

Solvents, thinners, and diluents

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4.1 Introduction

With the notable exception of water, all solvents, thinners, and diluents used in surface coatings are organic compounds of low molecular weight. There are two main types of these materials, hydrocarbons and oxygenated compounds. Hydrocarbons include both aliphatic and aromatic types. The range of oxygenated solvents is much broader in the chemical sense, embracing ethers, ketones, esters, ether-alcohols, and simple alcohols. Less common in use are chlorinated hydrocarbons and nitro-paraffins.

The purpose of these low molecular weight materials is implied by their names. Thus a solvent dissolves the binder in a paint. Thinners and diluents may be added to paints to reduce the viscosity of the paint to meet application requirements. These statements do not, however, go far enough to describe the complex requirements for solvents, thinners, and diluents to achieve their practical purpose. This purpose is to enable a paint system to be applied in the first instance, according to a pre-selected method of application; to control the flow of wet paint on the substrate and to achieve a satisfactory, smooth, even thin film, which dries in a predetermined time. They are rarely used singly, since the dual requirements of solvency and evaporation rate usually call for properties of the solvent that cannot be obtained from the use of one solvent alone.

In the foregoing we have been largely concerned with the use of solvents or solvent mixtures that dissolve the binder. There is a growing class of binders (see Chapter 2) that are not in solution, but nevertheless do require the use of a diluent, which is a non-solvent for the binder, for application. Water is thus a diluent for aqueous latex paints, and aliphatic hydrocarbons are examples of diluents for some non-aqueous polymer dispersions. Even these materials may require a latent solvent or coalescing agent to ensure that the dispersed binder particles coalesce to form a continuous film on evaporation of the diluent.

Factors that affect the choice of solvents and the use of solvent mixtures are their solvency, viscosity, boiling point (or range), evaporation rate, flash point, chemical

nature, odour, toxicity, and cost. Solvency is not an independent property of the liquid since it depends on the nature of the binder or film former. Odour, toxicity, and cost have become of increasing importance in recent years.

4.2 The market for solvents in the paint industry

Solvents are not produced for the paint industry alone. Nevertheless, the paint industry represents the largest outlet for organic solvents. The second largest sector is probably that for metal cleaning, i.e. principally degreasing, but this market is heavily dependent on chlorinated solvents. Other major industrial users of solvents are the adhesives and pharmaceutical industries.

The production of solvents has changed dramatically since the late 1960s because of two main factors: (i) environmental considerations that have led to considerable legislation particularly in the USA, and (ii) the economic recession. Solvent consumption dropped by almost 20% in 1975 and took almost ten years to recover, but with a different balance of solvents.

The main technical changes have been the decrease in the usage of aromatic solvents as a result of environmental legislation, notably the introduction of rule 66 in Los Angeles in 1967 and subsequently rules 442 and 443. This legislation was introduced to limit the emission of ultraviolet radiation absorbing materials into the atmosphere in an attempt to eliminate or minimize the well-known Los Angeles photochemical smog. It is important to note that legislation does not prohibit the use of solvents, only their emission into the atmosphere. This has meant that some users have not discarded aromatics and other atmospheric pollutants, but have had to seek alternative means of dealing with them. Two methods are commonly used: the introduction of solvent recovery plant enabling the re-use of solvents, for example the recovery of toluene and xylene in large printing works; and the use of 'after burners' on the fume extraction plant of industrial paint users. Both of these methods must be able to justify the capital expenditure. The savings resulting from recycling are obvious. In the case of the installation of after burners, the cost is recovered at least to some extent by utilizing the energy obtained by the combustion of the solvent.

Reliable data on the production and use of hydrocarbons are not available, largely because most hydrocarbons are produced for fuel and the solvent fractions represent only a minor proportion of the total. Data on oxygenated solvents are more reliable, but in some cases the solvent may be used as a raw material in chemical synthesis as well as a solvent, e.g. acetone, methanol. Ball [1] reviewed solvent markets and trends in the 1970s. Solvent consumption in Western Europe and the USA are compared in Table 4.1. Ten solvents commonly used in the paint industry are listed. It is interesting to note that although there continued to be a small increase in the use of organic solvents in Western Europe, overall the USA market shows a decline. This is due to the effects of the legislation referred to previously which has led to the development of alternative technology.

The use of aliphatic hydrocarbons was estimated to be at the rate of about two million tonnes per year in Western Europe in 1978. This compares with about 2.5 million tonnes in the USA for the same period, appearing to show a decline from a peak in 1987.

It is difficult to make direct comparisons between Ball's figures for solvent con-

Table 4.1 — Solvent consumption in Western Europe and the USA (000 tonnes) [1]

Solvent	Western Europe		USA	
	1974	1978	1974	1978
Methyl ethyl ketone	140	130	238	280
Methyl isobutyl ketone	65	50	86	70
Ethyl acetate	165	173	70	81
<i>n</i> -Isobutyl acetates	90	123	32	44
Perchlorethylene	350	375	292	315
Trichlorethylene	270	255	157	115
Isopropanol	250	250	427	360
Acetone	238	244	325	335
Methanol	250	265	270	240
Glycol ethers	142	150	121	140
Totals	1960	2015	2018	1980

Table 4.2 — Total solvent use in the USA (million tonnes) [2]

Solvent type	1987	1992	1997 (predicted)
Hydrocarbons	2.76	2.15	1.81
Alcohols/esters/ethers	1.64	1.90	2.07
Chlorinated solvents	0.91	0.63	0.31
Ketones	0.59	0.53	0.52
Glycols/esters/ethers	0.42	0.37	0.39
Other	0.10	0.12	0.15
Totals	7.42	5.70	5.25
Of which coatings applications employed:			
	4.58	3.10	2.77
	(61.%)	(54%)	(52.7%)

sumption (excluding hydrocarbons in 1974/78) and the more recent figures of Kirschner (Table 4.2). The latter includes data for 1987 and 1992 (with predictions for solvent usage in 1997), but the assumptions made and the methods of obtaining the data may be very different. However, it is probably safe to conclude that the use of organic solvents in paints has diminished over the past two decades and will continue to do so as a result of technological change stimulated largely by environmental considerations and more stringent legislation.

