8 Applications – Coatings and Other Filled Polymer Systems

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ABSTRACT

Hansen solubility parameters (HSP) are widely used in the coatings industry to help find optimum solvents and solvent combinations. They also aid in substitution to less hazardous formulations in various other types of products such as cleaners, printing inks, adhesives, etc. The discussion in this chapter includes the physical chemical reasons why solvents function as they do in many practical cases. The behavior of solvents in connection with surfaces of various kinds and the use of HSP to understand and control surface phenomena is especially emphasized. Products where HSP concepts can be used in a manner similar to coatings include other (filled) polymer systems of various types such as adhesives, printing inks, chewing gum, etc. There are many examples of controlled self-assembly.

INTRODUCTION

There are many applications documented in the literature where HSP have aided in the selection of solvents, understanding and controlling processes, and, in general, offering guidance where affinities among materials are of prime importance^{1–5} (see also the following chapters and examples below). This chapter emphasizes coatings applications and discusses the practical application of HSP to solvent selection. Computer techniques are helpful, but not necessary. The same principles useful for understanding the behavior of coatings are useful in understanding behavior in a larger number of related products, including adhesives, printing inks, and chewing gum, to mention a few. These contain widely different materials, both liquid and solid, which can be characterized by HSP. This allows their relative affinities to be established. Previous chapters have discussed how to assign HSP to solvents, plasticizers, polymers, and resins, as well as to the surfaces of substrates, pigments, fillers, and fibers. Various additives such as resins, surfactants, flavors, aromas, scents, drugs, etc., can also be characterized by HSP to infer how they behave in seemingly complex systems.

SOLVENTS

In order to find the optimum solvent for a polymer, one must have or estimate its HSP. Matching the HSP of an already existing solvent or combination of solvents can be done, but this procedure does not necessarily optimize the new situation. The optimum depends on what is desired of the system. A solvent with the highest possible affinity for the polymer is both expensive and probably not necessary and will rarely be optimum. In more recent years, optimization increasingly includes considerations of worker safety and the external environment. Volatile organic compounds (VOC) are to be reduced to the greatest extent possible. Chapter 11 is devoted to replacing ozone-depleting chemicals in cleaning operations.

Whereas hand calculations and plotting of data are still quite useful and at times more rapid than computer processing, it is becoming almost mandatory that computers be used. To this end, most solvent suppliers and many large users of solvents have computer programs to predict solution behavior as well as evaporation phenomena. In spite of these pressures to let the computer do the thinking, an experienced formulator can often arrive at a near-optimum result without recourse to paper or to computers. A major factor in this almost immediate overview is the decrease in the number of solvents useful in coatings. By putting this together with other necessary considerations such as flash point, proper evaporation rate, cost, odor, availability, etc., the experienced formulator who knows the HSP for the relatively few solvents possible in a given situation will be able to select a near-optimum combination by a process of exclusion and simple mental arithmetic. This does not mean the use of HSP is on the way out. The real benefit of this concept is in interpreting more complicated behavior, such as affinities of polymers with polymers and polymers with surfaces as described in the following. Much more work needs to be done in these areas, but the following gives an indication of what might be expected.

As indicated previously, computer techniques can be very useful but are not always necessary, and simple two-dimensional plots using δ_P and δ_H can often be used by those with limited experience with these techniques to solve practical problems. The nonpolar cohesion parameter, δ_D , cannot be neglected in every case, but, for example, when comparing noncyclic solvents in practical situations, it has been found that their dispersion parameters will be rather close regardless of structure. Cyclic solvents, and those containing atoms significantly larger than carbon, such as chlorine, bromine, metals, etc., will have higher dispersion parameters. The total solubility parameter for aliphatic hydrocarbon solvents is identical with their dispersion parameter and increases only slightly with increased chain length. This same trend is expected for oligomers of a polymer as molecular weight increases. Regardless of the means of processing data, the following examples are intended to illustrate principles on which to base a systematic course of action.

Most coatings applications involve solvents reasonably well within the solubility limit which is indicated by the boundary of a solubility plot such as that shown in Figure 8.1.¹ A maximum of cheaper hydrocarbon solvent is also desired and can frequently be used to arrive at such a situation for common polymers used in coatings. Some safety margin in terms of extra solvency is advised because of temperature changes, potential variations in production, etc. These can lead to a situation where solvent quality changes in an adverse manner. Balance of solvent quality on evaporation of mixed solvents is also necessary. Here again, computer approaches are possible, and calculations of solvent quality can be made at all stages of evaporation. It is usually good practice to include a small or moderate amount of slowly evaporating solvent of good quality and low water sensitivity to take care of this situation. These have frequently been slowly evaporating ketones and esters.

