

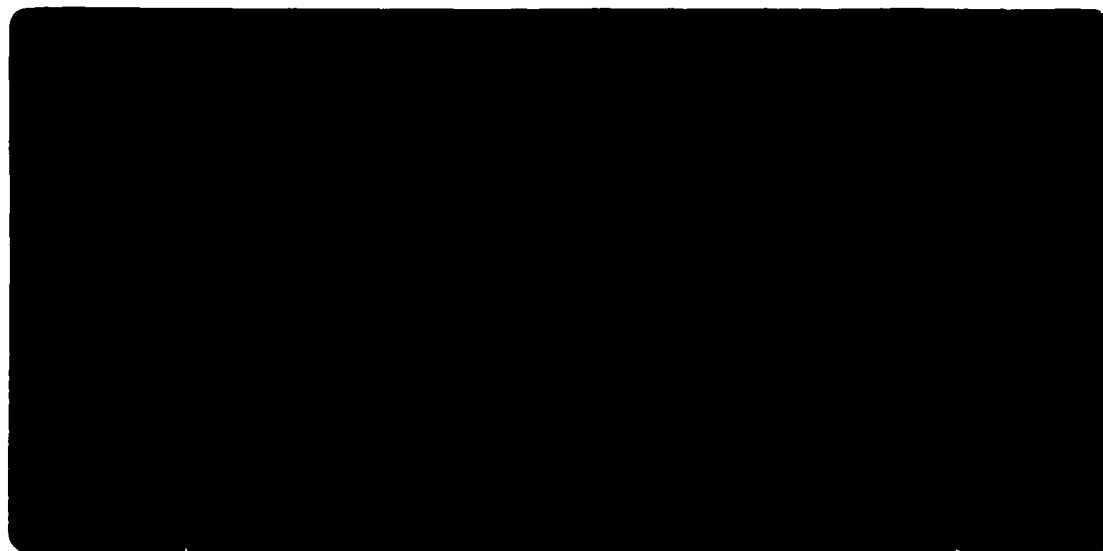


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**THE FLOTATION OF STICKY CONTAMINANTS  
FROM RECYCLED FIBER STREAMS**

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# The Flotation of Sticky Contaminants from Recycled Fiber Streams

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## The Flotation of Sticky Contaminants from Recycled Fiber Streams

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### INTRODUCTION

Removal of contaminants from secondary fiber ("deinking") is accomplished by washing, flotation, or a combination of the two. Washing is effective for removing particles smaller than about 10-20  $\mu\text{m}$  in extent<sup>1</sup>, while flotation works best for particles in the range 10-200<sup>1,2</sup>. Newsprint inks can be readily dispersed into small particles which can be removed by washing. Pulping of secondary fiber containing sticky contaminants such as hot-melt or pressure-sensitive adhesives typically results in the production of larger particles. We have examined the application of surface chemistry principles to the flotation of such sticky contaminants.

The process of removal of one type of solid particle from the presence of another by (froth) flotation has been used in ore beneficiation and deinking of paper for many years. Separation is dependent on there being a difference in surface free energy between the two types of solids (i.e., fiber and contaminant). When an air bubble attaches to a solid suspended in a liquid, a contact angle  $\theta$  can be defined as shown in Figure 1, i.e., the angle between the solid surface and the tangent to the air/liquid interface at the intersection with the solid surface. The angle is measured through the liquid phase.

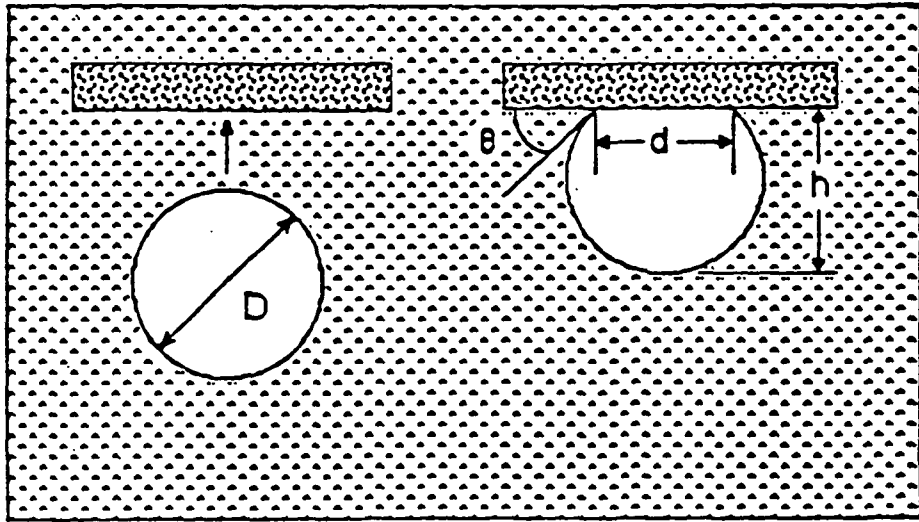


Fig 1. Schematic Representation of Bubble Attachment to a Sticky.

