

SOLVENTS IN TODAY'S COATINGS

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Introduction

The Clean Air Act (CAA) has been the driving force for change in the coatings industry for over twenty-five years. It addresses an assortment of air quality issues that include tropospheric (ground-level) ozone formation, and hazardous air pollution emissions. These two regulatory programs have had a significant impact on the use of solvents in the coatings industry.

Controlling VOC emissions is an important step in the control of ground-level ozone since VOCs are ozone precursors. The Environmental Protection Agency (EPA) defines a VOC as any volatile compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactivity.

Ozone is formed when VOCs react in the atmosphere with nitrogen oxides under the influence of heat and sunlight. Ozone is a major component of smog and is considered a health and environmental hazard.

Most solvents used in the coatings industry are considered volatile organic compounds. However, coatings account for only about 15% of the man-made VOC emissions in this country. Other significant sources include vehicles, petroleum production, storage and distribution, and industrial fuel combustion. Some compounds are exempt as VOCs by the EPA because they have negligible photochemical reactivity. Acetone and methyl acetate are two common solvents that have been granted VOC exemption.

The objective of the National Emission Standards for Hazardous Air Pollutants (NESHAP) regulations is to minimize cancer and long-term health risk by restricting the emissions of hazardous air pollutants (HAPs). The EPA has established a list of 188 compounds as HAPs. This list is controversial because some of the compounds are considered to be very hazardous while others are not. It includes many of the most widely used solvents in the coatings industry, such as MEK, MIBK, toluene, xylene, and ethylene glycol ethers and their acetates. The EPA must develop Maximum Achievable Control Technology (MACT) standards for many industrial source categories to reduce emissions of these compounds. They will be applied nationwide to sources that have the potential to emit, on an annual basis, 10 tons/year of any HAPs or 25 tons/year of all HAPs. Furthermore, the CAA provides EPA the authority to add or remove compounds from the list. Under those provisions, the Chemical Manufacturers Association (CMA) has requested the removal of ethylene glycol monobutyl ether (EB), MEK, MIBK, and methanol from the list. However, at the time of this writing, the EPA has not acted on these petitions.

To comply with VOC and HAP regulations, solvent users may choose from several strategies such as capture/recycle, incineration, change to another coatings technology that emits less solvent, or reformulate the solvent system to reduce VOCs and/or HAPs. The greatest reduction in emissions might be achieved by using a combination of strategies.

The major coating technologies used to comply with current VOC and HAP regulations are high-solids, waterborne, and solvent-free coatings such as powder and radiation cure. In some applications, such as wood coatings, low-solids lacquers and enamels are still used.

Solvents used in the Coatings Industry

Hydrocarbons. The most widely used solvents in the coatings industry are derived from petroleum. The most common types are aliphatics and aromatics. Most aliphatic solvents are mixtures of paraffinic, cycloaliphatic, and aromatic hydrocarbons. The proportions of these three components will significantly affect solvency and other properties. Aromatics have the highest solvent power, cycloaliphatics intermediate, and paraffins the lowest. Aliphatic solvents function as diluents in most coatings. A diluent is not a solvent for the resin but is included in the solvent blend primarily to reduce cost.

Aromatic hydrocarbon solvents, mainly toluene and xylene, are stronger solvents than aliphatics, and will, therefore, dissolve some resins that aliphatic hydrocarbons won't. Toluene and xylene are on the HAPs list. Cycloaliphatics with similar evaporation rates are being promoted as potential replacements for these products. Common hydrocarbon solvents and some of their physical properties are shown in Table 1.

Oxygenated Solvents. Oxygenated solvents are an important group of solvents because they have a wide range of solvencies and volatilities. Their solvencies diminish with increasing molecular weight and with increased branching of the molecule. Their evaporation rates also decrease with increasing molecular weight but increase with branching of the molecule. Esters, generally, are more polar than

hydrocarbons. Many resins that are not soluble in hydrocarbon solvents will dissolve in oxygenated solvents, because they have a wider range of solubility parameters and higher hydrogen bonding values. Oxygenated solvents are rarely used alone. They are normally blended with other types of solvents to obtain the proper solvency, overall evaporation rate, and cost. There are four major types of oxygenated solvents widely used in the coatings industry. They are ketones, esters, alcohols, and glycol ethers. The general structure for each of these families is shown in Table 8. The most widely used oxygenated solvents are discussed below.

Ester solvents used in coatings are mostly acetates. Acetate esters have moderate costs and pleasant, fruity odors. Their solvencies are less than ketones, in most cases, and their densities higher. They are less polar than ketones, alcohols, and glycol ethers, and consequently, have higher electrical resistances. The lower molecule weight esters are partially soluble in water. Common ester solvents and some of their physical properties are shown in Table 3.

