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The Removal of Hot Melt Adhesives from Recycled Paper Stock by the Froth Flotation Method

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THE REMOVAL OF HOT MELT ADHESIVES
FROM RECYCLED PAPER STOCK BY
THE FROTH FLOTATION METHOD.

by

Dennis G. Nivison

A Thesis submitted
in partial fulfillment of
the course requirements for
The Bachelor of Science Degree

Western Michigan University

Kalamazoo, Michigan

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ABSTRACT

The object of this report is to explore the area of flotation as a means of removing hot adhesive from recycled paper stock. The major area of research revolved around choosing a surfactant capable of good performance in enhancing the flotation of adhesive and minimizing fiber loss. This surfactant was chosen by using a combination of zeta - potential studies and a flotation study in which 3 surfactants were screened. The highest performance was given by Rohm and Haas Triton N-100 followed respectively by X-114 and X-165. Even though all the surfactants had approximately the same high level of adhesive removal, the performance difference was manifest in the area of fiber loss. It was then concluded that a nonionic surfactant with a larger hydrophobic chain will have a smaller rate of fiber loss as the level of surfactant addition increases and the oxyethylene group is varied in size.

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INTRODUCTION

Now more than ever ecological consciousness is becoming an American way of life. The paper industry, which is a part of this movement, is trying to do their part. They are recycling more paper every year. However, one of the hindrances to higher recycling are hot melt adhesives. Removal of these is very difficult in the recycling process and as a result can cause a variety of problems. The flotation process which has already been incorporated in some mills for deinking purposes, will here be used to try and remove adhesives also. Hopefully this method will show some positive results as to adhesive removal and thus allow the paper industry to increase the level of recycling and produce nearly an adhesive free product.

OVERVIEW OF HOT MELT PROBLEM

The onset of a large invasion of solid waste in the United States has raised a definite environmental problem. Each year municipalities must collect and dispose of an estimated 190 million tons of solid waste. This is expected to increase to 340 million tons per year in 1980 (1). Also in many areas, disposal is becoming increasingly difficult as available landfill space disappears(1).

As a contributor, the paper industries are trying to come to grips with their portion of the problem. A large portion of municipal solid waste consists of waste paper and paper products. Therefore recycling of waste-paper is being stressed as one way of reducing solid waste (1).

Figure (1), which covers the years between 1945 and 1970, gives a comparison of the rate that the paper and paperboard consumption has increased compared to waste paper consumption. It is obvious to see that the recycling rate is not increasing at a comparable rate(1).

A study of 1979 however, showed that waste paper recovery was at a record high. According to J. Rodney Edwards (31), vice president , paperboard group, for the American Paper Institute, about 18 million tons of

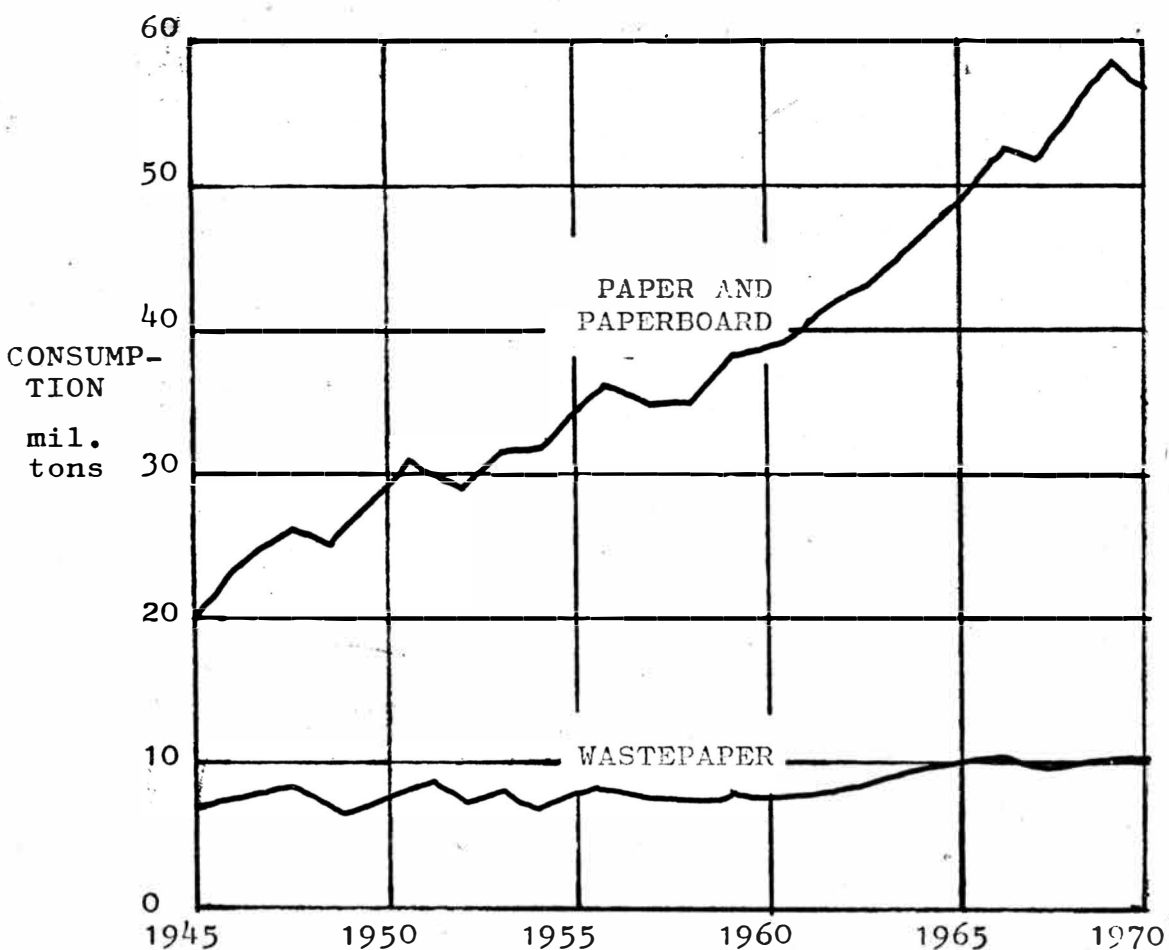


Fig. 1. United States consumption of paper, and wastepaper, 1945-1970.

waste paper were recovered in the United States in 1979, 7.2% more than 1978. The recovered tonnage represented 25% of the 72.5 million tons of paper and board products consumed in the United States last year, and 32% of the portion of consumption deemed recoverable. Of the total recovered, 15.6 million tons were used to make new paper

and board products. The rest was either exported or made into insulation. However even with the record increase, the percentage reused is still rather small compared to the consumption.

According to Kenworthy (2), some of the problems contributing to the fact of the small recycling rate; (1) collection cost, (2) market influences, (3) presence of contraries, (4) fiber degradation due to recycling, (5) effluent. Of these, the subject that will be keyed upon for this study is contraries; and, in particular, thermoplastic contraries.

Stokes, Baggaley and Temperly (3), have stated that until twenty years ago, recycling waste paper was relatively simple and straight forward recovery process. Since that time, technological improvements such as thermoplastics that have helped to increase paper and board consumption, have had a detrimental effect on recycling. The development of these improvements has led Bergstrom (4) to say, "Today, the most insidious and fastest growing cause of contamination in paper recycling is synthetic or rubber adhesives or coatings. These offset process efficiency and product quality in paper recycling more negatively than any other type of contamination".

The Composition of Hot Melts

Hot melts are 100% - solids thermoplastic adhesives. They are based on "plastic" polymers such as polyethylene (and it's copolymers), polypropylenes, polyvinyl acetates, polyamides and polyesters. Adhesive formulators compound hot melts with suitable resins, waxes, stabilizers etc. to give the desired adhesion, viscosity, flow characteristics, wetting ability and stability(5 and1).

