
6 Methods of Characterization — Surfaces

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ABSTRACT

Relations between cohesion parameters and surface energy parameters and their practical significance are discussed. Cohesion parameters (solubility parameters) can be used with full theoretical justification to characterize many surfaces, including substrates, coatings, plastics, pigment and filler surfaces, etc., in addition to the binder or polymer used in a given product. Important molecular relations between a binder in a coating or adhesive and its surroundings then become obvious. Use of cohesion parameters, i.e., Hansen solubility parameters in a total characterization of surface energy, clearly shows how the single point concepts of the (Zisman) critical surface tension and the wetting tension fit into a larger energy concept. A complete match of surface energies of two surfaces requires that exactly the same liquids (in a larger number of well-chosen test liquids) spontaneously spread on both surfaces. The dewetting behavior (wetting tension test) of the liquids must also be the same, in that the same liquids should not retract when applied to the surfaces as films.

INTRODUCTION

Interfacial free energy and adhesion properties result from intermolecular forces. It has been recognized for many years that molecules interact by (molecular) surface to (molecular) surface contacts to enable solutions to be formed.¹ As molecular surface-to-surface contacts control both solution phenomena and surface phenomena, it is not surprising that various correlations of cohesion parameters and surface phenomena can be found. This idea has been well explored and dealt with elsewhere.² The various treatments and correlations in the literature will not be explicitly dealt with here, other than those directly related to Hansen solubility parameters (HSP). In this chapter, solubility parameters are called *cohesion (energy) parameters* and refer more specifically to HSP. Solubility as such does not necessarily enter into the energetics of interfacial phenomena, but the energy characteristics of surfaces can still be correlated with HSP.

This chapter will emphasize methods of surface characterization using HSP. The orientation of adsorbed molecules is a significant added effect that must also be considered in many cases. The “like dissolves like” concept is extended and applied as “like seeks like” (self-assembly).

HANSEN SOLUBILITY PARAMETER CORRELATIONS WITH SURFACE TENSION (SURFACE FREE ENERGY)

Skaarup was the first to establish a correlation between liquid surface tension and HSP. This correlation with surface tension had been long lost in an internal report to members of the Danish Paint and Printing Ink Research Laboratory in 1967, as well as in an abstract for a presentation to the Nordic Chemical Congress in 1968.^{3,4}

$$\gamma = 0.0688V^{1/3}[\delta_p^2 + k(\delta_p^2 + \delta_H^2)] \quad (6.1)$$

γ is the surface tension, and k is a constant depending on the liquids involved. This k was reported as 0.8 for several homologous series, 0.265 for normal alcohols, and 10.3 for *n*-alkyl benzenes.

Beerbower independently published essentially the same type of correlation in 1971.^{5,6} With the exception of aliphatic alcohols and alkali halides, Beerbower found

$$\gamma = 0.0715V^{1/3}[\delta_D^2 + 0.632(\delta_P^2 + \delta_H^2)] \quad (6.2)$$

where γ is the surface tension. The constant was actually found to be 0.7147 in the empirical correlation. The units for the cohesion parameters are $(\text{cal}/\text{cm}^3)^{1/2}$, and those of the surface tension are dyn/cm in both Equation 6.1 and Equation 6.2. However, values in dyn/cm are numerically equal to those in mN/m . The constant was separately derived as being equal to 0.7152 by a mathematical analysis in which the number of nearest neighbors lost in surface formation was considered, assuming that the molecules tend to occupy the corners of regular octahedra.

The correlations presented by Koenhen and Smolders⁷ are also relevant to estimating surface tension from HSP. The author has never explored them in detail, however, so they are not discussed here.

It is interesting to note that δ_P and δ_H have the same coefficient in the surface tension correlations. They also have the same coefficient when solubility is correlated (see Chapter 1, Equation 1.9 or Chapter 2, Equation 2.6). The reason for this is the molecular orientation in the specific interactions derived from permanent dipole–permanent dipole and hydrogen bonding (electron interchange) interactions. The dispersion or London forces arise because of electrons rotating around a positive atomic nucleus. This causes local dipoles and attraction among atoms. This is a completely different type of interaction and requires a different coefficient in the correlations. It is this difference between atomic and molecular interactions that is basic to the entire discussion of similarity between HSP and the Prigogine corresponding states theory in Chapter 2. The finding that the polar and hydrogen bonding (electron interchange) effects require the same coefficient for both bulk and surface correlations suggests that the net effects of the (often mentioned) unsymmetrical nature of hydrogen bonding are no different from the net effects occurring with permanent dipole–permanent dipole interactions. The lack of specific consideration that hydrogen bonding is an unsymmetrical interaction led Erbil⁸ to state that HSP has limited theoretical justification, for example. The previous discussion and the contents of Chapter 1 and Chapter 2 clearly indicate that the author is not in full agreement with this viewpoint. In fact, it appears that this book presents massive experimental evidence, related both to bulk and surface phenomena, which shows that the geometric mean is valid for estimating interactions between dissimilar liquids. This includes dispersion, permanent dipole–permanent dipole, and hydrogen bonding (electron interchange) interactions.