An oxygenated solvent which is frequently added to hydrocarbon solvents and has been cost effective in increasing the very important hydrogen-bonding parameter has been *n*-butanol (or sometimes 2-butanol). The mixture of equal parts xylene and *n*-butanol has been widely used in conjunction with many polymers such as epoxies, but a third solvent, such as a ketone, ester, or glycol ether, is often included in small amounts to increase the polar parameter/solvency of the mixture. Neither xylene nor *n*-butanol satisfactorily dissolves an epoxy of higher molecular weight by itself. These are located in boundary regions of the solubility region for epoxies, but on opposite sides of the characteristic Hansen spheres (see Figure 8.2).¹ Glycol ethers also can be added to hydrocarbon solvents with advantage, and the polar and hydrogen-bonding parameters are higher than if *n*-butanol had been added to the same concentration. There are many possibilities, and a solubility parameter approach is particularly valuable in quickly limiting the number of candidates. The addition of glycol ethers or other water-soluble solvents can have adverse effects, such as increased water sensitivity and poorer corrosion resistance of the final film, as some solvent retention must be anticipated, and the least volatile solvent is enriched and left behind.

Relative costs for improving solvency from a hydrocarbon base solvent can be estimated by the relation $(\delta_{P}^{2} + \delta_{H}^{2})^{1/2}/\text{cost}$. This relation has generally pointed to the use of *n*-butanol, for

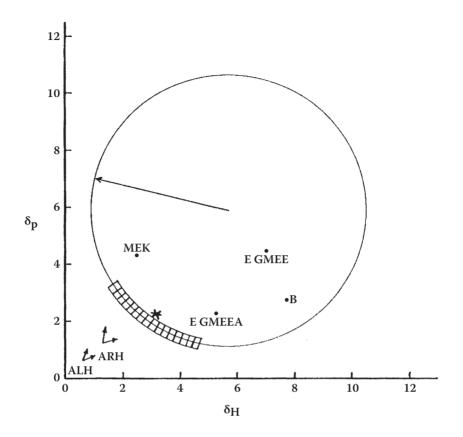


FIGURE 8.1 Sketch showing location of typical solvents relative to the HSP of a binder. Aliphatic hydrocarbons (ALH) and aromatic hydrocarbons (ARH) do not always dissolve well enough so other solvents must be added to bring the mixed solvent composition into the region of solubility for the binder. Ketones (MEK, methyl ethyl ketone), alcohols (B, *n*-butanol), or other solvents such as glycol ethers and their acetates (here ethylene glycol monoethyl ether and ethylene glycol monoethyl ether acetate) can be used to do this. The expected solvent improvement at least cost is discussed in the text as the quantity $(\delta_P^2 + \delta_H^2)^{1/2}$ /cost. Units in the figure are in (cal/cm³)^{1/2}. The choice of solvent today would involve glycol ethers based on propylene glycol as discussed in Chapter 18. (From Hansen, C.M., *Färg och Lack*, 17(4), 69–77, 1971. With permission.)

example, as a cost-efficient solvent to increase the hydrogen-bonding parameter in particular. Solvents can be ranked in this manner to arrive at the least cost solutions to given solvent selection problems.

Coalescing solvents in water-reducible coatings are often (but not always) those with somewhat higher hydrogen-bonding parameters than the polymer, which also means they are water soluble or have considerable water solubility. The distribution between the water phase and the dispersed polymer phase depends on the relative affinities for water and the polymer. Solvents which are not particularly water soluble will preferentially be found in the polymer phase. Such coalescing solvents may be preferred for applications to porous substrates, making certain they are where they are needed when they are needed. Otherwise, water-soluble coalescing solvents would tend to follow the aqueous phase, penetrating the substrate faster than the polymer particles, which also get filtered out and they are not therefore available to do their job in the film when the water evaporates. When water evaporates, the solvent must dissolve to some extent in the polymer to promote coalescence. Of course, this affinity of the coalescence solvent for the polymer is a function of its HSP relative to those of the polymer.