4.3 Solvent power or solvency

The dissolution of a polymer or a resin in a liquid is governed by the magnitude of the intermolecular forces that exist between the molecules of the liquid and the molecules of the polymer or resin. It is these same forces that govern the miscibility of liquids and the attraction between colloidal particles suspended in a liquid. Intermolecular forces have such an important bearing on so many of the factors that control practical paint properties that it is worth considering how they arise. There

are three kinds of intermolecular force: dispersion or London forces, polar forces, and hydrogen bonding. Dispersion forces arise as a result of molecular perturbation such that at any instant there is a transient but finite dipolar effect leading to an attraction between the molecules. In the case of hydrocarbons this is the only source of molecular attraction. Polar forces originate from the interaction between permanent dipoles (Keesom effect) or between dipoles and induced dipoles (Debye effect). Hydrogen bonds, largely responsible for the high anomalous boiling point of water, are well known to the organic chemist. When a hydrogen atom is attached to an electronegative atom such as oxygen or nitrogen, there is a shift in electron density from the hydrogen to the electronegative atom. Thus the hydrogen acquires a small net positive charge and the electronegative atom becomes slightly negatively charged. The hydrogen can then interact with another electronegative atom within a second molecule to form a so-called hydrogen bond. These forces are responsible for such fundamental properties as the latent heat of vaporization, boiling point, surface tension, miscibility, and of course solvency.

4.3.1 Solubility parameters

The concept of solubility parameters was introduced by Hildebrand and Soolt [3] who was concerned with its application to mixtures of non-polar liquids. It was derived from considerations of the energy of association of molecules in the liquid phase, in terms of 'cohesive energy density', which is the ratio of the energy required to vaporize 1 cm³ of liquid to its molar volume. The solubility parameter is the square root of the cohesive energy density of the liquid,

$$\delta = \sqrt{\frac{\Delta E_v}{V_m}}$$

where ΔE_v = energy of vaporization and V_m = molar volume. For liquids having similar values of δ , it is to be expected that they should be miscible in all proportions. Where δ is significantly different for two liquids it is unlikely that they will be miscible. Whilst this was an important step forward in an attempt to put solvency on a sound footing, it was of little immediate help to the paint technologists of the day who were dealing with a wide range of solvents, both polar and non-polar, and almost invariably used as mixtures. Moreover, since volatilization of polymers without degradation is impossible, the availability of data on polymers was not forthcoming at that time. Burrell [4] made the next major step forward in recognizing that a single parameter as defined by Hildebrand was insufficient to characterize the range of solvents in use in the paint industry. He did, however, recognize the potential of the solubility parameter concept and carried out some of the early experiments to determine solubility parameters of polymers by swelling. He saw the need to classify the hydrogen bonding capacity of solvents and proposed a system in which solvents were classified into one of three categories, poorly, moderately, and strongly hydrogen bonding. In doing so he established an empirical approach to the determination of the solubility parameters of polymers using a 'solvent spectrum'. A typical solvent spectrum is shown in Table 4.3. The solubility parameters of liquids can be calculated from experimentally determined energies of vaporization and their molar volumes. Solubility parameters of polymers can be determined empirically by contacting them with a range of solvents (e.g. the 'spectrum' in Table 4.3) and observing whether or not dissolution occurs. The solubility parameter is

Table 4.3 — A solvent 'spectrum' for determining the δ values of polymers

Group I δ (weakly H-bonded)	Group II (moderately H-bonded)	Group III (strongly H-bonded)
6.9 Low odour mineral spirits	7.4 Diethyl ether	9.5 2-ethyl hexanol
7.3 <i>n</i> -hexane	8.0 Methylamyl acetate	10.3 <i>n</i> -Octanol
8.2 Cyclo-hexane	8.5 Butyl acetate	10.9 <i>n</i> -Amyl alcohol
8.5 Dipentene	8.9 Butyl 'Carbitol'	11.4 <i>n</i> -Butanol
8.9 Toluene	9.3 Dibutyl phthalate	11.9 <i>n</i> -Propanol
9.2 Benzene	9.9 'Cellosolve	12.7 Ethanol
9.5 Tetralin	10.4 Cyclo-pentanone	14.5 Methanol
10.0 Nitrobenzene	10.8 Methyl 'Cellosolve'	
10.7 1-Nitropropane	12.1 2,3-butylene carbonate	
11.1 Nitroethane	13.3 Propylene carbonate	
11.9 Acetonitrile	14.7 Ethylene carbonate	
12.7 Nitromethane		

Note: Several of these solvents are highly toxic. They will not be used in practical situations as solvents for binders. The purpose of the 'spectrum' is to determine δ values for polymers only.

taken as the centre value of the range of δ values for solvents which appear to dissolve the polymer. An alternative method is to use a lightly crosslinked form of a particular polymer and to identify the solvent that is capable of causing the maximum swelling. The δ value for the polymer is then equated with that of the solvent.