How Contraries Get into Recycling

Some of the ways that these pernicious contraries get involved in recycling are; 1) hot melt laminated sealing tapes on corrugated containers, 2) hot melt book and ledger padding adhesives, 3) wax impregnable containers and waxed folding cartons, 4) hot melt curtain coated corrugated containers and folding cartons, 5) pressure sensitive adhesives on envelopes and corrugated boxes, 6) polyethylene extrusion coatings and laminations of paper and paperboard, 7) foamed polystyrene innerpacking in cartons and containers, as well as containers where foamed polystyrene replaces the normal fluted corrugating medium, 8) polyvinyl acetate emulsion adhesives used in side seaming cartons and containers as well as in cartons and case sealing applications, 9) hot melt adhesives used

for the same purpose as listed for polyvinyl acetate emulsion adhesives, and 10) rubber base printing inks (1&4).

Figure (2) gives an idea of how much scrap paper is generated by various operations and its cost (4).

(SRAC - Synthetic or Rubbery Adhesives and Coatings)

Generator	Annual Scrap Paper Generation (tons per year)	Percent Contaminated by SRAC	Uncon- taminated Scrap (per ton)	SRAC Contaminated Scrap (per ton)
Box shops	500-10,000 (20 ⁺ -5% Scrap rate)	10-12%	\$70-200	\$30-55
Book printers	5,000-25,000 (15 ⁺ -5% Scrap rate)	15-35%	\$50-200	\$10-25
Periodical printers	5,000-40,000 (15 ⁺ -5% Scrap rate)	40-50%	\$15-18 (Printed) \$90-130 (Unprinted)	\$8-12 (Printed) \$10-25 (Unprinted)
Envelope, forms & label houses	500-10,000 (25 ⁺ -5% Scrap rate)	5-10%	\$90-200	\$10-25

Fig. 2. These prices represent average prices to a recycling paper mill during the calendar year 1977.

Reasons for Using Hot Melts

The chief reason of their popularity is the instant bonding characteristic which they provide. This is a result

of setting by cooling rather than by adsorption or evaporation of the liquid vehicle in the conventional liquid adhesives. These conventional adhesives (wax, animal glue etc.) also do not have the high polymer plastic backbone that gives modern hot melts their strength, adhesion, and durability (5). These other advantages can be listed as well: 1) high speed production, short compression time, small space requirements, immediate shipping of sealed material, 2) improved glue line control, 3) bonding of impervious surfaces, 4) gap filling, 5) moisture resistance, barrier properties, 6) reduced maintenance and clean up costs, 7) storage problems minimized, and 8) no solvent hazards or air pollution problems (5).

However hot melts do incorporate some limitations: 1) They have limited toughness and heat resistance when compared with the best water based adhesives. 2) Because of their fast set, penetration into many surfaces is minimal. 3) Hot melts are organic materials which if overheated are subject to degradation (5). Their main limitation however is their resistance to removal in the recycling process.

There are some recyclable water based adhesives

on the market. But according to Ostle (7) these are and will continue to be more expensive than non-recyclable. Some may even cost 2 to 3 times as much as the others.

What Problems do They Cause?

Stickies can cause a variety of problems within a paper operation. First they will build up in mill whitewater systems. They then agglomerate on piping and finally break off in chunks to cause web breaks and spots in the sheet. Adhesive thermoplastics can retard the extraction of pulp from a hydropulper by agglomerate build up. Also more serious are the agglomerates on machine and cylinder wires, papermaking felts, and on press and dryer rolls. Spots on wires cause holes and web breaks. Press rolls and dryer accumulation often cause sheet picking or sticking. Filled felts often prevent proper water removal. When calendered, spots on finished sheets can become so called "shiners". Finally these spots can be very detrimental to a printing operation (1&4).

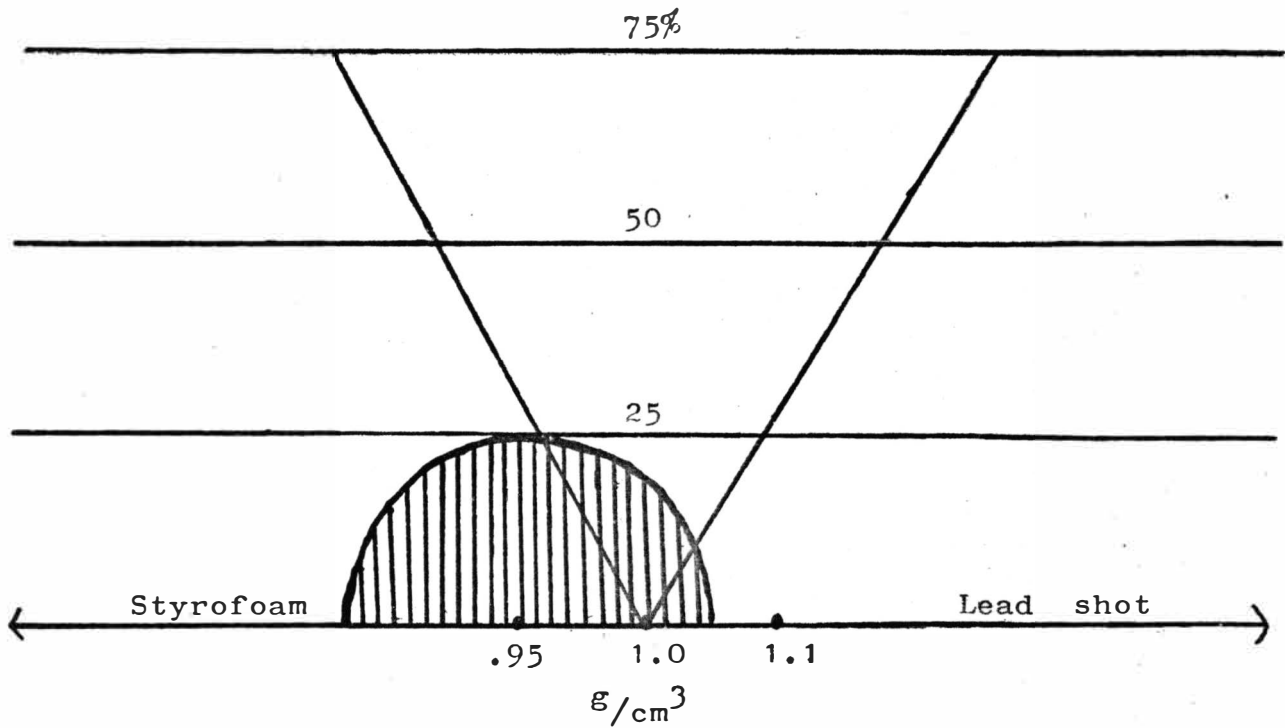
Why are they Hard To Remove?

The reason that pernicious contraries are so hard to remove can be better understood by looking at figure 3. Here it can be seen that the specific gravity of stickies is $(.95 \pm .1)$. This is very close to the specific gravity

(Figure 3)

Density Separation Efficiency

Cleaning
Efficiency



(decreasing)

Density

(increasing)

of water and fibers and therefore they are hard to separate centrifugally (4). Also some of the stickies are too small to screen out and too large to wash out (4). Finally they do not disperse even with prolonged agitation (4,8,9). State of the art techniques are therefore

not sufficient to remove these contaminants(4).

The paper industries are then going to have to try and solve the problem through new technology. If a new economically feasible method can be found to remove these contraries, the paper industry would have taken a major step in containing the invasion of solid waste. Paper that is now either dumped in a landfill or incinerated, could be recycled(4).