In order for a liquid to spread on a solid, the work of adhesion,  $W_{SL}$ , must be greater than the work of cohesion,  $W_{LL}$ , of the liquid. These quantities are related to the interfacial tensions as follows:

$$W_{SL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (1)$$

$$W_{LL} = 2\gamma_{LV} \quad (2)$$

where the subscripts indicate the solid, liquid, or vapor phase. The spreading coefficient,  $S_{L/S}$ , is given by

$$S_{L/S} = W_{SL} - W_{LL} \quad (3)$$

or, in terms of the interfacial tensions, as

$$S_{L/S} = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} \quad (4)$$

A necessary condition for flotation is that the air bubble be able to displace the liquid in order to become attached. This is equivalent to requiring that the liquid not spread on the solid or  $S_{L/S} < 0$ . The forces created by the interfacial tensions are shown in Figure 2. A force balance (in the plane of the surface of the solid) results<sup>3</sup> in Young's equation,

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (5)$$

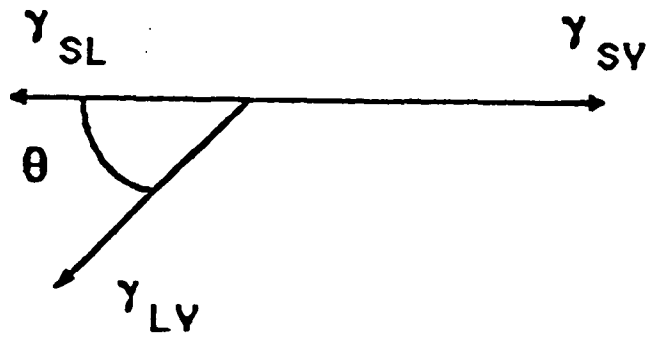


Fig 2. Balance of Surface Tensions at the Air-Liquid-Solid Interface.

When equation 5 is substituted into 4, the spreading coefficient becomes

$$S_{L/S} = \gamma_{LV} (\cos \theta - 1) \quad (6)$$

and the necessary condition for bubble attachment ( $S < 0$ ) is  $\cos \theta < 1$  or  $\theta > 0$ . Although necessary, this is not a sufficient condition for practical applications. In a flotation cell, the air bubble/solid attachment must be able to withstand the forces caused by the differential buoyancy of the two and the shearing forces produced by the bubble ascension and the turbulent mixing.

The strength of the attachment  $F_a$  is equal to the product of the perimeter of the bubble/solid interface and the liquid surface tension.

$$F_a = \pi d \gamma_{LV} \sin \theta \quad (7)$$

Here,  $d$  is the diameter of the circle formed by the attachment (see Figure 1), and the expression is multiplied by  $\sin \theta$  to produce the component of the surface tension perpendicular to the solid surface.

This can be rewritten in terms of the preattached bubble diameter  $D$  and the ratio  $d/D$  as

