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On the Use of Cohesion Parameters to Characterize Surfaces

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Examples of surface characterization using cohesive energy parameters and surface energy parameters are given. In general the two approaches yield essentially equivalent results. The predictive ability of the cohesive energy approach suggests its use where directed modification of surface properties is desired.

INTRODUCTION

The energy properties of surfaces can be studied by contact angle measurements using carefully selected liquids, either singly, in smaller series, or with a “total” approach using many liquids having widely different energy properties. This report will emphasize both the practical and theoretical advantages of the latter.

Cohesive energy interpretations of contact angle data have been used many times in the past, and a review of recent applications has been presented.¹

In the following the analogy between surface and cohesive properties of liquids is extended with selected examples being extracted from a larger study recently carried out at this Institute.²

EXPERIMENTAL

Six surfaces of interest to the coatings industry have been studied for

TABLE I

List of solvents used with their cohesive energy parameters, molar volumes, and surface tensions.

	δ_D (cal cm ⁻³) [‡]	δ_P (cal cm ⁻³) [‡]	δ_H (cal cm ⁻³) [‡]	V (cm ³ /mol)	γ_L^9 (mN/m)
1. Glycerine	8.5	5.9	14.3	73.3	62.3
2. Ethylene glycol	8.3	5.4	12.7	55.8	45.8
3. 1,3 Butanediol	8.1	4.9	10.5	89.9	36.6
4. Ethanol	7.7	4.3	9.5	58.5	21.4
5. <i>n</i> -Butanol	7.8	2.8	7.7	91.5	23.6
6. 2-Butanol	7.7	2.8	7.1	92.0	22.4
7. Ethylene glycol mono ethyl ether acetate	7.8	2.3	5.2	136.2	28.0
8. isoAmylacetate	7.5	1.5	3.4	148.8	23.9
9. <i>o</i> -Xylene	8.7	0.5	1.5	121.2	27.1
10. <i>n</i> -Hexane	7.3	0.0	0.0	131.6	17.3
11. Diethyleneglycol	7.9	7.2	10.0	95.3	43.4
12. Formic Acid	7.0	5.8	8.1	37.8	37.1
13. Ethylene glycol mono ethyl ether	7.9	4.5	7.0	97.8	27.7
14. Diethylene glycol mono ethyl ether	7.9	4.5	6.0	130.9	31.1
15. Diacetonealcohol	7.7	4.0	5.3	124.2	27.5
16. Toluene	8.8	0.7	1.0	106.8	27.8
17. Distilled water	7.6	7.8	20.7	18.0	69.8
18. Formamide	8.4	12.8	9.3	39.8	57.1
19. Dipropyleneglycol	7.8	9.9	9.0	131.3	32.3
20. 2-Pyrrolidone	9.5	8.5	5.5	76.4	44.4
21. <i>N,N</i> dimethylaceta- mide	8.2	5.6	5.0	92.5	34.0
22. Cyclohexanone	8.7	4.1	2.5	104.0	32.4
23. Methyl isobutyl ketone	7.5	3.0	2.0	125.8	23.4
24. Propylene carbonate	9.8	8.8	2.0	85.0	31.6
25. Nitroethane	7.8	7.6	2.2	71.5	31.0
26. 2-Nitropropane	7.9	5.9	2.0	86.9	27.9
27. 1,2 Dichlorobenzene	9.4	3.1	1.6	112.8	35.6

⁹ Measured values.

contact angle behavior when contacted with a large number of liquids (Table I) having widely varying cohesive energy densities. MPa[‡] is the preferred unit[‡] but unfortunately our work was still based on the older (cal/cm³)[‡] unit. Contact angles were taken as an average of 5 evaluations for both advancing and receding situations using 8 mm droplets. Both sides of the droplets were measured and standard deviations of between 1 and 3.5 degrees were found using a stereomicroscope with a goniometer eyepiece. In addition the "Wetting Tension" test was performed according to ASTM D 2578-67. This test involves application of a liquid

film and visually noting whether or not it breaks in 2 seconds. This test is, in fact, a self-contained de-adhesion test.