METHOD TO EVALUATE THE COHESION ENERGY PARAMETERS FOR SURFACES

One can determine the cohesion parameters for surfaces by observing whether or not spontaneous spreading is found for a series of widely different liquids. The liquids used in standard solubility parameter determinations are suggested for this type of surface characterization. It is strongly suggested that none of the liquids be a mixture, as this introduces an additional factor into the evaluations. The liquids in the series often used by the author are indicated in Chapter 5, Table 5.4 or Chapter 7, Table 7.2. Droplets of each of the liquids are applied to the surface and one simply observes what happens. If a droplet remains as a droplet, there is an advancing contact angle and the cohesion energy/surface energy of the liquid is (significantly) higher than that of the surface. The contact angle need not necessarily be measured in this simplified procedure, however. Contact angles have generally been found to increase for greater differences in cohesion parameters between the surface and liquid⁹ (see also Figure 6.5). If spontaneous spreading is found, there is presumed

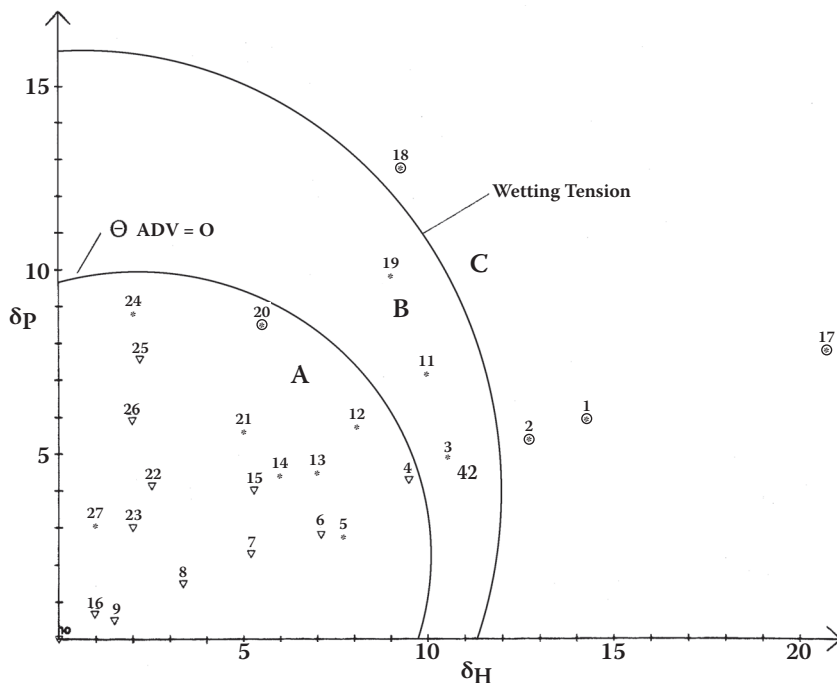


FIGURE 6.1 HSP surface characterization of an epoxy surface showing regions of spontaneous spreading of applied droplets (A), lack of dewetting of applied films (B), and dewetting of applied films (C). Note that this characterization may not be valid for all epoxy surfaces. Units are $\text{MPa}^{1/2}$. (From Hansen, C.M. and Wallström, E., *J. Adhes.*, 15[3/4], 281, 1983. With permission.)

to be some “similarity” in the energy properties of the liquid and the surface. The apparent similarity may be misleading. As discussed in greater detail later, the fact of spontaneous spreading for a given liquid does not mean that its HSP are identical with those of the surface being tested. If a given liquid does not spontaneously spread, it can be spread mechanically as a film and be observed to see whether it retracts. This can be done according to ASTM D 2578-84 or ISO 8296:1987 (E). This test determines whether or not there is a receding contact angle under the given conditions.