$$F_a = \pi D (d/D) \gamma_{LV} \sin \theta \quad (8)$$



# ATTACHED BUBBLE SIZE FACTOR

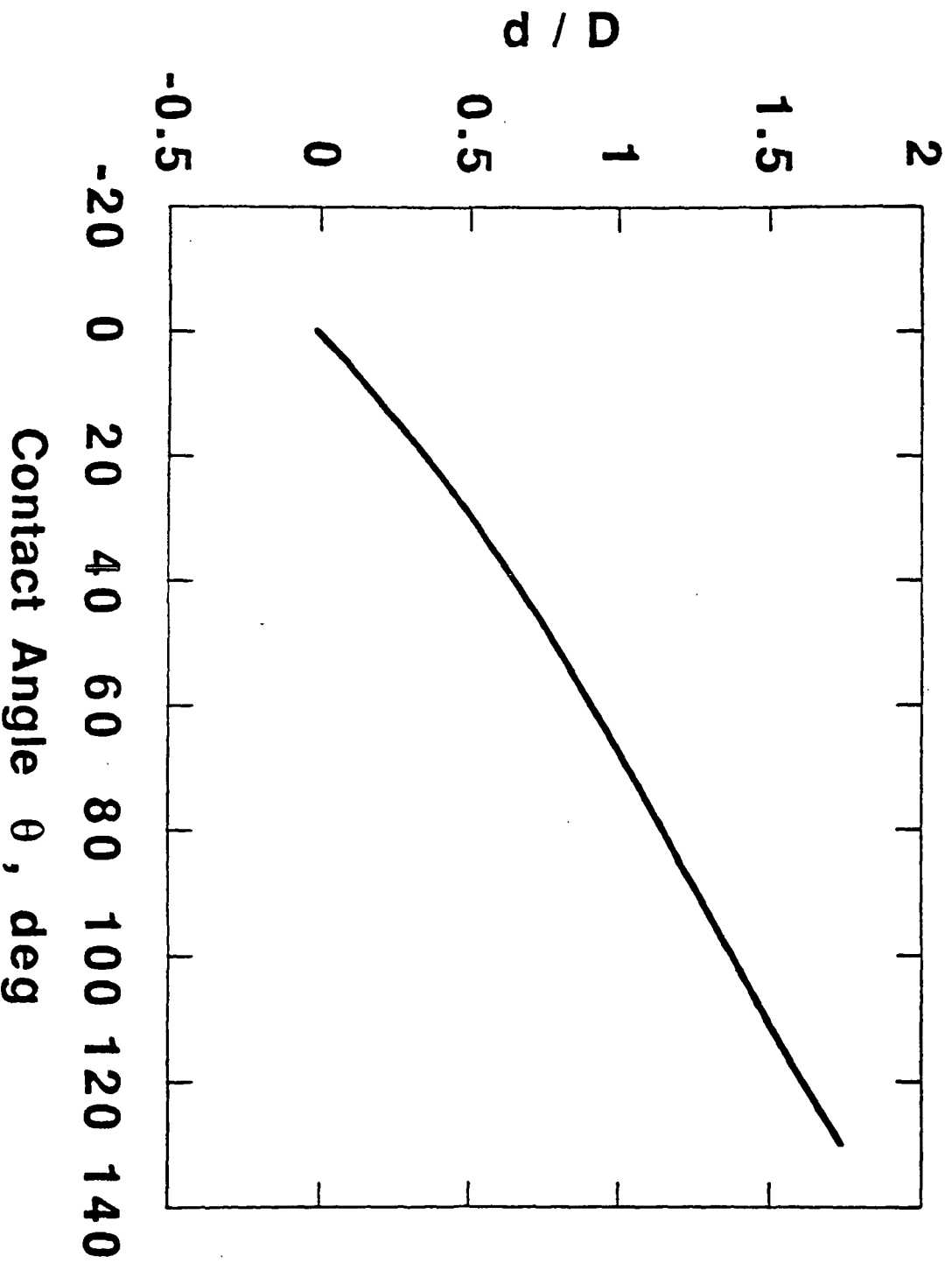


Fig. 3. Dependence of the Ratio  $d/D$  on the Contact Angle as Given by Equation 10.

Assuming that the volume of the bubble does not change upon attachment and that the attached bubble has the shape of a spherical segment, we can express the equality of the two volumes as

$$V = (\pi/6) D^3 = (\pi/24) h (4h^2 + 3d^2) \quad (9)$$

where  $h$  is the height as defined in Figure 1. By expressing  $h$  in terms of  $d$  and the contact angle  $\theta$ , equation 9 can be rearranged to

$$d/D = 2 \sin \theta / \left[ (1 + \cos \theta)^3 + 3(1 + \cos \theta) \sin^2 \theta \right]^{1/3} \quad (10)$$

This function is shown in Figure 3 where the almost linear dependence of  $d$  on contact angle for a given bubble size is seen. (Strong positive curvature occurs at still higher angles, but the latter are of no practical importance.) Over the more limited range  $0 < \theta < 65^\circ$  found experimentally in the present work, equation 10 can be closely approximated by

$$d/D \cong \sin \theta \quad (11)$$

The exact and approximate relations are compared in Figure 4.