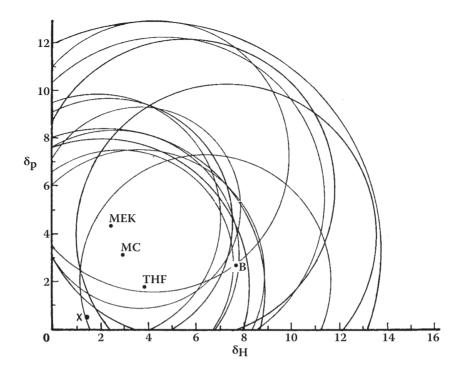


FIGURE 8.2 Sketch showing formulation principles using two relatively poor solvents in combination to arrive at a good solvent. Xylene (X) can be mixed with *n*-butanol (B) to arrive at a mixture which can be improved by additions of tetrahydrofuran (THF), methylene chloride (MC), or methyl ethyl ketone (MEK) among others. These three very volatile solvents have often been used in analytical work, paint removers, etc., because they dissolve all of the typical coatings binders shown in the figure. Labeling requirements have dictated other choices in more recent years. Units are (cal/cm³)^{1/2}. (From Hansen, C.M., *Färg och Lack*, 17(4), 69–77, 1971. With permission.)

Amines are frequently added to water-reducible coatings to neutralize acid groups built into polymers, thus providing a water-solubilizing amine salt. Amine in excess of that required for total neutralization of the acid groups acts like a solvent. Such amine salts have been characterized separately to demonstrate that they have higher solubility parameters than either (acetic) acid or organic bases.⁶ These salts are hydrophilic and have very little affinity for the polymers used in coatings, which means they are to be found in a stabilizing role in the interface in the aqueous phase while still being attached to the polymer. Electrostatic repulsion contributes to stability as well, and the dispersed solubilized polymer can be visualized in terms of a porcupine with raised quills.

Surface-active agents, whether nonionic or ionic, are also to be found where the affinities of the respective parts of their molecules dictate their placement; like seeks like. The hydrophilic end with a high hydrogen-bonding parameter will seek the aqueous phase, and the hydrophobic end will seek out an environment where energy differences are lowest (self-assembly). It might be noted here that some solvents have surfactant-like properties as well. Ethylene glycol monobutyl ether, in particular, has been shown to be a good coupling agent, as well as contributing to lowered surface tension.⁷ The hydrophobic end of such molecules may reside within the polymer if HSP relations dictate this. Otherwise, if the HSP differences are too great, the hydrophobic portion may be forced to remain in the interfacial region, not being accepted by the aqueous phase either.

Increases in temperature especially lead to lower hydrogen-bonding parameters (see Chapter 1, Chapter 3, and Chapter 10). For this reason, solvents with high hydrogen-bonding parameters, such as glycols, glycol ethers, and alcohols, become better solvents for most polymers at higher

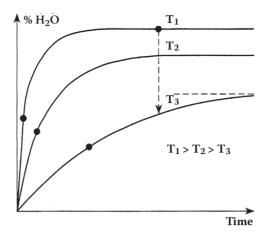


FIGURE 8.3 Sketch of water uptake in a polymer as a function of temperature. Higher temperature leads to more rapid uptake and to higher equilibrium levels. Quenching to a lower temperature (arrow) leads to excess water in the film and possibly to water blisters and delamination (see text for further discussion). (Reprinted from Hansen, C.M., New developments in corrosion and blister formation in coatings, *Prog. Org. Coat.*, 26, 113–120, 1995. With permission from Elsevier Science.)

temperatures. This can markedly affect hot-room stability in water-reducible coatings, for example, as more of the solvent will partition to the polymer phase, which swells, becomes more fluid, and has altered affinities for stabilizing surface-active agents. These may dissolve too readily in the swollen, dispersed polymer. When carefully controlled, these temperature effects are an advantage in water-reducible, oven-cured coatings, leading to higher film integrity, as poor solvents at room temperature become good solvents in the oven after the water has evaporated.

