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Studies on the Surface Chemistry of Wool

Part II — The Critical Surface Tension of Wool and Polymers — Some Results and a Reinterpretation of the Theory on Surface Interactions

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STUDIES ON THE SURFACE CHEMISTRY OF WOOL PART II — THE CRITICAL SURFACE TENSION OF WOOL AND POLYMERS — SOME RESULTS AND A REINTERPRETATION OF THE THEORY ON SURFACE INTERACTIONS

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ABSTRACT

A brief review of the theory and literature on interfacial phenomena is given. A statistical analysis of published data has shown that the value obtained for γ_S, *the surface free energy or surface tension of a solid, is dependent on the values of the dispersion and polar components of the liquid surface tension* (γ_L^d *and* γ_L^p) *used in its determination. It appears that the surface free energy of a solid can be correctly established by contact angle measurements with liquids only when the disperse fractions of the liquid* (D_L) *and that of the solid* (D_S) *are equal.*

The critical surface tension (γ_c) *of polyamide epichlorohydrin (® Hercosett) polymers was determined by contact angle measurements. The value obtained depended on the type of liquid used for the determination. Polar liquids tended to give significantly higher* γ_c *values than non-polar liquids.* m
Neutralisation of the polymer and its oisture content were also found to affect the γ_c *value.*

The γ_c *value of wool and of nylon 66 fibres was determined by the sink-float method. Various liquids produced different values. It seemed that* γ_c *was more sensitive to the type of liquid used in the case of nylon than in the case of wool.*

GENERAL INTRODUCTION

Nowadays it is common practice to render wool tops shrinkresistant by coating the fibres with a layer of polymer[1, 2]. It is generally accepted that a polymer will not spread on a wool fibre when the surface free energy of the wool is lower than that of the polymer[3]. In order to raise the surface free energy of the fibres to an acceptable level, the wool has to be modified by a chemical treatment which, in most cases, involves the use of strong oxidising agents such as chlorine[1, 2]. It is therefore important to know the surface free energy of the polymer and the wool fibres. Once the surface free energies are known, it is possible to establish whether or not a specific polymer will spread on a wool fibre. Furthermore, in these cases where the polymer does not spread, the level of chemical pretreatment required to increase the surface free energy of the wool to the level where such polymer spreading will occur, can be established. In addition, the information can be used to decide which way research should be directed, to obtain a polymer which will spread on wool *without* the application of a chemical pretreatment.

A study of the literature on adhesion, cohesion and spreading phenomena revealed several methods which can be used to determine the surface free energy (γ_S) of polymers and wool fibres. In the first method the contact angles (θ) of various liquids on the substrate are determined by plotting cos θ against γ_L (surface tension of the liquid). The value of γ_L where $\cos\theta = 1$ is obtained from the graph. This value has been defined by Zisman[4] as the critical surface tension (γ_c) of the surface. γ_c is an empirical parameter which can be used to characterise the critical surface tension of wetting and to compare the wettabilities of various surfaces.

The γ_c value of fibres can also be determined according to the sink-float method[5-7]. In this test, samples of fibres are placed on a series of liquids of progressively increasing surface tensions. The γ_c value of the fibre is that value lying between the surface tension of the liquid in which the fibre just sinks, and that of the liquid in which the fibre just floats.

A third method that can be used to determine the surface free energy of solids (γ_S), involves the calculation of γ_S from contact angle results by formulae proposed by various athors[8,9].

Theoretical aspects of the concept of surface free energy:

The surface properties of solids and liquids and their common interface can be investigated by measuring contact angles or interfacial tensions, or both.

Each of these can be and has been equated by the same expression[10]:

$$2(\gamma_1\gamma_2)^{1/2}\,\Phi = \mathrm{Wa} \quad (1)$$

$$= \gamma_1(1 + \cos\theta) \quad (2)$$

$$= \gamma_1 + \gamma_2 - \gamma_{12} \quad (3)$$

Where γ_1 is the surface tension of a liquid,

γ_2 is the surface tension of another liquid or a solid,

Φ is the bonding efficiency factor[10] which is a function of certain properties of the two substances,

Wa is the work of adhesion,

θ is the contact angle, and

γ_{12} is the interfacial tension.

By equating Wa, θ and γ_{12} as indicated, certain assumptions have been made, namely that the surfaces under consideration must be smooth and of low energy, θ is taken to be the equilibrium angle and the spreading pressure (π_e) must be negligible.

The surface free energy of a solid (γ_S) is of considerable importance in determining whether a liquid will spread on a surface. When spreading occurs, the work of adhesion will be at a maximum, the contact angle will be zero and the interfacial tension will be at a minimum. It is frequently accepted that the solid surface free energy is equal to the critical surface tension (i.e. $\gamma_S = \gamma_c$) when spreading occurs. The same assumption will be used in this publication, but it must be remembered that Owens and Wendt[8] state that Zisman has been careful to point out that γ_c is not necessarily equal to the solid surface free energy because it is not certain that $\pi_e = 0$ when $\theta = 0$.

The basic equations given above can be extented to take some further interactions into consideration. When two immiscible liquids 1 and 2 are in contact, the molecules of liquid 1 at the interface experience two net forces. The first force is the net attraction into the body of liquid 1 by the excess of the total number of molecules relative to the number of surface molecules, and is represented by γ_1. The second force is directed towards the second liquid and is dependent upon the attraction of the molecules of liquid 1 on those of liquid 2. This second force is the resultant of several different kinds of attraction, i.e. the London dispersion forces, Keesom polar forces, hydrogen bonding and dipoles, induced dipoles. etc.

Considering only the London dispersion forces, it is usually assumed that they can be represented by a fraction D_1 of the total γ_1 force so that this component $\gamma_1^d = D_1 \gamma_1$. Similarly liquid 2 has a component γ_2^d. If only dispersion forces are present then the second force can be represented by the *geometrical mean*[11] of these dispersion components, i.e. $(\gamma_1^d \; \gamma_2^d)^{1/2}$. Wu[9] however, claims that they can be better represented by their *harmonic mean* $\frac{\gamma_1^d \; \gamma_2^d}{\gamma_1^d + \gamma_2^d}$. Thus the resultant force on the surface molecules of liquid 1 which is directed into liquid 1 will be:

$$\gamma_1 - (\gamma_1^d \; \gamma_2^d)^{1/2}$$

Similarly liquid 2 will experience a resultant force of

$$\gamma_2 - (\gamma_1^d \; \gamma_2^d)^{1/2}$$

The interfacial surface will then be under tension, the force being

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\,(\gamma_1^d\ \gamma_2^d)^{1/2} \qquad (4)$$

Hence in this case $\Phi = (D_1\ D_2)^{1/2}$ (5)

Owens & Wendt[8] also introduced further terms into equation (4) to account for other forces. If P is the fraction due to polar forces, i.e. if all forces, which are not due to London dispersion forces, are assumed to be polar forces, then the bonding efficiency factor in equation (5) can be expanded to:

$$\Phi = (D_1\ D_2)^{1/2} + (P_1\ P_2)^{1/2} \qquad (6)$$

By a similar argument the P fractions have been further divided into an H fraction and a P fraction, where H is due to hydrogen bonding and P is the remainder[12].

Note that

$$D_1 + P_1 = 1 \qquad (7)$$

and

$$\gamma_1^d + \gamma_1^p = \gamma_1 \qquad (8)$$

Owens and Wendt[8] proposed the following equation as an extension of equation (4)

$$\gamma_{LS} = \gamma_L + \gamma_S - 2\,(\gamma_L^d\ \gamma_S^d)^{1/2} - 2\,(\gamma_L^p\ \gamma_S^p)^{1/2} \qquad (9)$$

where L refers to the liquid and S to the solid. Combinding equations (2), (3) and (9):

$$\frac{\gamma_L\ (1 + \operatorname{Cos}\,\theta)}{2} = (\gamma_L^d\ \gamma_S^d)^{1/2} + (\gamma_L^p\ \gamma_S^p)^{1/2} \qquad (10)$$

From equation (10) it can be seen that the surface free energy, γ_S, of a solid and the γ_S^d and γ_S^p values can be determined only when the γ_L^d and γ_L^p values for each of two liquids used for the determination and the contact angles of the liquids with the solid surface are known. If γ_S is also known then the γ_L^d and γ_L^p values of only one liquid and one contact angle are sufficient to determine the solid γ_S^d and γ_S^p values.

A survey of some results quoted in the literature for the surface free energy of polymers and other substances:

Several workers have measured the contact angles of liquids on solid surfaces and then applied the harmonic mean (Wu[9]), or the geometric mean (Owens & Wendt[8]) or the Fowkes[11] formulae to calculate the surface free energy of the solid. The formulae have also been used to calculate the disperse (γ_S^d) and the polar (γ_S^p) components of the surface tension. In some cases the results obtained were compared with γ_c values which were obtained according to the Zisman method.