Substituting the result of equation 11 into equation 8, we find

$$F_a \cong \pi D \gamma_{LV} \sin^2 \theta \quad (12)$$

# SIN $\theta$ APPROXIMATION

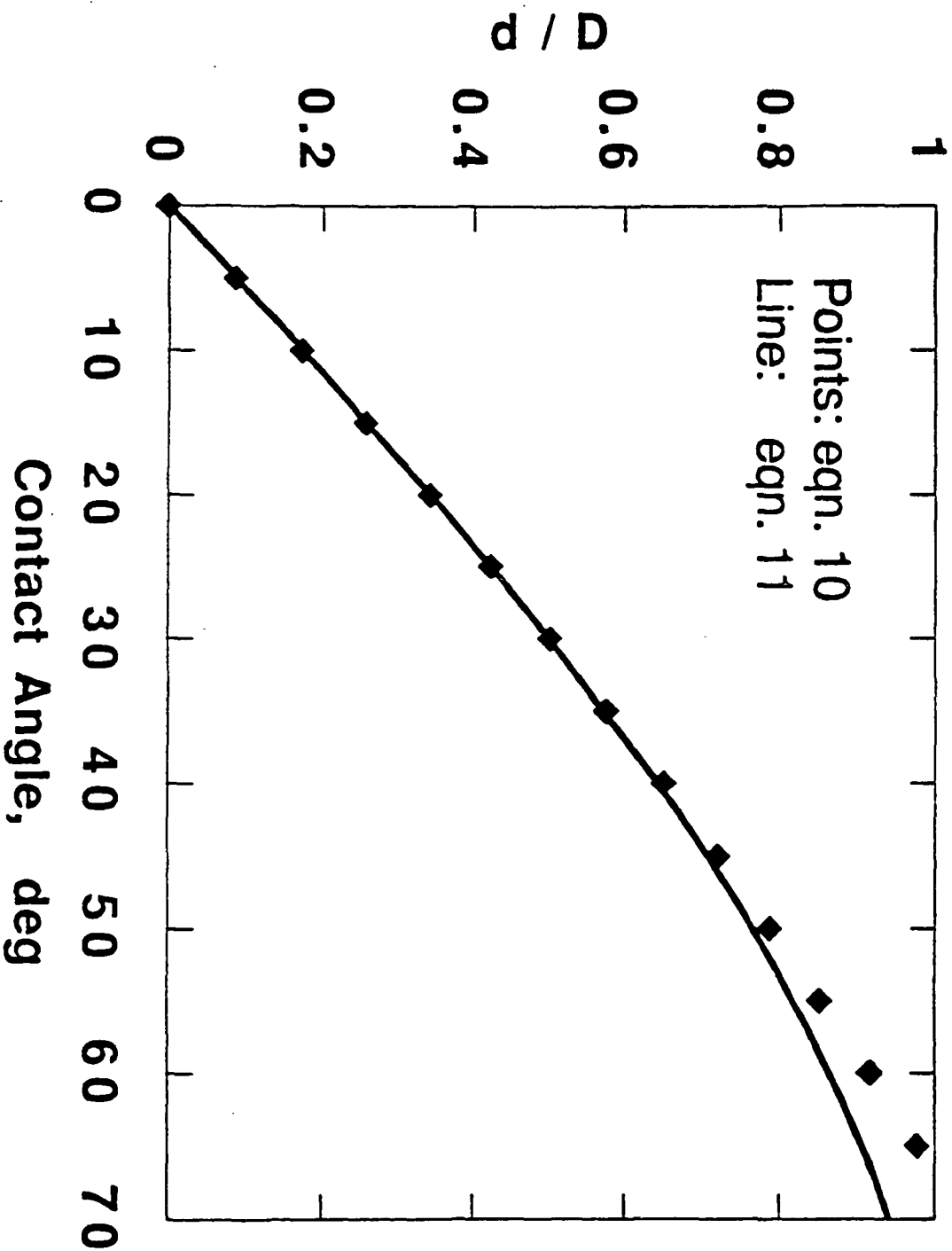


Fig. 4. Comparison of the exact (equation 10) and approximate (equation 11) expressions for the ratio  $d/D$ .

or

$$F_a \cong \pi D \gamma_{LV} (1 - \cos^2 \theta) \quad (13)$$

The strength of bubble attachment is thus strongly dependent on contact angle which in turn is determined by the surface energy of both the solid and the medium (equation 5).

To predict values of the contact angle from equation 5, the interfacial tension,  $\gamma_{SL}$ , between the solid and the medium is needed. Girifalco and Good<sup>4</sup> showed that this parameter can be calculated from the surface energies of the solid and the liquid,  $\gamma_{SV}$  and  $\gamma_{LV}$ , respectively.

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2 (\gamma_{SV} \gamma_{LV})^{1/2} \quad (14)$$

Fowkes<sup>5</sup> observed that, for the interaction of polar materials with nonpolar ones, only the London dispersion component of the intermolecular forces of the polar material was significant. He suggested separating the surface energy of the polar material into dispersion ( $\gamma^d$ ) and polar ( $\gamma^p$ ) contributions and that these were additive.

$$\gamma = \gamma^d + \gamma^p \quad (15)$$

For the interaction of an aqueous phase, for example, with a hydrophobic solid, Fowkes suggests that equation 14 be written as

$$\gamma_{SL} = \gamma_S^d + \gamma_L - 2(\gamma_S^d \gamma_L^d)^{1/2} \quad (16)$$

