (František, 1957) and PMMA heavily plasticized (textiles) (Pechoyá and Losos, 1957). The dispersions have been recommended for bone (Primal AC-61, AC-634, WS-24, WS-50 (Koob, 1984)) and wall-paintings (Primal AC-33 (Ferragni et al., 1984)). Acrylic dispersions have been much used to create heat-set adhesives for paper (Hey, 1970) (Primal AC-634, Plextol B500 (Macmullen, 1978); Primal AC-61 (Collings, 1983); Texicryl 13-002 (Hackforth-Jones, 1981)), liquid adhesives (Primal AC-33/ N580 (Hamm and Hamm, 1981)), and as consolidants (Plextols (Koura,

1981), Texicryl 13-002 (Das Gupta and Whitefield, n.d.)). Tissue coated with a dispersion of Texicryl 13-002 has been used by the ton for laminating paper at risk. Having experienced problems of blocking (self-adhesion of adjacent pages) in rebound volumes, Paraloid B-72 solution was emulsified into the Texicryl to create a less tacky adhesive layer (Archival Aids), though the amount of adhesive per unit area is also critical to the success of the treatment. The tissue can be removed by soaking the laminate in ethanol. Thickened Plextol B500 is used either as a wet adhesive or as a heat-set film applied to relining canvases (Mehra, 1984). Removal of the applied canvas and the adhesive is achieved by softening the polymer. Toluene is wiped over to moisten the canvas, which is then peeled off the painting with the rubbery, solvent-swelled, polymer attached. As many of the commercial products are changing and being withdrawn, materials specifically for conservation are being produced, e.g. by Lascaux (Hedlund and Johansson, 2005) for consolidation and lining canvas paintings. Dispersions are being reintroduced as heat and solvent set adhesives for textiles, particularly fragile silk (Karsten and Down, 2005).

Many of the polymers in the dispersions are nominally very close in composition. A review of the acrylic-based paints provides an insight into polymers used for conservation treatments (Jablonski et al., 2003). The polymer contents of Texicryl 13-002, Plextol B500 and various Primals (e.g. AC-634 and AC-33) are P(MMA/EA) copolymers (Howells et al., 1984). Unfortunately the properties of the films formed from these dispersions are extremely variable, presumably from batch to batch. For instance, Texicryl 13-002 has been described both as resistant to yellowing on heat ageing (Das Gupta and Whitefield, n.d.) and as darkening severely (Collings, 1983). The Primal grades AC-61 (Horie, unpublished research) and AC-634 (Howells et al., 1984; Horie, unpublished research) have been found to be both insoluble and soluble (AC-61: Collings, 1983; Koob, 1984; AC-634: Koob, 1984) in organic solvents. Primal AC-33 (Howells et al., 1984) seems to be more reliably soluble. Products tried and tested in practice have been discontinued, prompting the production of comparable, or better, replacements, specifically for conservation. Acronal 300D was widely used for consolidation of wood and polychromy, although it had considerable disadvantages of yellowing (Hedlund and Johansson, 2005) and promoting the corrosion of metals (Farnsworth, 1996). Lascaux has created a replacement material that aims to retain the positive and reduce the negative qualities of Acronal.

Primal N-560 has been used to form a temporary pressure-sensitive film where required (Notman and Tennent, 1980). PBA, with a small amount of dibutyl phthalate plasticizer probably applied from a dispersion, is the adhesive on a paper tape used for temporary attachment of paper (Archival Aids). A specially formulated acrylic/styrene polymer was made and its solution emulsified for textile conservation (Bengtsson, 1975).

TABLE 8.5 Properties of Some Commercial Acrylic Dispersions Used in Conservation (Manufacturer's Information Unless Otherwise Indicated)

Manufacturer Product	Monomer Composition	pH	Particle Size (μm)	Solids (%)	Viscosity (Pa.s)	MFFT ($^{\circ}\text{C}$)	T _g ($^{\circ}\text{C}$)	Elongation at break (%)	Notes
Rohm & Haas	Primal								
AC-33	EA (60)/MMA (40)/EMA (?)	9.7	(0.1)	46	6	8	16		Termed Rhoplex in North America ¹
AC-33	EA/MMA 66:34	9.3						1200	²
AC-61		9.8	(0.1)	46	0.06	18	16		
AC-73		9.5	(0.1)	46	0.25	37	32		
AC-73	EA (66)/MMA (34)	9.6						Brittle	²
AC-234	EA (>66)/MMA (<34)	9.2						1400	²
AC-634	MMA (65)/EA (35) ¹	9.8	(0.1)	46	1.2	12	7		Previously AC-34

TABLE 8.5 Properties of Some Commercial Acrylic Dispersions Used in Conservation (Manufacturer's Information Unless Otherwise Indicated) continued

Manufacturer Product	Monomer Composition	pH	Particle Size (μm)	Solids (%)	Viscosity (Pa.s)	MFFT ($^{\circ}\text{C}$)	T _g ($^{\circ}\text{C}$)	Elongation at break (%)	Notes
N-560		8	(0.1)	55	0.08	<0	-40		Used in pressure-sensitive adhesives
N-560	BA (>50)	7.4						>>500	²
Rohm, Hass, Acrysol									
WS24	nBMA ²	7	(0.03)	36	0.03	<10	39		Thickens considerably when alkali added
WS50		7.1		38		10	36		
Scott Bader Texicryl									
13-002	EA (65)/MMA (35)/EMA (?) ¹	9.2	0.25	55	1	6	16		Contained alkylphenoxy ethanoate surfactant; discontinued 2008
13-076									Similar to 13-002

continued

TABLE 8.5 Properties of Some Commercial Acrylic Dispersions Used in Conservation (Manufacturer's Information Unless Otherwise Indicated) continued

Manufacturer Product	Monomer Composition	pH	Particle Size (μm)	Solids (%)	Viscosity (Pa.s)	MFFT (°C)	T _g (°C)	Elongation at break (%)	Notes
PolymerLatex	Plextol								
B500	EA (60)/MMA (40)/EMA (?) ¹	9.5	0.1	50	1.1–4.5	7	9	600	Was Rohm until 1996
B500	EA (66)/MMA (34) ²								
D360	BA/MMA ³	8.0	0.3	60	1–3	0	–8	1000	Was Rohm until 1996, discontinued
D360	MMA/BMA/EMA								²
D498	BA/MMA ³	9.0		50		5	13		Was Rohm until 1996
BASF	Acronal								
300D	nBA/VAC/VC	5.2	0.3	50	0.01	17	26	350	Failed Oddy test ⁴

TABLE 8.5 Properties of Some Commercial Acrylic Dispersions Used in Conservation (Manufacturer's Information Unless Otherwise Indicated) continued

Manufacturer Product	Monomer Composition	pH	Particle Size (μm)	Solids (%)	Viscosity (Pa.s)	MFFT ($^{\circ}\text{C}$)	T _g ($^{\circ}\text{C}$)	Elongation at break (%)	Notes
500D		4.0	0.2	50	0.02	1		2500	Failed Oddy test ⁴
Lascaux									
498HV	BA (56)/MMA (44) ²								
360HV	BA (>50)/MMA (<50)	7.8						>800	²

¹Howells et al. (1984).²Down et al. (1996).³Lascaux website.⁴Farnsworth (1996).

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Miscellaneous Synthetic Thermoplastics

The properties of a selection of thermoplastics are summarized in [Table 9.1](#).

9.1 POLY(VINYL CHLORIDE) (PVC)

9.1.1 Background

PVC is a thermoplastic made by polymerizing the highly toxic monomer, vinyl chloride ([Figure 9.1](#)). The polymer is a stiff, hard material, soluble in a small range of organic solvents ([Figure A3.16](#)). Plasticizers or copolymers are frequently used to reduce the stiffness of the material. Although one of the most common polymers, it is one of the most unstable to both heat and light. PVC degrades by loss of HCl from the chain to produce double bonds ([Section 2.6](#)). Commercial formulations of PVC have large amounts of stabilizers added.

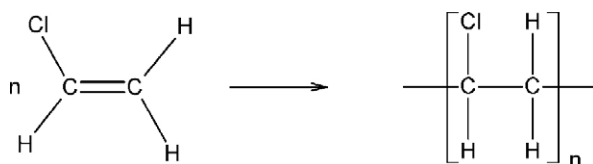


FIGURE 9.1 Polymerization of vinyl chloride to poly(vinyl chloride).

9.1.2 Conservation

PVC solutions have been used for consolidation of wood ([Domaslowski, 1958](#)) and in lifting archaeological objects ([Frere, 1958](#)), e.g. Archeoderm (which replaced Dermoplast SG and Filoform ([Wihr, 1977](#))). PVC films were applied with pressure-sensitive adhesives for the lamination of paper ([Plenderleith and Werner, 1958](#); [Belen'kaya, 1964](#)) as Mipofolie and Genotherm, although their use was discouraged in 1956 ([Minogue, 1956](#)). Removal of this film causes damage ([Wouters et al., 1990](#)).

PVC is too unstable to be used on objects. This property has been put to use by following the rapid deterioration of a PVC film as an indicator of the degrading influences of ultraviolet radiation in the museum environment ([Tennent et al.,](#)

TABLE 9.1 Properties of Miscellaneous Thermoplastics

Polymer	IUPAC Name	Abbreviation	T _g (°C)	n _D	Elongation at Break (%) / Stress at Break (MPa)	CAS No.	Note
Poly(vinyl chloride)	Poly(chloroethanediyl)	PVC	82	1.59	30%/60	9002-86-2	
Poly(vinylidene chloride)	Poly(1,1-dichloroethylene)	PVDC	-17	1.63	N.A./1550	9002-85-1	
Polystyrene	Poly(1-phenylethane-1,2-diyl)	PS	95	1.59	3%/60	9003-53-6	
Poly(vinyl pyrrolidone)	Poly[1-(2-oxo-1-pyrrolidiny)ethylene]	PVP	178	1.46	2%/16	9003-39-8	
Poly(p-xylylene)	Poly(1,4-phenylene-1,2-ethanediyl)	PPX	13	1.66	40%/45	25722-33-2	Parylene N
Poly(ethylene glycol)	Poly(oxyethylene)	PEG (PEO)	-22	1.45		25322-68-3	
N-Methoxymethyl nylon						11114-00-4	e.g. Calaton CB
Poly(2-ethyl-2-oxazoline)		PEtOx	70	1.52		25805-17-8	PEOX, Aquazol

1982). PVC objects in collections deteriorate, though the process can be slowed by appropriate storage conditions (Shashoua, 2003).

Plasticized PVC has been used for moulding (Nimmo and Prescott, 1968). A flexible material (e.g. Vinamold) is melted to a pourable liquid at 120–170 °C. The hot liquid is poured around the object. Even with a release agent such as cellulose acetate, the stress on an object can be very great. An alternative material was a PVC dispersion in a plasticizer, e.g. Vinagel. The paste was kneaded to a soft consistency and an impression taken. The impression was heated in an oven to 140 °C to fuse the particles together. The result was a hard, strong impression. Early workers (Unwin, 1950) did not remove the object before heating and this may have caused damage to the object.

9.2 POLY(VINYLDENE CHLORIDE) (PVDC)

PVDC (Brydson, 1999) is an intractable thermoplastic (Figure 9.2). Vinylidene chloride is therefore copolymerized, frequently with acrylonitrile, to produce polymers that can be used in solution (Figure A3.17). The major importance of PVDC lies in its very low permeability to vapours and gases. The polymers are unstable to heat and ultraviolet, degrading in a similar fashion to PVC. PVDC was tested as a moisture vapour barrier in the 1940s (Stevens and Johnson, 1950) to reduce the distortion of panel paintings (Saran F310; Dow) (Spurlock, 1978). A PVDC copolymer emulsion, Saran 150, has been suggested as a coating on ivory, though reservations were expressed about its stability (Lafontaine and Wood, 1982).

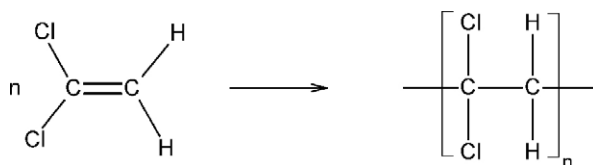


FIGURE 9.2 Polymerization of vinylidene chloride to poly(vinylidene chloride).

9.3 POLYSTYRENE (PS)

PS (Figures 9.3 and A3.18) is a rigid, transparent material that was recommended for optical uses as early as the 1840s. Expanded polystyrene has found uses as a lightweight modelling material and as a support or packing medium. Styrene can be copolymerized, e.g. in polyester casting resins. PS degrades by photolytic oxidation to form conjugated double bonds, ketone and phenyl groups, causing yellowing (Pickett, 2004). PS is resistant to water and acids. Polystyrene is in general too unstable and rigid to be used on objects. Because of its high glass transition temperature, it undergoes considerable shrinkage during drying from solution (Croll, 1980). Perhaps for this reason it was rejected as a picture varnish in the 1930s (Stout and Cross, 1937). PS has been used as a temporary protective resist during acid development of fossils in matrices from the 1940s (Rixon, 1949; Howie, 1984), though as the coating will shrink as the last of the solvent

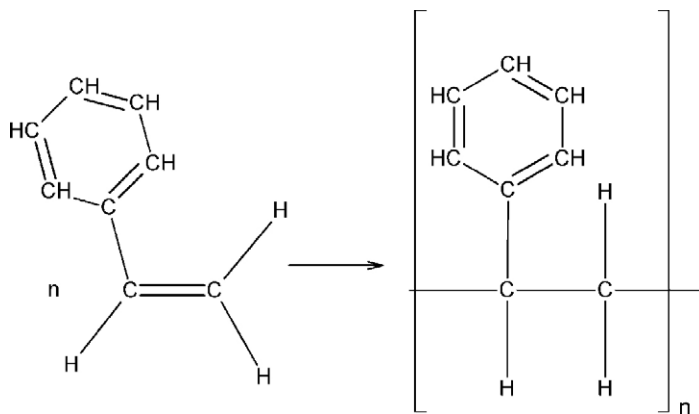


FIGURE 9.3 Polymerization of styrene to polystyrene.

evaporates, it has been replaced by PBMA (Rixon, 1976). In the past PS has been used as a consolidant (Halmagyi, 1958) and an adhesive (Organ, 1959b).

9.4 POLY(VINYL PYRROLIDONE) (PVP) (BLECHER ET AL., 1980)

PVP (Figure 9.4) is a stiff thermoplastic plasticized by water and soluble in both organic solvents and water (Figure A3.19). It has been proposed as a water-soluble, pressure-sensitive adhesive as a mixture with low-molecular-weight PEG (Feldstein, 2004). PVP is insolubilized by polyacids, but is less reactive to cellulose than carboxymethyl cellulose (Trost, 1963). PVP has been used as an adhesive for wood (Richards, 2002) and as a washing aid (Wight and Hanlan, 1978).

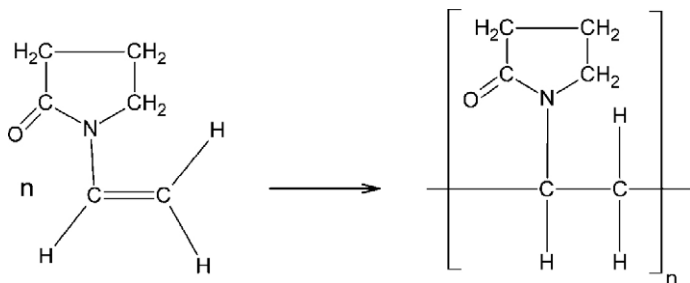


FIGURE 9.4 Polymerization of vinyl pyrrolidone to poly(vinyl pyrrolidone).

9.5 POLY(P-XYLYLENE) (PPX)

PPX (Figure 9.5) is deposited in a vacuum on to cool surfaces from an unstable monomer vapour (Szwarc, 1976). A number of variants exist, though Parylene C is the most commonly used. The polymer formed from the free-radical polymerization on the surface has a high molecular weight ($\approx 400,000$), is semi-crystalline and is soluble in hot solvents (such as chloronaphthalene) only above the crystalline melting point. It suffers from oxidative degradation on ultraviolet exposure (Pruden and Beaudoin, 2004). Ageing tests have shown that it cannot be considered stable enough for long-term conservation use (Bilz and Grattan, 1996).

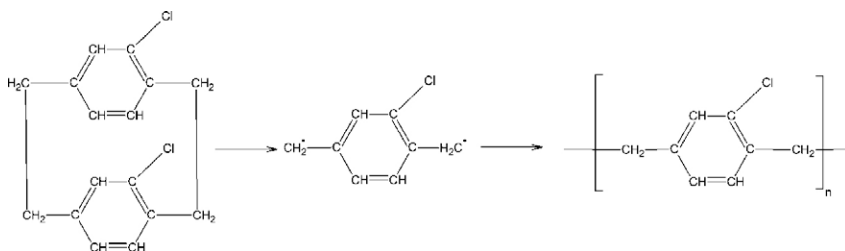


FIGURE 9.5 Polymerization of dichloro-di-*p*-xylylene to poly(*p*-chloroxylylene) (e.g. Parylene C).

It can be used as a coating for paper and other materials (Parylene; SCS) (Humphrey, 1984; Eusman et al., 2004), though considerable reservations have been expressed about its reversibility (Pascoe, 1985). Because it is unstable (Section 2.8.5), Parylene is used to strengthen only those objects that are so fragile that they are unlikely to survive environmental changes, movement or examination (Grattan et al., 1996).

9.6 LOW-MOLECULAR-WEIGHT RESINS

A number of different resin types have been produced for industrial purposes such as tackifiers, hardening coatings and pigment wetting, as ingredients in multicomponent products. Three types have been extensively studied for conservation use (Maines and de la Rie, 2005), with the incorporation of light stabilizers, e.g. Tinuvin 292, to reduce even further the rate of ageing. Ketone resins were introduced into conservation in the 1950s in order to replace natural isoprene resins. More recently, hydrogenated hydrocarbon resins and urea/aldehyde resins have been introduced with better light stability.

9.6.1 Background

Ketone resins are made by heating cyclohexanone, or methyl cyclohexanone for some products (Figure 9.6), at high pressure with a catalyst (Hill, 1948). Like many materials used in conservation, these are made and used for different purposes in industry. The commercial materials available have varied over the years since their introduction (Table 9.2). Taking MS2A as an example, on average about

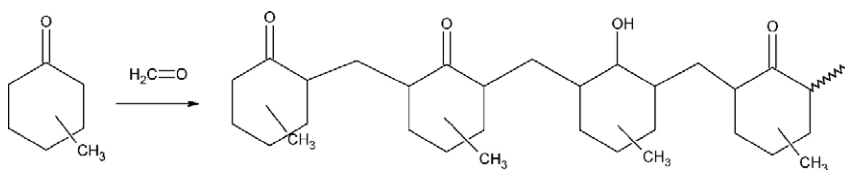


FIGURE 9.6 Indicative structure of Ketone Resin N and Laropal K80 derived from Domenech-Carbo et al. (2009). These resins are made by reacting methyl cyclohexanone with formaldehyde, to produce an oligomer of five to seven monomers with a couple of hydroxyl groups in each molecule. MS2A is made of different ingredients and is subjected to a further reduction process, producing a slightly different structure.

TABLE 9.2 Development and Introduction of Ketone Resins

Date	Product and Manufacturer	Composition ¹	M_w T_g (°C)	Notes
1926	I G Farbenindustrie (later BASF)	Ch		First patents issued
1941	Resin MS2 Howards	MCh		Produced from a mix of 90% methyl cyclohexanone isomers and 10% methyl cyclohexanol, Sextone B (i.e. methyl Sextone, MS)
1952–1967	AW2 I G Farbenindustrie	70% MCh/30% Ch		Recommended as a picture varnish ²
1958	MS2 Howards			Trials started at National Gallery UK for a picture varnish
1959	MS2A Howards	Borohydride reduction of MS2	920 ³	MS2 raw material selected for light colour
1962	MS2 Howards	MCh + paraformaldehyde		Rejected as feedstock for MS2A
1963	MS2B Howards	Reduced 70% MCh/30% Ch		MS2B made from AW2 (BASF) ⁴
1967–1980	Ketone Resin N I G Farbenindustrie	Ch	725 ⁵	Reduction product not light stable and rejected by the National Gallery
1968–1973	MS2A Howards	Borohydride reduction of MCh		MCh specially made and reduced. Sufficient MS2A made to last to 1980s

Table 9.2 Development and Introduction of Ketone Resins continued

Date	Product and Manufacturer	Composition ¹	M_w T_g (°C)	Notes
1980–present	Laropal K 80 BASF	Ch	725 ⁶ – 735 ⁷ 42 °C ⁸	
1984–1992	MS2A Laporte	Borohydride reduction of MCh	1144 ⁶ 57 °C ⁸	Methyl cyclohexanone is minimum 99% meta and para isomers
1993–2002	MS2A Linden (Widnes)	Borohydride reduction of MCh	1561 ⁶ 49 °C ⁸	
1998–present	MS2B Linden	Borohydride reduction of Ch	≈60 °C ⁸	
2003–present	MS2A Linden (Switzerland)	Borohydride reduction of MCh		Pure p-methyl cyclohexanone feedstock
2003–present	MS2B Linden (Switzerland)	Borohydride reduction of Ch		

¹ Ch, poly(cyclohexanone); MCh, poly(methyl cyclohexanone).

² Werner (1952), Koller and Baumer (2001).

³ Routledge (2006).

⁴ Thomson and Brommelle (1964).

⁵ Cruickshank (1985).

⁶ Maines and de la Rie (2005).

⁷ de la Rie and McGlinchey (1990b).

⁸ de la Rie and Shedrinsky (1989).

Source: Routledge (2006).

eight methyl cyclohexanone molecules join into one molecule, with the range of DP between 4 and 29 (Maines and de la Rie, 2005). A typical polymer molecule will contain carbonyl, methoxy, ether and hydroxyl groups (Roff and Scott, 1971). These contribute to the light absorption and susceptibility to oxidation. The polymer may be hydrogenated to reduce the carbonyl groups to hydroxyl groups, e.g. MS2A. The removal of carbonyl groups reduces the sensitivity to water vapour and the tendency to bloom (Thomson, 1963). The increased hydrogen bonding between the molecules increases the brittleness of the film, shown by the rise in T_g . The polymers are hard but, because of their low molecular weight, are weak and brittle. Thin films supported on aluminium foil cannot be bent around a 10-cm-diameter mandrel without cracking (de la Rie and Shedrinsky, 1989). The low molecular weight of the resin allows high-concentration solutions (>40%) to be made and applied (Figures A3.20 and A3.21). Accelerated ageing tests carried out under ultraviolet/air exposure showed that oxygen is absorbed, increasing the polarity of solvents required to dissolve the polymers (de la Rie and Shedrinsky, 1989). The molecular weight increases (Maines and de la Rie, 2005), though no insoluble material is created (Feller and Curran, 1975). Ketone resins have been observed to yellow in dark storage over some years. They are initially more stable than their natural counterparts, dammar and mastic, but eventually become more difficult to dissolve, though adding beeswax appeared to improve the long-term removability (Raft, 1985).

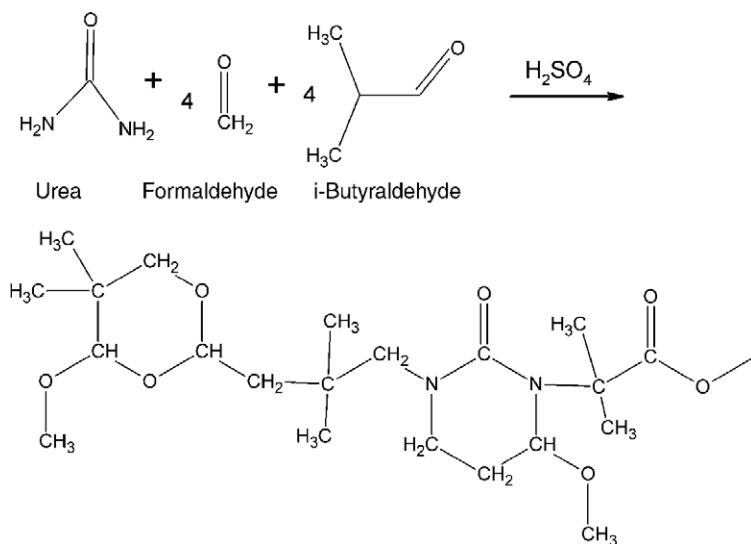


FIGURE 9.7 Aldehyde resin. Condensate of urea, formaldehyde and i-butyraldehyde, indicative structure (e.g. Laropal A 81).

Source: McKillip *et al.* (2002).

Urea/aldehyde resins (Figures 9.7 and A3.23) (de la Rie *et al.*, 2002) are made by condensing urea, formaldehyde and i-butyraldehyde. These resins wet pigment particles well because of their polar groups.

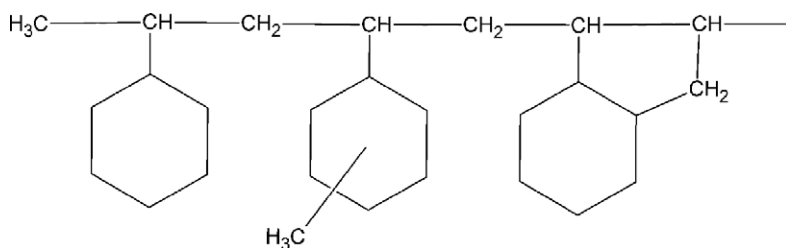


FIGURE 9.8 Hydrogenated hydrocarbon resin: styrene and methyl styrene monomers are polymerized to form an oligomer, which is then catalytically hydrogenated (e.g. Regalrez 1094).

Source: *Collin and Zander (2002).*

Hydrogenated hydrocarbon resins (Figures 9.8 and A3.24; e.g. Regalrez 1078, 1094) (de la Rie and McGlinchey, 1990b) are made by preparing oligomers of styrene and methyl styrene then hydrogenating the benzene rings to form saturated aliphatic compounds.

The ageing behaviour of these resins has been intensively studied, in comparison with the natural resins, dammar and mastic. The increase in the polarity of solvents required for removal of films on light ageing (Figure 9.9) reflects the underlying chemical changes, particularly incorporation of oxygen. Ketone resins, reduced and unreduced, and the hydrogenated hydrocarbon resins increase in molecular weight, while that of urea/formaldehyde resins is reduced (Maines and de la Rie, 2005).

9.6.2 Conservation

Ketone resins have been used primarily for picture varnishes (Werner, 1952; Koller and Baumer, 2001) and retouching (Prunet-Brewer and Routledge, 2001). A typical spraying varnish was made up of 100g resin in 220ml of slightly aromatic petroleum solvent (boiling range 150–220°C). An initial brushing varnish may need a small amount of butanol added to the solution to improve wetting (Lank, 1976). The glossiness of the surface can be adjusted by varying the spraying conditions or by adding a dispersion of microcrystalline wax in solvent (De Witte, 1975b). Ketone resins have been tried out as varnishes on iron (Barton, 1960) and to modify and harden wax (Chapter 6). Ketone resin is added to wax/EVA mixtures used for picture relining adhesives (BEVA) (Berger, 1976). Efforts have been made to reduce the yellowing and increase in polarity by adding stabilizers (Lafontaine and Wood, 1982; de la Rie, 1993) or modifying the material by hydrogen reduction and esterification (de la Rie and Shedrinsky, 1989; Routledge, 2000).

Following extensive testing, the urea/aldehyde resin Laropal A-81 has been introduced to create light-stable retouching paints (Leonard et al., 2000), and has been used as a varnish component (Arslanoglu and Learner, 2001) in combination with Paraloid B-72.

The hydrogenated hydrocarbon resin Regalrez 1094 has been used for saturating degraded paint films (Epley, 2000) and as a varnish component (Whitten, 1995). To counteract its inherent brittleness, a small amount of a stress-absorbing

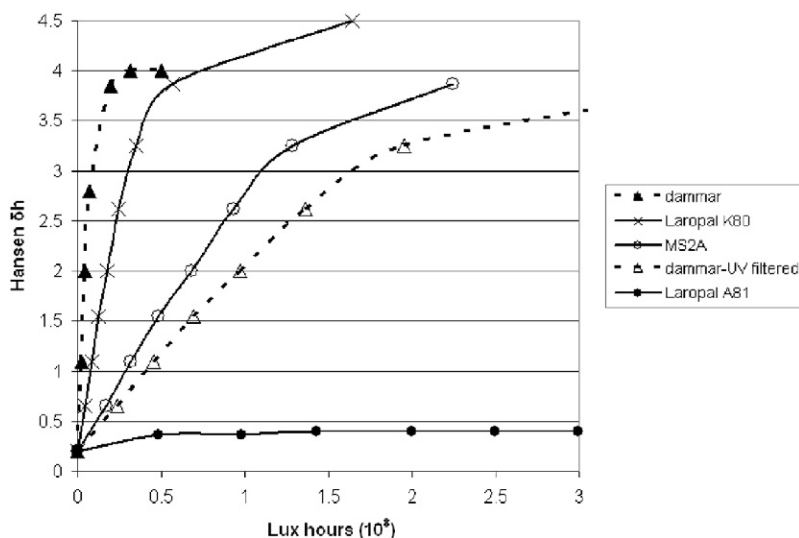


FIGURE 9.9 Accelerated ageing of low-molecular-weight resins in Weather-ometer, using simulated daylight passing through window glass. Relative rates of oxidation of dammar, ketone resins (Laropal K80 and MS2-A), and urea/aldehyde (Laropal A81). The rate for dammar exposed through a UV cut-off filter at 406 nm is shown for comparison. The oxidation states of the resins were assessed by their removability by swab using Feller's series of solvents, cyclohexane, toluene and acetone. The data were replotted against the solvents' hydrogen bonding parameters. Mastix (not shown) is slightly more unstable than dammar, so the graph shows the improvement of picture varnishes from top left to bottom right. **Sources:** *Feller and Curran (1975), de la Rie (1988), de la Rie and Shedrinsky (1989), de la Rie and McGlinchey (1990a, b), de la Rie et al. (2002).*

synthetic elastomer, Kraton G1650, can be added. The low molecular weight and ready solubility appear to make it sensitive when over-coating with other finishes or when handling (Piena, 2001).

Hostacoll C, a presumably low-molecular-weight condensate resin of ethylenimine, crotonic acid and ethylene glycol, was used in the 1950s as a coating and consolidant for stained glass (Jägers et al., 2000). It degrades to water-removable products.

9.7 POLYETHERS

9.7.1 Poly(Ethylene Glycol) (PEG)

Background (Powell, 1980; Bailey and Koleske, 1991; Dow, 2006a)

The term PEG is used commercially as a convenient acronym for the low-molecular-weight poly(ethylene oxides) polymerized from ethylene oxide (Figure 9.10). PEG is available in a number of grades, from liquids, e.g. PEG 200 with a

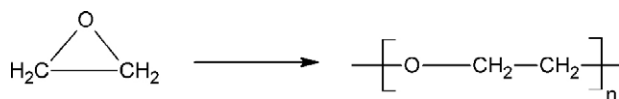


FIGURE 9.10 Polymerization of ethylene oxide to poly(ethylene glycol).

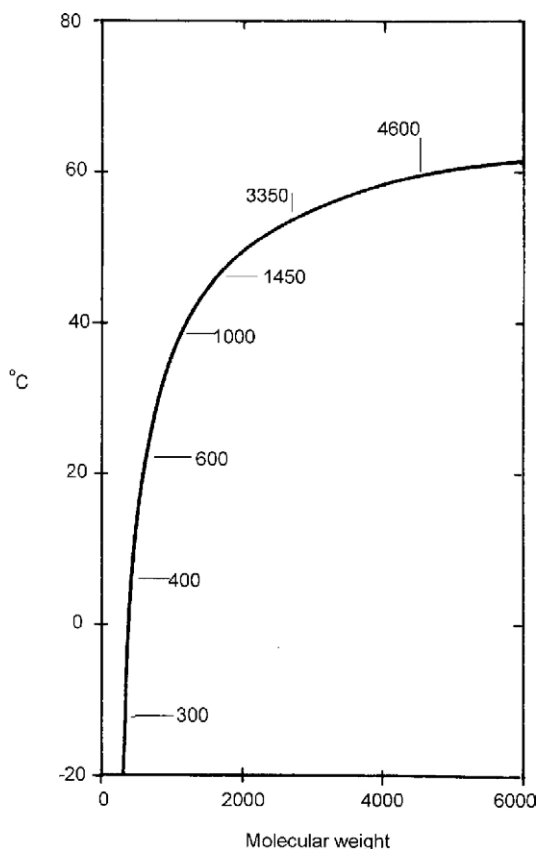


FIGURE 9.11 Melting points of PEGs. Because the materials are mixtures and subject to manufacturing variations, the melting and freezing occurs over a range of temperatures. **Source:** Dow (2006a).

DP of ≈ 4 , to hard waxy solids, e.g. PEG 8000 with a DP ≈ 170 (Figure 9.11). Higher-molecular-weight polymers, up to 8,000,000, are usually designated as poly(ethylene oxides) (PEO).

PEG is applied primarily as a solution in water to displace water from substrates and to provide bulking when the water has been removed. Both the viscosity in water and the solidification temperature of water solutions (Figure 9.12) are important in the choice of grade. The diffusion of a PEG molecule into a porous material depends on: the size of the molecule; the size of the hole into which it must diffuse;

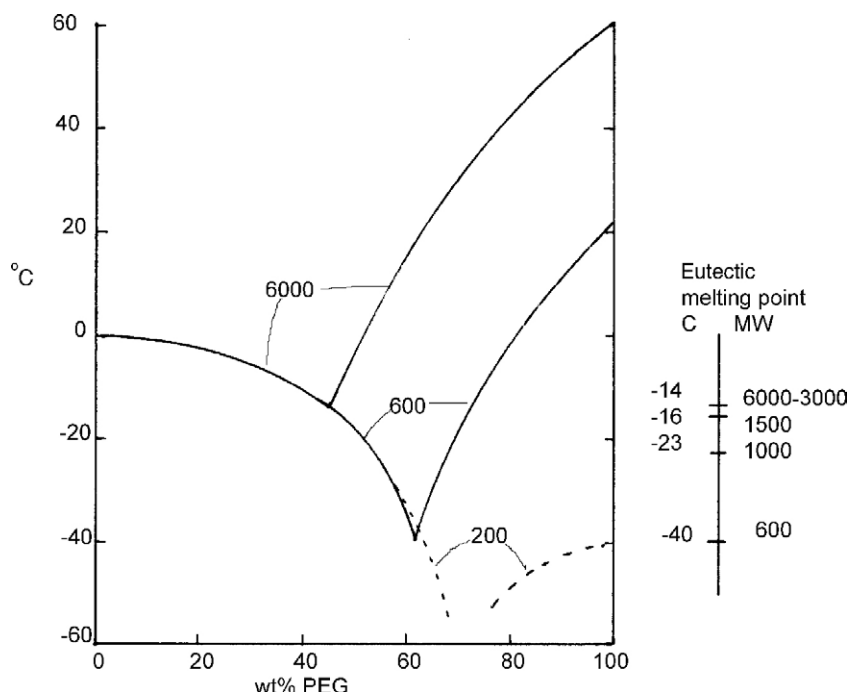


FIGURE 9.12 Phase diagram of representative PEG solutions in water. Above the line, the mixture is a liquid. Below the line, the mixture is frozen to a mixture of ice and PEG/water eutectic crystals. However, PEG 200 does not crystallize but freezes to a glass. **Sources:** *Murthy (2000), Huang and Nishinari (2001), Zobrist et al. (2003), Izutsu and Aoyagi (2005).*

the relative affinity of the molecule to the substrate (Jensen, 1997); and the temperature and concentration gradient (Dean et al., 1997). When freeze-drying from PEG solutions, it is important that the solution is frozen and provides support throughout the process (Chaumat et al., 2002). The lower-molecular-weight PEGs (up to PEG 560 (Huang and Nishinari, 2001)) supercool to a glass on cooling, down to -70°C . Higher-molecular-weight PEG solutions cool to form eutectic/ice crystal mixtures but can also supercool to form glasses. On warming, the glass may transform to a eutectic/ice mixture. On further warming, the eutectic will melt, e.g. PEG 1000 eutectic melts at $\approx -23^{\circ}\text{C}$ and PEG 3000 at $\approx -15^{\circ}\text{C}$, separating into a liquid PEG solution and ice (Antonsen and Hoffman, 1992). PEG freeze-dried from solutions showed that PEG 2000 and 4000 had considerable compressive strength, $\approx 20\text{ Pa}$ at 40% w/w in original water solution rising to $\approx 500\text{ Pa}$ at 100%. This strength was reduced to stickiness by even small amounts of PEG 200 ($>2.5\%$ w/w PEG 200/PEG 2000) (Bojesen Koefoed et al., 1999).

PEG is hygroscopic (Figure 9.13) and there is hysteresis in the response to variations in humidity. Organic solvents (Figure A3.25) may be used to apply or remove PEG without affecting water-sensitive materials. Many PEG commercial

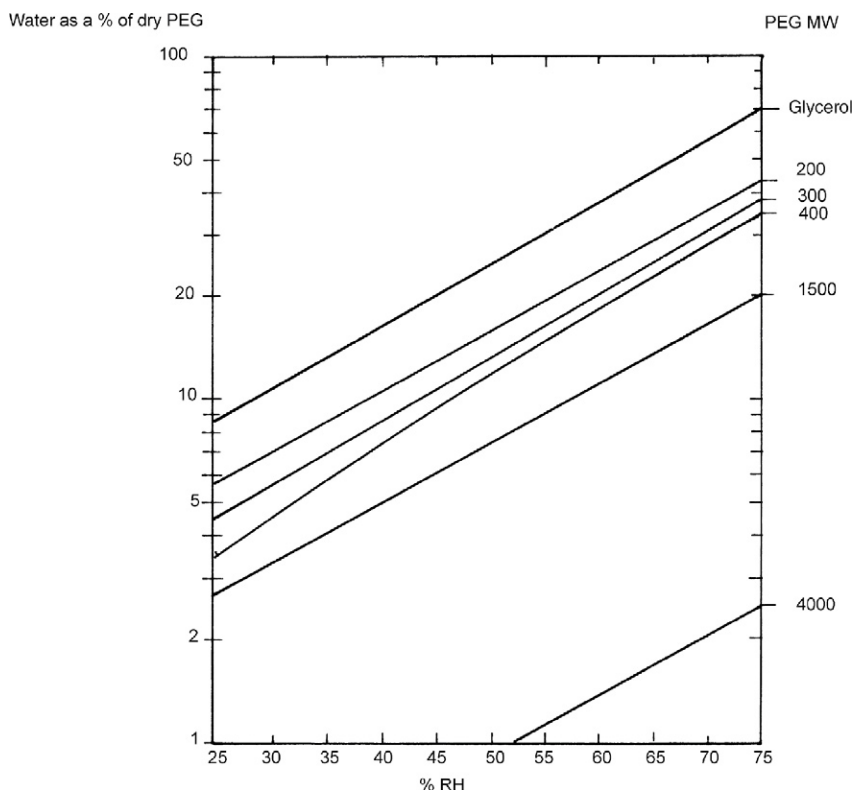


FIGURE 9.13 Absorption of water by PEG over a range of relative humidities. PEG exhibits hysteresis on absorption/desorption cycles, so values are approximate. **Sources:** *Blackshaw (1975), Powell (1980), Dow (2006a).*

materials produce acid solutions when dissolved in water (pH 4.9–7.2) (Blackshaw, 1975). This acidity could result from incorrect neutralization during manufacture or by oxidative degradation during storage. PEG solutions support biological activity so various biocides have been suggested, e.g. aluminium salts (Hoffmann, 1997) or copper/silver ions (Vere-Stevens et al., 1999), though acetic acid causes considerable loss of strength (Bojesen Koefoed et al., 1999).

PEG oxidizes rapidly with a severe drop in molecular weight by chain scission when exposed to air (Yang et al., 1996), a process accelerated by light (Decker and Marchal, 1973). This oxidation even at room temperature in the dark produces formaldehyde and long-chain aldehydes, which can be health hazards (Bergh, 1999). Butylated hydroxyanisole (BHA) (Bilz and Grattan, 1997) and butylated hydroxytoluene (BHT) (Dow, 2006b), taking regard for its toxicity, have been used as antioxidants for PEG. Oxidation can cause initially solid PEG to degrade to a material that will not solidify at room temperature. PEG will, if heated for long periods while exposed to the air, accumulate quantities

of highly inflammable vapour (Organ, 1959a). Heating for sufficient time to remelt PEG 4000 on objects (4 hours at 75 °C) causes severe degradation. Removal of the oxygen, by blanketing with nitrogen, can prevent the degradation (Padfield et al., 1990). Gallic acid (a tannin) acts as an inhibitor to oxidation (de Simone et al., 1991). Degradation is increased by the presence of metal ions in the solution, even those in tap water (Blackshaw, 1975). Metals such as iron can react with the acids etc. of the oxidized polymer to form soluble and insoluble salts (Argyropoulos et al., 2000). Lead, susceptible to attack by organic acids, is attacked very severely. Less severe attack occurs on various aluminium alloys, copper, mild steel, and both tin- and zinc-coated steel. Stainless steel may be corroded depending on the grade and conditions (Glastrup, 1990). However, few instances of degradation of PEG seem to have occurred within treated wood, perhaps because it is stabilized by the antioxidant properties of lignin (Hiron and Tran, 1999).

PEG, being well above its glass transition temperature at room temperature, can act as a solvent for inks and paint (Hey et al., 1960) or a plasticizer for polymers, e.g. PVAC, CN or colophony (Powell, 1980). It may cause stress cracking of moulded thermoplastics such as PE. It does not appear to attack beeswax or gelatine. The presence and quantity of PEG in a solution or thin section can be assessed by colour staining (Hoffmann, 1983; Bilz et al., 1999), but distribution within an object is frequently assessed by extracting the PEG from a core and using instrumental analysis to quantify the concentration (Hoffmann, 1989).

Conservation

Waterlogged Wood

The major use for PEG as a consolidant for waterlogged wood started in the 1950s. Air-drying waterlogged wood results in major collapse of the cells by surface tension as the water meniscus retreats through the degraded wood and by the shrinkage of the water-swollen cell walls (Grattan, 1989). Although earlier treatments replaced all the water by molten PEG, which was then cooled and solidified to provide consolidation (Organ, 1959a; Plenderleith and Werner, 1971), other strategies are now used. Placing the wood into high concentrations of PEG can cause surface cracking (Rosenqvist, 1959) because of osmotic shock. The wet material can be immersed directly in a solution of PEG in water or, after dewatering, in other solvents, i.e. 2-methylpropan-2-ol, methanol or 2-methyl-propan-2-ol (t-butyl alcohol) (Grattan and Clarke, 1987). Two methods of PEG-assisted stabilization are in current use: freeze-drying and cooling from a hot solution. The methods used need to be adjusted to suit the size and condition of the wood. Jensen (1997) has shown PEG 200 is the maximum size of molecule (diameter ≈ 5.5 Å) that can diffuse into the cell walls of the wood. However, as it has lower affinity to the wood than water, it cannot displace the water except at high concentrations. The presence of PEG 200 reduces considerably the shrinkage of the cell walls but contributes little to the strength

of the wood. Solid PEG (e.g. 3000 or 4000, molecular diameter $\approx 12 \text{ \AA}$) provides strength to highly degraded, usually outer, parts of the wood. It appears that PEG can be extracted from treated objects (Cooke et al., 1994).

Two-Step Process for Waterlogged Wood

It has been known for some time that two grades of PEG are needed to achieve stabilization: a low-molecular-weight and higher-molecular-weight material. Various mixtures and protocols have been tried (Grattan and Clarke, 1987), resulting in the development of a widely accepted two-stage process (Hoffmann, 2002). Over a number of years, the object is soaked in PEG 200 at increasing concentrations up to 40%, which enables the PEG to diffuse to the centre of even the well-preserved wood pieces. This solution is then replaced with a hot (40°C) 60% (rising to 70%) solution of PEG 3000, which diffuses into the outer, more degraded, wood layers and the excess PEG 200 diffuses out. The solution is drained off and the object cools and solidifies. The remaining water is allowed to evaporate naturally from the wood and excess PEG is removed by heating and wiping off.

Freeze-Drying Waterlogged Wood

The usual treatment for relatively small objects is to replace some of the water within the wood by soaking in a PEG solution (20–40%), then freeze-drying, though the grades used depend much on the state of the wood (Grattan and Clarke, 1987). In general, both low- (200–400) and high-molecular-weight (2000–4000) PEGs are used in a single treatment either as a mixture or one after the other. The internal processes of penetration, freezing and sublimation are not yet understood (Jensen et al., 2002) because of factors such as: super-cooling; the interaction on freezing of multiple components; the temperature of drying (whether the solution achieves solidity during freezing or maintains this state during drying); the rate of drying; the capabilities of the machinery; the time scale available for treatment; and the techniques used to follow the process (Chaumat et al., 2002; Schnell and Jensen, 2007).

Higher-molecular-weight PEGs (6000 and 12000) have been used for consolidating fossil bone (Baumgartner and Lanooy, 1982).

PEG was used originally as consolidant as a humectant/lubricant for leather and other skin products (Werner, 1957). Liquid, hygroscopic grades with a molecular weight in the region of 300–400 have been recommended. Ganiaris et al. (1982) concluded that glycerol provided better results than PEG when leather was treated by freeze-drying or acetone dewatering. However, the aldehydes produced during the degradation of PEG may well react with the collagen, fixing the PEG in situ (de Simone et al., 1991). Similar grades of PEG have been used for increasing flexibility in cellulose materials such as basketry and tapas (Schaffer, 1978; Bakken and Aarmo, 1981).

Other polyalkylene glycols based on copolymers of propylene oxide and ethylene oxide (BREOX) have been suggested as wood consolidants because of their reduced hygroscopicity and biogradability (Pournou et al., 1999). However, polypropylene glycols are more liable to oxidation than PEGs (Gallet et al., 2002).

9.7.2 Perfluoropolyethers

Perfluoropolyether (Figure 9.14) is a very unreactive liquid, being resistant to oxidation and hydrolysis and insoluble in all but fluorinated solvents. A moderately viscous grade (Fomblin YR; Solvay Fluor) has been suggested as a water repellent for stone (Frediani et al., 1982), applied in solution (as Fomblin YMET). It would gradually distribute itself throughout the bulk of porous material, and would therefore require periodic reapplications.

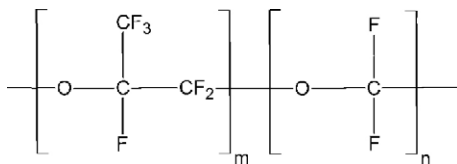


FIGURE 9.14 Structure of Fomblin Y (Montedison), a perfluoropolyether.

9.8 NYLONS

9.8.1 Background

Nylon is a generic name for a family of polyamides (Figure 9.15). The glass transition temperature of nylons is around room temperature at normal humidities and is reduced by moisture absorption. They are tough thermoplastics that are highly resistant to solvents because of the strong, regular, hydrogen bonds between adjacent chains. Solvents that can penetrate are phenol, formic acid, 2,2,3,3-tetrafluoropropanol and 1,3-dichloropropan-2-ol (Roff and Scott, 1971). Nylons in general are sensitive to oxidation, particularly photolytic oxidation. Two forms of soluble nylon are available: *N*-methoxymethyl nylon, which is a

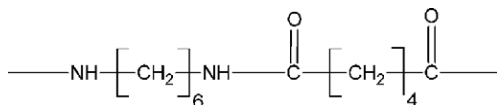


FIGURE 9.15 Monomer unit of nylon 66. The first 6 of the suffix indicates the number of carbon atoms in the diamine component (hexamethylene diamine). The second 6 indicates the number of carbon atoms in the diacid component (adipic acid). Nomenclature: poly(hexamethylene adipamide) and IUPAC poly[imino(1,6-dioxohexamethylene)imino]hexamethylene].

substituted nylon; and highly irregular copolymers. Soluble nylons are soluble in alcohol-based solvents. Commercial uses are as cross-linking components in coatings.

N-Methoxymethyl nylon (Bockhoff et al., 1984) is formed by heating nylon 66 with formic acid and methanol to produce short side chains (about 35% substitution) (Figure 9.16). This produces a polymer that is more flexible than the original nylon and that is soluble in ethanol or methanol if a small amount of water is added. Soluble nylon dissolves in hot solvent but forms a gel when cooled to room temperature. Films that are formed from the solution shrink on drying and must be heated to dissolve. The glass transition temperature of *N*-methoxymethyl nylon is sufficiently low when immersed in water to result in dirt pick-up (De Witte, 1975b). The side chains can be removed by reaction in acidic and alkaline conditions. The film is thus converted back to the original, intractable, nylon 66. The reaction occurs on standing – on opening a container of old *N*-methoxymethyl nylon the methanol can easily be smelled. An additional reaction in acidic conditions leads to cross-linking between the chains, which ensures complete insolubility. The cross-linked film is considerably stronger than the original film (Brydson, 1982).

Copolymers of widely different monomers (e.g. Elvamide 8061; Du Pont) are also soluble in alcohols etc. because disorder in the polymer chain disrupts the formation of coordinated hydrogen bonds. Films formed from solutions dried at room temperature are usually opaque white and must be heated to $\approx 80^{\circ}\text{C}$ to ensure transparency. The solutions gel at room temperature, so dissolve only by heating. These nylons suffer from the degradation reactions of the more common nylons.