Figure 6.1 shows a complete energy description for an epoxy polymer surface^{10,11} based on the testing procedure described previously. The Hansen polar and hydrogen bonding parameters δ_p and δ_H are used to report the data. Further explanation of these parameters themselves can be found in Chapter 1. The circular lines can be considered as portraying portions of HSP spheres, but the third Hansen parameter, δ_D , has not been specifically accounted for in the two-dimensional figure.

Figure 6.1 shows two curves that are concave toward the origin. The lower of these divides the test liquids into two groups based on spontaneous spreading or not. Below the line one finds that liquids applied as droplets will spontaneously spread. Liquids that are found in the region above the upper curve will retract when applied as films. A test method to determine this is found in the ASTM and ISO standards given previously, for example, except that one uses a large number of pure liquids instead of the liquid mixtures suggested in the standards. Receding contact angles will generally increase as one progresses to liquids with still higher HSP. Intermediate between the two curves in Figure 6.1 is a region where liquids applied as droplets will remain as droplets, whereas liquids applied as films will remain as films. This region deserves more attention in future research. The energy properties of these liquids are not as close to those of the surface as are the energy properties of the liquids that spontaneously spread. Spontaneous spreading is more related to adhesion since such liquids want to cover the surface spontaneously. The wetting tension test uses

an external force to spread the liquids, after which they may continue to remain as a film. The mobility of the surface layer(s) will play a role in the wetting tension test. Hydrophilic segments can (perhaps) rotate toward a water droplet at some rate, for example, and increase the hydrophilic nature of the surface accordingly. This is discussed more in Chapter 18.

As mentioned earlier, there is still a problem in simplifying these results for easier use and improved understanding. Hexane, for example, does not dissolve an epoxy polymer, but in [Figure 6.1](#) it is almost in the middle of the region describing spontaneous spreading of the liquids. Hexane will not contribute to a “bite” into an epoxy coating for improving intercoat adhesion with a subsequent coating. Hexane is within the region of spontaneous spreading because it has a lower surface energy (surface tension) than the epoxy surface. Nature reduces the free energy level of the surface by requiring hexane to cover the epoxy coating. The result of this is that the center of the normal HSP sphere for describing spontaneous spreading can be assigned sizable negative values.¹¹ This is both impractical and impossible. A better method of handling this situation is still desired, and until it is found, one must presumably refer to simple plots or other simple comparisons rather than to refined computer techniques, which are more desirable in most cases. In the meantime, interest will still be focused onto the usual test method(s) for determining surface tensions based on the Zisman critical surface tension plots (lack of advancing contact angle) or by using the ASTM procedure for wetting tension (lack of receding contact angle). The following discussion relates these to the HSP-type characterizations discussed earlier.

Additional surface characterization plots for spontaneous spreading and wetting tension using HSP are included in [Figure 6.2](#) for a plasticized polyvinyl chloride (PVC) and in [Figure 6.3](#) for a polyethylene (PE).

A CRITICAL VIEW OF THE CRITICAL SURFACE TENSIONS^{12,13}

The Zisman critical surface tension is determined by measuring the extent that affinity is lacking (contact angles) for a surface using pure liquids or liquid mixtures in a series. The surface tension of each of the liquids is known. One can then plot cosine of the contact angle vs. liquid surface tension and extrapolate to the limit where the contact angle is no longer present (see [Figure 6.4](#)). Liquids with higher surface tensions than this critical value allow measurement of a contact angle, whereas liquids with lower surface tensions than the critical value will spontaneously spread. The fact that the liquid with a surface tension just under the critical value spontaneously spreads is often taken as an indication of high affinity. This is difficult to understand and appears to be a misunderstanding. The limiting critical surface tension^{12,13} has very little to do with the “best” solvent for the surface. It is more appropriately compared with a very poor solvent which can only marginally dissolve a polymer, for example. This is similar to the condition for a RED number equal to 1.0 discussed in Chapter 1 and Chapter 2. Measuring the critical surface tension has been and still will be a useful technique to better understand surfaces, but it should be done with the following in mind.

Who would determine the solubility parameter for a polymer by the following method? One makes up a series of liquids with different, known solubility parameters. The polymer dissolves in some of them, and the degree of swelling of the polymer in question is measured in those liquids which do not dissolve it fully. One subsequently determines the solubility parameter of the polymer by extrapolating the degree of swelling to infinity, which corresponds to total solution. This extrapolation can be done by plotting $1/(\text{degree of swelling})$ vs. solvent composition (solubility parameter). One now focuses attention upon that liquid which (by extrapolation) just dissolves the polymer. One assumes that there is no better solvent than this one and, consequently, assigns the polymer solubility parameters corresponding to those of this boundary solvent. This is exactly what one does when the critical surface tension is measured. This method should clearly never be used to determine solubility parameters for polymers. At the same time, it sheds some light onto the true meaning of the critical surface tension.