Here,  $\gamma_L$  represents the combined contributions (equation 15) of the dispersion and polar components of the aqueous phase;  $\gamma_L^d$  is the dispersion component, and  $\gamma_S^d$  is the surface energy of the solid having only a dispersion component. The subscript V indicating the interface with air has been omitted for simplicity. Equation 16 can now be combined with that of Young (equation 5) to give an expression known as the Girifalco-Good-Fowkes-Young (G-G-F-Y) equation<sup>3</sup>.

$$\cos \theta = -1 + 2\left(\gamma_S^d \gamma_L^d\right)^{1/2} / \gamma_L \quad (17)$$

This equation gives explicitly the dependence of the contact angle on surface energy of the solid,  $\gamma_S^d$ , and that of the aqueous phase,  $\gamma_L$ . The dispersion component of the aqueous phase,  $\gamma_L^d$ , is expected to be a constant. We will test the validity of equation 17 for flotation systems by independently measuring  $\cos \theta$ ,  $\gamma_S^d$ , and  $\gamma_L$ . These results will then be combined with the concepts behind equation 7 to interpret flotation efficiency data. The experimental results were taken<sup>6</sup> from research contracted by the American Paper Institute.

## EXPERIMENTAL

Four "stickies" materials were chosen for study and are listed in Table 1. Their compositions were determined from FTIR spectra. The surface energy of the stickies was determined by measuring the contact angle of a 4 $\mu$ L drop of methylene iodide placed on the solid. The surface tension of methylene iodide is primarily due to dispersion forces with values of  $\gamma_L$  and  $\gamma_L^d$  of 50.8 and 50.4 mN/m, respectively. The measured contact angle and these values for  $\gamma_L$  and  $\gamma_L^d$  were substituted into equation 17 which was rearranged to yield  $\gamma_S^d$ . The calculated surface energies are listed in Table 1.

Table 1. Composition of Stickies

<u>Sticky</u>	Surface Energy <u>ergs/cm<sup>2</sup></u>	<u>Composition</u>
Wax-Coated Kraft (WCK)	28.0	Paraffin wax
<u>Hot-Melt Adhesives</u>		
HMD	27.1	Polyvinyl acetate + Polystyrene + Paraffinic Hydrocarbon (Wax or Polyethylene)
HMB	50.7	Glycerol Ester of polymerized rosin
HME	41.7	Polyethylene base

Contact angles of drops of several simulated deinking liquors on the stickies were measured immediately (five seconds) and as a function of time of contact up to 20 minutes. (The measurements were carried out in a humidified chamber to prevent drop evaporation.) Values of the contact angle between four different liquors and the four stickies measured at five seconds are listed in Table 2. The time dependence of the contact angle will be reported elsewhere.

The deinking liquors contained 0.1% by weight sodium silicate and sufficient nonionic surfactant (Triton X-100) to achieve the desired surface tensions listed in Table 2. The pH was adjusted with sodium hydroxide.

Table 2. Contact Angles at Five Seconds

<u>Liquor</u>	<u>pH</u>	$\gamma_L$ , <u>mN/m</u>	<u><math>\theta</math>, deg</u>			
			<u>WKC</u>	<u>HMD</u>	<u>HMB</u>	<u>HME</u>
1	12.4	39.2	76.3	71.3	54.0	58.7
2	12.4	29.9	47.7	43.0	22.0	29.0
4	10.1	39.4	75.0	69.3	54.0	63.0
5	10.1	29.7	47.3	43.7	23.3	28.3

Flotation studies were conducted using a pneumatic cell developed at the Institute of Paper Chemistry. The critical parameters are listed in Table 3.

Table 3. Flotation Parameters

Temperature:	73°F
pH:	10.1 or 12.4
Average Bubble Size:	260 $\mu\text{m}$ ( $\gamma_L = 29.7 \text{ mN/m}$ )
	350 $\mu\text{m}$ ( $\gamma_L = 39.4 \text{ mN/m}$ )
Sticky Particle Size:	57 - 420 $\mu\text{m}$
Time of Agitation	
Prior to Flotation:	1/4 - 60 min.
Time of Flotation:	1 min.

The results for the three (hot-melt adhesive) stickies with four deinking liquors and various agitation times are presented in Table 4.

Table 4. Flotation Results

<u>Sticky</u>	<u>Surface Tension, mN/m</u>	<u>Time of Agitation Prior to Flotation, min.</u>	<u>Apparent Contact Angle, deg</u>	<u>Sticky Removal %</u>
HMD	39.4	6	62.5	93.4
HMD	39.4	20	60.0	94.9
HMD	29.7	6	38.5	40.8
HMD	29.7	20	37.5	67.6
HMD	39.4	20	60.0	96.2
HMD	29.7	20	37.5	37.8
HMB	39.4	17	42.5	96.9
HMB	39.4	20	42.0	92.9
HMB	29.7	4	10.0	2.7
HMB	29.7	4	10.0	3.5
HMB	29.7	1/4	~20.0	6.3
HMB	39.2	60	~32.0	90.3
HMB	39.2	20	~32.0	84.5
HME	39.4	20	58.0	98.0
HME	39.2	20	47.0	96.3
HME	30.1	2	18.0	2.1
HME	30.1	1/4	24.0	11.1



## DISCUSSION

### Validity of the G-G-F-Y Equation

The G-G-F-Y equation is usually used to relate the surface energy interactions between pure liquids and pure solids. To use it in the flotation studies, it is necessary to show that it holds also for aqueous solutions of surfactants.