Results were plotted for selected liquid series as cosine of contact angle *versus* liquid surface tension according to Zisman,³ as well as by cosine of contact angle *versus* energy differences as reflected by cohesive energy considerations.

The two types of plots yield essentially equivalent results as seen below. An additional conclusion of our work² was that the liquid series used to construct these $\cos \theta$ plots should preferably consist of pure liquids which have cohesive energy parameters placing them on a reasonably straight line on cohesive energy plots as discussed below. In addition a uniform decrease of surface tension with decreasing cohesive energy density and low viscosities are desired.

Cohesive energy plots

Cohesive energy plots are readily constructed from “whether or not” data (contact angle, wetting tension film break, solubility, etc.) found for a large number of liquids. The liquids’ cohesive energy properties are best reflected by separation of the cohesive energy into parts which then lead to partial cohesive energy parameters, δ_i , as follows⁴⁻⁶:

$$\left(\frac{\Delta E_t}{V_M}\right) = \left(\frac{\Delta E_D}{V_M} + \frac{\Delta E_P}{V_M} + \frac{\Delta E_H}{V_M}\right)$$

$$\delta_t = \delta_D^2 + \delta_P^2 + \delta_H^2$$

ΔE_t = Total cohesive energy

ΔE_D = Dispersion energy contribution

ΔE_P = Permanent dipole—permanent dipole energy contribution

ΔE_H = “Hydrogen bonding” energy contribution

V_M = Molar volume of liquid

The total cohesive energy parameter, δ_t , was introduced by Hildebrand and Scott,⁷ and the partial cohesive energy parameter approach has evolved as reviewed by Barton.¹ Approximately 250 liquids have been characterized by these partial parameters.⁸⁻⁹ It is important to recognize that these partial parameters for liquids are based on the respective liquid’s molecular interaction with themselves. Evaporation breaks all these “bonds” and the total cohesive energy is taken as the energy of vaporization. Likewise it is noteworthy that the total experi-

mental energy of vaporization agrees with the sum of $\Delta E_D + \Delta E_P + \Delta E_H$ as found from independent calculations for each of these types of energy contribution. The cohesive energy parameters are therefore not empirical. Our understanding of a more unified theory showing how to use them best theoretically is lacking.¹⁰ We must currently use them in an empirical manner.

Such empiricism has shown that both polymer solubility and surface wetting (contact angle, wetting tension) phenomena can be described by the following equation¹¹

$$R_A^2 = [4(\delta_{D_1} - \delta_{D_2})^2 + (\delta_{P_1} - \delta_{P_2})^2 + (\delta_{H_1} - \delta_{H_2})^2]$$

where for $R_A < R_0$ an affinity is indicated.

Here

R_A = "distance" reflecting cohesive energy differences.

R_0 = Maximum allowable difference for positive interactions.
(No contact angle).

The subscripts are for the two materials involved, resp., 1 for liquid, and 2 for the material being tested.

If a sufficiently large enough number of liquids are included, R_0 can be found along with the partial parameters for the material under test with reasonable reliability. Typical data are included for our six test surfaces in Tables II and III. These data are calculated using a computer program. It is our experience that such values should not be considered as exact, and that several "spheres" with equivalent data fits can be calculated in these cases. One reason for the existence of these almost equivalent spheres is that the liquids used to determine the experimental data points are located in a very small part of the "optimum" sphere calculated by the computer regression technique. Cohesive energy parameters can be used to correlate the data, but the

TABLE II
Calculated regions of interaction for six surfaces based on advancing contact angles.

	δ_D	δ_P	δ_H	R_0	Data fit
PVC (Plasticized)	9.9	-21.3	5.0	24.6	0.99
PE (low density)	9.6	-15.3	8.8	20.0	0.98
Acrylic emulsion coating	6.5	-16.8	9.4	21.2	0.98
Epoxy coating	5.0	2.1	2.2	7.9	0.98
Aluminium	7.6	-10.5	8.1	14.8	0.95
Steel	1.4	-7.0	5.7	17.4	0.96

TABLE III
 Calculated regions of interaction for six surfaces based on wetting tension.

