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50 Years with solubility parameters—past and future☆

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Abstract

The developments leading from the Hildebrand solubility parameter (1950) to the Hansen solubility parameters (HSP) (1967) are discussed in the context of usage in coatings. Future applications will focus on predicting and controlling surface phenomena such as optimizing pigment surfaces, characterization and selection of surface active agents, self-assembly, and surface mobility. A large number of commonly used coatings raw materials are not yet characterized by HSP. This situation should be corrected as soon as possible.

Keywords: Solubility parameters; Surface characterization; Self-assembly; Surface mobility

1. Background

The solubility parameter was first introduced by Hildebrand and Scott in 1950, just over 50 years ago [1,2]. The Hildebrand solubility parameter, δ_t, is defined as the square root of the cohesive energy density (ced).

$$\delta_t = (\text{ced})^{1/2} = \left(\frac{\Delta E_v}{V}\right)^{1/2} \quad (1)$$

$$\Delta E_v = \Delta H_v - RT \quad (2)$$

δ_t is usually found by dividing the latent energy of vaporization, ΔE_v, by the molar volume, V, of the liquid involved, and taking the square root of this number as given in Eq. (1). The latent energy of vaporization is usually calculated by Eq. (2), where ΔH_v is the latent heat of vaporization, R is the universal gas constant, and T is the absolute temperature.

The original units and those that are still widely used, especially in the USA, are $(\text{cal/cm}^3)^{1/2}$. The SI units for the solubility parameter are $\text{MPa}^{1/2}$. These units are larger than the former units by a factor of 2.0455.

The author's extension of this single solubility parameter to what are now called Hansen solubility parameters (HSP) is described in [3] and in Appendix 1 of [4]. This was based on the fact that all types of physical bonds are broken when evaporation takes place, including those commonly called nonpolar, polar, and hydrogen bonding. This is discussed in detail in the following.

The solubility parameter concept is fundamentally sound, because it is based on well-defined and correct principles. It uses the so-called geometric mean of the interactions in two pure liquids to estimate the interaction between the unlike molecules in their mixtures. The use of the geometric mean has been shown experimentally to represent the data in a correct manner. This is true not only for the nonpolar interactions, but also for permanent dipole–permanent dipole and hydrogen bonding between the molecules as discussed in the following and in [3]. The hundreds of excellent HSP correlations for solubility, surface phenomena, etc. given for example in [3], witness the general validity of the geometric mean rule for all of these systems. This fact has not been widely anticipated.

The solubility parameter is very simple to use. First order estimates for liquid miscibility are easily obtained, for example, from the simple differences in the values for the liquids

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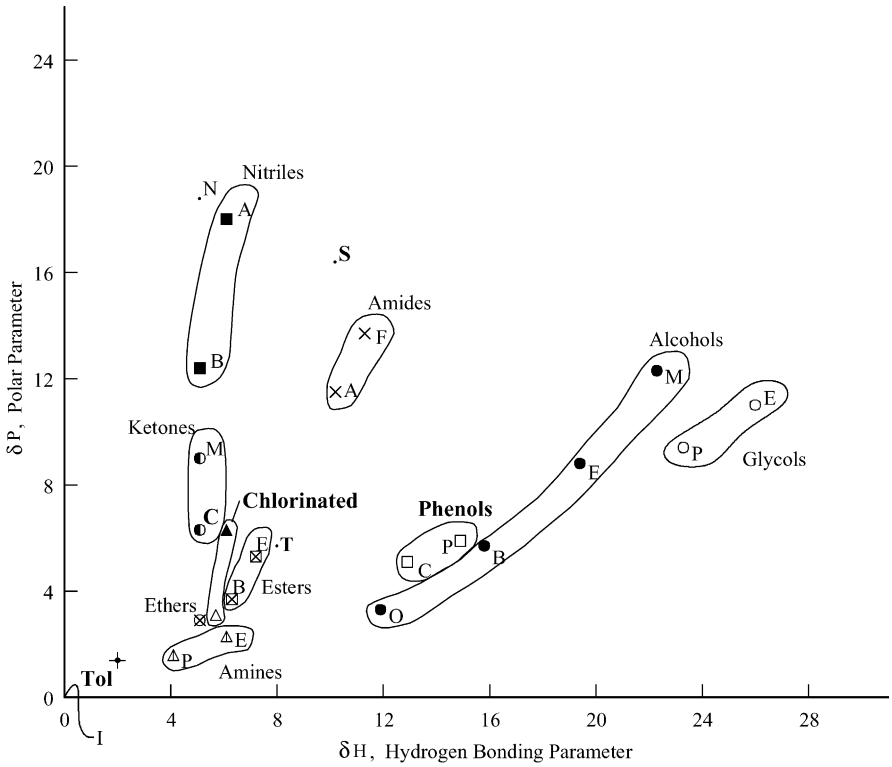