Of the four stickies considered here, the wax-coated kraft has the simplest composition. Its interactions with the liquors should consist of only dispersion forces. Equation 17 was solved for  $\gamma_L^d$  and the measured values of  $\theta$  (five seconds),  $\gamma_L$ , and  $\gamma_S^d$  for the WCK, and the four liquors (from Tables 1 and 2 above) were inserted. The average value for  $\gamma_L^d$  for the four liquors was 21.9 mN/m with a standard deviation of 0.6 mN/m. This value is in excellent agreement with the value found<sup>3</sup> for the dispersion component of water, 22 mN/m, and suggests that the surfactant liquors have dispersion interactions similar to water. Thus, the G-G-F-Y equation holds for the system WCK/deinking liquors with a constant value for  $\gamma_L^d$  of 22 mN/m.

For the hot-melt adhesives, the situation is more complex. From the compositional and surface energy information in Table 1, it is evident that polar components are present. It would appear that the interaction term in equation 14 should also contain polar contributions rather than just the dispersion contributions shown in equation 16. These contributions would then lead to a modified value for  $\gamma_L^d$  in the G-G-F-Y equation.

The applicability of the G-G-F-Y equation to the hot-melt adhesives was tested using the procedure outlined for the WCK and the data in Tables 1 and 2. The values calculated for  $\gamma_L^d$  are given in Table 5. Surprisingly, they do not differ greatly from the value for water. It can be argued that the correct value for  $\gamma_S^d$  to be used in the calculation is not that listed in Table 1 (obtained from interaction with methylene iodide) but should be modified to reflect adsorption of surfactant molecules onto the solid from the deinking liquors. In the absence of detailed information on this process and in order to follow relative changes, we will assume in subsequent calculations using the G-G-F-Y equation that the value for water is applicable to stickies/deinking liquors systems.

Table 5. Calculated Values for  $\gamma_L^d$

<u>Sticky</u>	<u>Liquor</u>	$\gamma_L^d$ , mN/m
HMD	1	24.7
	2	24.7
	4	26.2
	5	24.2
HMB	1	19.1
	2	16.4
	4	19.3
	5	16.0
HME	1	21.3
	2	18.8
	4	19.7
	5	18.7

## Flotation Studies

Flotation tests were carried out on particles of the three hot-melt adhesives. A variety of conditions of pH, liquor surface tension, and time of agitation prior to flotation were used. From the data in Tables 3 and 4, the force of attachment  $F_a$  was calculated from equation 8 using the exact expression (equation 10) for the factor  $d/D$ . The percent sticky removed during one minute of flotation is shown plotted against the corresponding force of attachment in Figure 5. Removal efficiency improves with increasing strength of attachment with most of the change occurring over a narrow range of forces. (The curve shown is a least squares fit to the hyperbolic tangent function.)

Although the dependence of removal efficiency on attachment force is believed to be a general relation, the particular "critical" force will be a function of the specific parameters of the flotation system. These parameters would include the ratio of bubble-to-particle size, mixing conditions in the flotation cell and the duration of flotation. The sensitivity to these factors needs to be examined in detail.

To gain a better appreciation of the influence of liquor and sticky surface energies on the attachment force, the G-G-F-Y equation can be substituted into equation 13 to give