Monohydric alcohols have a single hydroxyl group attached to a carbon atom. Alcohols are divided into three groups, primary, secondary, and tertiary, depending on their hydrocarbon segment configuration and the position of the hydroxyl group in the molecule. As a group, the alcohols have mild odors except for maybe the butanols. The lower alcohols are completely soluble in water. They also have low surface tensions, densities, and freezing points. Most form minimum boiling-point azeotropes with water. They also exhibit high hydrogen bonding which makes them important as solvents for many polymers. Some of the more common alcohols and some of their properties are shown in Table 4.

Glycol monoether solvents are synthesized by reacting ethylene oxide or propylene oxide with an alcohol. These solvents contain both an ether and an alcohol group as shown in Table 8. The ethylene glycol ethers are normally referred to as E-series glycol ethers and the propylene glycol ethers as P-series glycol ethers. The di and triglycol monoethers are formed as coproducts when the ethers further react with the remaining oxide and are separated by distillation. Glycol ether solvents typically have slow evaporation rates, high flash and freezing points, high densities, and low surface tensions. Almost all the E-series glycol ethers are completely soluble in water. The low molecular weight P-series glycol ethers are also completely soluble in water, but their higher homologs are only partially soluble in water.

Ethylene glycol monomethyl ether (EM) and ethylene glycol monoethyl ether (EE) have been removed from most applications because of concerns about their toxicity. However, extensive studies have found that the other ethylene glycol ethers do not exhibit the same toxicity as these two glycol ethers. However, these differences in toxicity are frequently not recognized. As a result, all the E-series glycol ethers and esters are on the HAPs list. Common E and P series glycol ethers and some of their physical properties are listed in Table 5.

The ethylene glycol and propylene glycol ether esters are produced by esterification of the hydroxyl group on a glycol ether with acetic acid. Sometimes the diglycol ethers are the basis of the molecule. The diglycol ethers are similar in solvency but slower evaporating than the derivatives of the simple glycols. Ethylene glycol monoethyl ether acetate (EE acetate), like EM and EE, has been removed from most

applications because of toxicity concerns. In most applications, it was replaced with PM acetate. Other potential replacements are Ethyl 3-Ethoxypropionate (EEP), and Exxate® 600 and 700 solvents. The common glycol ether acetates and some of their physical properties are listed in Table 5.

The estimated consumption of hydrocarbon and oxygenated solvents in coatings in 1997 is shown in Figure 1.

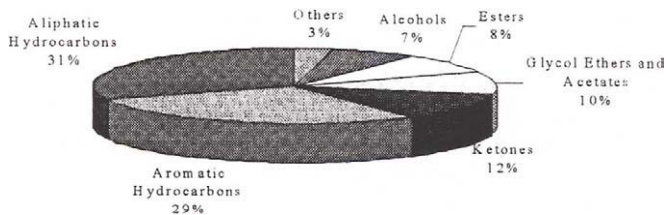


Figure 1 - U.S. Solvent Consumption by Type for Coatings in 1997
(Source: Skeist, Inc., 1998)

Solvent Properties

Solubility. The solvent system of a solventborne coating has two major functions. The first is to dissolve the resin and provide a clear, homogeneous solution. The second is to provide the proper coating viscosity.

Solubility parameters are often used to predict resin solubility in various solvents. The solubility parameter is a measure of the total attractive forces between molecules of a substance. These forces are of three major types: dispersion, polarity, and hydrogen bonding. Dispersion (London) forces are the result of temporary dipoles formed as continuous moving electrons within the molecule give rise to an unbalanced electrical field. Polar forces represent a combination of dipole-dipole (Keesom) and dipole-induced dipole (Debye) interactions. Hydrogen bonding is the attraction between polar molecules in which hydrogen is covalently bonded to electronegative elements. In order for a substance to dissolve in a solvent, the forces of attraction in the substance should be of the same order of magnitude as the forces of attraction in the solvent. Thus, dissolution will most often take place when the solubility parameters of the solute and solvent are similar. The solubility parameter, as defined by Hildebrand¹, is the square root of the cohesive energy density, and is the total molecular attraction per unit volume.

The mathematical expression is:

$$\delta = (E/V)^{1/2}$$

δ = solubility parameter

E = cohesive energy/mole

V = molar volume

Units = (calories/cm³)^{1/2} or (MPa^{1/2} cm³)

The cohesive energy is equal to the energy of vaporization. It can be measured experimentally from the heat of vaporization if the substance is volatile, where $\Delta E = \Delta H - RT$ and ΔH = heat of vaporization.

The solubility parameter of a solvent is commonly determined at 25° C, but it varies with temperature. Each solvent has a unique solubility parameter. On the other hand, a resin will have a range of values. The width of the range will vary widely for different types of resins. Resins are not volatile, and their heats of vaporization and solubility parameters cannot be measured directly. Hence, resin solubility parameters are commonly estimated from experimental solubility data.