9.8.2 Conservation

N-Methoxymethyl nylon, Calaton CA and CB (ICI; also called Maranyl C109/P), was recommended in the 1950s (Werner, 1958) for consolidating the painted surface of friable stone and pottery surfaces during soaking for removal

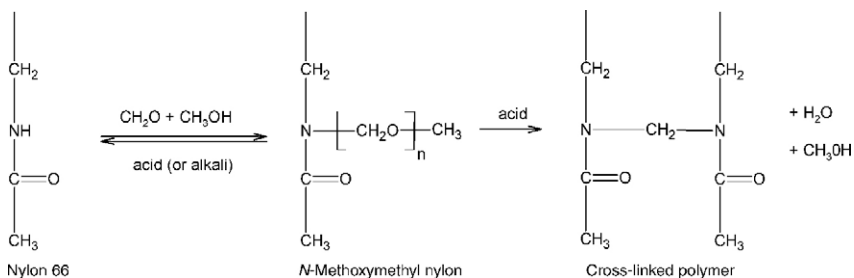


FIGURE 9.16 *N*-Methoxymethyl nylon is made by reacting nylon 66 with formaldehyde and methanol in acid conditions. In acidic (or alkaline) conditions, this can revert to nylon by loss of the hydroxymethyl group or can cross-link to form an insoluble material.

of salts. By the late 1960s, its use was being discouraged because of dirt pick-up (Torraca, 1968) and loss of strength and insolubility (Santucci and Plossi, 1969) after ageing. It has been suggested as a consolidant for paper (Belen'kaya and Strel'tsova 1964; Sauçois, 1981), pigments (King, 1972), canvas (Berger, 1974) and textiles (Agrawal, 1975), and as an adhesive for leather (Nikitina, 1981). The use of *N*-methoxymethyl nylon in conservation has been strongly discouraged (Sease, 1981; Fromageot and Lemaire, 1987; Hanna et al., 1988).

Soluble copolymer nylon (Zytel 61 = Elvamide 8061) has been rejected as a consolidant for paper (Baer et al., 1972) and stone (SPNHC, 1997).

A nylon 12 hot melt adhesive (Polyamide Textile Welding Powder No. 5065; Lascaux) has been introduced to join textile fibres, for instance in painting canvas.

9.9 POLY(2-ETHYL-2-OXAZOLINE)

This water- and organic-soluble polymer (Figures 9.17 and A3.26) was developed in the 1980s (Chiu et al., 1986) and introduced to conservation as a consolidant as a replacement for glue in the 1990s (Wolbers et al., 1998) with the trade names of PEOX and Aquazol.

It has been tried on a number of materials (Wolbers, 2008) because of its compatibility with many materials, solvents and other treatments, but is limited by its hygroscopic behaviour (Arslanoglu, 2005).

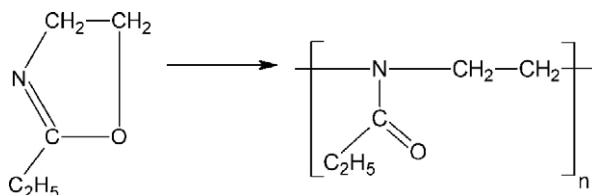


FIGURE 9.17 Polymerization of 2-ethyl-2-oxazoline to form poly(2-ethyl-2-oxazoline).

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Polymers Derived from Cellulose

Cellulose (Figure 10.1) is one of the most abundant polymers on earth, forming the bulk of the structural support of plants. It resists chemical (and physical) change because strong hydrogen bonds hold the chains in closely packed micro-crystals. It can be dissolved only by using extremely powerful solvents that disrupt the hydrogen bonds, such as ethylene diamine/potassium thiocyanate (Frey et al., 2006), *N*-methylmorpholine-*N*-oxide (NMNO) or water at $\approx 370^\circ\text{C}$. Most other liquids that dissolve cellulose, such as cuprammonium solution, react with and substitute the hydroxyl groups, creating a soluble form that may then be regenerated as solid cellulose, e.g. cellophane. In order to make soluble derivatives of cellulose, the hydroxyl groups must be replaced, at least in part, by other groups. The resultant materials are cellulose ethers or esters (Figure 10.2). A large range of different but similar products can be formulated, many of which are unique to a single manufacturer (Tables 10.1 and 10.2).

The number of hydroxyl groups substituted on each glucose unit of the chain is described as the degree of substitution (DS), with a maximum of 3. The average DS may be considerably less than 3, leading to differences between apparently similar polymers, with varying DS and how the substituents are distributed, both on different carbon atoms on each glucose unit and along the chain. One can have

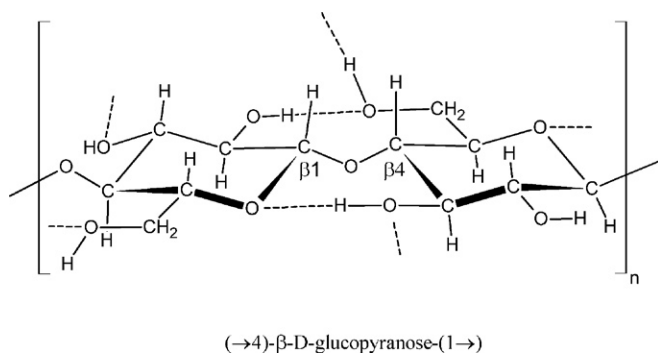
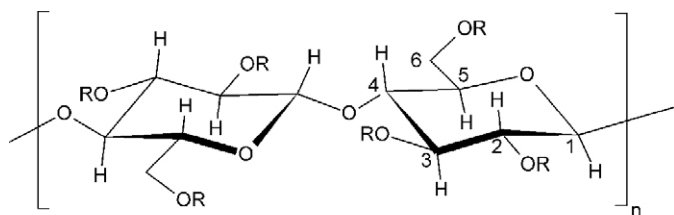


FIGURE 10.1 Structure of cellulose. Covalent bonds are shown solid, while hydrogen bonds are shown dotted connecting the molecule intra- and intermolecularly. The name of this compound defines the structural arrangement of the glucose monomers in the polymer.



R= H or a substituent

FIGURE 10.2 Structure of a substituted cellulose. The hydroxyl groups can be replaced with a number of different substituents. The position of the substitution can also affect the resulting properties, depending on which carbon atom (2, 3 or 6) the substituent(s) occur (see Table 10.1).

multiple substitutions on a single hydroxyl group, leading to a molar substitution (MS) different from the DS (Figure 10.3). Differences in molecular chain length, i.e. molecular weight, can also be used to vary the polymer properties.

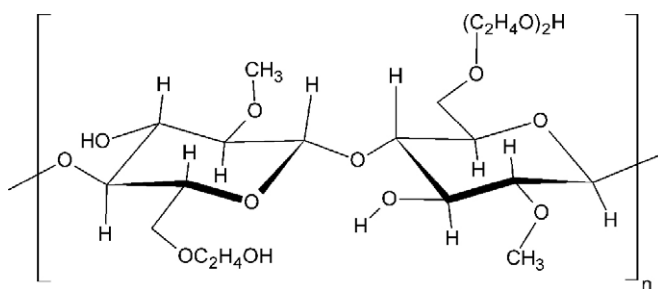


FIGURE 10.3 Describing the degree of substitution (DS) and molar substitution (MS). In this formula below of methyl hydroxyethyl cellulose, each glucose unit has one carbon atom with methyl group substituted, so has a DS of 1. Similarly, each glucose unit has one carbon atom with ethoxy groups substituted, so has a DS of 1. However, one of the glucose units has one ethoxy, but the other has two ethoxy groups attached, so giving an average MS of 1.5.

10.1 CELLULOSE ETHERS

10.1.1 Background (Feller and Wilt, 1990)

The ethers that are formed with cellulose can be divided into three types: alkyl, hydroxyalkyl and sodium carboxyalkyl (Table 10.1). The first stage is the reaction of cellulose with concentrated sodium hydroxide under heat and pressure (Figure 10.4). The alkali cellulose is then reacted with the appropriate substituent(s), again under heat and pressure. Alkyl, hydroxyalkyl and carboxyalkyl groups can be substituted in the same molecule. The molecular chain length is controlled by choosing an appropriate starting cellulose material or by oxidizing, i.e. degrading, the resultant polymer. The process creates by-products that are more or less removed by the manufacturer. In general, low degrees of substitution provide water-soluble, rather

TABLE 10.1 Representative Cellulose Ethers and Esters Used in Conservation (Manufacturers' Data)

Cellulose Derivative ¹	Abbreviation	Substituent(s)	Degree of Substitution on Monomer Unit	Molar Substitution on Monomer Unit	CAS No.	n_D of Film at 20 °C	Tensile Strength (MPa)/Elongation (%) at Break 25 °C 50% RH	Typical Products	Reference
Methyl	MC	-CH ₃	1.8		9004-67-5	1.49	69/12	Methocel A (Dow Chemical)	Greminger and Krumel (1980)
Ethyl	EC	-C ₂ H ₅	2.4–2.5		9004-57-3	1.47	131/10	Etholuse (Hercules ²)	Roff and Scott (1971)
Ethyl hydroxyethyl	EHEC	-C ₂ H ₅ -C ₂ H ₄ OH	0.9 (ethyl)	0.8 (hydroxyethyl)	118337-09-0	1.49	38/8	Bermocoll E (was Modocoll)	Lindenfors and Jullander (1973)
Methyl hydroxyethyl	MHEC	-CH ₃ -C ₂ H ₄ OH	1.25	0.5	9004-65-3			Tylose MH (Hoechst)	Greminger and Krumel 1980)

Continued

TABLE 10.1 Representative Cellulose Ethers and Esters Used in Conservation (Manufacturers' Data) continued

Cellulose Derivative ¹	Abbreviation	Substituent(s)	Degree of Substitution on Monomer Unit	Molar Substitution on Monomer Unit	CAS No.	n_D of Film at 20 °C	Tensile Strength (MPa)/Elongation (%) at Break 25 °C 50% RH	Typical Products	Reference
Hydroxyethyl	HEC	–C ₂ H ₄ OH	0.9	2.5	9004-62-0	1.51	27/35	Natrosol 250 G (Hercules ²)	Powell (1980)
Hydroxypropyl	HPC	–C ₃ H ₇ OH		≈ 4	9004-64-2	1.56	14/50	Klucel G (Hercules ²)	Butler and Klug (1980)
Sodium carboxymethyl	CMC	–CH ₂ COO [–] Na ⁺	0.7		9004-32-4	1.515	90/14	Blanose (Hercules ²) Cellulose Gum, Cellofas (ICI discontinued)	Stelzer and Klug (1980)
Acetate	CA	–COCH ₃	2.4		25395-31-7	1.48	50/25		
Nitrate	CN	–NO ₂	2.1		9004-70-0	1.5	86/15		

¹Ethers are designated as methyl cellulose, etc. Esters are designated cellulose acetate, etc.

²Hercules was acquired by Ashland Chemicals in 2008.

TABLE 10.2 Viscosity of Typical Cellulose Ethers, 2% Solution in Water (Manufacturers' Data)

Grade	Type	Molecular Weight M_n	Viscosity (mPa)	Manufacturer
Methocel A4M	MC	86,000	4000	Dow
Methocel A4C	MC	41,000	400	Dow
Culminal MC 2000	MC	70,000	2000	Hercules
Tylose MH 2000	MHEC		2000	SE Tylose (was Hoechst)
Natrosol 250 GR	HEC		300	Hercules
Klucel G	HPC	300,000	3000	Hercules
Klucel E	HPC	60,000	7	Hercules
Blanose 7HF	CMC	550,000	13,000	Hercules
Blanose 7LF	CMC	90,000	40	Hercules
Cellofas B-3500	CMC			(was ICI)

brittle materials. Increasing the amount of substitution increases the solubility in organic solvents and the plasticity of the polymer.

All the ethers are hygroscopic, with an equilibrium moisture content at 50% relative humidity (RH) varying from 14% for CMC to $\approx 7\%$ for MC, HEC and HPC. The mechanical properties of the ethers change considerably with increasing moisture content, becoming softer and even tacky at higher humidities.

Except for EC, the ethers used in conservation are all soluble in cold water, forming increasingly viscous and then thixotropic solutions (except HPC) at higher molecular weights. Many solutions can be spread on with a brush yet thicken when the force is removed (pseudoplastic). The polymers in water solution are distinguished by different responses to heating. MC forms a gel on heating to 50–90°C, depending on the grade. The gels melt on cooling. HPC and EHEC precipitate out of solution on heating to 40–45°C, while HEC remains in solution on heating. One can take advantage of this to help dissolve the powders of MC, HPC and EHEC, which can otherwise clump and form gelatinized lumps that are most difficult to disperse. The powder is poured into hot water, which is then stirred while cooling, e.g. by adding cold water, so the particles are wetted individually and dissolve. Alternatively, the powder can be dispersed in a small amount of water-miscible organic solvent, e.g. ethanol or acetone, and added as a slurry to the stirred water.

Solubility in organic solvents varies with the type of ether. EC is soluble only in organic solvents. HPC is soluble both in water and in polar solvents

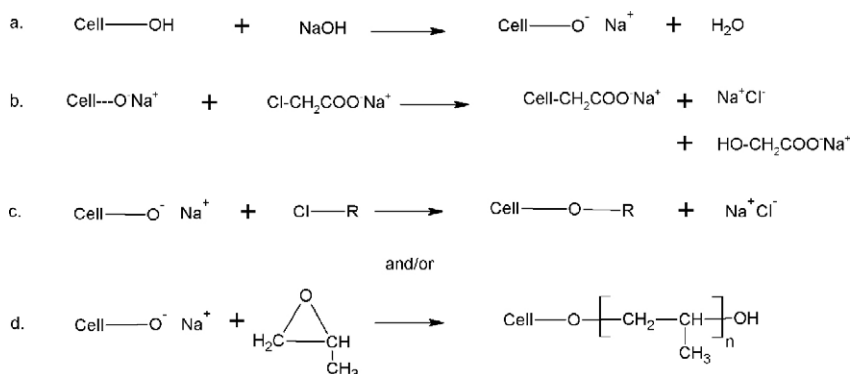


FIGURE 10.4 Reactions making cellulose ethers. (a) Reaction of cellulose to make sodium cellulose. (b) Reaction of sodium cellulose with chloroacetic acid to make sodium carboxymethyl cellulose. (c) Reaction of sodium cellulose with, e.g., methyl chloride to make, e.g., methyl cellulose. (d) Reaction of sodium cellulose with propylene oxide to make hydroxypropyl cellulose.

(Figure A3.27). MC, EHEC and HEC are soluble in only a few organic solvents such as dimethyl formamide and dimethyl sulphoxide.

Commercial CMC is available in many purities, from 99.5% CMC to 50%, containing as impurities the by-products of synthesis. The degree of substitution is normally around 0.7. With increasing molecular weight (up to 1 million), the strength, elongation and flexibility of films increase. Solutions of CMC in water are pseudoplastic, i.e. become thinner on stirring, and can be thixotropic, and high-molecular-weight materials may form gels on standing. Useful thixotropic solutions form at 2% concentration ($M_w = 7 \times 10^5$) or 5% ($M_w = 2.5 \times 10^5$).

The alkyl ethers, MC and EHEC, are resistant to biodeterioration in water solution whereas HEC and HPC are susceptible to attack. Storage of all the solutions should be in sterile, dark conditions to prevent algal growth. Solutions should not be stored for longer than 2–3 days.

Feller's work (1990) on the stability to heat and light of cellulose ethers has shown that EC and the alkoxy ethers are relatively unstable, showing discoloration and oxidation. MC, MHPC and CMC can be considered stable conservation materials. All cellulose ethers suffer from chain breaking, though MC appeared to form water-insoluble material on ageing. The oxidation will occur both in bulk storage and in situ, especially if there is light exposure. Considerable variation in ageing behaviour was found between different commercial products, some of which may be due to impurities from manufacture. As with all products, purified grades (usually food grades) of the ethers should be specified, rather than the technical grades, which may be made less carefully.

The non-ionic cellulose ethers do not form irreversible, insoluble, complexes with metal ions (in contrast to sodium carboxymethyl cellulose), but may be precipitated by high concentrations of salts. CMC forms a gel when reacted with divalent ions like Ca^{2+} (Clasen and Kulicke, 2001). CMC will react with iron, alu-

minium and other polyvalent ions to form cross-links. Films cast from mixtures of CMC and PEG are insoluble in water. CMC is adsorbed irreversibly from solution on to cellulose, especially in the presence of ions (Troost, 1963). All the ethers may be cross-linked in acid conditions through the hydroxyl groups by means of aldehydes and acids, which may be found on degraded organic materials.

10.1.2 Conservation

An early use for MC was as a lacquer for lead, being a more stable substitute for CN (Jenkinson, 1924). This MC was presumably applied in an organic solvent and so had a degree of substitution (DS) of more than 2.6. Water-soluble MC (DS of 1.5–2.0) is used in paper conservation as adhesives and consolidant (Asher, 1981; Ravines and Faurie, 1993). MC solutions have been used as a reversible facing on wall paintings (Kottulinsky, 1982); for pigment fixing (Belen'kaya et al., 1965; Ranacher, 1980); as a consolidant for waterlogged wood (Rosenqvist, 1959) and for basketry (Thomsen, 1981); as an adhesive for textiles (Masschelein-Kleiner and Bergiers, 1984; Durand, 1992); and as a poultice to carry enzymes (Lidle-Fürst et al., 1999). MC is added to starch adhesives (Anon, 1973) and polymer dispersions (Koller et al., 1980) to improve working properties.

EC is little used in conservation because better solvent-borne polymers are available. EC with a dibutyl phthalate plasticizer was suggested as a consolidant for leather (Belaya, 1958).

Solutions of HEC in water have been suggested for sizing paper (Santucci and Plossi, 1969), consolidating cellulose materials (Schaffer, 1978) and protecting pigments on unvarnished paintings (Brenner, 1974). HEC (Natrosol 250 GR (De Witte et al., 1984) and Natrosol 250HHR (Mehra, 1984)) are widely used for increasing the viscosity of dispersions, sometimes to form pastes, at a concentration of 1–2%. However, this addition seems to contribute to the yellowing of the dried films (Howells et al., 1984). EHEC has been used for textile consolidation (Geijer, 1961; Lodewijks and Leene, 1972). MHEC has also been used to increase the viscosity of aqueous reagents applied to surfaces (Tylose MH2000) (Hatton, 1977).

HPC, Klucel J (Berger, 1976) and Klucel G (Hofenk de Graaff, 1981) as a 2% solution in ethanol, has been suggested for pigment consolidation where a non-aqueous treatment is required. Klucel G is similarly used for leather consolidation (St John, 2000). HPC, like the other cellulose polymers, does not cause serious darkening of pigments. HPC has been applied as a film to adhere between layers, the films being activated with solvent (Gill and Boersma, 1997) or with water frozen on to the surface (Emberger et al., 2003). HPC has been used to make a solvent-swollen poultice to aid the removal of wax lining on paintings (Roznerska and Wójt, 2002).

The major use of CMC in conservation has been on paper, as an adhesive (Razdan, 1969), as a moisture-holding gel during aqueous surface treatments, as a pigment fixative (Brenner, 1974) and as paper consolidant by lamination

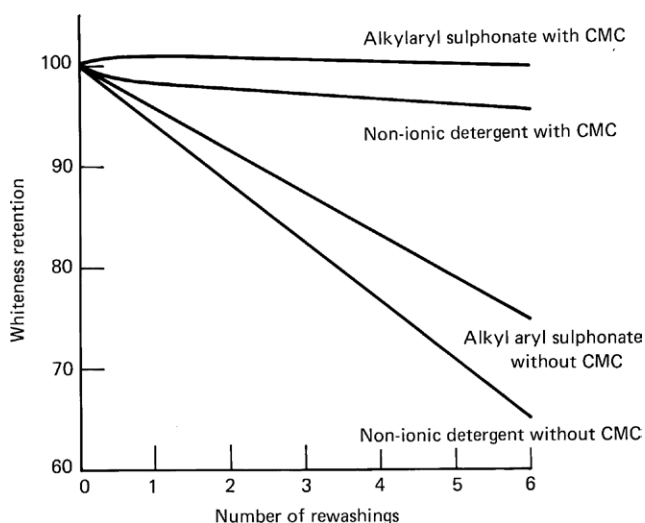


FIGURE 10.5 Use of sodium carboxymethyl cellulose (CMC) in detergents to prevent soil redeposition during washing of fabrics in dirty water. *Redrawn from Stelzer and Klug (1980).*

(Raff et al., 1967). While washing textiles with detergents, CMC at a concentration of 0.005% by weight in the solution prevents soil redeposition (Smith and Lamb, 1981; Lewis and Eastop, 2001). The most appropriate grade seems to have a DS of 0.6–0.8 with a molecular weight of 42,000–106,000. Figure 10.5 demonstrates the usefulness of including a suspending agent in the wash water. CMC is effective as an anti-redeposition agent only for cellulose-based fibres on to which it adsorbs; non-ionic ethers are better for wool and synthetics (Smulders, 2002). Mixed anti-redeposition agents are used for mixed fabrics.

Following the recommendations of Feller and Wilt (1990), it would be wise to use only MC and CMC in conservation, except for good explicit reasons. In general, the medium molecular weight grades are used, at a working viscosity of 400–4000 mPa, with 0.5–4% solutions.

10.2 CELLULOSE ESTERS

Various esters of cellulose have been manufactured but only the acetate and nitrate have been used extensively in conservation (Figure 10.6). Cellulose butyrate and its copolymer with the acetate do not seem to have been used.

10.2.1 Cellulose Acetate (CA)

Background

Cellulose acetate is manufactured by heating cellulose with acetic anhydride and a sulphuric acid catalyst. The chemical properties of CA change with increasing

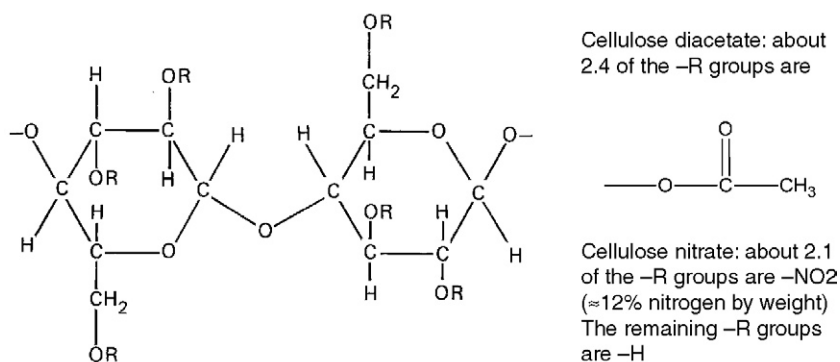


FIGURE 10.6 Two monomer units of a cellulose ester.

degree of substitution (DS). At a DS of about 2.4 (secondary acetates) the polymer is soluble in acetone and similar solvents (Figure A3.28). As the DS rises towards 3, the polymers require less polar solvents, e.g. chlorinated solvents. The molecular weight of CA used in solution is usually below 60,000 (Roff and Scott, 1971).

An intensive investigation into the properties of CA films was made by Wilson and Forshee (1959). CA with a DS of 2.4 will flow at $\approx 150^\circ\text{C}$, though this is lowered by plasticizers. CA oxidizes at room temperature, the molecular weight is reduced, and it becomes weaker and more brittle. Degradation is increased considerably by traces of acid catalysts remaining from manufacture. Old, impure samples can be expected to have degraded faster than modern equivalents. The process of degradation can be reduced by incorporating an acid acceptor, e.g. a buffer such as magnesium acetate. Ultraviolet absorbers and antioxidants can be added where an extended life is desired.

Conservation

Cellulose acetate in an acetone-soluble form became widely available during World War I as a coating for aircraft fabric, 'dope'. CA displaced cellulose nitrate, which was too inflammable. CA was first used, apparently without a plasticizer, in a solution in acetone for fixing pigments on paper and stone (Scott, 1923) and as a consolidant for cloth and other materials (Plenderleith, 1934). It was rejected in 1937 as a possible picture varnish (Stout and Cross, 1937). CA has been largely replaced for conservation uses by modern materials.

The greatest quantity of CA was used in the lamination of paper, starting around 1934 (Kimberly and Scribner, 1934). The heat-lamination process involves heating and pressing the paper between two sheets of CA so that the polymer flows into the paper. The degree of substitution, the molecular weight, the purity of the CA, the type and amount of plasticizer, the stabilizers used and the temperatures and pressures employed have been specified (Wilson and Forshee, 1959). Thin tissue was incorporated into the lamination by some

workers to improve the strength (Belen'kaya, 1964). Lamination can also be achieved by using solvents instead of heat to soften the polymer. The polymer films were wiped over with acetone then placed over the paper in a press (Kathpalia, 1966; Werner, 1968). Considerable difficulties have been caused by the degradation and increasing acidity of the CA films followed by the loss of compatibility with the plasticizer, which oozes out (Aubier et al., 1996).

CA has been widely used to copy cinema film images off old supports of CA or CN. However, much of the film stock used has deteriorated severely by metal-catalysed degradation and hydrolysis of the polymer (Allen et al., 1992), the 'vinegar syndrome'. The predicted lifetime of many CA films is c. 40 years, depending on the manufacture and storage conditions (Adelstein et al., 2002).

10.2.2 Cellulose Nitrate (CN)

Background (Miles, 1955; Selwitz, 1988)

Cellulose nitrate (CN) is prepared by soaking cellulose pulp in a mixture of concentrated nitric and (usually) sulphuric acids. For use as adhesives and lacquers the degree of substitution (DS) is usually 2.0–2.2 (11.2–12.3% nitrogen by weight) (Figure 10.6). The grade used in recent years for lacquers and adhesives is the ' $\frac{1}{2}$ second' grade, with a DP of ≈ 60 and molecular weight $\approx 25,000$ (Paist, 1977) (Figure A3.29). Higher-molecular-weight materials were used before the 1920s (Roff and Scott, 1971). CN has a high glass transition temperature and is usually compounded with plasticizers such as camphor (forming Celluloid), tri-phenyl phosphate and dibutyl phthalate. A typical adhesive formulation includes 5% plasticizer, 20% CN and 75% solvent. Camphor is still used as a plasticizer but it volatilizes rapidly, leading to shrinkage of the polymer film. Non-volatile plasticizers may migrate into adjacent porous material, producing similar shrinkage of the film. CN has strong intermolecular polar and hydrogen bonds that produce higher solution viscosity, though it releases solvent more quickly than other polymers. It has retained its usefulness as a lacquer and adhesive because it rapidly releases solvents to form a dry, strong film.

CN is an unstable material, apparently less stable than CA. The grades used for adhesives and lacquers are not supplied dry but are dampened with water or a solvent to reduce the chances of explosion when struck suddenly. This danger is eliminated by compounding with plasticizers. CN degrades at room temperature by a combination of oxidation and hydrolysis, which are catalysed by the presence of acid impurities and accelerated by light. These reactions result in a reduction of molecular weight and in the production of nitric oxides and acids. Yellowing also occurs (Koob, 1982). Many of these reactions appear to be related to the presence of the nitrogen oxides. If these are allowed to evaporate freely as in a free film or adhesive bond, the polymer is much more stable. CN will react in solution, and probably as a plasticized solid, with metal oxides to form an insoluble gel. The reactivity with the metals is greatest with lead, decreasing through calcium, silver, tin, iron, copper and zinc. This became

a severe problem during World War II when lead tubes of adhesive were inadequately coated internally. The material inside set to a gel, which could not be squeezed out (Anon, 1942). This effect has been noticed on copper alloy objects whose adhesives have had to be removed some years after application.

Conservation

Plasticized cellulose nitrate was first used for the conservation of objects during the late nineteenth century. Posse (1899) suggested Zapon, a CN/camphor solution in amyl acetate, for the coating of antiquities and strengthening of paper. It remained an adhesive, consolidant and coating of first choice in many applications for the first half of the twentieth century (Rathgen, 1905; Plenderleith, 1956) – ‘90% of one’s troubles can be overcome by “Celluloid in Acetone” (Leechman, 1931). Typical uses were as a consolidant for stone (Zellon) (Rathgen, 1926), earth (von Kock, 1914), wall paintings (Coremans, 1941), pigments (Bailey, 1938), plants (Jackson and Ghose, 1932), wood (Plenderleith, 1954) and general organic materials (Leechman, 1931); as an adhesive for pottery (Mibach, 1975); and as a coating for unstable glass (Pauzaurek, 1904) and stained glass paint (Jägers et al., 2000), silver (Majewski, 1973) and iron (Western, 1972).

Even in the early stages of its use, reservations were expressed about the stability of the polymer and the effect on objects (Posse, 1899). CN was displaced for some purposes during the 1920s and 1930s by CA (Plenderleith, 1934) and PVAC (Gettens, 1935). Although it has been reported as being used for picture varnishes (Johnson, 1977), few paintings seem to have been subjected to this treatment.

CN continues to be used in conservation, as an adhesive (Hanna et al., 1988) (Table 10.3), and for consolidating soil sections (van Baren and Bomer, 1979) and silver lacquers (Reedy et al., 1999). This is because of its ease of use and excellent appearance. It is packaged conveniently and dries rapidly. It is also,

TABLE 10.3 Some Cellulose Nitrate Adhesives Used in Conservation

Product	Manufacturer	Plasticizer ¹	Relative Stability ²
Durofix	Rawlplug	DBP (since before 1946)	2
HMG Waterproof adhesive	Guest	DBP (+ levelling agent)	3
Duco Cement	Decon		5
Cement	Randolph		1
UHU Hart	Lingner	DBP	4

¹Information from manufacturer or from infrared spectrophotometry; DBP, dibutyl phthalate.

²Approximate ordering, 1 being most stable, derived from Koob (1982).

in most cases, readily and completely soluble after long natural ageing and could be expected to last up to 100 years (Shashoua et al., 1992). Any proposed replacement must prove to have comparable properties and convenience before CN is displaced completely. Removal of lacquers with solvents is often not complete, leading to uneven tarnishing (Thickett and Hockey, 2003), so steam softening and stripping has been proposed (Ankersmit and van Langh, 2002).

However where CN is used in bulk, such as for cinema film or objects, it deteriorates and disintegrates (Edge et al., 1990; Fenn, 1995) with considerable risks to other objects, life and property (Robb, 2003).

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Natural Water-Soluble Polymers

The properties of a selection of natural water-soluble polymers are summarized in Table 11.1.

11.1 POLYSACCHARIDES

11.1.1 Starch

Background (Eliasson, 2004; BeMiller and Whistler, 2009)

Starch is a polymer made up, like cellulose, from glucose monomers (Figure 11.1). However, the joining of adjacent units is different, leading to very different

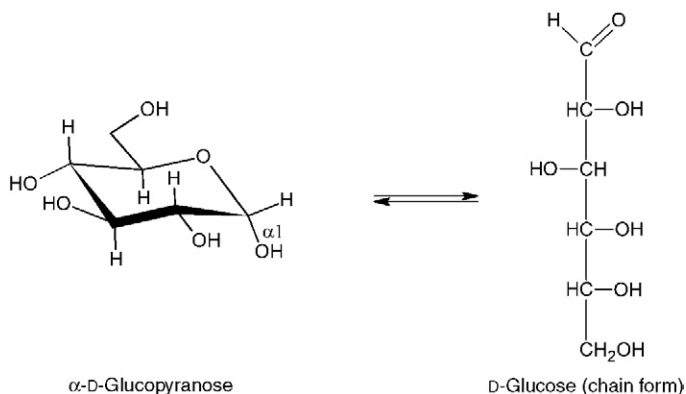


FIGURE 11.1 D-Glucose is the usual compound found in nature, with both the ring and chain forms coexisting in solution. α -Glucopyranose means that the glucose molecule is arranged in a ring with the hydroxyl group at carbon atom 1 arranged as shown.

properties. Two types of molecules make up the bulk of starch (Bertoft, 2004). Amylose is a largely linear molecule (Figure 11.2). The molecular weight of amylose lies between 130,000 and 890,000, being higher for tapioca and rice than for potato starch. Amylopectin molecules (Figure 11.3) are some of the largest molecules found in nature, the molecular weight being typically 10^7 to 10^8 . Amylose and amylopectin have different molecular architectures (Figure 11.4)

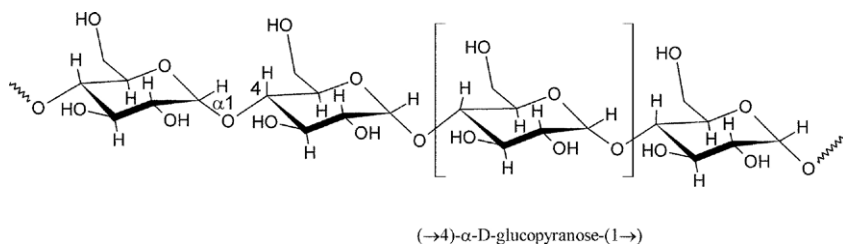


FIGURE 11.2 Straight-chain starch molecule, amylose (CAS 9005-82-7). It is made up of glucose units polymerized by dehydration to form ether links. Once incorporated into the chains, they are called anhydroglucose units. The α -links shown create a polymer that has a chemically similar monomer but is physically and chemically different from cellulose, formed using β -links (see Figure 10.1).

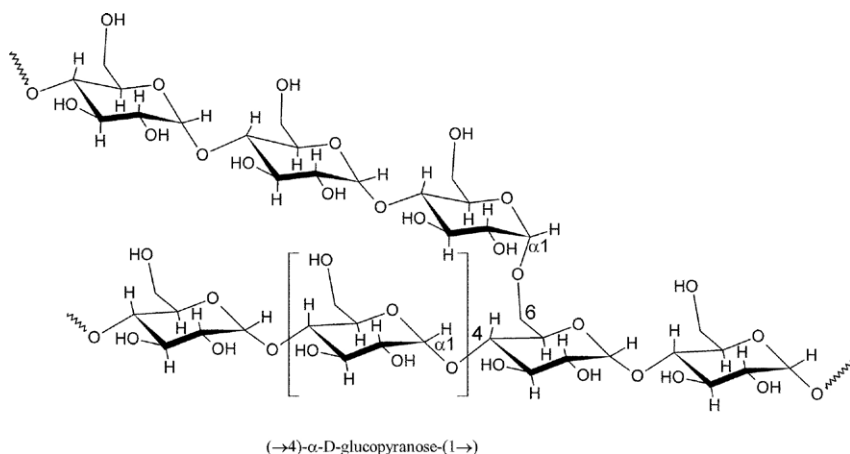


FIGURE 11.3 Amylopectin (CAS 9037-22-3) is a polymer molecule similar to amylose but with branching points at the C6 hydroxyl group.

leading to different properties, both in solution and as dry films. Both amylose and amylopectin are laid down as double helices in semi-crystalline form.

Starch is laid down in granules that are deposited in seeds, roots, tubers, etc., providing food storage for various plants (Moorphy, 2004). The granules are extracted by grinding the tissue then washing in water. The starch is insoluble in water until heated to the gelatinization temperature (55–80°C), when the granules swell and start to disrupt (Figure 11.5). The amylose component, largely on the periphery of the granule, dissolves out first while the swollen amylopectin granules interact to form a network. This causes a rapid rise in viscosity, reducing on cooking as the granules are dispersed. Remains of the original structure of the granule can survive 1 hour's heating at 100°C. Constant stirring is needed to prevent lumps forming. Vigorous stirring during cooking also reduces the molecular weight and the amount of granule ghosts remaining. On cooling, the amylose molecules associate into double helical regions, cross-linking the chains and causing the solution to gel. On standing, these cross-links

TABLE 11.1 Summary of the Properties of Natural Water-Soluble Polymers

Name	Monomers	CAS No.	Properties
Starch	Glucose	9005-25-8	Insoluble in water. Disperses in hot water to form a paste
Gum arabic	Arabinose, galactose	9000-01-5	Easily soluble with low viscosity
Agar-agar	Galactose	9002-18-0	Soluble in hot water, sets to a gel on cooling
Funori	Galactose sulphate		Soluble in cold water
Gelatine	Amino acids (characteristic hydroxy-proline)	9000-70-8	Soluble in hot water, sets to a gel on cooling
Casein	Amino acids	9000-71-9	Mixture of proteins, insoluble in water, soluble in alkalis
Egg white	Amino acids	9006-50-2	Mixture of ≈ 40 proteins, soluble in cold water, denatured by heat

are stabilized by loss of water and formation of stronger hydrogen bonds – ‘retrogradation’. The retrograded starch can be dissolved only by autoclaving and is resistant to enzyme attack.

The highly regular linear structure of amylose allows it to dry from solution to form strong films. Humectants may be added to prevent films becoming brittle at low relative humidities. Amylopectin, being more amorphous, forms weak films. Films of amylose will absorb up to four times their weight in water without dissolving. Amylopectin will dissolve in cold water to form viscous solutions with little tendency to form gels. Starch dissolves (but may be slightly degraded) in a few organic solvents, e.g. dimethyl sulphoxide and *N*-methyl-2-pyrrolidone.

The proportions and molecular weights of the amylose and amylopectin components determine the properties of the pastes and the final film (Table 11.2). A high proportion of amylose, e.g. in corn and wheat starches, will cause the solution to gel on cooling. A high-molecular-weight amylopectin will take longer to disperse and will form a high-viscosity solution.

Amylose has been shown to degrade by photo-oxidation and hydrolysis reactions on exposure to ultraviolet (Phillips, 1980), resulting in breaking of the chain and production of organic acids. Empirically, paste films have been found to be more stable if they are made from starch granules rather than flour (Clapp, 1978; Wills, 1984), whose gluten (protein) content will degrade faster (Radley, 1976). The paste made from flour has better proper-

ties of slip and adhesion during application than pure starch pastes. Potato and corn starches are more likely to be damaged during cooking, leading to yellowing (Rice, 1972). Rice starch has been found to be less stable than wheat starches on natural ageing (Clapp, 1978).

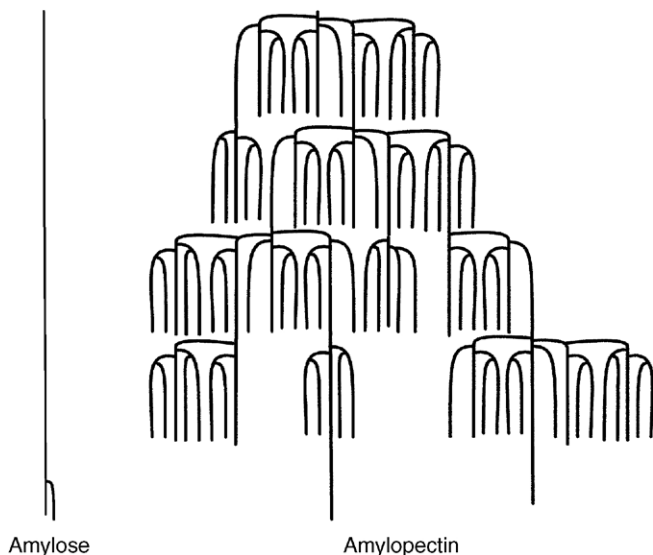


FIGURE 11.4 Indicative molecular structures of amylose and amylopectin.

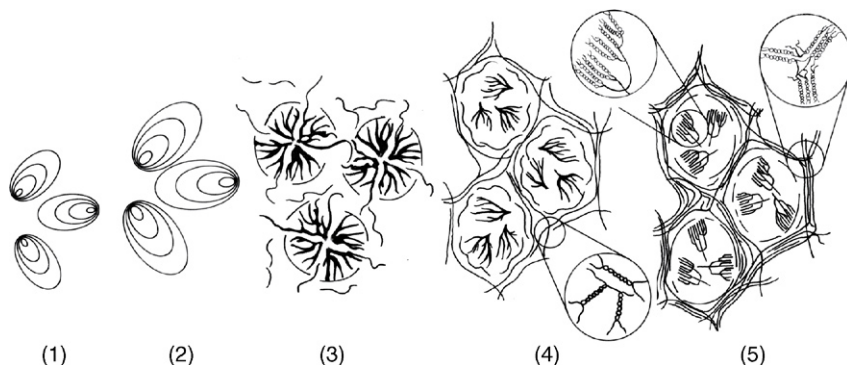


FIGURE 11.5 Changes in starch during the process of heating in water (cooking) and cooling (van der Borgh et al., 2005). (1) Dry native starch granules in their initial state. (2) Granules swelling in water at room temperature. (3) On heating to the gelatinization temperature, the granules absorb water and are disrupted, the starch molecules swell losing their helical structure and crystallinity, amylose molecules dissolve and disperse in the surrounding liquid, depending on the extent of heating and agitation, the amylopectin molecules swell but retain some of the shape of the original granules. (4) On cooling, the amylose molecules reform helical chains causing the liquid to gel. (5) On storage, the amylose helical regions expand and the amylopectin molecules reform helical regions (retrogression), becoming increasingly stiff and insoluble in water.

Image courtesy of Jan Delcour.

TABLE 11.2 Properties of Some Starches

Plant Type	Amylose Proportion in Starch (%)	Degree of Polymerization, DP_n		Gel Formation
		<i>Amylose</i>	<i>Amylopectin</i>	
Wheat	≈25	1300	7500	Strong
Rice	16–19	1100	10,000	Little
Potato	23	4900	11,200	Little
Rye	26			
Corn	22–28	930	16,000	Strong
Tapioca	17–22	2600		Little

Sources: Takeda et al. (2003), Vandeputte and Delcour (2004).

Furunori is a modified wheat starch made in Japan by ageing starch paste under water for years. The molecular weight of the starch is reduced considerably by microbial action and the amylose is almost totally retrograded (Daniels, 1988; Hayakawa et al., 2002). It has less tack and greater gel stiffness.

Starch is modified by hydrolysis and oxidation at elevated temperatures to produce easily soluble British gums and dextrans that have very low molecular weights and that have been widely used as remoistenable adhesives on paper tapes and labels. The molecular weight of starch can be modified more subtly by controlled hydrolysis of the molecules while still in the granules (Van Steene and Masschelein-Kleiner, 1980). When acid-catalysed hydrolysis is carried out below the gelatinization temperature, the starch molecules are attacked in the amorphous regions of the granule. This increases the proportion of unbranched but shorter polymer chains, resulting in a lower solution viscosity and an increased tendency to gelation (Taggart, 2004).

Starch is traditionally identified by the intense blue colour produced when amylose is reacted with an iodide solution. The iodide forms a complex with a surrounding amylose single helix, which amylopectin cannot form. This reaction works only with soluble amylose so retrograded amylose will react weakly, if at all.

Conservation

Flour pastes are traditional adhesives for paper and for use in book bindings, though starch pastes are now preferred. Typical proportions are (BS 4971:1, 1973):

- wheat starch, 400 g;
- water, 1150 ml.

The wheat starch is mixed to a cream in a small quantity of water. It is heated with the remaining water in a double boiler with continual stirring for 10 minutes at a simmer. It is then cooked for a further 1 hour. The final hour can be replaced by 20 minutes cooking in a pressure cooker at 200 kPa. The liquid is decanted into sterile containers. It will set to a firm gel or paste. This can be diluted by working in more water, 200 g paste in 1 litre of water previously heated to 100 °C for a few minutes to sterilize. Starch paste spoils easily. In use the paste should not sink into or release much water into the substrate (Plenderleith and Werner, 1971). A rice starch paste may be made as follows. Rice starch (30 g) is mixed to a cream with 30 ml water. Boiling water (600 ml) is poured into the cream with vigorous stirring. It is simmered in a double boiler for 1 hour. Wheat starch modified by acid hydrolysis is claimed to provide better qualities as both paste and adhesive (Van Steene and Masschelein-Kleiner, 1980). Starch has been used as a relining adhesive over many centuries, often mixed with glue (Marijnissen, 1967). A typical formula is (Bergeon et al., 1978):

- wheat flour, 375 g;
- rye flour, 188 g;
- skin glue, 94 g;
- Venice turpentine, 67 g;
- phenol, 8 g.

Although amylopectin is resoluble in water at room temperature, amylose is not. Starch adhesives are usually removed by swelling in water and scraping off the resultant gel. Even hot water is unlikely to dissolve amylose. Both enzymes (Daniels, 1995; van der Maarel et al., 2002; Schönbohm et al., 2004) and solvents such as *N*-methyl-2-pyrrolidone (Green and Bradley, 1988) and dimethyl sulphoxide (Kurtzman et al., 1973) can be used to dissolve starch, but may in the process dissolve or disrupt other components of the substrate.

11.1.2 Gum Arabic (Williams and Phillips, 2000; Verbeken et al., 2003)

Gum arabic is a high-molecular-weight polysaccharide exuded from wounds in *Acacia* species. Although the natural product is variable in composition (incorporating calcium, magnesium and potassium), it has two major components, arabinogalactan ($\approx 90\%$, $MW \approx 0.38 \times 10^6$) (Figure 11.6) and a glycoprotein ($\approx 10\%$, $MW \approx 1.5 \times 10^6$). Both are highly branched, compact, molecules. It is soluble in water at room temperature and forms viscous solutions with up to 50% by weight of gum and a pH of ≈ 5 . The gum lowers the surface tension of the liquid. It is an excellent suspending agent and acts as an emulsifier. Gum arabic probably degrades by hydrolysis and photo-oxidation in a similar fashion to starch. The molecules can be cross-linked and precipitated by trivalent metal ions, e.g. aluminium and iron salts, lead and mercury salts, and gelatine. Gum arabic is susceptible to biodeterioration.

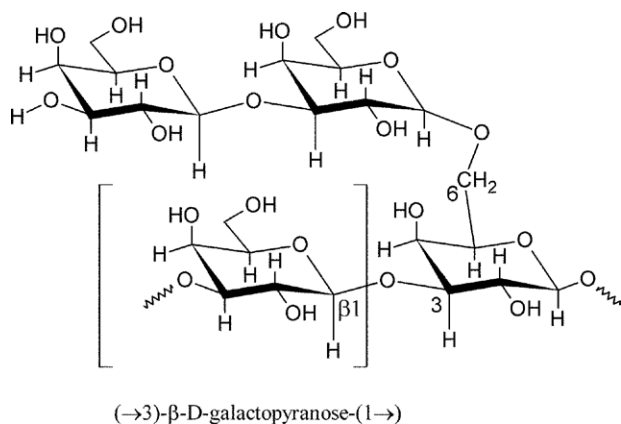


FIGURE 11.6 Gum arabic monomer unit. The molecules are probably constructed like bottle brushes with a long core from which branch numerous side chains.

Gum arabic has long been the medium in inks and water paints (Lucas, 1932) and it has been suggested as a fixative for pigments (Emmenegger, 1975; Flieder et al., 1981). The other major traditional use has been as an adhesive for paper tapes and labels, often plasticized with glycerol. Gum arabic has been used in the past as an adhesive for textiles (Lodewijks and Leene, 1972) and insects (Lewis, 1946). It should be removable by washing in water (Flieder et al., 1981).

11.1.3 Agar-Agar (Armisen and Galatas, 2000)

Agar is a polysaccharide extracted from the *Gelidium* and *Gracilaria* seaweeds. Having had lower-molecular-weight components removed during processing, the molecular weight is $\approx 125,000$ with a structure based on agarose (Figure 11.7). It will dissolve only in near-boiling-point water. At concentrations above 0.7%, the solution will set to a gel on cooling to 32–38 °C, by the formation of double helices that assemble into a three-dimensional network. Once formed, the gel requires heating to 88–94 °C in order to remelt it. On

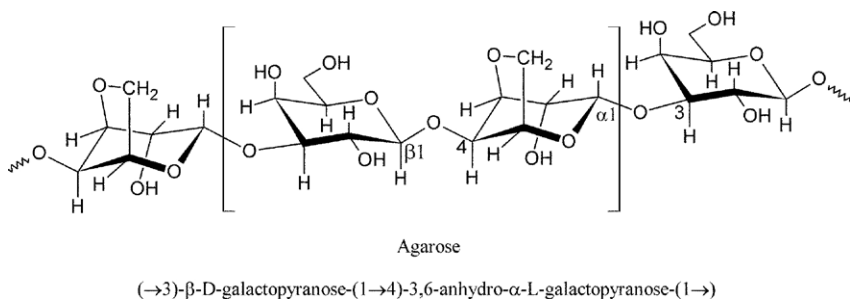


FIGURE 11.7 The major polysaccharide of agar-agar.

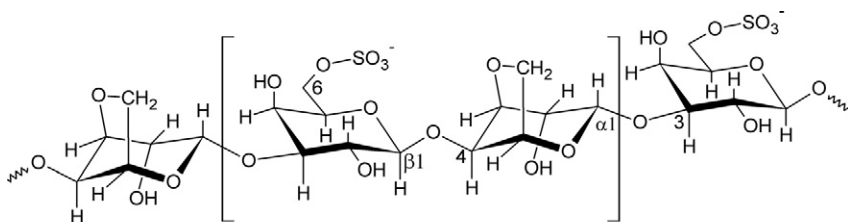
drying, the water-swollen film of agar undergoes considerable shrinkage. This probably accounts for the exfoliation of a pigment film that had been fixed with an agar/PVAL (whose films also form swollen gels) solution (Chemical Research Section and Research Section for Repairing Techniques, 1968).

Agar is likely to degrade by oxidation in a similar manner to other polysaccharides. It is resistant to biodeterioration, and is used as an inert growing medium for micro-organisms. Agar gels made with 5–17% by weight of gum in water have been used as moulding material. The warm solution sets to a rigid gel from which casts may be taken (Clarke, 1936).

Agar is one of a large number of seaweed extracts, including carrageen, which have slightly differing structures and properties, used for gelling and viscosity control in foods.