El-Shimi and Goddard[13] measured the contact angles of water and diiodomethane on 10 different surfaces and calculated γ_S, γ_S^d and γ_S^p for the solid surfaces. They found a good correlation between the γ_S values and values reported in the literature for γ_c. They furthermore employed the Zisman method, using alkanol/water mixtures, and found that γ_c was independent of the nature of the solid surface. The fact that the same γ_c value was obtained on 10 widely different surfaces was explained in terms of the adsorption of alcohol molecules onto the solid surfaces.

In his study of polymers Schwarcz[14] found that the harmonic mean equation sometimes could not be solved. This was not observed with the geometric mean equation and consequently he preferred this formula. He measured the contact angles of liquids on paraffin of known γ_S value and calculated γ_L^d and γ_L^p. The liquids subsequently were used to measure the contact angles of pairs of liquids on polymers, and the γ_S^p and γ_S^d values of the polymers were calculated by averaging the results. He obtained approximately the same γ_S values in all cases, despite the fact that widely different liquids were used.

Pittman et al[15] measured the contact angles of different liquid pairs on polymers and calculated the surface energy of the polymers from the results. Unlike Schwarcz, they found widely differing γ_S values for each set of liquid pairs.

Panzer[12] used the geometric mean equation to calculate γ_S^d and γ_S^p of the solid n-octacosane and obtained widely differing values, depending on the liquid pair used. Experiments were carried out to determine γ_S^d of polymethylmethacrylate with the aid of four different liquid pairs. When the harmonic mean equation was used to calculate γ_S^d, the following widely different values, viz. 12,9 14,1 30,4 and 24,7 mN/m, were obtained.

Fowkes[11] stated that if γ_c for a given solid was determined with liquids having only dispersion force interactions (e.g. hydrocarbons), then γ_c would be equal to γ_S^d. Baszkin[16], on the other hand, measured the contact angles of diiodomethane and decalin mixtures (which consisted of both γ_L^d and γ_L^p forces) on oxidised polyethylene and found that γ_c could not be equated to γ_S^d.

Wu[9, 17] measured the surface tension of molten polymers by the pendent drop method and calculated γ_S from these results. He compared these results with theoretical values calculated from parachor and found that they agreed within 3 mN/m. He also measured the contact angles of water and diiodomethane on these polymers and then used the harmonic mean equation to calculate the surface free energy of the polymers. He found good agreement between the γ_S values calculated from the contact angle results, and those calculated from the molten polymer results. Wu furthermore calculated the dispersion and polar force components of the polymers according to the geometric mean and the harmonic mean equations. He claimed that the harmonic mean equation gave results which were in agreement with those obtained in the case of the molten polymers, while the geometric mean equation gave significantly different results.

Dann[18] stated that the concept of γ_c being characteristic of the solid surface is not valid. He demonstrated that a specific surface showed different γ_c values, depending on the type of liquid used.

Kaelble[10] reported values for γ^d and γ^p for five liquids, and the work of adhesion for each of these liquids on nylon 66. He used these data together with the results from pairs of liquids to calculate the surface properties (γ_S^d and γ_S^p) of the solid, using the geometric mean equation. He concluded that the arithmetic mean values of γ_S^d, γ_S^p and γ_S "appeared to adsorb and normalise the eccentricities of the individual solutions, provided that the series of liquids chosen has a wide range of γ_L and γ_L^p values."

From the above literature survey it can be seen that various authors prefer different formulae for the calculation of the surface free energy of a substance. The results published by different authors are not always in agreement and in certain cases contradictory statements have been made. It was decided, therefore, to reinterpret the theory on surface free energy and to re-evaluate the various formulae suggested for the calculation of the surface free energy. It was also decided to conduct a statistical analysis of some results quoted in the literature. Finally, it was decided to determine the γ_c values of wool and nylon fibres by the sink-float method as well as the γ_c values of ®Hercosett samples by contact angle measurements.

EXPERIMENTAL

Materials:

Commercial ®Hercosett samples i.e. ®Hercosett 57 (10 *per cent* solids), ®Hercosett 125 (12,5 *per cent* solids) and ®Hecosett 70 (25 *per cent* solids) were polymerised into films. All the liquids used for the various tests were of the highest purity available.

Wool tops (64's) and nylon 66 fibres were cleaned successively with dichloromethane (three times), methanol (once) and distilled water (once) and dried at 60° C in a vacuum oven for three hours and then stored in a desiccator at room temperature.

Preparation of polymer surfaces:

The Hercosett solutions were diluted with water to a concentration of five *per cent* (m/v) and transferred to a petri dish lined with aluminium foil. The samples were first dried at room temperature for approximately three days, followed by oven drying at 60° C for 24 hours and then at 105° C for at least 24 hours. The samples were then transferred to a desiccator and stored at room temperature. In some cases the Hercosett resin solutions were neutralised with sodium bicarbonate prior to drying and these will be referred to as *neutralised* polymer films. The samples which were not treated with sodium bicarbonate will be referred to as *not neutralised*. One half of the dried film was exposed to atmospheric conditions for at least seven days before testing, and these will be referred to as conditioned samples. The moisture content of the conditioned samples was about 16 *per cent*.

Contact angle measurements:

The following liquids were used for the contact angle measurements:

non polar liquids*

bromobenzene

α - bromo naphthalene

chlorobenzene

1,2 - dibromoethane

diiodomethane

1,1,2,2 - tetrabromoethane

tricresyl phosphate

polar liquids*

aniline

benzaldehyde

ethylene glycol

formamide

glycerol

quinoline

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*Classification according to the γ^d and γ^p values of the liquids.

The polymer films were clamped between two metal plates in order to obtain a flat surface. A drop of the liquid (2 to 3 mm in diameter) was placed on the surface with the aid of a Hamilton syringe, and the contact angle was then measured with a reflection contact angle goniometer as described by Fort and Patterson[19]. In each case four different drops, each placed on a different location on the polymer film, were used. The average contact angle was then calculated.

Surface tension measurements:

The surface tension of each liquid was determined with a Du Noüy tensiometer (Cambridge), applying correction values according to the tables of Harkins and Feldman[20].

Critical surface tension measurements on wool and nylon 66 fibres:

The sink-float method[7] was used to measure the critical surface tension of wool and of nylon 66 fibres. The following liquids or liquid pairs were used for these experiments: Dioxane/water, butanol/water, benzaldehyde, aniline, α-bromonaphthalene, ethylene glycol, acetyl acetone, benzene and chlorobenzene.

RESULTS AND DISCUSSION

A. The critical surface tension of Hercosett polymers determined by contact angle measurements:

The critical surface tensions of the different Hercosett polymer surfaces were determined according to the method suggested by Zisman[4] i.e. by plotting cos θ against γ_L (where θ = contact angle) and γ_L = surface tension of the liquid giving the contact angle θ on the solid surface. Neatralised and not neutralised polymer films were examined. Figure 1 shows the results obtained on a neutralised, conditioned film of Hercosett 70. It can be seen that two different γ_c values were obtained, depending on the type of liquid used. Polar liquids gave a γ_c value of 42 mN/m, and non-polar liquids gave a γ_c value of 37 mN/m. In the case of the not neutralised polymer, non-polar liquids gave a much lower γ_c, i.e. about 31 mN/m (See figure 2). No value was obtained in the case of the polar liquids.

The effect of conditioning of the polymer on γ_c can be seen in Figures 3 and 4. Non-polar liquids gave a γ_c value of 31 mN/m in the case of the dried polymer and 36 mN/m in the case of the conditioned polymer (Figure 3). In the case of polar liquids, however, a γ_c value of 39 mN/m was obtained in the case of dried polymer and about 42 mN/m in the case of the conditioned polymer (Figure 4).

Differences were also observed between γ_c values of certain of the Hercosett polymers. Figures 5 and 6 show the results obtained with neutralised, conditioned Hercosett 57 and Hercosett 125, respectively. Both polymers had a γ_c value of about 39 mN/m when determined with polar liquids, and a γ_c value of about 31-32 mN/m when determined with non-polar liquids. These values are considerably lower than those found for Hercosett 70 (42 and 37 mN/m, respectively).

In the case of not neutralised, conditioned Hercosett 57 and Hercosett 125 (Figures 7 and 8), a γ_c value of about 31 mN/m was obtained when non-polar liquids were used for the determination. This is similar to the value obtained for Hercosett 70. Once again polar liquids gave significantly higher γ_c values (38 to 39 mN/m) than non-polar liquids.