Hansen proposed that the total solubility parameter of a solvent be divided into the contributions from the three major molecular forces which was discussed earlier. He expressed the total solubility parameter as the square root of the sum of the squares of these interactions as follows:

$$\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$$

where

δ_t = Total Solubility Parameter

δ_d = Dispersion forces

δ_p = Polar forces

δ_h = Hydrogen bonding forces

He determined values for these components empirically on the basis of experimental observations. Hansen solubility parameters for many common solvents are shown in Table 6.

Hansen represented solvents as points on a three-dimensional plot where the three parameters are axes. Solubility data determined experimentally on a given polymer in a spectrum of solvents permitted an estimation of the volume of solubility for that polymer in three-dimensional space. For most polymers, this volume of solubility is spherical if the scale of the dispersion axis relative to the other axes is doubled. Solvents within the polymer solubility sphere usually dissolve the polymer and those outside generally do not. So, a polymer's solubility parameter can be expressed as a center coordinate and a radius, which Hansen called the radius of interaction. Hansen solubility parameters for several polymers are shown in Table 7.

Solvency. A coating must have the proper viscosity for the selected application method. As the resin dissolves in the solvent, the solution viscosity increases—slowly at first, then very rapidly. How fast this transition occurs depends on two factors: (1) the solubility of the resin, and (2) the activity of the solvent. These factors, plus the viscosity of the solvent and resin, are important properties that influence the final viscosity of the coating.

A major influence on viscosity is the effect the solvent can have on the hydrodynamic volume of the resin molecules. Resin solution viscosity is generally regarded as arising from molecular entanglements between resin molecules. In the presence of a good solvent, the molecular interactions are strong and the resin molecules are fully extended into the solvent which produces high viscosity. However, in the presence of a poor solvent, the resin molecules stay coiled and the molecular interactions are weak, which produces low viscosity.

In dilute solutions, solution viscosity is proportional to the neat viscosity of the solvent. For example, isobutyl alcohol, has a neat viscosity more than five times that of VM&P naphtha, and solutions in these solvents will have viscosities that are proportional to the ratio of their neat viscosities.

The influence of the solvent's neat viscosity and solvency can be separated by calculating the specific viscosity². The specific viscosity

$$\eta_{sp} = \frac{\eta_{\text{solution}} - \eta_{\text{solvent}}}{\eta_{\text{solvent}}}$$

is the ratio of the viscosity increase occurring from dissolution to the viscosity of the solvent. Therefore, specific viscosity is dimensionless and indicates the thickening power of the resin. The effect of solvent viscosity is suppressed by treating the viscosity increase relatively.

Two solvents can provide identical viscosity reduction curves for a resin if their neat viscosities and solvencies are identical, which is unlikely. Most oxygenated solvents have higher neat viscosities than hydrocarbons, but their solvencies are usually greater at a given molecular weight.

Neat Solvent Evaporation. Since ambient conditions vary widely, evaporation rates are measured and reported on a comparative basis. Measurements of relative evaporation rates are made with an evaporometer. A weighed sample is evaporated under carefully controlled conditions of temperature, humidity, and air flow rate. A plot of time versus weight percent evaporated is obtained. It is routine to make comparisons of evaporation rates at 90% evaporation so that high boiling impurities won't substantially effect the evaporation rate. The evaporation time of a solvent is compared to that of a reference material such as n-butyl acetate, which is commonly set to 1 or 100. Humidity affects the evaporation of water miscible solvents. However, humidity has no significant effect on the evaporation of water immiscible solvents.

Molecular interaction affects the evaporation of components from a mixture, especially if one component is hydrogen bonded and another is not.³ For ideal

systems, which occur only when the blend components are very similar, the vapor pressure and resulting evaporation rate are governed by Raoult's Law:

$$P_1 = P_1^\circ X_1$$

Where P_1 = Partial pressure of a component in the mixture
 P_1° = Vapor pressure of pure component
 X_1 = Molar concentration of liquid component

This simplest form of Raoult's Law says that the partial pressure of a component in a mixture will be proportional to its molar concentration and to its vapor pressure in the pure state. For non-ideal systems, it is necessary to include in the equation an activity coefficient:

$$P_1 = \gamma_1 P_1^\circ X_1$$

Where γ_1 = Activity coefficient

The activity coefficient for a given component is the ratio of its actual partial pressure to its ideal partial pressure calculated from Raoult's Law.

Today most of the major solvent producers have computer programs that use a formula similar to the one above to calculate the evaporation rates of solvent blends. These programs typically have the physical properties of most commercially available solvents stored in files. Using this data, they estimate properties of the solvent blend such as solubility parameters, surface tension, neat viscosity, density, flash point, evaporation rate, evaporation profile (solvent composition versus weight percent evaporated), and cost. Some of these programs can even estimate the effect of temperature, humidity, and resin on solvent evaporation, and resin solubility as solvent composition changes during the evaporation process.

