

# DETERMINING THE SURFACE FREE ENERGY OF SOLIDS USING POLAR PROBE LIQUIDS

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## Abstract

A new method is described for determining the surface free energy (SFE) of a film or flat solid sample in terms of its polar and non-polar (dispersion) energy components. The method is based on the static contact angle technique, but offers an alternative to the use of methylene iodide or bromonaphthalene for determining the non-polar component. Instead, contact angles of two polar liquids (such as ethylene glycol and dipropylene glycol) which are chemically similar but which differ in degree of polarity are taken. It is not necessary to know the polar and non-polar components of these probe liquids since only the total surface tension for each is used in the calculations. The cosines of these two contact angles are extrapolated to determine the non-polar component of the surface free energy of the solid. The polar component is then calculated from the contact angle of water on the solid. Advantages of using this method include greater availability of the probe liquids, lower solvency power of the probe liquids, and greater reliability of results as compared with methods using methylene iodide or bromonaphthalene. Evidence is also presented for a predictable reduction in the efficiency of dispersion force interaction with increasing polarity of the solid surface.

## Introduction

The phenomenon of a liquid wetting a solid surface is critical in many industries and applications, including the printing industry. For instance, in printing it plays a key role in the proper transfer and distribution of inks and fountain solutions throughout the press and is especially important in obtaining desired ink lay and adhesion on the printing substrate. It is therefore important to be able to evaluate the wettability of polymer films and other substrates in order to know whether they will accept and hold a printed ink film.

Wetting is dependent on the degree of surface free energy interaction between the solid and the liquid involved. In order to understand the surface interactions taking place we must be able to characterize the surface free energy (SFE) of both the solid and the liquid, not only in terms of the total SFE of each, but also in terms of the dispersion and polar SFE components.

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The total SFE of a liquid is equivalent to its surface tension and is relatively simple to measure directly using any of several commercially available instruments. Determining the SFE of a solid surface and differentiating between its polar and non-polar components, however, requires measuring the interaction of the unknown surface with known reference liquids and using the observed data to calculate the unknown SFE values. Many workers have used liquid-solid contact angles to provide an indication of the magnitude of SFE interaction taking place, building on the work of Young (1805) which related solid-liquid interfacial tension to the cosine of the contact angle.

Fox and Zisman (1950) described the wettability of a solid surface in terms of its "critical surface tension",  $T_c$ . To determine  $T_c$  for a solid sample, contact angles,  $\alpha$ , are measured for a homologous series of probe liquids on the solid surface. A plot is made of  $(\cos \alpha)$  vs.  $T_L$ , where  $T_L$  is the surface tension of the probe liquid. The plot is extrapolated to find value of  $T_L$  at which the contact angle goes to zero ( $\cos \alpha = 1$ ). This is taken as the critical surface tension for the solid.