The Escher Wyss process, Boi-z cleaners and other screening and cleaning systems are examples of newer technology. But they have had only marginal success since they are not much more than glorified methods of previous technology(4,9-13).

Solvent removal is a possibility, but solvent removal is costly. The use of additives to increase the specific gravity of hot melts thereby enhancing density separation is also a possibility. The use of water-based recyclable adhesives should also be mentioned. But as stated before these are very costly. One other alternative, with which very little experimentation has been done, is flotation(4). Flotation is the method which will be keyed upon in this study.

FLOTATION

Flotation is a process by which particles are separated from a solution by means of being attached to an air bubble and floated to the surface. Once on the surface, the particles are held in a froth and skimmed off (14). This process has been used for many years by the mining industry to separate ores (15). However within the past 30 years the paper industry has adapted this method in deinking, whitewater reclamation and effluent control.

Theory

There are three general phases which one needs to be familiarized with to understand flotation; 1) liquid 2) solid 3) gas. The liquid used in froth flotation is water. To this, various reagents (collectors, frothers, modifiers) are added for selective control of the wettability of various surfaces and to achieve the desired frothing (16).

The gas generally used in flotation is air. This can be introduced into the system either through agitation or by means of injection of compressed gas (16).

Finally, there is the solid phase, which is probably the most important in flotation (16). The solids which will be dealt with are the hot melts adhesives.

When a solid is introduced into the flotation system, it generally needs help to perform in the correct manner. It usually does not of itself connect with an air bubble and float to the surface. A collector is therefore needed, and acts as a tie between the solid and air bubble. A collector therefore has a dual role in the flotation process, to connect to the solid and to be attracted to the air bubble(17).

Since the collector plays such an important part in flotation, it will be worth going a little more in depth to look at the theory behind its role. Collectors which are actually surface active agents (surfactants) are substances which when present at low concentration in a system, can change the system. This is accomplished by adsorbing onto surfaces or interfaces of the system and by altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). The term interface indicates a boundary between any two immiscible phases; the term surface denotes an interface where one phase is a gas, usually air(32).

The reason that surfactants have the ability to adsorb onto surfaces or interfaces is, that they possess one polar and one non-polar portion(18). They can also

have a nonionic characteristic (no ionic charge), or a zwitterionic characteristic in which both positive and negative charges are present. The non-polar group, which has no attraction for the solvent (usually water), is generally called a hydrophobic group. On the other hand, the polar group which has a strong affinity for water is called the hydrophilic group. This is known as an amphipathic structure(32). Because of this amphipathic structure a surfactant will arrange itself at the surface of a liquid. Here it will cause a reduction in surface tension and orient itself with the hydrophilic head in the aqueous phase and the hydrophobic group towards the air (32).

Structures of Surfactants

To give an idea of what surfactants look like, here are some examples of their structures. 1) Anionic- the surface active portion of the molecule bears a negative charge, for example, $R-\overset{\overset{O}{\parallel}}{C}-O^{-}Na^{+}$ (soap), $RC_6H_4SO_3Na^{+}$ (alkylbenzene sulfonate). 2) Cationic - the surface-active portion has a positive charge, for example, $RNH_3^{+}Cl^{-}$ (salt of a long chain amine), $RN(CH_3)_3^{+}Cl^{-}$ (quaternary ammonium chloride). 3). Zwitterionic - both positive and negative charges may be present in the surface-active portion, for example, $R^{+}NH_2CH_2COO^{-}$ (long chain

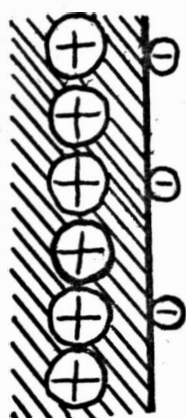
amino acid), $\text{RN}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ (sulfobetaine). 4) Non-ionic - the surface-active portion bears no apparent ionic charge, for example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long - chain fatty acid), $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alkylphenol) (32).

Adsorption of Surfactants on Solids

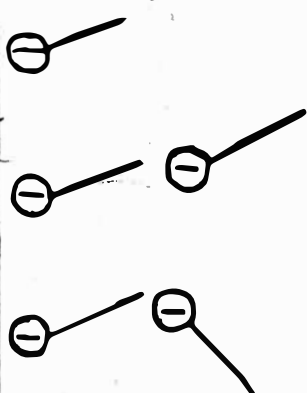
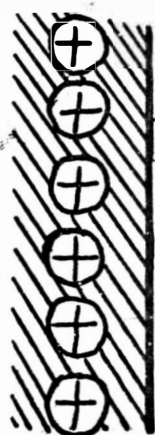
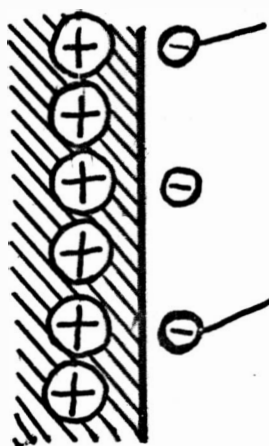
The adsorption of surfactants at the solid / liquid interface is influenced by a number of factors: 1) the nature of the structural groups on the solid surface - whether the solid has positive or negative potential determining ions, or is non-polar; 2) the structure of the surfactant being absorbed, ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic; and 3) the nature of the aqueous phase which will be discussed later. Since adsorption of surfactants onto solids involves single ions rather than micelles, a concentration of surfactant in the bulk solution below the CMC is beneficial for adsorption. The various mechanisms by which absorption can take place are as follows:

1. Ion exchange (Figure 3) - involves replacement of counterions adsorbed onto the substrate from the solution by similarly charged surfactant ions.
2. Ion pairing (Figure 4) - adsorption of surfactant

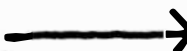
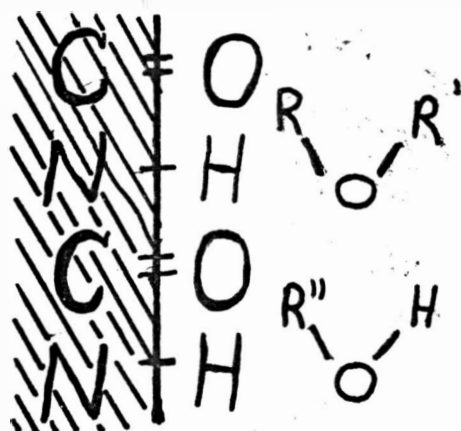
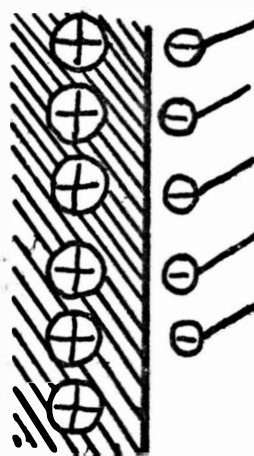
solution



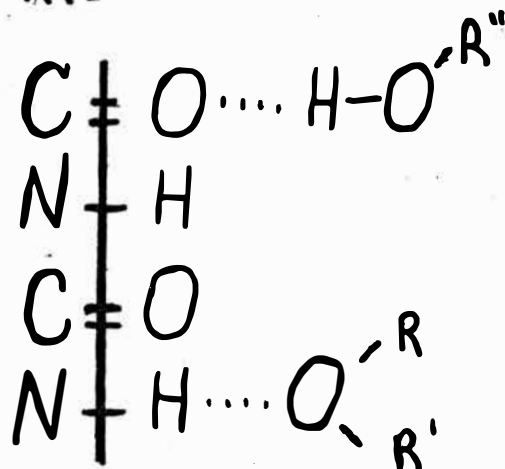
Ion Exchange
Fig. 3



Ion Pairing
Fig. 4



Hydrogen Bonding
Fig. 5



ions from solution onto oppositely charged sites occupied by counterions.