	δ_D	δ_P	δ_H	R_0	Data fit
PVC (plasticized)	10.0	0.0	4.0	8.7	1.0
PE (low density)	6.5	-15.2	4.0	21.4	0.95
Acrylic emulsion	11.0	0.1	6.3	10.0	0.92
Epoxy coating	5.2	4.0	0.0	12.0	0.99
Aluminium	1.7	1.5	4.0	14.8	0.99
Steel	5.2	4.0	2.4	10.4	0.99

correlations often given negative values (Tables II and III). This fact also reflects our lack of a basic understanding at present as to how best to interpret such data in terms of a more general theory.

Typical cohesive energy plots are given in Figures 1 to 3 for a polyethylene, a plasticized polyvinyl chloride, and an epoxy coating.

The data fit (Tables II and III) indicates the degree to which the criteria given above satisfy the observed contact angle data. Figures 4

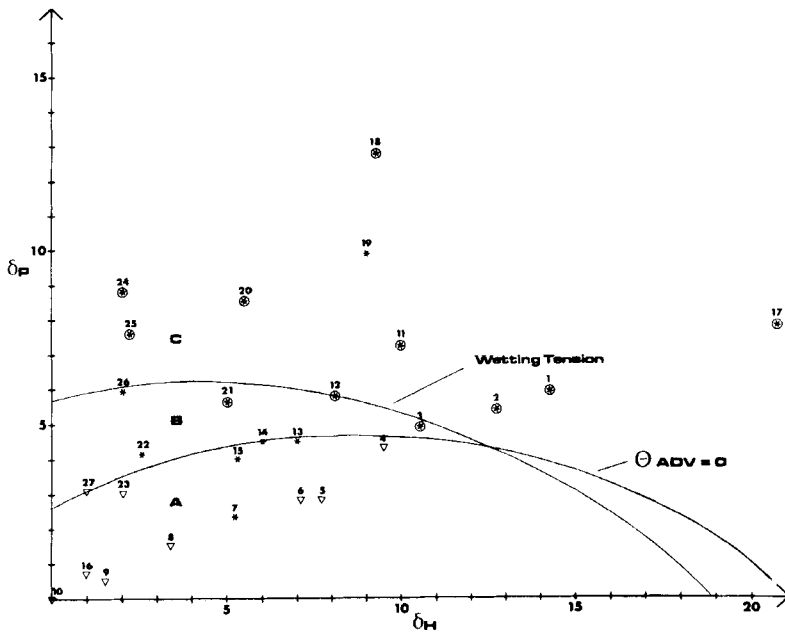


FIGURE 1 Cohesive energy plot of contact angle and wetting tension data for a low density polyethylene substrate.

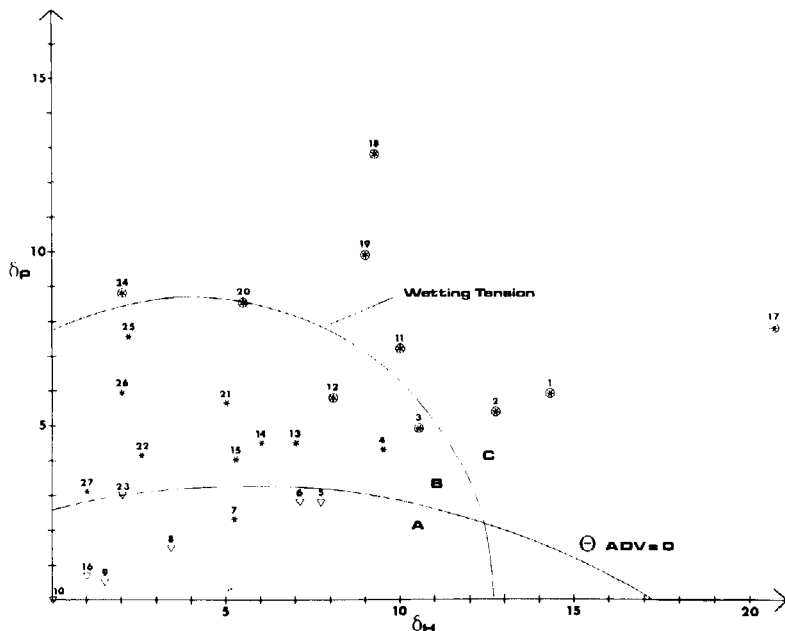


FIGURE 2 Cohesive energy plot of contact angle and wetting tension data for a plasticized polyvinyl chloride substrate.