$$F_a \cong 4\pi \gamma_L D (x - x^2) \quad (18)$$

where

$$x = \left( \gamma_S^d \gamma_L^d \right)^{1/2} / \gamma_L \quad (19)$$

# FLOTATION EFFICIENCY-ATTACHMENT FORCE

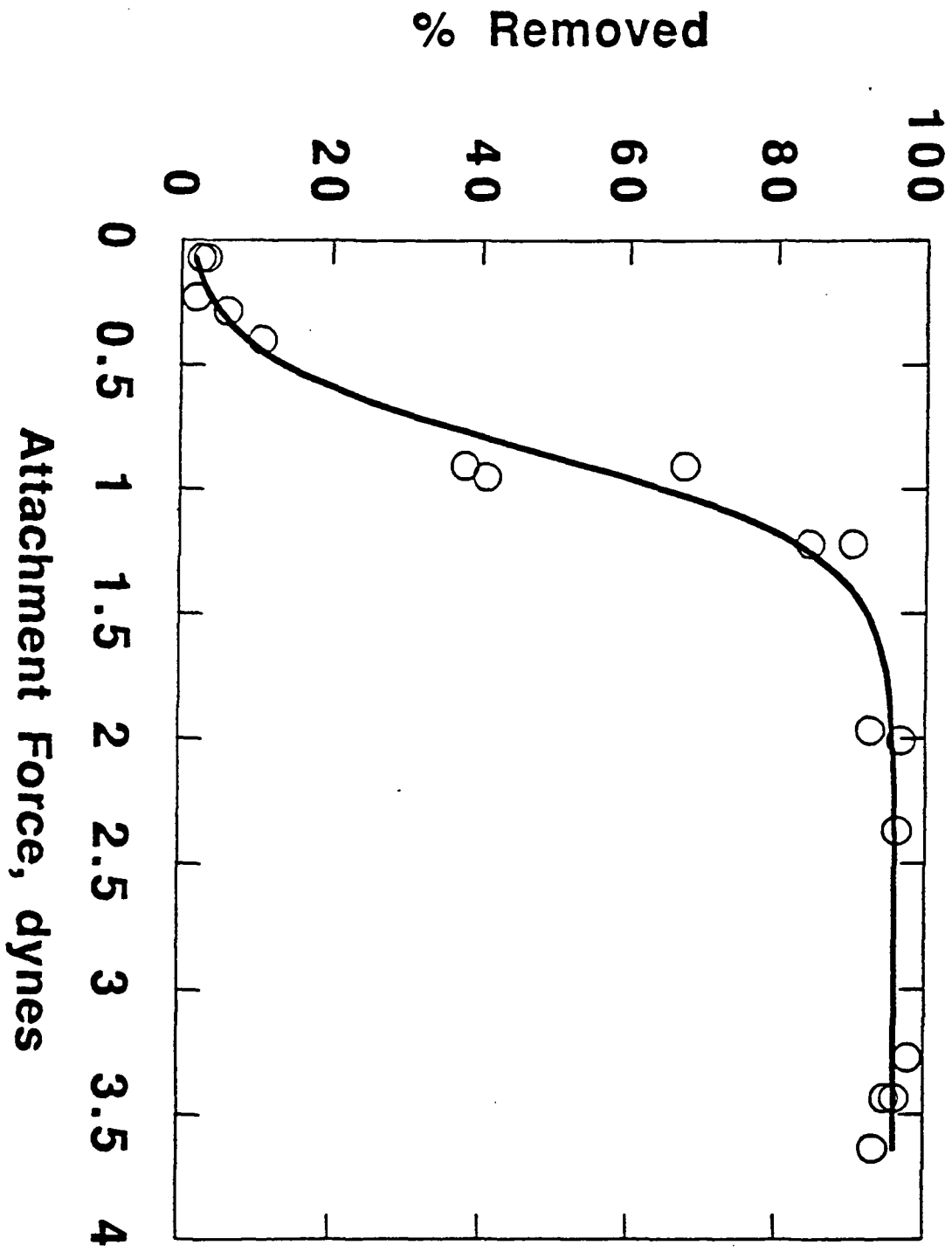


Fig 5 . Dependence of stickies removal efficiency by flotation on the force of attachment between air bubble and sticky, the latter calculated from equation 8.

The ratio  $(\gamma_s^d)^{1/2} / \gamma_L$  is seen to be the critical parameter.

Upon substituting the exact equation 10 into equation 8 and simplifying, the force of attachment can be found as a function of the  $\text{Cos } \theta$ .

$$F_a = 2\pi\gamma_L D \left[ \left( 1 - \text{Cos}^2\theta \right) / \left( 4 + 6 \text{Cos}\theta - 2 \text{Cos}^3\theta \right)^{1/3} \right] \quad (20)$$

Equation 17 can then be used to evaluate this function. A map showing the dependence of the attachment force on the sticky surface energy is shown in Figure 6. The curves represent conditions of constant liquor surface tension at the indicated values obtained from equation 20 and the G-G-F-Y equation. The dashed lines indicate levels of the attachment force required to reach the given recovery efficiencies. These levels were obtained from Figure 5. For a particular sticky with a given surface energy, a vertical line can be drawn at that energy to intersect the level of recovery desired. The deinking liquor must then have a surface tension equal to (or greater than) that at the intersection. Intermediate values for  $\gamma_L$  can be interpolated (approximately linearly) between the values for the indicated curves.