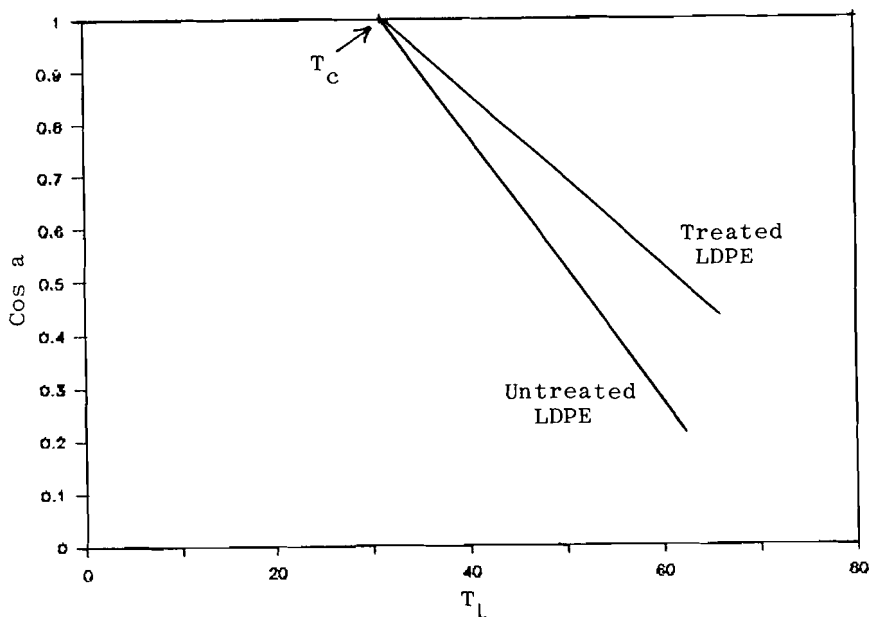


Figure 1. Critical Surface Tension Plot. Lines shown for treated and untreated polyethylene represent typical data.

A problem arises, however, in the case of polyethylene film. There is little or no difference in  $T_c$  values obtained for treated and untreated polyethylene (see Figure 1), even though there is a

considerable difference in the wettability of the two films. It is thus apparent that  $T_c$  alone cannot adequately describe the wetting properties of a solid surface.

Fowkes (1962) described surface free energy forces in terms of independent additive components, dispersion (non-polar) forces and polar forces (such as hydrogen bonding). For the special case in which one of the two interacting surfaces is totally non-polar, so that only dispersion forces need be considered, he related the contact angle of a liquid on a solid to the dispersion SFE components of the solid and liquid according to Equation 1.

$$(1 + \cos a) = \frac{2\sqrt{d_L d_S}}{T_L} \quad (1)$$

where

$T_L$  = Liquid total surface tension  
 $d_L$  &  $d_S$  = Dispersion SFE components

Fowkes showed that a plot of  $(1 + \cos a)$  vs.  $\sqrt{d_L}/T_L$  yields a straight line passing through the origin and intersecting the " $(1 + \cos a) = 2$ " line at  $\sqrt{d_L}/T_L = 1/\sqrt{d_S}$ . Although this is a valuable concept and provides a better understanding of liquid-solid surface interactions, its application is limited to situations in which either the liquid or the solid is totally non-polar. Since most printing substrates and printing inks have appreciable polar SFE components a more comprehensive equation is needed to describe their surface interactions.

For cases in which the SFE interaction involves both polar and non-polar forces, Owens and Wendt (1969) extended Equation 1 to include a polar interaction term.

$$(1 + \cos a) = \frac{2\sqrt{d_L d_S} + 2\sqrt{p_L p_S}}{T_L} \quad (2)$$

They suggested the use of two probe liquids of known  $d_L$  and  $p_L$  to determine  $d_S$  and  $p_S$  for an unknown solid. The contact angle data for the two liquids are inserted into Equation 2, yielding two equations in two unknowns,  $d_S$  and  $p_S$ , which can then be solved by the method of simultaneous equations. The two probe liquids they selected were methylene iodide and water. They used the SFE values shown in Table 1 in their calculations.

This approach provided a means by which to calculate not only the dispersion SFE component of a solid substrate or film, but also the polar SFE component.

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TABLE 1. Surface free energy values used by Owens and Wendt (1969)

	Water	Methylene Iodide
Dispersion, $d_L$	21.8	49.5
Polar, $p_L$	51.0	1.3
Total, $T_L$	72.8	50.8

Note: All values are in dynes/cm

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A problem occurs in practice, however, in that methylene iodide dissolves polystyrene, a commonly used printing substrate. Considering the strong solvency typical of short chain halogenated hydrocarbons it seems reasonable to expect that other common polymer films might also be solvated to varying degrees by methylene iodide. This may appreciably affect the contact angle, while producing little, if any, visually apparent change in the test surface.

In selecting an alternative probe liquid certain considerations must be kept in mind.