11.1.4 Funori

Funori is the adhesive extracted from *Gloiopeltis furcata* seaweed found on the coast of Japan and China. The extract (funoran) is a mixture of polysaccharides, one major (Figure 11.8) and three minor components (Takano et al., 1998). Funori is obtained by dissolving the seaweed in warm-to-hot water. A small amount of the seaweed does not dissolve and is filtered off. Unlike agar, funori solutions do not gel on cooling. Funori has been used traditionally in Japan as an adhesive and for refixing pigment (Winter, 1984; Swider and Smith, 2005). In order to reduce the natural variation in properties, a refined version, Junfunori, has been made available (Geiger and Michel, 2005). On artificial ageing by UV and heat, funori undergoes relatively little change.



Agarobiose 6-sulphate

(→3)-β-D-galactopyranose-6-sulphate-(1→4)-3,6-anhydro-α-L-galactopyranose (1→) unit

FIGURE 11.8 The major (≈85%) polysaccharide in funoran.

11.2 PROTEINS

11.2.1 Glue

Gelatine is the soluble protein made by heating, breaking down and dissolving collagen from animal connective tissues, such as skin (including

parchment) and bones. Glue is an impure form of gelatine. Collagen (Woodhead-Galloway, 1980) is the strong, white fibrous protein in skin and bone. Methods employed to remove the other components have considerable influence on the resultant glue. Collagen is a polyamide (Figure 11.9) polymerized from amino acid monomers in the body as a long rod about 300 nm long and 1.5 nm in diameter. The collagen molecule is a helix of three sub-chains, each with a molecular weight of about 100,000, wound around each other then assembled into increasingly complex structures (Figure 11.10). When first made, the collagen molecules can be easily separated from one another. As the animal ages, cross-links form both within and between the chains. When collagen is heated, the helix uncoils releasing the chains. The collagen network denatures and shrinks, and the gelatine can be dissolved out (Figure 11.11a). The temperature at which this happens is called the shrinkage temperature. Mammal collagens from cattle, pig, rabbit, etc. are fairly similar and have similar shrinkage temperatures, around 37–42 °C. However, fish collagens have fewer hydroxyproline amino acid units, resulting in shrinkage temperatures between 6 and 32 °C (Burjanadze, 2000). On cooling, gelatine becomes a gel (Figure 11.11b) at a temperature depending on the source species, the molecular weight and concentration.

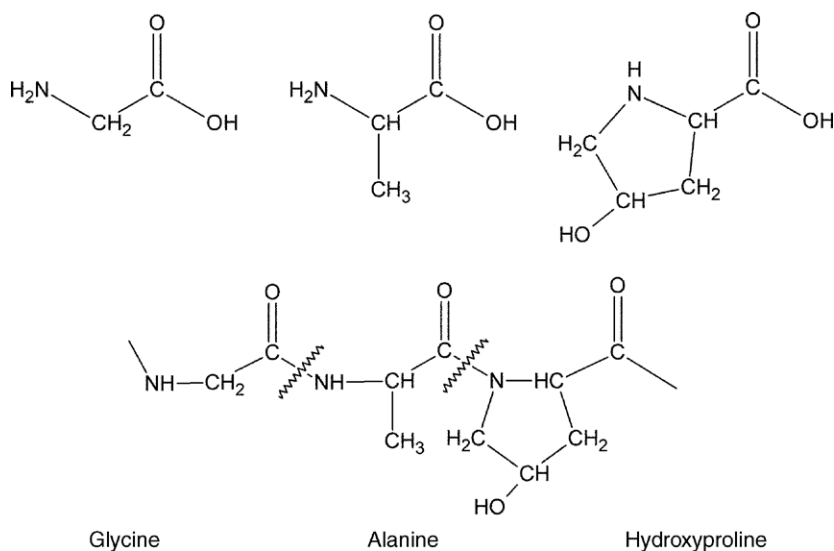


FIGURE 11.9 A typical amino acid sequence in collagen, formed from glycine, alanine and hydroxyproline. A collagen sub-chain normally has over 1000 amino acid units, drawn from a pool of 20 different amine acids. The triplet sequence in the helical region is invariably glycine followed by two other amino acids, of which proline, hydroxyproline and alanine are the most abundant. **Source:** Bhattacharjee and Bansal (2005).

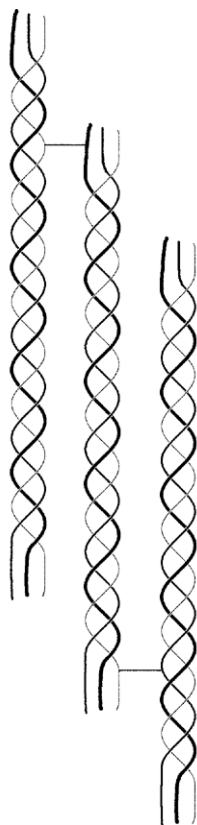


FIGURE 11.10 Schematic collagen network. The collagen molecules (the triple helix) are packed closely by cooperating hydrogen bonds, at the correct spacing to enable covalent cross-links to form over time with the correct chemical environment (e.g. enzymes, oxygen).

Glue Production

Acids, alkalis and enzymes are used to clean the collagen networks for extraction, though the different pretreatments have effects on the resultant gelatine (Ledward, 2000). The first extract releases complete denatured chains that are lightly bound to their neighbours. These large molecules produce the strongest glue with the lightest colour. As the extraction conditions become more severe, the cross-linked molecules are degraded and released from the network, making weaker, more coloured glues. The solution is then evaporated to create the solid glue, which may contain fats and minerals. Collagen in young animals (e.g. rabbits) has fewer cross-links and the extracted gelatine will be less degraded.

The least degraded samples contain molecules with multiples of the component chains. The largest molecules may be formed of up to five chains held together by the original cross-linking. More commonly, molecules with one, two or three chains are found. More severe conditions break down the molecules, resulting in solutions of shorter chains, even down to MW 10,000.

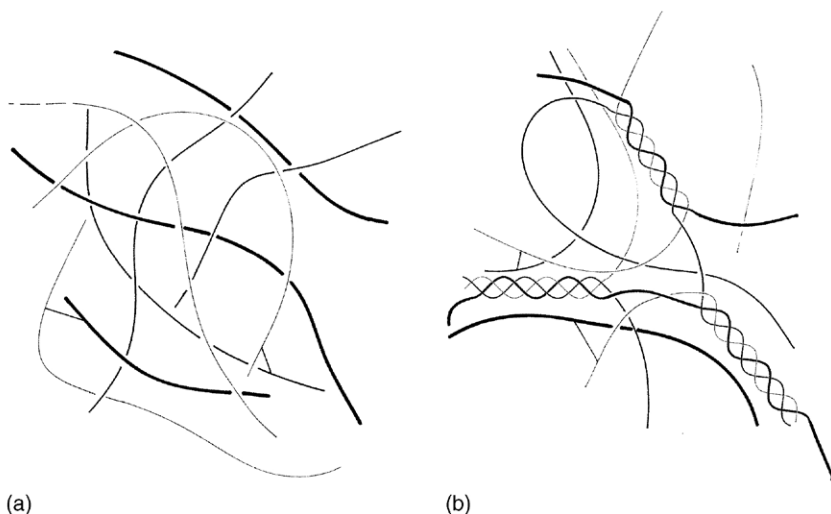


FIGURE 11.11 (a) Denaturation of a collagen network when heated in water. The triple helix unwinds, the collagen molecules are hydrolysed causing chain scissioning, but some of the resistant cross-links survive. (b) When cooling, thermo-labile triple helical cross-links are formed, creating a gel.

Because fish collagen has few cross-links, less severe conditions are required to make the glue. Isinglass, made from the swim bladder of the sturgeon (and now other fishes), needs far less preparation. The swim bladder is fairly pure collagen (Hickman et al., 2000), which can be cut out of the fish and cleaned mechanically. When soaked then heated in water, the swim bladder will almost totally dissolve. After filtering, the glue is ready to use. Glue made from other parts of the fish body tends to be less pure and more degraded.

Gelatine producers supply highly specified products for the pharmaceutical and optical industries. These also supply glues but many glues are made by craft producers.

Glue Properties

On cooling, gelatine solutions set to gels when the molecules associate and re-establish the triple helix structure in small areas, acting as heat-sensitive cross-links (Figure 11.11b). Mammal glue solutions form a gel at room temperature and most fish glue solutions need refrigeration to gel (Simon et al., 2003). Gels melt on heating when the helices unwind. The strength of solid glue films is difficult to measure so in practice the properties of glue solutions are used for specification. The strength of the gel in g Bloom (ISO 9665:2000, 2000) is a standard method; the higher the value, the stronger will be the gel and the glue. A 300 Bloom gelatine will have a high proportion of multiple chain molecules, whereas a 150 Bloom gelatine will have about 40% molecules smaller than single chains. The viscosity of a gelatine solution also decreases as the average

molecular size decreases. If a glue solution is kept molten at high temperature, the glue degrades. Keeping it liquid for 24 hours at 60 °C causes the gelling potential to drop by 2%. Solutions are easily spoiled by micro-organisms, which also cause degradation.

Most mammal glues will solidify/gel at 20–40 °C. On cooling, high Bloom gelatines gel sooner while low Bloom gelatines will remain liquid, “open”, for longer. When the concentration of gelatine is increased so is the gel strength, as are the melting temperature and the viscosity. When a glue solution sets, the strength of the gel rises over a few hours as the cross-links develop. The gelation of the solution can be prevented by adding gel depressants, so creating mammal glues that remain liquid at room temperature. Gel depressants such as urea, thiourea and ammonium thiocyanate can be used at 8–20% of the weight of glue (Brandis, 1989).

As the glue sets in position, it passes through various stages. Initial cooling of the solution forms a gel. This then starts losing water and shrinks in the process. On drying from the initial gel to ≈50% relative humidity (RH), the film shrinks by more than 70% and builds up an internal tension of ≈14 MPa (Mecklenburg, 1988). This is considerably more than the stresses occurring with modern synthetic adhesives. There are indications that humidity cycling allows some of the tension to be dissipated (Payne et al., 1999). Shrinkage of glue films is strong enough to pull the surface off glass, and it is used for glue etching (Mitchell, 1989).

Glue is hygroscopic. Mammal gelatine (Kozlov and Burdygina, 1983; Sobral and Habitante, 2001) contains about 6% water at 10% RH, 12–16% water at 50% RH and 30% at 84% RH at room temperature. The more impure grades are more hygroscopic. Glue becomes extremely stiff and glassy when it is dry. As it absorbs more water, it becomes more flexible and is a jelly at 84% RH. Changing from its glassy state to a rubbery one depends on both the moisture content and the temperature. With no water, it changes from a glass to plastic at 220 °C. More interestingly, at 50% RH the transition is about 45 °C, while at 80% RH the transition is around room temperature. Glycerol (Brandis, 1989), at 5–25% as a proportion of the dry weight of glue, sucrose and magnesium sulphate, can be included in the dry glue to make it more flexible, either to increase the flexibility directly or to absorb extra water and so increase flexibility. The increased flexibility of the glue results in a lower strength and less shrinkage. Fish glues form gels only at low temperatures and the films convert from rigid to gels at ≈60% RH (13% water) (Fraga and Williams, 1985). They are less rigid than mammalian glues.

Gelatine is soluble in some unusual solvents at room temperature, e.g. 2,2,2-trifluoroethanol and formamide (Miller et al., 1998) whereas water, glacial acetic acid, ethane-1,2-diol and dimethyl sulphoxide require heating (Umberger, 1967). It is degraded rapidly in acid (pH < 3) or alkaline (pH > 9) conditions and by enzymes. Like its parent molecule, glue can be cross-linked by a number of different chemicals, such as trivalent metal ions (e.g. iron, aluminium

and chromium), tannins or aldehydes. These are used where water resistance and higher strength are required, e.g. photographic emulsions, abrasive papers. Cross-linking also makes dismantling a join very difficult.

Glue will last remarkably well in dry, neutral conditions. Even after 8000 years in a dry cave (Bar-Yosef and Schick, 1989), the glue was identifiable. If it reacts similarly to its parent collagen, it will degrade oxidatively in acid conditions (Horie, 1990). This might be a problem if alum, an acidic compound, has been added to glue solution to cross-link it. Pollutants have been shown to degrade gelatine (Nguyen et al., 1997). A greater problem is likely to be the hydrolytic and micro-organism degradation of glue at high relative humidities. Glue contains DNA from its source animal (or even humans) and this can cause significant contamination when analysing objects (Nicholson et al., 2002).

Conservation

Glue was one of the strongest adhesives available before the development of synthetic materials and has a 10,000-year record of use. It has been used in ancient Egypt (Lucas and Harris, 1962), mediaeval Europe (Theophilus, 1963), through the Industrial Revolution (Neumann, 1773) and into the present (Brandis, 1989). Glue commonly used as a size in paper has been shown to be protective against ageing (Barrett and Mosier, 1994). Glue/starch pastes were introduced for the relining of canvas paintings in the seventeenth century (Ackroyd, 1995) and have been used on other textiles (Section 11.1.1). Glue is still the usual adhesive for the conservation of furniture (Kjelland, 1997; Rivers and Umney, 2003), following traditional methods in its construction (Table 11.3). Glue is

TABLE 11.3 Recommended Mixing Ratios of Glue in Solution to Make a Strong Bond

Bloom Grade (g)	Porous Woods		Non-Porous Woods (% w/w)
	% w/w	Gel setting point (°C)	
380	25	41	24
315	29		27
250	31	37	29
192	36		33
136	44	35	40

25% w/w means 25 g of glue in 75 g of water, making up a solution of 100g. Gel setting data from www.gelita.com, 29.6.05.
Adapted from Anon (1951).

also used for the production of Japanese art materials (Morita, 1984; Winter, 1984). The shrinkage of glue has been employed to remove paint layers from substrates from the seventeenth century (Marijnissen, 1967), especially during the transfer of wall paintings (Mora et al., 1984). These facing adhesives incorporate considerable amounts of plasticizing materials such as molasses in order to increase impact strength and flexibility. Modern investigations have demonstrated that traditional additives have merit. Dedicated research has shown that beer (containing both alcohol and polysaccharides) improves glue adhesion to brass (Triboulot, 1999).

Gelatine solutions were used widely for adhering and consolidating objects: ivory (Anon, 1852; Lowe, 1910), palaeontological bone (Howie, 1995), wood (Petrie, 1904; Cronyn and Horie, 1985), shale (Plenderleith, 1934), pottery (Rathgen, 1905; Watkins and Scott, 2001) and porcelain (Thiacourt, 1868). Glues may have been protected from mould growth with mercuric chloride (corrosive sublimate) or formaldehyde (Rathgen, 1905). The use of formaldehyde to strengthen gelatine consolidant on parchment manuscripts was deprecated (Nicholson, 1898). The former would remain as a toxic impurity and a contaminant for analysis; the latter would cause cross-linking and insolubilization of the gelatine. The insolubilization reaction between glue and tannins was proposed as a method of consolidation of waterlogged wood (Augusti, 1959).

Reversing glued joints in wood has traditionally been achieved by feeding water into cracks and pulling the gelled joint apart. If the joint is not sufficiently weakened by just swelling the glue, applying heat, e.g. iron or hot towels, may induce sufficient softening. Energy can be concentrated in the wet glue by using radio frequency heating (Neher, 1995). Glued joints may be renovated by swelling the glue in water but only if heated sufficiently to liquefy the glue line to allow the adhesive to flow over the surfaces.

The swelling of glue applied to fragile surfaces can cause further damage during removal. This may be reduced by using mixed solvents, such as ethanol/water.

Glue (Pataki, 2005) and isinglass (Takami and Eastop, 2002) have been increasingly used for the consolidation of friable paint and ground layers because of good wetting and flow characteristics.

11.2.2 Casein

Background (Ennis and Mulvihill, 2000)

Casein is the main milk protein precipitated from skimmed milk as curds or cheese by acidifying. This casein is a mixture of many proteins, with molecular weights around 20,000–25,000. Although casein is insoluble at $3.5 < \text{pH} < 5$, it will dissolve in neutral and alkaline solutions. These solutions are fairly heat stable but very viscous above concentrations of 15%. Casein films deposited from dilute sodium and potassium hydroxide solutions will redissolve on warming, though ammonia solutions dry to insoluble films. Calcium and similar

multivalent alkalis create cross-links, forming an insoluble product. Calcium caseinate is the most usual form for adhesives. Mediaeval (Theophilus, 1963) and nineteenth-century (Spon, 1888) recipes involved mixing dispersions of casein and slaked lime in water (Gettens and Stout, 1942). Modern formulations employ mixed dry ingredients to which water is added when required (Bye, 1989). Casein films are brittle but can be plasticized with glycerine or sugars. Casein supports mould growth and cannot be used in a damp environment, even if fungicides are added.

Conservation

Calcium caseinate is a traditional adhesive (Lucas, 1932) for wood (Hayward, 1976) and plaster restoration (Mora et al., 1984). Skimmed milk has been applied to lime plasters and will form a cross-linked film. Casein has been used as a surface consolidant for stone (Warnes, 1926) and for pigments on paper (Kishore, 1952). One use has been as an adhesive for detached wall paintings (Mora et al., 1984). The shrinkage of the calcium caseinate gel applied to pigments on wall paintings has created damage and difficulties in reversal (Nisbeth, 1980). Although the alkaline conditions make enzyme removal more difficult, this method has been successfully used to reverse casein coatings (Klein and Beutel, 2002).

11.2.3 Egg White (Schreiber et al., 2002)

Egg white is a solution in water, $\approx 12\%$ solids, primarily the glycoproteins (protein joined to a carbohydrate) ovalbumin (57%) and conalbumin, and a number of other proteins, with molecular weights of 10,000–70,000. Some of the proteins denature and coagulate on heating. On drying, egg white becomes insoluble.

Egg white has long been used as an adhesive (Theophilus, 1963) and as a picture varnish; this is known to cause problems (Woodhuysen-Keller, 1999). Calcium albumate, made from white of egg, has also been used as an adhesive (Standage, 1931).

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Natural Resins

12.1 TERPENES

Many natural resins are obtained as exudates from trees. These plant resins are based on the terpene skeleton, which contains 10 carbon atoms. This can be arranged in a large variety of ways (Figure 12.1). Oleoresins can be extracted from a large number of plants. Monoterpenoids are frequently liquids, and act as solvents for larger resin molecules in the exudate. These volatile chemicals are important in flavouring and scents, and many have antiseptic properties. Fortunately for analysis and identification, the diterpenoids and triterpenoids do not occur naturally in the same resin. The resins display characteristic differences in chemical composition and properties. Many of the terpenes are important biologically and can have biological effects. All the terpenes tend to oxidize readily and many are partly oxidized during processing for use (Scalarone et al., 2005). Most of the terpenes occur in a number of different structures, enantiomers, that differ only in how the atoms are arranged in space. Those resins that are likely to have been used in the manufacture or conservation of objects have been well reviewed (Mills and White, 1994).

12.2 MONOTERPENOIDS (TABLE 12.1)

Turpentine, the exudates from various pines around the world, is separated by distilling the volatile oils ($\approx 20\%$) from solid resin. The largest components of the oil are usually α -pinene and β -pinene with many other components, mostly liquids but containing some materials solid at room temperature. These occur in varying proportions depending on the source trees and the blending, though the oil will contain a number of other monoterpenes. However, the original name turpentine is derived from the terebinth, the broad-leaved *Pistacia terebinthus*, a small Mediterranean tree, whose volatile exudate also contains α -pinene and β -pinene (Kivcak et al., 2004). Oil of turpentine is distilled off at $\approx 155\text{--}165^\circ\text{C}$. Because the hydrocarbons are unsaturated, they tend to react with oxygen in the air, becoming increasingly polar with the formation of peroxides (Ancel et al., 2004). These can then polymerize to form insoluble and yellow products. These oxidized components will in turn cause any solutes, such as other polymers, to oxidize, deteriorate and cross-link. This has been known for at least 200 years

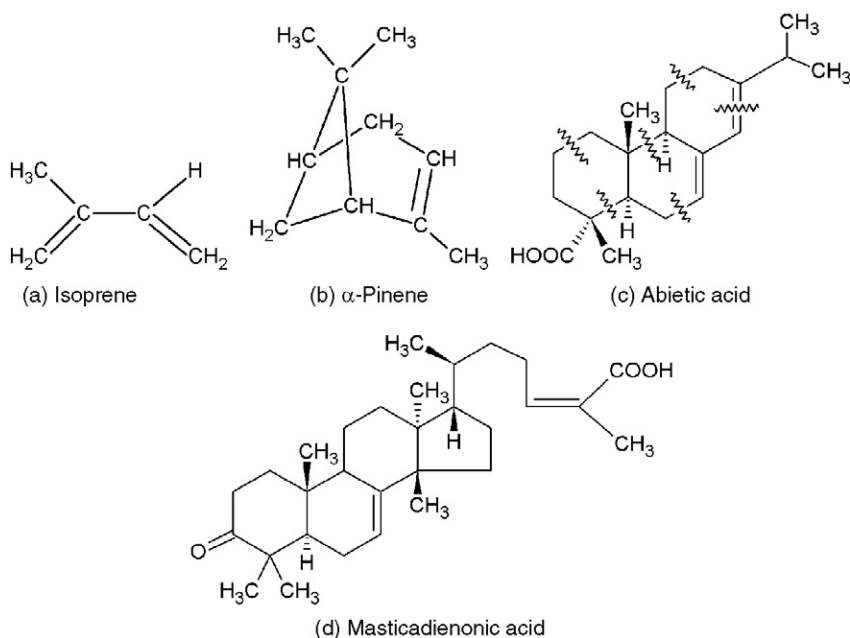


FIGURE 12.1 Typical terpenes. (a) Isoprene is the nominal building block of the terpenoids. (b) Pinene is a major constituent of oil of turpentine. (c) Abietic acid is a major constituent of rosin (colophony). (d) Masticadienonic acid is a major constituent of mastic resin. The wavy lines in (b) and (c) indicate the junctions between the five carbon monomer units (isoprene), two of which form a terpene.

(Margueron, 1797). For that reason, oil of turpentine is not recommended to be used for conservation purposes (Feller, 1971). Oil of turpentine has physiological effects and can be toxic in high doses.

12.2.1 Solid Monoterpenoids

Camphor

The natural source of high-purity camphor is a tree, *Cinnamomum camphorae*, native to south-east Asia but cultivated more widely. In the early twentieth century, camphor was one of the first organic materials to be synthesized industrially from inorganic starting materials. Camphor sublimates at room temperature (see below). Camphor was one of the earliest and best plasticizers (at 25–40%) for cellulose nitrate plastics (Miles, 1955) though it has largely been replaced by liquid plasticizers.

Menthol

Menthol, like camphor, is a waxy crystalline solid that sublimates at room temperature. It is, however, more polar and dissolves in alcohols.

Camphene

Camphene is a minor component of many terpene oils from which it is purified. It is a waxy solid, which sublimates at room temperature. Because it contains a reactive double bond, it tends to oxidize to form non-volatile oxidation products. For this reason, the commercial product is normally compounded with an antioxidant.

Tricyclene

Tricyclene is a minor component of many terpene oils from which it is purified. It is made industrially by isomerization of pinenes. It is a waxy solid that sublimates at room temperature. However, it usually occurs with camphene, from which it is separated with difficulty.

Cyclododecane

Cyclododecane is not a terpene but is included here because it is used in conservation for similar purposes. It is a waxy solid that sublimates at room temperature and dissolves in a number of solvents (Figure A3.30).

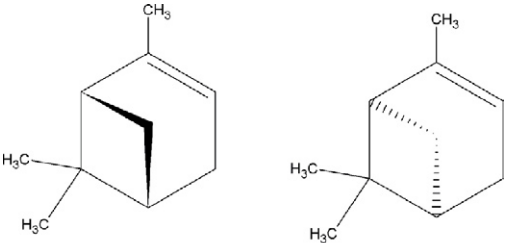
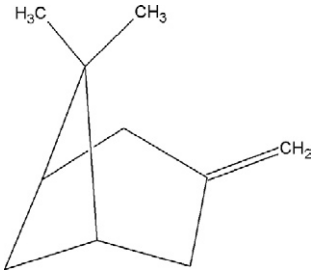
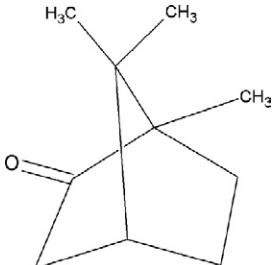
12.2.2 Conservation

The solid, subliming materials – camphene, tricyclene, menthol and cyclododecane – have been used as temporary, volatile consolidants and release agents (Jägers & Jägers, 1999; Cleere, 2005). These have been chosen to be suitable because of their ease of use and resistance to polar solvents. Of these, cyclododecane is the preferred material because it is the most stable to degradation, has fewer impurities, and has fewer health and safety risks. It is important that the material applied contains as little as possible non-volatile material, which will remain after treatment as a contaminant.

These materials are applied to fragile surfaces either in solution or molten. Films applied from different solvents tend to deposit as crystals so are less coherent and resistant to penetration by liquids, such as water. Films applied from molten materials are stronger, more coherent and solvent resistant. Mixtures of compounds may form strong films with smaller crystals, by analogy with similar findings from industrial practice (Araki and Halloran, 2004). The rate of sublimation of the consolidant depends on the vapour pressure of the material, the temperature, the rate of air movement and the depth of penetration into a porous surface. For the high-melting-point, low-volatility materials such as cyclododecane and menthol, it can take many weeks for the consolidant to leave. The more volatile materials will leave faster.

Both the solvent carrier for the consolidant and the molten consolidant itself can act as solvent for components of an object. For instance, when protecting ink on sensitive paper during washing, the cyclododecane consolidant causes migration in paper and ink components, while not fully protecting the ink from attack by the washing solution (Keynan and Eyb-Green, 2000).

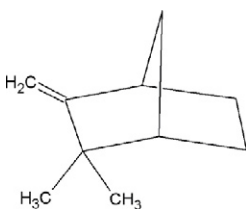
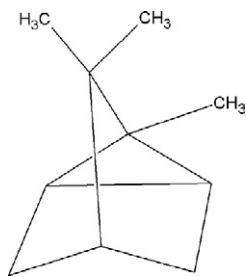
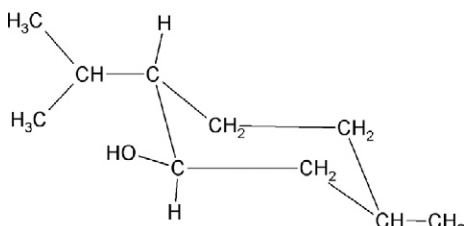
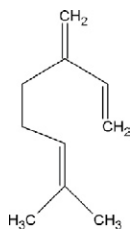
TABLE 12.1 Monoterpenes and Cyclododecane

Name Structure	Formula Systematic Name CAS No.
α-Pinene  (-)-α-pinene (+)-α-pinene	$C_{10}H_{16}$ (1<i>S</i>,5<i>S</i>)-2,6,6-Trimethyl bicyclo[3.1.1]hept-2-ene 2437-95-8
β-Pinene 	$C_{10}H_{16}$ (1<i>S</i>,5<i>S</i>)-6,6-Dimethyl-2- methylenebicyclo[3.1.1] heptane 18172-67-3
Camphor 	$C_{10}H_{16}O$ 1,7,7-Trimethyl- bicyclo[2.2.1]heptan- 2-one 76-22-2 (unspecified) 464-49-3 ((+)-camphor)

Melting Point (°C) Boiling Point (°C) Vapour Pressure Solid/Liquid Density (g/cm ³)	Hansen Solubility Parameters (MPa ¹) D, P, H	Flash Point (°C) Toxicity	Production	References
M.p. -55 B.p. 155–156 3 mmHg Density 0.858	(16.4, 1.4, 0.4 turpen- tine)	F.p. 33 Eye, skin and respiratory irritant. May be absorbed through the skin	A major component of turpentine	Barton (1983)
M.p. -61 B.p. 165–168 2 mmHg at 20°C Density 0.859		F.p. 32 Flammable Skin, eye and respiratory irritant	A major component of turpentine	
M.p. 177 B.p. 207 Density 0.99 (solid)	(16)		Exudation from camphor laurel, <i>Cinna- monum cam- phora</i> . Now synthesized industrially	

Continued

TABLE 12.1 Monoterpenes and Cyclododecane continued

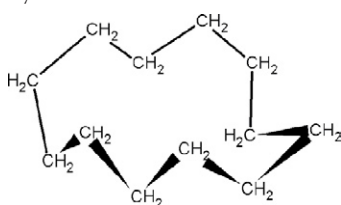
Name Structure	Formula Systematic Name CAS No.
Camphene 	$C_{10}H_{16}$ 2,2-Dimethyl-3-methylene-bicyclo[2.2.1]heptane 79-92-5
Tricyclene 	$C_{10}H_{16}$ 1,7,7-Trimethyltricyclo[2.2.1.02,6]heptane 508-32-7
(-)-Menthol 	$C_{10}H_{20}O$ 2-(2-Propyl)-5-methyl-cyclohexanol 89-78-1 (racemic) 2216-51-5 ((-)-menthol)
β-Myrcene 	$C_{10}H_{16}$ 7-Methyl-3-methylene-1,6-octadiene 123-35-3

Melting Point (°C) Boiling Point (°C) Vapour Pressure Solid/Liquid Density (g/cm ³)	Hansen Solubility Parameters (MPa ^{1/2}) D, P, H	Flash Point (°C) Toxicity	Production	References
M.p. 45–46 B.p. 156–160 0.33 kPa (20 °C); 21.5 mbar (50 °C) Density 0.842 (20)	16.9, 1.8, 3.1	F.p. 41 Flammable Low toxicity	Extracted from plants, produced industrially by modification of pinene. Normally contains 10–18% tricyclene	Hansen (2005)
M.p. 64–65 B.p. 152–154			Minor component of many essential oils. Produced industrially by modification of pinene. Cannot be easily separated from camphene	
M.p. 36–45 B.p. 212 Density 0.890 (20)	16.6, 4.7, 10.6	F.p. 93 Irritant flammable	Extracted from peppermint oil, <i>Mentha x piperita</i> . Now synthesized industrially	Hansen (2005)
M.p. < –10 B.p. 165			Obtained from essential oils. Can be produced industrially	

TABLE 12.1 Monoterpenes and Cyclododecane continued

Name	Formula
Structure	Systematic Name
	CAS No.

Cyclododecane

 $C_{12}H_{24}$

294-62-2

12.3 DITERPENOIDS

12.3.1 Background

Trees of the *Pinus* genus exude a thick liquid, once called common turpentine. A similar material is extracted from waste products of the forestry industry (Coppen and Hone, 1995). Oil of turpentine ($\approx 20\%$) is distilled off by heating, leaving the highly modified solid rosin. Rosin (colophony) is composed of a number of diterpenoid molecules, predominantly abietic acid (Table 12.2) (Mills and White, 1994). Rosin is initially soluble in a wide range of solvents, which evaporate to deposit glossy clear films. The rapid oxidation of the resin causes loss of gloss, yellowing and increased water sensitivity. Because of its small molecular size, rosin is very brittle. Rosin may be modified by hydrogenation to reduce yellowing and oxidation, or reacted to produce esters.

Similar exudations from other trees have been used, for instance Venice turpentine from *Larix decidua* and Canada balsam from *Abies balsamea* (Mills and White, 1994). Their overall composition based on mono- and diterpenes and properties are similar, varying slightly with differences in composition.

Naturally and artificially aged films formed from these resins oxidize and polymerize (Scalarone et al., 2002). The oxidation results in increasing dehydroxyabietic acid and its oxidation products, while their precursors are reduced.

12.3.2 Conservation

An early conservation use of pine resin was as a hot-melt coating applied to degraded wool in the eleventh century (Cronyn and Horie, 1985). The oleoresin and the rosin derived from it have been included in recipes for artistic materials

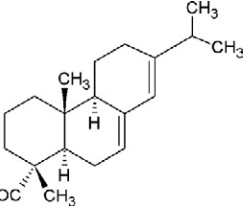
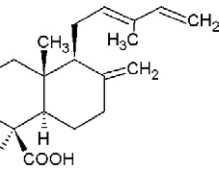
Melting Point (°C) Boiling Point (°C) Vapour Pressure Solid/Liquid Density (g/cm ³)	Hansen Solubility Parame- ters (MPa ¹) D, P, H	Flash Point (°C) Toxicity	Production	References
M.p. 58–61 B.p. 243 Density 0.79	16.4, 0, 0	F.p. 98 Flammable		Hansen (2005)

since the ninth century (Gettens and Stout, 1942). Picture varnishes and media were made by mixing oil and resin with or without heating (van Schendel, 1958). Later, rosin was used as a spirit varnish, being found on globes (Mills and White, 1994), and was probably an adulterant of more expensive resins such as mastic (Brommelle, 1956).

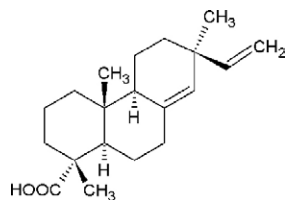
The solubility of rosin in acetone increases from 40% at room temperature to 67% at 52 °C (Bryce et al., 1975). This property is the basis for the consolidation with rosin of waterlogged wood that has been dewatered in baths of acetone (Ganiaris, 1990). After the wood has reached equilibrium with a saturated rosin solution at 52 °C, the impregnated wood is allowed to cool. About 40% of the rosin precipitates during cooling. Setting of the other 60% occurs during subsequent evaporation of the acetone. The solvent takes some months to evaporate, during which time the consolidant is still flexible (Oddy, 1975). Cellolyn 21 (Hercules) (phthalate ester of abietyl alcohol) is used as a relatively stable (Autenrieth, 1977) tackifying resin for BEVA 371, a hot-melt adhesive for canvas pictures (Berger, 1976). This continues the long-established tradition of the use of rosin in picture lining adhesives (Laurie, 1932). Rosin and its derivatives are widely used, as in pressure-sensitive adhesives based on rubbers (Autenrieth, 1977). Up to 60% of the composition may be rosin derivatives. Adhesives incorporating rosin derivatives are not designed for long-term use and should be avoided in conservation (Magnelli, 1982). Rosin also increases the rate of degradation of paper to which it has frequently been added in manufacture (Richardin et al., 1990).

Venice turpentine has been used in picture varnishes and as a tackifying resin in adhesives partly because it increases the flexibility of the film, though this effect will diminish as the monoterpenes evaporate. Canada balsam was widely used for mounting specimens on microscope slides and as a glass adhesive, though again the evaporation leads to shrinkage and distortion.

TABLE 12.2 Di- and Sesquiterpenoids

Name Structure	Formula Systematic Name CAS No.	Melting Point (°C) Boiling Point (°C)	Occurrence/ Production
Abietic acid 	$C_{19}H_{29}COOH$ 13-Isopropylpodocarpa-7,13-dien-15-oic acid 514-10-3	M.p. 173	
Communic acid 	$C_{20}H_{30}O_2$ Decahydro-1,4a-dimethyl-6-methylene-5-(3-methyl-2,4-pentadienyl)-1-naphthalenecarboxylic acid 2761-77-5	M.p. 121	

Pimaric acid

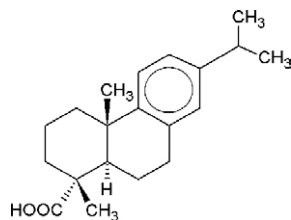
 $C_{20}H_{30}O_2$

M.p. 210

7-Ethenyl-1,2,3,4,4a,4b,5,6,7,9,10,10a-dodecahydro-1-,4a,7-trimethyl-1-phenanthrenecarboxylic acid

127-27-5

Dehydroabietic acid (DHA)

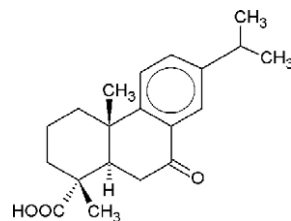
 $C_{20}H_{28}O_2$

M.p. 172

1,2,3,4,4a,9,10,10a-Octahydro-1,4a-dimethyl-7-(1-methylethyl)-1-phenanthrenecarboxylic acid

1740-19-8

7-Oxo-DHA

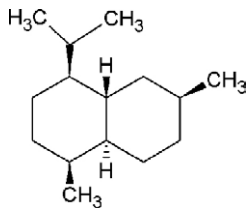
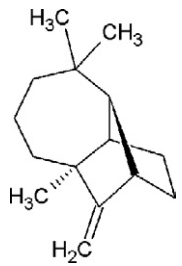
 $C_{20}H_{26}O_3$

1,2,3,4,4a,9,10,10a-Octahydro-1,4a-dimethyl-7-(1-methylethyl)-9-oxo-1-phenanthrenecarboxylic acid

18684-55-4

Continued

TABLE 12.2 Di- and Sesquiterpenoids continued

Name Structure	Formula Systematic Name CAS No.	Melting Point (°C) Boiling Point (°C)	Occurrence/ Production
Cadinene 	$C_{15}H_{26}$ Decahydro-1,6-dimethyl-4-(1-methylethyl)-naphthalene 29350-73-0	B.p. 136	Sesquiterpene, found polymerized in dammar 'wax'
Longifolene 	$C_{15}H_{24}$ Decahydro-4,8,8-trimethyl-9-methylene-1,4-methanoazulene 475-20-7	B.p. 258	Sesquiterpene

12.4 TRITERPENOIDS (TABLE 12.3)

12.4.1 Dammar

Background

Dammar is a hydrocarbon, triterpenoid resin, obtained from various species of the Diptocarpaceae. Dammar, like other natural resins, is composed of a mixture of similar molecules (Scalarone et al., 2003) whose proportions vary from sample to sample (Figure 12.1c). Typical samples contain upwards of nine triterpenoid molecular species (Table 12.3, a–d), plus some higher-molecular-mass compounds up to 850. As collected, dammar contains about 10–16% of polymer polycadinene (Table 12.3, g) (Van Aarssen et al., 1990), dammar ‘wax’, which dissolves only in hydrocarbon solvents. This is usually removed before the resin is made up into a varnish (Mantell et al., 1942). Dammar is a hard brittle resin, is easily scratched and has little flexibility, though more than ketone resins (Feller, 1971). Although pure triterpenoids of dammar do not form coherent films by themselves, the mixture is able to do so (van der Doelen and Boon, 2000). The low molecular weight allows mobile solutions to be prepared at much higher solids content than with high-molecular-weight polymers, and in a wider range of solvents (Figure A3.31). The mobility of the molecules in solution enables the solution to flatten before ceasing to flow, thus forming a glossy surface. This makes surfaces to which it is applied appear more saturated in colour (Berns and de la Rie, 2003) than do those varnished using high-molecular-weight polymers. Solvent is retained in dammar varnishes for upwards of 6 months, during which time hardness and brittleness gradually increase.

When a solution of dammar dries in high relative humidities, a bloom made up of small crystals of ammonium sulphate can occur on the surface. Dammar films can develop wrinkles during drying. The wrinkling appears to be the result of an initial oxidation of the resin combined with movement of the underlying solution. Mastic, which develops fewer wrinkles than dammar (Thomson, 1957), retains less solvent than dammar (Feller, 1957b, 1958).

The molecular composition of dammar changes as it absorbs oxygen (up to six oxygen atoms per molecule) during exposure to ultraviolet in air and there is an increased number of larger molecules (de la Rie and McGlinchy, 1989; Scalarone et al., 2005). This increases the polarity of the solvents needed for dissolution and the difficulty of getting the resin into solution (Figure A3.32). The films become more brittle due to increased polar and hydrogen bonding. The yellowing of dammar has been shown to occur largely by thermal rearrangements including dehydration working on the products of UV auto-oxidation (de la Rie, 1988) and is associated with the formation of high-molecular-weight material (van der Doelen and Boon, 2000). Exposure to light or UV causes bleaching of the chromophores. Dammar oxidizes rapidly when exposed to UV and existing stabilizers do not seem to prevent this. However, most dammar films are exposed in very low UV conditions. It has been found that dammar films exposed to UV filtered light can be stabilized by a hindered amine light stabilizer (HALS), 3%

TABLE 12.3 Dammar and Mastic Constituents

Typical constituents found in dammar and mastic resins. Scalarone, #2005
These are major components alongside many minor ones. Compounds **a**, **b**, and **c** are major components of dammar. **b**, **c**, and **d** are found in both resins, while **e** and **f** are found in mastic but not in dammar so can be used as markers for its presence. **g** and **h** are polymers found in small quantities in dammar and mastic respectively. **i** is a typical oxidation product of dammar and mastic.

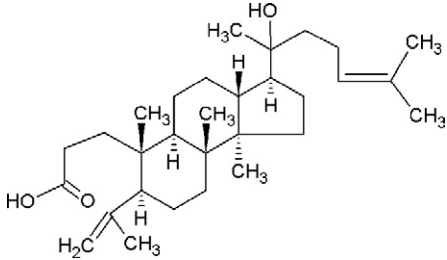
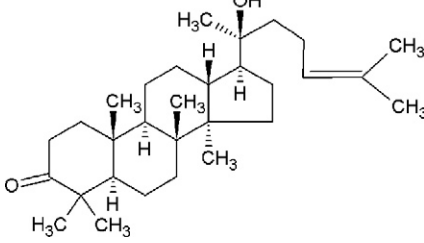
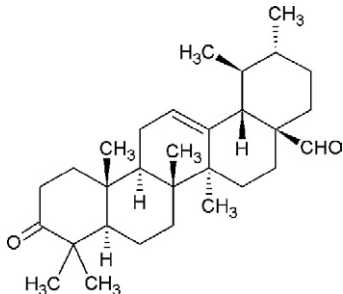
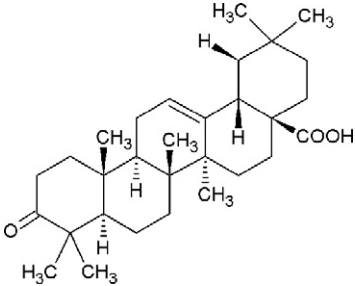
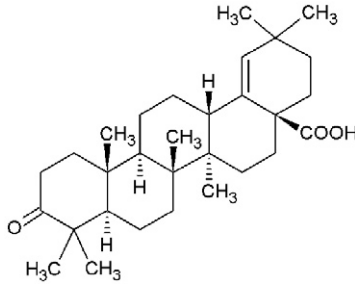
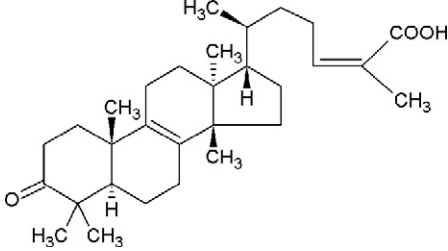
Trivial name, structure	IUPAC name molecular formula CAS no. melting point
a. Dammarenolic Acid 	Dodecahydro-3-[(1S)-1-hydroxy-1,5-dimethyl-4-hexenyl]-6,9a,9b-trimethyl-7-(1-methylethenyl)-1H-benz[e]indene-6-propanoic acid $C_{30}H_{50}O_3$ 34336-09-9 m.p. 140 °C
b. Hydroxydammarenone 	20-Hydroxy-dammar-24-en-3-one $C_{30}H_{50}O_2$ 471-69-2 m.p. 136 °C
c. Ursonic Aldehyde 	3-Oxo-urs-12-en-28-al $C_{30}H_{46}O_2$ 35936-63-1

TABLE 12.3 Dammar and Mastic Constituents continued

Typical constituents found in dammar and mastic resins. {Scalarone, #2005}
 These are major components alongside many minor ones. Compounds **a**, **b**, and **c** are major components of dammar. **b**, **c**, and **d** are found in both resins, while **e** and **f** are found in mastic but not in dammar so can be used as markers for its presence. **g** and **h** are polymers found in small quantities in dammar and mastic respectively. **i** is a typical oxidation product of dammar and mastic.

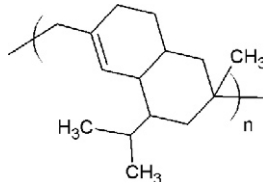
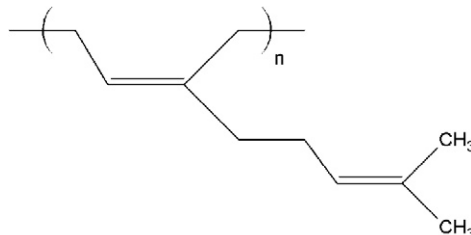
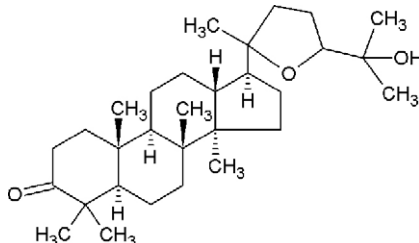
Trivial name, structure	IUPAC name molecular formula CAS no. melting point
d. Oleanonic Acid 	3-Oxo-olean-12-en-28-oic acid $C_{30}H_{46}O_3$ 17990-42-0 m.p. 184 °C
e. Moronic Acid 	3-Oxo-olean-18-en-28-oic acid $C_{30}H_{46}O_3$ 6713-27-5 m.p. 193 °C
f. Iso-masticadienonic Acid 	3-Oxo-lanosta-8,24-dien-26-oic acid $C_{30}H_{46}O_3$ 5956-26-3 m.p. 167 °C

Continued

TABLE 12.3 Dammar and Mastic Constituents continued

Typical constituents found in dammar and mastic resins. {Scalarone, #2005}

These are major components alongside many minor ones. Compounds **a**, **b**, and **c** are major components of dammar. **b**, **c**, and **d** are found in both resins, while **e** and **f** are found in mastic but not in dammar so can be used as markers for its presence. **g** and **h** are polymers found in small quantities in dammar and mastic respectively. **i** is a typical oxidation product of dammar and mastic.

Trivial name, structure	IUPAC name molecular formula CAS no. melting point
g. Polycadinene 	(For monomer see Table 12.2)
h. Cis-1,4-poly-β-myrcene 	29463-45-4 (For monomer see Table 12.1)
i. 20,24-Epoxy-25-hydroxy-dammaran-3-one 	$C_{30}H_{50}O_3$ 19865-90-8 (Stereo-specific enantiomer at C20 is called ocotillone, CAS 19865-62-2, m.p. 170°C)

Source: Scalarone et al. (2005).

Tinuvin 292, increasing its useful lifetime (assessed by yellowing and solubility) potentially up to 136 years (de la Rie and McGlinchey, 1990).

Conservation

Dammar was introduced early in the nineteenth century by German restorers as a more stable material than mastic for picture varnishes (Lucanus, 2002), and was used by adventurous English (Hanson, 1954) and American (Mayer and Myers, 2002) painters by the middle of the century. However, the friability of dammar prompted the incorporation of plasticizing materials, e.g. rubber solutions and drying oils. Both of these will oxidize, rapidly becoming insoluble. Dammar requires increasingly polar solvents, e.g. acetone or alcohols, for removal (Boon and van der Doelen, 1999). Various solvents that have been used to apply films have been shown to increase the rate at which yellowing occurs, e.g. turpentine (Feller, 1976) and Stoddard's solvent (Lafontaine, 1979), so toluene and other solvents that do not tend to oxidize should be used. Dammar has been shown to be less stable and yellow in solution (de la Rie and McGlinchey, 1990; van der Doelen and Boon, 2000). Solutions of dammar should be made up freshly and kept in the dark and in dark bottles.

Dammar applied in solution has been used for the consolidation of iron (Rathgen, 1905), waterlogged wood (Barker, 1973; Blackshaw, 1974) and other materials (Hübner, 1934; Plenderleith, 1934).

On ageing, dammar polymerizes and some parts even become cross-linked, yellow and insoluble (Boon and van der Doelen, 1999). Dissolving coatings with solvents will therefore leave coloured insoluble material on the surface. For this reason, a mechanical method of removal should also be considered when the application and reversal of a dammar coating are being proposed.

12.4.2 Mastic

Background

Mastic is exuded and collected from a bushy tree, *Pistacia lentiscus* (Mills and White, 1994). The solid resin is composed (van den Berg et al., 1998) of a mixture of primarily triterpenoids (Table 12.3, b–f), with small amounts of a volatile oil ($\approx 2\%$; primarily α -pinene (Koutsoudaki et al., 2005)) and a polymer, *cis*-1,4-poly- β -myrcene (Table 12.3, h), with a molecular weight up to 100,000 (van den Berg et al., 1998) (Figure 12.2). Having a low molecular weight, the resin is brittle with little extensibility, though it forms solutions with high solids content. Portions of the resin are soluble in all the organic solvents (Figure A3.33), but complete solution requires moderately polar solvents (Mantell et al., 1942). Mastic films applied from solution release solvents relatively quickly and approach their final properties of hardness and brittleness in upwards of a month (Feller, 1957b). They are less likely to wrinkle than are dammar films (Section 12.1). On photo-oxidation under daylight fluorescent lamps, mastic absorbs up to eight oxygen atoms per molecule, forms increasingly larger molecules such as dimers, and becomes more polar, thus requiring more polar solvents for dissolution (Scalarone et al., 2005).

Mastic is less stable than dammar in this respect. Mastic, like dammar, alters its composition as a result of both UV exposure and heating (Stern et al., 2003).