It would appear, therefore, that γ_c of the Hercosett resin, determined according to the Zisman method, depends on the type of liquid used for the contact angle measurements. Polar liquids tended to give significantly higher γ_c values than non-polar liquids. The moisture content of the polymer in certain cases also appeared to affect the γ_c values. The three different polymer samples (not neutralised) had approximately the same γ_c value when determined with non-polar liquids. Neutralisation of the polymers, however, resulted in large differences between the γ_c values of Hercosett 57, 70 and 125. It must be pointed

TABLE I

THE CRITICAL SURFACE TENSION OF WOOL AND NYLON 66 AS DETERMINED BY THE SINK-FLOAT METHOD

Solvents	Critical surface tension (mN/m)	
	Nylon 66	Wool
Butanol/water mixtures	< 27 - 29,5	< 29 - 33(a)
Benzaldehyde and aniline	> 39,9 - < 41,2	—
α-Bromonaphthalene and ethylene glycol	> 43,8 - < 47,2	—
Acetyl acetone and benzene	—	< 28,6 - 31
Chlorobenzene, benzene and dioxane	—	< 28,6 - 32,9
Dioxane/water mixtures	40,3 - 42,3(b)	—
Dioctyl ether/o-diethyl phthalate mixture	27,0 - 27,8(b)	—
Non-polar liquids	—	28(c) 33(d)

(a) Reference (7)

(b) Reference (5)

(c) Lincoln Wool 45% RH - reference (6)

(d) Lincoln Wool 0% RH - reference (6)

out that the acid content of the different polymer solutions varied and consequently different amounts of alkali had to be employed for neutralisation. This probably had some effect on the spreading behaviour of the liquids used for the determinations.

There are very few publications describing the determination of γ_c of polyamide epichlorohydrin polymers. Most of the recent reports refer to the value reported in a publication[3] which appeared in 1964. In that investigation the polymer solution was dried and the spreading behaviour of various butanol/water mixtures on the polymer film was determined. The solution with the highest surface tension which would immediately spread on the polymer was taken to be γ_c of the polymer. The γ_c value of the polyamide epichlorohydrin polymer was found to be 52 mN/m, when determined according to this method. This is significantly higher than the values obtained from the contact angle measurements in the present study.

B. The γ_c value of wool and nylon 66 fibres determined by the sink-float method:

When a sample is available in the form of a fibre, its γ_c can be determined by the sink-float method described by Mutchler et al[5-7]. The γ_c's of wool and nylon fibres were determined according to this method, using various liquids and the results obtained are given in Table I, together with some values reported in the literature. Nylon 66 fibres have a γ_c value of between <27 - 29,5 mN/m, when determined with butanol/water mixtures. When other liquids were used, however, significantly higher γ_c values were obtained. Results quoted in the literature for the γ_c of nylon 66 fibres also varied from relatively low to very high values, depending on the type of liquid used for the determinations. This is, therefore, in agreement with the results obtained in the present study and it is evident that the γ_c values obtained for nylon 66 fibres by the sink-float method depend on the liquid used.

γ_c of merino wool fibres determined in this investigation with the aid of various liquids was found to be $<28{,}6$ to 32,9 mN/m. In earlier studies, where butanol/water solutions were used, γ_c was found to be in the region 29 to 33 mN/m[7]. It seems that γ_c of the wool fibres was not as dependent on the type of liquid used for the determination as is the case with nylon 66 fibres.

C. A re-interpretation of the theory on surface free energy and some comments on the contradictory findings reported to date:

As a result of the anomalous results frequently obtained by different workers, it was decided to re-assess the surface free energy theory and the various interpretations of this theory. It seems that the following argument, originally used by Kaelble[21], may explain the dependence of γ_S of a polymer or fibre at the critical point on the specific liquid used for the determination.

From equations (1) and (6) it can be seen that

$$Wa = 2(\gamma_L \ \gamma_S)^{1/2} \left[(D_L \ D_S)^{1/2} + (P_L \ P_S)^{1/2} \right] \tag{11}$$

If, when spreading occurs, Wa is at a maximum then the bonding efficiency factor, Φ must be at its maximum value of unity for a given γ_L and γ_S, i.e.:

$$\frac{Wa}{2(\gamma_L \ \gamma_S)^{1/2}} = \Phi = (D_L \ D_S)^{1/2} + (P_L \ P_S)^{1/2} = 1 \tag{12}$$

This requires that $D_L = D_S$ and hence $P_L = P_S$. The dispersion fractions of the liquid and the solid must therefore match, as must also the polar fractions. The requirement that $D_L = D_S$ has very important implications. Many of the anomalous results reported in the literature can probably be attributed to this requirement frequently not being met. To illustrate the implications of the requirement that $D_L = D_S$ in greater detail, consider the following:-

Figure 9 shows the relation of equation (12) in the form of a series of of Φ versus D_L for several D_S values. It can be seen that each curve exhibits a maximum ($\Phi = 1$) *only* when $D_L = D_S$.

A similar behaviour will be observed in cases where cos θ is plotted against γ_L for liquids having different D_L values. Such a case is illustrated in Figure 10, which shows a plot of equation (10) for a given γ_S and D_S. If an assumed value for γ_S of 30,0 mN/m and for D_S of 0,9 are used, it can be seen that, at the critical point of the spreading or wetting, i.e. when cos $\theta = 1$ and $\gamma_L = \gamma_S = \gamma_c$, a value of 30 mN/m for γ_c will only be obtained when $D_L = 0{,}9$. The implication is that, if γ_S is known to be 30,0 mN/m this value will only be found from a series of liquids with different γ_L values when their D_L fraction is 0,9. Other liquids with different D_L values will give different and erroneous γ_S values. For example, when $D_L = 0{,}6$ a γ_S value of 26,2 mN/m will be found, while $D_L = 0{,}2$ will give a γ_S value of about 15 mN/m.

Considering equations (2) and (6) against the criterion for spreading ($\theta = 0$), the following equation is obtained:

$$\left[\frac{\gamma_L}{\gamma_S} \right]^{1/2} = (D_L \ D_S)^{1/2} + (P_L P_S)^{1/2} \tag{13}$$

Combining equations (7) and (13) and rearranging the equation to relate γ_S to D_S:

$$\gamma_L^{1/2} = \gamma_S^{1/2} \left[(D_L \ D_S)^{1/2} + \left[(1 - D_L)(1 - D_S) \right]^{1/2} \right] \tag{14}$$

TABLE II

THE γ_L^d VALUE OF LIQUIDS DETERMINED FROM THE γ_S^d AND γ_S^p VALUES OF NYLON 66, POLYTETRAFLUOROETHYLENE AND POLYETHYLENE USING THE HARMONIC MEAN EQUATION

Liquid	γ_L^d **(mN/m)**		
	Nylon 66*	**PTFE***	**Polyethylene***
Formamide	27,6	—	34,5
Benzylalcohol	—	41,8	32,1
Tricresylphosphate	20,8	41,3	35,1
Ethylene glycol	25,4	—	29,6
Glycerol	26,2	—	42,0
Dibutyl phthalate	—	36,9	27,4
Dibromo ethane	18,4	40,2	—

*γ_S^d and γ_S^p values as calculated by Kaelble[10] i.e. γ_S^d and γ_S^p values for the solids are respectively 33,5 and 7,8 mN/m (Nylon 66), 14,4 and [illegible],1 mN/m (PTFE) and 31,3 and 1,1 mN/m (Polyethylene).

Curves of this function have been drawn in Figure 11 for several γ_L, D_L and D_S values. It can be seen that, when spreading occurs, i.e. when $\theta = O$ and assuming that the liquid $\gamma_L = 20$ mN/m and $D_L = 0,4$ and for the solid $D_S = 0,80$, then the γ_S value of the solid, calculated from the above equation, will be 24 mN/m. If, however, $\gamma_L = 40$ mN/m and $D_L = 0,4$, with $D_S = 0,80$, then γ_S will be 48 mN/m. In the case where $\gamma_L = 20$ mN/m and $D_L = 0,7$, with $D_S = 0,80$, γ_S will be 20,3 mN/m. Obviously the value obtained for γ_S depends on the value used for γ_L, D_L and D_S.

Not all the situations illustrated in Figure 11 will occur in practice, because of the limitations imposed by available liquids. Nevertheless, the variation in derived γ_S values will still be large in certain cases. The fact that different γ_c values have been obtained in this investigation, when various liquids were used to characterise a specific surface, can probably be explained by the possibility that the D_L and D_S values did not meet the requirements as discussed above.

So far it has been shown that the solid surface properties can be calculated from contact angle results and the liquid γ_L^d and γ_L^p values. On the other hand it can also be assumed that the solid surface properties, the contact angle and γ_L are known and the γ_L^d and γ_L^p have to be calculated. In this manner equation (10) was used to calculate the γ_L^d and γ_L^p values of various liquids from published results[10]. The results obtained are given in Table II from which it can be seen that the γ_L^d value depended on the solid surface which was used for the contact angle measurement. In general, the γ_L^d values were found to be high in the case of PTFE, low in the case of nylon 66, while polyethylene gave intermediate values.