3. Hydrogen bonding (Figure 5) -adsorption by hydrogen bond formation between substrate and adsorbate.

4. Adsorption by polarization of π electrons -occurs when the adsorbate contains electron-rich aromatic nuclei and the solid adsorbent has strongly positive sites. Attraction between electron-rich aromatic nuclei of the adsorbate and positive sites on the substrate results in adsorption.

5. Adsorption by dispersion forces-occurs via London-van der Waals dispersion forces acting between adsorbent and adsorbate molecules. Adsorption by this mechanism generally increases with increase in the molecular weight of the adsorbate, and is important not only as an independent mechanism, but also as a supplementary mechanism in all other types. For example, it accounts in part for the pronounced ability of surfactant ions to displace equally charged simple inorganic ions from solid substrates by an ion exchange mechanism.

6. Hydrophobic bonding-occurs when the combination of mutual attraction between hydrophobic groups of the surfactant molecules and their tendency to escape from an aqueous environment becomes large enough to permit

them to adsorb onto the solid adsorbent by aggregating their chains. Adsorption of surfactant molecules from the liquid phase onto or adjacent to other surfactant molecules already adsorbed on the solid adsorbent also may occur by this mechanism (32).

If the adsorption takes place in the fashion that the hydrophobic tail is oriented toward the bulk of the solution it can be said that the solid has gained hydrophobicity. This hydrophobic solid will now want to escape from the aqueous solution. This then is exactly the position to be in to enhance flotation. If air is introduced into the system the particles because of their hydrophobicity will want to join to the air bubbles for exactly the same reason that the surfactant itself wanted to go to the air/liquid interface (to escape from the water). Here, the importance of contact angle also comes into play. The surfactant on the solid makes the basic modifications needed to give the correct contact angle (14). The various interfacial energies, after contact, are related to the contact angle created by the air bubble on the solid surface in solution by Young's equation. $V_{SA} = V_{SL} + V_{LA} \cos\theta$

Here V_{SA}, V_{SL}, V_{LA} are the interfacial tension at the solid/air, solid/liquid and liquid/air interfaces

respectively and θ is the contact angle. For adhesion of the air bubble to the particle in solution a contact angle of fairly larger than 0° but less than 90° is required. This is because at 0° the liquid will completely wet the particle (18).

There are other important factors that affect flotation. One is a frothing agent or a foam-stabilizing additive. The most effective additive for increasing the stability of the foam produced by surfactant solutions appear to be long-chain, often water insoluble, polar compounds with straight chain hydrocarbon groups of approximately the same length as the hydrophobic group of the surfactant (32). Pine oil is the most commonly used, long-chain alcohols and phenols are also used. The purpose is not only to help produce good film elasticity of the bubble but to help gain a stable bubble by establishing like charges around the bubble. This in turn makes them repel each other and thus not join together before they reach the surface (17).

The other major additive in a flotation cell are modifiers. As was stated before the nature of the aqueous phase very much affects the adsorption of surfactants at the solid/liquid interface. The variables involved here are pH, electrolyte content, the

presence of any additives such as short-chain polar solutes (alcohol, urea, etc.) and the temperature (32). Probably the most important of these are the pH regulators. Adjusting the pH is a major method of achieving selectivity between species in flotation. For the materials whose potential determining ions are H^+ and OH^- the role of pH altering the surface charge is quite obvious. In other systems pH may indirectly affect the potential-determining ions through chemical equilibria which alter the concentration of the potential determining ions. Also the pH controls the ionization of the collector from molecular to ionic species, which in turn influences the type of adsorption of the collector and so the subsequent flotation (16).

Activators are added to permit better surfactant attachment to the material to be floated (16). For example, electrolytes such as Ca^{++} can tie up the negative charge on particles in solution and thus allow an anionic surfactant to adsorb on the surface. Depressants are also added as another means of obtaining selectivity (14 & 16). Dispersants are added in order to separate the materials from those which need to be floated (16).

The temperature affects the adsorption of the sur-

factant on the solid since it can change the critical micelle concentration of the surfactant. This in turn will as mentioned before, determine whether the surfactant will be in solution as individual ions or in micelles, the ion form being more effective for adsorption.

Theory Application

Now this theory of flotation can be applied to the problem of floating hot melts out of a fiber dispersion . One very important factor that should first be dealt with here is to find the zeta-potential of the hot melts in solution. This will be necessary to determine the type of collector, (anionic, cationic, non-ionic) and pH that will be used during flotation. Nowadays, however, most of the flotation work done in industry is with deinking. Therefore it would be nice to incorporate floating these hot melt particles with the ink particles. One of the first steps of deinking is to add chemicals to disperse and separate the ink particles from the fibers (19-26). The chemicals which many deinking processes use are NaOH, Sodium Silicate (water glass) and Hydrogen Peroxide. Therefore the zeta-potential of the hot melts in this solution could be different than when they are alone present in water.

Also the paper fibers could have some effect on the zeta-potential of the hot melts.

Another factor which should be taken into account is water hardness (20 & 29). Pornpaitoonsakul showed that the addition of CaCl_2 to increase water hardness raised the zeta-potential on dispersed ink particles. The amount of Ca^{++} electrolyte as mentioned before, also probably has an effect on zeta-potential of adhesive in dispersion.

Besides adsorption at the S/L interface, temperature has other effects in the recycling system. In the pulping cycle of deinking, temperatures of up to 50°C could possibly cause the hot melts to agglomerate thus these larger particles could be more easily separated by screening. (Temperature above 50°C however are found to be detrimental to the H_2O_2 bleaching chemical) (19). However when the actual screening takes place as low a temperature as possible should be maintained. This is because plastic contaminants are more rigid at the lower temperature and thereby would not so easily deform and slip through the screen (30).

As mentioned before very little work has been done in the field of floating hot melts. One previous study has been done in treating of plastic mixtures. Here a mixture of waste polypropylene, polyethylene, poly-

styrene, nylon, methacrylate and PVC was crushed and mixed with NaAlkylarylsulfonate and pine oil. This solution was then bubbled with the result of only the PVC remaining in dispersion. The others were floated (27).

Also a German Patent shows the process for the recovery of fiber from plastic coated waste paper and, waste paperboard by the flotation method (28). The plastics are first screened and the remaining particles floated to the surface.

These previous studies give at least some direction to be followed in conducting the study of flotation of hot melts.

EXPERIMENTAL DESIGN

The purpose of this study is to choose the correct surfactant which would optimize removal of hot melt adhesives during flotation. To perform in an optimum fashion means the surfactant should remove a high level of adhesive and the least amount of fiber as possible. The first part was designed to choose the type of charge desired on the surfactant (anionic, cationic, etc.) The second part was designed to screen several surfactant structures (with varying hydrophobic and hydrophilic groups) to find the best performer.

Part 1. Zeta-Potential Studies.

A. Distilled water-adhesive system.

1. Varying pH

B. Distilled water-Fiber system.

1. Varying pH

(This was actually a separate study)

Part 2. Flotation Studies.

A. Three different surfactants used.

1. Three levels of addition.

a. Surfactant added in molar quantities. (mol/liter)

2. Three replicates at each level.

B. Variables held constant.

1. Temperature
2. pH
3. Type of adhesive
4. Stock freeness
5. Cell consistency
6. Flotation dwell time
7. .2 - .25% Adhesive (based on Fiber)

C. Results calculated.

1. Percent fiber loss
2. Percent adhesive removal

EXPERIMENTAL PROCEDURE

As mentioned before, the zeta-potential studies were actually done separately. A detailed procedure will therefore not be given for this part, however the basic results will be shown.