Conservation

Mastic has been used since at least Roman times (Pliny the Elder, book 12, ch. 36). Mastic was the picture varnish material of first choice for many years (Hendy, 1947) because of its good working and film properties. However, it has been increasingly replaced by dammar (Lucas and Brommelle, 1953) since the early nineteenth century (Brommelle, 1956). A major deficiency of mastic as a varnish is its brittleness. This can be counteracted by adding a drying oil, but this creates the same types of problem as it does with dammar. Its brittleness could be an asset during removal, as the film can be powdered on the painting by scraping or crushing (Ruhemann, 1968). Mastic mixed with the oleoresin of *Larix decidua*, Venice turpentine, was used in the nineteenth century as a hot-melt adhesive for ceramics (Thiacourt, 1868).

12.5 SHELLAC

12.5.1 Background (Misra and Sengupta, 1970; Mills and White, 1994)

A scale insect (*Tacchardia lacca*) of south Asia secretes a protective covering on twigs. The twigs, sticklac, are collected and the resin is extracted by melting and cooling in various shapes, shellac and beadlac (Parry, 1935). Shellac has a variety of components with the composition varying with the source and extraction, $\approx 75\%$ 'resin', $\approx 6\%$ colouring material, $\approx 6\%$ 'wax'. The resin component can be further separated into 'soft' (low molecular weight, e.g. dimers of aleuritic acid and terpene acids) and 'hard' (larger molecules MW ≈ 1000 , with eight monomers) (Figure 12.2). Some 30–40% of shellac resin is aleuritic acid, which is combined with sesquiterpene acids such as epishellolic acid (Table 12.4) (Colombini et al., 2003). The latter are unsaturated as well as having alcohol and aldehyde groups. Butolic acid can be used as a marker for recognizing shellac on an object. The red dye extracted from lac was long used for colouring textiles. The wax, which is insoluble in alcohol and soluble in benzene, is a mixture of long-chain alcohols (such as myricyl alcohol, $\text{CH}_3(\text{CH}_2)_{28}\text{CH}_2\text{OH}$), fatty acids and their esters (such as lacceryl lacceroate, $\text{CH}_3(\text{CH}_2)_{30}\text{CH}_2\text{O}-\text{CO}-\text{CH}_2(\text{CH}_2)_{30}\text{CH}_3$) (Manjunath and Douch, 1965, p. 86). Shellac is available in various grades – filtered resin (button lac), dewaxed or bleached.

Shellac dissolves in hydrogen-bonding solvents, ethanol commonly being used (Figure A3.34). The solutions dry to glossy films with good adhesion and toughness (Hauser, 1912). The molecules can be degraded by hydrolysis, e.g. in dilute alkali or by autoclaving with water. Shellac cross-links by two mechanisms. On heating, acetal links are formed. On prolonged room-temperature storage, a different mecha-

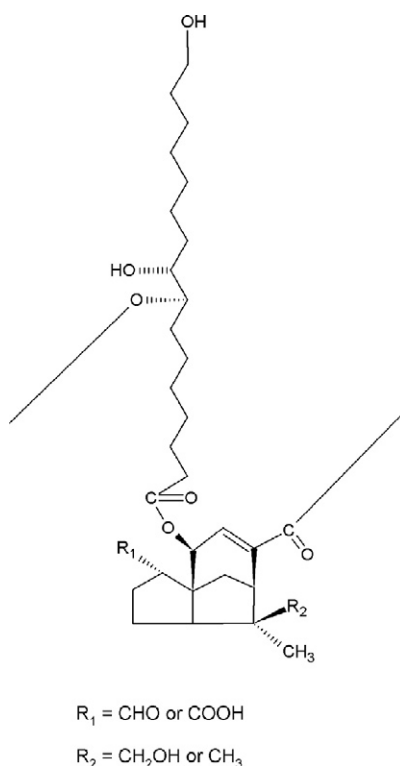


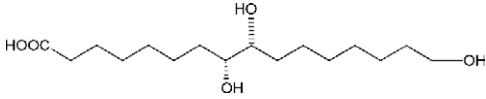
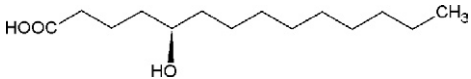
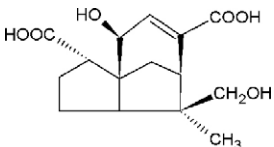
FIGURE 12.2 Shellac: schematic diagram of a typical repeating unit of the oligomer of aleuritic acid and epishelloic acid.

nism results in insolubility in cold alcohol, though heating may cause dissolution (Roff and Scott, 1971). Pyridine may disrupt intractable films (Koob, 1979).

12.5.2 Conservation

Use of shellac resin has been recorded since 1300 BC, particularly for coating wood (Pliny the Elder, book 12, ch. 36). Shellac has been used in Europe from the early nineteenth century for the finishing and refinishing of woodwork, as French polish (Hayward, 1960), a solution of approximately 30 g of shellac in 100 ml of denatured alcohol. The dewaxed grades are used when recoating is planned as the wax reduces adhesion, while the inclusion of the wax component improves the gloss of the coating on rubbing. Shellac has been applied as a molten liquid to heated ceramic sherds (Koob, 1979), either alone or fused with sulphur (Thiacourt, 1868). Alternatively it has been used as a viscous solution (Thiacourt, 1868; Petrie, 1888). Solutions of shellac have been used for general mending and consolidation (Bather, 1908; Plenderleith, 1934). Heat-activated

TABLE 12.4 Some Components of Shellac (CAS No. 9000-59-3)

Name Structure	Formula Systematic Name CAS No.
Aleuritic acid 	$C_{16}H_{32}O_5$ 9,10,16-Trihydroxy- hexadecanoic acid 17941-34-3
Butolic acid 	$C_{15}H_{28}O_3$ 6-Hydroxy- tetradecanoic acid 24205-54-7
Epishellolic acid 	$C_{15}H_{20}O_6$ 2,3,4,7,8,8a-Hexa- hydro-4-hydroxy- 8-(hydroxymethyl)- 8-methyl-1H-3a,7- methanoazulene-3,6- dicarboxylic acid 6718-99-6

films of shellac have been used for commercial ‘dry-mounted’ paper-laminating processes. The adhesive becomes insoluble in alcohol but may be broken down in 2-methoxyethanol (Baynes-Cope, 1972).

12.6 BEESWAX

Beeswax is obtained from the hives of honey bees and is usually purified by melting (m.p. 63 °C) and filtering. It is a complex mixture of at least 284 compounds, principally esters, hydrocarbons and free fatty acids (Figure 12.3) (Tulloch, 1980). Its composition can be modified by heat treatment or fractionation (Bonaduce and Colombini, 2004) and is discoloured by heating above 85 °C. It is slightly soluble in a small range of solvents (Figure A3.35), increasing considerably with temperature. Although it will yellow, presumably due to oxidation of the unsaturated components, it can remain soluble over millennia in Egyptian tombs. Beeswax has been widely used, mixed with natural resins and fillers, for relining paintings (Marijnissen, 1967). The wax-resin lining adhesive can prove difficult to remove and even with solvent extraction with a poultice will leave some within the structure of the painting (Roznerska and Wójt, 2002).

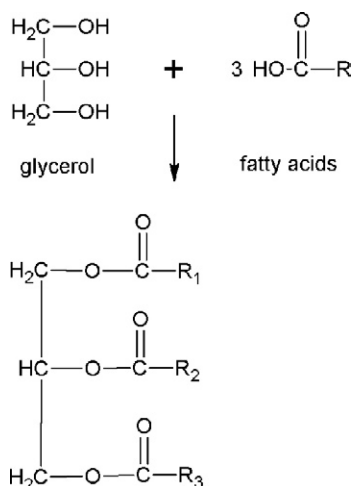


FIGURE 12.4 Formation of triglycerides from glycerol and fatty acids. The reverse reaction is also important in creating soaps, etc. A wide range of fatty acids can be incorporated in the triglyceride, providing both gross and subtle differences in properties.

All the unsaturated fatty acids will oxidize, for instance causing rancidity in foods. The drying of an oil to a solid is by oxidative cross-linking polymerization (Figure 12.5) (van den Berg et al., 1999; van Gorkum and Bouwman, 2005). This is catalysed by metal ions added as driers or pigments. The process is initiated by the double bond, so the reactivity of the fatty acid with oxygen increases with the number of double bonds present (Porter et al., 1995). In the early stages of auto-oxidation, volatile degradation products, e.g. carboxylic acids, aldehydes and carbon dioxide, are produced (Hancock et al., 1989; Christensen et al., 2002); most will evaporate. The oxidative scission of the fatty acids leads to the creation of C_9 acids such as azelaic acid ($\text{HOOC}(\text{CH}_2)_7\text{COOH}$). The increasing acidity of the film leads to the hydrolysis of the triglyceride, releasing the glycerine and any unreacted fatty acids. These can be solvent extracted or evaporate from the film (Schilling et al., 1999; Sutherland, 2003). The film shrinks over time, becomes much more polar and becomes more brittle from increased cross-linking, ionic bonds between the acid groups and ions in pigments, and loss of plasticizing small molecules.

The drying reaction can be speeded up by heating the oil with oxygen (boiled or blown) as a pretreatment. A vinyl-type polymerization can be achieved by heating the oil in the absence of air (stand oils). This increases the molecular weight and reduces the susceptibility to oxidation. Yellowing occurs when oxidation is in the dark or under low illumination (Mallegol et al., 2000). The yellowing can be bleached by sunlight and oxidizing agents and can reappear in dark ageing as the conjugated double bonds are created by oxidation. The source of the yellowing appears to be oxidation to contaminants in the oil, rather than one of the major fatty acids. Although the hardness of paints is achieved in

TABLE 12.5 Typical Fatty Acids in Fats and Oils

Fatty Acid Component	Formula of Acid		IUPAC Name	M.p. (°C)	CAS No.
Palmitic	$\text{HOOC}_{15}\text{H}_{31}$	$\text{HOOC}(\text{CH}_2)_{14}\text{CH}_3$	Hexadecanoic acid	63	57-10-3
Stearic	$\text{HOOC}_{17}\text{H}_{35}$	$\text{HOOC}(\text{CH}_2)_{16}\text{CH}_3$	Octadecanoic acid	70	57-11-4
Oleic	$\text{HOOC}_{17}\text{H}_{33}$	$\text{HOOC}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3$	<i>Cis</i> -9-octadecenoic acid	16	2027-47-6
Linoleic	$\text{HOOC}_{17}\text{H}_{31}$	$\text{HOOC}(\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_4\text{CH}_3$	All- <i>cis</i> -9,12-octadecadienoic acid	-5	60-33-3
Linolenic	$\text{HOOC}_{17}\text{H}_{29}$	$\text{HOOC}(\text{CH}_2)_7(\text{CH}=\text{CHCH}_2)_3\text{CH}_3$	All- <i>cis</i> -9,12,15-octadecatrienoic acid	-11	463-40-1
α -Elaeostearic	$\text{HOOC}_{17}\text{H}_{29}$	$\text{HOOC}(\text{CH}_2)_7(\text{CH}=\text{CH})_3(\text{CH}_2)_3\text{CH}_3$	<i>Cis,trans,trans</i> -9,11,13-octadecatrienoic acid	49	13296-76
Erucic	$\text{HOOC}_{21}\text{H}_{41}$	$\text{HOOC}(\text{CH}_2)_{11}\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3$	<i>Cis</i> -13-docosenoic acid	34	112-86-7
DHA	$\text{HOOC}_{21}\text{H}_{31}$	$\text{HOOC}(\text{CH}_2)_2(\text{CH}=\text{CHCH}_2)_6\text{CH}_3$	All- <i>cis</i> -4,7,10,13,16,19-docosahexaenoic acid		6217-54-5

TABLE 12.6 Major Components of Some Triglycerides (Typical Values)

Source of Oil	Major Fatty Acid Components, Typical	Type of Oil ¹	Iodine Number ²	CAS No.
Cow/sheep	30% palmitic, 30% stearic, 35% oleic	N	50–60	
Olive	13% stearic, 69% oleic, 13% linoleic	N	77–94	8001-25-0
Cottonseed	20% stearic, 33% oleic, 44% linoleic	S	100–110	8001-29-4
Poppyseed	10% palmitic, 16% oleic, 72% linoleic	D	135	8002-11-7
Walnut	5% palmitic, 18% oleic, 73% linoleic	D	140–150	8024-09-7
Linseed	10% palmitic, 15% oleic, 16% linoleic, 56% linolenic	D	170–190	8001-26-1
Tung	9% oleic, 10% linoleic, 79% elaeostearic	D	145–175	8001-20-5
Fish	12% palmitic, 15% oleic, 12% erucic, 13% DHA	D	185	

The exact composition depends on many factors such as growth conditions, variety, processing and modification.

¹D, drying oil; N, non-drying oil; S, semi-drying oil.

²The iodine number is a measure of the degree of unsaturation in the oil. Higher values indicate greater unsaturation.

part by addition of pigments, oil varnishes have traditionally been made from oils reacted with resins at high temperatures (Coffignier, 1923).

The cross-linked oil will continue to oxidize. The physical state changes from a mobile liquid to a gel to a tough film. This is insoluble but is swollen by solvents (Figure A3.36). Both the density and the refractive index increase. Subsequently the film will become brittle and finally friable as the structure starts to break down. The loss of degradation products and consequent shrinkage of the film causes cracking. Oxidation of non-drying and semi-drying oils also takes place but without causing the formation of an insoluble network.

Alkyd resins (Paul, 1985; Deligny and Tuck, 2000) are formed by reacting drying oils with polyols, typically pentaerythritol ($\text{C}(\text{CH}_2\text{OH})_4$) and phthalic anhydride. A polymer is produced with a much higher molecular weight, $\text{MW} \approx 2000\text{--}10,000$ (Vareckova et al., 2006), than the oil. The number of cross-links and therefore the amount of unsaturation required for the insolubilization of the film is reduced. This improves resistance to oxidation, degradation and

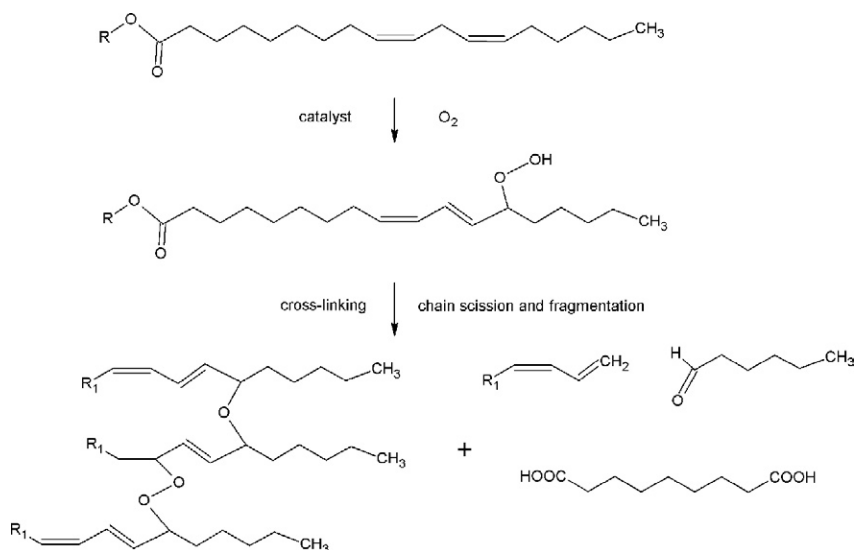


FIGURE 12.5 Oxidative cross-linking of linoleic acid: typical reactions.

yellowing. Because of their higher molecular weights, the alkyds have a higher viscosity and are usually applied as a solution, e.g. 50% solids, in hydrocarbon solvents. Setting is thus a two-stage process. Viscosity increases during evaporation of the solvent, and this is followed by a slow cross-linking and insolubilization. During manufacture, the viscosity of the resin, drying time, hardness and stability of the film can be optimized to suit a particular application.

12.8.2 Conservation

Walnut and linseed oils have long been used in the creation (Gettens and Stout, 1942; Mills and White, 1994) and restoration (Marijnissen, 1967) of paintings. Walnut oil was often preferred for paints, especially light colours. However, its slow drying and instability in storage have reduced its use. Linseed oil has been used for consolidation of iron corrosion products (Rathgen, 1905) and stonework (Rathgen, 1905; Stois, 1934). The latter use was criticized in the 1920s for its harmful effects on stone (Warnes, 1926). Linseed oil emulsions with vinegar and turpentine were suggested as a polish and dirt remover for furniture (Plenderleith and Werner, 1971). A mixture of ethanol, aliphatic solvent and glacial acetic acid was found to remove the resultant tacky deposit effectively (Martin, 1978).

Animal fat (tallow) was used as a consolidant in the nineteenth century for preserving iron objects (Rathgen, 1905). Lanolin, the grease derived from sheep fleeces, is, after thousands of years, still employed as a corrosion-inhibiting coating on iron objects. It is not a triglyceride but a complex mixture of thousands of lipids, esters of fatty acids with long-chain alcohols and sterols (Jover

et al., 2002; Moldovan et al., 2002). It used to be applied to dry and waterlogged leather in order to improve its flexibility though, because the surface becomes progressively stickier, this treatment usually has to be reversed by solvent extraction (Peacock, 2001).

Japanese swords have traditionally been very lightly coated with choji, clove oil mixed variously with camellia seed oil and light mineral oil. Camellia oil has large amounts of oleic acid in its triglyceride (Firestone, 1999).

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Cross-Linking Polymers

13.1 SILICON-CONTAINING POLYMERS

13.1.1 Background

The chemistry of silicones is potentially as diverse as that of carbon-based organic compounds. The scientific nomenclature is derived from silane (SiH_4), analogous to methane. Thus a typical compound might be methyltriethoxysilane (Figure 13.1). Silicon atoms form chains not by simple Si–Si bonds but with linking oxygen atoms, i.e. Si–O–Si, a siloxane bond.

Monomeric silane derivatives (Wheeler, 2005) used in conservation are tri- or tetrafunctional derivatives, such as tetraethoxysilane (synonyms ethyl silicate, tetraethyl silicate, TEOS). The polymerization, initiated by traces of water, is by hydrolysis and condensation (Figure 13.2). Not all the silanol Si–OH groups will condense to form cross-links (Amoroso and Fassina, 1983). The polymer formed from a tetrafunctional monomer will be similar to silica gel. Care must be taken to ensure anhydrous storage of silanes to prevent premature polymerization. Trifunctional monomers such as methyltrimethoxysilane react in a similar fashion but retain the Si–C bond. The polymer formed from this monomer is resistant to solvents and photo-oxidation. It is tough but not flexible (Moncrieff, 1976). The silanol groups will react with –OH groups on a surface to create chemical links.

By using trialkoxysilanes with organic groups that interact with organic adhesives (coupling agents) (Table 13.1), a chemical bond, formal or informal, between the surface and the adhesive can be ensured. The bond thus formed is more resistant to failure, mechanically or chemically. Coupling agents are therefore used to promote adhesion on glass (Hand et al., 1998). The best adhesion is created when very thin, nearly monomolecular, layers are formed by reacting the coupling agent then washing off excess silica gel, which forms a weak layer. The chemical link between the silicon atom and attached carbon chain will eventually hydrolyse. The coupling agent does not stop corrosion of the glass by water, but helps maintain the adhesion of the resin to the glass (Whittle et al., 2001).

The usual chain-forming unit of silicone oils and rubbers is dimethylsiloxane (Figure 13.3). Organic substituents other than methyl groups are used for special purposes, e.g. phenyl and fluorinated alkyls. The silicones are made with

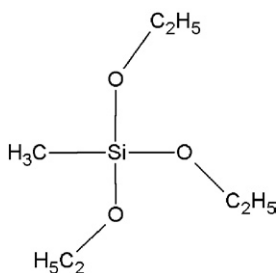


FIGURE 13.1 Methyltriethoxysilane (MTEOS).

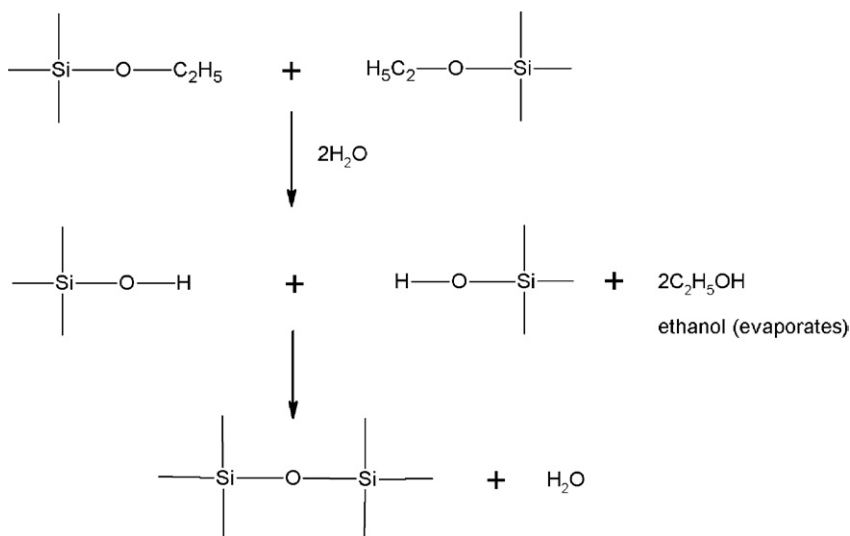


FIGURE 13.2 Condensation polymerization of ethoxysilanes. Increasing water concentration increases the rate of reaction. Acid and base catalysts increase the rate of hydrolysis of the alkoxy-silane bond. Tin compounds (and other catalysts) also increase the rate of reaction between the silanol groups and alkoxy-silane groups.

various molecular weights, from thin fluids (degree of polymerization, $DP \approx 3$ – anti-foaming agents) to very viscous liquids ($DP \approx 20,000$ – release agents).

The chains can be cross-linked to form rubbers if suitable reactive groups are incorporated in the molecule (Moretto et al., 2002). There are two major classes of room-temperature vulcanizing (RTV) rubbers (Thomas, 1993). The majority (both two-part and one-part) set by a condensation reaction (Figure 13.4, Table 13.2). Two-part RTV-2 rubbers are formulated of: the silicone polymer ($MW \approx 10,000$) with $-OH$ at either end mixed with a filler (usually finely divided silica), a small amount of water and frequently some unreactive silicone oil to reduce viscosity of the mix and increase flexibility of the rubber; the cross-linking agent (commonly TEOS) and a dialkyl tin catalyst.

TABLE 13.1 Silane Coupling Agents

Name Abbreviation (CAS No.)	Chemical Formula	Application
γ -Methacryloxypropyltrimethoxysilane MPS (2530-85-0)	$ \begin{array}{c} \text{H}_3\text{C} \quad \text{O} \\ \quad \\ \text{H}_2\text{C}=\text{C}-\text{C}-\text{O}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3 \end{array} $	Polyester resin
γ -Glycidoxypropyltrimethoxysilane GPS (2530-83-8)	$ \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{H}_2\text{C}-\text{CH}-\text{CH}_2-\text{O}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3 \end{array} $	Epoxy
γ -Aminopropyltrimethoxysilane APS (13822-56-5)	$\text{H}_2\text{N}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3$	General purpose

The coupling agents are usually applied to a cleaned surface as dilute ($\approx 1\%$), partly hydrolysed solutions in water or alcohol. The methoxy groups hydrolyse to form silanols, which then react to form oligomers. These then can react with the surface to form a chemically bonded monolayer, upon which build up layers and clumps of more or less bonded siloxane polymer.

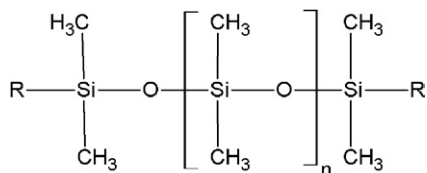


FIGURE 13.3 Monomer unit and end groups of dimethylsiloxane polymers. Dimethylsiloxane is the common unit of most silicone polymers. If $\text{R}=\text{CH}_3$, the end groups are trimethylsilane. The polymer is an unreactive silicone oil or grease, depending on the molecular weight. If $\text{R}=\text{OH}$, the end groups are dimethylsilanol. The polymer will react and cross-link with suitable reagents to form a rubber (condensation type). If $\text{R}=\text{H}$, the end groups are dimethylsilane. The polymer will react and cross-link with suitable reagents to form a rubber (addition type).

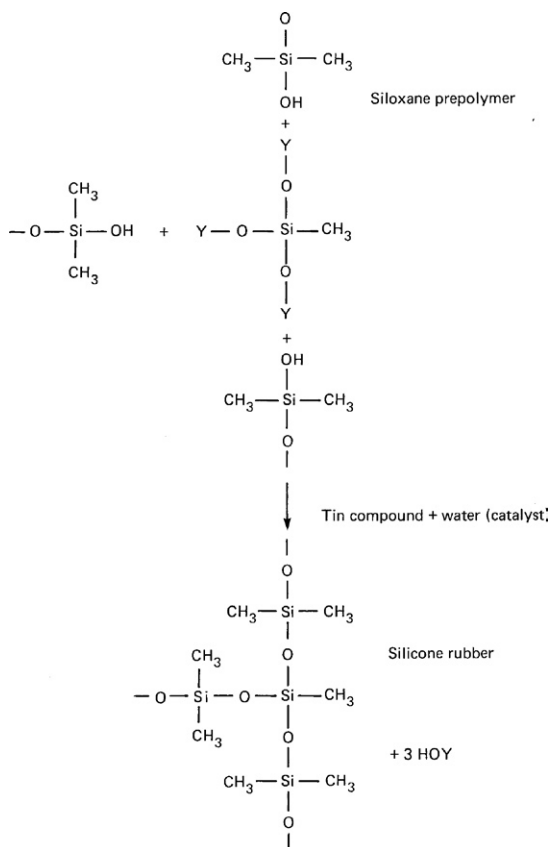


FIGURE 13.4 Cross-linking of silicone rubber pre-polymer by condensation polymerization.

This cures giving off ethanol. One-part RTV-1 acetoxy rubbers contain the silicone polymer, filler, the cross-linking agent and a tin catalyst. The second part of a RTV-1 rubber is water, which diffuses into the polymer promoting the hydrolysis of the cross-linker and cross-linking of the polymer. The

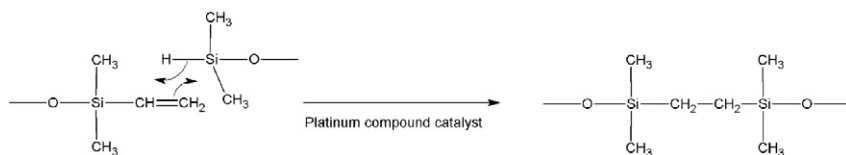
TABLE 13.2 Some Typical Cross-Linking Agents, $\text{CH}_3\text{-Si(-Y)}_3$, of Condensation-Type Silicone Rubbers

Reactive Group, Y	Curing Rubber Gives Off
$\text{---O---}\overset{\text{O}}{\underset{\text{ }}{\text{C}}}\text{---CH}_3$	Acetic acid
$\text{---O---CH}_2\text{---CH}_3$	Ethanol
$\text{---O---N=C}\begin{matrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{matrix}$	Methylethyl oxime

cross-linking agent is usually methyltriacetoxysilane (releasing acetic acid on curing) because it needs less (or no) catalyst and has better adhesion. For non-corrosive RTV-1 products, the silane polymer is terminated with dimethoxy groups (releasing methanol), uses a titanium catalyst and frequently incorporates a silane coupling agent to promote adhesion to surfaces. In these condensation reactions, the volatile fragment evaporates, resulting in shrinkage on setting, up to 3% linear, which increases on ageing.

The other type of two-part RTV-2 rubber is vinyl-terminated siloxanes cross-linked by methyl hydrogen siloxanes, setting by an addition reaction catalysed by platinum compounds (Figure 13.5), though this cross-linking reaction may be inhibited by many substrates, release agents, etc. (Hamilton Waters, 1983). The silicone polymer is one of the parts while the cross-linking agent is the other. The platinum catalyst may be carried in either, depending on the manufacturer. These materials are notable for having much lower shrinkage on setting, typically 0.2%, as no volatile products are produced. Also, because they have no groups that can hydrolyse to a reactive silanol, they are much less likely to react with and fix to a surface.

Silicone rubbers have low strength and extensibility, which are increased by adding fillers (especially aerosol silicas) to about half that of hydrocarbon

**FIGURE 13.5** Addition cross-linking of silicone rubber achieved by incorporating vinyl groups in the pre-polymer, which is reacted with hydrogen in a silane.

rubbers. Fillers also reduce the cost. Silicone rubbers allow fast diffusion of gases through the flexible structure. The rubbers have a very low glass transition temperature and are therefore likely to pick up and hold dirt particles. The cross-linked polymers can be swollen by solvents (Figure A3.37). The stoichiometry of the reactants is important to achieve the correct cross-linking, so ingredients should be measured to $\pm 3\%$, followed by thorough mixing (Gomersall, 2005). Double mixing is recommended, i.e. mix in one vessel, scrape and transfer to another and remix, so as to prevent unmixed components being transferred to the mould. This mixing causes air to be entrained, which is frequently removed by evacuating. However, too much bubbling will evaporate the water needed to promote cross-linking, so preventing the cure. The filler will agglomerate into clumps over time, causing inhomogeneities in the mix and leading to uneven cure. High-speed stirring will redisperse the mix. Cured condensation-type rubbers have a limited life around 2 years, especially in damp conditions. The cross-linking sites seem liable to rehydrolyse under the influence of the catalyst and atmospheric humidity, resulting in the bonds reverting and the mould becoming cheesy. This defect is increased if too much catalyst or cross-linker is added. A mould can also distort as the cross-links are broken and remade when put under strain, e.g. folded. Addition-type moulds are more stable and should last many decades. Good-quality addition-type RTV-2 silicone rubbers should be used for any moulds taken for archival purposes.

The strength of silicone rubbers can be assessed in various ways but the three most important for use in conservation are the tear strength, elongation at break and hardness. By choosing a low-tear-strength material, one can reduce the possible stresses on the object. A rubber that has a high elongation at break is likely to withstand pulling out of deep undercuts or doubling back on itself in a sleeve mould. The harder rubbers are more rigid and more likely to be self-supporting in thin sheets than the softer polymers. As silicone rubbers have a high oxygen and water transmission rate, the setting of some polymers, especially polyester resins, can be inhibited. Special measures such as curing in a vacuum or nitrogen or the use of carefully chosen polyester resins may be employed.

13.1.2 Conservation

Silanes

Wheeler (2005) has reviewed the history of silanes for stone consolidation from early use in the 1920s. The polymerization reaction requires the presence of water and usually a catalyst. A gel is formed swollen by the remaining monomer, any solvent and the alcohol generated during the hydrolysis. The gel shrinks with further polymerization then dries as the alcohols evaporate, causing stresses and cracking on the micro and macro scale. Tetraethoxysilane (TEOS) has been used for stone consolidation because of the similarity of the polymerized gel to many stone materials. From the 1960s, methyltrialkoxysilanes were used to make the stone water-repellent. Because the hydrolysis of the alkoxy groups is

catalysed in acid conditions and inhibited in alkaline, silanes are deposited more readily in sandstones than limestones. As a result, silanes tend to evaporate from limestones before they have time to react and also form less coherent and less adhering internal films than in sandstones. Although the evaporation losses can be reduced by using pre-polymerized materials, the differences in bonding to internal stone surfaces is not affected. The polymerized gel can bridge gaps up to 50 μm but provides little reinforcement above this, presumably because the shrinkage of the swollen polymerized mass causes too many fault lines above this thickness. Silanes cannot therefore adhere large grains or flakes, for which other materials such as acrylic, silicone or epoxy resins must be used.

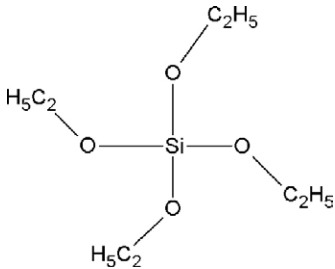
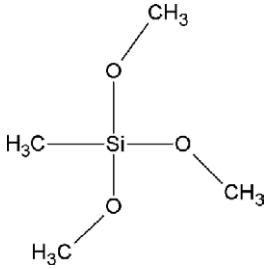
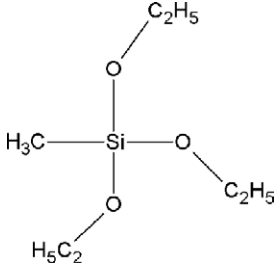
The silanes can be supplied and applied in many formulations (Young et al., 2003) (Tables 13.3 and 13.4). The TEOS applied up to the 1960s appeared to have been oligomeric, and later largely monomeric. TEOS is now usually applied as a slightly pre-polymerized solution in order to: improve the initial rate of cross-linking and gelling; reduce evaporation of the silane; reduce the viscosity (increasing penetration) of the solution; and (with ethanol as a co-solvent) improve the penetration of the silane into water-filled areas of the stone. MTMOS, though initially applied as a pure monomer, is now usually applied as part of a mixture with TEOS. Increasingly, water is included in the formulation as reliance on water in the stone or atmosphere leads to unreliable gellation.

Silanes have two effects, strengthening friable stone and reducing water absorption. The strengthening effect requires penetration in depth by the silane consolidant. This has a limited life on external stonework as the polymer breaks down near the surface and needs to be repeated after 7–20 years (Martin et al., 2002). The consolidation can change the surface colour of the stone, but in many cases the colour returns to near the original stone colour as the silane degrades. The water-repellent effect appears to be separate and can cause difficulties with subsequent treatments of masonry using standard water-based materials such as mortars. Water repellence may best be achieved by a separately designed and applied treatment. In recent years, the materials (and associated techniques) have been increasingly matched to the properties of the object being treated. The water-repellent effect of applied siloxane resins is diminished over time (Wendler, 1997).

The differential consolidation by TEOS of sand grains (poor) and fossil bone (good) has been exploited to strengthen the fossil while enabling the surrounding matrix to be removed easily (Biscula et al., 2009). Treatment using TEOS has been attempted on organic objects such as wood, basketry and paper (Paleos et al., 1981), though with limited success (Grattan, 1982; Jespersen, 1982). The polymerization of silanes that leads to more flexible polymers, e.g. using a mixture of difunctional and trifunctional silanes, has been suggested (Smith, 2002). All silane treatments are irreversible.

Silane coupling agents (Plueddemann, 1991) (Table 13.1) have been widely used to increase the durability of the adhesion between an adhesive and glass; this has been suggested as a pretreatment for consolidation of stone

TABLE 13.3 Silane Stone Consolidant Monomers

Name Abbreviation (CAS No.)	Formula	B.p. (°C)	F.p. (°C)	Viscosity (mPa.s)
Tetraethoxysilane TEOS (78-10-4)		168	46	0.65
Methyltrimethoxysilane MTMOS (1185-55-3)		102	11	0.48
Methyltriethoxysilane MTEOS (2031-67-6)		142	23	

(Wheeler et al., 2000). Once the silane end has reacted with the glass (or other substrates), the organic component may be reacted with the adhesive, e.g. epoxy or polyester, or be used to increase the wetting of the surface by a thermoplastic in solution (Errett et al., 1984). It is important to use very small quantities of coupling agent, enough for a layer only a few molecules thick that is firmly reacted with the glass surface. Excess amounts lead to the creation of a weak separation layer of silica gel, though this may be washed off in water (Hand et al., 1998). The strength and durability of the consolidating effect of Paraloid B-72 on fragile painted surfaces on stained glass has been shown to be increased by pretreating

TABLE 13.4 Silane Stone Consolidation Products

Product Manufacturer	Composition: Silane Solvent Catalyst	Notes
OH Wacker	75% TEOS + dimer + oligomers 25% butanone + acetone 1% dibutyltin dilaurate	
H Wacker	75% TEOS-MTEOS (1:1) + dimers + oligomers 25% butanone + acetone 1% dibutyltin dilaurate	
SILRES BS OH100 Wacker	TEOS	
Conservare OH ProSoCo	TEOS Tin compound	
Silex OH Keim	TEOS oligomers Toluene Dibutyltin dilaurate	Early versions silane mostly monomer with some dimer, now mostly oligomers. Less fracturing than ketone dissolved forms in gel on polymerization
Tegovakon V Goldschmidt	65% TEOS monomers z+ dimers 34%: 17% naphtha, 17% ethanol Tin compound	Gels are less fractured than Wacker products
Tegovakon V Goldschmidt	65% TEOS-MTEOS monomers + dimers 34%: 17% naphtha, 17% ethanol Tin compound	Gels are less fractured than Wacker products
Funcosil OH Remmers	75% TEOS oligomers 25% butanone Tin catalyst	
Funcosil 100 Remmers	<75% TEOS oligomers >25% butanone Tin catalyst	
Motema 20 Iteracryl	TEOS oligomers Ethanol <0.1% tin catalyst	≈20% SiO ₂ equivalent weight. Ethanol helps these products form a solution with water in the stone

Continued

TABLE 13.4 Silane Stone Consolidation Products continued

Motema 28 Iteracryl	TEOS oligomers Ethanol	≈28% SiO ₂ equivalent weight. Ethanol helps these products form a solution with water in the stone
Motema 29 Iteracryl	TEOS oligomers Ethanol <0.3% tin catalyst	≈29% SiO ₂ equivalent weight. Ethanol helps these products form a solution with water in the stone
RC70 Rhone-Poulenc	70% TEOS oligomers White spirit Tin catalyst	
RC80 Rhone-Poulenc	60% TEOS oligomers + methylsiloxane White spirit + 8% xylene Tin catalyst	
RC90 Rhone-Poulenc	60% TEOS oligomers + methylphenylsiloxane White spirit + 8% toluene Tin catalyst	Fewer cracks in gel, used for coating stained glass
SS-101 COLCOAT	TEOS Butanone + acetone Tin compound	
Brethane	MTMOS (64 ml) Ethanol + water (13 ml) 0.06% lead naphthenate	Miscible with water in stone, short gel time, 2–6 h, less fractur- ing of gel (Martin et al., 2002)

with γ -aminopropyltriethoxysilane (Jägers et al., 2000). Silanes have been used without an additional coating for reducing the hydrolysis of sensitive glass surfaces (Rathouský, 1960; Hogg et al., 1998).

Siloxanes

Silicone oils have been used in conservation to reduce the foaming of polymer dispersions (Werner, 1952), and may indeed be incorporated as an undeclared processing aid in many industrial products. They have been suggested as protective coatings for metal objects, e.g. iron (Gyermek, 1964), copper and zinc (Cejka, 1975), and as liquid storage media for fossils (Rixon, 1976). However, silicone liquids will drain away over time, leaving surfaces uncovered. Advantage is taken of the lack of adhesion in the use of these oils as release agents (Rixon and Meade, 1960; Wang, 1977; Ketnath, 1978). They should not, of course, be used on materials that absorb them, e.g. rubber, paint and porous materials. Silicone liquids are notorious for being difficult to remove from substrates, where they prevent the adhesion of another surface coating. Repeated washing with solvents such as toluene is usually necessary and often unsuccessful.

Silicone RTV-1 rubbers were widely adopted for edge bonding of stained glass (Bettembourg, 1975) and for sealing around plated fragments (Jägers et al., 2000) that are to be replaced in situ. However, the silicones will not dissolve (Erhardt, 1983) and the bond with glass will only be broken by chemical degradation of the polymer and/or glass surface, this being the corollary of its stability. The low glass transition temperature enables the polymer to absorb dirt. Uncured silicone adhesive must not be allowed to come into contact with anything other than the surfaces to be bonded. The range of silicone rubbers is being improved and non-corrosive products with better adhesion properties are becoming available. Although the acetic acid by-product of many RTV-1 silicones does not seem to have caused corrosion of lead came in stained glass windows, one case has been noted of a silicone adhesive apparently absorbing manganese colourant from a glass (Cole, 1977). Silicone rubbers contain a small proportion, typically 2–6%, of unreacted silicone oil. This will tend to migrate into porous materials and may creep out of joints on to exposed surfaces. Silicone rubbers have been developed as pressure-sensitive adhesives for textiles (Fabri-sil; Shelley) (Fieux, 1984). A thermoplastic silicone resin (Vani-sil; Shelley) (Fieux, 1984) has been suggested as a picture varnish, though its T_g (137 °C) appears too high for this purpose. A cross-linked in situ silicone rubber has been tried for consolidating a composite dewatered water-logged wood/textile button (Smith, 2002). RTV-2 rubber bulked with microballoons has been used as low-modulus fills for large voids in wood (Grattan and Barclay, 1988).

Some silicone adhesives can be modified by thinning with anhydrous hydrocarbon solvents such as toluene or cyclohexane. Moisture-activated curing will be retarded as the solvent evaporates. Pigments (Rhodia) may be incorporated into the thinned adhesive.

Silicone RTV-2 rubbers are used for taking moulds of objects because of their ease of use and excellent detail reproduction (dinosaur) (Larsen, 1994; Daxner, 1996) (Table 13.5). Moulding an object is a significant treatment to an object and care must be taken in deciding on both materials and methods. The uncritical use of silicone rubbers can cause damage to objects, e.g. pulling the surface off Easter Island statues (Van Tilburg, 1990), staining of terracotta surfaces (Figure 5.9) and interfering with subsequent conservation treatments to stone (Bromblet, 2003). These are due to the penetration of the liquid silicone polymer (unreactive or cross-linking) into the surface. Although a double release layer of gum arabic applied over cyclododecane reduced considerably the staining to porous terracotta, there remains a significant possibility of contamination (Brückle et al., 1999). The lower modulus (higher flexibility) rubbers tend to have silicone oils added to increase plasticity, so should be avoided. Food-grade silicone rubbers contain much lower amounts of extractables so should cause less staining. Preliminary tests of the material proposed for use should be carried out to ensure that contamination can be prevented or reduced to specified limits.

TABLE 13.5 Typical Silicone Rubbers (Manufacturers' Information)

Product	Manu- facturer	Cross- Link Type ¹	Viscosity (mPa.s)	Pot Life/ Handling ² (hours)	Elonga- tion at Break (%)	Tear Strength (N/mm)	Hardness Shore A	Shrinkage (1 week) (linear %)	Colour	Use with Casting Materials ³	
										Recom- mended	Unsuitable
Silastic3110	Dow	Cond	12,500	0.1–4/0.3–48	180	22	45	0.6	White	PE	PU, E, M
Silastic9161	Corning	Cond	16,000	0.1–1/24	150	22	38	1	Off-white	M	
SilasticE		Add	60,000	2/24	400	160	35	0.1	White	PE, PU	E
SilasticJ		Add	100,000	2/24	250	150	60	<0.1	Green	PU	M
RTV-ME426	Wacker	Cond	10,000	0.3–1.5/4–24	120	5.3	60		Red	M, PU, PE	
RTV-M531		Cond	28,000	0.5–1.5/15	380	20	19		White	PE, E, PP	
RTV-M533		Cond	35,000	0.5–.5/8–20	350	20	25	0.41	Pearl	PP, PE, E	A
RTV-M539		Cond	>100,000	0.5–3/6–24	600	28	20	0.6	Milky	PP, PE	A
RTV-M540		Cond	48,000	0.1–1/15–20	300	20	38		White	PU, E	
Rhodorsil RTV5335	Rhone- Poulenc	Cond	60,000	0.5–2/18	130	32	60	0.5	Beige	PP, PE	
CAF3		Cond ⁴	150,000		300	4	30		Translucent		

¹Add, addition; Cond, condensation.²Usually depends on the choice of catalyst.³A, acrylic resin; E, epoxy resin; M, low-melting-point metals; PE, polyester resin; PP, plaster of Paris; PU, polyurethane resin.⁴Cures on contact with atmospheric moisture to give off acetic acid.

13.2 POLYESTER RESINS

13.2.1 Background (Boenig, 1988; Malik et al., 2000)

The basis for two-part polyester resin formulations is the unsaturated polyester resin pre-polymer (UP) (Brydson, 1999) (Figure 13.6). This pre-polymer is dissolved in a reactive monomer, styrene, to form a liquid with a convenient viscosity while a small amount of inhibitor ($\approx 0.3\%$) is added to ensure the stability of the mixture in processing. The other part is a peroxide initiator, usually $\approx 1\%$ of butanone peroxide (methyl ethyl ketone peroxide, METKP) (TLV 0.2 ppm, Section 3.2). Copolymerization is by free-radical vinyl of the styrene with the unsaturated groups in the polyester component, initiated by combining the two. The generation of free radicals is catalysed by an accelerator, typically cobalt naphthenate, incorporated in the initial resin solution at $\approx 0.2\%$. The accelerator and the initiator must never be mixed as they form an explosive combination. Increased concentration of accelerator ($>2\%$) causes discoloration of the cured polymer. Polyester formulations are available which provide a range of properties in the cured polymer, e.g. increased flexibility, stability to light and fire resistance. Various types of addition can be made. Fillers (e.g. calcium carbonate or microspheres), reinforcing materials (e.g. glass fibre) or colorants (e.g. dyes and pigments) are available (Chapter 14).

The vinyl polymerization (Figure 13.7) results first in gelation of the liquid then hardening of the solid. Considerable heat is produced that can lead to distortion and, in extreme cases, charring. The rate of reaction can be reduced by employing less accelerator and initiator. Polymerization also results in shrinkage,

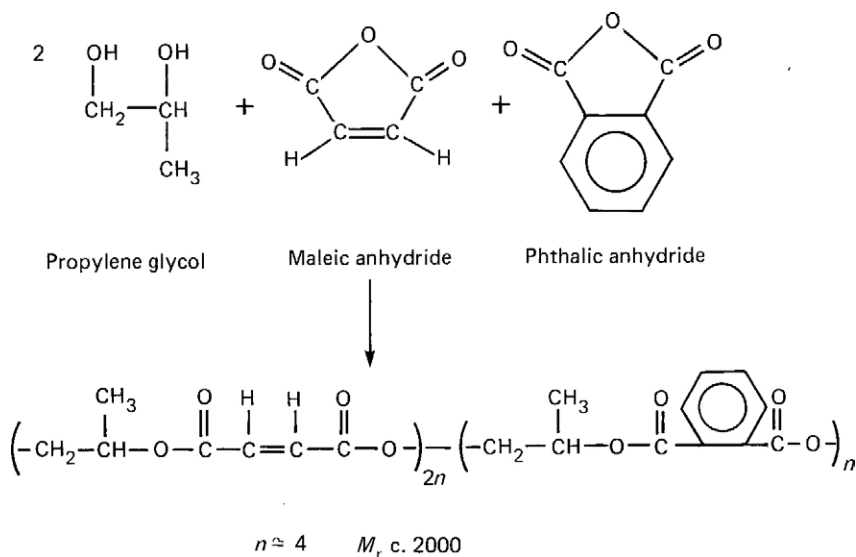


FIGURE 13.6 Components of a typical polyester laminating resin.

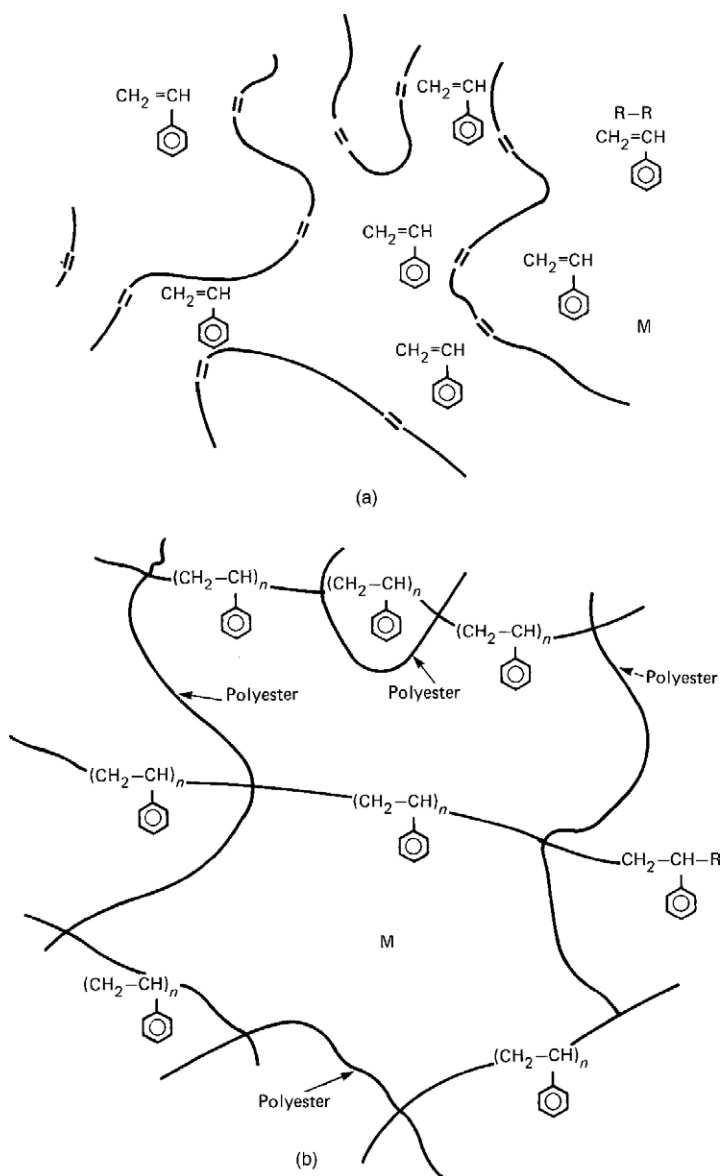


FIGURE 13.7 The curing of a polyester resin. (a) Components of a resin ready for application: low-molecular-weight unsaturated pre-polymer molecules; reactive diluent molecules, usually styrene (30–35%); initiator ('catalyst') molecules ($\text{R}-\text{R}$), which decompose to form free radicals; catalyst ('accelerator') molecules (M), which are metal compounds. (b) Structure of the cured polyester resin. The pre-polymer is cross-linked by the vinyl copolymerization with the styrene. The value of n is variable but averages 2 in many polymers (Boenig, 1988). The polymerization changes with conversion, from initially within the polyester chains and later incorporating more styrene in the polymer (Mortaigne and Vivien, 1996). Adapted from Brydson (1982).

up to 8% by volume, which can be minimized by reducing the rise in temperature. The reaction continues for some months (Marais et al., 2000), leaving significant number of styrene and polyester double bonds unreacted. Cross-linking will stop when the reactive groups can no longer diffuse together, i.e. around the $T_g \approx 65^\circ\text{C}$ (Jasso-Gastinel and Vivero-Marin, 2004). Therefore to achieve maximum cure, polyester moulding materials are heated above this T_g , for a 'post-cure' to achieve a final T_g of $\approx 95^\circ\text{C}$. The remaining unreacted unsaturated groups are a source of instability. Oxygen and water interfere with the polymerization reaction, preventing cross-linking and leaving the surfaces of the resin exposed to the air tacky. This interference can be minimized by reducing the amount of accelerator used or by adding wax to the resin (Brydson, 1999).