Equation (9) can be used to calculate the dispersion and polar components of surface tension of a solid if the surface tension components of the liquid (γ_L^d and γ_L^p), as well as the interfacial tension between the solid and liquid, are known. However, as yet no method is available to measure the interfacial tension between solids and liquids. The interfacial tension between two liquids, on the other hand, has been determined by methods other than contact angle measurements. It was decided to evaluate equation (9) for the case of liquid/liquid interactions using results obtained by techniques different from those used for liquid/solid interfaces. Table III shows the results obtained, using values quoted in the literature for the interfacial tension of the liquid/water system as well as the surface tension of the liquid. The values published in the literature[9] for the dispersion and polar fractions of the surface tension of water were used. Both the harmonic mean and geometric mean equations were used. It can be seen that the harmonic mean equation generally produced higher γ_L^p values than the geometric mean equation. Furthermore, the value for γ_L^p generally increased when the interfacial tension value decreased. When the interfacial tension was less than 15 mN/m, neither equations gave a solution, except in the case of aniline, which gave a solution when the geometric mean equation was employed. Table III also shows that the water/liquid interfacial tension decreases when more polar liquids were used.

When the geometric mean equation is used to determine the γ_S^d, γ_S and D_S values for a solid, from the results obtained with different liquid pairs, the solid properties appear to vary in a systematic manner with the particular two liquids used for the determination. This was, for example, observed in the results reported by Kaelble for nylon 66. (See geometric mean equation results in Table IV). The harmonic mean results showed similar variation. To investigate this systematic variation in more detail the ten geometric mean results were fitted to the following mathematical model:

$$y = a_1 x_1 + a_2 x_1^2 + a_3 x_1 x_2 + a_4 x_2 + a_5 x_2^2 + a_0 \qquad (15)$$

TABLE III

A COMPARISON OF THE γ^d AND γ^p VALUES CALCULATED BY THE GEOMETRIC MEAN AND HARMONIC MEAN EQUATIONS FROM LIQUID/WATER INTERFACIAL TENSION DATA(a)

Liquid	γ_{LS}	γ_L	Geometric mean equation		Harmonic mean equation	
			γ_L^d	γ_L^p	γ_L^d	γ_L^p
Dekalin	51,4(b)	29,9(b)	29,9	0	29,8	0,1
n-Hexane	51,1(b)	18,4(b)	18,4	0	18,4	0
n-Heptane	50,2(b)	20,4(b)	20,4	0	20,2	0,2
Cyclohexane	50,2(b)	25,5(b)	25,5	0	25,3	0,2
Diiodomethane	48,5(b)	50,8(b)	50,5	0,3	46,7	4,1
Carbon disulphide	48,36	31,38	31,3	0,1	30,2	1,2
Carbon tetrachloride	45,0	26,66	26,5	0,2	24,6	2,0
α- Bromonaphthalene	42,07	44,59	43,7	0,9	39,5	5,1
Iodobenzene	41,84	39,70	39,0	0,7	35,3	4,4
Diiodomethane	41,6(b)	50,8(b)	49,6	1,2	44,3	6,5
Bromoform	40,85	41,53	40,6	0,9	36,4	5,1
Ethyliodide	40,0	29,9	29,2	0,7	25,8	4,1
Bromobenzene	39,82	36,26	35,4	0,9	31,5	4,7
Chlorobenzene	37,41	33,08	31,9	1,2	27,8	5,3
Dibromoethane	36,54	38,71	37,2	1,5	32,4	6,3
Toluene	36,1	28,4	27,1	1,3	22,8	5,6
Benzene	35,00	28,86	27,4	1,5	22,7	6,1
Chloroform	32,80	27,13	25,2	1,9	19,9	7,2
Nitrobenzene	25,66	43,38	38,2	5,2	31,5	11,9
Diethyl phthalate	16,27	37,34	27,6	9,7	19,8	17,5
Benzaldehyde	15,51	40,04	29,5	10,5	22,0	18,0
Diethyl ether	10,7	17,1	c	c	c	c
Methyl butyl ketone	9,73	25,49	c	c	c	c
n-Octyl alcohol	8,52	27,53	c	c	c	c
Heptanoic acid	7,00	28,31	c	c	c	c
Ethyl acetate	6,8	24,3	c	c	c	c
Aniline	5,77	42,58	22,3	20,3	c	c
Benzyl alcohol	4,75	39,71	c	c	c	c
Cyclohexanol	3,92	34,23	c	c	c	c
n-Butanol	1,8	24,6	c	c	c	c

γ^d and γ^p for water was taken as 22,1 and 50,7 mN/m respectively [(Ref. (9)]

γ_{LS} and γ_L data from reference (22)

(a) all values in mN/m (b) data from reference (9) (c) no solution possible.

where

y is the dependent variable γ_S^d or γ_S or D_S

x_1 is the D value of one liquid

x_2 is the D value of the other liquid

a is a constant.

After rejection of non-significant variables the best fit equations were:

$$\gamma_S^d = 213\, x_1 - 217\, x_1 x_2 + 101\, x_2 - 62 \qquad r = 0{,}934$$

$$\gamma_S = 110\, x_1 - 122\, x_1 x_2 + 57\, x_2 - 9 \qquad r = 0{,}901$$

$$D_S = 3{,}0\, x_1 - 2{,}8\, x_1 x_2 + 1{,}4\, x_2 - 0{,}6 \qquad r = 0{,}945$$

The confidence limits of the coefficient are such that each equation can, with suitable scaling, be represented by

$$y = 2\, x_1 - 2\, x_1 x_2 + x_2 \qquad (16)$$

This simple empirical relation possibly reflects the relations illustrated in Figure 9. The same statistical treatment was applied to data published in the literature[10] for PVC, paraffin, polyethylene and PTFE. The results are shown in Table V. Once again it can be seen that the surface properties of a solid vary in a simple systematical manner with the liquids used for their determination.

The finding that the surface properties of a solid vary systematically with the liquids used for their determination, throws some doubt on the validity of the assumption which has frequently been made by various authors, namely that the results obtained from a large number of liquids can be normalised to "absorb the eccentricities" of individual so-called "erratic" results.

SUMMARY AND CONCLUSIONS

Two methods which have been proposed for the determination of the surface free energy of a low energy surface, have been applied to wool and nylon 66 fibres and ®Hercosett polymers used for the shrink-resist treatment of wool. When contact angle measurements were used to determine the critical surface tension of wetting ($\bar{\gamma}_c$) of Hercosett polymer films, more than one γ_c value were obtained. When polar liquids were used for the determination, significantly

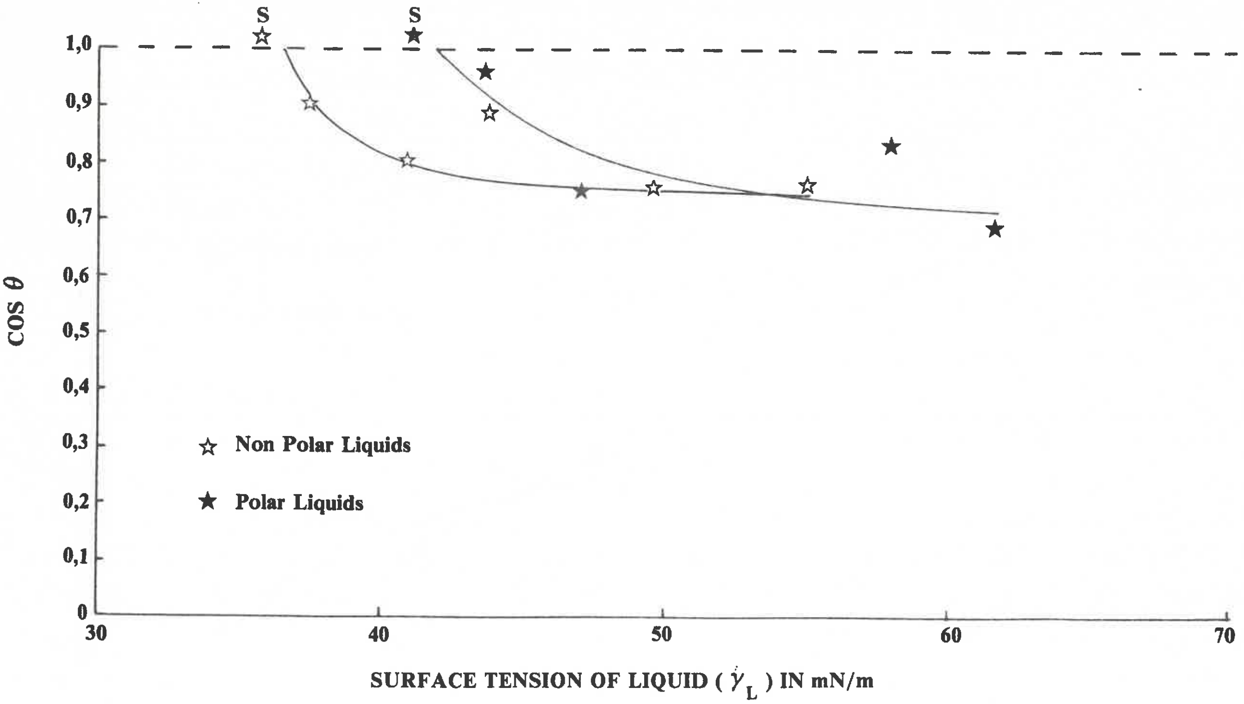

Fig. 1 The critical surface tension of Hercosett 70 (neutralised and conditioned)