Fig. 1. δ_P vs. δ_H plot showing the location of various common solvents. The glycols are ethylene glycol (E) and propylene glycol (P). The alcohols are methanol (M), ethanol (E), 1-butanol (B), and 1-octanol (O). The amides include dimethyl formamide (F) and dimethyl acetamide (D). The nitriles are acetonitrile (A) and butyronitrile (B). The esters are ethyl acetate (E) and *n*-butyl acetate (B). The amines are ethyl amine (E) and propyl amine (P). The phenols are phenol (P) and *m*-cresol (C). The ethers are represented by diethyl ether. Bold type indicates relatively high δ_D.

concerned. The solubility parameter has been widely used in many practical applications for this reason and because of the general availability of solubility parameters for most common liquids. Many of these applications are summarized in handbooks, for example [3,5–7], and will not be discussed here. Burrell [8] was the champion of the concept in the coatings industry. The success was significant, but still somewhat limited since the simple Hildebrand or total solubility parameter could not handle hydrogen bonding. The competing theories of polymer solubility presented by Prigogine and coworkers and Huggins/Flory could not account for hydrogen bonding either [3,5]. Patterson was the only one who seemed to be able to make the very complex (unmanageable) Prigogine theory understandable. Patterson's work contributed significantly to the author's later theoretical developments that are likewise reviewed in [3,5]. Even though the Prigogine approach was theoretically very appealing (both it and the HSP are based on corresponding states theories), it never achieved any practical success. The Flory parameter continues to be widely used, primarily in academic contexts.

In the mid 1960s, the author realized that all of the cohesive bonds holding a liquid together were broken when it evaporates. This clearly means that "nonpolar" bonds, permanent dipole–permanent dipole bonds, and hydrogen bonds are all broken in the evaporation process. These must all be accounted for within the energy of vaporization itself. This led to the division of the cohesive energy, i.e. the Hildebrand solubility parameter, into the three parameters, δ_D, δ_P, and δ_H to quantitatively describe atomic, nonpolar interactions (D), molecular, dipolar interactions (P), and molecular, hydrogen bonding interactions (H), respectively.

$$(\delta_t)^2 = (\delta_D)^2 + (\delta_P)^2 + (\delta_H)^2 \quad (3)$$

δ_D, δ_P, and δ_H are now called Hansen solubility parameters. δ_D is found from corresponding states principles at 25 °C, δ_P is found with the aid of dipole moments and other parameters, and δ_H is usually found by what is left over in Eq. (3) or by group contributions. The locations of common solvents relative to each other on a δ_P versus δ_H plot are shown in Fig. 1. The parameters for mixed solvents are found by volume (or weight) additivity of the respective parameters. The "distances" between materials (Ra) on such plots are given by Eq. (4).