through 9 show plots using cosine θ for the same substrates described by Figures 1, 2, and 3. Interpretation is possible both with surface free energy (surface tension) and R_A found from cohesive energy parameters. The same trends and minor deviations within the data are found for the same liquids in both interpretations in these cases. The correspondence of the two approaches has been confirmed once more. Similar data have been accumulated and reported for all six of the substrates listed in the Tables.²

If one compares the interaction spheres for the three surfaces reported here, it can be seen that several polar liquids do not yield contact angles with the epoxy but do so with the other two surfaces. The epoxy is more polar. The Zisman $\cos \theta$ curve is also located closer to $\cos \theta = 1$ for the epoxy most probably as a consequence of this higher relative polarity.^{1,2} The hydrogen bonding parameter has an influence on all three surfaces as seen from the interaction spheres, but does not reflect differences as clearly. Based on our limited data for six surfaces² including these three, it appears that the slope of the Zisman type curve is largely determined by the polar character of the surfaces. We have no

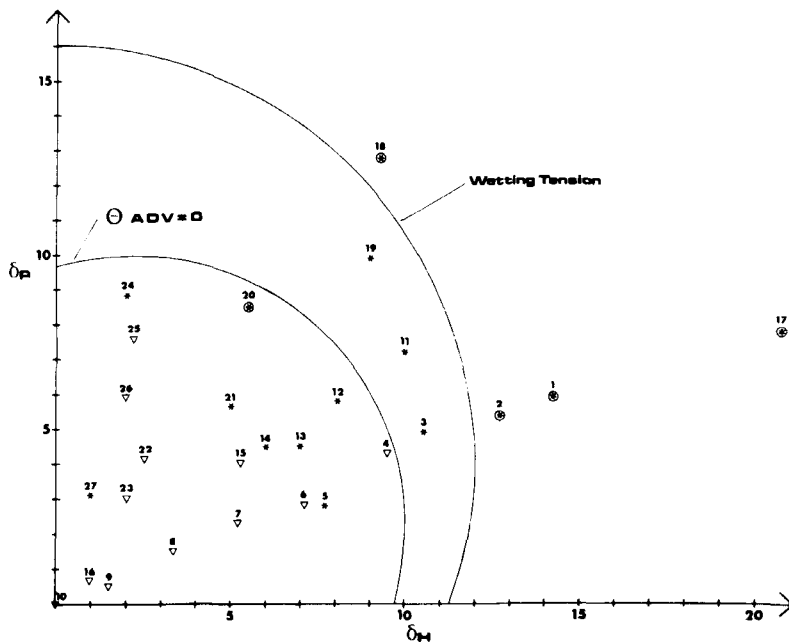


FIGURE 3 Cohesive energy plot of contact angle and wetting tension data for an epoxy coating.

proven explanation for this, although adsorbed water on the surfaces may be important. Those liquids tending toward higher hydrogen bonding parameters have a relative greater affinity for water than those of more polar character.

DISCUSSION

There are several advantages of the cohesive energy parameters which are not found when the energetic interactions are described by other parameters.

From a practical point of view one need not give up characterizing a surface because contact angles can not be determined. One need only note whether or not a contact angle is found for the liquid and substrate being tested. This type of surface characterization offers a positive approach (wetting, lack of contact angle) *versus* the customary negative approach based on lack of affinity.