1. Although a liquid with no polar SFE component, such as a saturated hydrocarbon, would simplify calculations and would probably reduce solvation problems, these liquids typically have relatively low surface tensions. This results in spreading of these liquids on many of the test surfaces of interest, limiting their utility as probe liquids.
2. Low polarity liquids having higher surface tensions can be found by considering those containing halogens or phosphorus. These liquids, however, typically exhibit higher solvency toward the polymer films commonly used as printing substrates, thus presenting the same problem as methylene iodide.
3. Liquids with a significant degree of hydrogen bonding offer the desired properties of increased surface tension and decreased solvency toward the commonly used printing substrates. However, application of the simultaneous equation solution with polar probe liquids yields unreasonably low  $d_S$  values. Another means of determining  $d_S$  must be utilized if polar probe liquids are to be used.

The objective of the work presented here was to develop a reliable alternative method for determining the dispersion and polar SFE components of solid surfaces which would allow the use of polar probe liquids because of their desirable physical properties and ready availability.

## DISCUSSION

For a series of liquids which are chemically similar, variations in the total surface tension,  $T_L$ , are due primarily to variations in the polar SFE component,  $p_L$ , with  $d_L$  remaining fairly constant. Thus, as  $T_L$  decreases,  $p_L$  approaches zero and the polar term in Equation 2 drops out, leaving Equation 1. Also, as  $p_L$  approaches zero,  $\sqrt{d_L}/T_L$  approaches  $1/\sqrt{T_L}$ . Thus, a plot of  $1/\sqrt{T_L}$  vs  $(1 + \cos a)$  should cross the " $(1 + \cos a) = 2$ " line at  $1/\sqrt{d_S}$ , which is the same point as for the plot of  $\sqrt{d_L}/T_L$  vs  $(1 + \cos a)$  described by Fowkes (1962). In other words, it should be possible to determine  $d_S$  using chemically similar polar probe liquids for which only the total surface tensions are known.

In order to test this approach, comparative  $d_S$  values were determined for two substrates, polypropylene and polyvinyl chloride, using both the method of Fowkes and the proposed method. In applying Fowkes' method, mineral oil ( $T_L = d_L = 31.9$  dynes/cm) was used as a non-polar probe liquid to establish the location of the  $\sqrt{d_L}/T_L$  vs  $(1 + \cos a)$  line. The mineral oil was confirmed to be totally non-polar ( $p_L = 0$ ) by measuring its interfacial tension with water (51.3 dynes/cm) and solving Equation 3 for the polar component.

$$T_{12} = T_1 + T_2 - 2(\sqrt{d_1 d_2} + \sqrt{p_1 p_2}) \quad (3)$$

In the proposed method dipropylene glycol ( $T_L = 32.6$  dynes/cm) and ethylene glycol ( $T_L = 42.7$  dynes/cm) were used to establish the  $1/\sqrt{T_L}$  vs  $(1 + \cos a)$  line. The resulting plot for one of the test substrates, a cold formed polyvinyl chloride film for shrink wrap packaging, is shown in Figure 2. Results for both test substrates are summarized in Table 2. The data shows excellent agreement between the two methods.

It should be noted here that neither the test substrates nor the probe liquids used in this work were subjected to any special purification steps, with the exception of the water, which was commercial high purity (HPLC grade) water.

The reasoning for using "off the shelf" materials is that they are representative of the materials encountered in day-to-day operations, and that any method for measuring wettability must be valid with these materials in order to be practical.

Table 2. Comparison of  $d_S$  values obtained from plots of  $\sqrt{d_L}/T_L$  using mineral oil and  $1/\sqrt{T_L}$  using dipropylene glycol and ethylene glycol as shown in Figure 2.