The equation for Ra, or rather $(Ra)^2$, is:

$$Ra^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 \quad (4)$$

An additional extremely useful parameter is the RED number. This is Ra divided by Ro, the largest value for Ra allowed where solubility (or other interaction being correlated) is allowed. Ro is frequently called the radius of a Hansen solu-

bility parameter sphere.

$$\mathrm{RED} = \frac{\mathrm{Ra}}{\mathrm{Ro}} \quad (5)$$

The subscripts are for the polymer, 1, and challenge chemical, 2, respectively. Good solvents will have RED less than 1.0. Progressively poorer solvents will have increasingly higher RED numbers. On two-dimensional plots the circles for binders encompass those solvents that dissolve them. The radius of these is given by the Ro found from computer correlations of experimental data for a large number of well-defined solvents. These correlations use Eqs. (4) and (5) to optimize a data fit.

The state of the art for usage of HSP is largely described in a single volume [3]. There have been some relevant developments of importance for coatings since [3] appeared. Some of these are included in the discussion below. The rest of this report deals with applications useful or potentially useful in the coatings industry, with an emphasis on newer and less traditional applications. Comparative examples are drawn from nature.

2. Current applications of HSP in coatings

2.1. Solvent-reducible coatings

It has been possible to optimally formulate a solvent-based product taking account of solubility parameter differences in various solid components, solubility parameters for single or mixed solvents, legislation, relative evaporation rates, flash points, etc. for many years. Hot and/or cold room stability and other solvent related properties can be improved, if required, by adjusting solvent quality, and latent solvents and diluents can be used to reduce costs. These types of applications in solvent-reducible coatings are now considered traditional, and will not be discussed here.

The formulation of thixotropic alkyds is also based on HSP concepts, although this is not generally recognized. Polymer segments (polyamide) not soluble in the solvent of the continuous phase (mineral spirits) are attached to alkyd molecules as blocks in a latter stage of their production. These segments then associate, not being soluble in the solvent, and a rheology-building structure is attained. The loose bonding can be broken by high shear application, and will restore itself, and the high viscosity, as the insoluble segments find each other again. This is an example where the insoluble segments have a higher HSP than the solvent in the continuous phase. Water, which also has a higher HSP than the continuous phase, can enter the associated regions and cause problems. The higher HSP polyamides will also tend to locate at higher HSP filler surfaces (see below). Thus, variations in fillers and excess water, and particularly their combination, can provide adequate basis for instability in this type of coating. Additions of alcohols, such as *n*-butanol, will tend to reduce or destroy the polyamide association, since these segments are soluble in *n*-butanol. These relations are portrayed in Fig. 2.

2.2. Water-reducible coatings

Some help in terms of understanding what is going on in water-reducible coatings can also be found from HSP concepts. The binders here are (usually) dispersed (i.e. not truly soluble) in water. The fact that δ_H falls more rapidly with temperature than δ_P or δ_D allows skillful use of alcohol-group containing glycol ethers, for example, to improve coalescence in an oven, while maintaining in-can stability at room temperature. These relations are shown in Fig. 3. The solvent should remain in the aqueous phase at room temperature. Coalescing solvents having a close match in HSP with the binder will tend to locate within the binder, whereas those with larger differences will either distribute between the binder and aqueous phase, or appear almost totally in the aqueous phase. This has been important for coatings on porous substrates, in particular, because coalescing solvent in the aqueous phase may disappear into the substrate, and not be available in the film itself, where it is required. Coatings without volatile coalescing solvents avoid this problem in another way.

The usual rule has been “like dissolves like”. This is now extended to encompass “like seeks like”. Thus, similarity of HSP (or more generally, energy characteristics) governs what appears where. This is why surface active agents function as they do. Those segments most resembling water will preferably appear in the aqueous phase, and those segments resembling given surfaces, dispersed solids, or other materials, will appear where energy matches are best. This has particular importance for water-reducible coatings. In terms of nonsoluble or only partly soluble systems, this means that those components or segments of components with similar energies (HSP) will tend to aggregate with their own kind. The aggregation is promoted by the insolubility or partial insolubility of the given segments in the aqueous phase. The presence of solvents in this phase will clearly affect, and probably reduce, the degree of the aggregation found in some types of (associative) thickeners, for example. This would affect the rheology. In principle, this is the same situation as with the thixotropic alkyds discussed above, where water or alcohols affect the rheological behavior by residing at places that should otherwise promote the aggregation of larger entities.