Small [5] proposed a method for calculating the δ value for a polymer from the simple equation,

$$\delta = \frac{\rho \sum G}{M}$$

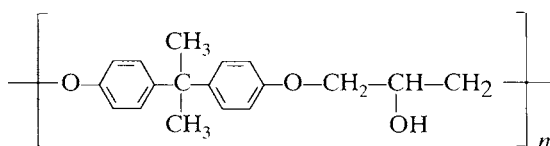
where ρ is the density of the polymer and M its molecular weight. G is the 'molar attraction constant' for the constituent parts of the molecule which are summated. Although this is only in most cases a crude approximation it serves to give a value which is a guide to the choice of the range of solvents that one might select for either of the experimental methods mentioned above. Small's approach is not satisfactory for many of the polymers that are currently used in the paint industry. In the case of those polymers that are of low molecular weight and are converted at a later stage in the film-forming process into higher molecular weight products, the reactive group in the molecule may have a disproportionate effect on the solubility of the polymer. With high molecular weight polymers there has been a growth in the use of amphiphathic polymers for many purposes. These may be block or graft copolymers in which different parts of the molecules have very different solubility characteristics. The implications of these structural considerations, e.g. in the context of non-aqueous dispersion polymerization (see Chapter 2), illustrate this point. Molar attraction constants (G values) are given in Table 4.4.

The need to use solvent mixtures arises for a number of reasons. We have already mentioned the need to control evaporation rate. On the other hand, a suitable single solvent may not be available. If available it may be too expensive or too toxic, or it may be particularly malodorous. It is therefore useful to predict as accurately as possible the solvency of mixtures having known individual δ values. A reasonable

Table 4.4 — Molar attraction constants at 25°C according to Small [5]

Group	<i>G</i>	Group	<i>G</i>
—CH ₃	214	H	80–100
—CH ₂ —	133	O (ether or hydroxyl)	70
$\begin{array}{c} \\ -\text{CH}- \\ \end{array}$	28	CO (carbonyl)	275
$\begin{array}{c} -\text{C}- \\ \end{array}$	-93	COO (ester)	310
CH ₂ =	190	CN (nitrile)	410
—CH=	111	Cl (mean)	260
>C=	19	Cl (single)	270
Ch ≡ C—	285	Cl (twinned as in > CCl ₂)	260
—C ≡ C—	222	Cl (triple as in — CCl ₃)	250
Phenyl	735		
Phenylene	658		
Naphthyl	1146		
5-membered ring	105–115		
6-membered ring	95–105		
Conjugation	20–30		

Example: Epikote 1004



Equivalent molecular mass of repeating unit,

$$\text{C}_{18}\text{H}_{20}\text{O}_3 = 284; \quad \rho = 1.15 \text{ g/cm}^3$$

ΣG :	2 ether O	@	70 = 140
	1 hydroxyl O	@	70 = 70
	1 hydroxyl H	@	100 = 100
	2 phenylene	@	658 = 1316
	2 methyl	@	214 = 428
	2 methylene	@	133 = 266
	1 tert C	@	-93 -93
			$\Sigma G = 2227$

$$\text{Thus, } \frac{\Sigma G}{M} = \frac{1.15 \times 2227}{284} = 9.02$$

approximation is to calculate the δ value for the mixture simply from the volume fraction of the constituent solvents. For example, a polyester resin that is readily soluble in ethyl acetate ($\delta = 9.1$, Group II) is not soluble in either *n*-butanol ($\delta = 11.4$, Group III) or xylene ($\delta = 8.8$, Group I). However, it is soluble in a mixture of xylene and butanol in the ratio 4/1, by volume. The average δ value of the mixture is 9.3.

Interesting as these observations may be it is clear that the single value Hildebrand solubility parameter, even when used in conjunction with a broadly defined hydrogen bonding capacity, falls short of what is required to define solvent power

in the paint industry. Nevertheless it did have sufficient promise as a method for predicting solubility for subsequent workers in this field to attempt to refine the concept and to improve its validity.

4.3.2 Three-dimensional solubility parameters

All subsequent developments in this field have been based upon the resolution of the single 'solubility parameter' into three constituent parts related to the three types of inter molecular forces described above, namely dispersion forces, polar forces, and hydrogen bonding. Crowley, Teague, & Lowe [6] were the first to put forward a scheme which used a solubility parameter δ (equivalent to that of Hildebrand), the dipole moment of the molecule, μ , and a hydrogen bonding parameter, γ . The hydrogen bonding parameter, γ , was derived from the spectroscopic data published by Gordy [7]. Although an improvement on the original Hildebrand solubility parameter as applied by Burrell to paint polymer and resin systems, the Crowley method has not gained the acceptance within the industry as have two subsequent treatments, due to Hansen [8] and Nelson, Hemwall, & Edwards [9].

More recently, work on the prediction of solubility using the solubility parameter concept has been directed at the behaviour of solvent blends, particularly during the evaporation stage of coating formation [10].

4.3.2.1 The Hansen solubility parameter system

Hansen considered that the cohesive energy density of a solvent results from the summation of energies of volatilization from all of the intermolecular attractions present in the liquid,

$$\frac{\Delta E_t^v}{V_m} = \frac{\Delta E_d^v}{V_m} + \frac{\Delta E_p^v}{V_m} + \frac{\Delta E_h^v}{V_m}$$

where ΔE^v , subscripts T, d, p, and h respectively represent the energies per mole of solvent, and energy contributions arising from dispersion, polar, and hydrogen bonding respectively. V_m is the molar volume. Alternatively, this may be written in terms of the solubility parameter δ , in the form

$$\delta_s^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

where δ_s , δ_d , δ_p , and δ_h are the solubility parameters corresponding to the solvent, dispersion, polar, and hydrogen bonding respectively. Hansen used a homomorph concept to estimate the value of δ_d for a given solvent. This involves the assumption that a hydrocarbon having approximately the same size and shape as the solvent molecule will have the same energy of volatilization at the same reduced temperature (the ratio of the absolute temperature to the critical temperature) as the solvent, i.e. the dispersion force contributions are likely to be the same.