A very special destructive effect of water is caused by the reduction of its hydrogen-bonding parameter with increases in temperature. The solubility of water in most polymers is higher at a higher temperature than it is at a lowered temperature because the HSP for the polymer and water match better at the higher temperature. It has been documented in many cases that a rapid quench from hot water to cold water can cause blisters in coatings.⁸ Previously dissolved water within the film now becomes in excess of that soluble in the film. This can be seen in Figure 8.3 where water uptake curves are shown for three temperatures. The amount and rate of uptake is higher for the higher temperatures. Rapid cooling to below the solubility limit at a lower temperature means the system is supersaturated. Excess water freed by this mechanism has been called SWEAT (soluble water exuded at lowered temperatures). If the SWEAT water cannot rapidly diffuse out of the coating, it will appear as a separate phase, perhaps first as clusters, but ultimately at hydrophilic sites or at a substrate. The coating fails by blistering or delamination. This special effect has been noted by the author in coatings (alkyd, polyester, and epoxy), in rigid plastics such as poly(phenylene sulfide) and poly(ether sulfone), and even in EPDM rubber. Examples of measurements of this type are shown in Chapter 12, Figure 12.3 and Figure 12.4 for an EPDM rubber gasket and for a poly(ether sulfone) tensile bar. This effect is not restricted to water; it has also been seen for an epoxy coating that was repeatedly removed from room temperature methanol to measure weight gain. The cooling due to the methanol evaporation was sufficient to produce methanol blisters near the air surface of the coating because of excess amounts of methanol over that soluble at the lower temperature resulting from the methanol evaporation.

The use of supercritical gases as solvents has become possible in recent years. The solubility parameters for carbon dioxide have been reported ⁹ earlier and in the first edition of this handbook, based on the room temperature solubility of the gas in different liquids. These are now revised as discussed in Chapter 10 to δ_D , δ_P and δ_H equal to 15.7, 6.3, and 5.7. HSP values are reported as a

function of temperature and pressure. This same type of analysis can be used to evaluate the temperature and pressure effects for other gases. See also Chapter 3. These parameters are found using the solvents that dissolve more than the theoretical amounts of carbon dioxide that are reported in Table 10.2. The use of such gases is considered an advantage for the environment, but their use has been limited to relatively smaller items because of the size of pressure equipment.

Solvent technology has also been used in a wide variety of other products and processes as listed by Barton.² One can mention the formulation of solvent cleaners based on vegetable oils as an additional example.¹⁰ Such "green" products have found increasing use, as have those solvents with low volatility, low VOC, and low labeling requirements.

TECHNIQUES FOR DATA TREATMENT

As mentioned earlier, a simple approach to many practical problems is to make a two-dimensional plot of polar vs. hydrogen-bonding parameters with a circle (or estimated circle) for the polymer in question. The circle should encompass the good solvents. One can then plot points for potential solvents and quickly arrive at a starting composition for an experiment. Subsequently, this can be adjusted if necessary. A linear mixing rule based on the volume (or weight) fractions of the solvent components is usually satisfactory. Plasticizers should be included in the calculations. They will be very slow to dissolve rigid polymers, in particular, and are, of course, nonvolatile for all practical purposes.

A special plotting technique for solvent selection developed by Teas¹¹ is used frequently by those who restore old paintings. The art involved in this stage of the conservation process is to remove the old varnish without attacking the underlying original masterpiece. HSP principles have been used since the late 1960s for selecting solvents and solvent blends for this purpose.¹² The triangular plotting technique uses parameters for the solvents, which, in fact, are modified HSP parameters. The individual Hansen parameters are normalized by the sum of the three parameters. This gives three fractional parameters defined by Equation 8.1 to Equation 8.3.

$$f_{d} = 100\delta_{\rm D}/(\delta_{\rm D} + \delta_{\rm P} + \delta_{\rm H}) \tag{8.1}$$

$$f_{\rm P} = 100\delta_{\rm P}/(\delta_{\rm D} + \delta_{\rm P} + \delta_{\rm H}) \tag{8.2}$$

$$f_{\rm h} = 100\delta_{\rm H}/(\delta_{\rm D} + \delta_{\rm P} + \delta_{\rm H}) \tag{8.3}$$

The sum of these three fractional parameters is 100 in the form the equations are written. This allows use of the special triangular technique. Some accuracy is lost, and there is no theoretical justification for this plotting technique, but one does get all three parameters onto a two-dimensional plot with enough accuracy that its use has survived for this type of application (at least). The Teas plot in Figure 8.4 includes an estimate of the solubility/strong attack of older, dried oil paint. A varnish which could be considered for use is Paraloid[®] B72, a copolymer of ethyl methacrylate and methyl methacrylate from Rohm and Haas. There is a region in the lower, right-hand part of this plot where the varnish is soluble and the dried oil is not. The varnish remover should be in this region. Mixtures of hydrocarbon solvent and ethanol are located in this region and could be considered. HSP correlations for materials of interest in restoration of older paintings are included in Table 8.1.