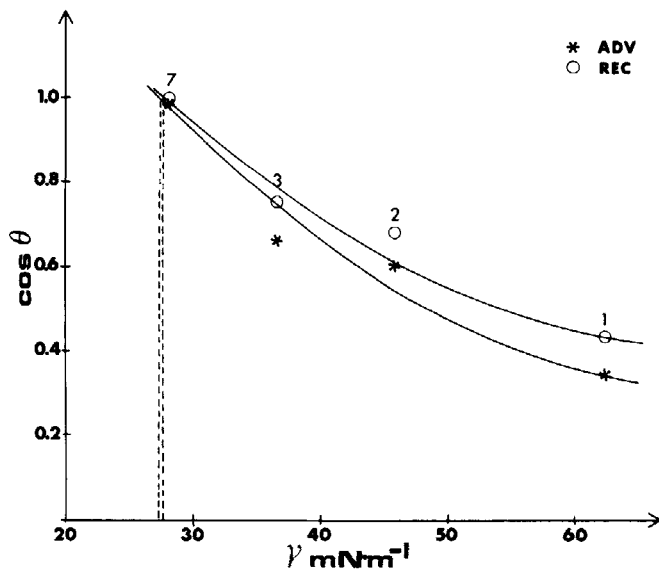


FIGURE 4 $\cos \theta$ versus surface tension for a low density polyethylene substrate.

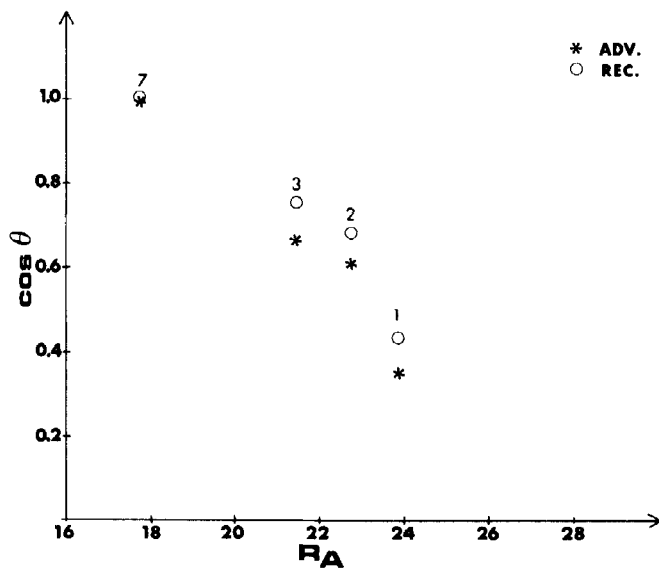


FIGURE 5 $\cos \theta$ versus energy difference R_A , for a low density polyethylene substrate.

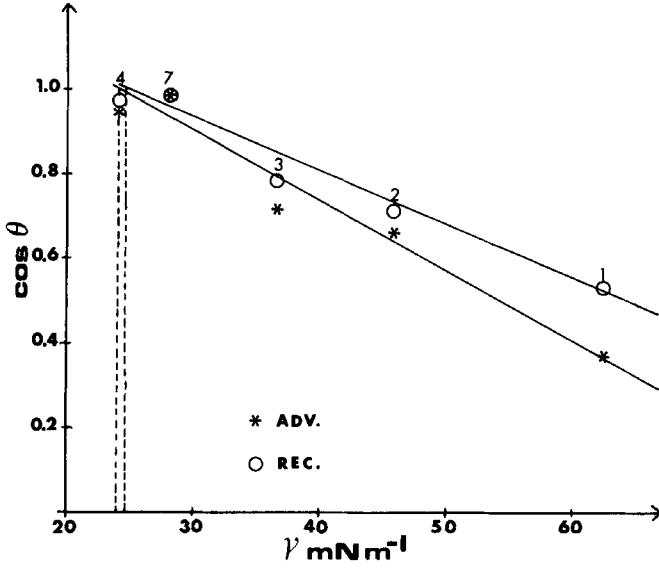


FIGURE 6 Cos θ versus surface tension for a plasticized polyvinyl chloride substrate.