Solvent Evaporation from Solution. Solvent evaporation is significantly affected by the addition of a resin solute. Initially, evaporation is essentially equal to that of the neat solvents and is controlled by their volatilities. At some point in the process, solvent evaporation slows suddenly and diffusion becomes the limiting factor in this evaporative process. Resin plasticization increases solvent diffusion because solvent molecules will diffuse much faster through resins that are above their glass transition temperatures than through ones below. Small amounts of solvent are sometimes retained in the film for long periods of time. Their retention time depends on the types of resins and solvents selected.

During this evaporative process, the function of the solvent is to control flow characteristics as the film forms. If solvent evaporation is too fast, the film will not level or wet the substrate which can cause film defects such as poor gloss and adhesion. If solvent evaporation is too slow, the film will sag and perhaps become too thin. If the solvent's activity decreases significantly during evaporation, precipitation of the resin

can occur resulting in poor film formation. Thus, the evaporation rate of the solvent system can have a major impact on coating quality.

Solvent Selection in Today's Coatings

Lacquers. Lacquers are thermoplastic coatings that form films by solvent evaporation. In these coatings, a blend of solvents is typically used to achieve the proper solvency, evaporation rate, and cost. A good example is a thinner blend for a nitrocellulose resin, which contains three types of solvents: active, latent, and diluent. Ketones or esters are active solvents for this resin. An alcohol is a latent solvent, which simply means that it is not an active solvent, but in combination with an active solvent, will produce a synergistic effect. The combination of the two will be a better solvent than either one alone. Hydrocarbons are diluents and are included to reduce cost. A balanced blend of high, medium, and low boilers is selected from the three types of solvents. The exact combination depends on many factors such as application technique (spray or brush), substrate to be coated, desired drying time, cost, and VOC restrictions.

High-solids Coatings. High-solids coatings are formulated with low molecular weight resins that have low polydispersity to obtain application viscosity at high solids. These resins contain functional groups that are crosslinked to produce high performance coatings. The viscosity of these coatings is highly dependent on temperature. Thus, many are often heated to reduce their viscosity to the appropriate range for application.

According to Wicks, Jones, and Pappas⁴, resins that contain hydroxyl or carboxyl functional groups tend to associate with each other. This can cause substantial increases in viscosity. To minimize these interactions, they suggest choosing polar solvents with single hydrogen bonding acceptor sites such as ketones, ethers, or esters. Furthermore, they suggest that the effect the solvent has on the hydrodynamic volume of the resin molecules can also influence viscosity. In addition, Sprinkle⁵ reported that ketones are more effective in reducing the viscosity of high-solids resins for a given weight of solvent. He attributed these results to their higher solvencies and lower densities. If high-solid coatings are applied with electrostatic spray equipment, esters or hydrocarbon solvents are sometimes added to adjust electrical resistance. In some high-solids coatings (polyol/melamine), alcohols are commonly added to improve viscosity stability. In urethane crosslinked high-solids coatings, urethane-grade solvents are utilized because low alcohol, water, and acid content are important in these coatings.

Latex Coatings. Latexes are dispersions of high molecular weight polymers in water. They are divided into two major categories by their glass transition temperatures (T_g), low and high. The major end uses for low T_g latexes are interior and exterior architectural house paints. These latex coatings don't form films at moderate to low temperatures. Hence, solvents, known as coalescing aids, are added to aid film formation. They plasticize (soften) the polymer particles, allowing them to fuse together. After film formation, the coalescing aids slowly diffuse to the film surface and

evaporate. Coalescing aids should have low solubility in water if the latex paint will be applied to porous substrates such as dry wall or cinder blocks. Coalescing aids are usually very slow evaporating solvents such as glycol ethers, glycol ether esters, and ester-alcohols. In addition to reducing the minimum film formation temperature of the latex coating, coalescing aids improve weatherability, scrubability, cleanability, touch-up ability, and color development. The most widely used coalescing aid for low T_g latex coatings is 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, commonly known as Texanol® ester-alcohol. It has very low solubility in water and excellent hydrolytic stability, allowing it to be used with a wide variety of latexes including those with high pH. Other solvents that are used as coalescing aids for low T_g latex coatings include: propylene glycol monophenyl ether (PPh), diethylene glycol monobutyl ether (DB), dipropylene glycol n-butyl ether (DPnB), ethylene glycol 2-ethylhexyl ether (EEH), and ethylene glycol monophenyl ether (EPh). Glycol ether esters such as DB acetate are also used as coalescing aids, but their usefulness is limited because of poor hydrolytic stability.

The major end uses for high T_g latexes are OEM and industrial maintenance coatings. High T_g latex coatings generally require higher levels of coalescing aids than their lower T_g counterparts for satisfactory film formation. Faster evaporating coalescing aids are often used with the high T_g latex coatings because faster drying and hardness development are required.