A helpful simplifying relation to use in solvent selection calculations using solubility parameters is that the resultant values for mixtures can be estimated from volume fraction averages for each solubility parameter component. Solvent quality can be adjusted by the RED number concept, which is discussed in Chapter 1 (Equation 1.10), or graphically as described above.

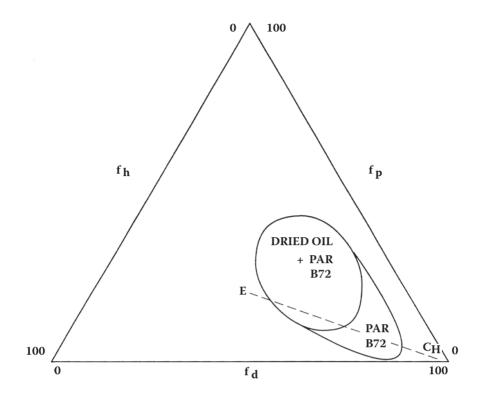


FIGURE 8.4 Teas plot for a typical painting conservation situation where a varnish is to be removed or applied without attacking the underlying original oil painting. Solvents indicated are cyclohexane (C), heptane (H), and ethanol (E) (see text for further discussion).

TABLE 8.1HSP Correlations for Materials of Interest in theConservation of Older Paintings						
MATERIAL	δ	δ_{P}	$\delta_{\rm H}$	Ro	FIT	G/T
Paraloid® 22 solubility	17.6	7.4	5.6	9.4	1.000	17/26
Dammar gum dewaxed	18.4	4.2	7.8	8.3	0.915	30/56
Dried oil (estimate)	16.0	6.0	7.0	5.0	1.000	9/22

A computer search with the SPHERE computer program (Chapter 1) for "nearest neighbors" for a given single solvent has been used many times to locate alternates for a wide variety of product types including coatings of various descriptions, cleaners, etc. A similar application is to predict which other solvents will probably be aggressive to a chemically resistant coating where very limited data have indicated a single solvent or two are somewhat aggressive. A nearest neighbor search involves calculation of the quantity Ra (Chapter 1, Equation 1.9) for a whole database, for example, and then arranging the printout in RED number order (Chapter 1, Equation 1.10). The potentially most aggressive liquids are at the top of the list. Solvents with RED less than 1.0 are "good" and therefore easily recognized. Sorting out these possibilities considering toxicity, evaporation rate, cost, etc. leads to the most promising candidates for the substitution.

SOLVENTS AND SURFACE PHENOMENA IN COATINGS (SELF-ASSEMBLY)

Chapter 6 and Chapter 7 have been devoted to the characterization of surfaces for substrates, pigments, fillers, and the like. This means the interplay between solvent, polymer, and surfaces can be inferred by their relative affinities. These depend on their HSP relative to each other, and the RED number concept can be quite useful.

As stated previously, the desired solvent quality in many coatings is just slightly better than that of a marginal solvent. This means RED numbers just under 1.0 relative to the polymer will be sought. One reason for the desired marginal solvent quality is that this will ensure that the polymer adsorbed onto pigment surfaces during pigment dispersion has little reason to dissolve away from that surface. The dispersion stabilizing polymer should remain on the pigment surface where it is desired. If this polymer is dissolved away, the result is most likely pigment flocculation, which leads to color change, undesired settling, and perhaps even rheological difficulties. The solvent in this case should have a RED number for the pigment surface greater than 1.0, or at least reasonably high, to aid in the planned affinity approach to pigment dispersion stability. Of course, the polymer, or some portion of it, and the pigment surface should have high affinity for each other. A sketch of the optimum relations in coatings is given in Figure 8.5 where the marginal solvent is number 1. Solvent 2 would probably be too expensive and, in addition, will probably dissolve the polymer too well.