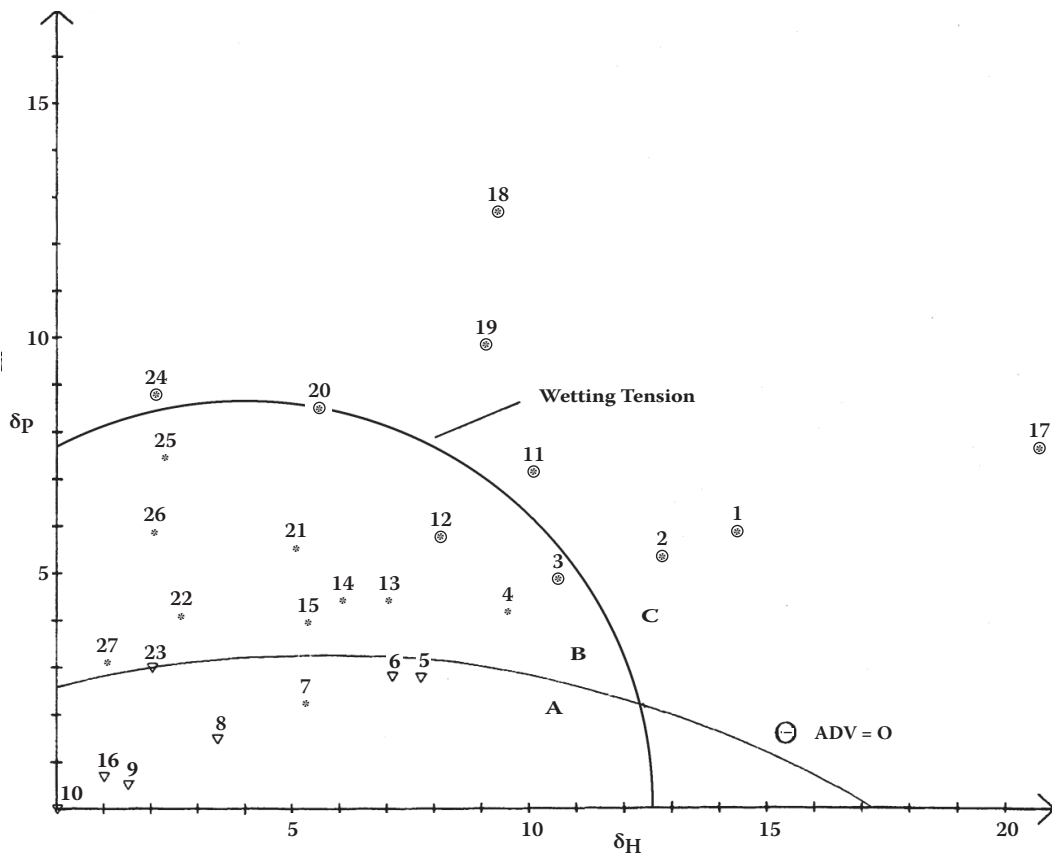


FIGURE 6.2 HSP surface characterization of spontaneous spreading of applied droplets and wetting tension for applied films for plasticized polyvinyl chloride (PVC). Note that these characterizations may not be valid for all PVC surfaces. Units are $\text{MPa}^{1/2}$ (From Hansen, C.M. and Wallström, E., *J. Adhes.*, 15[3/4], 280, 1983. With permission.)

If we now consider the region for spontaneous spreading in [Figure 6.1](#) to [Figure 6.3](#), it can be seen that the critical surface tension is a point on its boundary. In practice, one finds different critical surface tensions for the same surface depending on which liquids (or liquid mixtures) are used. This is explained by the fact that the cohesion parameter regions of the type shown in [Figure 6.1](#) to [Figure 6.3](#) are not symmetrical around the zero axis. The individual liquid series used to determine the critical surface tension will intersect the cohesion parameter spontaneous spreading boundary at different points. The corresponding total surface tension will vary from intersection to intersection as mentioned earlier. Hansen and Wallström¹¹ compared the critical surface tension plotting technique with one where a difference in HSP was used instead of liquid surface tension. One arrives at the same general conclusions from both types of plotting techniques. This comparison is made in [Figure 6.4](#) and [Figure 6.5](#).