The type and level of coalescing aid are determined predominately by drying conditions (temperature and humidity), but polymer hardness and coating stability are also factors. Ethylene and propylene glycol ethers are typically used as coalescing aids for these types of latexes. Of these glycol ethers, ethylene glycol monobutyl ether (EB) is the most widely used. If the relative humidity is high (70% to 90%) or heat is applied to accelerate drying, the addition of higher-boiling coalescing aids such as Texanol® ester-alcohol may be necessary to ensure satisfactory film formation.

Water-reducible Coatings. Water-reducible coatings are used mainly as industrial coatings for cans and metal substrates. They are typically thermosetting coatings made from polymers with acid or amine functional groups on their backbones. These polymers become water dispersible when the pendant groups are neutralized with volatile amines or acids. Cross-linkers are then added and the coating is diluted with water. Ethylene and propylene glycol ethers are widely used as cosolvents for these water-reducible coatings. The most commonly used one is EB, but others are also used. Alcohols are sometimes included as part of the cosolvent mainly to improve coating stability, but they also reduce the surface tension of water and accelerate the evaporation of water by forming low-boiling azeotropes with water. The level and composition of the cosolvent are adjusted to control solution viscosity behavior, improve flow-out and leveling, control evaporation characteristics of the solvent/water system, keep the film open during drying, and control sagging and running.

The Future

The EPA is phasing out the current National Ambient Air Quality Standard for ozone (1-hour standard, 0.12 ppm limit) and replacing it with an 8-hour standard with a limit of 0.08 ppm. The old standard will not be revoked in a given area until that area has met the old standard for three consecutive years. The new standard will create more non-attainment areas and will continue to apply pressure on the coating industry to reduce VOCs from all major sources. Long-term, this change may reduce the size of the U. S. solvent market.

The EPA is also developing MACT standards for many source categories to reduce the emissions of HAPs. A number of surface coating processes will be affected such as can, coil, large appliances, etc. These regulations will most likely reduce the quantity of HAPs solvents used in the coating industry.

The California Low Emissions and Reactivity Program, commonly known as the CLEAR program, will provide a voluntary alternative method to comply with VOCs limits for some commercial and consumer products. This method allows the option of meeting photochemical reactive-based CLEAR limits rather than the mass based VOC limits.

If this compliance method spreads from California to other states, the solvents that are more photochemically reactive will be replaced with solvents that are less photochemically reactive. If this occurs, it could drastically change the makeup of the U. S. solvent market.

APPENDIX OF TABLES

Table 1—Aliphatic and Aromatic Hydrocarbon Solvents and Some of Their Properties

Solvent	API ^a Gravity	Specific Gravity, 60°F	lbs/gal	Distillation Range, °F	Flash Point TCC, °F ^b	Mixed Aniline Point, °F	Kauri- Butanol Value
Aliphatic Hydrocarbons							
Hexane	78	0.675	5.62	152-157	<0	150	30
Rubber solvent	71	0.699	5.82	175-225	<0	142	34
Lacquer diluent	57	0.751	6.25	200-220	20	120	38
VM&P naphtha	56	0.755	6.28	250-300	60	140	34
Stoddard solvent	53	0.767	6.39	310-370	100	148	35
Mineral spirits	52	0.771	6.42	310-400	100	150	36
140°F solvent	49	0.784	6.53	360-415	140	157	30
Deodorized kerosene	43	0.811	6.75	350-510	140	160	30
Aromatic Hydrocarbons							
Toluene	30.8	0.872	7.26	230-232	45	49	105
Xylene	31	0.871	7.26	281-284	80	51	98
Medium-flash aromatic naphtha	30.7	0.872	7.26	311-344	110	56	91
High-flash aromatic naphtha	25.4	0.902	7.51	362-410	150	60	95

(a) API = American Petroleum Institute. API gravity is an arbitrary, standard scale for petroleum products.

(b) TCC = Tag Closed Cup.

Table 2—Ketones and Some of Their Properties

Solvent	Specific Gravity, 20°C/20°C	lbs/gal 20°C	Boiling Point, °C	Flash Point TCC °F	Solubility at 25°C % by weight		Evaporation Rate (n-BuOAc=1)
					In Water	Water In	
Acetone	0.792	6.6	57	-4	Complete	Complete	5.7
Methyl ethyl ketone	0.802	6.67	80	16	27.1	12.5	3.8
Methyl n-propyl ketone	0.807	6.74	103	46	3.1	4.2	2.3
Methyl isobutyl ketone	0.802	6.67	116	60	2	1	1.6
Methyl isoamyl ketone	0.813	6.76	145	96	0.5	1.2	0.5
Methyl n-amyl ketone	0.818	6.8	150	102	0.5	1.3	0.4
Diisobutyl ketone	0.811	6.76	169	120	0.05	0.7	0.2
Cyclohexanone	0.948	7.89	156	111	2.3	8	0.3
Diacetone alcohol	0.94	7.82	158	126	Complete	Complete	0.12
Isophorone	0.922	7.67	215	179	1.2	4.3	0.03