The difference between the energies of volatilization of the homomorph and the solvent will thus give a measure of the contributions from polar and hydrogen bonding forces. In solubility parameter terms this means,

$$\delta^d \text{ for solvent} = \delta \text{ for homomorph}$$

therefore

$$\delta_s^2 - \delta_d^2 = \delta_p^2 + \delta_h^2$$

Hansen determined the values of δ_p and δ_h initially by an empirical method involving a large number of solubility experiments for several polymers and then selecting values of δ_p and δ_h which gave the best 'volumes' of solubility for the system. Later he used another method of calculating δ_p and δ_h independently and found generally good agreement with his previous empirical values. Because the concept uses three numerical values it is convenient to plot them on three axes, hence the term 'volume' of solubility which is simply a reference to the volume on a three-dimensional plot representing the three parameters, into which the parameters of a given solvent would have to fall if the solvent is to dissolve a given polymer or resin. In Hansen's case this would be an oblate spheroid. However, for convenience the scale for the dispersion contribution is doubled to convert the volume of solubility into a sphere. In this form the sphere of solubility of a polymer or resin can be defined in terms of its position relative to the three axes, i.e. by the coordinates of its centre and its radius, R_p . An alternative way of treating solubility data is to use two-dimensional plots, where one is in effect using the projection of the sphere of solubility onto one or other of the two-dimensional axes as indicated in Fig. 4.1. The third parameter defines the circle which should enclose solvents for the polymer or resin in question. There is, however, no sound theoretical basis for the assumption that all solvents for a given polymer will fall within the sphere of solubility, particularly as the sphere is only arbitrarily defined and without resorting to the artifice of doubling the scale for one of the parameters would not be a

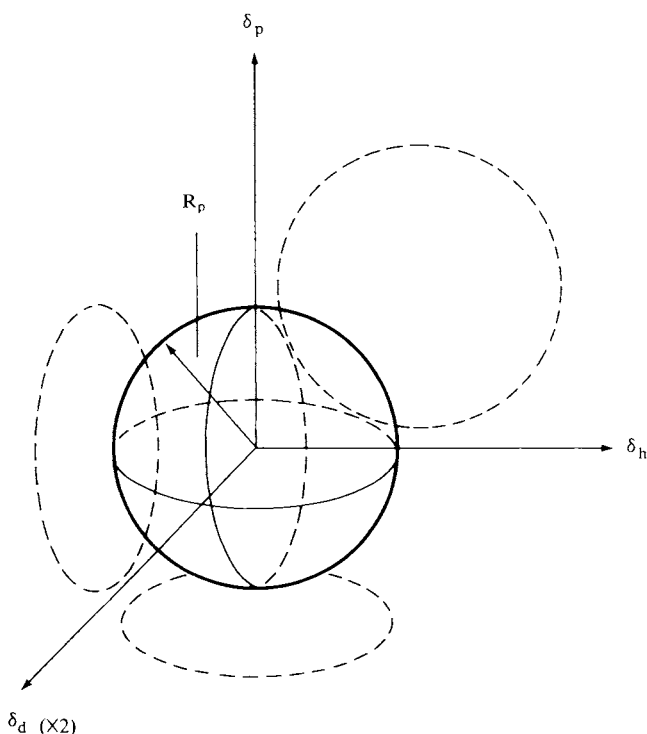


Fig. 4.1 — Diagrammatic representation of a polymer solubility plot based on Hansen's parameter system. (The dotted circles represent projections of the 'sphere of solubility'.)

sphere at all. Since the sphere is determined empirically the concept does have a certain simplicity which makes it easy to apply to practical systems, and many workers have adopted Hansen's method because of this.

The distance, R_s , between the three-dimensional coordinates of the solubility parameters of the solvent and the coordinates of the centre of the sphere of solubility of the polymer determines whether or not the polymer will be soluble in the solvent. That is, if $R_p > R_s$ the polymer will be soluble in the solvent because the coordinates for the solvent fall within the sphere of solubility for the polymer.

As an illustration of this point it is worthwhile seeing how the Hansen method compares with the Burrell method for predicting the solubility of the polyester of our previous example (Section 4.3.1) in the 4/1 mixture of xylene and *n*-butanol.

$$R_s = \left[4(\delta_{d_0} - \delta_d)^2 + (\delta_{p_0} - \delta_p)^2 + (\delta_{h_0} - \delta_h)^2 \right]^{\frac{1}{2}}$$

From Tables 4.5 and 4.6 the Hansen solubility parameters are as follows:

	δ_d	δ_p	δ_h	
<i>n</i> -butanol	7.8	2.8	7.7	
xylene	8.7	0.5	1.5	
saturated polyester (Desmophen 850)	10.53	7.30	6.0	$R_p = 8.2$

Since the solvents are in the proportion 1/4, butanol/xylene, the equivalent solubility parameters for the mixture are:

	δ_d	δ_p	δ_h
20% butanol	1.56	0.56	1.54
80% xylene	6.96	0.40	1.20
therefore			
mixture	8.52	0.96	2.74

$$\begin{aligned} R_s &= \left[4(10.53 - 8.52)^2 + (7.30 - 0.96)^2 + (6.0 - 2.74)^2 \right]^{\frac{1}{2}} \\ &= [16.16 + 40.20 + 10.63]^{\frac{1}{2}} \\ &= (66.99)^{\frac{1}{2}} = 8.18 \end{aligned}$$

Since R_s is less than R_p this predicts that the polyester will be soluble in this solvent mixture. But since the values are almost equal it suggests that the polyester is only just soluble. It can be argued, therefore, that Hansen's method can give more information than the Burrell method, since the latter does not give any indication of the influence of degree of disparity between the δ values for polymer and solvent. A selection of the Hansen δ values for solvents is given in Table 4.4, a selection of δ and R_p values for polymers in Table 4.5 and δ and R_p values for a selection of pigments in Table 4.7. A more extensive range of values will be found in reference [11].

As has been indicated in the foregoing discussion of the three-dimensional solubility parameter concept, early work was concerned mainly with aspects of solvent miscibility and the dissolution of polymers in solvents and mixtures thereof. It is now recognized that it has even wider applications, such as in polymer compatibility, interactions at pigment surfaces (wetting and adsorption properties), and in predicting the chemical and solvent resistance of the coatings [12].