2.3. Coatings and biological systems

The author has always thought it curious that thinking based on solubility parameter considerations and practiced in coatings formulation can be also extended from understanding coatings behavior to understanding behavior in biological systems, such as those involving proteins. The reverse should also be true. Proteins are dispersed in water. They are not soluble. Proteins have some (hydrocarbon type) segments with such low solubility parameters that they are not water-soluble. This leads to the aggregation of these segments by

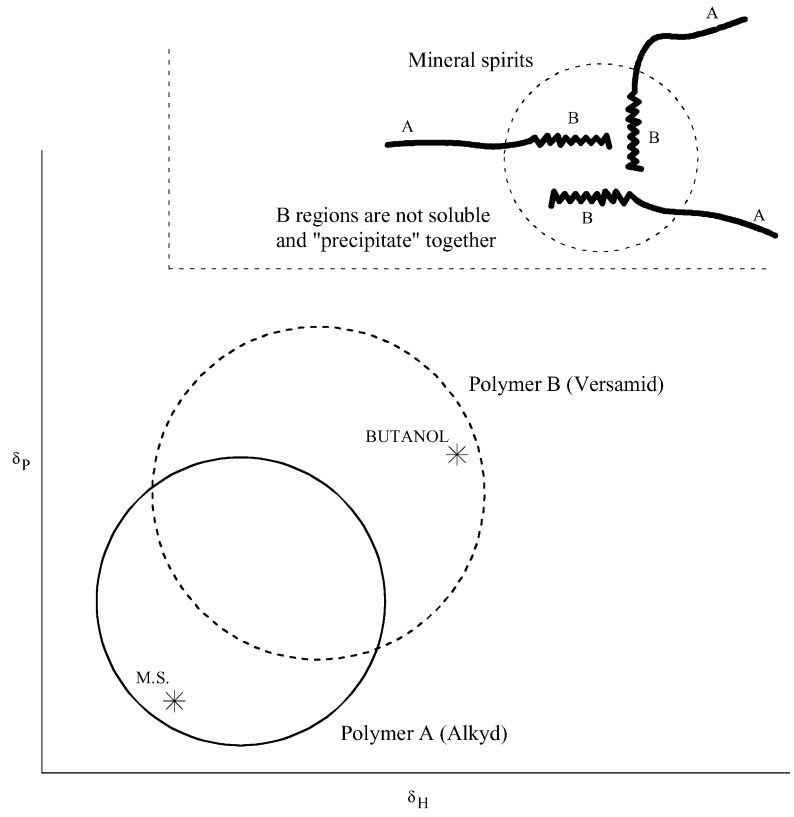

Fig. 2. HSP relations for establishing thixotropy in an alkyd-type paint. The polyamide segments associate because they are not soluble in mineral spirits. Addition of *n*-butanol or other alcohol destroys the thixotropic effect, since the solvent then becomes too good for the polyamide segments. Similar relations exist for the solution (denaturing) of proteins by addition of urea to water.