Cured polyesters yellow on exposure to light. Oxidation will also be accelerated by the oxygen absorbed into the polymer during storage and curing. Polyester resins are susceptible to swelling, hydrolysis and degradation by water and aqueous solutions (Abeyasinghe et al., 1982). This is worst at the defective surfaces formed during curing.

13.2.2 Conservation

Soon after their introduction in the 1940s, UP resins were used for encapsulating natural history objects (Purves and Martin, 1950). This use has probably been abandoned for objects that must be preserved. One example has been published of a transparent resin that went opaque (Meurgues, 1982). Polyester resins deteriorate when exposed to weathering (Beloto, 1994), though it is possible to specify grade and application methods to reduce the tendency.

UP resins have been used for consolidation of wood (Plenderleith, 1956; Werner, 1978) and stone both chemically and radiation (Ramiere and Tassigny, 1976) initiated. However, because of shrinkage during curing with consequent risk of cracking (Donis and Sneyers, 1961), this use has stopped (Unger et al., 2001).

UP resins have a long and continuing use as stone adhesive for the reasons stated early in its use (Hempel, 1968) – the commercial products can be readily modified to suit the needs of stone workers, and can be further adjusted in the field. UP resins are similarly used as strong adhesives for coarse ceramics where the viscosity prevents penetration into the porous substrate (Buys and Oakley, 1996).

The high transparencies of some embedding resins have been found useful in the restoration of glass (Hussons and Wihr, 1954; Davison, 2003). Colouring materials must be chosen that are stable when exposed to the oxidizing free-radical chemistry; some may inhibit the curing of the resin. The number of dyes that are also light stable is even more limited (Schmidt-Ott, 1996). Stable pigments can sometimes be used in a transparent fill if a slight amount of clouding is acceptable. UP resins are used for gap-filling lacunae in objects, nowadays usually with a separating layer to aid reversal (Minney, 1994; Garland and Rogers, 1995; Buys and Oakley, 1996). Commercially, putties are frequently compounded with various

fillers depending on the proposed application, so relatively weak and easily carved products are available with low shrinkage. Ranges of polyester resins are available from local manufacturers and agents. The cured polymers cannot be dissolved in organic solvents but may be removed from smooth surfaces after swelling in resin disintegrators, e.g. based on dichloromethane (Figure A3.38).

13.3 POLYURETHANE POLYMERS

13.3.1 Background (Oertel, 1993; Brydson, 1999)

The urethane bond is produced by reaction between an isocyanate group and an alcohol group (Figure 13.8). By varying the isocyanate component, R (Table 13.6), and the alcohol component, R', the polyurethanes, from fibres to coatings, are made. Di- and polyisocyanates and alcohols are used to build up linear and cross-linked polymers. Most polyurethane formulations are proprietary and the ingredients undeclared. All the isocyanates are highly toxic. For this reason, less volatile di-isocyanates are preferred. The aromatic isocyanates, such as MDI, have lower volatility but tend to create less light-stable polymers than aliphatic ones such as HDI. In order to reduce the toxicity, higher-molecular-weight adducts are frequently used. Isocyanates can react with most –OH groups, so eliminating water contamination from surfaces and creating chemical links between the polymer and the surface. However, in many situations, the isocyanate reacts preferentially with any water present rather than the hydroxyl groups on the substrate (Jansen et al., 1993; Weaver and Owen, 1995). These reactions increase adhesion considerably. Polyurethane polymers are sensitive to thermal- and photolytic-induced oxidation (Thapliyal and Chandra, 1990) and are therefore usually compounded with stabilizers.

Foams make up a large volume of the polyurethanes used both for making objects and for their conservation. The polyol-containing component may be based on a polyester or a polyether. The polyester-type foams frequently have better mechanical properties but are more susceptible to photolytic, hydrolytic and oxidative breakdown. The foam can yellow and disintegrate into a friable sticky mass. Where longer life is required, polyether foams are used. Polyurethane foams are not greatly affected by organic solvents but may be broken down by vigorous treatments, e.g. hot alcoholic alkali or 95% sulphuric acid (Roff and Scott, 1971). It is therefore advisable to avoid contact between

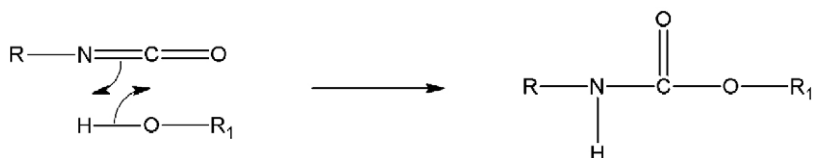
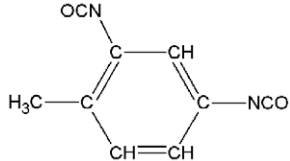
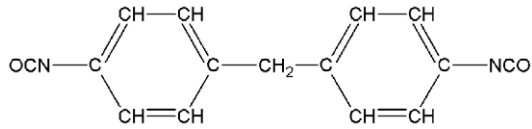
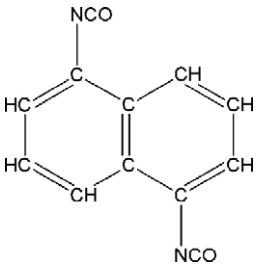


FIGURE 13.8 The formation of the urethane link: reaction of an isocyanate group with an alcohol.

TABLE 13.6 Commonly Used Isocyanates and Their Uses

Name	Abbreviation CAS No.	Formula	Viscosity (mPa.s)	Toxicity, TLV (ppm)	Uses
2,4-Toluene di-isocyanate	TDI 26471-62-5		5	0.005	Foams, adhesives
4,4'-Di-isocyanato-diphenylmethane (impure)	MDI 101-68-8		600	0.005	Foams, adhesives
1,5-Naphthalene di-isocyanate	25551-28-4		280		Rubbers
Hexamethylene di-isocyanate	HDI 822-06-0	OCN-(CH ₂) ₆ -NCO	3	0.005	Coatings, frequently used as adduct with water or other polyols

the foaming materials and objects. The pre-polymers may be dissolved in pyridine, dimethyl sulphoxide or formic acid.

Various forms of polyurethane coatings are available. For maximum toughness and light stability, an acrylic polyol and a light-stable polyisocyanate, e.g. the HDI derivatives, may be applied (Thapliyal and Chandra, 1990). Polyisocyanates and derivatives are frequently added to alkyd resins to improve their properties of toughness and adhesion. They suffer from many of the instabilities of the parent alkyds.

Polyurethane adhesives are frequently applied in solution as thermoplastics made from reacting diols, such as polyesters or polyethers with hydroxyl end groups, with di-isocyanates. These materials are rubbery, tough and, because of the urethane and other polar groups, have good adhesion to textiles and leathers. In addition they are more resistant to oxidation than diene-type rubbers. However, they are still unstable. They can be cross-linked and bound to the substrate by incorporating a small quantity of di-isocyanate either free or attached to the polyol. Strength is increased and resistance to solvents is ensured.

13.3.2 Conservation

One-part formulations are composed of an isocyanate pre-polymer in an anhydrous solvent. As the solvent evaporates, cross-links are produced to form the polymer. Isocyanate and polyol in the two-part formulation react when they are mixed. Except when applied to a smooth unreactive surface, a polyurethane treatment is irreversible.

Xylamon LX Hardening N (Desowag), a resin dissolved in a petroleum solvent, sets to a solid (perhaps a polyurethane) on exposure to the moisture of the air. It was extensively used from the 1950s for the consolidation of fragile wood (Packard, 1971). Modified isocyanate solutions have been used for consolidating earth (Steen, 1971; Sawada, 1981). Aliphatic isocyanates have been proposed for consolidation of very porous building materials such as adobe, where silanes cannot provide the bulking or strength improvements (Coffman et al., 1991; Papp, 1993).

Commercial polyurethane rubbers, applied as solutions, have been adapted to the conservation of leather, both as adhesives (White, 1980) and as consolidants (Haines, 1991). The most effective, and irreversible, of these materials are composed of flexible polyurethane polymers with active isocyanate groups which cross-link on to the substrate.

A two-part polyurethane coating has been applied to stained glass for protection and consolidation (Bettembourg, 1976), though coating glass frequently provides only short-term protection until the adhesion between polymer and glass deteriorates. By using an acrylic-based polyol (Viacryl) and an aliphatic isocyanate (Desmodur N75), a more light-stable polymer can be formed. The cured polymer is removed by swelling in solvents (Appendix 3), e.g. dichloromethane-based resin disintegrators, and scraping off the resulting gel.

Rigid polyurethane foams have been used for temporary facing supports when treating pictures with high impasto (Honig, 1974; Kottulinsky, 1982) using an

appropriate isolating varnish. The bulk of the foam is removed mechanically, with the final, adhering layer being removed when the separating layer is dissolved. Rigid preformed foams have also been used as more permanent support for display, which must be removed as it deteriorates (Jordan, 1999). The foam support may be degraded by contact with other storage and treatment substances such as PEG (Kreß, 1999). Foam is widely used in the lifting and temporary support of archaeological objects (Price, 1992). Foaming polyurethane generates a large amount of heat (up to 133 °C) and is an excellent insulator (Macgregor, 1993). Damage by heating should be considered before the foam is applied. Because adhesion is so strong, the reacting polyurethane should be kept rigorously isolated from objects while in the liquid state.

13.4 EPOXY RESINS

13.4.1 Background (Ellis, 1993; Pham and Marks, 2005)

An epoxy resin system is made up of two parts – one incorporates the epoxide group, and the other is the hardener that reacts with the epoxide and cross-links the molecules (Figure 13.9). A wide range of polymers can be produced by changing the epoxide and cross-linking components. Further modification can be achieved using catalysts, diluents, plasticizers and solvents. Epoxy adhesives and gap-fillers have high strength and good adhesion to many substrates.

The common epoxide resin of industry is the diglycidyl ether of bisphenol A (DGEBA), a viscous (or solid) oligomer (Figure 13.10). The benzene ring in the chain ensures that the resin cures to a strong rigid polymer in a short time. Although the smallest member of the series ($n=0$) is a crystalline solid when pure, in practice the mixtures of oligomers are liquids, which have a tendency to

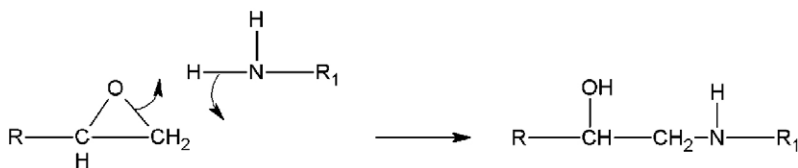


FIGURE 13.9 Epoxy-amine cross-linking reaction. Many other cross-linking reactions are used to achieve different properties, though most require high temperatures for curing.

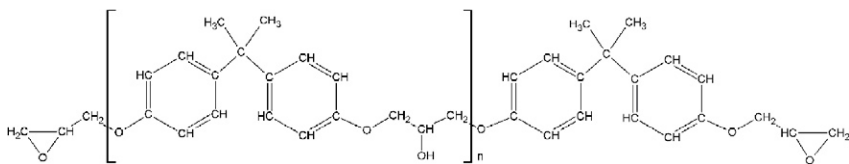


FIGURE 13.10 Typical DGEBA epoxy resin (diglycidyl ether of bisphenol A). The epoxy resins used in conservation are mixtures of short oligomers with the average value of $n < 1$. Each molecule has two epoxy groups where cross-linking can take place (CAS no. 1675-54-3, $n=0$, MW 340).

crystallize at low temperatures or if purified. In order to be able to calculate the correct proportions of epoxy resin and amine, one must know the number of epoxide groups in a known quantity. The equivalent weight is defined as the molecular weight of the epoxy divided by the number of epoxide rings in each molecule.

The hardeners for room temperature use are the aliphatic amines and amides (Table 13.7). Other materials such as acid anhydrides are used in high-temperature curing. The amount of amine required for reaction is described in the same way as for the epoxy resin. The molecular weight is divided by the number of active hydrogen atoms. In practice, a slightly smaller proportion of amine is required to allow for the reaction of the resin with the hydroxyl groups produced during curing. All amines are toxic. For this reason less unpleasant pasty or liquid polyamides are made for domestic use. Many require a catalyst for curing within reasonable times (days). The low-viscosity amines cause serious skin irritation, have unpleasant and toxic vapours, are hygroscopic, and may cause staining on copper alloy substrates (Tuttle, 1983). These amines have small equivalent weights and small quantities of them are required. Great care has to be exercised in each aspect of their use.

DGEBA resins are frequently too viscous for easy application and form stiff polymers on curing. Low-viscosity formulations based on DGEBA resins can be made in various ways. Mono- or di-epoxy diluents, e.g. butyl glycidyl ether, can be used more successfully. During consolidation, differential movement of the components will result in uneven curing. It is usually better to choose resins that are inherently more suitable, e.g. low-molecular-weight aliphatic epoxide resins (Table 13.8), which have low viscosity. However, their disadvantages are slowness in setting, greater sensitivity to water action and the high cross-linking density. This latter property results in a rigid polymer and can only be circumvented by attaching the epoxide groups to either end of a flexible chain, frequently of a polypropylene glycol oligomer.

The curing process occurs in two stages, in the liquid state and later when the polymerizing mixture has passed its T_g (Francis et al., 2002). The first stage is (relatively) fast, depending on the formulation, but the second stage can last months or years as the unreacted groups diffuse through the glassy mass (Croll, 1980). Total shrinkage on setting is $\approx 5\%$, of which about half occurs after gelation. The restrained shrinkage of epoxy resins produces stresses between the adhesive and adherend. The force exerted by a room-temperature-setting resin was found to be 4.4 MPa (Igarashi et al., 1979). The stresses are reduced by curing at high humidity (Abdelkader and White, 2002) – presumably the reacting chains are plasticized by water. Serious stresses, loss of adhesion and damage by shrinkage can result when added solvents or plasticizers are lost after curing (Croll, 1980).

The aromatic DGEBA is prone to degradation and yellowing by light, ultra-violet absorption and heat (Mailhot et al., 2005). Aliphatic epoxy resins create polymers that are more stable to weathering (Pham and Marks, 2005). Many commercial products contain reactive impurities that contribute to the yellowing (Tennent, 1979). Both the epoxide and the amine components are reactive chemicals and will deteriorate in storage, causing the resultant cross-linked

TABLE 13.7 Typical Amine Cross-Linking Agents

Name (CAS No.)	Formula	Comment
Diethylenetriamine, DETA (111-40-0), $n=1$ Triethylenetetra-amine, TETA (112-24-2), $n=2$	$\text{H}_2\text{N} \left[\begin{array}{c} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{NH} \\ \qquad \qquad \\ \text{CH}_2 \qquad \qquad \text{H} \end{array} \right]_n$	Low viscosity, high vapour pressure, toxic (e.g. dermatitis), reacts with CO_2 and H_2O , short pot life, polymers with epoxy tend to yellow
Trimethyl-1,6-hexanedi-amine, TMD (25620-58-0)	$\begin{array}{c} \text{HC}=\text{CH} \text{---} (\text{CH}_2)_7 \text{---} \text{C}(=\text{O}) \text{---} \text{NH} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{NH}_2 \\ \qquad \qquad \\ \text{CH} \qquad \qquad \text{CH} \\ \qquad \qquad \\ \text{CH}_3(\text{CH}_2)_5 \text{---} \text{CH} \text{---} \text{CH} \text{---} \text{CH}=\text{CH} \text{---} (\text{CH}_2)_7 \text{---} \text{C}(=\text{O}) \text{---} \text{NH} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{NH}_2 \\ \\ (\text{CH}_2)_5\text{CH}_3 \end{array}$	Low viscosity, high reactivity, irritant and tendency to react with CO_2 , in Araldite 2020
Typical polyamide	$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\ \qquad \quad \\ \text{H}_3\text{C} \text{---} \text{C} \text{---} \text{CH}_2 \text{---} \text{C} \text{---} \text{CH}_2 \text{---} \text{NH}_2 \\ \qquad \quad \\ \text{H}_2\text{C} \qquad \quad \text{CH}_2 \\ \qquad \quad \\ \text{CH} \\ \\ \text{NH}_2 \end{array}$	Very viscous, low toxicity

Continued

TABLE 13.7 Typical Amine Cross-Linking Agents continued

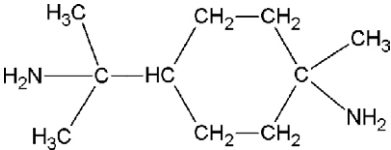
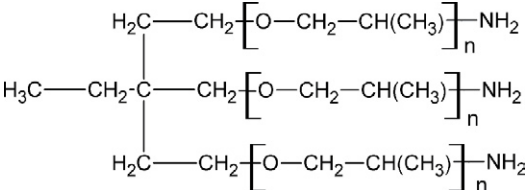
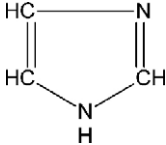
Name (CAS No.)	Formula	Comment
Isophoronediamine, IPDA (2855-13-2)		Low viscosity, irritant, and tendency to react with CO ₂ , in Araldite 2020
1,8-Menthanediamine (80-52-4)		Low viscosity, irritant and tendency to react with CO ₂ , very slow cure, in Rurapox I-93/1
Poly(ethylene glycol)-diethylamine adduct	HO-CH ₂ -CH ₂ -NH-CH ₂ -CH ₂ -NH-CH ₂ -CH ₂ -NH ₂	Fast cure, low toxicity, sensitive to water
Glycidyl-diethylamine adduct	R-CH ₂ -CHOH-CH ₂ -NH-CH ₂ -CH ₂ -NH-CH ₂ -CH ₂ -NH	Fast cure
Poly(propylene glycol) amine (9046-10-0)	 Total $n \approx 5$	Low viscosity, low reactivity, in Hxtal NYL-1

TABLE 13.7 Typical Amine Cross-Linking Agents continued

Name (CAS No.)	Formula	Comment
Imidazole (288-32-4)	The chemical structure of Imidazole is a five-membered aromatic heterocycle. It consists of two nitrogen atoms and three carbon atoms in a ring. One nitrogen atom is at the bottom position, bonded to a hydrogen atom (NH). The other nitrogen atom is at the top position, bonded to a hydrogen atom (NH). The carbon atoms are at the 2, 4, and 5 positions. The carbon at position 2 is bonded to a methyl group (CH₃) and a hydrogen atom (H). The carbon at position 4 is bonded to a methyl group (CH₃) and a hydrogen atom (H). The carbon at position 5 is bonded to a hydrogen atom (H) and a hydrogen atom (H). The structure is shown as a skeletal formula with all atoms and bonds explicitly labeled.	Solid accelerator, in Hxtal NYL

TABLE 13.8 Low-Viscosity Epoxy Pre-Polymers

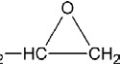
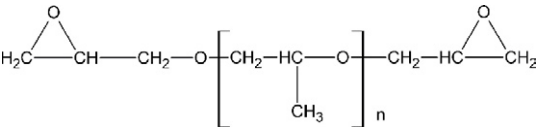
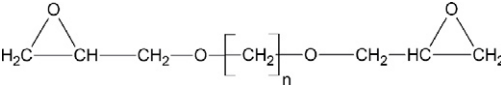
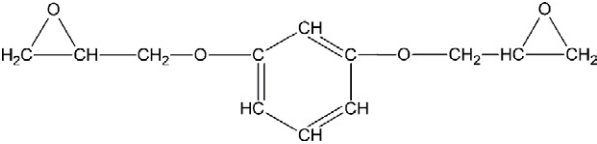
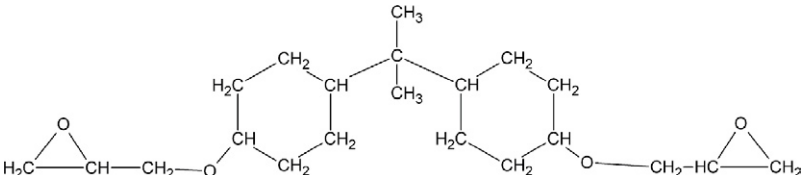
Name (CAS No.)	Formula	Viscosity (mPa.s)	Comments
Butyl glycidyl ether (2426-08-6)	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{HC}-\text{CH}_2$ 		Reactive diluent for epoxy resins
Poly(propylene glycol) diglycidyl ether (26142-30-3)	$\text{H}_2\text{C}-\text{CH}-\text{CH}_2-\text{O}-\left[\text{CH}_2-\underset{\text{CH}_3}{\text{HC}}-\text{O}\right]_n-\text{CH}_2-\text{HC}-\text{CH}_2$ 	30–100	Imparts flexibility, water sensitive
1,4-Butyl diglycidyl ether (2425-79-8) (n = 4)	$\text{H}_2\text{C}-\text{CH}-\text{CH}_2-\text{O}-\left[\text{CH}_2\right]_n-\text{O}-\text{CH}_2-\text{HC}-\text{CH}_2$ 	≈20	Imparts flexibility, in Araldite 2020 and Rurapox I-93/1
Resorcinol diglycidyl ether (101-90-6)	$\text{H}_2\text{C}-\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_2-\text{O}-\text{CH}_2-\text{HC}-\text{CH}_2$ 	≈30	Stiffer than the aliphatic types, in Rurapox I-93/2

TABLE 13.8 Low-Viscosity Epoxy Pre-Polymers Continued

Name (CAS No.)	Formula	Viscosity (mPa.s)	Comments
4,4-Isopropylidenedicyclohexanol-epichlorohydrin (1675-54-3)			In Hxtal NYL-1

polymer to yellow. Cured polymers yellow in the dark (Down, 2001), presumably by formation of conjugated groups. It was found that the polyamide types of hardener, often found in household packs, produced unacceptably unstable polymers. There is no reliable method of assessing the likely yellowing of commercial products, which vary from batch to batch.

The cross-linked polymers are not soluble but are swelled by solvents (Figure A3.40), which enable the gel to be removed mechanically (Daniels, 1981). The adhesion of epoxy resins to glass deteriorates sharply above a critical RH ($\approx 70\%$) due to the absorption of water by the hydroxyl groups in the epoxy and loss of hydrogen bonding to the glass by displacement by water (Lefebvre et al., 2000). This can be reduced by choosing an appropriate silane coupling agent (Whittle et al., 2001).

Formulation and availability of epoxy resins and hardener systems lend themselves to modification for specific applications. It is to be hoped that epoxy resin formulations will be produced with known, and declared, ingredients of a purity comparable to the other polymers used in conservation, designed in combination with application techniques. Formulations of materials that cure to form thermoplastics should also be possible, thus enabling the application of the versatile epoxies to a much wider range of problems.

13.4.2 Conservation

Epoxy resins were made available in the late 1940s and were soon introduced into conservation. Epoxy adhesives for wood (Werner, 1952), metal (Organ, 1959) and ceramics, and as consolidants for wood, were developed during the 1950s (Anon, 1961).

The use of epoxies for stone conservation has been reviewed (Selwitz, 1992). The requirement for good penetration means that low-viscosity formulations, <2 mPa.s, must be used. The early applications were of DGEBA with triethylene tetramine as a 15% solution in methanol/toluene (Domaslowski, 1971). Because of its low viscosity, a low-molecular-weight aliphatic epoxy (with TEOS as a diluent) was used for the consolidation and restoration of stone (Munnikendam, 1973). The lowest-molecular-weight epoxies and amines have a viscosity of ≈ 10 mPa.s, but also tend to be more sensitive to hydrolysis and weathering. Currently, epoxy formulations are applied in solution. Alcohols and water accelerate the curing, ketones retard the curing, while hydrocarbon solvents have little chemical effect. The different solvents also affect whether the cross-linked polymer is deposited as a coherent film from say acetone or xylene, leading to shrinkage and cracking, or a non-coherent (and presumably relatively unswollen) precipitate from a mixed solvent such as methanol/toluene. A cycloaliphatic epoxy (EP 2101) with a low-molecular-weight polyamine (K 2101) as a 25% solution in propan-2-ol/toluene is widely used.

Epoxy adhesives for glass in the museum environment have been tested and reviewed (Down, 2001). They have been widely used for glass (Rathouský,

1960; Davison, 2003) and ceramics (Buys and Oakley, 1996). Epoxies have been developed for adhering glass, Hxtal NYL-1 and Fynebond specifically for conservation, and Araldite 2020 commercially. For the best visual effect, the refractive index should be matched with the glass. This can be achieved by mixing Hxtal with a higher-refractive-index epoxy (Augerson and Messinger, 1993) such as XTR-311. Epoxies have long been known to fail as glass adhesives when exposed to weather, shown by the failure of appliqué stained glass windows (Anon, 1973). Even so, epoxies without silane coupling agents are still used for the edge adhesion of stained glass exposed outside. A small range of fluid adhesives whose refractive index may be modified has been tested (Table 13.9).

Two epoxy resins were specially developed for consolidating wood (Rutapox 1-93/2) and leather (Rutapox 1-93/1) (Munnikendam, 1978). The low viscosities of these low-molecular-weight resins result in deep penetration of porous substrates. The 1-93/2 forms a hard tough polymer because of the stiffening effect of the aromatic group. The 1-93/1 is flexible and rubbery. Both polymers are a light yellow colour but cause considerable darkening of the material they are consolidating.

Epoxy resins have been used in canvas picture conservation. An unfortunate use as a varnish caused problems in identification and removal (Keck and Feller, 1964). Epoxy resin adhesives have been used for sticking threads across tears in canvases and also as a filler (Berger and Russell, 1993). The formulations need to be of sufficiently high viscosity to prevent absorption into the canvas, but must be flexible enough to respond to movement in the fabric.

13.5 FORMALDEHYDE RESINS

13.5.1 Background (Brydson, 1999)

The formaldehyde family of resins are highly cross-linked polymers formed by condensation reactions. The group has three main members: phenol–formaldehyde (PF), urea–formaldehyde (UF) and melamine–formaldehyde (MF) resins. The process of polymerization takes place in two stages. The first stage is the creation of water-soluble oligomers of formaldehyde combined with phenol, urea or melamine (Roff and Scott, 1971). These are used immediately to impregnate moulding materials. Stable solutions of oligomers can be produced by using appropriate grades of resin and pH conditions (Figure 13.11). The oligomers are then cross-linked by acid catalysts and/or heat. Initially a gel is formed, which reacts further to create a polymer that is highly cross-linked. During the process of polymerization, a large amount of water is produced. The polymers can be used as coatings if the films are thin enough to allow the water to escape. The polymers are hard, brittle materials. UF resins can be modified with butanol to create oligomers that are readily applied in organic solvents. These cure to form more flexible polymers than the unmodified UF polymers.

TABLE 13.9 Low-Viscosity Epoxy Formulations

Product (Reference)	Manu- facturer	Epoxy/Hardener Components ¹	Viscosity (mPa.s)	Working/ Setting Time ² (h)	Shrinkage (linear %)	n_D^3	Elastic Modulus (MPa)	T_g^4 (°C)	Stability, Useful Life ⁵ (years)	Comments
Hxtal-NYL-1		4,4-Isopropylidenedi- cyclohexanol- epichlorohydrin/ poly(oxymethyl-1, 2-ethanediyl), α -hydro- ω -(2- aminomethylathoxy)- ether with 2-ethyl- 2-(hydroxymethyl)- 1,3-propanediol (3:1) with imidazole accelerator	250	2/7 days	0.02	1.52	2100	45	100	
EPO-TEK 301	EPO-TEK	DGEBA, 1,4-butanediol diglycidyl ether (3:1)/2,2,4-trimethyl-1,6-hexanediamine	150	1.5/24	1.3	1.57	2260	65	50	
EPO-TEK 301-2	EPO-TEK	DGEBA/polyoxypropylenediamine	325	8/48	0	1.59	1710	80	100	
Fynebond	Fyne Conservation Services	DGEBA, $M_n < 700$ /polyoxypropylenediamine		9/30		1.565		46	50	
Ablebond 342-1	Abelstik (ICI)	DGEBA/polyoxypropylene	200	8/48	0.3	1.566	3280	54	50	Available 1979–1989

Continued

TABLE 13.9 Low-Viscosity Epoxy Formulations continued

Product (Reference)	Manu- facturer	Epoxy/Hardener Components ¹	Viscosity (mPa.s)	Working/ Setting Time ² (h)	Shrinkage (linear %)	n_D ³	Elastic Modulus (MPa)	T_g ⁴ (°C)	Stability, Useful Life ⁵ (years)	Comments
Heloxy modifier HD/Epikure 943	Hexion	Diglycidylether of 1,6-hexandiol/ isophoronediamine, 10:3 by weight	20	8	0.04	1.576		−10		Was Rutapox 1-93/1, before then 1210
Rutapox I-93/2	Bakelite	As Heloxy HD/ Epikure 943 with resorcinol	27	1.5	0.5	1.53		16		Was 1200, dis- continued c. 1995
Araldite AY103/ HY951	Ciba- Geigy	DGEBA/triethylene- diamine	800	1.5/24	0.2	1.58	2800		50	Discontinued
Araldite 2020 (XW396/XW397)	Huntsman	DGEBA, $M_n < 700$ / isophoronediamine	150	0.75/16				40	50	Available in Europe
XTR-311	His Glass- works	Phenol,4,4'-(1- methylethylidene) bis-(chloromethyl) ox- irane, n-butyl glycidyl ether (0-20%)/1-pro- panamine-3,3'- (oxybis(2,1-ethaned- yloxy))bis	500	2/24		1.58				Can be mixed with Hxtal to modify the refrac- tive index

¹DGEBA, diglycidyl ether of bisphenol A.²At room temperature ($\approx 25^\circ\text{C}$), reaction speeded with heating.³Refractive index: manufacturers' information and Tennent and Townsend (1984).⁴Glass transition temperature: manufacturers' information and values courtesy Perkin Elmer (UK) Ltd, measured by differential scanning calorimetry at $10^\circ\text{C}/\text{min}$.⁵Stability to yellowing with light exposure (Down, 1986, 2001).

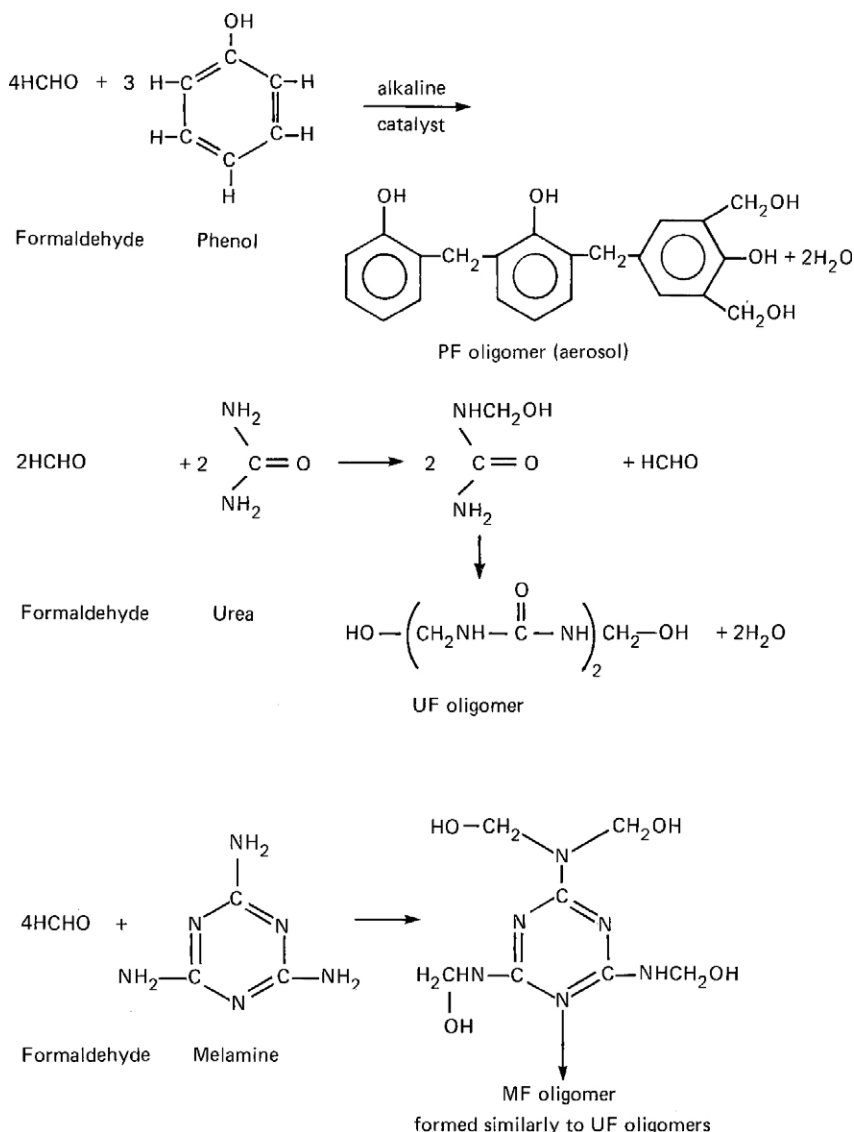


FIGURE 13.11 First stage in the polymerization of formaldehyde resins. The oligomers that are formed are mixtures whose composition depends on the proportion of reactants and the reaction conditions.

The materials used in conservation have usually been acid-catalysed formulations. The polymers are entirely insoluble but can be decomposed by concentrated acids and alkalis or molten phenols. Water-white polymers can be produced if low-temperature acid cure is employed. The melamine resins show the greatest resistance to yellowing.

13.5.2 Conservation

Fossil bones were soaked in PF (Bakelite) varnish solutions and allowed to dry and cure at room temperature for up to 6 months (Case, 1925; Nichols and Orr, 1932). An alternative was to bake at 93 °C. Numerous different Bakelite solvent grades were employed up to the 1960s for fossil bone and wood (Howie, 1984).

UF resins were used initially as transparent encapsulating resins for plants (Schmidt, 1939). UF resins were more widely adapted from commercial use and used as consolidants (Takakage, 1952) and adhesives for wood (Rawlins and Werner, 1949; Plenderleith, 1956; Hayward, 1976).

An MF resin, Kauramin CE 5549, was proposed as a consolidant for water-logged wood and lacquerwork (Hoffmann and Wittköpper, 1999) as a replacement for Arigal C and Lyofix DML (Haas, 1969; Grattan and Clarke, 1987). The pre-polymer is applied as a solution in water. It was cured in solution using an added catalyst and heat. Butylated amino-formaldehyde resins were used as coatings, especially for ceramics (Chinaglaze) (Tennent, 1983). The resin solution is mixed with an acid catalyst before application. Chinaglaze was a UF resin modified by the addition of an alkyd (phthalic acid polyester), which yellows badly.

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Fillers and Colourants

14.1 FILLERS

Fillers are added to polymers for many reasons (Gächter and Müller, 1993) (Table 14.1). A filler reduces the volume and cost of polymer used in a formulation. Calcium carbonate is frequently added to polyester casting resins as an extender. Hollow spheres, e.g. glass or phenol micro-balloons (Nishiura, 1981) or vermiculite (Bradley et al., 1983), can be used to reduce the weight of an adhesive layer. The reduced polymer volume also restricts the possible shrinkage (Larkin and Makidrou, 1999). The size of filler particles determines the amount of filler that can be incorporated into the liquid polymer. A mixture of large particles with small particles that partially fill the voids between them enables most complete filling of the polymer. Sufficient polymer must be added to fill the voids between the particles if strength retention is required.

Fillers alter the mechanical properties of the set polymer. Frequently the filler is used to increase strength and hardness. Sand and larger aggregate is used in building restoration (Lawrence et al., 2006). Weak fillers are incorporated into polymers to allow the set material to be reworked by drilling or sanding. These can be solid, e.g. talc and calcium carbonate, or hollow microspheres.

Added filler will increase the viscosity and resistance to flow of a polymer. This is essential in adhesives, which would drain out of the joint by gravity or be sucked out of the glue line by capillary attraction. Viscosity increase becomes larger as the particle size is reduced. Fumed (aerosol) silica, a filler that introduces a structure to the liquid, can produce a thixotropic mixture (Anon, n.d.; Byrne, 1984). Ease of handling of a liquid adhesive can be improved by additions to the polymer of 3–10% of its own weight in silica. The thickening effect is greatest in non-polar solvents when the powder is well dispersed.

14.2 COLOURANTS

Colourants for polymers may be divided into two groups, pigments and dyes. Pigments remain as solids dispersed in polymers and increase its opacity, while dyes dissolve in polymers, producing transparent colours. Many colourants

TABLE 14.1 Fillers for Polymers

Type	Supplier ¹	Use
Calcium carbonate	Chem	Reducing volume of polymer, as extender
Talc	Chem	Can provide some reinforcement
Purified sand	Buil	
Glass fibre	Poly	Reinforcement
Carbon fibre	Poly	Reinforcement
Precipitated silica	Degussa	Flatting (matting) agent, thickening agent for liquids
Fumed silica	Degussa	
Micro-balloons		
Phenolic	Union Carbide	Extending, reducing weight, increasing
PVCC	Dow	Workability of set polymer
Glass	Emmerson	
Fly ash	Fillite	
Vermiculite	Pack	

All these fillers are available in various purities and sizes.

¹*Buil, builders' suppliers (fillers must be dried); Chem, chemical suppliers; Pack, packaging and insulation suppliers; Poly, suppliers of polyester resins.*

tend to fade when exposed to light (Allen, 1991). A wide variety of inorganic and organic pigments are available that are very light-stable. Pure pigments are available from colourmen and can be bound into the appropriate polymer liquid. Colourants may be designed for use with specific polymers: polyesters, silicones and epoxies. Some pigments react adversely with cross-linking polymers. The light stability of many pigments is affected by the medium. Powdered metals may react with components of the polymer, e.g. amines in epoxy formulations will react with copper alloys. Powdered metals, e.g. lead, bronze and copper, can be purchased separately or ready mixed in epoxy resins.

Dyes are exposed in the full depth of the coloured polymer, so especially stable materials are needed. Unfortunately, there are few dyes that approach pigments in light-fastness (Table 14.2). Finely ground pigments may be used to achieve coloration with some loss of transparency. Problems of incompatibility are greater with dyes than with pigments. For a critical use, preliminary tests of compatibility and fastness should be made.

TABLE 14.2 Light-Stable Dyes (Orosol, Ciba)

Dye Name	Solvent-Borne Acrylic	Polyurethane	Epoxy	Polyester Acrylic Resin	
Yellow	2GLN	1	8	6	6–7
	3R	–	8	–	X
Orange	G	–	8	–	X
	RLN	–	8	6	6–7
Brown	GR	–	8	–	X
	2GRL	–	7–8	–	
	2RL	5–6	6–7	–	
	5R	–	6–7	–	X
	6RL	–	8	–	–
Red	3GL	–	7–8	–	6–7
	GLN	–	7–8		–
	2BL	–	8	–	
	G	–	7–8	X	–
	B	–	7–8	–	–
	2B		8	5–6	–
Violet	RN	–	8	–	X
Blue	GN	6	–	–	6–7
	2GLN	5–6	X	–	6–7
Black	BA		8	X	X
	CN	–	8	–	X
	RL	–	8	5–6	X

Many dyes react with cross-linking resins and some combinations are unsuitable, indicated by 'X'. The numbers indicate the blue wool light-fastness equivalent (Section 2.2). Lack of a number indicates that light-fastness is poor. Similar dyes are available from other manufacturers, e.g. BASF.

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Polymer Properties

These data are derived from many sources and refer to the set polymer without modifications. The values given will be only approximate, but should enable qualitative comparisons of properties. The values will vary with molecular weight, grade, method of measurement, etc. Good manufacturers will provide information about properties and test methods for their products, even obsolete ones.

Chapter or Section No.	Trivial Name ¹	IUPAC Abbreviation ²	Structural Name ³	CAS No. ⁴	T_g^5 (°C)	n_D
6.1	Polyethene	PE	Polymethylene	9002-88-4	-20	1.49–1.52
6.1	Hydrocarbon wax			8002-74-2		
6.1	Poly(ethene/vinyl acetate)	EVAC		24937-78-8	-24	1.48
6.2	<i>Cis</i> -1,4-polyisoprene	Rubber	Poly(1-methyl- <i>cis</i> -1-butenylene)	9003-31-0	-75	1.53
6.2	Gutta-percha			9000-32-2	39	1.51
6.2	Chlorinated rubber					1.55–1.60
7.1	Poly(vinyl acetate)	PVAC	Poly(1-acetoxy-ethylene)	9003-20-7	18–29	1.47
	Poly(vinyl acetate) dispersion	PVAC				
7.2	Poly(vinyl alcohol)	PVAL	Poly(1-hydroxy-ethylene)	9002-89-5	#75	1.5
7.3	Poly(vinyl butyral)	PVB	Poly[(2-propyl-1,3-dioxane-4,6-diyl)-methylene]	63148-65-2	45–66	1.49
8	Poly(methyl acrylate)	PMA	Poly[1-(methoxycarbonyl)-ethylene]	9011-14-7	8	1.479
8	Poly(ethyl acrylate)	PEA	Poly[1-(ethoxycarbonyl)-ethylene]	9003-21-8	-22	1.46
8	Poly(<i>n</i> -butyl acrylate)	PBA	Poly[1-(<i>n</i> -butoxycarbonyl)-ethylene]	9003-49-0	-54	1.474

Chapter or Section No.	Trivial Name ¹	IUPAC Abbreviation ²	Structural Name ³	CAS No. ⁴	T_g^5 (°C)	n_D
8	Poly{2-ethyl hexylacrylate)	PEHA	Poly[1-(2-ethylhexoxycarbonyl)-ethylene]	9003-77-4	-55	
8	Poly(methyl methacrylate)	PMMA	Poly[1-(methoxycarbonyl)-1-methyl ethylene]	9011-14-7	105	1.489
8	Poly(ethyl methacrylate)	PEMA	Poly[1-(ethoxycarbonyl)-1-methyl ethylene]	9003-42-3	65	1.484
8	Poly(n-butyl methacrylate)	PnBMA	Poly[1-n-butoxycarbonyl)-1-methyl ethylene]	9003-63-8	20	1.483
8	Poly(i-butyl methacrylate)	PiBMA	Poly[1-(i-butoxycarbonyl)-1-methyl ethylene]	9011-15-8	55	1.486
8	Poly(methyl cyanoacrylate)		Poly[1-(methoxycarbonyl)-1-cyano ethylene]	25067-29-2	165	1.49
9.1	Poly(vinyl chloride)	PVC	Poly(1-chloro-ethylene)	9002-86-2	83	1.54
9.2	Poly(vinylidene chloride)	PVDC	Poly(1,1-dichloro-ethylene)	9002-85-1	75	1.62
9.3	Polystyrene	PS	Poly(1-phenyl-ethylene)	9003-53-6	80	1.59
9.4	Poly(<i>N</i> -vinyl pyrrolidone)	PVP	Poly[1-(2-oxypyrrolidin-1-yl)-ethylene]	94800-10-9	#86	1.53
9.5	Poly(<i>p</i> -xylylene)	PPX	Poly(1,4-dimethylene benzene)	25722-33-2	60-80	1.669
9.6	Cyclohexanone polymer	Ketone resin		9003-41-2	≈100	1.515

Young's Modulus ⁷ (MPa)	Elongation at Break ⁷ (%)	Solubility Chart No. ⁸	δ_d^9 (MPa $^{1/2}$)	δ_p^9 (MPa $^{1/2}$)	δ_h^9 (MPa $^{1/2}$)	R^9	Stability ¹⁰	Introduction Commercial	Introduction ¹¹ Conservation
B									
3000	4	3.10	18.6	10.5	7.5	8.6	A	1932	1937
	10	3.11	17.6	9.7	4	10.6	A	1933	1940
	300	3.12	16.2	6.8	5.7	9.1	B		1932?
	1						B		1932?
3700		3.41					B	1950s	1968
3000	15	3.16	18.4	6.6	8	3	T	1930s	1958
20–60		3.17	17.5	7.6	40.8	6.1	T	1939	1949
3000	1	3.18	22.3	5.8	4.3	12.7	C	1930	1937
	100	3.19	24	14.8	16.2	19.9		1940s	1978
2400	12						T	1965	1984
		3.20 and 3.21	21.7	1.9	7.6	14.9	B	1926	1952

Chapter or Section No.	Trivial Name ¹	IUPAC Abbreviation ²	Structural Name ³	CAS No. ⁴	T_g^5 (°C)	n_D
9.7	Poly(ethylene glycol)	PEOX	Polyoxyethylene	25322-68-3	-55	1.46
9.7	Perfluoropolyether					1.304
9.8	<i>N</i> -Methoxymethyl nylon	Soluble nylon		11114-00-4		1.53
9.9	Poly(2-ethyl-2-oxazoline)	PEOX		25805-17-8	55	
10.1	Methyl cellulose	MC		9004-67-5	140	1.49
10.1	Ethyl cellulose	EC		9004-57-3		1.49
10.1	Hydroxyethyl cellulose	HEC		9004-62-0		1.51
10.1	Hydroxypropyl cellulose	HPC		9004-64-2		1.56
10.1	Methyl hydroxyethyl cellulose	MHEC		9032-42-2		
10.1	Ethyl hydroxyethyl cellulose	EHEC		9004-58-4		
10.1	Sodium carboxymethyl cellulose	CMC		9004-32-4		1.515
10.2	Cellulose diacetate	CA		9035-69-2	180	1.47
10.2	Cellulose nitrate	CN		9004-70-0	56	1.51
11.1	Starch			9005-25-8		1.53

Young's Modulus ⁷ (MPa)	Elongation at Break ⁷ (%)	Solubility Chart No. ⁸	δ_d^9 (MPa ^{1/2})	δ_p^9 (MPa ^{1/2})	δ_h^9 (MPa ^{1/2})	R^9	Stability ¹⁰	Introduction ¹¹ Commercial	Conservation
15 (nylon 66–210)		3.25	15.9	7.2	24.5	19.9	B	1930s	1957
							A	1970s	1982
							T	1948	1958
	370-36 (8–73% RH)	3.26	18.4	13	10.9	11.6		1980s	1998
	12						B	1920s	1924
							B	1920s	1961
							B	1920s	1968
	414	3.27	24.6	10.2	19.7	19.9	B	1920s	1976
								1920s	
								1920s	1972?
	14						B	1930s	1966
2000	20	3.28	18.2	12.4	10.8	7.4	B	1910s	1923
2500	13	3.29	15.4	14.7	8.8	11.5	C	1877	1899
3.5							B	Traditional	

Chapter or Sec- tion No.	Trivial Name ¹	IUPAC Abbre- viation ²	Structural Name ³	CAS No. ⁴	T_g^5 (°C)	n_D
11.1	Gum arabic			9000-01-5		1.48
11.1	Agar-agar			9002-18-0		
11.1	Funoran	Funori		9083-24-3		
11.2	Gelatine			9000-70-8	210	
11.3	Casein			9000-71-9		1.53
	Cyclododecane			294-62-2		
12.1	Dammar			9000-16-2	100	1.53
12.2	Mastic			61789-92-2	72	1.54
12.3	Rosin			8050-09-7		1.525
12.4	Shellac			9000-59-3	40	1.52
12.5	Polymerized linseed oil	linoxyn				1.48–1.57
13.1	Silane					
13.1	Siloxane	Silicone rubber			–125	1.4
13.2	Polyester resin	Unsaturated polyester				1.55
13.3	Polyurethane resin	PUR				

Young's Modulus ⁷ (MPa)	Elongation at Break ⁷ (%)	Solubility Chart No. ⁸	δ_d^9 (MPa ^{1/2})	δ_p^9 (MPa ^{1/2})	δ_h^9 (MPa ^{1/2})	R^9	Stability ¹⁰	Introduction ¹¹ Commercial Conservation	
							B	Traditional	
							B	Traditional	
							B	Traditional	
3700							B	Traditional	
37								Traditional	
		3.30	17.7	2.6	2.1	6.9			1995
2200		3.31 and 3.32	19	2	9	9	B	1826	1829
910		3.33	23.4	10	13.4	17.9	B	Traditional	
2500							C	Traditional	
1340		3.34	17.8	8.5	13.7	8.2	C	Traditional	
		3.36	16	6	7	5	C	Traditional	
							A	1920s	1923
3	300	3.37					B	1940s	1950s
2000	2	3.38					C-B	1946	1950
		3.39						1930s	1969

Chapter or Section No.	Trivial Name ¹	IUPAC Abbreviation ²	Structural Name ³	CAS No. ⁴	T_g ⁵ (°C)	n_D
13.4	Epoxy resin	EP				1.56
13.5	Phenol formaldehyde	PF	Phenol methanal polymer	90	1.7	
13.5	Urea formaldehyde	UF	Urea methanal polymer			1.55
13.5	Melamine formaldehyde	MF	Melamine methanal polymer	2		1.65

¹This list follows International Union of Pure and Applied Chemistry (IUPAC) recommendations (Maréchal and Wilks, 2001). The trivial name is usually derived from the monomers used to construct the polymer, if only nominally. If the polymer is derived from a natural product, this is used as the source for the name.