Table 4.5 — Hansen's solubility parameters for a selection of solvents

Solvent	δ_d	δ_p	δ_h
<i>n</i> -hexane	7.3	0	0
Cyclohexane	8.2	0	0.1
Toluene	8.8	0.7	1.0
Xylene	8.7	0.5	1.5
Acetone	7.6	5.1	3.4
Methyl ethyl ketone	7.8	4.4	2.5
Methyl isobutyl ketone	7.5	3.0	2.0
Ethyl acetate	7.7	2.6	3.5
<i>n</i> -Butyl acetate	7.7	1.8	3.1
Ethanol	7.7	4.3	9.5
<i>n</i> -Propanol	7.8	3.3	8.5
<i>n</i> -Butanol	7.8	2.8	7.7
Ethoxyethanol	7.9	4.5	7.0
Tetrahydrofuran	8.2	2.8	3.9
Ethylene glycol	8.3	5.4	12.7
Glycerol	8.5	5.9	14.3
Dichloromethane	8.9	3.1	3.0
Carbon tetrachloride	8.7	0	0.3
Water	7.6	7.8	20.7

Table 4.6 — Hansen's solubility parameters for a selection of polymers

Polymer type	Trade name	Supplier	Computed parameters			
			δ_d	δ_p	δ_h	R_p
Short oil alkyd (34% oil length, OL)	Plexal C34	Polyplex	9.04	4.50	2.40	5.20
Long oil alkyd (66% OL)	Plexal P65	Polyplex	9.98	1.68	2.23	6.70
Epoxy	Epikote 1001	Shell	9.95	5.88	5.61	6.20
Saturated polyester	Desmophen	Bayer	10.53	7.30	6.00	8.20
Polyamide	Versamid 930	General Mills	8.52	-0.94	7.28	4.70
Isocyanate (Phenol blocked)	Suprasec F5100	ICI	9.87	6.43	6.39	5.70
Urea/formaldehyde	Plastopal H	BASF	10.17	4.05	7.31	6.20
Melamine/formaldehyde	Cymel 300	American Cyanamid	9.95	4.17	5.20	7.20
Poly(styrene)	Polystyrene LG	BASF	10.40	2.81	2.10	6.20
Poly(methyl methacrylate)	Perspex	ICI	9.11	5.14	3.67	4.20
Poly(vinyl chloride)	Vipla KR	Montecatini	8.91	3.68	4.08	1.70
Poly(vinyl acetate)	Mowilith 50	Hoechst	10.23	5.51	4.72	6.70
Nitrocellulose	H23 ($\frac{1}{2}$ sec)	Hagedorn	7.53	7.20	4.32	5.60

Table 4.7 — Hansen’s solubility parameters for a selection of pigments [12]

Pigment	δ	δ	δ	R_p
Zinc silicate	23.5	17.5	16.8	15.6
TiO ₂ (Kronos RN 57)	24.1	14.9	19.4	17.2
Heliogen blue LG	21.9	10.2	13.3	12.3
Aluminium powder	19.0	6.1	7.2	4.9
Red iron oxide	20.7	12.3	14.3	11.5

With respect to the use of solubility parameters in describing the wetting and de-wetting of surfaces in general, the surface tension of liquids has been correlated quite successfully with the three Hansen parameters according to the equation.

$$\gamma = 0.0715V^{1/3}[\delta_D^2 + 0.632(\delta_P^2 + \delta_H^2)]$$

It has been shown that in pigmented systems colour development is at a maximum when the solvent quality for the binder is only moderate. Too poor a solvent leads to excess binder on the surface of the pigment, in a flatter configuration than for a slightly better solvent which allows for polymer chain segment extension into liquid phase. Too good a solvent can cause the binder to be desorbed and the colloidal stability of the system deteriorates.

An efficient aid to the reformulation of solvent systems for paints has been developed by Shell Chemicals in the form of a series of computer programs, under the name ‘Shell Solvent Computer Programs’ (SSCP), that assist the paint technologist by reducing the number of formulations that have to be evaluated experimentally. The procedure is not limited to a simple calculation of the properties of solvent blends, but also includes data on properties that relate directly to the performance of the paint formulation. For example, the changes in the solvent parameters as a result of changes in the solvent composition that accompany evaporation can be examined for quite complicated systems, thus reducing the need for extensive experimental work [10].

4.3.2.2 *The Nelson, Hemwall, and Edwards solubility parameter system*

Nelson and co-workers developed their system almost contemporaneously with Hansen, but quite independently. They proposed a system which uses the Hildebrand solubility parameter δ , a fractional polarity term, and a ‘net hydrogen bond accepting index’, θ_A . The latter allows for differences in hydrogen bonding characteristics of the various solvent types. It thus attempts to quantify what Burrell had recognized as an important factor (cf. his ‘solvent spectrum’).

$\theta_A = K_\gamma$, where γ is the spectroscopic value for hydrogen bonding [6]. The coefficient K has three values: -1 for simple alcohols, 0 for glycol-ethers, and $+1$ for all other solvents.