A CRITICAL VIEW OF THE WETTING TENSION

A region larger than that for spontaneous spreading will be found on a δ_p vs. δ_H plot when one plots data for those liquids that remain as films (do not break up or contract) when they are applied as films. This type of experiment measures the wetting tension. Mixtures of formamide and ethylene glycol monoethyl ether are usually used in practice for these measurements according to ASTM

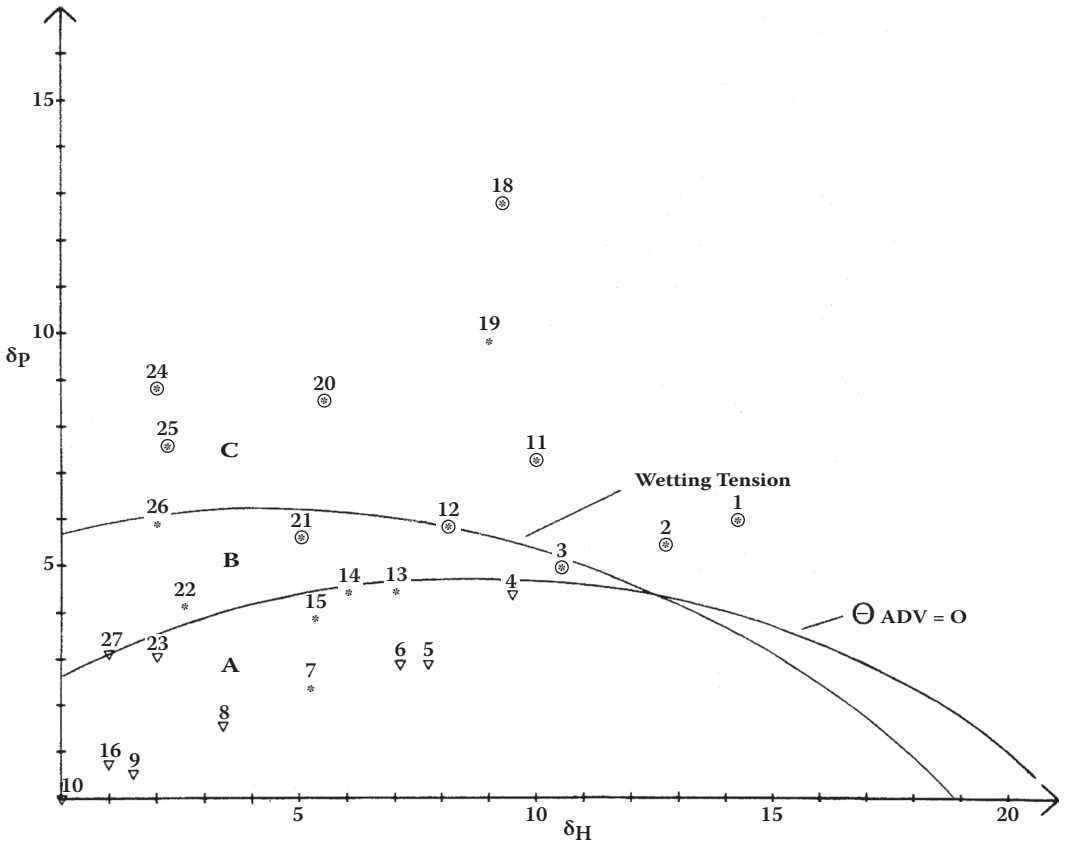


FIGURE 6.3 HSP surface characterization of spontaneous spreading of applied droplets and wetting tension for applied films for a polyethylene (PE) surface. Note that these characterizations may not be valid for all PE surfaces. Units are $\text{MPa}^{1/2}$. (From Hansen, C.M. and Wallström, E., *J. Adhes.*, 15[3/4], 279, 1983. With permission.)

D 2578-84 or ISO 8296:1987 (E). One can also use the same liquids suggested earlier for cohesion parameter determinations and make a plot like that in Figure 6.1. If two different surfaces are to have the same wetting tension behavior, their plots must be the same.

The results of the ASTM test are usually stated in terms of the surface tension of the liquid or liquid mixture which just stays intact as a film for 2 sec. This simple single point determination corresponds to determining a single point on the boundary of the HSP plot describing wetting tension for all liquids. A single point determination may not always be sufficient information and certainly neglects the complete picture possible from HSP considerations. Comments identical in principle to those included in the earlier section, “A Critical View of the Critical Surface Tensions,” on measurement of the critical surface tension are also valid here.