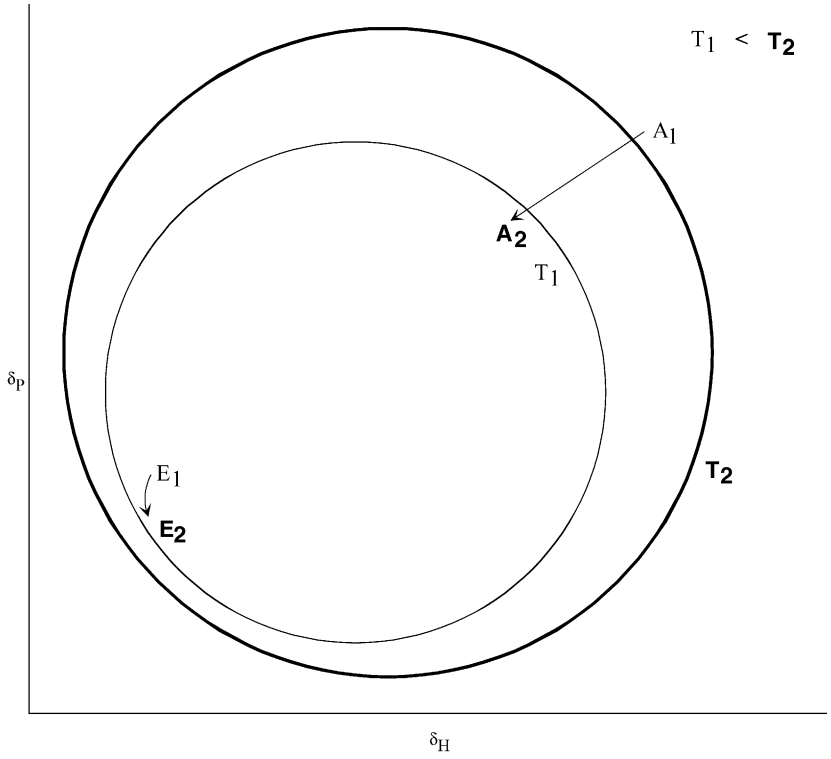

Fig. 3. The effect of higher temperature on solubility is an enlarged HSP region. In particular, solvents containing alcohol groups, such as alcohols, glycols, and glycol ethers, become better for most binders used in coatings as the temperature increases.

"hydrophobic" bonding, just like the aggregation of thickeners commonly used in water-reducible paints. Proteins also have some segments with solubility parameters too high to be dissolved in water, and this state of affairs leads to the (helical) structures they assume because these segments associate. These segments are also hydrophobic enough to not seek placement in the aqueous phase. The term "hydrophobic bonding" has already been applied to the aggregation of nonsoluble hydrocarbon segments, so what shall this be called? "Hyperphilic bonding" is as close as I can come. Can this concept be used in coatings? Why not? In fact it already has been used, since this is exactly the principle discussed above for designing thixotropic alkyds. In a similar manner to the addition of *n*-butanol to the alkyds, the solubility of proteins in water can sometimes be improved by addition of urea or given salts to the aqueous phase. The resulting (denaturing) solubility is because of a better HSP match between the aqueous phase and the previously "hydrogen bonded" helices.

2.4. Barrier properties, chemical resistance, and chemical protective clothing

The discussion above demonstrates that use of solubility parameters is not restricted to solvent selection, as many may suppose. Resistance to solvent uptake, barrier properties, selection of suitable protective clothing, and the like depend on lack of similarity of solubility parameters. These topics will continue to be of interest.

The barrier properties of polymers are only poorly correlated with HSP alone. The size and shape of the challenge molecules must be considered to arrive at reliable correlations with good predictive ability. All other things being equal, smaller and more linear molecules diffuse faster in polymers than do molecules with larger or more complex structure. The author has traditionally used the molar volume as a size parameter, but this is not fully satisfactory since the shape of the molecules is not specifically included. Work is needed here to establish a simple, more general way to include the effects of molecular size and shape along with the HSP. Reference is made to Chapter 8 in [3].

Chemical resistance testing data are not always suitable for direct correlation with HSP. This is not because of any particular problem with HSP but rather because equilibrium is not usually reached by challenge chemicals with larger molecules during normal testing times. Simultaneous consideration of the size and shape of the challenge chemicals allows HSP correlations with reliable predictive ability. Reference is made to Chapter 7 in [3].