The system is commonly used in the form of ‘solubility maps’ an example of which is shown in Fig. 4.2. This illustrates the application of the method to Epikote 1004, an epoxy resin (ex Shell Chemicals plc). A and B on the map represent the solubility parameters of xylene and *n*-butanol respectively, neither of which is a solvent for the resin. However, the line joining these two points intersects the region

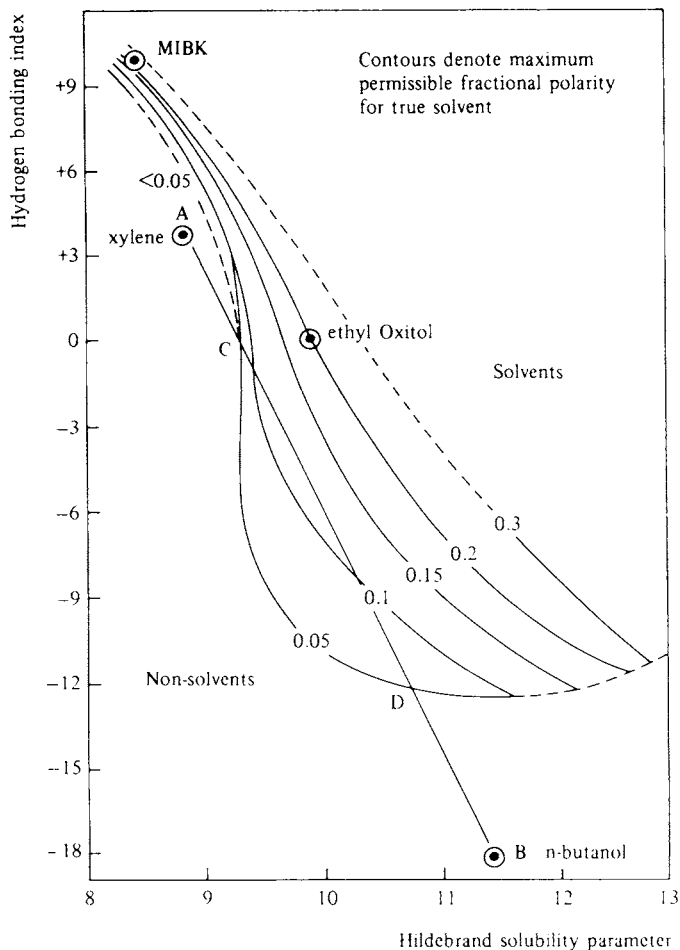


Fig. 4.2 — Solubility map for Epikote 1004 (solids > c. 30% W).

of solubility at the two points C and D, so that it would be expected that Epikote 1004 will be dissolved by mixtures of xylene and *n*-butanol for all compositions lying between C and D. Since the solubility parameters combine linearly, the composition of the mixtures at C and D can be calculated. They turn out to be 85% xylene, 15% *n*-butanol at C, and 25% xylene and 75% *n*-butanol at D. These blends now have to be checked against the fractional polarity contours on the map. Neither mixture may have a fractional polarity of greater than 0.05 if they are to be true solvents. The fractional polarity for xylene is 0.001 and for *n*-butanol is 0.096. Thus the average fractional polarities for the two mixtures are

$$\text{Blend C } 85/15 \text{ xylene/butanol} = 0.00085 + 0.0144 = 0.01525$$

$$\text{Blend D } 25/75 \text{ xylene/butanol} = 0.00025 + 0.072 = 0.07225$$

These results indicate that Blend C would be a solvent for the resin, but that Blend D would not. Clearly one would only have to calculate the proportions of

these two solvents to give a value of fractional polarity equal to or less than 0.05 in order to achieve solubility. A number of solubility maps of this sort have been published, and for more detailed information the reader is directed to reference [13].

Both the Hansen method and the Nelson, Hemwall, and Edwards method lend themselves readily to computerization, e.g. in Rocklin & Edwards [14].

4.4 Solvent effects on viscosity

Establishing that a given solvent or mixture of solvents is capable of dissolving the resinous or polymeric components of a paint is only the first step in solvent selection. The solubility parameter concept may aid in choosing solvents for a given system, but it does not tell us anything about the condition of the polymer or resin in solution; i.e. the intermolecular forces described previously also control the disentanglement and extension of the polymer chains. A 'good' solvent will tend to maximize (at relatively low polymer concentration) the viscosity of the solution at a given concentration. For solvents of similar solvent power the viscosities of a particular polymer at the same concentration in each will be in the ratio of the solvent viscosities. This implies that the solvent/polymer interactions in both solutions are equal. It is not generally understood that good solvents tend to give more viscous solutions, although it is recognized that the addition of a non-solvent for a polymer to a solution of that polymer in a good solvent can reduce the viscosity of that solution. There is a point at which precipitation will take place when the polymer will have collapsed back on itself, no longer being solvated by the 'good' solvent. This effect is used to characterize polymers such as aminoplasts which are usually dissolved in aromatic hydrocarbon/butanol mixtures. Their tolerance to a non-solvent such as hexane is a measure of the degree of butylation and molecular weight.

Solvents are Newtonian fluids. That is, their viscosity is independent of shear rate. Likewise, most polymer solutions are Newtonian, although some may be non-Newtonian at high concentrations. A few polymers such as polyamides are designed to produce non-Newtonian effects, but it is debatable if they are in true solution, and it is believed that the non-Newtonian behaviour (in this case shear thickening or thixotropy) is due to structure developing through a dispersed micro-particulate phase.

It is convenient to compare the viscosities of polymer solutions under standard conditions, since this enables direct comparisons to be made between solvents with respect to solvent power, or comparisons to be made between the same polymer type, but with differing molecular weights. The following terms have come into use:

$$\text{Relative viscosity} = \frac{\text{Solution viscosity}}{\text{Solvent viscosity}}$$

$$\begin{aligned} \text{Specific viscosity} &= \frac{\text{Solution viscosity} - \text{Solvent viscosity}}{\text{Solvent viscosity}} \\ &= \text{Relative viscosity} - 1 \end{aligned}$$

$$\text{Reduced viscosity} = \frac{\text{Specific viscosity}}{\text{Concentration (g per decilitre)}}$$

Relative viscosity and specific viscosity are dimensionless quantities; reduced viscosity has the dimension decilitres per gram. If reduced viscosities are measured for a range of dilute solutions, e.g. <1% concentration, and they are plotted against concentration, a quantity known as the intrinsic viscosity of the polymer can be obtained by extrapolation to zero concentration. The intrinsic viscosity of a polymer is related to its molecular size and thus its molecular weight.