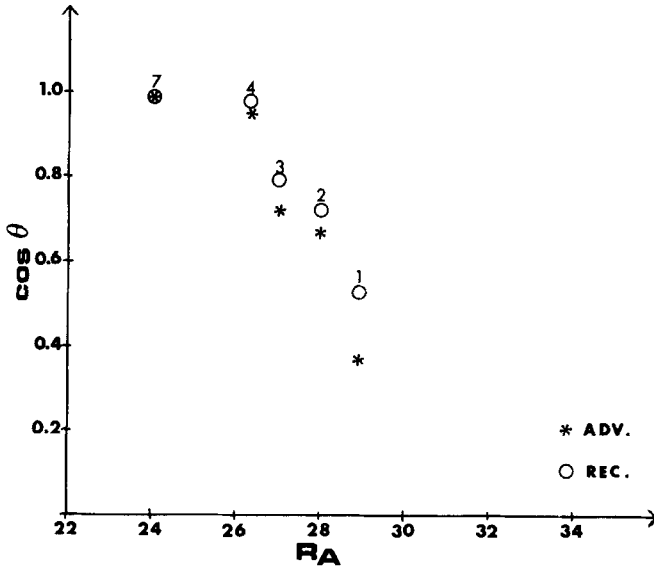


FIGURE 7 Cos θ versus cohesive energy difference, R_A , for a plasticized polyvinyl chloride substrate.

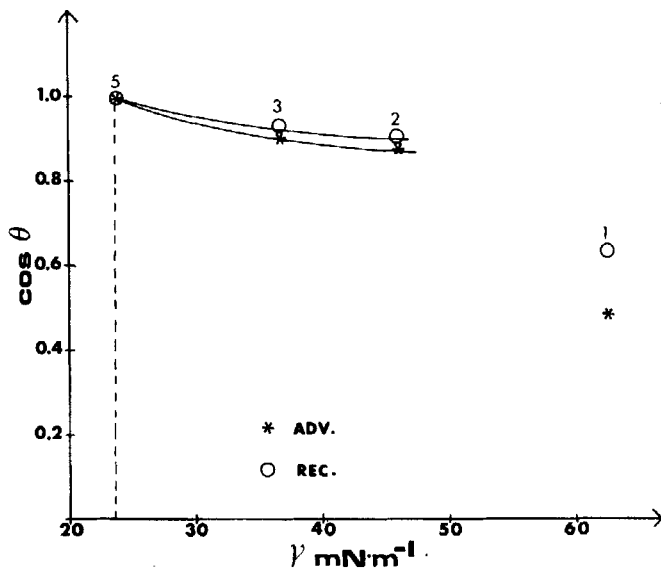


FIGURE 8 $\text{Cos } \theta$ versus surface tension for an epoxy coating. Solvent no. 1 (Glycerol) deviates from the Zisman curve as a result of a relatively higher viscosity.

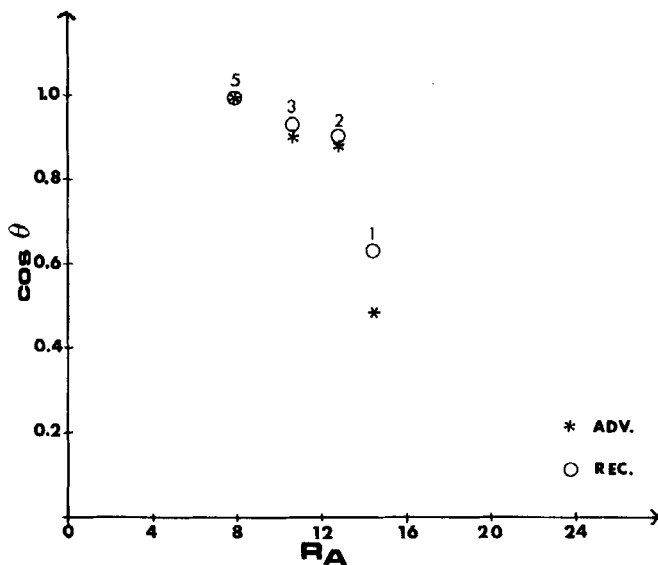


FIGURE 9 $\text{Cos } \theta$ versus cohesive energy difference, R_A , for an epoxy coating.