Substrate	Contact Angles ( $^\circ$ )			$d_S$ (dynes/cm)	
	Min. Oil	DPG	EG	Fowkes' Method	Proposed Method
PVC, #2	28	35	63	28.3	29.0
Treated PP, #1	13	20	51	31.1	31.0

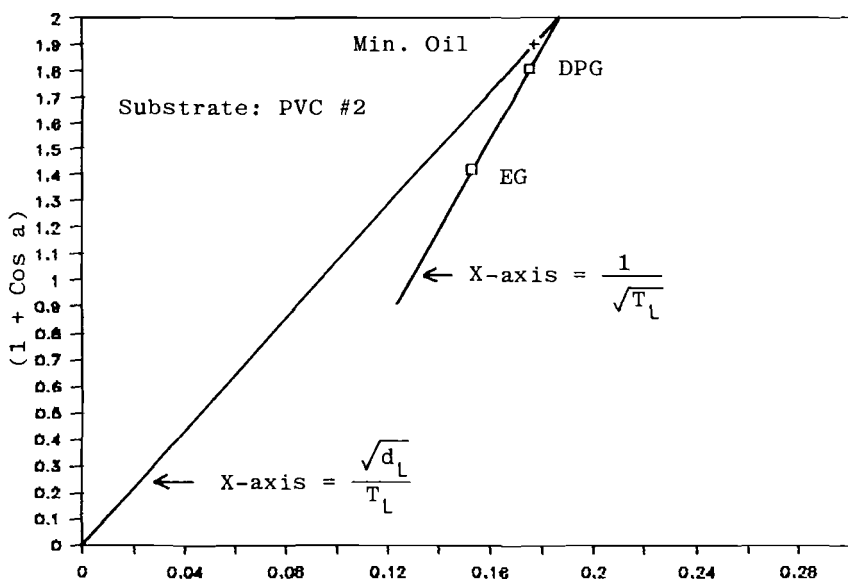


Figure 2. Convergence of  $\sqrt{d_L}/T_L$  and  $1/\sqrt{T_L}$  plots. Data is summarized in Table 2.

Once  $d_S$  has been determined,  $p_S$  can be determined from the contact angle of water, using the commonly accepted values of  $d_L$  and  $p_L$  for water shown in Table 1. This calculation is accomplished by solving Equation 2 for  $p_S$ , yielding Equation 4.

$$p_S = \left[ \frac{T_L(1 + \cos a) - 2\sqrt{d_L}d_S}{2\sqrt{p_L}} \right]^2 \quad (4)$$

Tables 3 and 4 list typical results obtained on several substrates tested in our laboratory.

Table 3. Observed contact angles for several representative substrates.

Substrate	Contact Angles ( $^{\circ}$ )		
	DPG	EG	Water
1. Polyethylene, Untreated	37	68	90
2. Polyethylene, Treated	22	55	75
3. Polypropylene, Treated, #1	20	51	69
4. Polypropylene, Treated, #2	20	43	56
5. Polystyrene	26	60	79
6. Polyvinyl Chloride, #1	29	51	71
7. Polyvinyl Chloride, #2	35	63	85
8. Polyvinyl Chloride, #3	26	56	73
9. Photopolymer Printing Plate	23	49	67
10. Paraffin Wax	55	81	108

Table 4. Surface free energy results obtained from the contact angle data shown in Table 3.

Substrate	SFE Values (dynes/cm)		
	Disp.	Polar	Total
1. Polyethylene, Untreated	29.1	2.5	31.6
2. Polyethylene, Treated	31.1	7.7	38.8
3. Polypropylene, Treated, #1	31.0	10.8	41.8
4. Polypropylene, Treated, #2	30.3	19.0	49.3
5. Polystyrene	30.7	6.0	36.7
6. Polyvinyl Chloride, #1	28.8	10.8	39.6
7. Polyvinyl Chloride, #2	29.0	4.3	33.3
8. Polyvinyl Chloride, #3	30.3	8.9	39.2
9. Photopolymer Printing Plate	30.3	12.2	42.5
10. Paraffin Wax	25.7	0.0	25.7