It is hoped the reader now better understands the total energy context of the simple ASTM wetting tension measurements.

ADDITIONAL HANSEN SOLUBILITY PARAMETER SURFACE CHARACTERIZATIONS AND COMPARISONS

Beerbower¹⁴ has reported many other correlations of surface phenomena with HSP. Examples include the work of adhesion on mercury; frictional properties of untreated and treated polyethylene

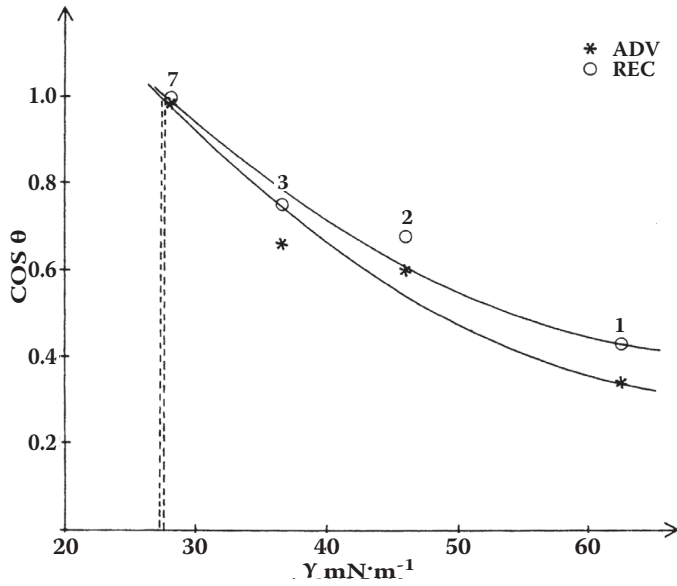


FIGURE 6.4 Zisman critical surface tension plot of cosine of the static advancing and receding contact angles vs. liquid surface tension for low density polyethylene. The same data are used in Figure 6.5. (From Hansen, C.M. and Wallström, E., *J. Adhes.*, 15[3/4], 282, 1983. With permission.)

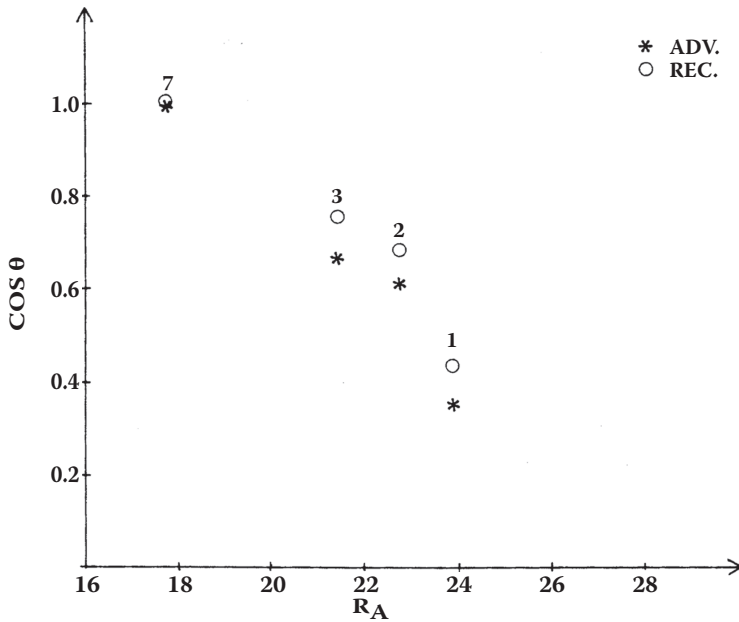


FIGURE 6.5 Critical HSP plot of cosine of the static advancing and receding contact angles vs. the HSP difference as defined by Chapter 1, Equation 1.9 for low density polyethylene. The same data are used in Figure 6.4. (From Hansen, C.M. and Wallström, E., *J. Adhes.*, 15[3/4], 282, 1983. With permission.)

for 2 and 5 min, respectively, with $\text{H}_2\text{S}_2\text{O}_7$; the Joffé effect — effect of liquid immersion on fracture strength of soda-lime glass; and the Reh binder effect — crushing strength of Al_2O_3 granules under various liquids. Beerbower has also brought cohesion parameters into the discussion of wear and boundary lubrication.¹⁴ It appears that these factors should still have some consideration, even though recent progress and understanding in the area are much more advanced.¹⁵