The flotation studies were carried out with a stock of fibers (50% H.W. and 50% S.W.) beaten to 500 freeness in the Valley beater. This remained constant throughout the experimentation. The adhesive used was National Starch Instant-Lok 34-2812. With it, draw-downs were made with a coating roll bar on base stock and cut into small strips. These strips were beaten in a Waring blender and floated under the following conditions in a laboratory Voith flotation cell.

- 1) Consistency - .3%
- 2) Temperature - 20°C
- 3) pH \approx 10 (adjusted with NaSilicate).
- 4) Surfactants:
 - a. Triton N-100 (nonionic) .2-.4-.6 ($\times 10^{-5}M$)
 - b. Triton X-114 (nonionic) .75-1.0-1.25 ($\times 10^{-5}M$)
 - c. Triton X-165 (nonionic) .50-.75-1.00 ($\times 10^{-5}M$)
- 5) Dwell time - 12 minutes.
- 6) Water used - tap water

Evaluation

A standard set of handsheets (3 grams) were made on the Noble and Wood handsheet machine before flotation. The specks of adhesive were counted and then compared to the amount of specks that were in the same weight of handsheet after flotation. Thus a percent of hot melt removal was calculated.

During flotation the froth from the cell was collected and filtered through a Buchner funnel. The remaining pad was weighed and compared to the original amount of fiber in the system. Thus the % loss of fiber could be calculated. For the detailed procedure see Appendix 1.

Levels of addition, along with how to calculate amount of addition can also be seen in Appendix 1. (It should be noted that the range of addition varied for each surfactant because they had different foaming characteristics).

PRESENTATION OF RESULTS AND DISCUSSION

PART 1. Zeta-Potential Studies

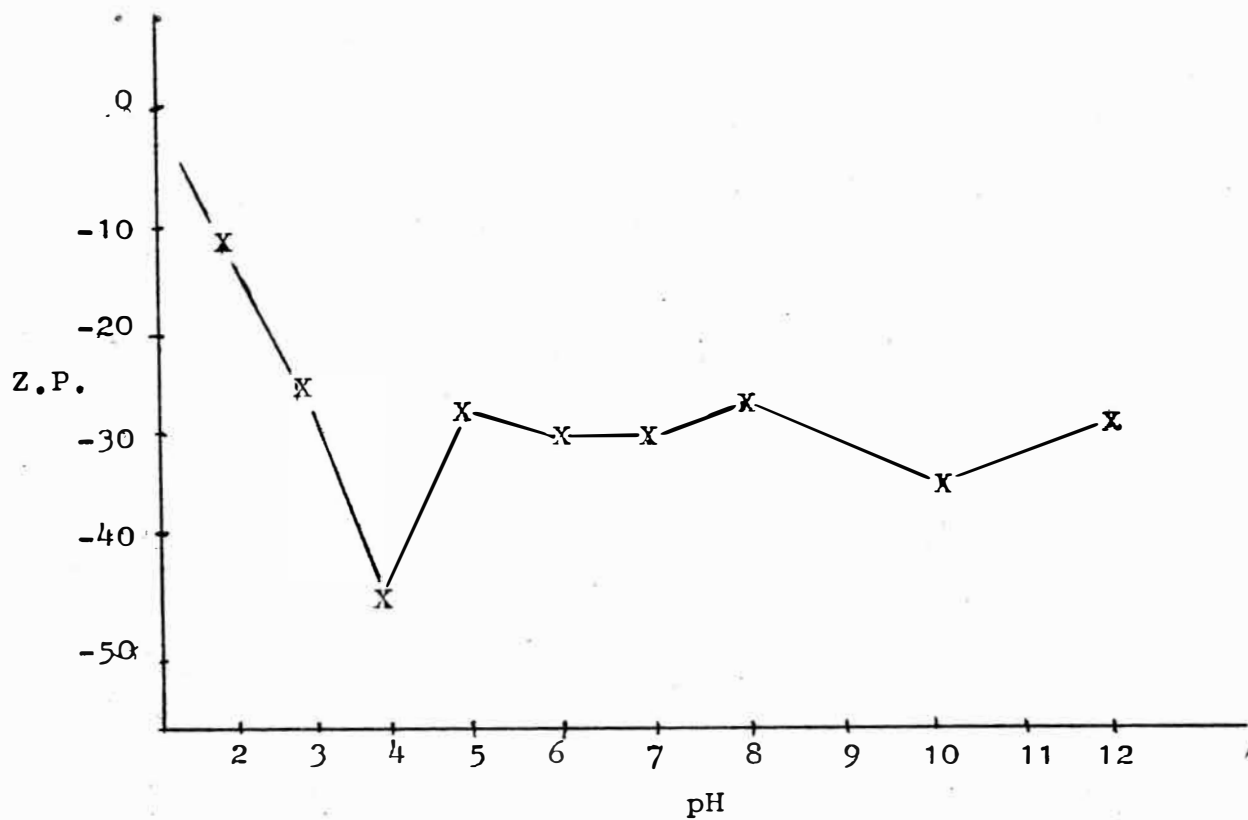
The zeta-potential of fibers and adhesive was studied in a distilled water system varying the pH from 2 to 12. The results are presented in the following table. The graph of these results can be seen in Figure 7 & 8.

pH	2	3	4	5	6	7	8	9	10	11	12
Z-P of fibers	12.7	25.2	46.7	28.	31	31.9	27.5		35.6		30
Z-P of Adh.	0		23.0		29.4	28.8	30.9		13.2		0