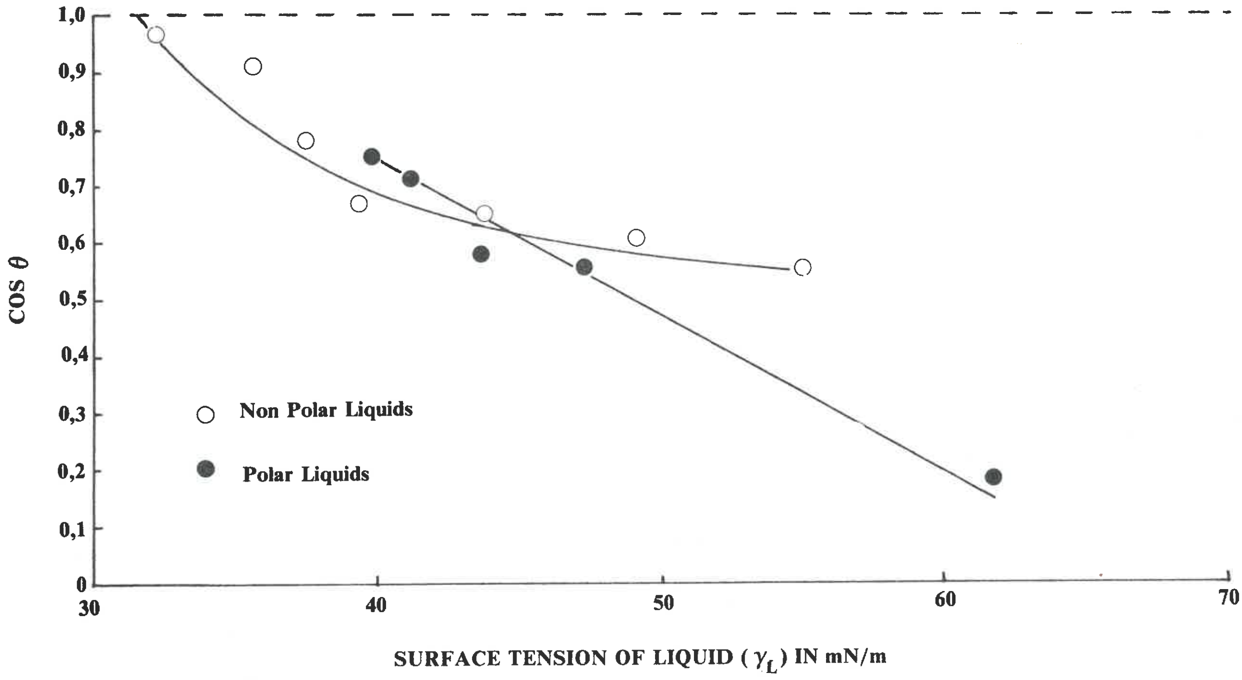

Fig. 2 Critical surface tension of Hercosett 70 (not neutralised and conditioned)

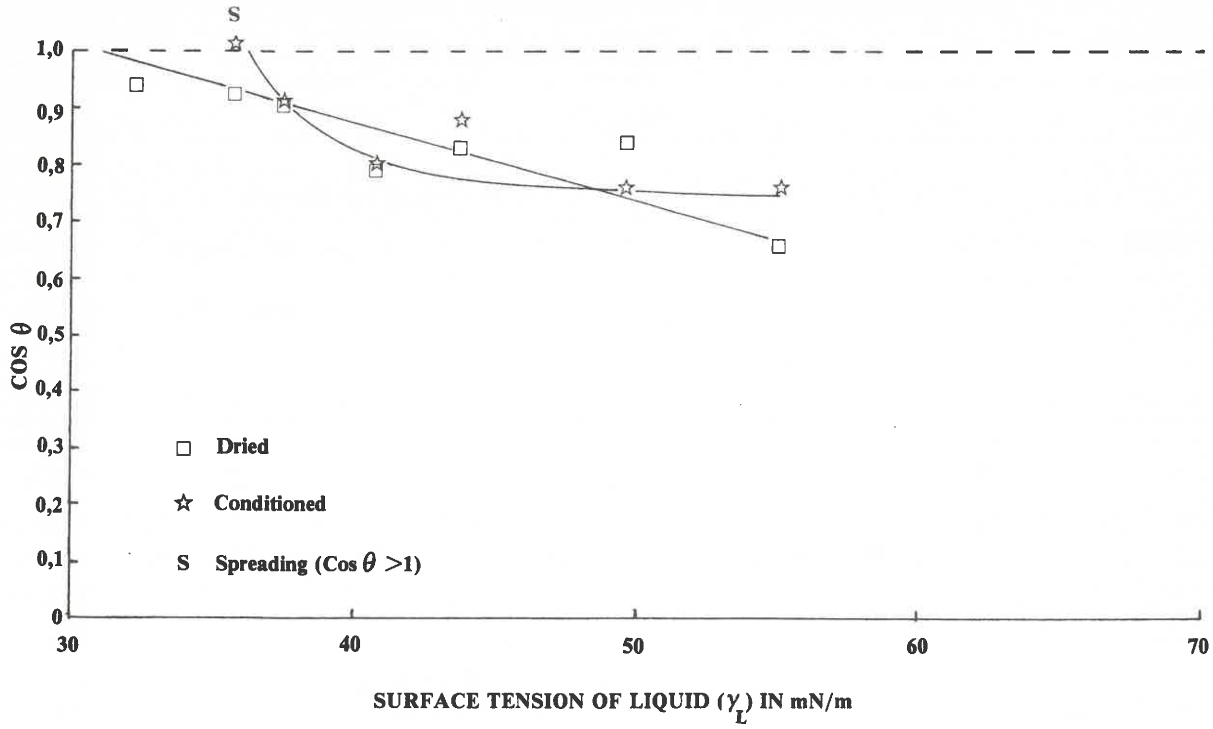

Fig.3 The critical surface tension of Hercosett 70 (neutralised) using non polar liquids

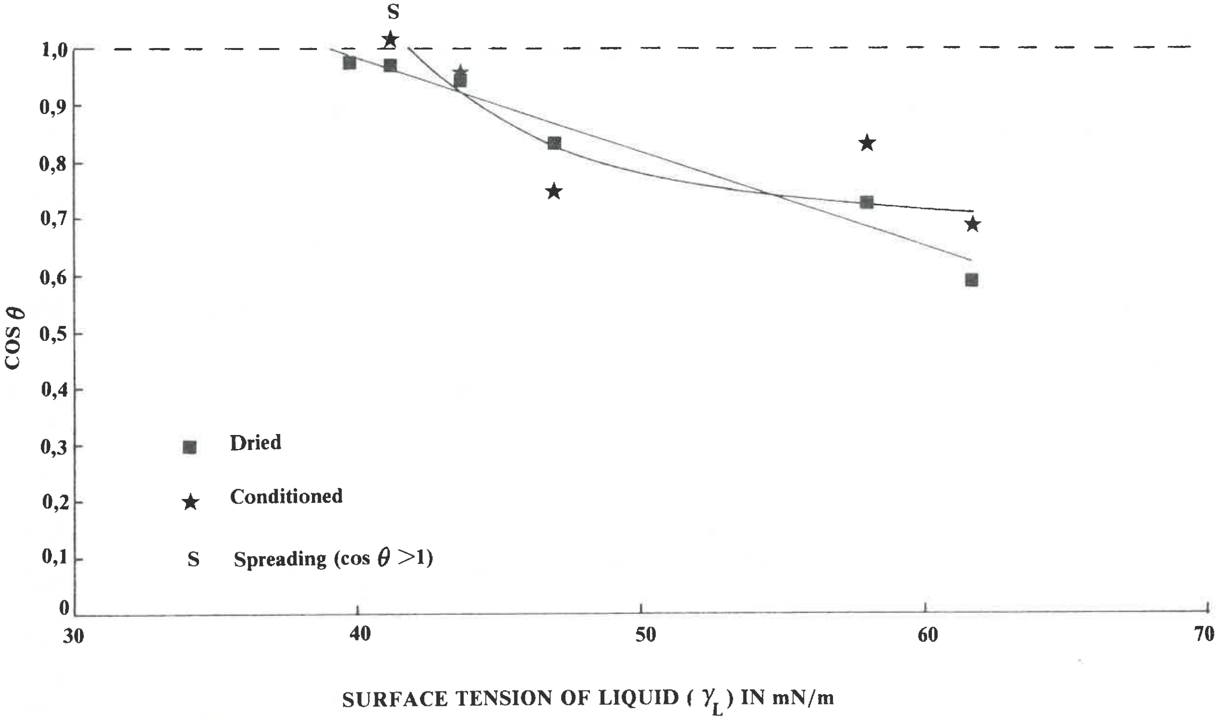

Fig. 4 The critical surface tension of Hercosett 70 (neutralised) using polar liquids