Schröder¹³ (BASF) confirms that the optimum polymer adsorption will be found when the binder and pigment surface have the same HSP. He indicates that the solvent should be very poor for the pigment and located in the boundary region for the binder. He prefers the pigment to have HSP values placing it intermediate between the solvent and binder. This is suggested for conditions where the solvent has higher HSP than the pigment, as well as for conditions where the solvent has lower HSP than the pigment. This situation, with the solvent and binder on opposite sides of the pigment, means the composite vehicle has parameters very closely matching those of the pigment. A very similar type of result was found by Skaarup,¹⁴ who especially emphasized that optimum color strength was found for solvents marginal in quality for the binder and poor for the pigment in question.

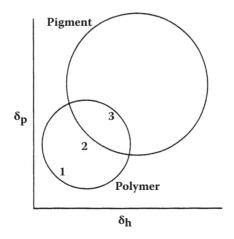


FIGURE 8.5 Sketch showing influence of solvent quality on expected pigment dispersion stability (see text and Figure 1.1 for discussion). (Reprinted from Hansen, C.M., *Paint and Coating Testing Manual*, 14th ed. of the Gardner-Sward Handbook, 1995, p. 400. With permission. Copyright ASTM.)

In special applications, an extended polymer chain configuration is desirable, but a solid anchor to the pigment surface is also desired. This means a better-than-marginal solvent for the polymer is desired. A good anchor has high affinity for the pigment surface and marginal affinity for the solvent. Solvent 3 (Figure 8.5) would adsorb onto the pigment surface preferentially, and pigment dispersion stability would be poor. An extension of this thinking may be required for pigment pastes and other very highly filled products. In these cases, there is little dispersing vehicle relative to the pigment, and the solvent must be considered as being part of the dispersing vehicle. In such cases the solvent may have high affinity for the pigment surface as well as for dispersing polymer. An ideal situation here is where all the ingredients have the same HSP.

POLYMER COMPATIBILITY

In some cases, closer-than-usual matches between solvent and polymer solubility parameters are required. This is true when two polymers are mixed and one of them precipitates. This is most likely the polymer with the larger molecular weight, and it must be dissolved even better. Lower RED numbers with respect to this polymer are desired, while still maintaining affinity for the other polymer. Miscible blends of two polymers have been systematically found using a solvent mixture composed exclusively of nonsolvents.¹⁵ This is demonstrated schematically in Figure 8.6, where it can be seen that different percentage blends of solvents 1 and 2 will have different relative affinities for the polymers. No other alternative theory of polymer solution thermodynamics can duplicate this predictive ability. Polymer miscibility is enhanced by larger overlapping solubility regions for the polymers as sketched in Figure 8.7. Polymers A and B should be compatible, whereas polymer C would not. Such a systematic analysis allows modification of a given polymer to provide more overlap and enhanced compatibility. The advantages of a copolymer containing the monomers of A or B and C should also be evident. Such a copolymer will essentially couple the system together.

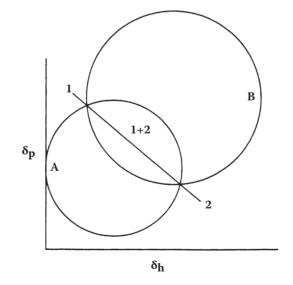


FIGURE 8.6 Sketch showing how two otherwise immiscible polymers can be brought into a homogeneous solution by the use of mixed nonsolvents. (Reprinted from Hansen, C.M., *Paint and Coating Testing Manual*, 14th ed. of the Gardner-Sward Handbook, 1995, p. 400. With permission. Copyright ASTM.)

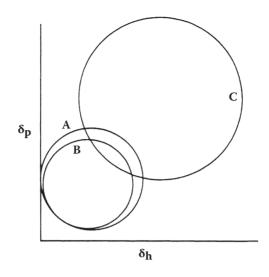


FIGURE 8.7 Sketch describing expected polymer miscibility relations (see text for discussion). (Reprinted from Hansen, C.M., *Paint and Coating Testing Manual*, 14th ed. of the *Gardner-Sward Handbook*, 1995, p. 401. With permission. Copyright ASTM.)