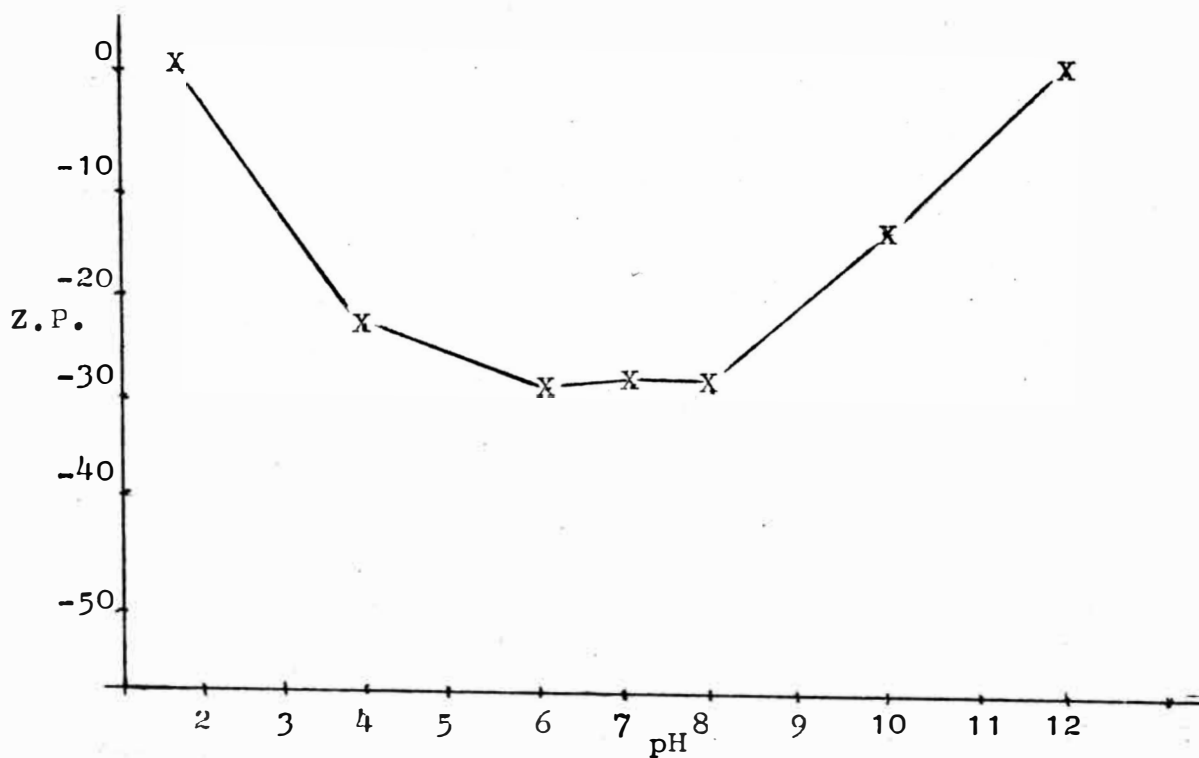
Discussion

From the graphs of the results it can be seen that the use of a cationic surfactant would not be very feasible. The cationic surfactant would attach to fiber in the system because of its negative charge. This would result in a high fiber loss. However an anionic surfactant could possibly work at high pH since the zeta-potential on adhesive at high pH is much less negative. Consequently the repulsion between adhesive and surfactant would be smaller. Also a nonionic surfactant would be a very logical choice since there would be no charge effects between surfactant and fibers or adhesive. The adsorption at the solid/liquid inter-

(Figure 7)
Z.P. vs. pH
(Fibers)



(Figure 8)
Z.P. vs. pH
(Adhesive)

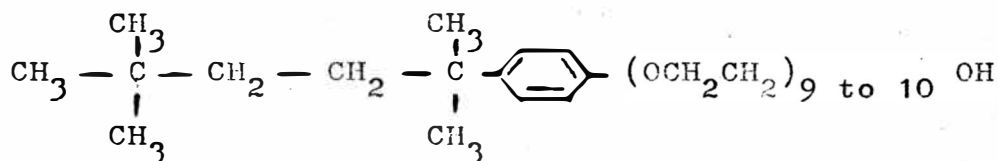


face would be something other than ionic. Nonionic surfactants then, were finally chosen since not enough information could be found on anionic surfactants. Companies are very confidential with the molecular formulas and molecular weight of their surfactants. Therefore three Triton nonionic surfactants were chosen for the flotation studies.

PART 2. Flotation Studies

The effect of these different surfactants on fiber loss and percent adhesive removal were measured after 9 flotation cells were run for each surfactant. The results and discussion for each individual surfactant will first be presented. It will be followed by a general discussion with a comparison of all the surfactants.

1. The first surfactant used in flotation study was Triton N-100. This surfactant is an alkylaryl polyether alcohol and it has a density of 8.7 lbs/gal. The structural formula is :



Molecular Weight: 638 gr/mol CMC: $7.5 \times 10^{-5} \text{M}$

Where CMC is critical micelle concentration. (32&33)

The results received with this surfactant are presented in the following table. (Table I).

Table I

N-100

RUNS	$.2 \times 10^{-5} M$		$.4 \times 10^{-5} M$		$.6 \times 10^{-5} M$	
	% Fiber loss	% Adh. Removal	% Fiber loss	% Adh. Removal	% Fiber loss	% Adh. Removal
#1	2.5	99.5	2.8	99.3	4.4	99.2
#2	3.5	98.3	3.7	99.5	3.7	99.6
#3	3.7	98.5	4.5	97.5	4.2	99.5
Avg.	3.3	98.8	3.7	98.8	4.1	99.4

	Coeff. of Deter.	Mult. Corr. Coeff.	Slope
Over all pts.	.30783	.55483	216668
Avg..of pts.	1.0000	1.0000	200000

$$F_{\text{calc}} = .8098$$

F_{calc} is not greater
than 5.1433.

Discussion

From the table it can be seen that the average overall adhesive removal was very similar in all three levels of addition. The F - test results give support to this statement since it could not be proven that there was any difference between the levels of addition. Therefore it can be assumed that within this range of addition a higher level surfactant shows no extra removal of adhesive.

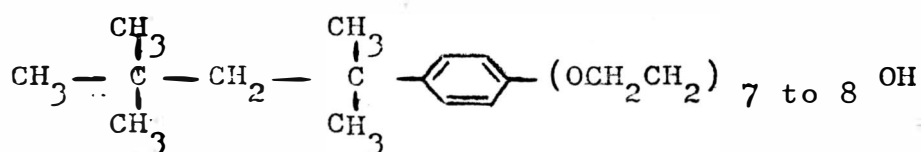
A regression analysis was run on % adhesive removal and no significant correlation was found. Overall, however, it can be seen that the % adhesive removal for N-100 was very high.

The results of a regression analysis for % fiber loss over-

all points of addition, and the three replicates at each level, showed fairly poor correlation (Figure 9). The coefficient of determination (how well points fit the line) and the multiple correlation coefficient (how accurate the slope is) were approximately 30% and 55% respectively. However, when the average of the replicates was taken and a regression run, perfect correlation was found (Figure 10). It can then be assumed there is a relationship between the percent fiber loss and level of addition of surfactant.

2. The second surfactant used in the flotation study was Triton X-114. This surfactant is also an alkylaryl polyether alcohol with a density of 8.8 lbs/gal (32 & 34).

The structural formula is :