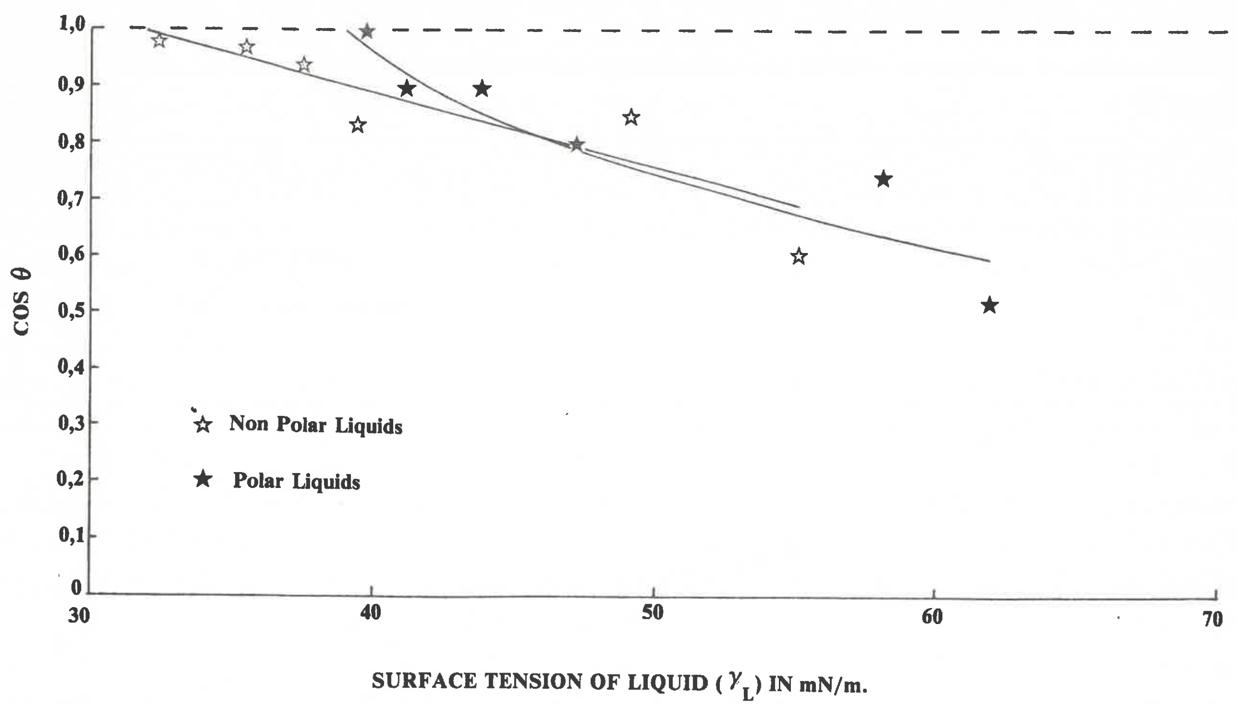

Fig. 5 The critical surface tension of Hercosett 57 (neutralised and conditioned)

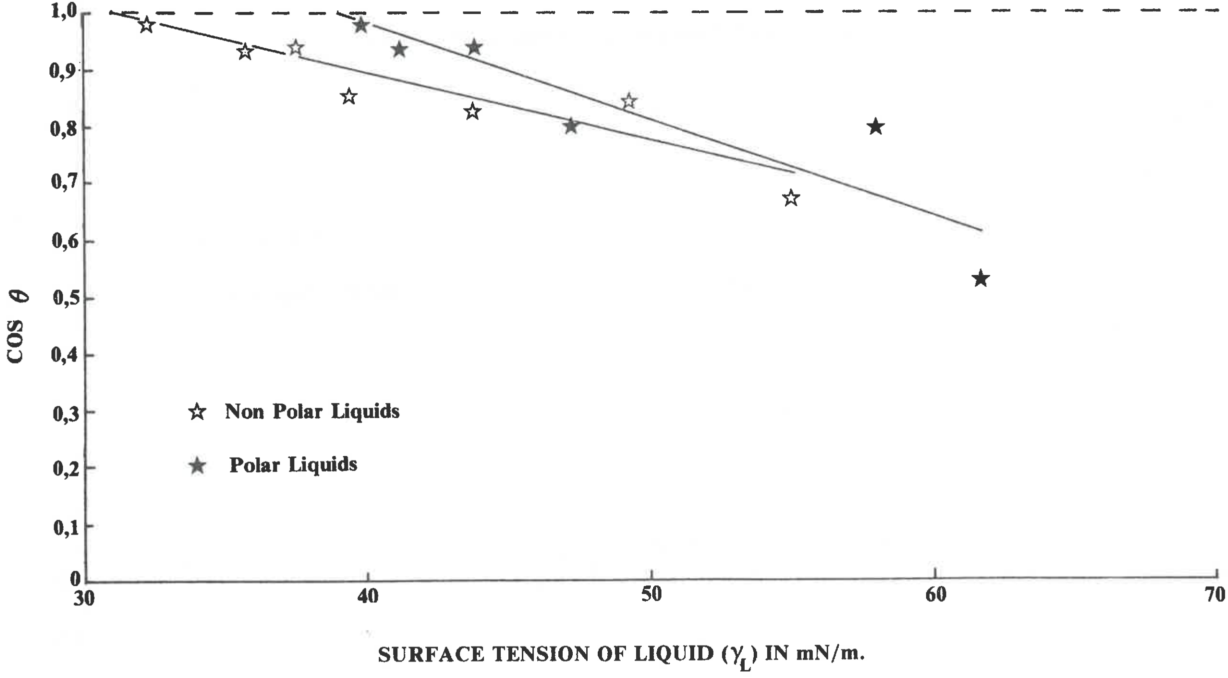

Fig. 6 The critical surface tension of Hercosett 125 (neutralised and conditioned)

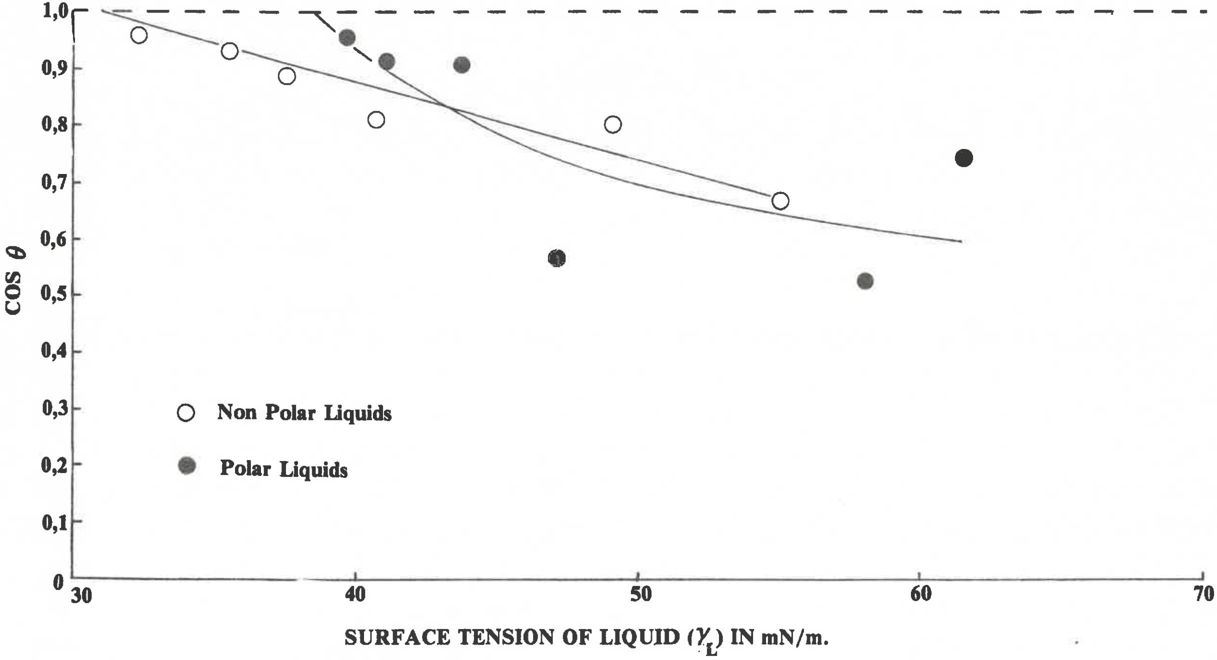

Fig. 7 The critical surface tension of Hercosett 57 (conditioned and not neutralised)