Van Dyk et al.¹⁶ have correlated the inherent viscosity of polymer solutions with HSP. The inherent (intrinsic) viscosity used in this study, $[\eta]$, is given by Equation 8.4.

$$[\eta] = (\eta_s / \eta_0) / c \tag{8.4}$$

 η_s is the solution viscosity, η_0 is the solvent viscosity, and c is the solution concentration. The concentration used was about 0.5 g/dl. This is an expression reflecting polymer chain extension in solution, with higher values reflecting greater chain entanglements because of greater polymer extension. This is interesting in that the solubility parameter is a thermodynamic consideration, whereas the viscosity is a kinetic phenomenon. Higher [η] were found for solvents with HSP nearest those of the polymer.

As stated above additional uses of HSP (and the total solubility parameter) in solvent technology can be found in Barton,² but these are too numerous to include here. However, a couple of examples relating to guided polymer compatibility are worthy of special mention. These are the formulation of asymmetric membranes for separations,^{17,18} where polymer solutions — having given HSP relations — and at least one solvent soluble in water are used. The solution is immersed in water, the solvent quality becomes bad, and a controlled porous membrane results. Another example of controlled phase relations during a dynamic process is found in the formulation of self-stratifying coatings. This is discussed in Chapter 6 in terms of the creation of interfaces and therefore interfacial surface tension. The HSP principles involved in this type of coating can be seen in Figure 8.8. The solvent must dissolve both the topcoat and primer and allow the lower surface tension topcoat to migrate to the surface during film formation. Formulation principles have been discussed in detail elsewhere.^{19,20} Before concluding this section, some of the recent work on miscible polymer blends should also be noted.^{21,22} This work used group contribution estimates of the δ_P and δ_H parameters only in an effort to correlate interfacial tension between polymers, assuming that the δ_D parameters would not be too different. Although this is a good starting point to prove the procedure has possibilities, further differentiation between the polymers and improved group contribution methods may offer even more improvement.

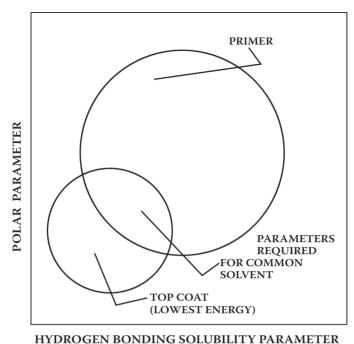


FIGURE 8.8 Sketch illustrating the principles of solvent selection for self-stratifying coatings. (From Birdi, K.S., Ed., *Handbook of Surface and Colloid Chemistry*, CRC Press, Boca Raton, FL, 1997, p. 324. With permission.)

HANSEN SOLUBILITY PARAMETER PRINCIPLES APPLIED TO UNDERSTANDING OTHER FILLED POLYMER SYSTEMS

Recent characterizations of inorganic fillers and fibers²³ have confirmed that HSP concepts can be applied to engineered fiber-filled systems such as those based on polypropylene.

The behavior of chewing gum can also be analyzed in terms of solubility parameter principles.²⁴ In addition to rheological behavior, appearance, and other performance considerations, a desired product characteristic is that the release of the taste components should be controlled. Greater differences in solubility parameters between flavoring agents and wax-free gum bases lead to enhanced flavor release. Similarity of HSP can lead to stopping the desired release too soon.

Perhaps the most important practical work dealing with solubility parameters and the stability of pigment dispersions is that attributable to Stephen.²⁵ He concludes that all the (solid) ingredients in a paint formulation should have the same energy characteristics. If they do not, there will be a driving force for this to occur. This can lead to problems. One can just as well make the formulation stable from the start, and then everything will remain stable just where it is because there are no driving forces for anything to move around. Although this sounds expensive, obvious, and perhaps too simple, the truth of the matter is well documented in very practical terms.

CONCLUSION

Many practical uses of the solubility parameter concept have been described in detail, including optimizing solvent selection, improving polymer compatibility, and enhancing pigment dispersion. When all of the materials involved in a given product and application can be characterized with the same affinity (solubility/cohesion) parameters, the possibility exists to predict interactions

among them. This is true even in complicated situations, such as the formulation of various types of filled systems including coatings, printing inks, adhesives, and other filled polymer systems including chewing gum.