Chemical protective clothing will still be used in the next 50 years. HSP correlations can be used to exclude hopeless alternatives and to quickly lead to the most promising choices for the best protective material [9]. The current requirements that coatings manufacturers more precisely specify appropriate chemical protective clothing has made this interesting at the present time.

2.5. Environmental stress cracking (ESC)

The plastics industry now realizes the excellent ability of HSP to identify the challenge chemicals that can cause environmental stress cracking (ESC) [10–13]. ESC chemicals hasten the physical cracking of many polymers. Indeed some polymers can crack immediately on contact with given liquids. ESC liquids are typically those which only absorb to a small amount, and sometimes only to a very small amount. HSP correlations and predictions can be used to locate these and to predict the behavior of untested systems since such swelling liquids generally have RED numbers slightly larger than 1.0 in a HSP correlation of true solubility.

3. Surface applications

3.1. Pigment surface optimization

The major new applications for HSP in coatings will be found in surface science. Hundreds of pigment and fiber surfaces have been characterized, but who uses the information? Typical data are included in Table 1.

These data quickly indicate which binders are best for which pigments, and vice versa. A good match in HSP is desired. If there is no good HSP match between the pigment and binder, then the same principles can be used to achieve the desired match by either systematic modification of the binder or systematic modification of the pigment surface so they match better.

These surface characterizations have largely been made by observing relative sedimentation rates of the particles or fibers in a large number of well-chosen liquids [3]. They have been done as early as 1967 [14–17], but there still exists a certain reluctance for raw material suppliers to provide this kind of data. When those liquids that dissolve a binder are the same ones that selectively retard sedimentation of a given pigment, then one can deduce that the binder will also adsorb well onto the pigment surface. The HSP of pigment surface and binder will match. This promotes dispersion stability, of course. Many, including the author, have already achieved success with this direct and systematic approach. Even complicated systems can be analyzed in this manner by characterizing each of the ingredients making them up.

The author's most recent writings of a general nature on HSP and surface science are found in [3,18]. The first presentation of some of these ideas relating to surface science was in 1997 in Färg og Lack Scandinavia [19]. One needs to consider a qualitative, HSP energy characterization characteristic of a given additive, together with a quantification of this by, for example, degree of surface coverage attained. This has been shown in unpublished studies where a bare fiber surface was extremely difficult to assign HSP values, but when the surface coverage of a silane treatment increased, the clarity of the correct HSP assignment became better and better. This was because more and more test solvents within a region de-

Table 1
HSP correlations for typical pigments and fillers

Material	δ_D	δ_P	δ_H	Ro	FIT	*G*/*T*
Organic pigments						
Paliotol Gelb L1820 BASF	18.9	3.5	10.5	5.4	0.99	3/35
Heliogen Blau 6930L BASF	18.0	4.0	4.0	4.0	1.00	5/34
Socco Rosso L3855 BASF	17.3	5.7	2.7	4.1	0.99	4/34
Perm Rubin F6B Hoechst	16.7	3.7	3.1	4.8	0.88	6/33
Perm Gelb GRL02 Hoechst	16.7	2.5	3.7	4.5	0.945	5/37
Perm Lackrot LC Hoechst	19.0	5.0	5.0	4.0	1.00	7/28
Inorganic pigments, fillers, etc.						
Kronos RN57 TiO_2	24.1	14.9	19.4	17.2	[a]	[a]
Aluminum Pulver Lack	19.0	6.1	7.2	4.9		[a]
Red iron oxide	20.7	12.3	14.3	11.5	[a]	[a]
Cabot Hochdisperse[b]	16.7	9.3	11.5	11.7	–	23/23
Cabot Hochdisperse	19.3	9.5	10.3	12.7	0.788	23/31
Zeta potential for Blanc Fixe	26.5	19.1	14.5	20.0	0.948	5/19