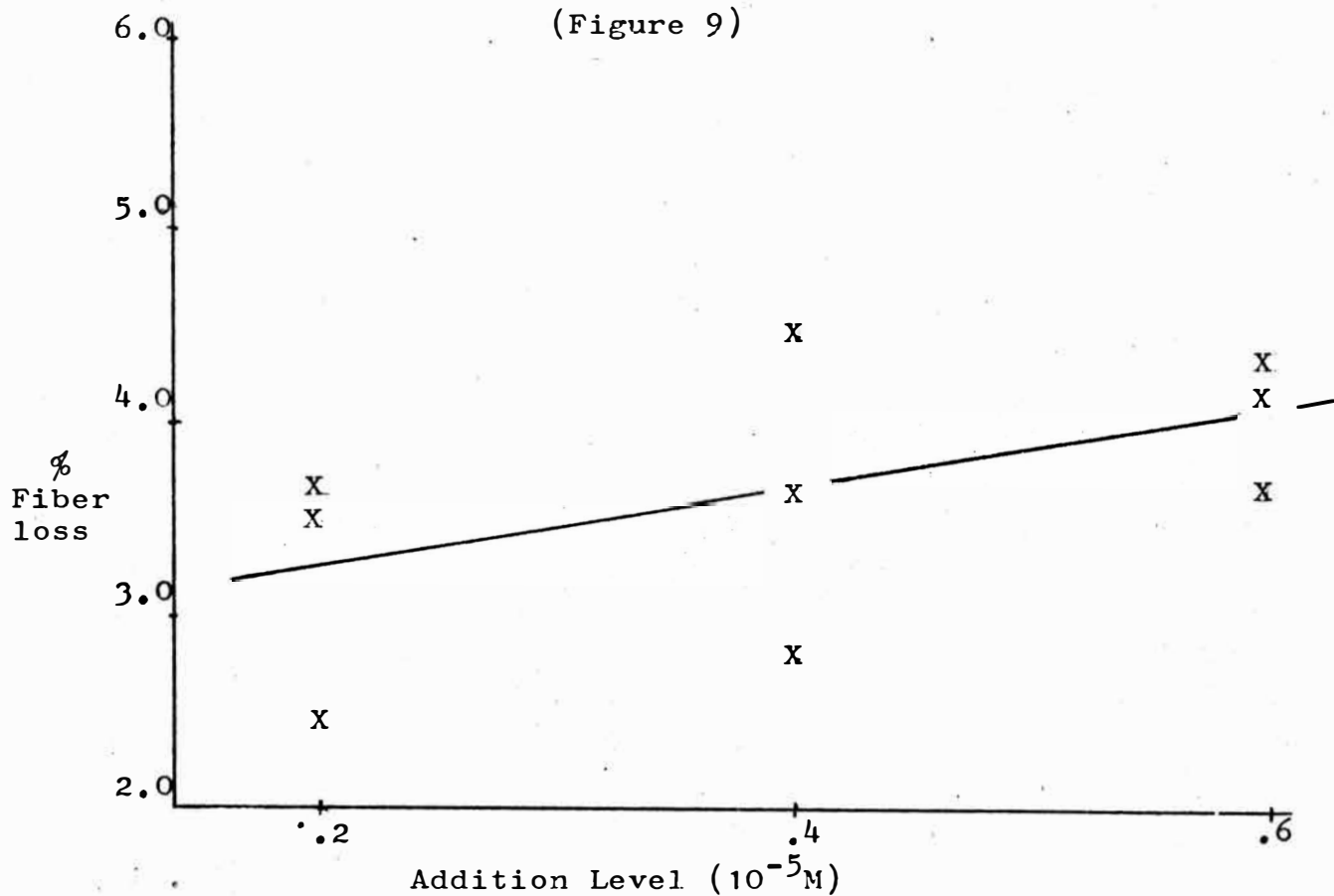


Molecular Weight: 536 gr/mol CMC: $2.7 \times 10^{-4} \text{M}$

The results recieved with this surfactant are presented in the following table (Table II).

N-100 % Fiber loss vs. Level of Addition

(Figure 9)



N-100 % Fiber loss vs. Level of Addition
(Average of points)

(Figure 10)

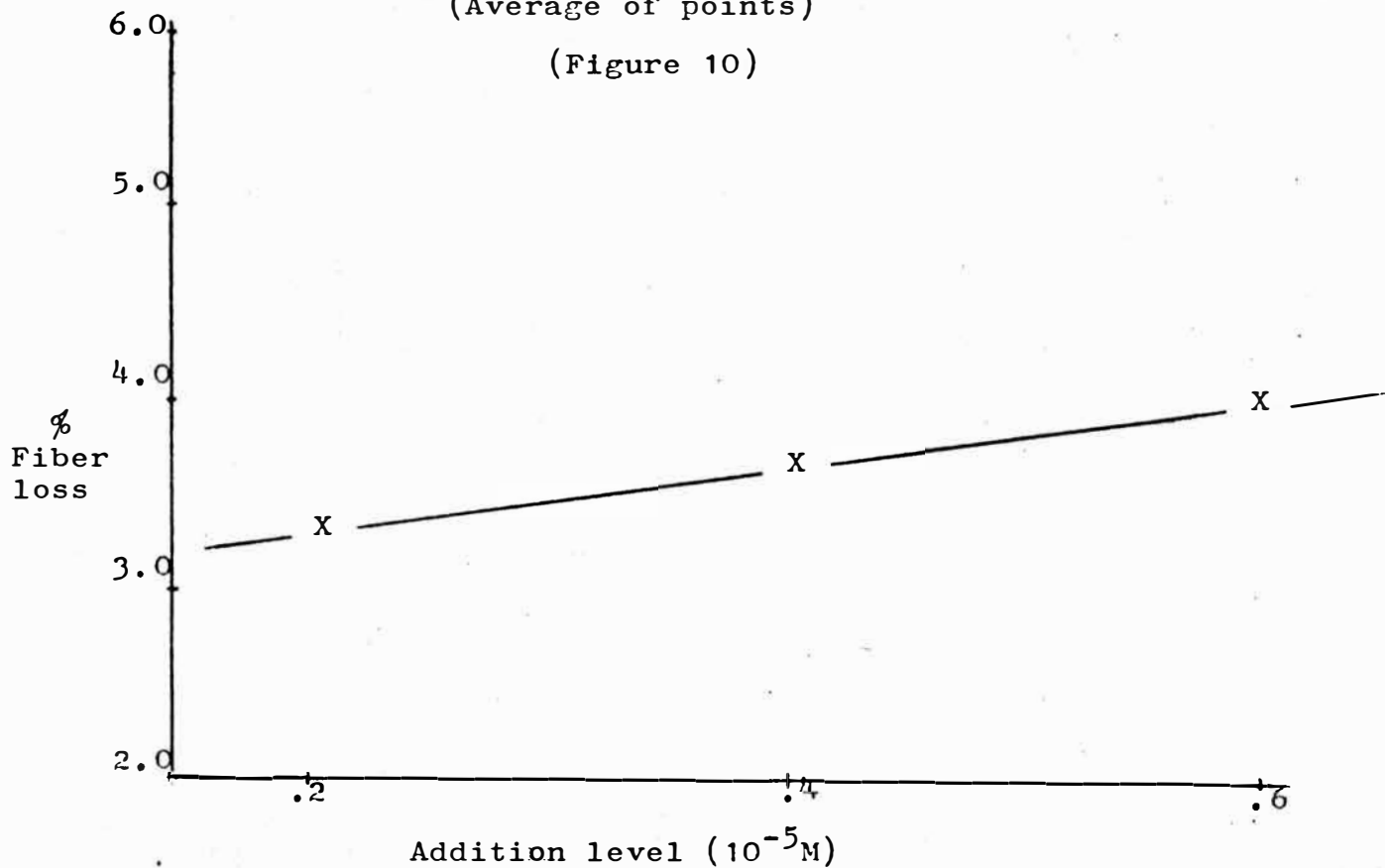


Table II

X-114

RUNS	$.75 \times 10^{-5}M$		$1.0 \times 10^{-5}M$		$1.25 \times 10^{-5}M$	
	% Fiber loss	% Adh. Removal	% Fiber loss	% Adh. Removal	% Fiber loss	% Adh. Removal
#1	4.0	99.0	5.8	99.8	8.6	99.4
#2	4.4	97.5	5.9	99.1	8.6	99.6
#3	4.1	98.9	7.0	98.8	9.3	99.6
Avg.	4.2	98.5	6.2	99.2	8.9	99.5

	Coeff. of Deter.	Mult. Corr. Coeff.	Slope	$F_{calc} = 2.816$ F_{calc} is not greater than 5.1433.
Over all pts.	.95772	.97683	933333	
Avg. of pts.	.99266	.99632	940000	