Table 3—Esters and Some of Their Properties

Solvent	Specific Gravity 20°C/20°C	lbs/gal 20°C	Boiling Point, °C	Flash Point TCC °F	Solubility at 25°C % by weight		Evaporation Rate (n-BuOAc=1)
					In Water	Water In	
Methyl acetate	0.94	7.7	58	9	22	7.3	5.3
Ethyl acetate (99%)	0.901	7.51	77	24	7.4	3.3	4.1
Ethyl acetate (85%-88%)	0.884	7.36	75	27	7.4	3.1	4.2
Isopropyl acetate	0.873	7.26	88	35	2.9	1.8	3.0
n-Propyl acetate	0.889	7.39	101	55	2.3	2.6	2.3
Isobutyl acetate	0.87	7.25	116	69	0.7	1.6	1.4
n-Butyl acetate	0.883	7.34	127	100	0.7	1.2	1.0
n-Butyl propionate	0.876	7.3	145	100	0.2	<0.02	0.45
p-Amyl acetate (95%)	0.876	7.29	146	106	0.2	0.9	0.4
Isobutyl Isobutyrate	0.855	7.13	148	104	<0.1	<0.2	0.4
Exxate 600	0.874	7.3	170	134	0.02	0.7	0.17
Ethyl 3-ethoxypropionate	0.95	7.91	168	136 ^a	2.9	2.2	0.12
2-Ethylhexyl acetate	0.873	7.27	202	160	0.03	0.6	0.04
Exxate 800	0.875	7.3	201	160	0.02	0.35	0.03
Ethylene Glycol Diacetate	1.107	9.22	190	191	16.4	7.6	0.02
Dibasic Esters	1.092	9.09	214	212	5.3	3.1	0.007
Exxate 1000	0.871	7.26	235	212	<0.1	0.2	0.006
Texanol ester-alcohol	0.95	7.9	257	248 ^b	<0.1	0.9	0.002
Exxate 1300	0.88	7.3	260	261	0	0.2	0.001

^a Setflash Point^b Cleveland Open Cup

Table 4—Alcohols and Some of Their Properties

Solvent	Specific Gravity, 20°C/20°C	lbs/gal 20°C	Boiling Point, °C	Flash Point TCC °F	Solubility at 25°C % by weight		Evaporation Rate (n-BuOAc=1)
					In Water	Water In	
Methanol	0.792	6.6	65	50	Complete	Complete	3.5
Ethanol, anhydrous	0.79	6.58	78	70	Complete	1.7	
Ethanol, 95%	0.812	6.76	78	75	Complete	Complete	1.9
n-Propanol	0.804	6.71	97	74	Complete	1.0	
Isopropanol, 99%	0.786	6.54	82	55	Complete	1.7	
Isobutanol	0.803	6.68	108	85	9.5	14.3	0.6
n-Butanol	0.811	6.75	118	97	7.9	20.8	0.5
Secondary butanol	0.81	6.73	100	72	20.6	30.7	0.9
Tertiary butanol	0.788	6.56	82	52	Complete	1.0	
Methyl isobutyl carbinol	0.808	6.73	132	103	1.6	6.3	0.3
Cyclohexanol	0.962	8.01	161	156	0.1	11.8	0.05
2-Ethylhexanol	0.833	6.94	185	164	0.1	2.6	0.01

Table 5—Glycol Ethers and Their Acetates, and Some of Their Properties

Solvent	Specific Gravity, 20°C/20°C	lbs/gal 20°C	Boiling Range, °C	Flash Point TCC °F	Solubility at 25°C % by weight		Evaporation Rate (n-BuAc=1)
					In Water	Water In	
Ethylene Glycol							
Monoethyl Ether	0.931	7.75	134-136	110	Complete	Complete	0.3
EE							
Monoethyl ether acetate	0.973	8.11	150-160	130	23.8	6.5	0.2
EE Acetate							
Monopropyl ether	0.913	7.59	150-154	120	Complete	Complete	0.2
EP							
Monobutyl ether	0.902	7.51	169-173	143	Complete	Complete	0.09
EB							
Monobutyl ether acetate	0.941	7.84	186-194	160	1.1	1.6	0.03
EB Acetate							
Propylene Glycol							
Monomethyl ether	0.923	7.69	117-125	91	Complete	Complete	0.7
PM							
Monomethyl ether acetate	0.97	8.06	140-150	114	20	5.9	0.4
PM Acetate							
Monopropyl ether	0.885 ^b	7.38 ^b	150 ^c	119	Complete	Complete	0.21
PnP							
Monobutyl ether	0.884 ^b	7.37 ^b	170 ^c	138	6.4	16	0.08
PnB							
Monophenyl ether	1.063 ^b	8.80 ^b	243 ^c	240	1.1	7	0.002
PPh							