Additional surface characterizations using HSP are reported in Chapter 7. These include characterizations of the surfaces of pigments, fillers, and fibers. Both organic and inorganic materials have been characterized. The test method used is to determine sedimentation rates for the materials of interest in the same large number of solvents traditionally used in HSP studies. Adsorption of given liquids onto the particle or fiber surface slows the sedimentation rate, and indeed some (fine) particles with rather high densities suspend for years in organic liquids with rather modest densities. A significant advantage in this testing method is that hexane, for example, is not able to retard sedimentation where it may spontaneously spread, as discussed above. Hexane is not an isolated example of this behavior. The characterizations using standard HSP procedures indicate it is truly high affinity for the surface, which is important in these characterizations and not just spontaneous spreading. The reason for this may be the extent (or depth) of the adsorption layer, as well as whether the adsorption occurs at specific sites, or both. Results may be affected when molecules in a surface can orient differently from their original state upon contact with a liquid, for example, with water (see the discussion in Chapter 18).

An indirect correlation between HSP and the phenomena discussed above, spontaneous spreading and dewetting, has been established through measurements of environmental stress cracking (ESC).¹⁶ As discussed in Chapter 14, ESC correlates with the strain and the HSP and molecular size and shape of the cracking agent. The polymers polycarbonate (PC), cyclic olefinic copolymer (COC), and acrylonitrile/butadiene/styrene (ABS) terpolymer could be described in terms of the regions A, B, and C as shown in Figure 6.1 to Figure 6.3. A large number of test liquids in each category were used to evaluate the critical strain required for ESC. It was found that in every case tested, category A liquids gave ESC. All category B liquids also gave ESC, but the critical strains were somewhat higher on an average. Category C liquids could also give ESC in some cases. *n*-hexane was a category C liquid for some of these polymers in spite of its low surface tension. The HSP differences outweighed the expected spreading based on surface tension differences. Although these observations should not replace testing, a simple test of applying a droplet of liquid and possibly spreading it, if it does not do so itself, is a rapid way to assess a potential problem.

Before leaving this section, it is appropriate to mention that thinking of the type described above has led to a Nordtest Method, NT POLY 176, "Spreading Surface Tension by the Applied Droplet Method." This method is based on visual observation of droplets of known surface tension after they are applied to a test surface. The test surface may be a polymer, metal, or other material. The spreading surface tension is found to within ± 1 mN/m by locating two liquids in a series where one of them spreads spontaneously and the other with a slightly higher surface tension does not. The preferred set of liquids is made with ethanol and water with a difference of 2 mN/m between them. Surfaces of many different geometries (from 4 μm diameter wire to ships being painted), states of contamination (from clean for internal medical use to contamination with oil, silicones, pressure sensitive adhesive, etc.), and orientation (ceiling in a tunnel, inside pipes, etc.) have been tested with remarkable success using this simple test. The usual procedure is to assign a value to a clean(ed) surface and then compare test surfaces, wherever they may be, against this to determine the presence of contamination.

SELF-STRATIFYING COATINGS

A newer development in the coatings industry is to apply a single coat of paint which separates by itself into a primer and topcoat. A special issue of the journal *Progress in Organic Coatings* was devoted to this type of coating.¹⁷ Misev has also discussed formulation of this type of product using

HSP concepts.¹⁸ The separation of the binders into primer and topcoat must occur while the coating is still liquid enough to allow the necessary transport processes to occur. The solvent must just dissolve the binders such that they become incompatible when it begins to evaporate. The binder with the lowest energy (surface tension/cohesion parameters) will naturally migrate toward the low energy air interface and, therefore, this determines which of the binders makes up the topcoat. There are a number of other factors which are important for the process, including polymer molecular weight, rate of solvent evaporation, etc., but these will not be discussed here. This discussion is included because it once more demonstrates how cohesion parameters are coupled with surface energy and also to interfacial energy. The interface between the topcoat and primer is formed from an otherwise homogeneous system. The previous considerations lead to the expectation that the magnitude of the interfacial surface tension between two incompatible polymers is closely related to the difference in their cohesion parameters. Without going into greater detail, it is widely known among those who work with partially compatible polymers that this is indeed the case.^{19,20} See also Chapter 9 where partial compatibility in bitumen (asphalt) is discussed.