It is also possible to use a modification of the technique described here to determine the dispersion and polar surface tension components of a liquid sample. To do so it is necessary to use a totally non-polar reference solid, such as freshly cast paraffin wax. Using dipropylene glycol and ethylene glycol contact angles, the value of  $d_s$  is established for the reference solid and the  $\sqrt{d_L}/T_L$  vs  $(1 + \cos a)$  line is drawn (see Figure 3). The contact angle of

the unknown liquid is measured on the reference surface and the value of  $\sqrt{d_L}/T_L$  is determined from the plot. The value of  $d_L$  can then be calculated. It is important that the reference surface be as free of polar constituents as possible. This can be verified from the contact angle of water. If the data point for water falls above the  $\sqrt{d_L}/T_L$  line it indicates the presence of polar constituents in the solid surface. However, because of the difficulty in obtaining a surface totally free of polar sites, a slight displacement of the water data point is almost unavoidable. Table 5 shows results thus obtained for dipropylene glycol and ethylene glycol.

Table 5. Surface free energy components determined for dipropylene glycol and ethylene glycol using paraffin wax as a non-polar reference solid (See Figure 3).

	$d_L$	$p_L$	$T_L$
Dipropylene Glycol	25.9	6.7	32.6
Ethylene Glycol	23.7	19.0	42.7

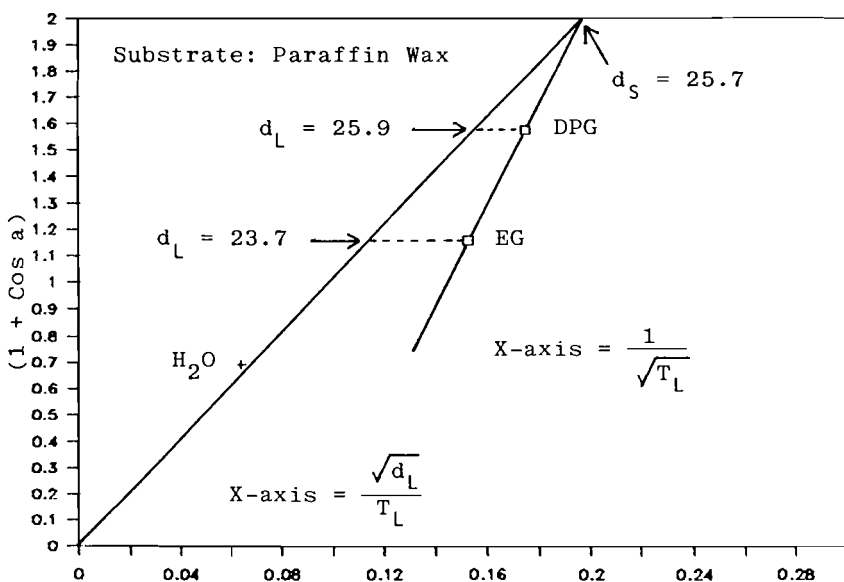


Figure 3. Determination of the dispersion SFE component for dipropylene glycol and ethylene glycol using paraffin wax as a non-polar reference solid. (See Table 5 for a summary of results.)



Knowing the dispersion and polar SFE components for a specific solid-liquid pair should allow one to calculate their contact angle with a reasonable degree of accuracy. However, if we use the values shown in Tables 4 and 5 to calculate expected contact angles for dipropylene glycol and ethylene glycol on the various surfaces, the predicted angle is always smaller than the angle actually observed (see Table 6). In order to correctly predict the contact angle of dipropylene glycol, for instance, would require a different dipropylene glycol  $d_L$  value for each different substrate surface, and in many cases  $d_L$  would have to be well below 20 dynes/cm.

Table 6. Comparison of predicted and observed contact angles for dipropylene glycol and ethylene glycol on various substrate surfaces.