Diethylene Glycol

Monomethyl ether DM	1.021	8.5	192-196	191	Complete	Complete	0.02
Monoethyl ether DE	0.99	8.25	198-204	195	Complete	Complete	0.02
Monoethyl ether acetate DE Acetate	1.012	8.42	214-221	225 ^a	Complete	Complete	0.008
Monobutyl ether DB	0.955	7.94	230-235	232 ^a	Complete	Complete	0.004
Monobutyl ether acetate DB Acetate	0.98	8.16	235-250	240 ^a	6.5	3.7	0.002

Dipropylene Glycol

Monomethyl ether DPM	0.950 b	7.91 ^b	184 ^c	167 ^d	Complete	Complete	0.02
Monopropyl ether DPnP	0.922 b	7.70 ^b	212 ^c	190 ^d	19	20.5	0.015
Monobutyl ether DPnB	0.906 b	7.55 ^b	229 ^c	212 ^d	5	12.5	0.01

^aCleveland Open Cup

^b 25 °C

^c Boiling Point

^d Setaflash Point

Table 6—Hansen Solubility Parameters of Various Solvents (MPa^{1/2} cm³)

Solvents	δ_D	δ_P	δ_H	δ_T
Acetone	15.5	10.4	7.0	20.0
Aromatic 100	17.8	0.6	1.4	17.8
Aromatic 150	17.8	0.6	1.4	17.8
n-Butyl acetate	15.8	3.7	6.3	17.4
n-Butyl alcohol	16.0	5.7	15.8	23.1
sec-Butyl alcohol	15.8	5.7	14.5	22.1
γ -Butyrolactone	19.0	16.6	7.4	26.3
Cyclohexane	16.8	0	0.2	16.8
Cyclohexanol	17.4	4.1	13.5	22.5
Cyclohexanone	17.8	6.3	5.1	19.6
Diacetone alcohol	15.8	8.2	10.8	20.9
Dibasic esters (DBE)	16.2	4.7	8.4	18.8
Diethylene glycol n-butyl ether	16.0	7.0	0.6	20.5
Diethylene glycol butyl ether acetate	16.0	4.1	8.2	18.4
Diethylene glycol n-ethyl ether	16.2	9.2	12.3	21.9
Diethylene glycol methyl ether	16.2	7.8	12.7	21.9
Diethylene glycol n-propyl ether	16.0	7.2	11.3	20.9
Diethylene glycol ethyl ether acetate	16.8	6.4	15.8	19.2
Diethyl ketone	15.8	7.6	4.7	18.1
Diisobutyl ketone	16.0	3.7	4.1	16.9
Dipropylene glycol n-butyl ether	15.4	5.6	9.0	18.7
Dipropylene glycol methyl ether	15.5	5.7	11.2	20.0
Ethyl acetate	15.8	5.3	7.2	18.1
Ethyl alcohol	15.8	8.8	19.4	26.6
Ethyl benzene	17.8	0.6	1.4	17.8
Ethyl 3-ethoxypropionate	16.2	9.2	9.4	18.6
Ethylene glycol diacetate	16.4	10.5	12.9	19.4
Ethylene glycol n-butyl ether	16.0	5.1	12.3	20.9
Ethylene glycol butyl ether acetate	15.3	4.5	8.8	18.2
Ethylene glycol 2-ethylhexyl ether	16.0	4.1	5.1	17.2
Ethylene glycol n-propyl ether	16.0	6.2	13.3	22.7
2-Ethyl hexanol	16.0	3.3	11.8	20.3
2-Ethylhexyl acetate	15.7	2.9	5.1	16.8
n-Heptane	15.3	0	0	15.3
n-Hexane	14.9	0	0	14.9

Solvents	δD	δP	δH	δT
Isobutyl acetate	15.1	3.7	6.3	16.8
Isobutyl alcohol	15.1	5.7	16.0	22.7
Isobutyl isobutyrate	15.1	2.9	5.9	16.5
Isophorone	16.6	8.2	7.4	19.9
Isopropyl acetate	15.6	3.3	8.8	17.6
Isopropyl alcohol	15.8	6.1	16.4	23.5
Methyl acetate	15.5	7.2	7.6	18.7
Methyl alcohol	15.1	12.3	22.3	29.6
Methyl n-amyl ketone	16.2	5.7	4.1	17.6
Methyl ethyl ketone	16.0	9.0	5.1	19.0
Methyl isoamyl ketone	16.0	5.7	4.1	17.4
Methyl isobutyl carbinol	15.4	3.3	12.3	19.8
Methyl isobutyl ketone	15.3	6.1	4.1	17.0
Methyl n-propyl ketone	15.8	9.0	7.6	18.2
N-Methyl 2-pyrrolidone	18.0	12.3	7.2	22.9
Methylene chloride	18.2	6.3	6.1	20.3
Nitroethane	16.0	15.5	4.5	22.7
Nitromethane	15.8	18.8	5.1	25.1
2-Nitropropane	16.2	12.1	4.1	20.6
n-Propyl acetate	16.4	6.6	8.2	17.6
n-Propyl alcohol	16.0	6.8	17.4	24.5
Propylene glycol n-butyl ether	15.6	5.8	11.2	18.4
Propylene glycol t-butyl ether	15.4	6.8	9.3	19.6
Propylene glycol phenyl ether	18.7	5.7	11.3	21.5
Propylene glycol n-propyl ether	15.5	6.3	12.4	19.4
Propylene glycol methyl ether	15.6	6.3	11.6	20.5
Propylene glycol methyl ether acetate	16.1	6.1	6.6	19.2
Texanol ester-alcohol	15.1	6.1	9.8	19.0
Toluene	18.0	1.4	2.0	18.2
Xylene (mixed isomers)	17.6	1.0	3.1	17.8
VM&P naphtha	15.1	0	0.2	15.1