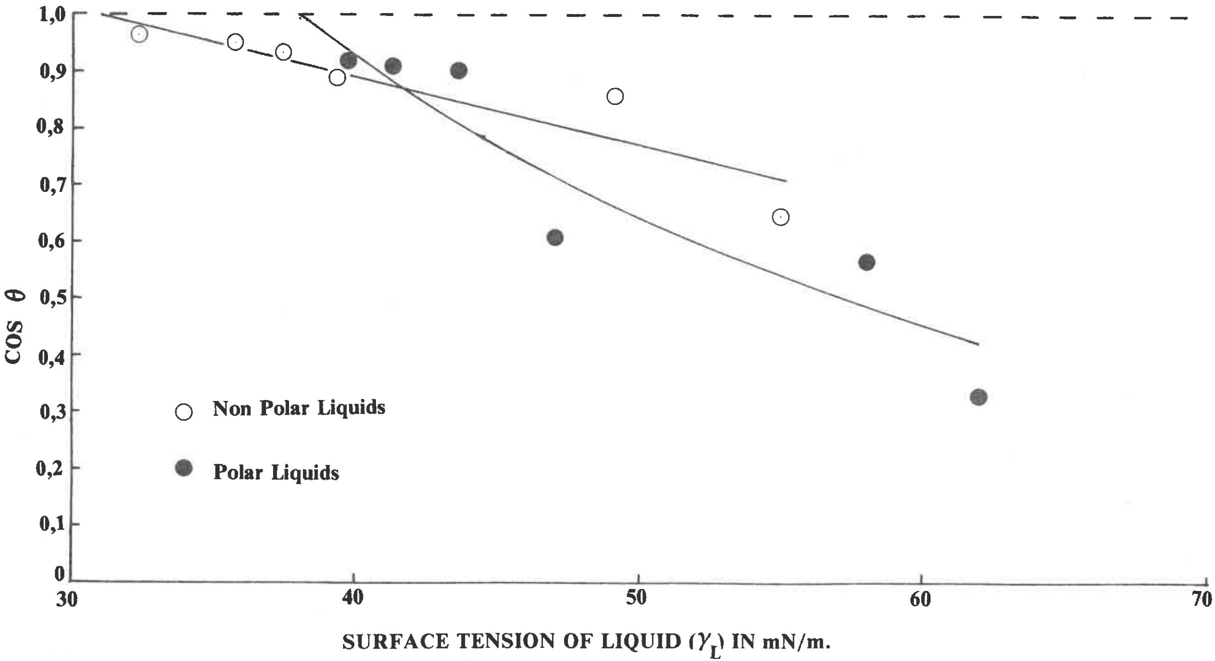

Fig. 8 The critical surface tension of Hercosett 125 (conditioned and not neutralised)

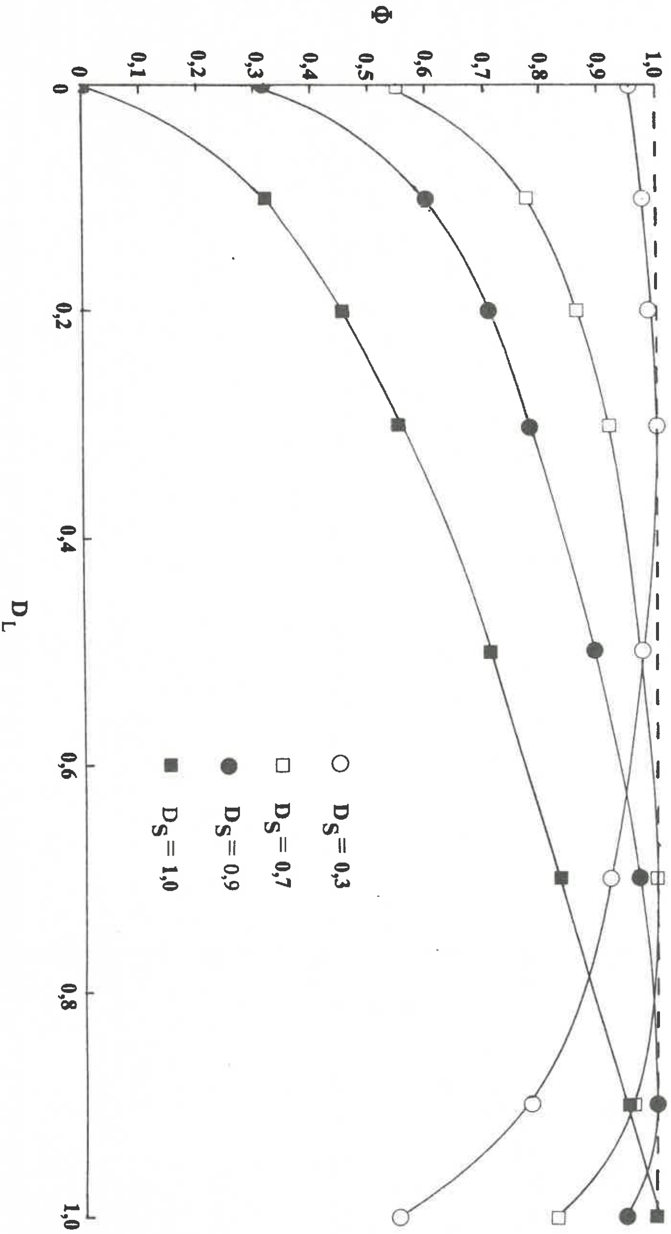

Fig. 9 The effect of different D_S and D_L values on the bonding efficiency factor (Φ)

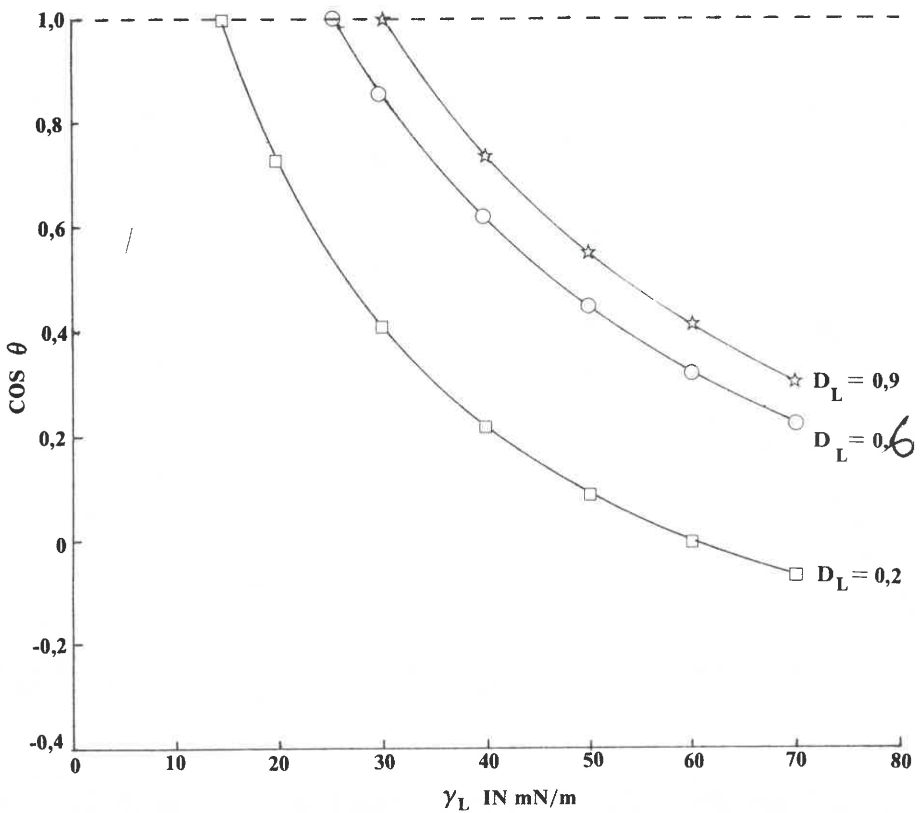

Fig. 10 A theoretical relationship between cos θ and γ_L for different values of D_L ($\gamma_S = 30$ and $D_S = 0,9$)