REFERENCES

- 1. Hansen, C.M., Solubility in the coatings industry, Färg och Lack, 17(4), 69-77, 1971.
- Barton, A.F.M., Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press, Boca Raton, FL, 1983; 2nd ed., 1991.
- Gardon, J.L. and Teas, J.P., Solubility parameters, in *Treatise on Coatings, Vol. 2, Characterization of Coatings: Physical Techniques*, Part II, Myers, R.R. and Long, J.S., Eds., Marcel Dekker, New York, 1976, chap. 8.
- Beerbower, A., Boundary Lubrication Scientific and Technical Applications Forecast, AD747336, Office of the Chief of Research and Development, Department of the Army, Washington, D.C., 1972.
- 5. Hansen, C.M. and Beerbower, A., Solubility parameters, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Suppl. Vol., 2nd ed., Standen, A., Ed., Interscience, New York, 1971, pp. 889–910.
- Hansen, C.M., Some aspects of acid/base interactions (Einige Aspekte der Säure/Base-Wechselwirkung, in German), *Farbe und Lack*, 83(7), 595–598, 1977.
- 7. Hansen, C.M., Solvents in water-borne coatings, Ind. Eng. Chem. Prod. Res. Dev., 16(3), 266–268, 1977.
- 8. Hansen, C.M., New developments in corrosion and blister formation in coatings, *Prog. Org. Coat.*, 26, 113–120, 1995.
- 9. Hansen, C.M., 25 years with solubility parameters (25 År med Opløselighedsparametrene, in Danish), *Dan. Kemi*, 73(8), 18–22, 1992.
- Rasmussen, D. and Wahlström, E., HSP-solubility parameters: a tool for development of new products
 — modelling of the solubility of binders in pure and used solvents, *Surf. Coat. Int.*, 77(8), 323–333,
 1994.
- 11. Teas, J.P., Graphic analysis of resin solubilities, J. Paint Technol., 40(516), 19-25, 1968.
- 12. Torraca, G., *Solubility and Solvents for Conservation Problems*, 2nd ed., International Centre for the Study of the Preservation and the Restoration of Cultural Property (ICCROM), Rome, 1978. (13, Via Di San Michelle, 00153 Rome)
- 13. Schröder, J., Colloid chemistry aids to formulating inks and paints, Eur. Coat. J., 5/98, 334–340, 1998.
- 14. Skaarup, K., The three dimensional solubility parameter and its use. II. Pigmented systems, skandinavisk tidskrift for *Fårg och Lack*, 14(2), 28–42, 1968; 14(3), 45–56, 1968.
- 15. Hansen, C.M., On application of the three dimensional solubility parameter to the prediction of mutual solubility and compatibility, *Färg och Lack*, 13(6), 132–138, 1967.
- Van Dyk, J.W., Frisch, H.L., and Wu, D.T., Solubility, solvency, solubility parameters, *Ind. Eng. Chem. Prod. Res. Dev.*, 24(3), 473–478, 1985.
- 17. Klein, E. and Smith, J.K., Assymetric membrane formation, *Ind. Eng. Chem. Prod. Res. Dev.*, 11(2), 207–210, 1972.
- 18. Chawla, A.S. and Chang, T.M.S., Use of solubility parameters for the preparation of hemodialysis membranes, *J. Appl. Polym. Sci.*, 19, 1723–1730, 1975.
- 19. Misev, T.A., Thermodynamic analysis of phase separation in self-stratifying coatings solubility parameters approach, *J. Coat. Technol.*, 63(795), 23–28, 1991.
- 20. Special issue devoted to self-stratifying coatings, Prog. Org. Coat., 28(3), July 1996.
- Luciani, A., Champagne, M.F., and Utracki, L.A., Interfacial tension in polymer blends. Part 1: Theory, *Polym. Networks Blends*, 6(1), 41–50, 1996.
- 22. Luciani, A., Champagne, M.F., and Utracki, L.A., Interfacial tension in polymer blends. Part 2: Measurements, *Polym. Networks Blends*, 6(2), 51–62, 1996.
- Hennissen, L., Systematic Modification of Filler/Fibre Surfaces to Achieve Maximum Compatibility with Matrix Polymers, Lecture for the Danish Society for Polymer Technology, Copenhagen, February 10, 1996.

- 24. Song, J.H. and Reed, M.A., Petroleum Wax-Free Chewing Gums Having Improved Flavor Release, U.S. Patent No. 5,286,501, February 15, 1994, assigned to Wm. Wrigley Jr. Company, Chicago, IL.
- 25. Stephen, H.G., Parameters controlling colour acceptance in latex paints, J. Oil Colour Chem. Assoc., 69(3), 53–61, 1986.