The foregoing is applicable to linear flexible homopolymers or random copolymers in solution. With block or graft copolymers it is possible for the polymer to be dissolved by a solvent for one component block or graft, the remaining component remaining unsolvated and collapsed into a tight coil. In these cases the polymer is likely to be in a colloidal state, in micellar solution. Such a solvent is described as a 'hemi-solvent' for the polymer. The effects of solvent on polymer configuration will be described in more detail in connection with the use of polymer stabilizers for dispersion (see Chapter 8).

4.5 Evaporation of solvents from coatings

In arriving at a suitable solvent blend for a surface coating, one has to consider the rate of evaporation of the solvent from the paint in relation to the conditions of application and cure. For example, thinners supplied for motor refinishing may be formulated for rapid or slow evaporation according to the ambient conditions. Also, the rate of solvent loss from a thin film governs the propensity of the coating to flow, so that it may be important to use a solvent blend of two or more solvents. This enables a rapid increase in viscosity to occur by the evaporation of a volatile component, and flow to be controlled by a less volatile one.

Evaporation takes place in essentially two stages. Initially the solvent loss is dependent on the vapour pressure of the solvent and is not markedly affected by the presence of dissolved polymer. As the polymer film is formed, solvent is retained within the film and is lost subsequently by a diffusion-controlled, slow process. This latter stage may be dominant when as much as 20% of the solvent is retained in the film.

The initial rates of evaporation can be predicted from an application of Raoult's Law, from a knowledge of activity coefficients of the components of a mixture of solvents and its composition. The measurement of evaporation rates is done very simply by a gravimetric method. Shell have developed an automatic evaporimeter which is now accepted as an ASTM Standard, No. D 3539.76 [15].

Two methods are commonly used, evaporation from a thin film of the liquid, or from a filter paper, using equal volumes of liquids in each case. The results obtained are comparable for all except the most volatile of solvents. The filter paper method is preferred by many since the evaporating surface remains constant throughout the determination. Newman and Nunn [16] quote relative evaporation rates for some common solvents and tabulate their order of retention. It is common to use *n*-butyl acetate as a standard for evaporation and to quote all other solvents in comparison with butyl acetate, taken as unity. It is interesting to note from Table 4.8 that the retention of a given solvent is not related to its relative initial evaporation rate or its molar volume. However, within a homologous series the expected order of retention seems to apply, e.g. acetone, methyl ethyl ketone, and methyl isobutyl ketone.

Table 4.8 — Order of solvent retention (data from reference [16])

Solvent	Relative evaporation rate	Molar volume (cm ³ /mole)	
Methanol	3.2	40	Increasing order of retention ↓
Acetone	7.8	73	
2-Methoxyethanol	0.51	79	
Methyl ethyl ketone	4.6	90	
Ethyl acetate	0.35	97	
2 Ethoxy ethanol	4.3	97	
<i>n</i> -Heptane	3.3	146	
2 <i>n</i> -Butoxyethanol	0.076	130	
<i>n</i> -Butyl acetate	1.0	132	
2 Methoxyethyl acetate	0.35	117	
2 Ethoxyethyl acetate	0.19	135	
Toluene	2.3	106	
Methyl isobutyl ketone	1.4	124	
Isobutyl acetate	1.7	133	
Cyclohexane	4.5	108	
Methyl cyclohexane	3.5	126	
Cyclohexanone	0.25	103	
Methyl cyclohexanone	0.18	122	

4.6 Flashpoint

The flashpoint of a solvent mixture is important to those concerned in the manufacture, handling, storage, transport, and use of solvent-containing products. A considerable amount of legislation has been enacted to control the use of flammable liquids because of the fire hazards they represent, and standard methods have been established for the determination of flashpoint.

The flashpoint of a liquid may be defined as the lowest temperature at which the liquid, in contact with air, is capable of being ignited by a spark or flame under specified conditions. Two methods of determining flashpoint are in common use, the Abel method (Institute of Petroleum Test Method 170) and the Pensky-Marten closed cup method (ASTM D93). Each calls for a specific piece of equipment designed for the test. The apparatus and its method of use is described in each of the test methods referred to.

There have been many attempts to predict the flashpoints of paints containing solvent mixtures [17, 18]. They are based broadly on the assumption that the flashpoint is related inversely to the vapour pressure of the solvent and its activity coefficient. These predictive approaches have gained little support, however, since to meet most regulations related to transportation and storage an experimentally determined value by a specified method is almost always required. In practice it is necessary to know whether a product has a flashpoint above a specified limit to satisfy regulations regarding shipment. For example in the UK a product is not classed as 'highly flammable' unless it has a flashpoint below 32°C and is combustible. Flashpoints of a number of common solvent constituents of paints are given in Table 4.9.

As a general guide the flashpoint of a mixture of solvents can be assumed to be that of the solvent with the lowest flashpoint. However, this is not always the case, and lower values are sometimes obtained experimentally.

Table 4.9 — Boiling points (BP), flashpoints (FP), and threshold limit values (TLV) for some common solvents

Solvent	BP (°C)	FP (°C)	TLV (ppm)
Ketones			
Acetone	57	-17	750
Methyl ethyl ketone	80	-4	200
Methyl isobutyl ketone	116	13	100
Diacetone alcohol	168	54 [†]	50
Di isobutyl ketone		47	
Esters			
Ethyl acetate	77	-3	400
Isobutyl acetate	118	16	
<i>n</i> -Butyl acetate	127	25	150
2-Ethoxyethyl acetate	156	52 [†]	50
2-butoxyethyl acetate	1	115 [†]	
Alcohols			
Methanol	65	10	200
Ethanol	78	12	1000
<i>n</i> -Propanol	97	22	200
Isopropanol	82	10	400
<i>n</i> -butanol	118	33	50
Isobutanol	108	27	50
Sec butanol	100	14	
Hydrocarbons			
Toluene	111	5	100
Xylene	138-144	24	100
White spirit (LAWS)	155-195	39	500
SBP 6	138-165	28	—

FP by Abel method, except [†] which were by the Pensky-Marten closed cup method. TLV quoted is time weighted average (TWA).