	Contact Angles ( $^{\circ}$ )			
	DPG		EG	
	Calc'd	Obs'd	Calc'd	Obs'd
1. LDPE, Untreated	21	37	56	68
2. LDPE, Treated	< 0	22	33	55
3. PP, Treated, #1	< 0	20	20	50
4. PP, Treated, #2	< 0	20	< 0	42
5. Polystyrene	< 0	26	40	60
6. PVC, #1	< 0	29	27	51
7. PVC, #2	< 0	35	49	63
8. PVC, #3	< 0	26	30	56
9. Photopolymer Plate	< 0	23	15	49

One possible explanation for this discrepancy between predicted and observed contact angles might be the effect of steric hindrance resulting from preferred orientation of the liquid molecules at the solid surface. At a polar site on the solid surface a liquid molecule will orient itself to maximize the polar interaction, reducing the freedom of the molecule to maximize its dispersion interaction with the surface. In addition it may also sterically hinder the approach of other liquid molecules to the surface in the immediate vicinity of the polar site, further reducing dispersion force interactions in that immediate area.

If, in fact, steric hindrance is causing a reduction in the dispersion interaction efficiency, it should be possible to represent the fractional efficiency by means of a factor, "k", inserted into the

dispersion term of Equation 2. This yields Equation 5. A similar interaction factor was proposed by Good and Girifalco (1960), except that polar and dispersion type interactions were not separated in their equation.

$$(1 + \cos a) = \frac{2\sqrt{kd_L d_S} + 2\sqrt{p_L p_S}}{T_L} \quad (5)$$

Using the contact angles and SFE values tabulated in the foregoing tables, Equation 5 was solved for the value of  $k$  for dipropylene glycol and ethylene glycol on each of the test surfaces. The  $k$  values thus obtained are listed in Table 7. Also listed is the relative polarity of each substrate, expressing  $p_S$  as a percentage of  $T_S$ .

Noting that  $k$  seems to decrease with increasing polarity of the solid surface, plots of  $k$  vs substrate polarity were prepared for dipropylene glycol (Figure 4) and for ethylene glycol (Figure 5). The straight line correlation shown in these plots supports the validity of including the dispersion interaction efficiency factor,  $k$ ,

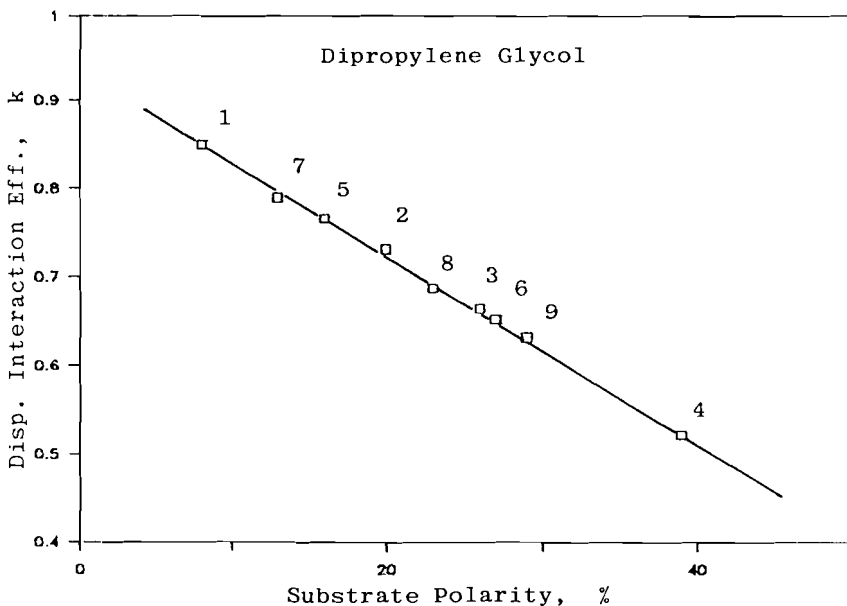


Figure 4. Variation of dipropylene glycol dispersion interaction efficiency factor,  $k$ , with substrate polarity. Numbers refer to substrates listed in Table 7.

as shown in Equation 5. The fact that the solid surfaces are of varying chemical composition further indicates that  $k$  is primarily influenced by the degree of polarity of the solid surface rather than by the specific chemical composition of the solid.