Figure 6.6 shows the principles involved for selecting the solvent which can make these work. The polymer with HSP nearest the origin will be the topcoat, as it has the lower (surface or cohesion) energy of the two. A solvent is required which dissolves both polymers, so it will be located in the common region to the spheres portrayed. Mutual solubility of two polymers is promoted when the solvent favors the polymer which is most difficult to dissolve.²¹ This is usually the one with the higher molecular weight. It is clear that selection of the optimum solvent for this process of designed generation of an interface is aided by systematic use of HSP. This is a prime example of self-assembly where proper formulation can be aided by the concepts discussed above.

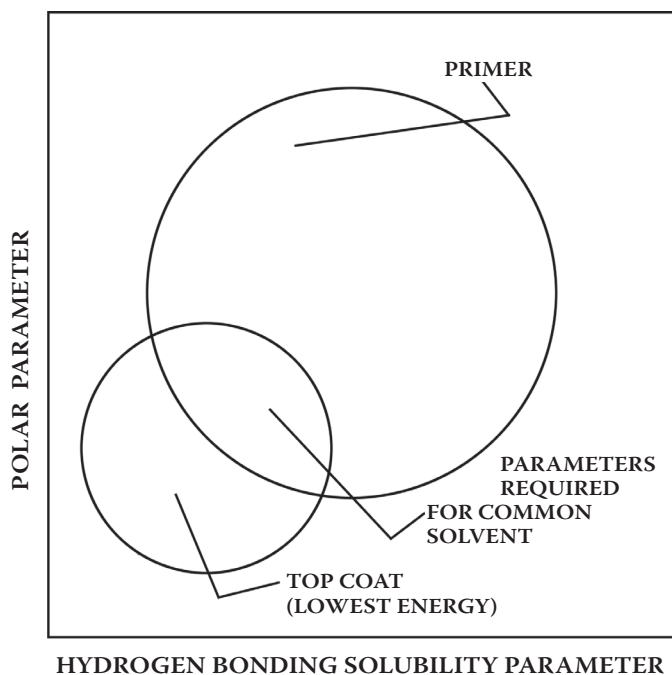


FIGURE 6.6 Sketch of HSP principles used to formulate a self-stratifying coating from an initially homogeneous solution (see discussion in text). (From Birdi, K.S., Ed., *Handbook of Surface and Colloid Chemistry*, CRC Press, Boca Raton, FL, 1997, p. 324.)

MAXIMIZING PHYSICAL ADHESION

If one wishes to maximize physical adhesion, the physical similarity (same HSP) of the two interfaces being joined must be as close as possible. The previous discussion suggests that physical similarity can be obtained when two criteria are met. The first criterion is that exactly the same liquids spontaneously spread on each of the surfaces to be joined. The second criterion is that exactly the same liquids maintain films when spread (ASTM method for wetting tension) on each of the surfaces to be joined. Any differences in this spontaneous spreading or wetting tension behavior can be interpreted as being a difference in physical similarity. The differences in the behavior of liquid droplets or films that are observed may suggest which steps can be taken to minimize differences, if this is required. Should one add aliphatic segments to reduce the polar and hydrogen bonding contributions? Should alcohol and/or acid groups be incorporated to increase the hydrogen bonding in the system? This type of approach can be used to establish guidelines for action relative to each of the HSP parameters. Aromatic character and halogens other than fluorine characteristically increase δ_D ; nitro and phosphate groups characteristically increase δ_P ; and alcohol, acid, and primary amine groups characteristically increase δ_H . Reference can be made to the table of group contributions in Chapter 1 (Table 1.1) for more precise comparisons. The discussion of forming good anchors on pigments and other surfaces found in Chapter 8 is also relevant to the present discussion, as such anchors can also be used to enhance adhesion.

CONCLUSION

Greater insight into the makeup of a product is possible when one not only knows the cohesion parameters, i.e., HSP, for polymers and solvents it contains, but also the HSP for the various surfaces which these encounter. The surfaces of substrates, pigments, fillers, plastics, fibers, and other materials can also be characterized by HSP (see Chapter 5 and Chapter 7). This allows mutual interactions to be inferred by comparisons of which materials are similar and which materials are different in terms of their HSP. Similar materials in this context have similar HSP regardless of differences in composition.

The critical surface tension and wetting tension are single point determinations. Cohesion parameters allow a more complete characterization of surfaces than do these single point measurements and, at the same time, allow insight as to how the single point measurements fit into the overall energy picture for the product. Guidelines for systematically changing the affinities of surfaces can also be obtained from HSP concepts.

Both the spontaneous spreading region and the wetting tension region on HSP plots for two different surfaces must be identical if they are to have identical overall surface characteristics.

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