Once a substrate has been characterized in terms of cohesive energy parameters, it fits readily into an already existing situation where many liquids, polymers^{1,5,8} pigments,¹¹ and numerous other types of materials have already been characterized.^{1,9,13}

Cohesive energy parameters allow systematic analysis of a situation and lead the way to create the systematic and predictable changes desired in product development. As an example assume one wishes the cohesive (or surface) energies of two different materials to be the same (this should promote "compatibility," for example). Each of them can be characterized by the partial cohesion energy parameters. If there are energy differences, some liquids will behave differently on one material when compared with behavior on the other. The energy properties of these differing liquids then provide the clue to implement systematic changes in composition in the direction desired. When "all" liquids behave similarly with respect to both materials, energetic similarity is achieved.

There are also disadvantages to a cohesive energy approach including the large number of liquids required. Likewise higher energy surfaces, where only water or only a few liquids provide contact angles, yield no reliable characterization. In this case surface energy parameters and contact angles are a better approach. Whether to use the one approach or the other depends largely on what is being dealt with and what is desired, since both have advantages and disadvantages.

It is not the purpose of this discussion to delve further into advantages or disadvantages of one approach or the other. The message here is that there are certain situations where a cohesive energy approach to surface characterization can be an advantage, if used properly. Computer descriptions and plots greatly simplify the use of the cohesive energy parameters, should the practical details of testing and evaluation be a major problem.

CONCLUSION

Surfaces can be described energetically in terms of their interactions with liquids having well defined energy properties. This has been termed ESLA (Energy Spectroscopy by Liquid Analysis).¹⁰ These energy properties can be expressed both in terms of the customarily used surface free energies (surface tension) and in terms of partial cohesive energy parameters. This article has emphasized the ease of use and generality of application of the cohesive energy approach, and in particular, its predictive capability. At the same time it is apparent that precise surface

characterizations based on contact angle data have not been found and some scatter of data is present regardless of the principles used to interpret the experimental results.

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References

1. A. F. M. Barton, *J. Adhesion* **14**, 33 (1982).
2. E. Wallström, I. Svenningsen and C. M. Hansen, *Karakterisering av Ytor-Metodstudie — Ytspänning och Löslighetsparameterbetraktelser* (Research Report T5-82, Scand. Paint Print. Ink Res. Inst., 1982) (in Swedish).
3. W. A. Zisman, *Ind. Eng. Chem.* **55** (10), 18 (1963).
4. C. M. Hansen, *The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient* (Thesis, Technical Univ. Denmark, Danish Technical Press, Copenhagen, 1967).
5. C. M. Hansen, *J. Paint Technol.* **39**, 104 (1967).
6. C. M. Hansen and K. Skaarup, *J. Paint Technol.* **39**, 511 (1967).
7. J. H. Hildebrand and R. L. Scott, *The Solubility of Non-Electrolytes*, 3rd ed. (Reinhold, New York, 1950).
8. A. Saarnak and C. M. Hansen, *Löslighetsparametrar—Karaktärisering av färgbindemedel och polymerer* (Research Report T10-82, Scand. Paint Print. Ink Res. Inst., 1982) (in Swedish).
9. C. M. Hansen and A. Beerbower, *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd Ed. Suppl. Vol. (Wiley, New York, 1971), p. 889.
10. C. M. Hansen, *Macromolecular Solutions*, R. B. Seymour and G. A. Stahl, Eds. Pergamon, New York, 1982) p. 1.
11. C. M. Hansen, *J. Paint Technol.* **39**, 505 (1967).
12. E. Wallström and I. Svenningsen, *Ytspänningsmätningar på Korrosionsskyddande Färger—Metodstudie*. (Research Report T10-81, Scand. Paint Print. Ink Res. Inst., 1981) (in Swedish).
13. A. F. M. Barton, *Chem. Rev.* **75**, 731 (1975).