²The IUPAC abbreviations for polymers (BS EN ISO 1043-1, 2002; Jones et al., 2009) are followed here. Many different abbreviations are used for polymers and plastics (Elias, 1999).

³This structural name follows IUPAC recommendations, though there are potentially a number of equally valid names (Kahovec et al., 2002). The properties of the polymer depend on the structure of the molecule, and little on the properties of the monomer from which it is derived.

⁴The Chemical Abstract Service Registry number (CAS Registry, 2009) provides a stable reference for a chemical, though the assignment of the number to a chemical by users is frequently loose. The CAS nomenclature varies considerably from the IUPAC recommendations.

⁵The measured glass transition temperature, T_g , is sensitive to the details of the measurement technique and its interpretation. Because of this variability, the methodology is being standardized. As a result, past values are unlikely to be directly comparable to current values. # indicates that the value will be affected by water content due to humidity changes.

⁶The refractive index (n_D) is normally measured using sodium light (the D line at 589 nm) at room temperature, and is sensitive to processing and impurities that change the density, e.g. solvents and water content.

⁷Mechanical properties of the polymer depend on the sample shape and speed of testing.

⁸See Appendix 3.

⁹Hansen solubility parameters in MPa^{1/2}, δ_d , δ_p , δ_h , at the centre of the polymer's solubility sphere. R is the radius of the sphere (Hansen, 2007).

¹⁰Stability of polymer in its normal use environment, using Feller's (1978) scale of useful life (Section 2.7). A > 100 years, 100 years > B > 20 years, 20 years > C > 6 months, 6 months > T.

¹¹Dates drawn from available literature. The earliest date for the use of the polymer, usually the date of publication of an article describing the application. Many of these dates are much later than the first use in conservation.

[illegible]

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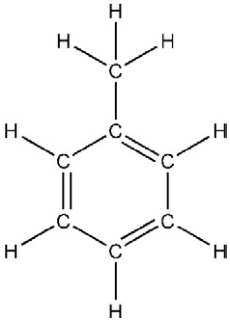
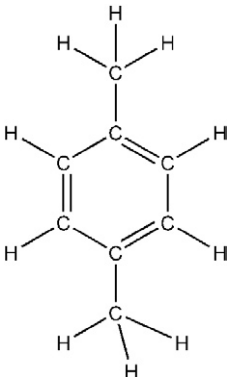
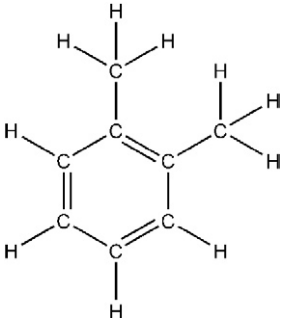
Solvent Properties

The solvents listed are those that have been used to apply, remove or assess materials. Many are not suitable for use in conservation treatments but illustrate the range of solvent properties. Particular circumstances may require knowledge of other properties, for which standard or specialist texts may be consulted (Wypych and Wypych, 2007).

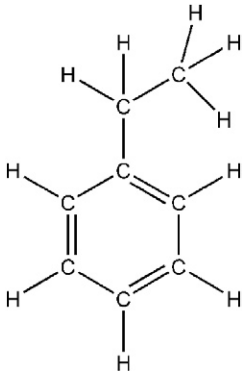
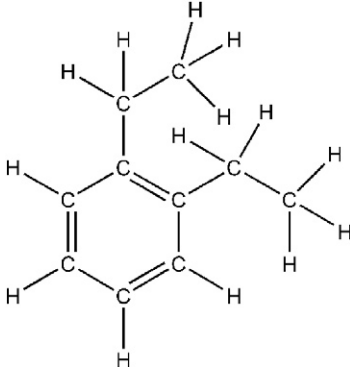
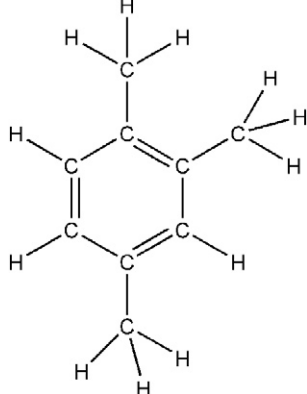
The values of properties listed here have been drawn from a large number of different sources. It is likely that the sets of data are not self-consistent, so direct comparisons should be made with caution.

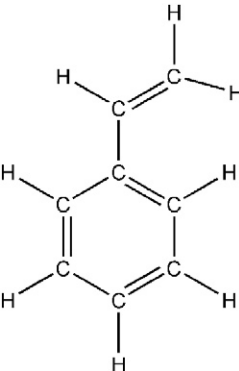
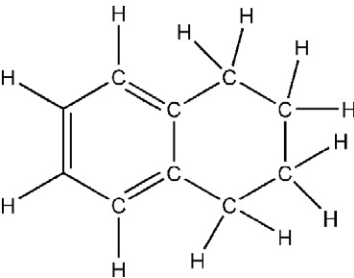
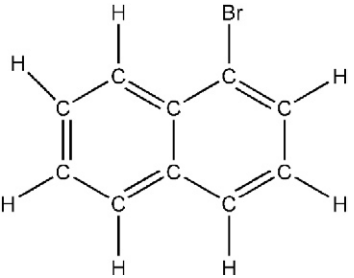
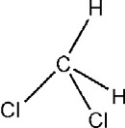
Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo-ration Rate ⁴
1 Hexane		142-82-5		69	8.1
2 Heptane		110-54-3		98	2.8
3 Cyclo-hexane		110-82-7		81	4.5
4	Odourless mineral spirits				
5 Shellsol D38		64742-88-7		149–185	0.21
6 Benzene		71-43-2		80	5.4

Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
0.38	20	−21	131.6	100	0	0	14.9	0	0	KB no. 30
0.42	400	−5.5	147.4	100	0	0	15.3	0	0	
1	100	−18	108.7	99	0	1	16.8	0	0.2	
				98	1	1				Appen- dix 2.2
1.19		37.8		96	2	2				Appen- dix 2.2
0.65	1(C)	−11	89.4	90	0	10	18.4	0	2	KB no. 100

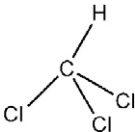
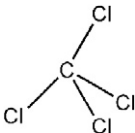
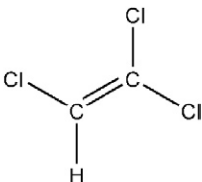
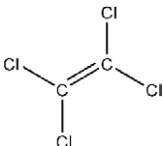
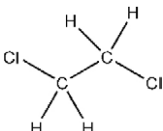
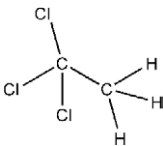
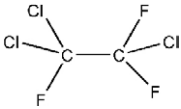
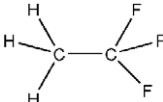
	Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo- ration Rate ⁴
7	Toluene	Methyl benzene	108-88-3		110	2.3
8	<i>p</i> -Xylene	1,4-Dimethyl benzene	106-42-3		138	
9	<i>o</i> -Xylene	1,2-Dimethyl benzene	95-47-6		138	0.75

Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
0.58	50(N,S)	4	106.8	84	7	9	18	1.4	2	
0.65	50(S)	25	123.3	81	5	14	17.6	1	3.1	
0.63	50(S)	30	121.2	81	5	14	17.8	1	3.1	KB no. 94 (mix- ture of isomers)

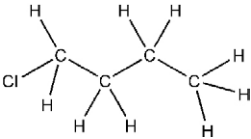
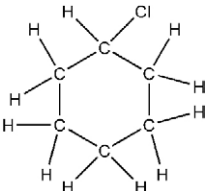
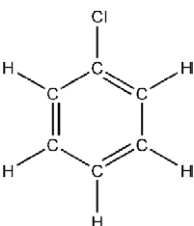
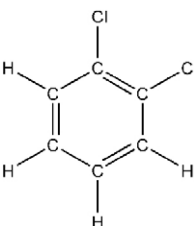
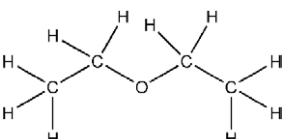
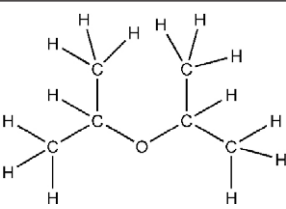
Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo- ration Rate ⁴
10 Ethyl benzene		100-41-4		136	
11 1,2-Diethyl benzene		135-01-3		183	
12 1,2,4- Trimethyl benzene		95-63-6		171	

Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point	Evapo-ration Rate ⁴
(°C)					
13	Styrene	Vinyl benzene	100-42-5		146
14	1,2,3,4-Tetrahydronaphthalene	Tetralin	119-64-2		207
15	Turpentine		9005-90-7		150–170
16	1-Bromonaphthalene		90-11-9		283
17	Dichloromethane	Methylene chloride	75-09-2		40
					6.4

Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
0.75	100	31	115.6	78	4	17	18.6	1	4.1	
2.2		77	136	80	8	12	19.6	2	2.9	Rapidly oxidizes
	100	>32		77	18	5				Rapidly oxidizes
		128	140	74	11	15	20.3	3.1	4.1	
0.43	100(N)	—	63.9	59	21	20	18.2	6.3	6.1	KB no. 136

Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evaporation Rate ⁴	
18	Chloroform	Trichloromethane	67-66-3		61	
						
19	Carbon tetrachloride		56-23-5		77	
						
20	Trichloroethene		79-01-6		87	4.9
						
21	Tetrachloroethene	Perchloroethylene	127-18-4		122	1.29
						
22	1,2-Dichloroethane	Ethylene dichloride	107-06-2		84	
						
23	1,1,1-Trichloroethane	Methyl chloroform	71-55-6		74	4.7
						
24	1,1,2-Trichlorotrifluoroethane	Freon 113	76-13-1		48	
						
25	1,1,1-Trifluoroethane		420-46-2		-47	
						

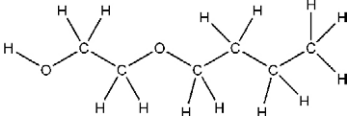
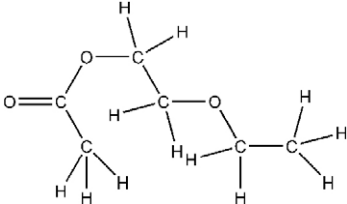
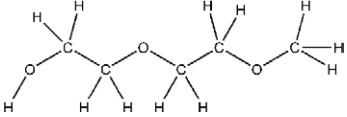
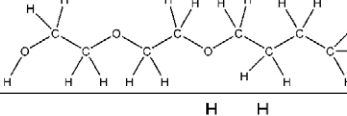
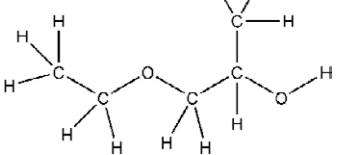
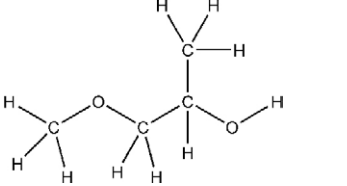
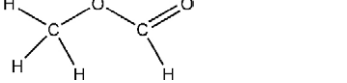
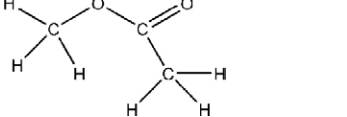
Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
0.57	2(N,C)	–	80.7	67	12	21.42857	17.8	3.1	5.7	
0.97	2(N,C,S)	–	97.1	66	34	0	16.1	8.3	0	KB no. 114
0.57	100(N,C)	–	90.2	68	12	20	18	3.1	5.3	KB no. 132
0.9	50	–	101.2	76	24	0	18.3	5.7	0	KB no. 90
0.84	5	13	84.2	60	29	11	16.5	7.8	3	
1.1	100(N)	–	99.3	73	19	9	16.8	4.3	2	KB no. 124
0.69	1000	–	119.2	90	10	0	14.7	1.6	0	KB no. 31
			64.6	58	42	0	14.6	10.7	0	

	Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evaporation Rate ⁴
26	1-Chlorobutane		109-69-3		79	
27	Cyclohexyl chloride		542-18-7		142	
28	Chlorobenzene		108-90-7		131	
29	o-Dichlorobenzene		95-50-1		180	
30	Diethyl ether		60-29-7		35	-11
31	Di-isopropyl ether		108-20-3		69	

Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
		-6.7	104.5	68	23	8	16.2	5.5	2	
		28.9	118.6	70	22	8	17.3	5.5	2	
	1	29	102.1	75	17	8	19	4.3	2	
	25	66	112.8	67	22	11	19.2	6.3	3.3	
0.25	100(N)	-40	104.8	64	13	23	14.5	2.9	5.1	Forms perox- ides on storage
		-28	140.9	69	20	12	13.7	3.9	2.3	

Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evaporation Rate ⁴
32 Furan		110-00-9		31	
33 Tetrahydrofuran	THF	109-99-9		65	-4.9
34 Di(2-chloroethyl) ether	1,1'-Oxybis(2-chloroethane)	111-44-4		179	
35 1,4-Dioxacyclohexane	1,4-Dioxane	123-91-1		101	-1.7
36 Methylal	Dimethoxymethane	109-87-5		42	
37 2-Ethoxyethanol	Cellosolve	110-80-5		135	0.35
38 2-Methoxyethanol	Methyl Cellosolve	109-86-4		125	0.51

Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
		−35	72.5	71	7	21	17.8	1.8	5.3	
0.48	50(N,C)	−22	81.7	55	19	26	16.8	5.7	8	Forms perox- ides on storage
		55	117.2	56	27	17	18.8	9	5.7	
1.52	25(S)	11	85.7	67	6	26	19	1.8	7.4	Forms perox- ides on storage
	1000	−18	169.4	59	7	34	15	1.8	8.6	
2.1	10(S)	42	97.8	41	23	36	16.2	9.2	14.3	Forms perox- ides on storage
1.7	5(C)	37	79.1	39	22	39	16.2	9.2	16.4	Forms perox- ides on storage

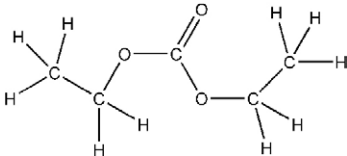
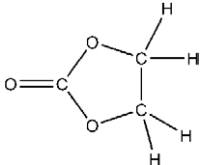
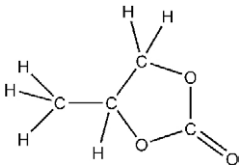
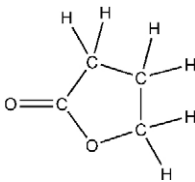
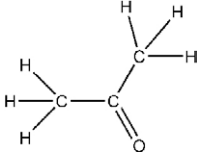
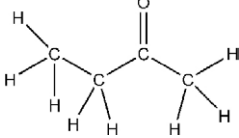
Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo-ration Rate ⁴
39 2-Butoxy-ethanol	Butyl Cellosolve	111-76-2		171	0.076
40 2-Ethoxy-ethyl acetate	Cellosolve acetate	111-15-9		156	0.19
41 Diethylene glycol methyl ether	2-(2-Methoxyethoxy) ethanol	111-77-3		194	
42 Diethylene glycol butyl ether	2-(2-Butoxyethoxy) ethanol	112-34-5		230	
43 1-Ethoxy-2-propanol	Propylene glycol ethyl ether	1569-02-4		131	
44 1-Methoxy-2-propanol	Methyl proxitol; propylene glycol methyl ether	107-98-2		118	
45 Methyl formate		107-31-3		32	
46 Methyl acetate		79-20-9		57	6.9

Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
3.2	25(S)	60	131.6	48	15	37	16	5.1	12.3	Forms perox- ides on storage
	10(S)	51	131.6	51	15	34	15.9	4.7	10.6	Forms perox- ides on storage
	10	84	118	44	21	34	16.2	7.8	12.6	
	10	100	170.6	48	21	32	16	7	10.6	
		46	115.6	48	20	32	15.7	6.5	10.5	
	100	34	93.8	47	19	35	15.6	6.3	11.6	
			62.2	45	25	30	15.3	8.4	10.2	
0.38	200	-10	79.7	51	24	25	15.5	7.2	7.6	

	Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evaporation Rate ⁴
47	Ethyl acetate		141-78-6		77	4.3
48	i-Propyl acetate		108-21-4		89	3.3
49	n-Butyl acetate		123-86-4		126	1
50	Pentyl acetate	n-Amyl acetate	628-63-7		149	
51	i-Amyl acetate	3-Methyl butyl acetate	123-92-2		142	

Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
0.45	200(N,C)	−4	98.5	56	19	25	15.8	5.3	7.2	
0.52	250(N,C)	12	117.1	54	16	30	14.9	4.5	8.2	
0.73	150	25	132.5	61	14	24	15.8	3.7	6.3	
			148	61	14	25	15	3.3	6.1	
		25	148.8	60	12	28	15.3	3.1	7	

	Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evaporation Rate ⁴
52	Methyl methacrylate	Methyl-2-propenoate	80-62-6		101	
53	Isobutyl isobutyrate	2-Methyl-2-methylpropyl propanoate	97-85-8		144	
54	Ethyl lactate	Ethyl 2-hydroxypropanoate	97-64-3		154	
55	Butyl lactate	Butyl 2-hydroxypropanoate	138-22-7		189	
56	Ethyl acetoacetate	Ethyl 3-ketobutyrate	141-97-9		181	
57	Benzaldehyde		100-52-7		178	
58	Dimethyl carbonate		616-38-6		90	

	Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo- ration Rate ⁴
59	Diethyl carbonate		105-58-8		127	
60	Ethylene carbonate	1,3-Dioxolan-2-one	96-49-1		261	
61	1,2-Propane-diol carbonate	Propylene carbonate; 4-methyl-1,3-dioxolan-2-one	108-32-7		242	
62	γ-Butyrolactone	4-Butanolide	96-48-0		204	
63	Acetone	Propanone	67-64-1		56	7.8
64	Butanone	Methyl ethyl ketone (MEK)	78-93-3		80	4.6

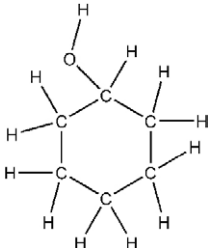
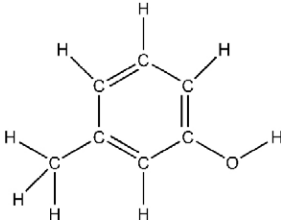
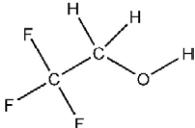
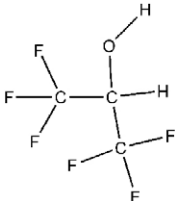
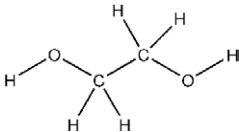
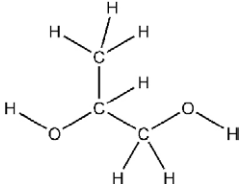
Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
		31	121	61	25	14	15.1	6.3	3.5	
		150	66	42	47	11	19.4	21.7	5.1	
2.8	(25C)	–	85	48	43	10	20	18	4.1	
2	–	94	76.8	44	39	17	19	16.6	7.4	
0.32	500	–17	74	47	32	21	15.5	10.4	7	
0.42	200(N)	–1	90.1	53	30	17	16	9	5.1	

65	Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point	Evapo-ration
	Pentan-2-one	Methyl propyl ketone	107-87-9		101	
66	Cyclohexanone		108-94-1		157	0.25
67	Methyl isobutyl ketone	4-Methyl-2-pentanone	108-10-1		117	1.4
68	Methyl isoamyl ketone	2-Methyl-5-hexanone	110-12-3		144	
69	Di-isobutyl ketone	2,6-Dimethyl-4-heptanone	108-83-8		168	-0.2
70	Acetophenone	Phenyl methyl ketone	98-86-2		202	

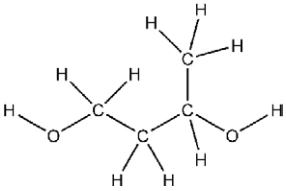
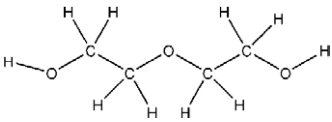
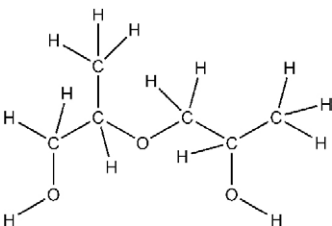
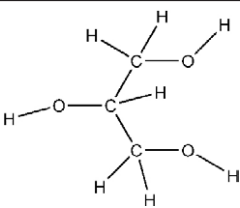
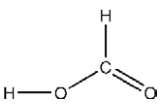
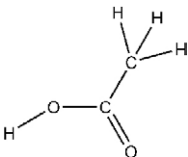
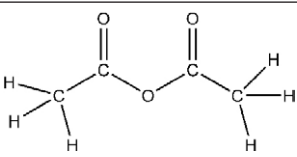
	Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo- ration Rate ⁴
71	Diacetone alcohol	2-Hydroxy- 2-methyl-4- pentanone	123-42-2		166	
72	Isophorone	3,5,5-Trimethyl- cyclohexyl- 2-eneone	78-59-1		215	
73	Mesityl oxide	4-Methyl- pent-3-ene- 2-one	141-79-7		129	
74	Methanol	Methyl alcohol	67-56-1		65	4.1
75	Ethanol	Ethyl alcohol	64-17-5		78	-2.4
76	1-Propanol		71-23-8		97	

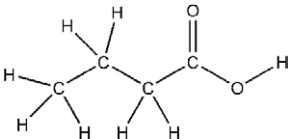
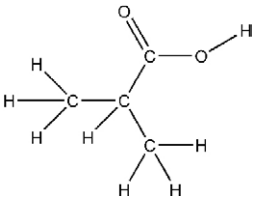
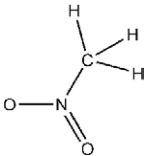
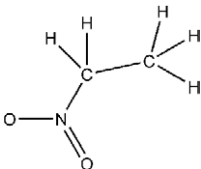
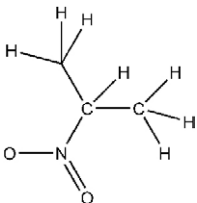
Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
	50	62	124.2	45	24	31	15.8	8.2	10.8	
		84	150.5	52	25	23	16.6	8.2	7.4	
		87	115.6	57	21	21	16.4	6.1	6.1	
0.61	200(N,C,S)	11	40.7	30	25	45	15.1	12.3	22.3	
1.2	1000(N)	12	58.5	36	20	44	15.8	8.8	19.4	Pure ethanol
1.9	200	15	75.2	40	17	43	16	6.8	17.4	

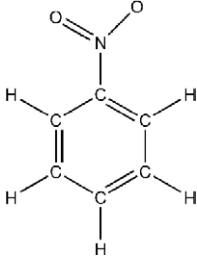
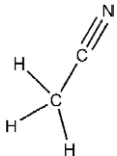
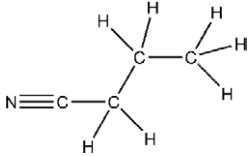
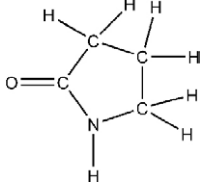
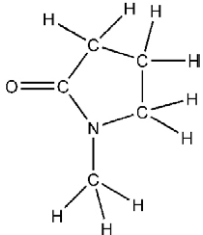
Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo-ration Rate ⁴
77	2-Propanol	i-Propyl alcohol	67-63-0	82	2.2
78	1-Butanol	n-Butyl alcohol	71-36-3	118	0.46
79	2-Ethyl-1-butanol	97-95-0		146	
80	1-Pentanol	71-41-0		138	
81	2-Ethyl-hexanol	104-76-7		184	
82	4-Methyl-pentan-2-ol	Methyl isobutyl carbinol	108-11-2	134	

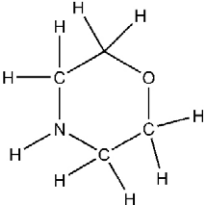
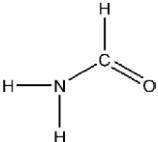
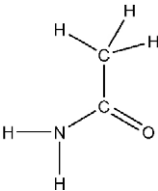
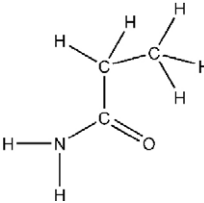
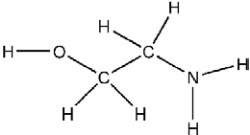
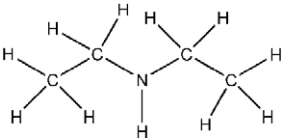
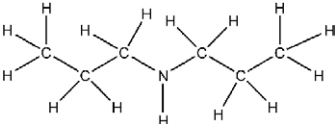
	Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo-ration Rate ⁴
83	Cyclo-hexanol		108-93-0		161	
84	<i>m</i> -Cresol	3-Methyl phenol	108-39-4		203	
85	2,2,2-Trifluoroethanol		75-89-8		78	
86	Hexafluoro-2-propanol	1,1,1,3,3,3-Hexafluoro-2-propanol	920-66-1		58	
87	1,2-Ethane diol	Ethylene glycol	107-21-1		197	
88	1,2-Propane diol	Propylene glycol	57-55-6		188	

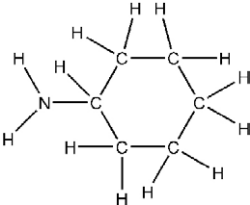
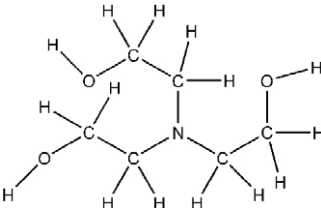
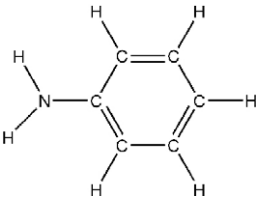
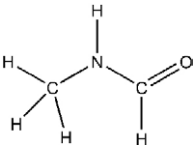
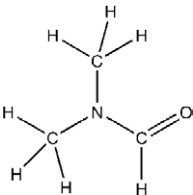
Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
41	50	67	106	50	12	39	17.4	4.1	13.5	
184		86	104.7	50	14	36	18	5.1	12.9	
		29	72.3	38	21	41	15.4	8.3	16.4	
1.7		0	105.3	47	12	40	17.2	4.5	14.7	
21	20	119	55.8	31	20	48	17	11	26	
	150	107	73.6	34	19	47	16.8	9.4	23.3	

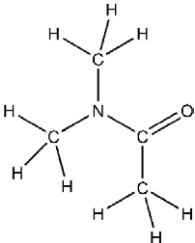
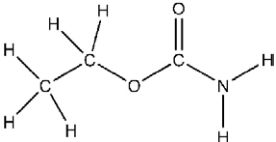
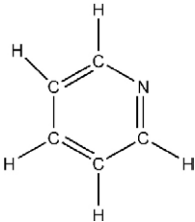
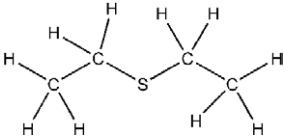
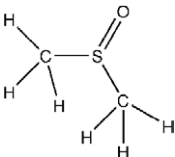
	Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evaporation Rate ⁴
89	1,3,-Butanediol		107-88-0		207	
90	Diethylene glycol	(2-Hydroxyethoxy)ethan-2-ol	111-46-6		244	
91	Dipropylene glycol	4-Oxa-1,7-heptandiol	25265-71-8		230	
92	Glycerol	1,2,3-Propane triol	56-81-5		290	
93	Formic acid		64-18-6		101	
94	Acetic acid	Ethanoic acid	64-19-7		118	
95	Acetic anhydride		108-24-7		140	

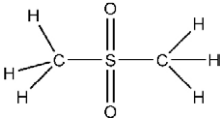
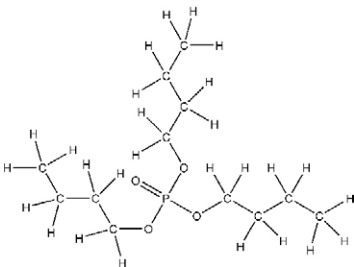
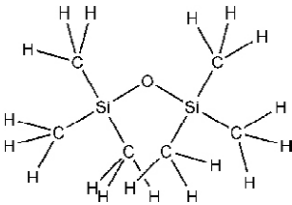
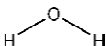
	Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo- ration Rate ⁴
96	Butyric acid	n-Butanoic acid	107-92-6		164	
97	2-Methylpropionic acid	Isobutyric acid	79-31-2		155	
98	Nitromethane		75-52-5		101	
99	Nitroethane		79-24-3		115	
100	2-Nitropropane		79-46-9		121	

Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo-ration Rate ⁴
101 Nitrobenzene		98-95-3		211	
102 Ethane nitrile	Acetonitrile	75-05-8		82	
103 Butyronitrile		109-74-0		117	
104 2-Pyrrolidone		616-45-5		245	
105 N-Methyl-2-pyrrolidone		872-50-4		202	

Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evaporation Rate ⁴
106	Morpholine	110-91-8		129	
107	Formamide	75-12-7		210	
108	Acetamide	60-35-5		222	
109	Propionamide	79-05-0		213	
110	Ethanolamine	141-43-5		170	
111	Diethylamine	109-89-7		55	
112	Dipropylamine	142-84-7		111	

Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evaporation Rate ⁴
113 Cyclohexylamine		108-91-8		134	
114 Triethanolamine	TEA	102-71-6		335	
115 Aniline	Phenylamine	62-53-3		184	
116 N-Methylformamide		123-39-7		199	
117 N,N-Dimethylformamide	DMF	68-12-2		155	

Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo-ration Rate ⁴
118 <i>N,N</i> -Dimethyl acetamide		127-19-5		164	
119 Ethyl carbamate	Urethane	51-79-6		185	
120 Pyridine		110-86-1		115	
121 Carbon disulphide		75-15-0	$\text{S}=\text{C}=\text{S}$	46	
122 Diethyl sulphide	1,1'-Thio-bis-ethane	352-93-2		92	
123 Dimethyl sulphoxide		67-68-5		189	

Name ¹	Synonym ²	CAS No. ³	Chemical Structure	Boiling Point (°C)	Evapo-ration Rate ⁴
124 Dimethyl sulphone	Sulphonyl-bismethane	67-71-0		238	
125 Tri-n-butylphosphate		126-73-8		289	
126 Hexamethyldisiloxane	OS-10; 1,1,1,3,3,3-hexamethyl-disiloxane	107-46-0		101	3.8
127 Water		7732-18-5		100	0.27

¹Common name.

²Trivial or International Union of Pure and Applied Chemistry (IUPAC) name.

³Chemical Abstract Service registry number (CAS Registry, 2009).

⁴Evaporation rate, relative to *n*-butyl acetate = 1.

⁵HSE (2007).

⁶Note that cm³/mol is expressed in cgs units not SI.

⁷These Teas fractional values have been recalculated using the recent Hansen solubility parameters. They should not be used in conjunction with values from other sources.

⁸Hansen solubility parameter values are taken from Hansen (2007) and Abbott and Hansen (2008).

Viscosity (mPa•s)	WEL ⁵ (ppm)	Flash Point (°C)	Molar Volume ⁶ (cm ³ / mol)	Fractional Solubility Param- eters ⁷			Hansen Solubility Parameters ⁸			Com- ments
				100f _d	100f _p	100f _h	δ _d	δ _p	δ _h	
		143	75	37	38	24	19	19.4	12.3	
		120	274	61	23	16	16.3	6.3	4.3	
0.5	200	-3	212.4	100	0	0	12.4	0	0	
1	-	-		18	28	54	15.1- 18.1	16- 20.4	16.9- 42.3	

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Hydrocarbon Solvents

These are typical products, whose designations, specifications and manufacturers change over time. Data are mostly drawn from manufacturers' information. In general, these grades have low sulphur and benzene content.

Name	CAS ¹	Manu- facturer	Boiling range (°C)	Evapo- ration rate ²	KB No. ³	Aniline point ⁴	Comments ⁵
n-Pentane	109-66-0	BP	32–37	12	29	71	TLV of pure pentane 600 ppm
Heptane	110-54-3		98	2.8	30	70	
Cyclohexane	110-82-7		81	4.5	55	65	
Benzene	71-43-2		80	5.4	110	8	
Toluene	108-88-3		110	2.3	105	9	
<i>p</i> -Xylene	106-42-3						
<i>o</i> -Xylene	95-47-6		138	0.75	98		
Ethyl benzene	100-41-4		136				
1,2-Diethyl benzene	135-01-3						
1,2,4-Trimethyl benzene	95-63-6						

Name	CAS ¹	Manu- facturer	Boiling range (°C)	Evapo- ration rate ²	KB No. ³	Aniline point ⁴	Comments ⁵
ShellSol TD		Shell	174–187	0.16	26	84	
ShellSol OMS		Shell	171–210	0.1	29	84	
SBP 60/95 LNH	64742- 49-0	Shell	70–92	6.3	33	61	A C ₆ –C ₇ hydro- carbon, <3% n-hexane
VM&P naphtha HT		Shell	118–149	1	36	60	Varnish makers' and painters' f_d 94, f_p 3, f_h 300 ppm similar to Stoddard's solvent
ShellSol D40		Shell	162–181	0.23	32	68	
Kristalloel 30		Shell	160–198	0.13	36	55	Typical white spirit
ShellSol D38		Shell	159–181	0.21	34	66	Was called 340HT, specially low im- purities (Bechtold and Pool, 2004)
ShellSol A		Shell	165–185	0.25	90		Mostly trimethyl benzenes, discon- tinued
ShellSol A100		Shell	167–180	0.2	90	14	A C ₉ –C ₁₀ aromatic hydrocarbon sol- vent, was Cyclosol 100 (Bechtold and Pool, 2004)
Xylene S		Shell	139–142	0.7	90	10	
Solvesso 100		Exxon- Mobil	164–178	0.19	95	14	US – Aromatic 100
Solvesso 200 ND		Exxon- Mobil	242–299		92	14	ND = naphthalene depleted

¹Chemical Abstract Service registry number.²Evaporation rate, relative to *n*-butyl acetate = 1.³Kauri-butanol number (ASTM D1133-09, 2009).⁴Aniline point (ASTM D611-07, 2007).⁵Teas solubility parameters taken from Barton (1991).

REFERENCES

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- ASTM D1133-09. (2009). *Standard test method for kauri-butanol value of hydrocarbon solvents*. ASTM.
- Barton, A. F. M. (1991). *CRC handbook of solubility parameters and other cohesion parameters*. CRC Press.
- Bechtold, S-L., & Pool, M. (2004). Mineral spirits: characteristics and hazards. *American Institute for Conservation News*, 29(2), 9–10.

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Hazards and Warnings (European Union Labelling)

These symbols, usually printed black on an orange background, are standard across Europe for indicating hazards (HSE, 2009). A hazard symbol will normally be accompanied with risk and safety phrases summarizing the hazard and appropriate action. This system will be replaced by a worldwide system in 2015 (see [Appendix 2.4](#)).

Toxicity

Toxic



Toxicity may be apparent through various routes: swallowing, contact with skin, or by inhalation. Precautions must be taken to prevent exposure by all of these routes to the worker directly involved and to those in the area or who might later come into contact with contaminated materials and facilities

Harmful



Corrosiveness

Corrosive



Corrosive materials usually cause damage and rapid pain to skin, eyes, etc. Precautions against possible contact with the material should be made

Irritant

Irritant substances cause damage more insidiously by damaging or irritating the skin

Flammability**Highly flammable**

There are various grades of 'flammable':

Extremely flammable – flash point $<0^{\circ}\text{C}$ and boiling point $<35^{\circ}\text{C}$

Highly flammable – flash point $>0^{\circ}\text{C}$ and $<21^{\circ}\text{C}$

Flammable – flash point $>21^{\circ}\text{C}$ and $<55^{\circ}\text{C}$ (does not require a hazard label).

Explosive

May explode as the result of shock, ignition, etc

Oxidizing agent

Oxidizing agents are those that can cause fire in combustible materials

Environment**Danger to aquatic life**

These materials may be dangerous to any part of the environment, including the ozone layer

REFERENCE

HSE. (2009). *Approved Classification and Labelling Guide: Chemicals (Hazard Information and Packaging for Supply) Regulations 2009 (CHIP 4), Approved Guide*. Health and Safety Executive.

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Hazards and Warnings (Globally Harmonized System Labelling)

A Globally Harmonized System of Classification and Labelling of Chemicals (GHS) has been proposed (UNECE, 2009). The increasing transport and use of materials across borders led to confusion and considerable costs in dealing with hazardous materials. In the UK and in stages up to 2015, the different national labelling rules will be progressively replaced by the GHS. The following table illustrates the pictograms. The change of labelling enabled a re-evaluation of hazards and their categories. Each of these categories and pictograms is augmented by phrases and classifications that provide extra levels of information (and complication) on the labelling.

The labels have a red square outline with the black hazard pictogram on a white background. The appropriate 'signal word' (e.g. Warning) and a 'hazard statement' (e.g. Harmful if swallowed) is printed in black below the pictogram.

Hazard	Pictogram
Explosive	
Flammable	

Hazard	Pictogram
Oxidizing	
Corrosive	
Toxic – danger	
Toxic – warning	
Specific danger, e.g. carcinogen	
Aquatic toxicity	

REFERENCE

UNECE. (2009). *Globally harmonized system of classification and labelling of chemicals (GHS)*. United Nations Economic Commission for Europe.

Polymer Solubility Charts

The following charts are based on the Teas charts discussed in Section 3.2 (Gardon and Teas, 1976). Much of the polymer testing was carried out some decades ago. The indicated manufacturer is that which supplied the tested polymer. The values of fractional parameters have been recalculated from the Hansen solubility parameters (Hansen, 2007), so the values cannot be compared with data from other sources. The solvent numbers relate to those listed in Appendix 2.1. The solubility properties have been drawn from a number of sources, with a methodology matching as closely as possible to ASTM D3132-84 (1996). Because of overlap of plotted points, some solvents have been omitted from the charts but are listed below each chart. The range of solvents included provide a comprehensive indication of the solubility properties. The inclusion of a solvent is not an indication that its use by a conservator or on an object is a good idea.

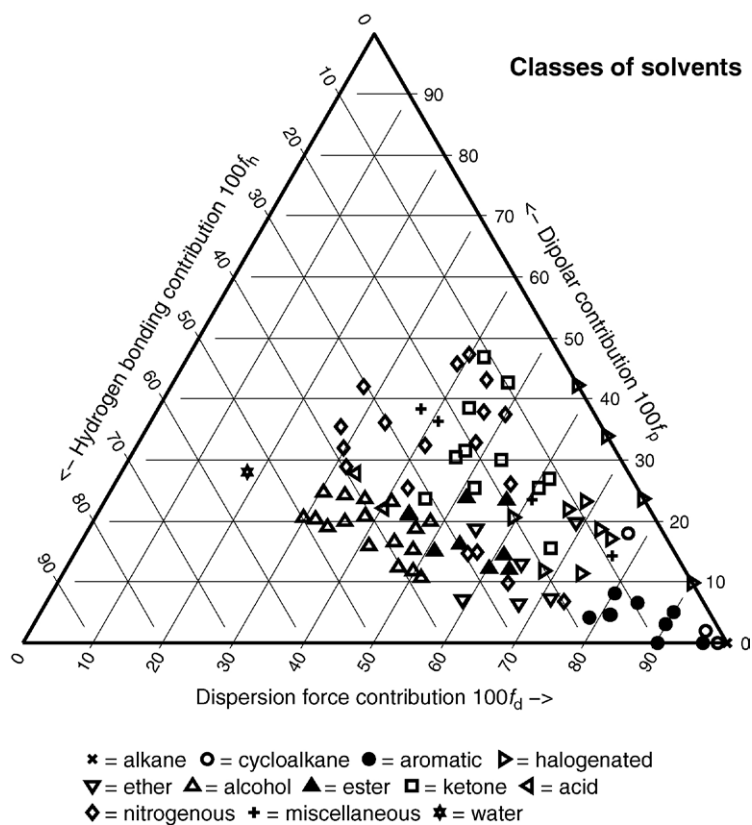


FIGURE A3.1 Major classes of solvents and their position on the Teas chart.

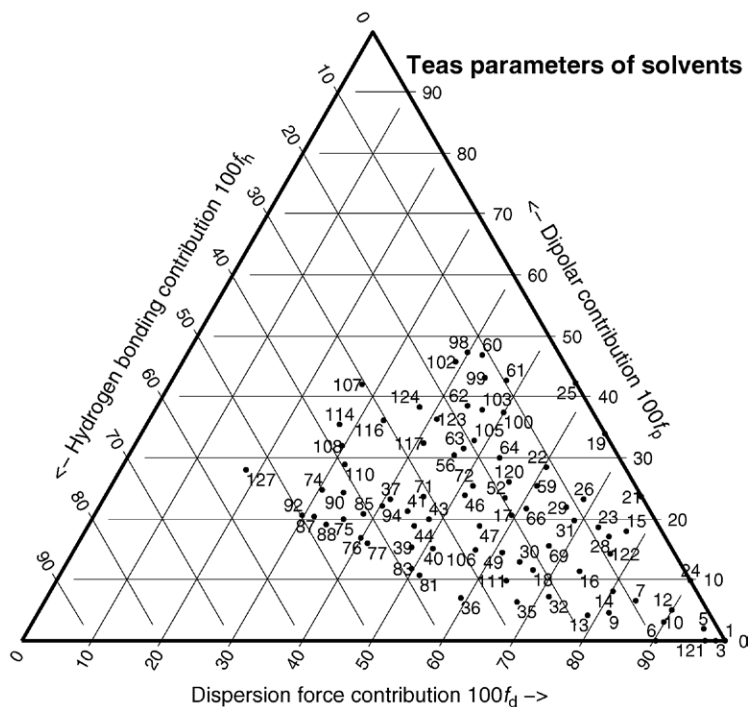
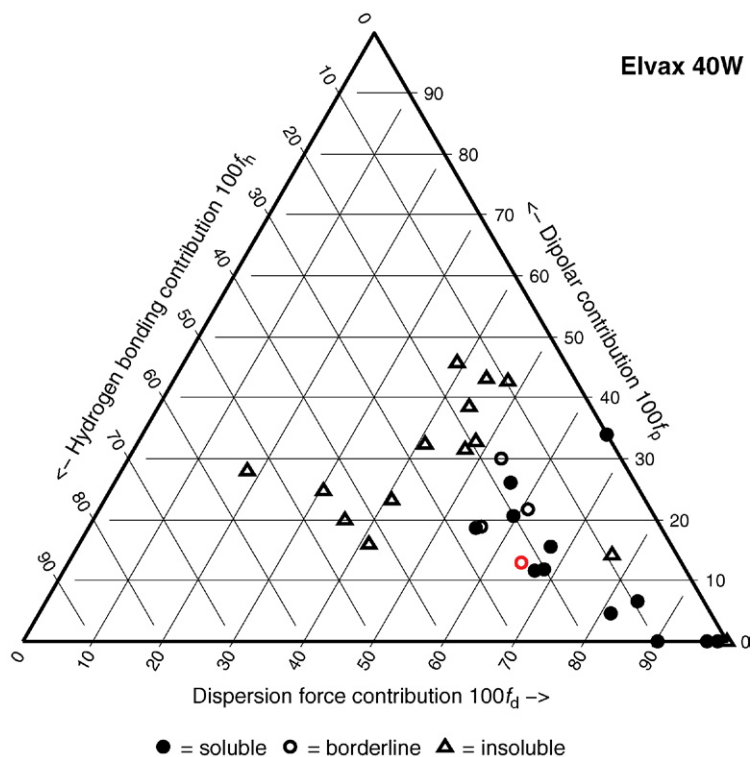


FIGURE A3.2 Location of solvents listed in [Appendix 2.1](#).



soluble: 3 6 7 9 17 18 19 20 33 69 120 121

borderline: 30 47 64 66

non-solvent: 2 37 61 62 63 74 75 77 99 102 105 117 122 127

FIGURE A3.3 Solubility of a medium-molecular-weight poly(ethene/vinyl acetate) 60:40 (Elvax 40W; du Pont).

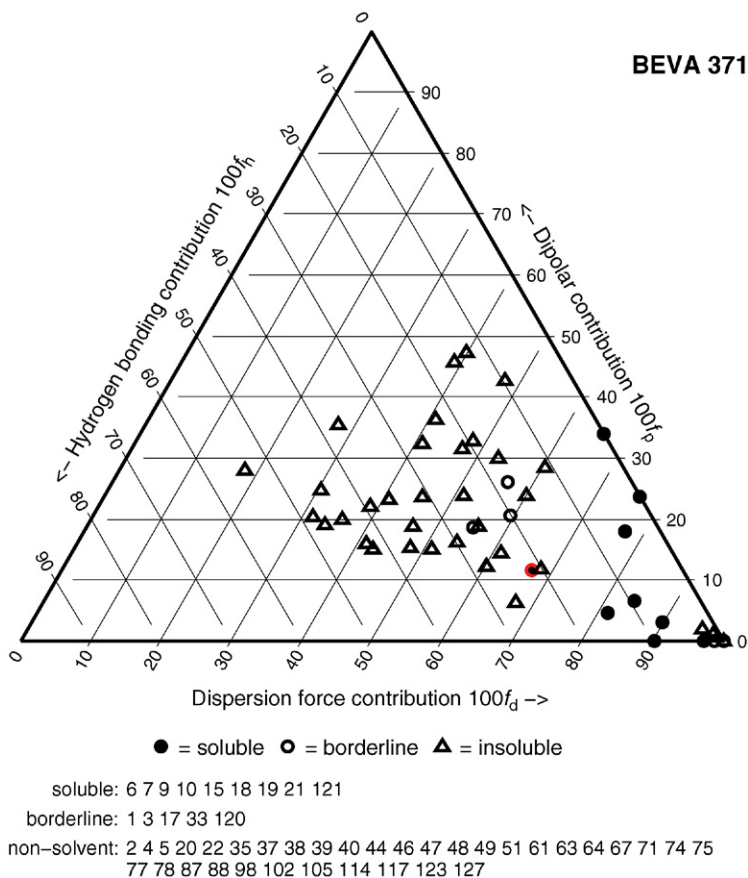
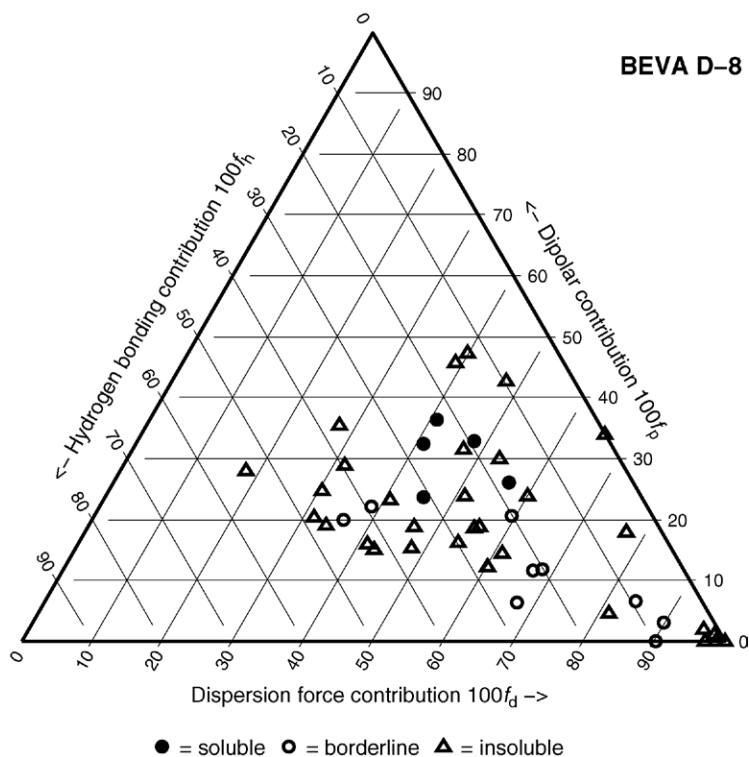


FIGURE A3.4 Solubility of BEVA 371 film. Data kindly provided by Dr Greg Smith and Classes of 2009, 2010 and 2011 of the Art Conservation Department at Buffalo State College.