It is emphasized that these levels (dashed lines) pertain only to the particular flotation conditions used to generate the data in Figure 5. For a different set of operating parameters, the attachment force required to achieve a given recovery level would need to be determined experimentally. Once this is done and the level of attachment force is entered on the map in Figure 6, the necessary conditions for liquor surface tension for particular types of stickies can be determined.

## CONCLUSIONS

1. The G-G-F-Y equation can be used to correlate the experimental data on stickies/deinking liquors systems.
2. The flotation efficiency results can be explained by a theory based on the need for strong air bubble-sticky attachment. It includes the effects of bubble size, liquor surface tension, and the surface energy of the sticky.

# STRENGTH OF BUBBLE ATTACHMENT AS A FUNCTION OF LIQUID AND SOLID SURFACE ENERGIES

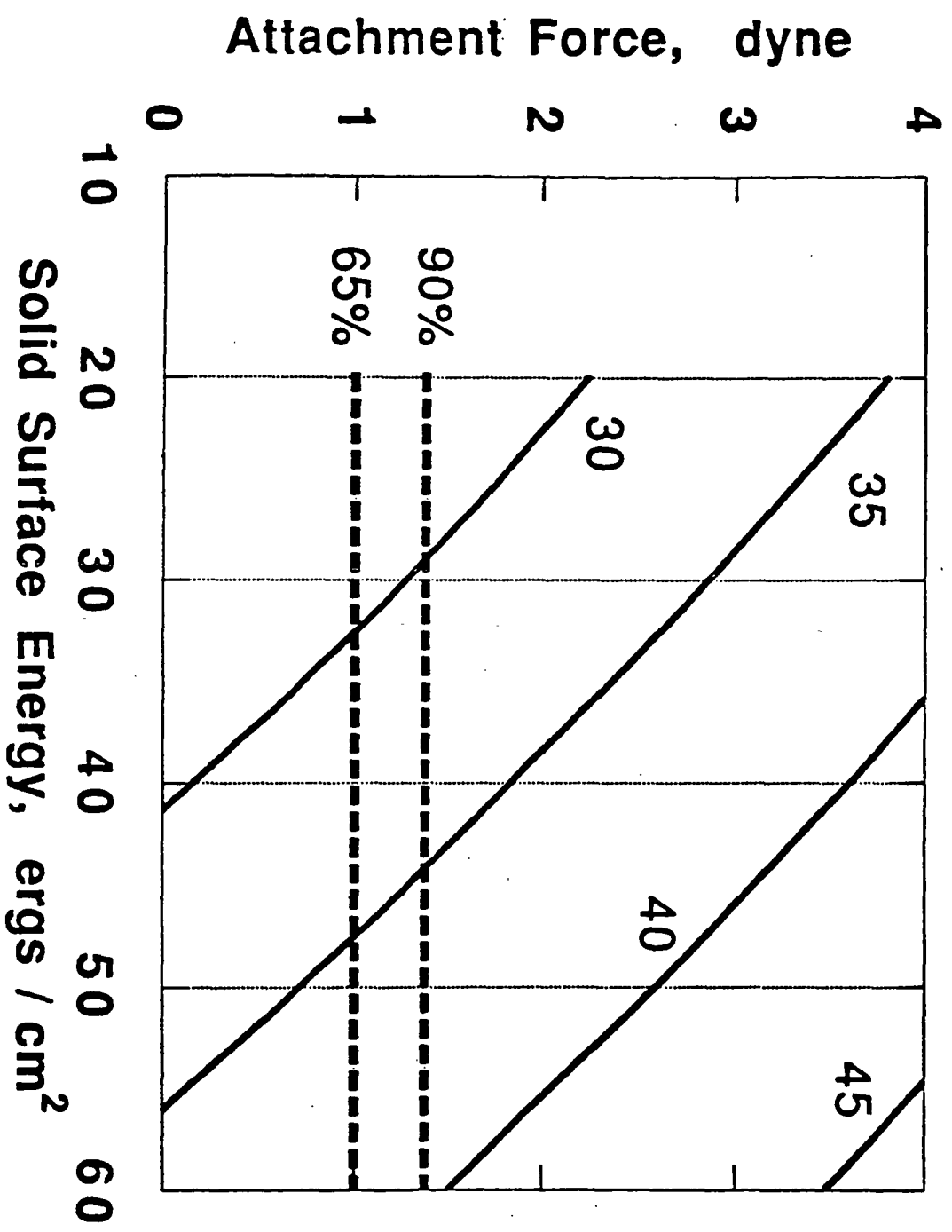


Fig. 6. Map of dependence of force of attachment (between air bubble and sticky) and the surface energy of the sticky at several levels of deinking liquor surface tension. Also shown are the levels of attachment force required with the present flotation cell to achieve 65 or 90% removal efficiency.

## ACKNOWLEDGEMENTS

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