[a] Not available, not recorded at time of study.
[b] Special technique where the "sphere" encompasses all good solvents, and neglects bad ones. A FIT of 1.0 means all the "good" solvents have Ra less than Ro. The number of "good" solvents is *G* and the total number of liquids in the correlation is *T*. See [3] for a more detailed discussion. The zeta potential data for Blanc Fixe are found in Winkler [Zeta potential of pigments and fillers, *Eur. Coat. J.* 97 (1–2) (1997) 38–42].

fined by the same Ro were able to retard sedimentation on a relative basis. In continuation of comparisons with nature let it be noted that dentin (teeth) has been characterized by HSP to confirm the reason for improved adhesion using given adhesives [20].

3.2. Characterization and selection of wetting agents

As indicated above, many pigments and fillers have been characterized by HSP. But what does the coatings formulator do when he can neither change the pigment nor the binder? Many additives have also been characterized or can be characterized by HSP [3,21]. Some help may be gotten from changing the solvent. For many systems the solvent should be neither too good nor too bad. There is often an optimum. The most common remedy, however, is clearly to seek a suitable pigment dispersant (surface wetting agent). In the past this has not been easy and even HSP has had difficulties in characterizing such materials. This is because pigment dispersants dissolve in practically all of the test solvents, and it has not been possible to find the (two?) HSP, one for each end of the molecule, in a definitive manner. Calculations have also been uncertain since there are two distinctly different ends to these molecules. These ends are frequently termed hydrophilic and hydrophobic, but this generalization does not allow precision formulation. Acid–base considerations are widely used in this respect, but these are generally derived from studies that could equally well be interpreted from a HSP point of view. It has been clearly shown hundreds of times that surfaces can be very well characterized in terms of their nonpolar, polar, and hydrogen bonding interactions with well-defined liquids, i.e. by HSP. A study of the usual assignment of acid or base character leads one to a generality that acidic generally involves higher δ_H and "positive", while basic generally involves δ_P and negative. This can change somewhat depending on circumstances, whereas HSP do not.

In the future, comparisons of HSP for "bare" and surface treated pigments/fillers/fibers are recommended to find the capabilities of given wetting agents. Most bare fillers give HSP characterizations with poor data fits, often resembling the HSP that might be expected for a thin water layer. They sediment very rapidly in most organic test liquids. It has sometimes been a matter of belief, rather than voluminous quantitative data, when HSP have been assigned to some fillers. The relative sedimentation rate data do seem to indicate a resemblance to a thin water layer on the surfaces of the fillers in many of these cases, but the data fits are poor due to lack of a significant number of liquids that significantly retard sedimentation. The adsorption of solvent on a filler surface is substantially different and more difficult than a corresponding "adsorption" onto a polymer chain in a polymer system. The preferred adsorption sites on the filler surface are rigidly fixed, whereas as such "sites" in a flexible polymer system may be able to move and may even be supplied by more than one polymer molecule, thus enhancing the adsorption/solubility process and giving much better HSP correlations. There will be less net adsorption if the spacing between the preferred adsorption sites on the surface does not match with a corresponding spacing on an adsorbing molecule, even though HSP comparisons may indicate similarity. The HSP of the filler with adsorbed dispersant or surface treatment will yield a characterization of what may be called the HSP "quality", meaning given sphere and radius, of the surface treatment. This HSP quality will be enhanced by intense adsorption or treatment with high surface coverage. The intensity of the adsorption or surface coverage is therefore also clearly important, since little adsorption does not change the filler properties, even though the additive potentially giving the correct HSP is in the system. Here, again

the solvent will also be an important factor affecting the intensity and nature of the adsorption. The surface-active agent should generally not be too soluble in the liquid system. A list of the expected HSP attainable by given pigment dispersants would be very useful to the skillful formulator.