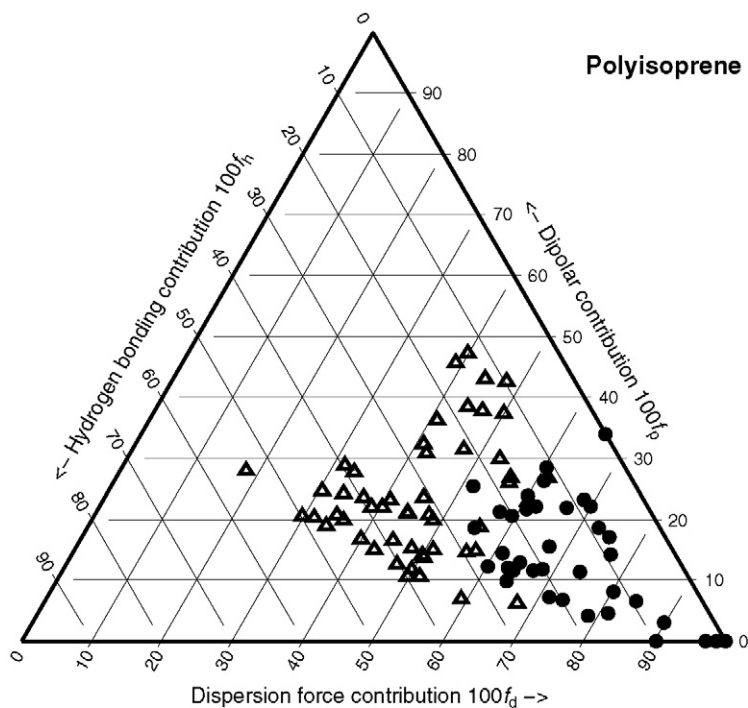


soluble: 71 105 117 120 123

borderline: 6 7 10 17 18 20 35 38 75

non-solvent: 1 2 3 4 5 9 15 19 33 37 39 44 46 47 48 49 51 61 63 64 67 74 77 78
87 88 98 102 110 114 121 127

FIGURE A3.5 Solubility of BEVA D-8 film. Data kindly provided by Dr Greg Smith and Classes of 2009, 2010 and 2011 of the Art Conservation Department at Buffalo State College.



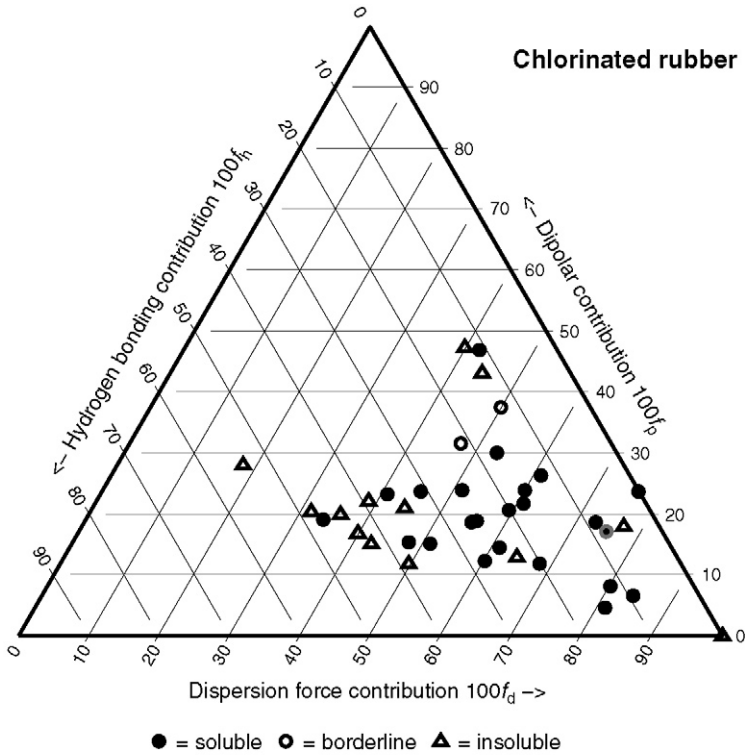
● = soluble ○ = borderline ▲ = insoluble

soluble: 1 3 6 7 8 10 13 14 16 17 18 19 20 22 23 26 27 28 29 30 32 33 49 51
53 66 67 68 69 72 73 101 111 112 113 121 122

borderline:

non-solvent: 34 35 36 37 38 39 40 41 42 47 54 55 57 61 62 63 64 70 71 74 75 76
78 79 80 81 82 83 84 87 88 89 90 91 92 93 94 95 96 98 99 100 102
103 106 110 115 117 120 123 127

FIGURE A3.6 Solubility of a high-molecular-weight *cis*-1,4-polyisoprene (Cariflex IR305; Shell). **Source:** Hansen (2007).

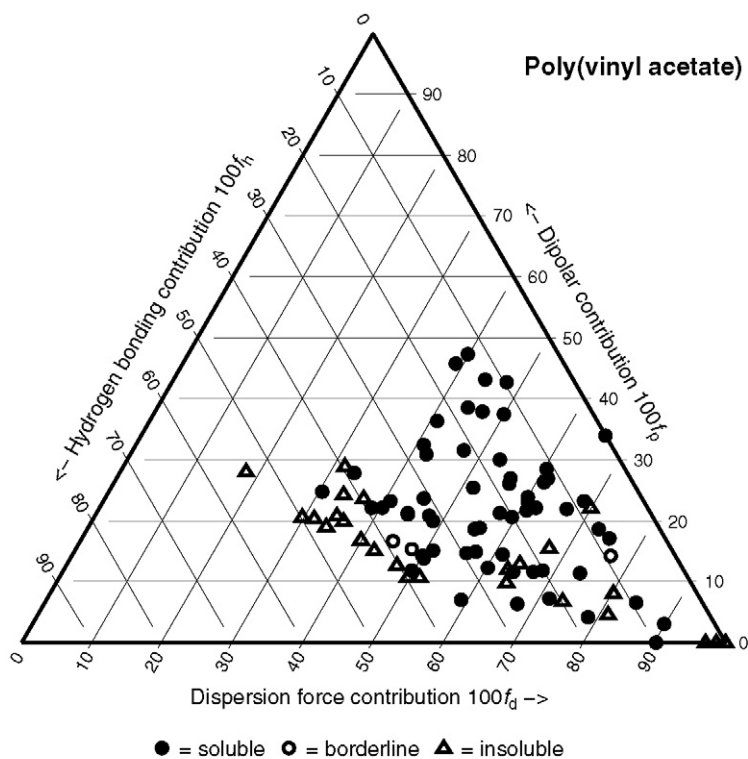


soluble: 7 8 14 17 20 21 23 28 33 37 39 40 46 47 49 51 60 64 66 67 71 88 101

borderline: 63 100

non-solvent: 1 15 30 38 54 75 76 78 83 87 98 99 127

FIGURE A3.7 Solubility of chlorinated rubber. **Source:** *Parker (1967)*.



soluble: 6 7 10 13 16 17 18 19 20 22 23 26 28 29 32 33 34 35 36 37 38 40 41
42 47 49 51 54 55 57 61 62 63 64 66 67 68 70 71 72 73 74 83 84 93
94 95 96 98 99 100 101 102 103 106 113 115 117 120 123

borderline: 39 80 122

non-solvent: 1 3 8 14 27 30 53 69 75 76 78 79 81 82 87 88 89 90 91 92 110 111
112 121 127

FIGURE A3.8 Solubility of poly(vinyl acetate) (Mowilith 50; Hoechst). **Source:** Hansen (2007).

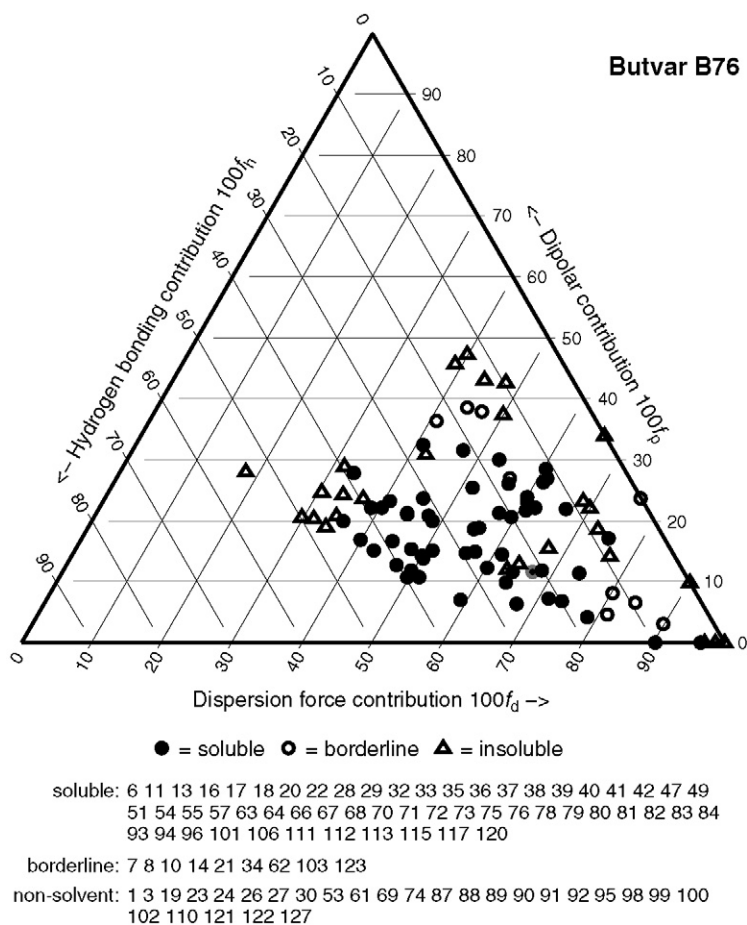


FIGURE A3.9 Solubility of medium-molecular-weight poly(vinyl butyral) with a low (11%) vinyl alcohol content (Butvar B-76; Monsanto). **Source:** Hansen (2007).

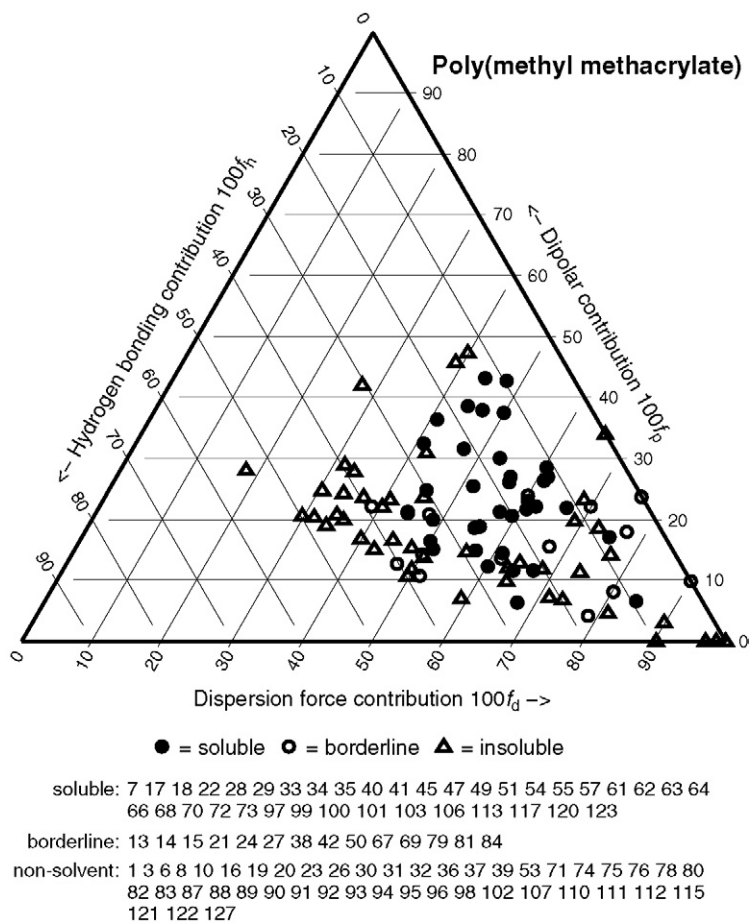
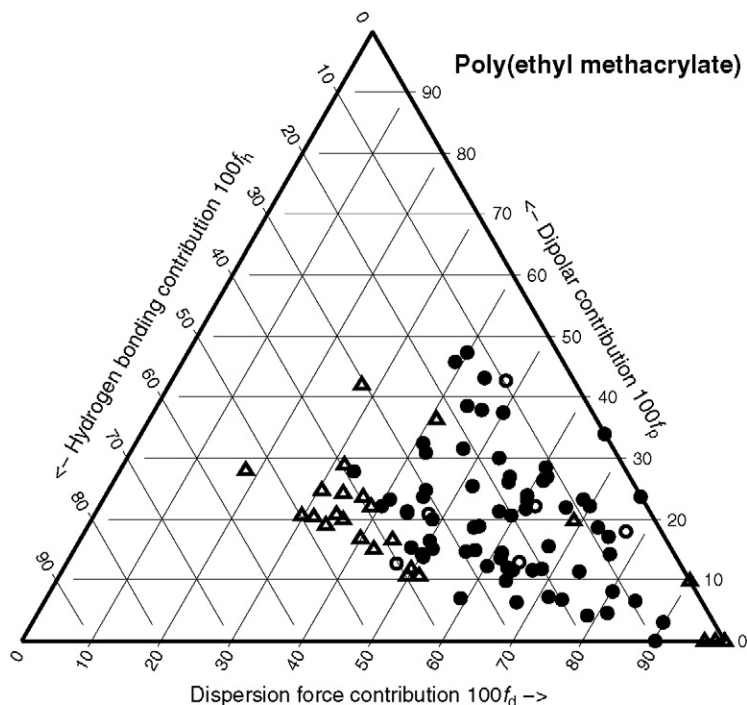


FIGURE A3.10 Solubility of poly(methyl methacrylate) (Rohm & Haas). **Source:** Hansen (2007).



● = soluble ○ = borderline ▲ = insoluble

soluble: 6 7 8 10 13 14 16 17 18 19 20 21 22 23 26 27 28 29 32 33 34 35 36
37 39 40 41 45 47 49 50 51 53 54 55 57 62 63 64 66 67 69 70 71 72
73 93 94 95 96 97 98 99 100 101 102 103 106 111 112 113 115 117
120 122

borderline: 15 30 42 61 68 79 84

non-solvent: 1 3 24 31 38 74 75 76 78 80 81 82 83 87 88 89 90 91 92 107 110

FIGURE A3.11 Solubility of poly(ethyl methacrylate) (Lucite 2042=Elvacite 2042; du Pont).

Source: Hansen (2007).

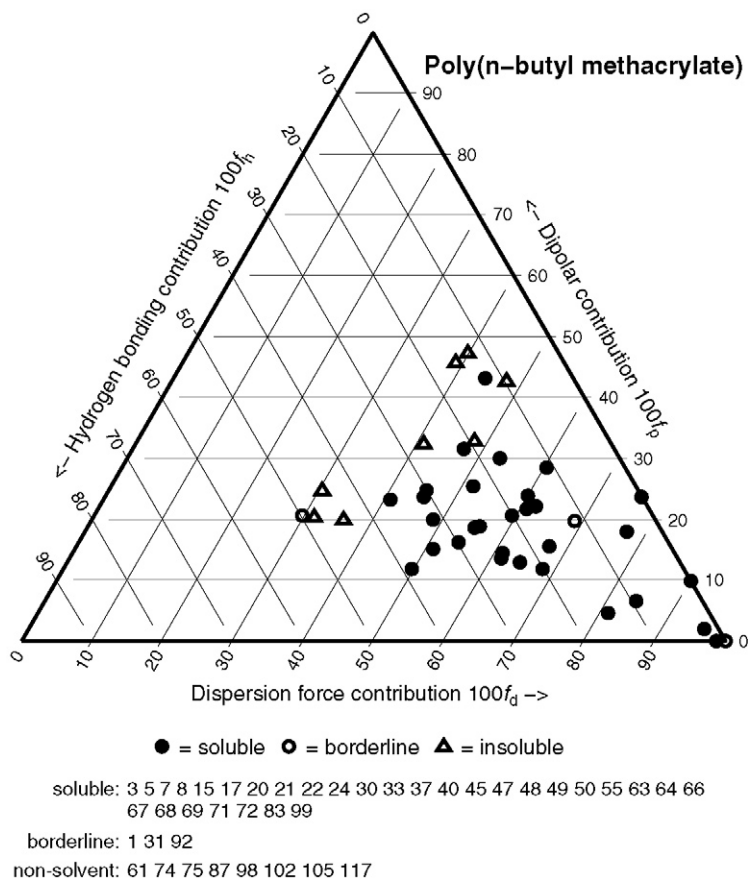
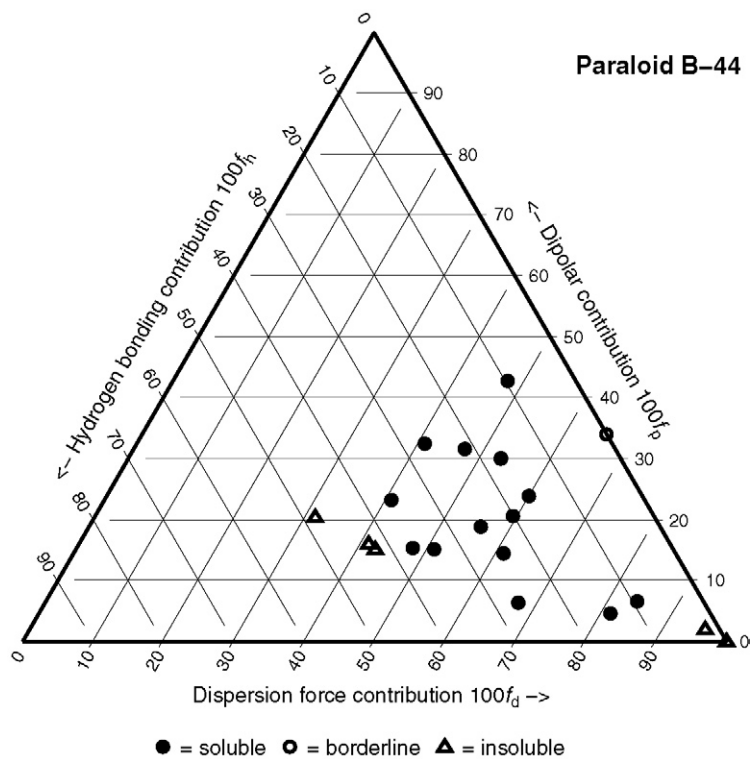


FIGURE A3.12 Solubility of poly(n-butyl methacrylate) (Elvacite 2044; du Pont), manufacturers' data. Solubility of poly(iso-butyl methacrylate) is similar.

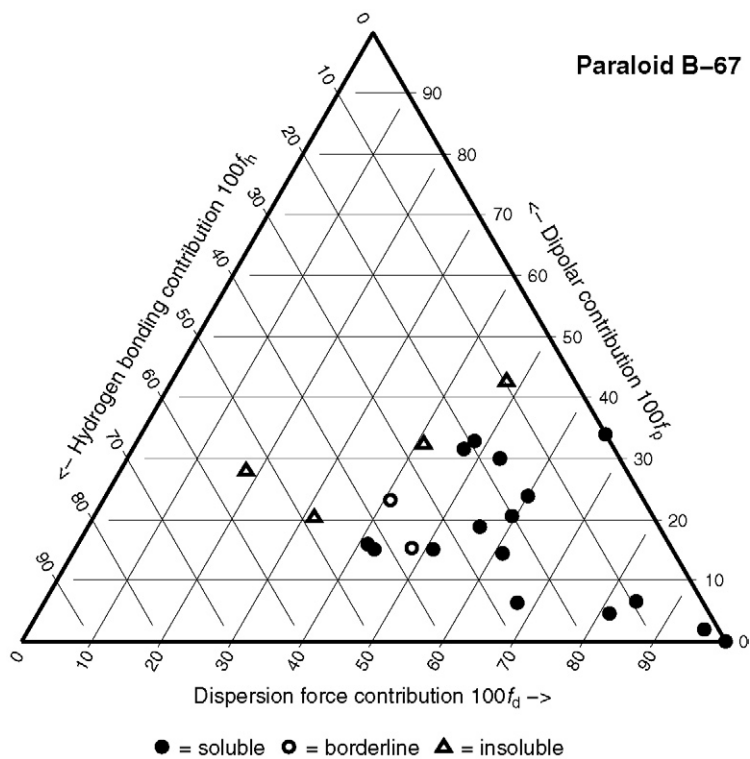


soluble: 7 9 17 35 37 39 40 47 49 61 63 64 67 117

borderline: 19

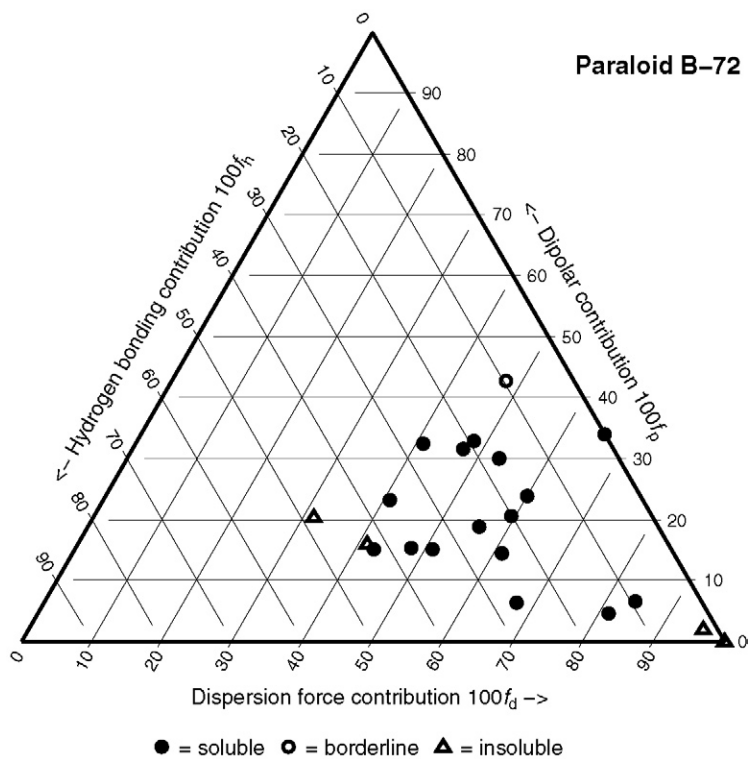
non-solvent: 2 5 77 78 87

FIGURE A3.13 Solubility of Paraloid B-44 (Rohm & Haas), manufacturers' data.



soluble: 2 5 7 9 17 19 35 40 47 49 63 64 67 77 78 105
borderline: 37 39
non-solvent: 61 87 117 127

FIGURE A3.14 Solubility of Paraloid B-67 (Rohm & Haas), manufacturers' data.



soluble: 7 9 17 19 35 37 39 40 47 49 63 64 67 78 105 117

borderline: 61

non-solvent: 2 5 77 87

FIGURE A3.15 Solubility of Paraloid B-72 (Rohm & Haas), manufacturers' data.

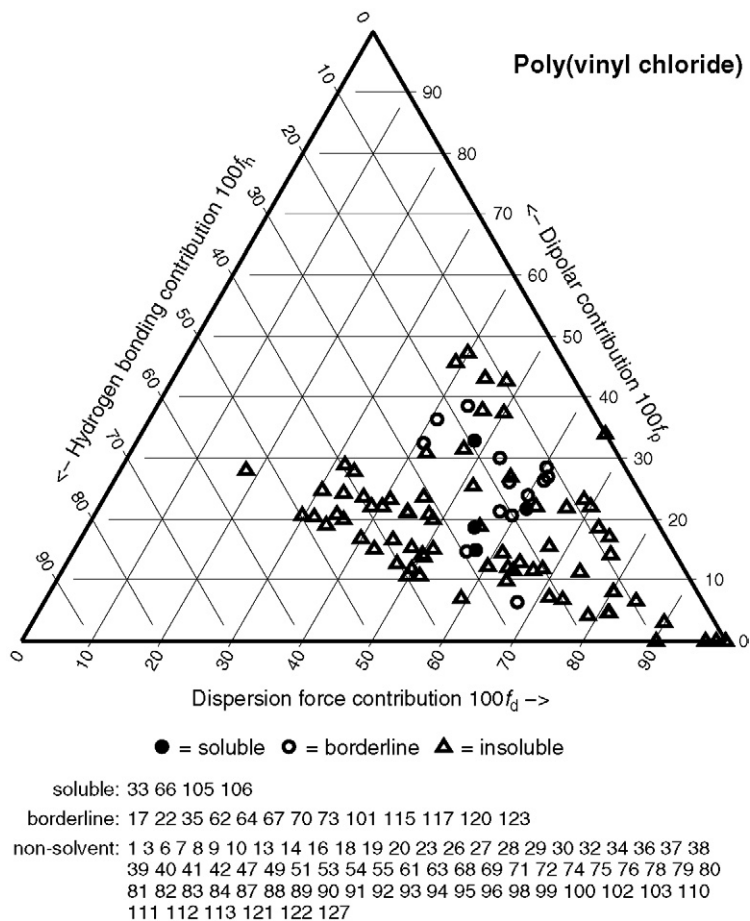
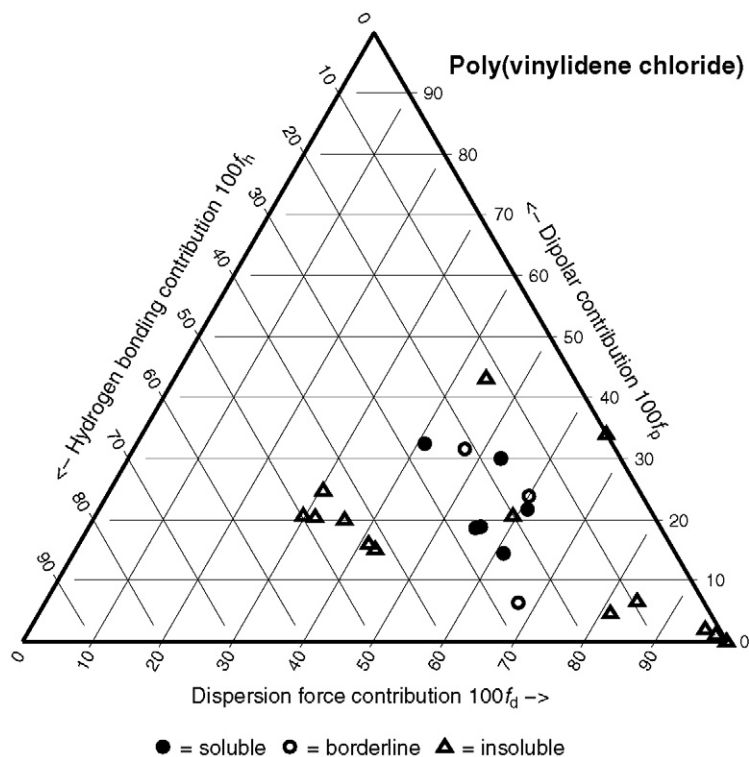


FIGURE A3.16 Solubility of poly(vinyl chloride) (Vipa KR; Montecatini). **Source:** Hansen (2007).



soluble: 33 47 49 64 66 117

borderline: 35 63 67

non-solvent: 2 4 5 7 9 17 19 74 75 77 78 87 92 99

FIGURE A3.17 Solubility of poly(vinylidene chloride/acrylonitrile) 70:30 (Saran F310; Dow Chemical). **Source:** Hansen (2007).

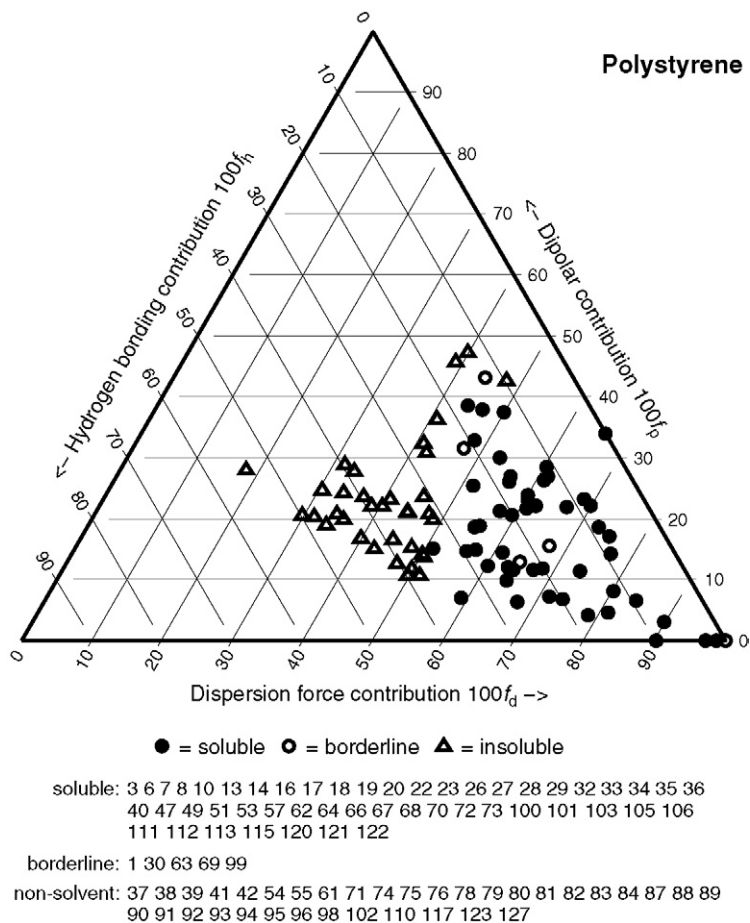


FIGURE A3.18 Solubility of polystyrene (Polystyrene LG; BASF). *Source:* Hansen (2007).

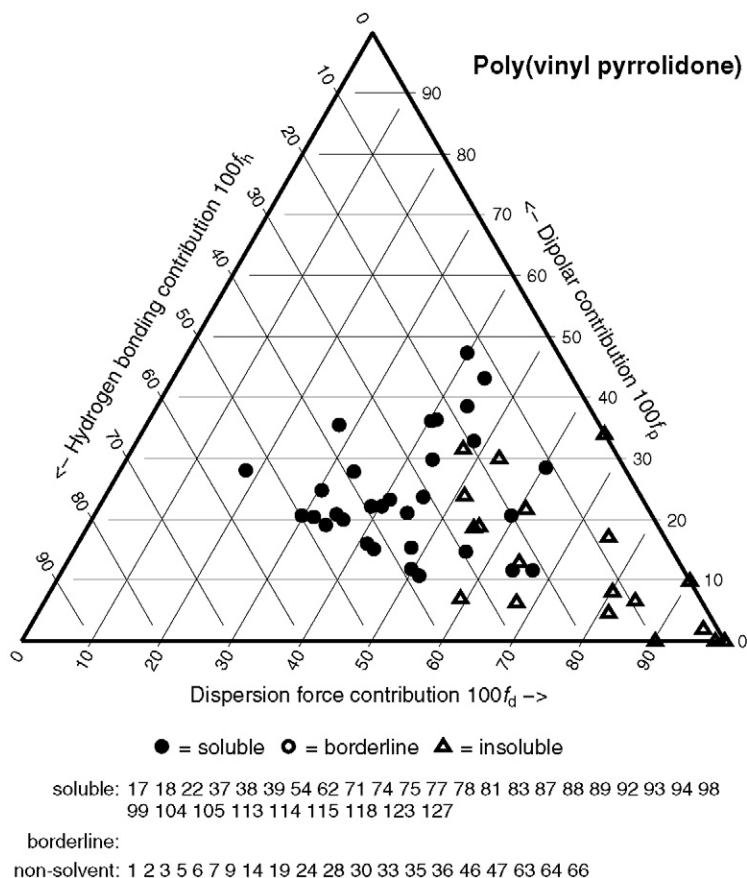


FIGURE A3.19 Solubility of poly(*N*-vinyl pyrrolidone) (GAF). **Source:** *Blecher et al. (1980).*

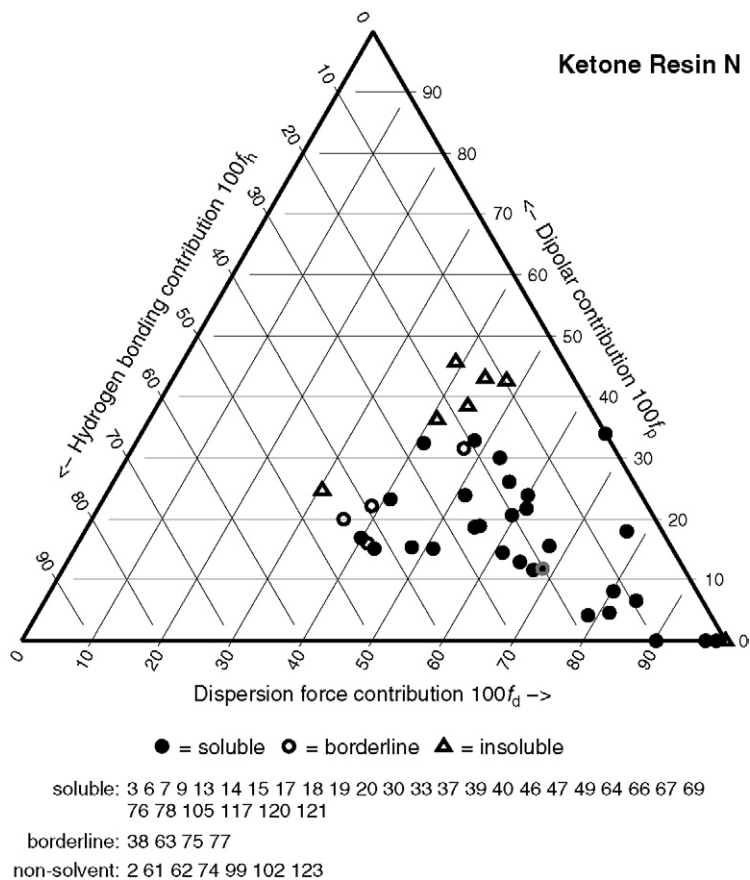
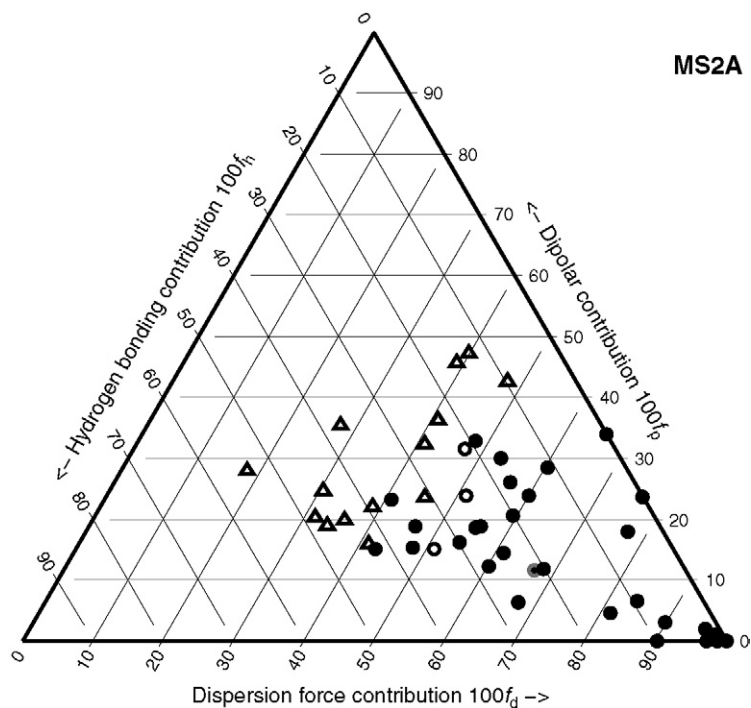


FIGURE A3.20 Solubility of a ketone resin (Ketone Resin N; BASF), manufacturers' data.



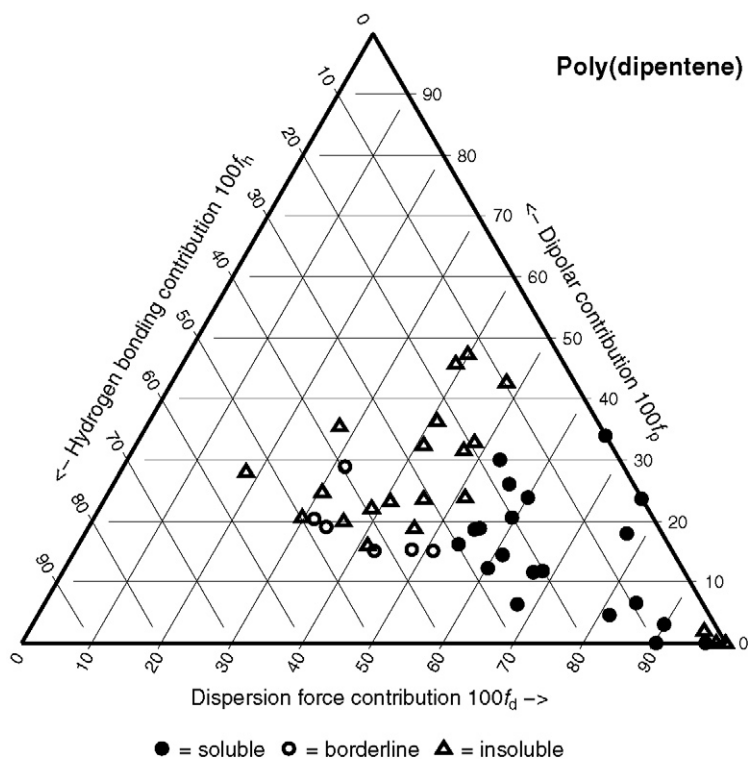
● = soluble ○ = borderline ▲ = insoluble

soluble: 1 2 3 4 5 6 7 9 10 15 17 18 19 20 21 22 33 35 37 39 44 47 48 49 51
64 67 78 105 120 121

borderline: 40 46 63

non-solvent: 38 61 71 74 75 77 87 88 98 102 114 117 123 127

FIGURE A3.21 Solubility of a ketone resin (MS2A; Linden). Data kindly provided by Dr Greg Smith and Classes of 2009, 2010 and 2011 of the Art Conservation Department at Buffalo State College.

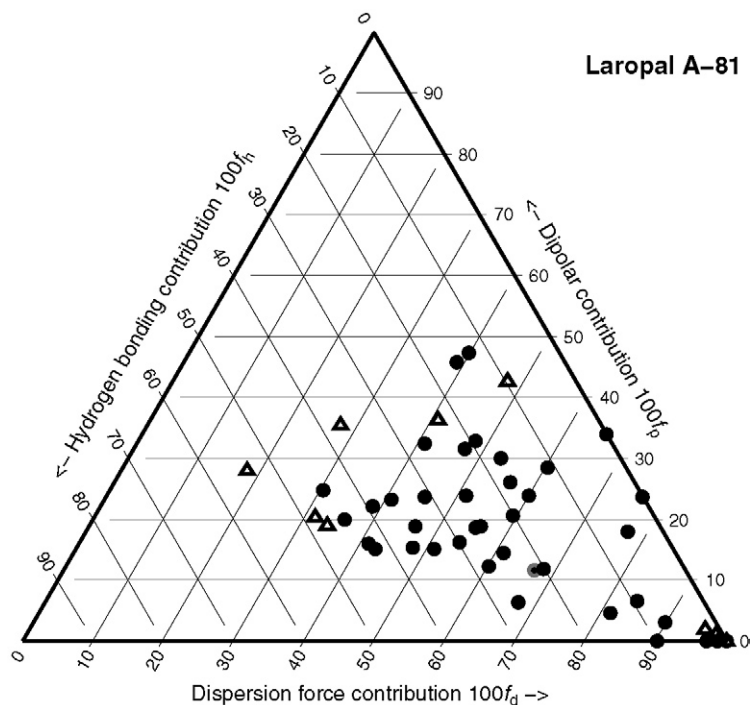


soluble: 6 7 9 10 15 17 18 19 20 21 33 35 47 48 49 51 64 67 120 121

borderline: 39 40 78 87 88 110

non-solvent: 1 2 3 4 5 37 38 44 46 61 63 71 74 75 77 92 98 102 105 114 117 123 127

FIGURE A3.22 Solubility of a poly(dipentene) used as a tackifier in picture lining adhesives (Zonarez 7085; Arizona Chemicals, manufactured 1975) (Beardsley, 1978). Data kindly provided by Dr Greg Smith and Classes of 2009, 2010 and 2011 of the Art Conservation Department at Buffalo State College.



● = soluble ○ = borderline ▲ = insoluble

soluble: 3 6 7 9 10 15 17 18 19 20 21 22 33 35 37 38 39 40 44 46 47 48 49
51 63 64 67 71 74 75 77 78 98 102 105 117 120 121

borderline: 2

non-solvent: 1 4 5 61 87 88 114 123 127

FIGURE A3.23 Solubility of a low-molecular-weight aldehyde resin (Laropal A 81; BASF). Data kindly provided by Dr Greg Smith and Classes of 2009, 2010 and 2011 of the Art Conservation Department at Buffalo State College.

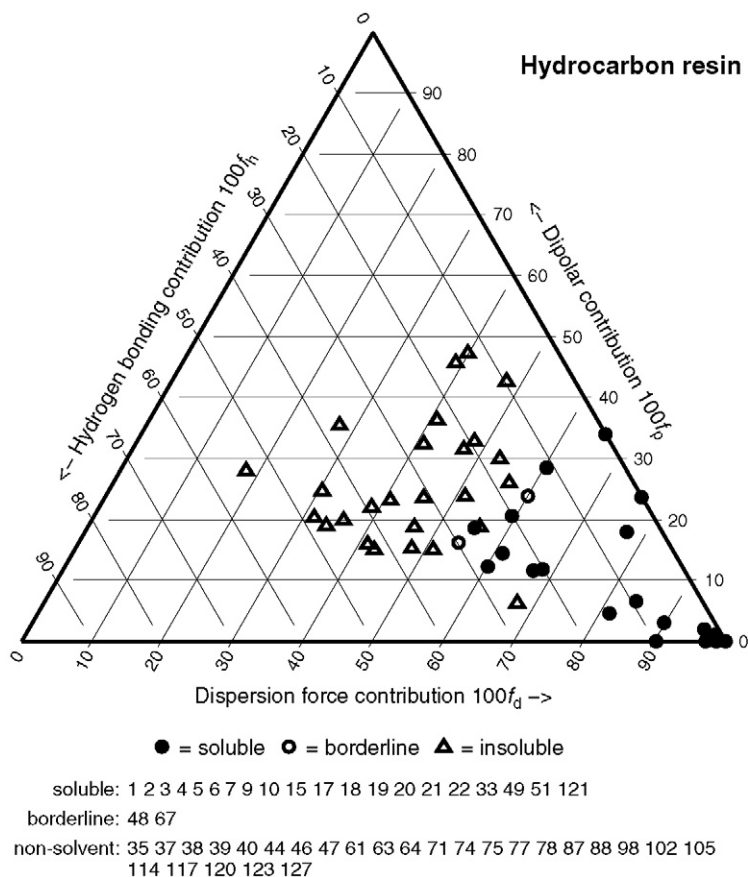
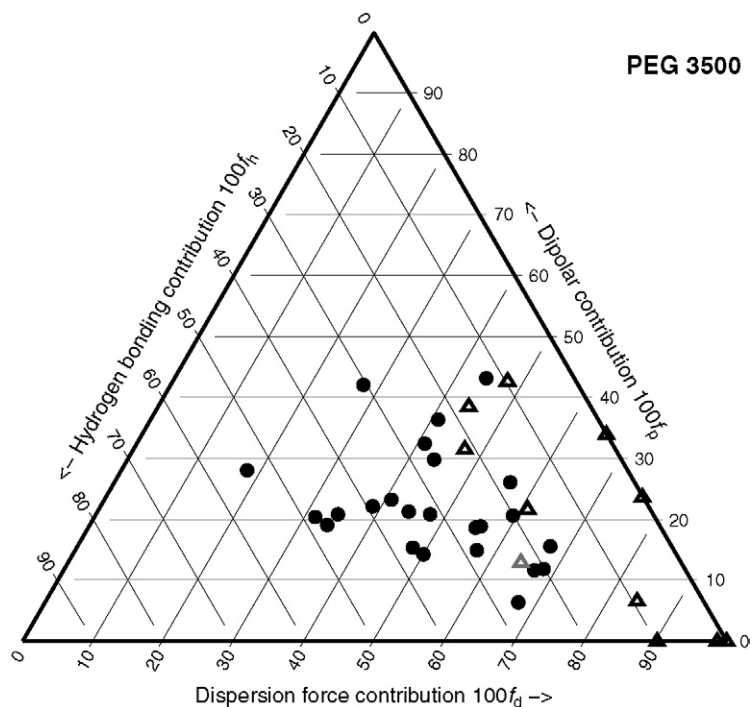


FIGURE A 3.24 Solubility of a low-molecular-weight hydrocarbon resin (Regalrez 1094; Eastman). Data kindly provided by Dr Greg Smith and Classes of 2009, 2010 and 2011 of the Art Conservation Department at Buffalo State College.



● = soluble ○ = borderline ▲ = insoluble

soluble: 17 18 20 33 35 37 38 39 41 42 47 69 84 87 88 89 99 106 107 117
118 120 123 127

borderline:

non-solvent: 2 3 6 7 19 21 30 61 62 63 66

FIGURE A3.25 Solubility of poly(ethylene glycol) (Carbowax PEG 3350; Union Carbide).

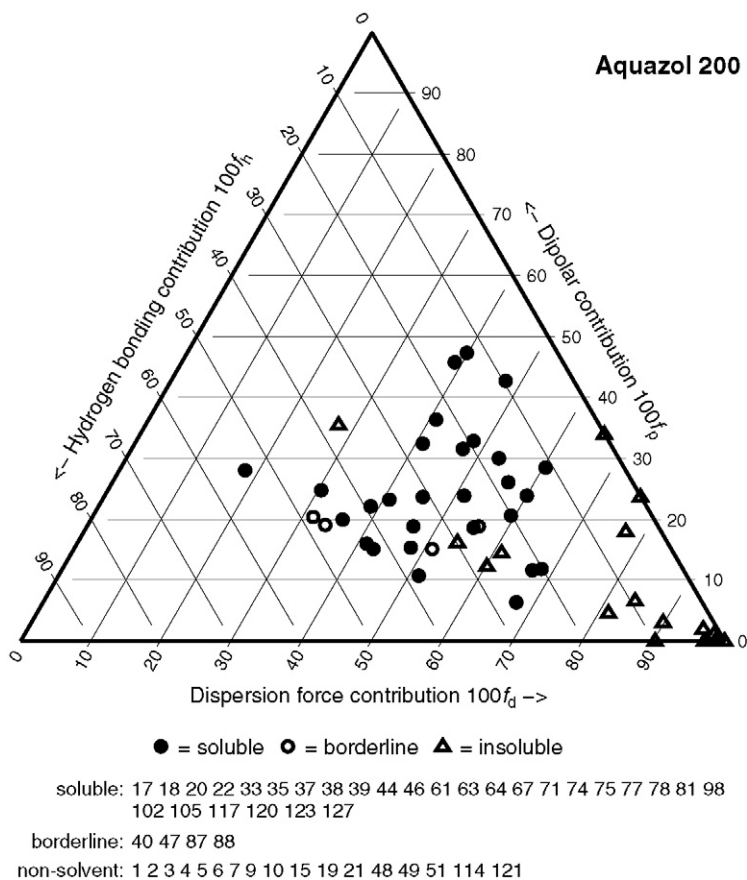
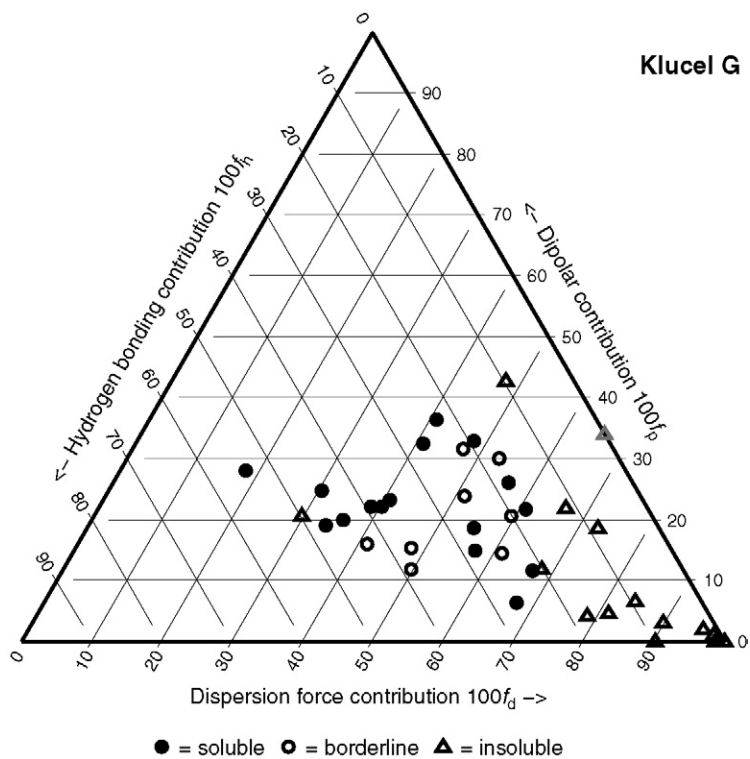


FIGURE A3.26 Solubility of poly(2-ethyl-2-oxazoline) (Aquazol 200; Polymer Chemistry Innovations). Data kindly provided by Dr Greg Smith and Classes of 2009, 2010 and 2011 of the Art Conservation Department at Buffalo State College.



soluble: 18 33 35 37 38 66 74 75 88 94 105 106 117 120 123 127

borderline: 17 39 46 49 63 64 77 83

non-solvent: 1 3 4 5 6 7 9 10 13 19 20 23 29 61 92

FIGURE A3.27 Solubility of hydroxypropyl cellulose (Klucel G; Hercules), manufacturers' data.