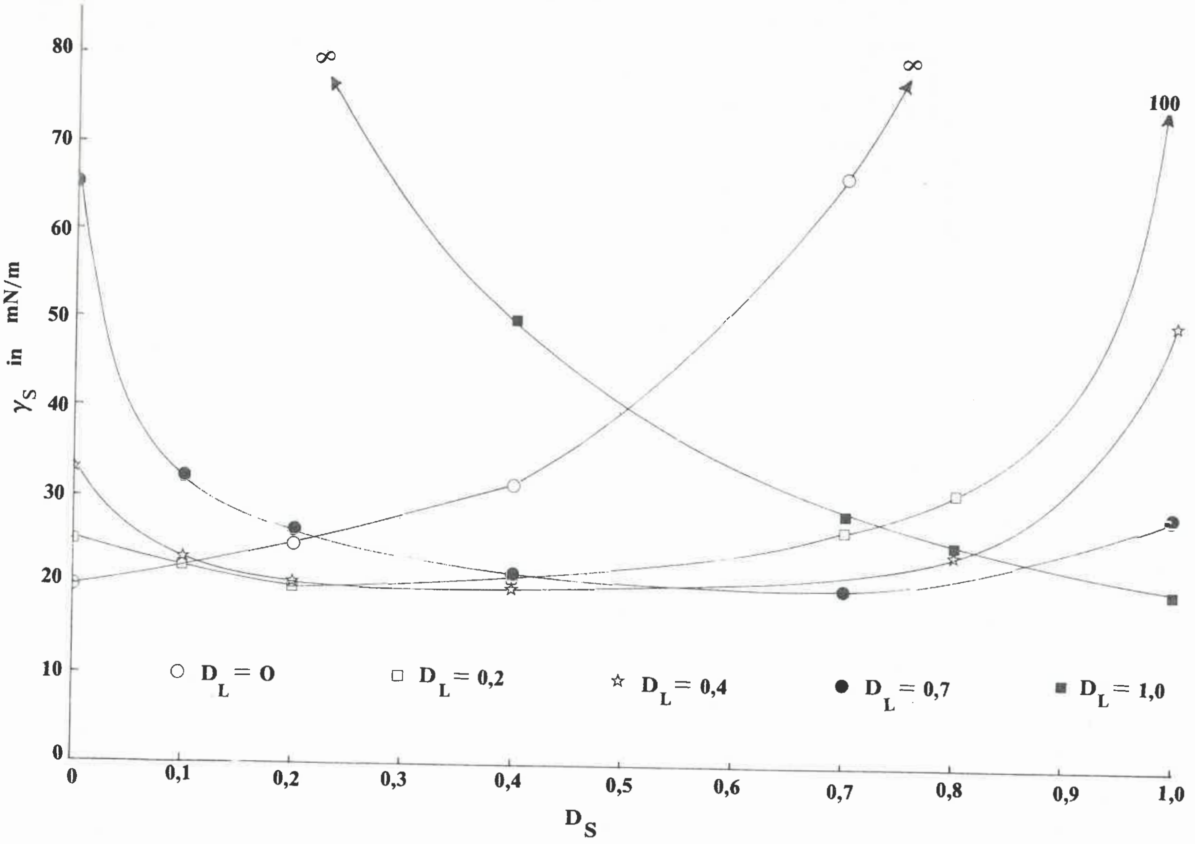

Fig. 11 Theoretical relationship between γ_S and D_S for liquids having $\gamma_L = 20$ mN/m and different D values for the case where *$\theta = O$*

TABLE IV

SOME SURFACE PROPERTIES OF NYLON 66 AS CALCULATED FROM THE CONTACT ANGLE RESULTS OF TWO LIQUIDS USING THE GEOMETRIC MEAN AND HARMONIC MEAN EQUATIONS

Liquid 2 / Liquid 1	GEOMETRIC MEAN*												HARMONIC MEAN											
	Glycerol			Formamide			Diiodomethane			Trichlorobiphenyl			Glycerol			Formamide			Diiodomethane			Trichlorobiphenyl		
	γ_S^d	γ_S	D_S	γ_S^d	γ_S	D_S	γ_S^d	γ_S	D_S	γ_S^d	γ_S	D_S	γ_S^d	γ_S	D_S	γ_S^d	γ_S	D_S	γ_S^d	γ_S	D_S	γ_S^d	γ_S	D_S
Water	20,7	35,7	0,58	27,8	39,3	0,71	32,8	42,4	0,77	37,9	45,8	0,83	18,6	38,6	0,48	23,8	41,3	0,58	35,0	49,0	0,71	39,6	52,6	0,75
Glycerol				44,6	46,4	0,96	35,0	40,0	0,88	40,2	43,2	0,93				35,6	42,7	0,83	35,7	42,8	0,83	40,1	45,5	0,88
Formamide							34,2	40,7	0,84	39,9	43,4	0,92							35,7	42,7	0,84	40,1	45,2	0,89
Diiodomethane										58,3	91,8	0,64										**	**	**

* Part of this table quoted by Kaelble [(Ref. (10)]

** Equation could not be solved.

TABLE V

VALUES OF COEFFICIENTS IN THE REGRESSION EQUATIONS RELATING TO SURFACE PROPERTIES OF A SOLID TO THE D FRACTIONS OF TWO LIQUID PAIRS

Solid Surface	Property of Solid	TERMS OF REGRESSION EQUATION					
		x_1	x_1^2	x_2	x_2^2	$x_1 x_2$	Constant a_o
PVC	γ_S^d	2010			410	- 2090	- 340
	γ_S	1610			330	- 1680	- 260
	D_S	15	1		3	- 16	- 2
Paraffin	γ_S^d			29			-3
	γ_S			28			-1,5
	D_S	0,4		0,3		-0,5	0,7
Polyethylene	γ_S^d	-120		-420	260	- 140	190
	γ_S	-60	70	-310	220		150
	D_S	-4,5		-5,5	2,7	4,9	3,7
PTFE	γ_S^d	-380		-104		390	120
	γ_S	-310		-86		320	100
	D_S	-1,2				1,1	0,7

higher γ_c values were obtained (about 38 mN/m) than when non-polar liquids were used (about 31 mN/m). It was found furthermore that the moisture content of Hercosett (i.e. dried and conditioned surfaces) affected the γ_c value. Neutralisation of the polymer solutions prior to drying also affected the γ_c values. The second method which was used to determine the γ_c values of wool and nylon 66 fibres was the sink-float method, using various liquids. In the case of nylon 66 the γ_c value appeared to depend on the liquids used for the determination. In the case of wool, however, γ_c was less sensitive to the type of liquid and varied between 28 and 33 mN/m.

A brief review of the theory and literature on critical surface tension of wetting, interfacial tension, contact angles, work of adhesion and dispersion and polar components of surface tension, was also undertaken. Analysis of published data showed that the surface free energy of a solid is dependent on the dispersion and polar components of the surface tension (γ_L^d and γ_L^p respectively) of the liquids chosen for the determination. This dependence appeared to be systematic. Furthermore, the geometric mean and harmonic mean equations gave significantly different values for the dispersion and polar components of surface tension of the solid (γ_S^d and γ_S^p) respectively.

The γ_L^d and γ_L^p components of various liquids were calculated from published data. It was found that the value obtained from the dispersion component is dependent on the solid surface which was used. For example, γ_L^d was found to be high in the case of PTFE and low in the case of nylon 66, while polyethelene gave intermediate values.

In the case of liquid/liquid interfaces, where the interfacial tension was determined by different methods (other than the contact angle method which was used for solid/liquid interfaces) it was also found that the theoretical equations sometimes could not be solved. Where the interfacial tension was less than about 15 mN/m, no solution was possible.

From these observations, and from the literature survey given earlier, it can be concluded that the geometric mean equation is to be preferred, since the harmonic mean equation could not be solved in several instances. This does not necessarily imply that the geometric mean equation offers an adequate explanation of the experimental data. Since the derived surface tension value for a solid appears to depend systematically on the particular two liquids used in its determination, the result obtained from two arbitrarily chosen liquids may not necessarily be the correct value. It is probably also incorrect to assume, even though the absolute values may be wrong, that the relative ordering of several substances (viz. polymers and wool) will be independent of the liquids or methods used in the determinations.

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THE USE OF PROPRIETARY NAMES

®Hercosett is a registered trade mark of Messrs Hercules Inc. The fact that products with proprietary names have been used in this report in no way implies that there are not others as good or even better.

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