Table 7. Values of dispersion interaction efficiency,  $k$ , calculated for dipropylene glycol and ethylene glycol on various surfaces.

Substrate	Substrate Polarity, %	D.I.E. Factor, $k$	
		DPG	EG
1. LDPE, Untreated	8	0.850	0.742
2. LDPE, Treated	20	0.732	0.636
3. PP, Treated, #1	26	0.664	0.573
4. PP, Treated, #2	39	0.522	0.454
5. Polystyrene	16	0.766	0.636
6. PVC, #1	27	0.652	0.613
7. PVC, #2	13	0.790	0.709
8. PVC, #3	23	0.688	0.576
9. Photopolymer Plate	29	0.632	0.564

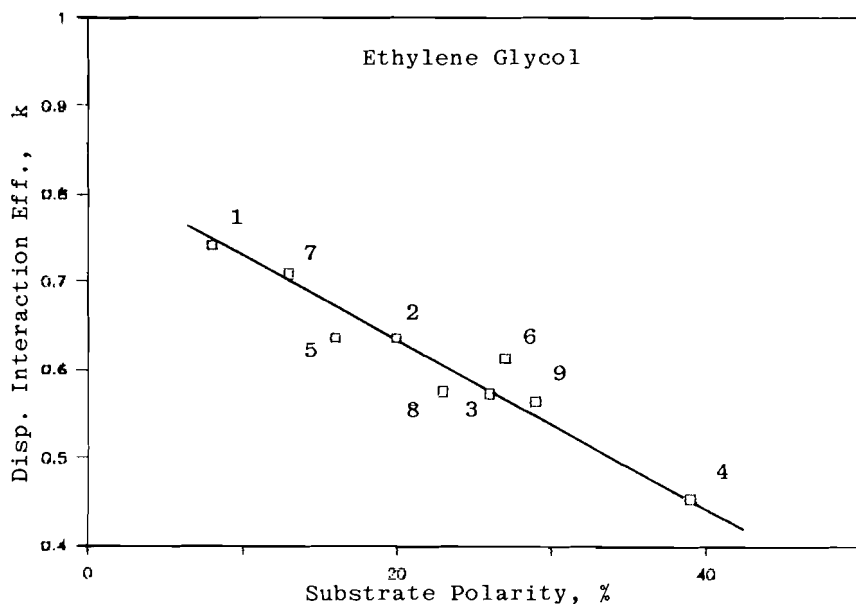


Figure 5. Variation of ethylene glycol dispersion interaction efficiency factor,  $k$ , with substrate polarity. Numbers refer to substrates listed in Table 7.

It is expected that this relationship will also hold for other liquids, which should significantly improve our ability to predict the wetting behavior of inks and fountain solutions on various substrates. Also, since molecules of dissolved resin in an ink have the freedom of movement to orient themselves as would a liquid molecule, we may be able to apply the same type of calculation to predict adhesion properties of a dried ink film to specific substrates.

#### SUMMARY

This work has shown that it is possible to determine  $d_s$  for a solid surface reliably using polar liquids for which only the total surface tension of each is known. The value of  $d_s$  thus determined can then be used in conjunction with a measured contact angle for water to determine  $p_s$ , providing both the polar and the dispersion SFE components for the solid. In addition it has been shown that polar organic liquids exhibit a reduced dispersion force interaction efficiency when in contact with a polar substrate surface. This decreased dispersion interaction efficiency can be represented by a factor,  $k$ , which, for a given liquid, varies in an inverse linear fashion with the polarity of the solid surface.

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