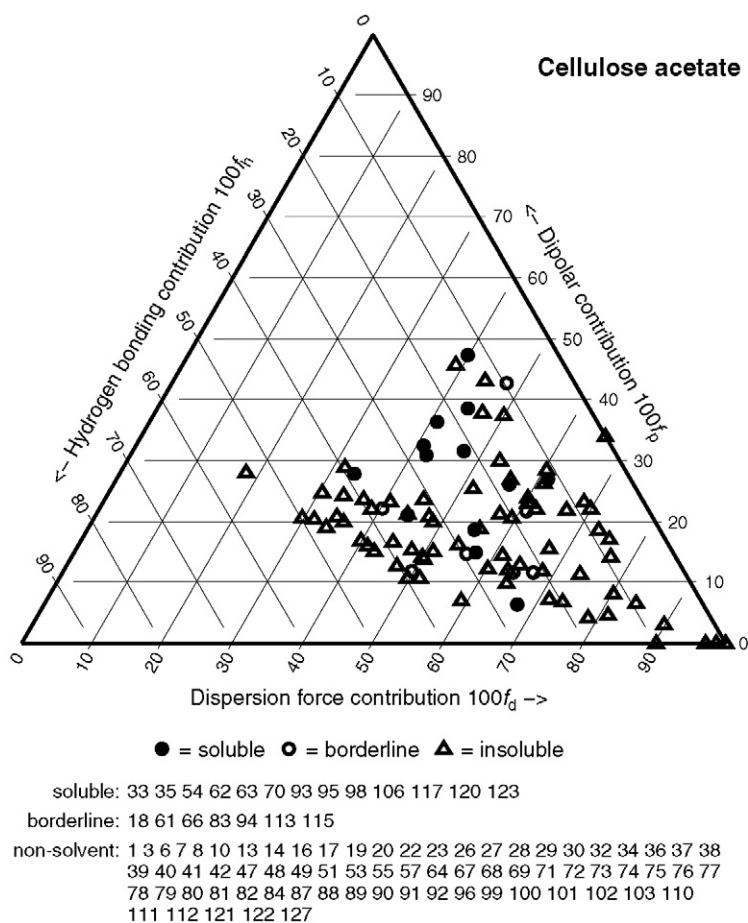


FIGURE A3.28 Solubility of medium-molecular-weight cellulose acetate. **Source:** Hansen (2007).

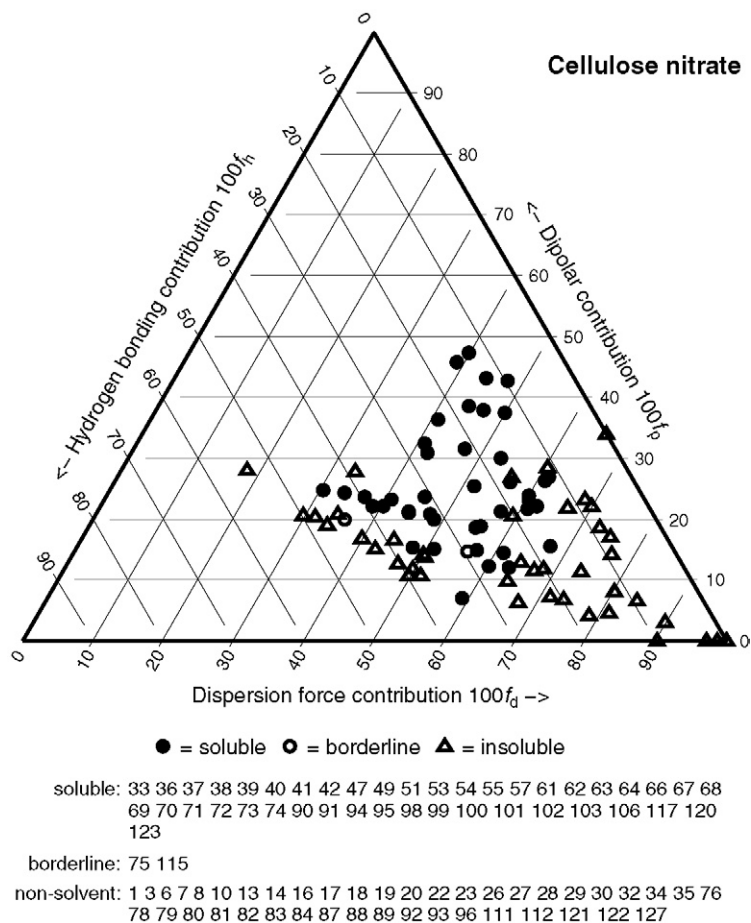


FIGURE A3.29 Solubility of medium-molecular-weight cellulose nitrate, half second grade.

Source: Hansen (2007).

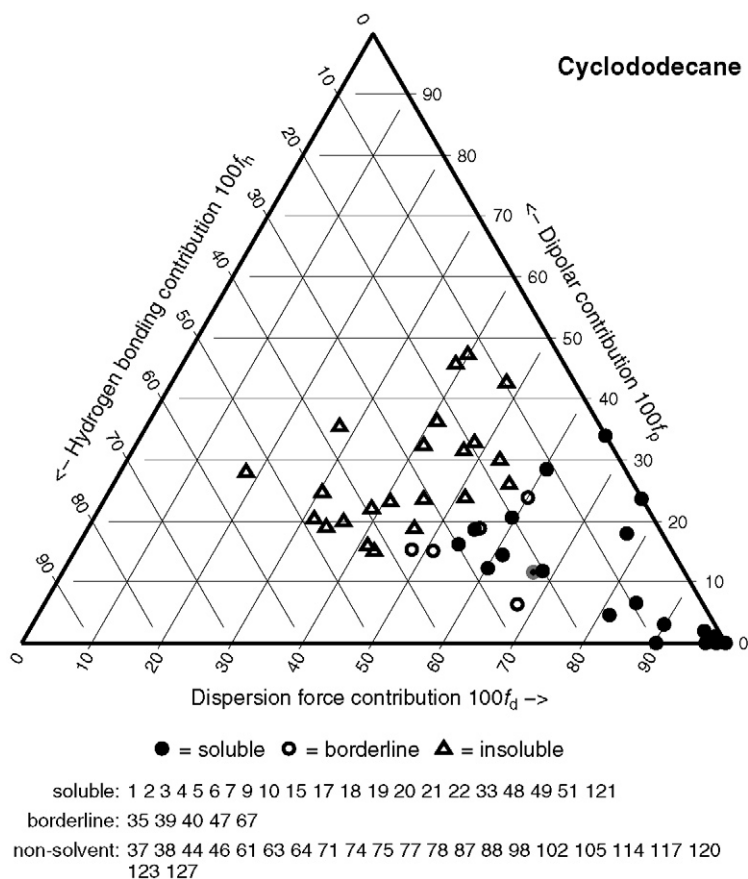
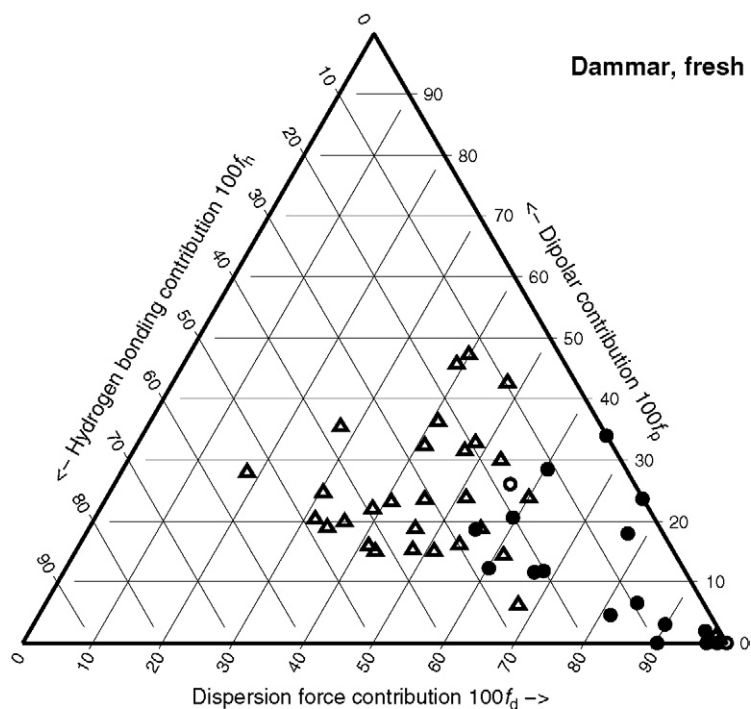


FIGURE A3.30 Solubility of cyclododecane. Data kindly provided by Dr Greg Smith and Classes of 2009, 2010 and 2011 of the Art Conservation Department at Buffalo State College.



● = soluble ○ = borderline ▲ = insoluble

soluble: 3 5 6 7 9 10 15 17 18 19 20 21 22 33 51 121

borderline: 1 2 120

non-solvent: 4 35 37 38 39 40 44 46 47 48 49 61 63 64 67 71 74 75 77 78 87 88
98 102 105 114 117 123 127

FIGURE A3.31 Solubility of fresh dammar. Data kindly provided by Dr Greg Smith and Classes of 2009, 2010 and 2011 of the Art Conservation Department at Buffalo State College.

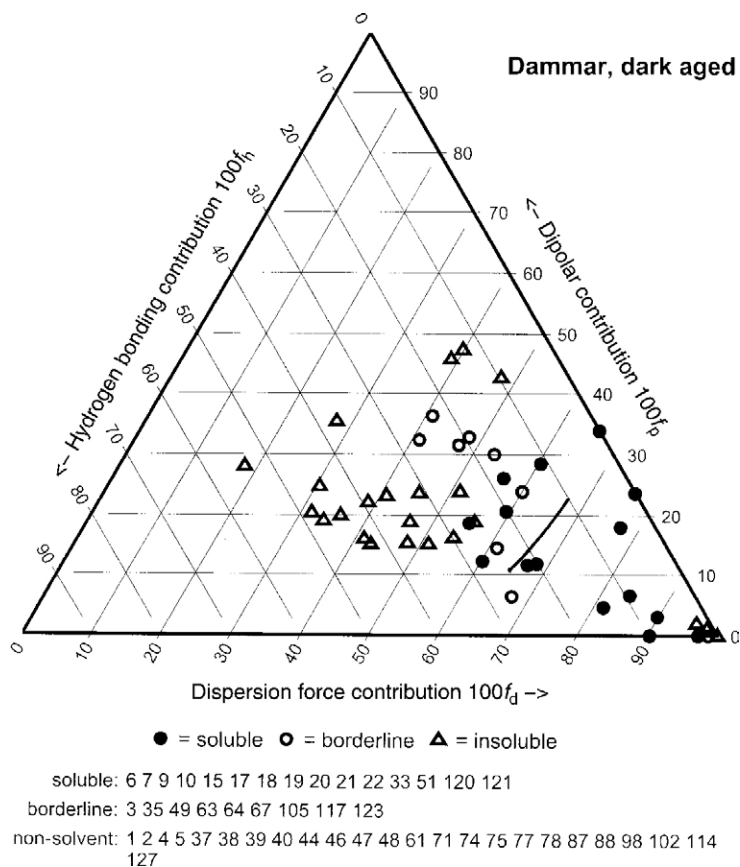
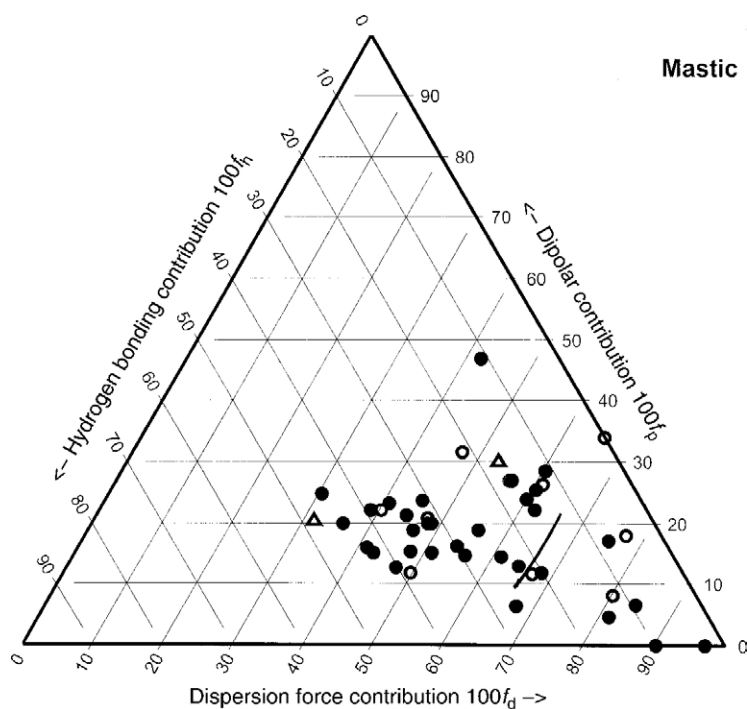


FIGURE A3.32 Solubility of dark aged dammar. — indicates the approximate limit of solubility when exposed to light and oxidation equivalent to 100 years on a gallery wall (Feller and Curran, 1975 of A3.33). Data kindly provided by Dr Greg Smith and Classes of 2009, 2010 and 2011 of the Art Conservation Department at Buffalo State College.



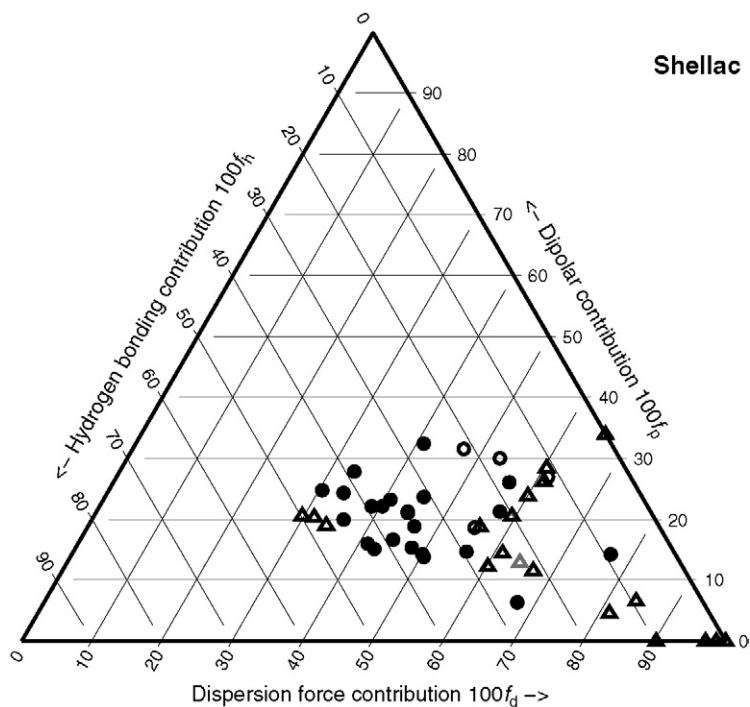
● = soluble ○ = borderline ▲ = insoluble

soluble: 6 7 9 20 22 28 30 34 35 37 38 39 40 41 43 44 47 48 49 59 60 65 67
68 71 74 75 77 78 79 115 121

borderline: 14 15 18 19 42 55 63 83 94 101

non-solvent: 64 87

FIGURE A3.33 Solubility of mastic. — indicates the approximate limit of solubility when exposed to light and oxidation equivalent to 100 years on a gallery wall (Feller and Curran, 1975).
Source: Mantell *et al.* (1942).



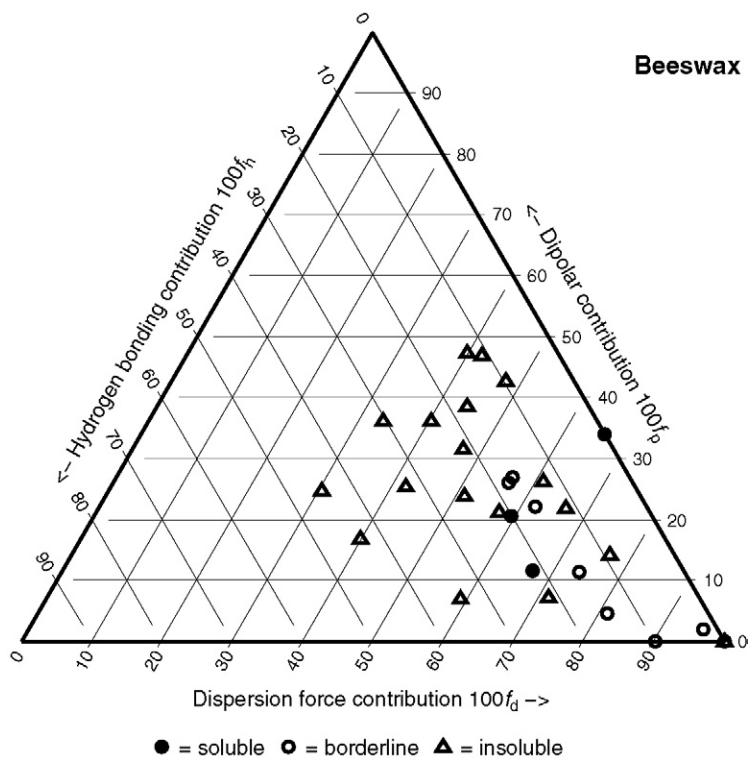
● = soluble ○ = borderline ▲ = insoluble

soluble: 35 37 38 39 41 44 54 71 73 74 75 77 78 80 84 90 93 94 96 115 117
120 122

borderline: 33 63 64 70

non-solvent: 1 3 6 7 9 17 18 19 22 30 47 49 51 67 87 88 92 101 121

FIGURE A3.34 Solubility of shellac. **Source:** *Russell (1965).*

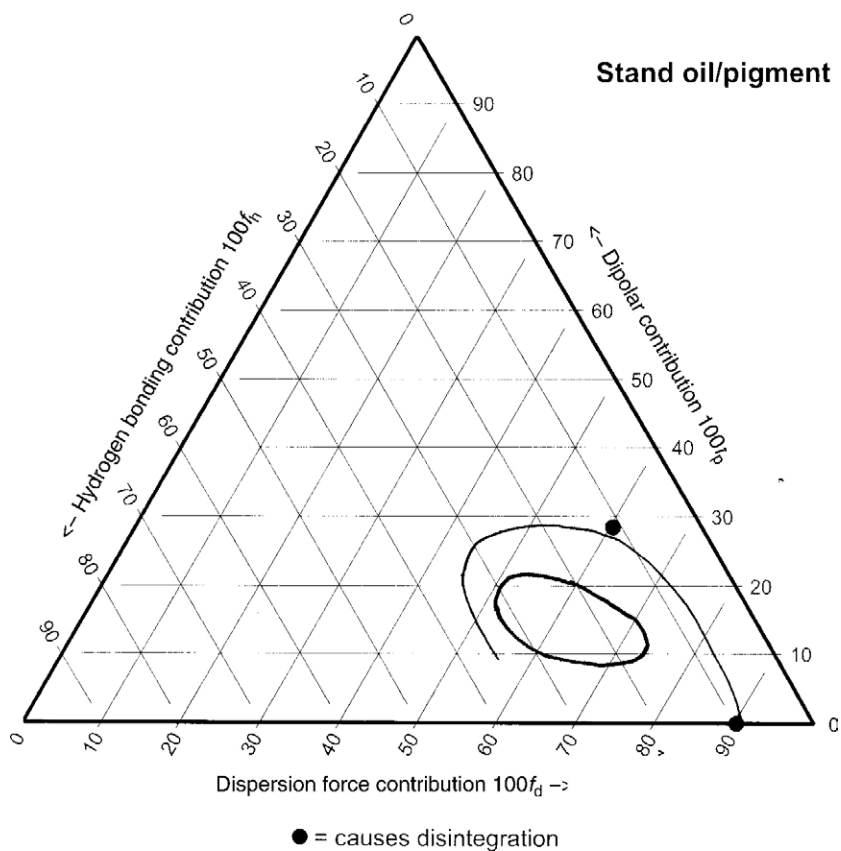


soluble: 17 18 19

borderline: 2 5 6 8 16 65 68 120

non-solvent: 1 29 32 36 46 60 61 62 63 73 74 76 98 101 104 116 119 122 126

FIGURE A3.35 Solubility of beeswax.



solvents causing disintegration: 6 22

FIGURE A3.36 Swelling behaviour of polymerized linseed oil films, open pot stand oil (19%) and white lead pigment (81%), aged at 32 °C. Contours are shown at 60% swelling for a film aged 27 weeks (—) and a film aged 14 years (—). The older film is obviously more resistant to swelling and is less affected than the younger film by low-polarity solvents. **Sources:** *Stolow (1956, 1957).*

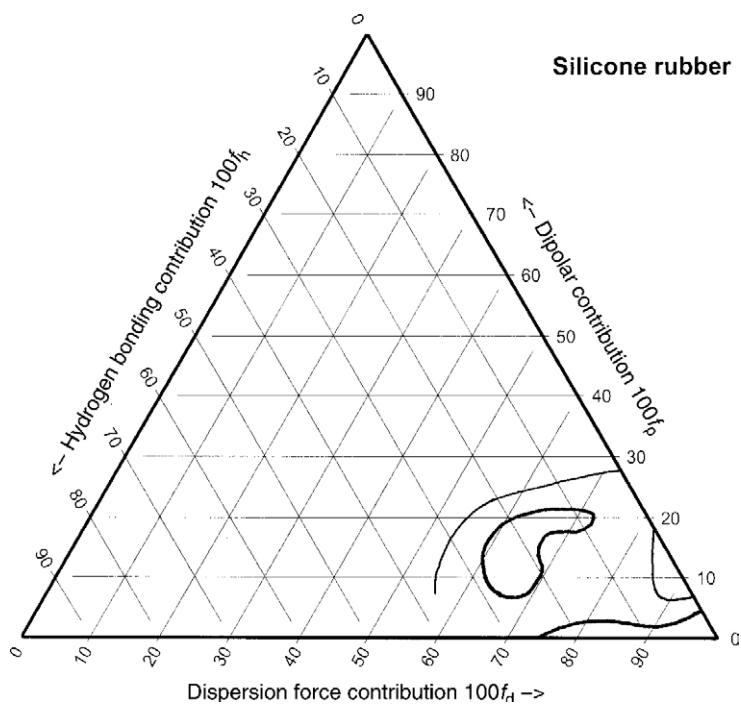


FIGURE A3.37 Swelling behaviour of a silicone rubber (GAF 3; Rhone-Poulenc). Contours are shown at 150% (—) and 300% (---) swelling in solvent.

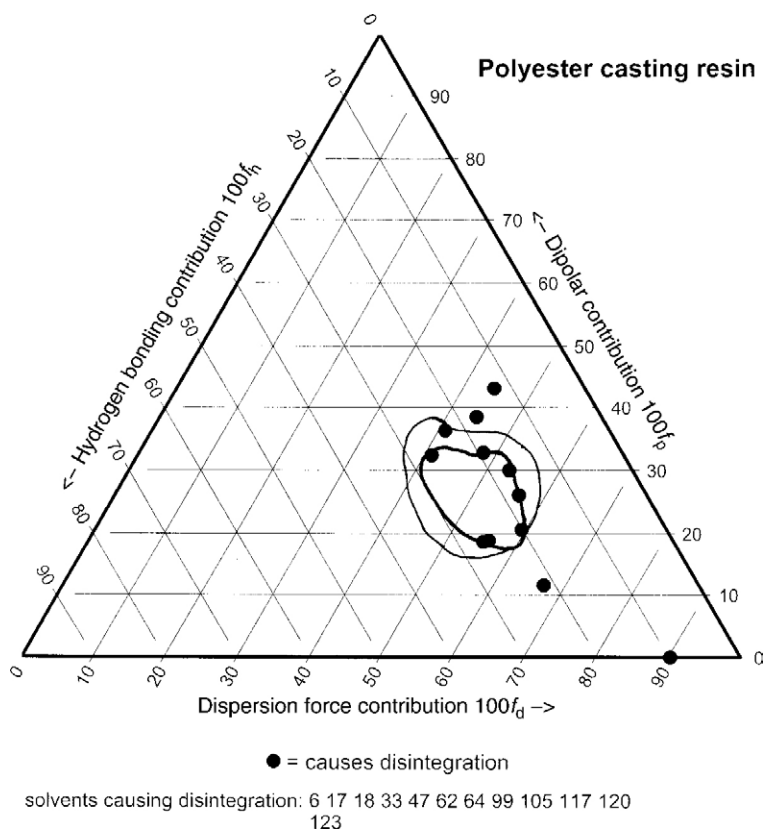


FIGURE A3.38 Swelling behaviour of a polyester casting resin (Polymaster; Warwick). Contours are shown at 50% (—) and 100% (—) swelling in solvent.

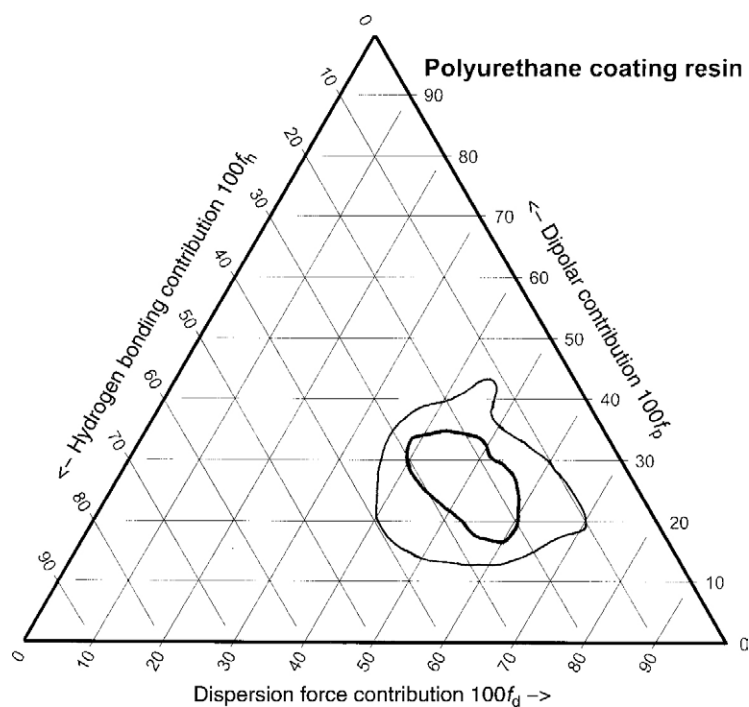
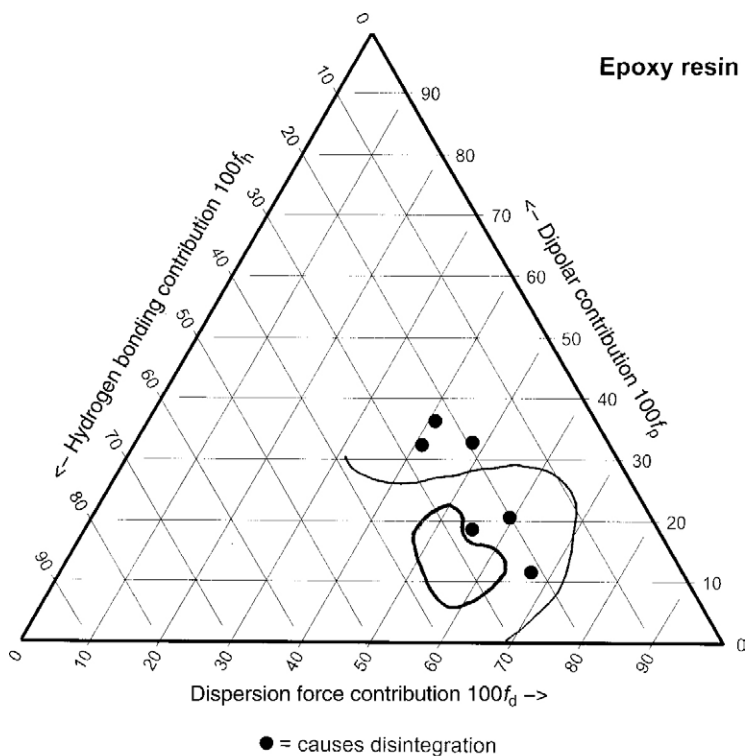
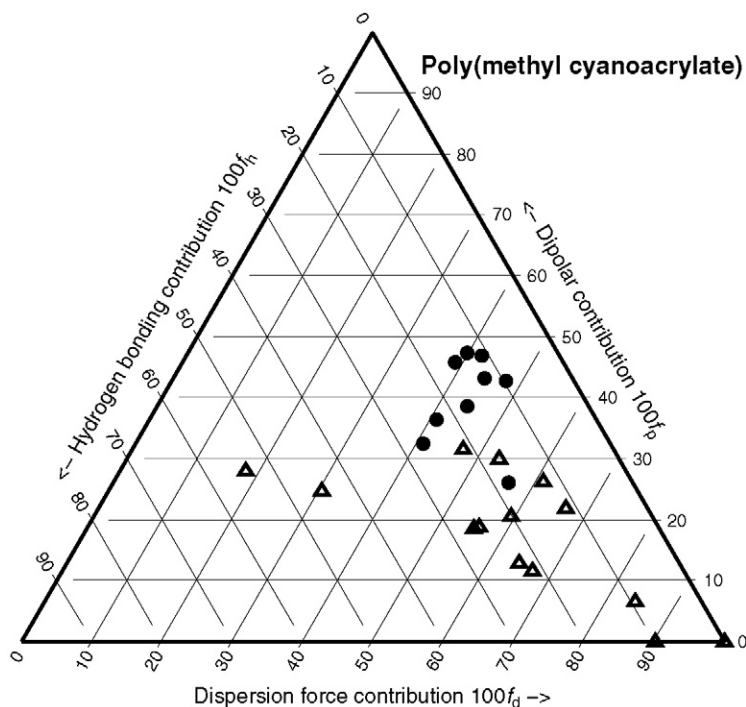


FIGURE A3.39 Swelling behaviour of a polyurethane coating resin (Viacryl/Desmodur). Contours are shown at 100% (—) and 200% (—) swelling in solvent.



solvents causing disintegration: 17 18 33 105 117 123

FIGURE A3.40 Swelling behaviour of an epoxy resin (Araldite AY103/HY951; Ciba-Geigy). Contours are shown at 20% (—) and 40% (—) swelling in solvent.



soluble: 60 61 62 98 99 102 117 120 123

borderline:

non-solvent: 1 6 7 17 18 29 30 33 47 63 64 74 101 127

FIGURE A3.41 Solubility of poly(methyl 2-cyanoacrylate). **Source:** Donnelly and Pepper (1981).

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Glossary

The precise and consistent use of language aids communication. Indeed, the vocabulary one uses defines the concepts one is able to conceive then express. Most technical vocabularies grew out of common language, adapting words to specialized meanings. For instance, in common English, ‘stress’ and ‘strain’ are used interchangeably for the effect of pulling. However, in mechanics, stress is defined as the force applied to a material and strain is defined as the resultant extension in the material. One needs to be clear to oneself, then to any reader, what range of meaning is being applied. English tends to use the same word for all parts of an application. For instance, ‘coating’ is used for the liquid applied to a surface, the solid material formed after setting and the process of applying the liquid. One can be led, and can lead others, into confusion by assuming that the single word ‘coating’ describes a single underlying concept or physical attribute, when there are at least three.

Disciplines advance by distinguishing concepts in finer detail, defining them and giving them special names. In every subject, the definition and term (signifier) develop as understanding of the concept evolves. Frequently, in each discipline, there are a number of competing standards of terminology and one must be clear which of these one is using. For instance, there are national variants of the IUPAC chemical naming conventions. It is good practice to state in a report what terminology standard one is using. This is especially important when using specialist terms or abbreviations, which should be separately defined if there is potential for confusion.

Conservation is beginning to develop its own specialist vocabulary (Horie and Tzanne, 2001), which needs to be agreed if it is to be useful for communication (prEN 15898, 2010). A useful general dictionary is Lackie (2007). The following list is derived from a number of sources and is based on the glossary for the ‘Adhesives for Conservators’ course developed by the Foundation of the American Institute for Conservation of Historic and Artistic Works (2005). Its aim is to provide a common vocabulary when using this book. Although many of the definitions are based on industrial and scientific usage, some have been modified to reflect conservation practice where this has specific concept.

Term	Definition	Note
Adhere	Two surfaces adhere when they are held together by an adhesive.	Deprecated term: stick or glue.
Adherend	An adherend is a body that is held to another body by an adhesive.	Substrate is a broader term.
Adhesion	Adhesion is the state in which two surfaces are held together by interfacial forces.	Adhesion acts between a substrate and a coating, adhesive or consolidant.
Adhesive	An adhesive is a substance that holds two surfaces together by interfacial forces.	The adhesive in place should be distinguished from the liquid material which sets to form the adhesive.
Adhesive failure	Adhesive failure is the rupture of the adhesive bond, such that the separation appears to occur at the adhesive/adherend interface.	
Ageing	Ageing is the combination of the irreversible changes in the properties of a material which occur with the passage of time.	
Artificial ageing	Artificial ageing is the exposure of a material to laboratory conditions in order to study the changes on ageing.	The environmental conditions are usually increased, in time or intensity, over that experienced by the material in normal use.
Batch	A batch of a product is the result of a single making of a formulation.	It is expected that there will be little variation between samples taken from the same batch, with significantly more batch-to-batch variation.
Binder	The binder in a liquid coating is the solid polymer component of the medium.	A liquid coating might be made up of pigments, dyes, a binder and solvents.
Blocking	Blocking is the unwanted adhesion of two surfaces.	Blocking can occur in books whose pages have been reinforced using a consolidant with too low a glass transition temperature.

Term	Definition	Note
Blooming	Blooming is the unwanted deposit on the surface of a film usually rising from within the film or by chemical reaction between the film and the environment.	For example, some oils contain waxes that separate and appear on the surface as the film sets.
Blushing	Blushing occurs as a milky opalescence within a film of lacquer.	Blushing can occur when a liquid coating absorbs water from the environment or object, causing the dissolved polymer to precipitate.
Bond	To bond two adherends is to join them with an adhesive.	Deprecated term: glue.
Bond line	The bond line is the layer of adhesive that attaches the two adherends.	
Bond strength	The bond strength is the force needed to break an adhesive assembly with failure occurring near the plane of the bond line.	
Casein adhesive	A casein adhesive is an aqueous dispersion of casein, compounded with other reactants, especially alkalis.	
Catalyst	A catalyst is a substance that changes the rate of a chemical reaction but is not changed by the reaction.	
Chain polymerization	Chain polymerization is the growth of a polymer by successive reaction of a monomer with a reactive site on the growing chain, with a reactive site being regenerated.	This results commonly from a free radical, but also ionic, reaction.
Chain scission	Chain scission is a chemical reaction resulting in the breaking of the main chain bonds.	
Chalking	Chalking is the appearance of a loosely adherent powder on a film resulting from the degradation of the binder.	

Continued

(continued)

Term	Definition	Note
Coating	A coating is a continuous layer formed after application of a coating material to a substrate.	Narrower terms: varnish, lacquer, paint.
Coating material	A coating material is a product that, when applied to a substrate, forms a film with specific properties.	Most coating materials are liquids that form a liquid film. However, some materials are applied as vapours to form a solid film. Narrower terms: varnish, lacquer.
Cohesion	Cohesion is the state in which the particles of a substance are held together by primary or secondary valence forces.	
Cohesive failure	Cohesive failure is the loss of cohesion within the body of a material.	Cohesive failure can take place in the adhesive, termed cohesive failure of the adhesive, or in the adherend, termed cohesive failure of the adherend.
Collagen	Collagen is the major fibrous protein making up bone and skin.	Degraded collagen is the major component of glue and gelatine.
Consolidant	A consolidant is a solid material that changes the properties of a porous object by filling the pores or joining the particles.	A consolidant is usually used for strengthening, but can also change the optical properties or the hydrophobicity.
Consolidant material	A consolidant material infiltrates a porous substrate then sets to form a consolidant.	
Consolidation	Consolidation is a treatment designed to change a porous substrate by incorporating a consolidant.	
Contact adhesive	A contact adhesive has the property of auto adhesion.	
Copolymer	A copolymer is composed of more than one type of monomer.	This term might be elaborated, like terpolymer (three monomers). See <i>Polymer</i> .

Term	Definition	Note
Creep	Creep is the time-dependent strain in an adhesive resulting from a sustained stress.	
Cross-link	A cross-link is a part of the polymer molecule where at least four chains emanate.	The cross-link is usually formed by covalent bonds, but may result from weaker chemical interactions, such as hydrogen bonds. The result of many cross-links is a three-dimensional network.
Cure	When a liquid cures to form a solid material, it sets as a result of a chemical reaction.	
Curing	Curing is the increase in molecular size by chemical reaction.	For example, linseed oil cures by polymerization to form a solid film.
Curing agent	A curing agent is an additive to a liquid material that promotes curing by taking part in the reaction.	For example, styrene forms cross-links during the curing of a polyester resin.
Curing temperature	The curing temperature is the temperature to which the adhesive must be heated to cure the adhesive.	
Curing time	The curing time is the time necessary during which an assembly is subjected to heat to cure the adhesive.	The time will vary with the temperature of cure which should be stated, e.g. room temperature, 40 °C, etc.
Deformation	A material is deformed when its shape has been changed.	The change of shape can be reversible or irreversible.
Degradation	Degradation occurs when a large molecule is broken into smaller molecules by chemical reactions.	For example, collagen is degraded in the process of forming gelatine.
Delamination	Delamination is the separation of layers in a laminate because of the failure of the adhesive, either in the adhesive itself or at the interface of the adhesive and adherend.	

Continued

(continued)

Term	Definition	Note
Depolymerization	Depolymerization is the process of converting a polymer into a monomer.	Not to be confused with degradation. For instance, PMMA can be converted back to its monomer by heating.
Dirt pick-up	Dirt pick-up is the tendency of a dry film to attract soiling material to its surface.	The soiling may be resting on the surface, and so be more or less removable, or be retained within the structure of the film.
Dirt retention	Dirt retention is the tendency of a dry film to attract and hold soiling material on or in its surface.	
Dispersion	A dispersion is a two-phase system in which one phase is particles suspended in another phase.	Both the dispersed and continuous phases can be solids, liquids or gases (except one cannot have a gas/gas dispersion). Smoke, beaten egg whites and dispersion adhesives are all dispersions.
Distortion	A material suffers distortion when its shape has been changed more than it can recover elastically.	
Dry	When a liquid dries to form an adhesive, consolidant or coating, it sets as a result of loss of solvent.	
Drying time	The drying time is the period of time during which a liquid material on a substrate is allowed to dry.	This is often assessed by the loss of tack to a finger (or thumb).
Elasticity, modulus of	The modulus of elasticity is the ratio of stress to strain when a material is deformed elastically.	Young's modulus applies to tensile forces. Compression, torsion strains, etc. also have elastic moduli.
Elastomer	An elastomer is a polymer that returns rapidly to approximately its initial dimensions and shape after a substantial deformation by a weak stress and release of the stress at room temperature.	

Term	Definition	Note
Emulsion	An emulsion is a stable two-phase system in which small droplets of one liquid (the internal phase) are dispersed in a second continuous liquid phase (the extended phase).	Deprecated: latex.
Failure	The failure of a joint occurs when the adherends separate totally or in part.	Failure can occur in the adherend, in the adhesive or at the interface.
Fill	A fill is a replacement of a missing piece of an object.	
Filler	A filler is a solid material used to modify the properties of an adhesive or gap-filler.	Fillers may be used to increase strength or weatherability, reduce weight, etc.
Film	A film is a layer of applied material.	A film could be the result of applying a liquid adhesive, a coating material or a liquid consolidant, from initial application to a final solid state. Film is used in other contexts to mean a thin flexible polymer sheet.
Flash point	The flash point is the lowest temperature at which a product emits sufficient vapour to be ignited by a source of ignition.	A measured flash point depends on the condition of test.
Flow	Flow is the movement of a liquid before it sets or gels.	
Gap-filling adhesive	A gap-filling adhesive bridges the existing space between two adherends.	
Gel	A gel is a polymer highly swollen with a liquid.	
Gel point	The gel point is reached during the transition from liquid to solid when the film starts to exhibit elastic properties.	Gelation may occur because of cross-linking of the polymer or because the viscosity has risen so the film can no longer flow.
Gelatine	Gelatine is a protein adhesive made from collagen broken down and extracted from parts of animals.	Glue is an impure form of gelatine.

(continued)

Term	Definition	Note
Glass transition	The glass transition is a reversible change in an amorphous polymer between a viscous rubbery condition and a hard brittle condition.	This property can be measured by a number of different properties, such as optical and volumetric.
Glass transition temperature	The glass transition temperature is the approximate midpoint of the temperature range over which glass transition takes place.	The exact specification of the methodology and the point chosen makes a considerable difference to the value quoted, so needs to be explicit, e.g. ASTM E1356-08 (2008).
Gloss	The gloss of a surface is its ability to reflect light specularly.	There is variation in glossiness, from matt through eggshell to mirror, whose value is determined by the method of test.
Glue	Glue is a protein adhesive made from collagen broken down and extracted from parts of animals.	Gelatine is a purer form of glue.
Gum	A gum is a water-soluble or dispersible adhesive (frequently composed of polysaccharides) obtained from plants.	Examples are gum arabic and dextrin.
Hardener	A hardener is one component of a multi-pack product that takes part in a chemical reaction to form a solid material.	In a two-pack epoxy adhesive, the hardener is usually an amine compound.
Heat-activated adhesive	A heat-activated adhesive is a dry film that is made tacky by heat applied to the assembly.	For example, BEVA is heat activated above 68 °C.
Heat-setting adhesive	A heat-setting adhesive is one that sets on the application of heat.	For example, many epoxy resin mixtures may be kept cold to prevent the normal curing process that occurs at room temperature.
Homopolymer	A homopolymer is a polymer made up of only one type of monomer.	See <i>Polymer</i> .
Hot melt adhesive	A holt melt adhesive is rendered fluid by heating and forms the bond on cooling.	

Term	Definition	Note
Hydrolysis	Hydrolysis is a degradation reaction resulting from reaction with water.	For example, starch can be hydrolysed to smaller molecules by extended storage in water.
Hygroscopic	A hygroscopic material is capable of absorbing from and releasing water to the environment.	
Interface	The interface is the area of contact between the adherend and adhesive.	
Isinglass	Isinglass is a gelatine made from the swim bladders of fishes.	Sturgeon is the traditional source of isinglass.
Joint	The joint is the location at which two adherends are held together by an adhesive.	
Laminate (noun)	A laminate is made by joining together two or more layers of material or materials.	
Laminate (verb)	To laminate is to make an assembly by bonding layers of materials together.	
Levelling	The levelling of a coating material is its ability to flow after application to minimize irregularities caused by the application process.	
Liquid adhesive	A liquid adhesive is one that when applied to a substrate sets to form an adhesive.	
Matting agent	A matting agent is an additive incorporated into a coating material to reduce the gloss of the dry coating.	Synonym: flattening agent.
Medium	The medium is all constituents of the liquid phase of a coating material.	The medium will include dissolved polymer, solvents, dispersing agents, etc.
Melting point	The melting point of a polymer is the temperature at which both amorphous and crystalline components of a polymer have become liquid.	

Continued

(continued)

Term	Definition	Note
Molecular weight	The molecular weight is the weight of one mole of the molecules.	Abbreviation: MW. Synonym: molecular mass. Strictly, molecular mass is the mass of one molecule and the molar mass is the mass of N (Avogadro's number) x molecular mass.
Monomer	A monomer is a low-molecular-weight compound that can react with two or more other monomers to form a polymer.	
Monomer unit	A monomer unit is the repeating constituent of a polymer molecule.	Monomers change significantly when they react to form a polymer, so one should not confuse the properties of the original monomer with the structure of monomer units in the polymer.
Natural	A natural polymer is one that has been prepared from animal or plant material with little or no chemical modification.	Few natural polymers are used without significant processing. Gum arabic and mastic are examples.
Oligomer	An oligomer is a very-low-molecular-weight polymer whose properties differ significantly depending on the degree of polymerization.	Ketone resins and PEG are examples.
Open time	The open time is the period between applying the liquid to the adherends and the assembly of the joint.	The open time is usually the period until the viscosity of the liquid rises too high to allow it to flow and wet the surfaces. For example, a joint made with a hot glue solution has a limited open time before the glue gels.
Paint	Paint is a pigmented coating material that forms an opaque coating.	
Paste	A paste is semi-solid plastic gel.	In conservation, paste frequently refers to a mixture of starch and water.

Term	Definition	Note
Peel	Peel is the force applied to a joint in which one or both of the adherends is flexible and in which the force is concentrated at a boundary line.	
Penetration	Penetration occurs when the liquid material enters a substrate.	
Plasticity	Plasticity is the property that enables a material to retain its shape under a force not exceeding its yield value and to flow above this value.	
Plasticizer	A plasticizer is an unreacting additive to the liquid material which makes the resulting solid material more flexible.	
Polycondensation	Polycondensation is the growth of a polymer by means of condensation reaction.	For example, a polyester is made by stepwise addition of monomers reacting with the elimination of water.
Polymer	A polymer is a large molecule formed by the reaction of many smaller monomer molecules.	The term is also used collectively to describe material used.
Polymer molecule	A polymer molecule is formed of multiple repeating units, monomers.	
Polymerization	Polymerization is the process of converting monomers into a polymer.	
Pot life	The pot life is the time during which a multi-part adhesive can be used after mixing the components.	Synonym: working life.
Pre-polymer molecule	A pre-polymer molecule is a polymer or oligomer molecule that can enter into subsequent polymerization.	Polyester and epoxy resins are made by reacting pre-polymers with cross-linking molecules, frequently also oligomers.

Continued

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Term	Definition	Note
Pressure-sensitive adhesive	A pressure-sensitive adhesive is a viscoelastic material, which in solvent-free form remains permanently tacky.	For example, the adhesive on a self-adhesive tape.
Primer	A primer is a coating applied to the substrate, prior to application of the liquid material, to improve the performance of the bond.	For example, a coupling agent can be applied to produce chemical bonding between the adherend and the adhesive.
Release agent	A release agent is a coating intended to prevent or reduce adhesion.	Release agents are used when making or taking a mould.
Resin	A resin is an amorphous polymer or oligomer.	Resin is increasingly used for low-molecular-mass materials, such as natural resins.
Retrogradation	Retrogradation is the change of starch pastes from low to high viscosity on standing.	
Sample	A sample is a portion of a material intended to be representative of the whole.	Samples may be taken for current or delayed analysis.
Set	A liquid sets to form a solid, when it has developed its cohesive strength and other physical and chemical properties.	Setting may be by chemical (curing), physical (cooling) or evaporation (drying) means.
Setting time	The setting time is the time needed for the liquid to form a solid.	
Shear	Shear is the force applied to a joint that acts in the plane of the bond line.	
Size	A size is a gelatine that has been applied to a surface to reduce penetration of a liquid or to increase adhesion.	Application of the gelatine solution is called sizing, and is used for paper, plaster, etc.
Slippage	Slippage occurs when the adherends move during the bonding process.	

Term	Definition	Note
Solvent	A solvent is a liquid that dissolves another material.	The term solvent is sometimes (erroneously) used to mean a mobile liquid.
Solvent-activated adhesive	A solvent-activated adhesive is a dry film that is rendered tacky just prior to use by the application of a solvent.	
Solvent adhesive	A solvent adhesive has a volatile liquid as the vehicle.	
Specimen	A specimen is a portion of a sample used in a test.	
Storage life	The storage life is the time during which the liquid material will remain in usable condition, under specified circumstances.	Deprecated term: shelf life.
Strain	Strain is the unit change due to force in the size of a body relative to its original size.	Strain can be measured in tension, compression, torsion, etc.
Stress	Stress is the force exerted per unit area at a point within a plane.	
Stress-strain diagram	A stress-strain diagram is one where stress and strain are plotted against one another.	
Substrate	A substrate is a material to which a liquid material is applied.	A substrate can be the object to which an adhesive, coating or consolidant is bonded.
Surface tension	Surface tension is the energy needed to increase the surface area of a liquid by a defined value.	
Surfactant	A surfactant is a material added to a liquid to lower its surface tension.	Colloquial: wetting agent.
Synthetic	A synthetic polymer is one that has been prepared from monomers.	

(continued)

Term	Definition	Note
Tack	Tack is the property of a material that enables it to form a bond of measurable strength immediately on contact with another surface.	The tack of a film is related to its viscosity. Tack is commonly tested with a finger.
Tensile force	A tensile force is applied by pulling along the line of the object being tested.	
Thermoplastic	A polymeric material is thermoplastic if it can be repeatedly softened by heating and hardened by cooling.	Not all un-cross-linked polymers are thermoplastics, e.g. cellulose.
Thermosetting	A material is thermosetting if it is cured to a polymer by heating.	Many thermosetting polymers are now available that require heating only to room temperature.
Thixotropy	Thixotropy is the decrease of apparent viscosity under shear stress, followed by a gradual recovery when the stress is removed.	Pastes are thixotropic, i.e. they have very high viscosity or are solids at rest but can be made more liquid by stirring or brushing.
Varnish	A varnish is a clear coating material.	
Viscoelasticity	A material demonstrates viscoelasticity in response to a stress when it has both elastic and viscous behaviour.	Many coatings are solid elastic materials but can flow to absorb dirt.
Viscosity	The viscosity of a liquid is its resistance to flow.	
Water-borne	A water-borne adhesive is one where the volatile carrier of the adhesive material is water, either acting as a solvent or as a dispersing phase.	
Wetting	The wetting of a substrate occurs when a liquid spreads over its surface.	
Wetting agent	A wetting agent is an additive or pretreatment used to improve the contact between a liquid and a solid.	A wetting agent can be used to help the dispersion of pigments in a medium, or the coverage of a liquid material over a substrate.

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