Table 7— Hansen Solubility Parameters of Polymers

Polymers	Tradename	Supplier	δD	δP	δH	Radius
Acrylic (PEAM)	Eiacite 2042	Du Pont	17.6	9.7	4.0	10.6
Acrylic (PMMA)	Perspex	ICI	18.6	10.5	7.5	8.6
Acrylic	Paraloid P400	Rohm&Haas	19.2	9.6	9.3	12.2
Alkyd, long oil (66% Oil Length)	Plexal P65	Polyplex	20.4	3.4	4.6	13.7
Alkyd, short oil (34% Oil Length)	Plexal C34	Polyplex	18.5	9.2	4.9	10.6
Nitrocellulose	H-23, 1/2 sec.	Aqualon	15.4	14.7	8.8	11.5
Epoxy	Epon 828	Shell	21.3	14.2	6.1	17.7
Epoxy	Epon 1001	Shell	20.0	10.3	10.1	10.0
Epoxy	Epon 1004	Shell	17.4	10.5	9.0	7.9
Hexamethoxymethyl melamine	Cymel 300	Cytec	20.4	8.5	10.6	14.7
Isocyanate, phenol blocked	Suprasec F5100	ICI	20.2	13.2	13.1	11.7
Phenolic	S. Beckacite 1000	Reichhold	23.3	6.6	8.3	19.8
Polyamide	Versamid 930	Henkel	17.4	-1.9	14.9	9.6
Polyester	Desmophen 850	Bayer	21.5	14.9	12.3	16.7
Polyvinyl butyral	Butvar B-76	Monsanto	18.6	4.4	13.0	10.6
Urea-formaldehyde	Plastopal H	BASF	20.8	8.3	12.7	12.7
Vinyl chloride	Vipla KR	Montecatini	18.2	7.5	8.3	3.5
Vinyl chloride / vinyl acetate	UCAR VYHH	Union Carbide	17.4	10.2	5.9	7.8

Table 8—General Chemical Structures for Various Types of Solvents

Hydrocarbons Groups		Oxygenated Groups	
Methyl	— CH ₃		$\begin{array}{c} \text{O} \\ \\ \text{R} - \text{C} - \text{R}^a \end{array}$
Ethyl	— CH ₂ CH ₃	Ketone	
Propyl	— CH ₂ CH ₂ CH ₃	Alcohol	R — OH
Isopropyl	$\begin{array}{c} \text{— CH — CH}_3 \\ \\ \text{CH}_3 \end{array}$	Glycol ether	HO — R — O R
Butyl	— CH ₂ CH ₂ CH ₂ CH ₃	Ester (Acetate)	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \quad \quad \\ \text{CH}_3\text{C} - \text{O} - \text{R} \end{array}$
Isobutyl	$\begin{array}{c} \text{— CH}_2\text{ CH CH}_3 \\ \\ \text{CH}_3 \end{array}$	Ester (Propionate)	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2 - \text{C} - \text{O} - \text{R} \end{array}$
Amyl	— CH ₂ CH ₂ CH ₂ CH ₂ CH ₃		

^a R = Hydrocarbon (alkyl) group

LITERATURE CITED

- (1) Hildebrand, J. H., "The Solubility of Non-electrolytes," Third Edition, Reinhold Publishing Corp., New York, 1949.
- (2) Lambourne, R., "Paint and Surface Coatings: Theory and Practice," Ellis Horwood, Limited, Chichester, West Sussex, England (1993).
- (3) Ellis, W.H. and Goff, P.L., "Precise Control of Solvent Blend Composition During Evaporation," JOURNAL OF PAINT TECHNOLOGY, 44, No. 564, 79 (1972).
- (4) Wicks W. Z., Jones F. N., and Pappas S. P., "Organic Coatings, Science and Technology, Volume 1, Chapter XV, 1992.
- (5) Sprinkle, G. P., "Selecting Solvents for High Solids Coatings," Modern Paint and Coatings, April, 44, (1983).
- (6) Hansen, C. M., Private communication, 1987