3.3. Self-assembly

Without going into great detail, it should be recognized that the coatings industry has been practicing controlled or self-assembly of molecular segments ever since it has been in existence. That this special name has evolved in recent years should not deter continuing the practices already established in our industry. The coatings industry has found out how to control rheology by addition of structure-building additives using segments of molecules that are not soluble in the continuous phase. This is true for both solvent and water-reducible coatings. The coatings industry has also learned to use adhesion promoters, surfactants, and other molecules of this type. These locate by themselves at given surfaces to accomplish a given task. Self-assembly involves like seeking like, and most often includes some degree of insolubility (rejection) to enhance and control the process. One can use HSP to predict and develop better coatings based on self-assembly [3]. Self-stratifying coatings are an excellent example [22]. The initial homogeneous liquid product separates into a primer and topcoat in a controlled manner. Examples in nature can be found where similarity of energy (HSP) leads to self-assembly into desired configurations (ultrastructure). Proteins have been discussed above. The molecular orientation found in wood cell walls has been discussed in [23] from an HSP point of view. Very briefly, the hemicelluloses have different kinds of side chains. Those side chains with alcohol groups (high δ_H) will orient toward cellulose (with its many alcohol groups), and those side chains with acetyl and other low-HSP groups will orient toward the lower HSP lignin. The side groups will not penetrate the lignin, due to short length and lack of a good HSP match. These side groups will therefore lie in the interface between the hemicelluloses and the lignin, and allow undamaging movement (sliding?) not possible with a more rigid attachment. This is presumed to be the reason trees can tolerate such high bending, and still be able to return back to a normal situation. Generally speaking, the hemicelluloses function like special polymeric surface-active agents by binding the lignin regions to the cellulose fibers. This is clearly a concept, which has usefulness in coatings.

3.4. Surface mobility

Polymer segments in surfaces are known to be able to rotate at the surface if a given liquid, such as water, is applied to the surface [3]. Higher energy segments or side groups are normally buried toward the bulk of the polymer, since these have a higher energy than air. Low energy hydrocarbon segments, for example, will tend to orient toward the air surface. But if water, or another higher HSP liquid, is applied to the surface, the polymer segments with higher energies will rotate to face the liquid if they can. This type of rotation is easily seen in peat moss, for example. Water droplets pearl for a few minutes, after which they absorb readily into the bulk. The surface molecules of the peat moss have rotated, changing the surface to one of hydrophilic character rather than hydrophobic. This is nature's automatic valve to conserve water within the relevant systems. Evaporation is limited in dry periods, and water is readily taken in when it is available. Rotation of the surface molecules or segments of these molecules is an important factor for the performance of many types of coatings, even though this may not be recognized as such. The phenomena relate directly to dirt retention and the ability of water to either bead up or to form a continuous film and run off. Many years ago, a coating was developed for a water evaporator based on this concept [24]. Water beaded up on the fresh coating, which was not acceptable. When the coating was immersed in water overnight, it allowed water to spontaneously spread on the evaporator surface, thus enhancing evaporation. The surface molecules had rotated. This rotation of polymer segments in the surface when contacted with "matching" HSP liquids is currently thought to be a cause of ESC in given plastics. Significant absorption of ESC-promoting, higher molecular weight oils (olive oil, butter, hand creams, etc.) cannot be measured, but such rotation of polymer segments at the surface can initiate the crazes and cracks that lead to the catastrophic failure that occurs in far too many cases.

If surface mobility can be controlled or predicted, HSP concepts can aid in doing it.

4. Conclusion

An attempt has been made to review new and expected future applications of Hansen solubility parameters that will find use in the coatings industry. The past has been used to project into the future. The best comprehensive collection of past data and interpretations is "Hansen Solubility Parameters—A User's Handbook" [3]. It is concluded that solubility parameters will be useful for at least the next 50 years as they have been for the past 50 years. The major area of future applications will be the control of surface phenomena.

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