4.7 Toxicity and environmental pollution

In recent years it has become evident that many of the solvents in common use represent a health hazard, and legislation has been introduced to control their use. In addition, even with solvents of low toxicity their odour may be unacceptable both in the working environment and in the vicinity of manufacturing and user plants. As has been mentioned previously, solvent emission into the atmosphere can be controlled by the use of afterburners on extraction systems or by recycling.

Studies of the toxicity of solvents, as with any chemical compound, cover a comprehensive range of standard test procedures, including animal testing for toxic effects arising from skin contact with the liquid, exposure to vapour at a range of well-defined concentrations, and by ingestion. Data have also been collected over many years on the effects of exposure of workers in most industries to the chemicals which they use. These data, which are constantly being revised as more information is obtained, are used to define acceptable working conditions for those exposed to the solvents in their daily work.

The most commonly applied limit on solvent concentration in the atmosphere is the 'threshold limit value' (TLV). This is usually applied as a time weighted average

value which takes into account the period that an individual may be exposed during his or her working day, e.g. eight hours. Thus the TLV gives the average concentration (ppm) that should not be exceeded within the working day. Such exposure is regarded as being insufficient to be a health hazard. Clearly the concentration may be exceeded for a short period if most of the time an individual is working in an atmosphere in which the concentration of the solvent is less than the TLV. An exception to this is if a 'ceiling' value for a given material has been defined. In this case the concentration of the material must not exceed the 'ceiling' value if a health hazard is to be avoided. Fortunately, few solvents come into this category. Some TLVs are given in Table 4.9.

4.7.1 Volatile organic compounds and environmental legislation

The presence of toxic solvents in the atmosphere of the work-place is not the only problem giving concern in recent years. It is now well established that the emission of volatile organic compounds (VOCs) into the atmosphere can have serious environmental implications. Thus, effects on the concentration of ozone in the stratosphere (resulting in the depletion of ozone (particularly in the polar regions) have been much publicized as 'holes in the ozone layer', which give rise to increased ultraviolet radiation penetration of the earth's atmosphere. The mechanism of this process, in which chlorinated hydrocarbons play an important part, is well understood. A consequence of the increased intensity of UV light in the troposphere is an increase in the incidence of skin cancers. The formation of summer smogs (associated with large conurbations such as Los Angeles and Athens) is a result of ozone creation in the troposphere which is also encouraged by VOC emissions. It has also been observed that a smog can be formed at substantial distances from the original emission source. Smogs can cause eye irritation and respiratory problems in human beings and animals, and can be harmful to crops and trees. The World Health Organization guideline levels are an 8 hour average exposure of 50–60 p.p.b., but higher levels are frequently recorded in the UK and continental Europe. The 'greenhouse effect' which is caused mainly by increases in the carbon dioxide concentration in the atmosphere is also exacerbated by some VOCs. 'Acid rain', although caused principally by sulphur dioxide and nitrogen oxides in the atmosphere, can contain small amounts of hydrochloric acid that is derived from chlorofluorocarbons (CFCs) [19].

All of these effects of the release of chemicals in the atmosphere were recognized as major issues during the 1970s and 1980s as requiring global action to achieve significant improvement. This realization resulted in the United Nations taking an increased role in setting up Conventions to address these issues. Various agencies of the United Nations organization are involved, including the UN Environment Programme (UNEP), UN Economic Commission for Europe (UNECE), and the UN Conference on Environment and Development (UNCED). These bodies provide a forum for discussion and cooperation, make recommendations, and publish detailed Convention statements and Protocols. However, ultimately it is for national governments to introduce and enforce the implementation of any legislation introduced to their statute books.

The paint industry in the USA, for example, is attempting to minimize (or to eliminate) the use of solvents to reduce the costs of dealing with hazardous wastes as well as other chemical emissions for which mandatory limits have been laid down according to the 'Toxics Release Inventory' (TRI), published by the US Environ-

mental Protection Agency. The TRI is applied in conjunction with the '33-50' programme which calls for voluntary emission reductions of 17 chemicals, including 6 commonly used solvents. The 33-50 programme is so-called because companies agreed to reduce releases of the 17 listed chemicals by 33% by 1992 and by 50% by 1995, as measured against 1988 data. The EPA reported that its 33% target was achieved, a reduction of 40% being reported in 1992.

The representatives of the member states of the Montreal Protocol met in September 1997 and some optimism was expressed to the effect that the tightening of global controls on ozone-depleting substances had resulted in a thickening of the ozone layer by 15-20% in the previous year [20]. Optimistically, it is stated that 'the ozone layer is expected to start to recover within a few years, and to recover fully by the middle of next century'. This is in spite of considerable in-fighting between Canada and the USA on the one hand and the EC on the phasing out of HCFCs.

Of the three main types of solvent that are subject to legislation (hydrocarbons, oxygen-containing solvents, and chlorinated solvents), the replacement of chlorinated solvents provides the biggest challenge. Ozone-depleters, such as 1,1,1-trichloroethane and CFC-113, are subject to a production and import ban in the USA with effect from 1 January 1996 under the Montreal Protocol on 'Substances that Deplete the Ozone Layer'. The Montreal Protocol was signed by the representatives of 60 governments in September 1987, committing those governments to actions the end of the millennium [2].

In the USA the Clean Air Act Amendments 1990 extended existing law by adding over 700 pages of new and amended requirements, and sets an agenda that will extend well into the twenty-first century. The major provisions of this document which affect the paint industry have been discussed by Wigglesworth [19].

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