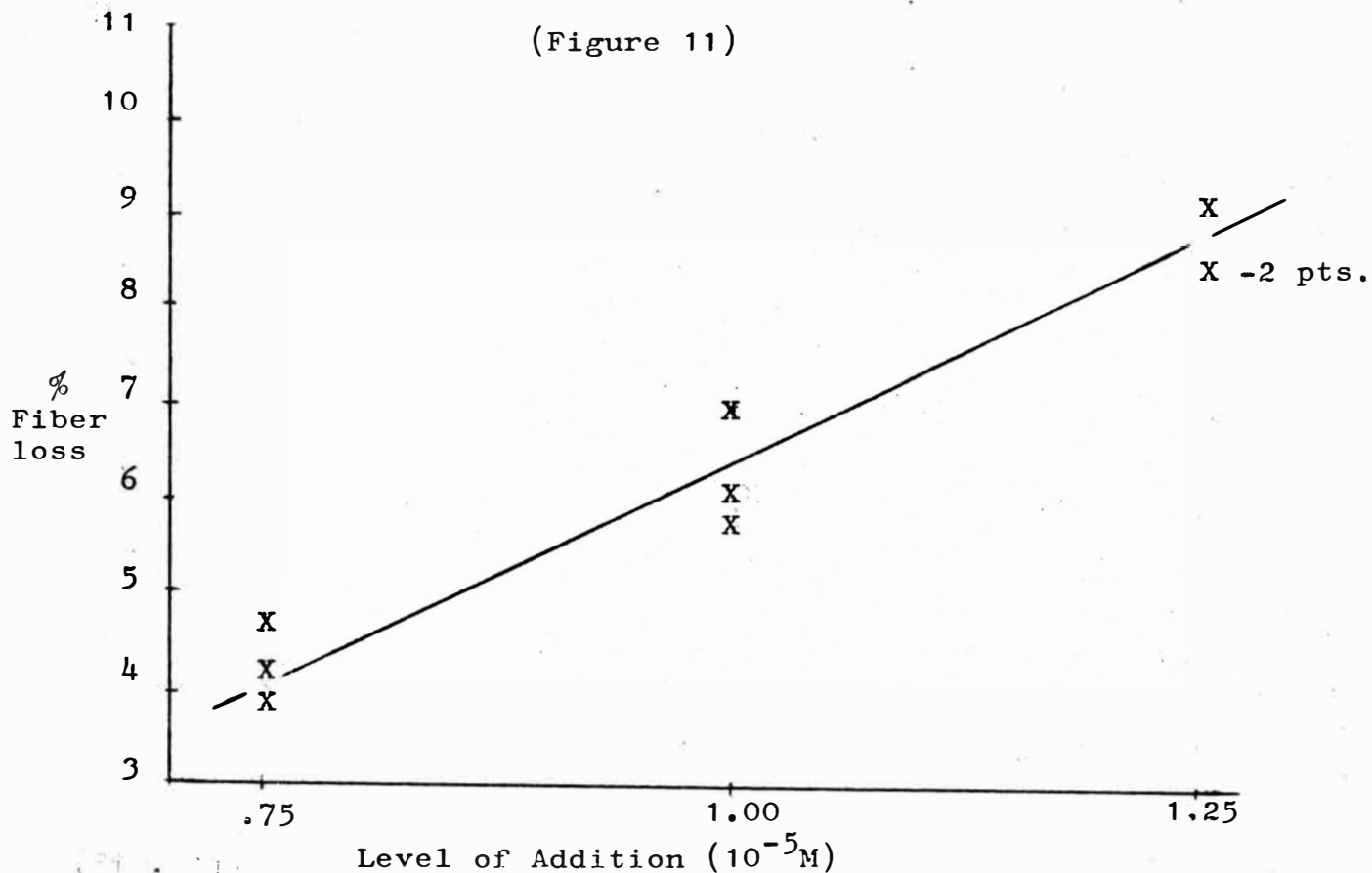
Discussion

From the table it can be seen again that the average overall adhesive removal was very similar in all three levels of addition. An F - test supported this observation. Also it again can be seen that the % adhesive removal was not only similar but very high (around 99%).

The results of a linear regression analysis overall points of addition, and the three replicates at each level, showed very good correlation (Figure 11). When the average of the replicates was taken and a regression run, the correlation again was nearly perfect (Figure 12). Therefore it definitely looks as if there is a relation of higher fiber loss with level of addition.

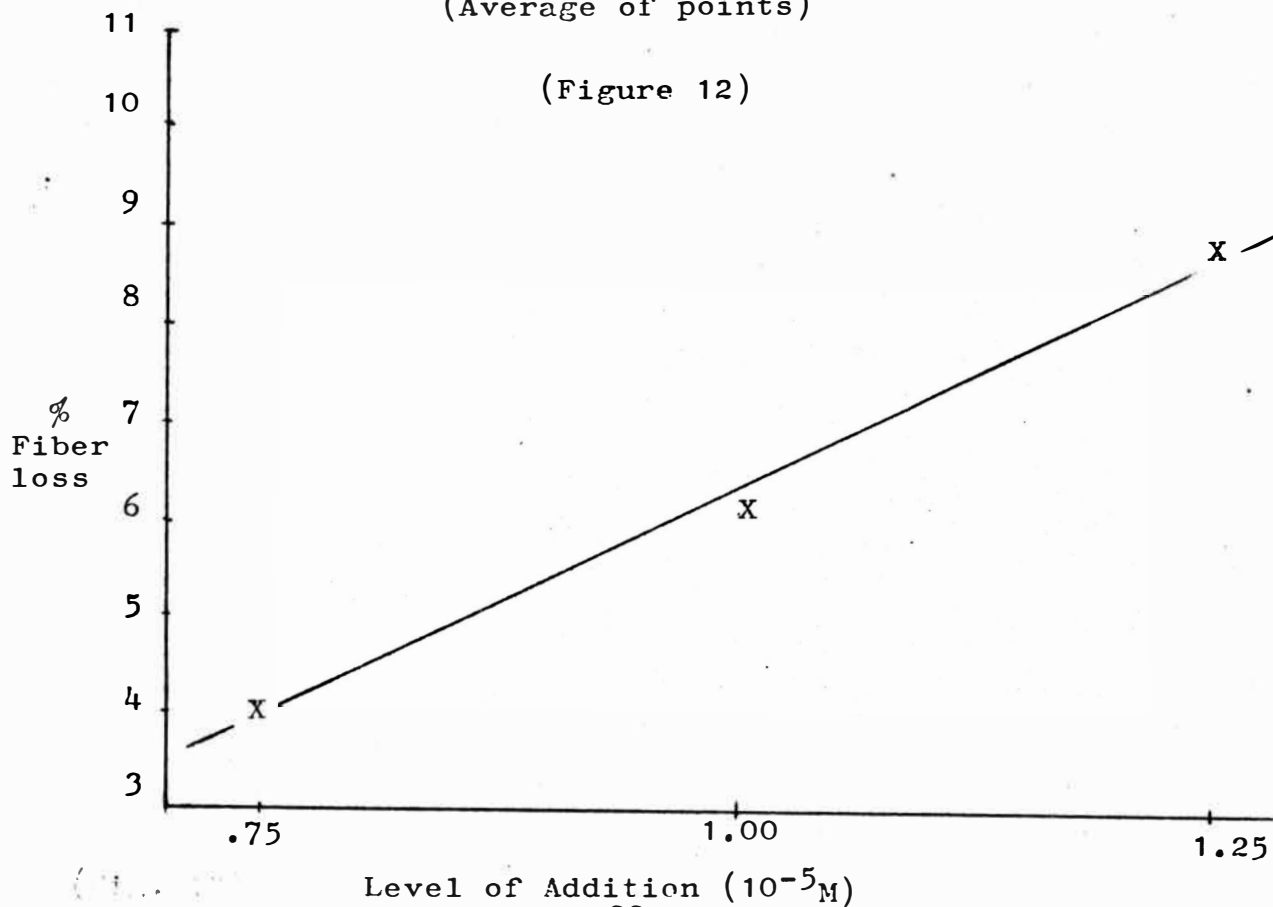
X-114 % Fiber loss vs. Level of Addition

(Figure 11)



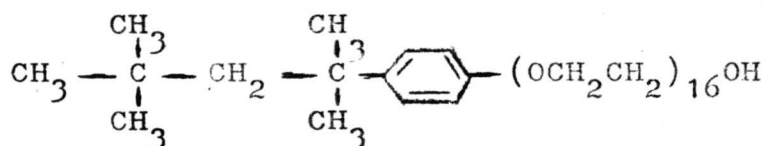
% Fiber loss vs. Level of Addition
(Average of points)

(Figure 12)



3. The third surfactant used was Triton X-165.

This surfactant is an alkylaryl polyether alcohol and it has a density of 9.0 lbs/gal (32&35). The structural formula is :



Molecular Weight: 910 gr/mol CMC: $4.5 \times 10^{-4}\text{M}$

The results recieved from this surfactant are presented in the following table (Table III).

Table III
X-165

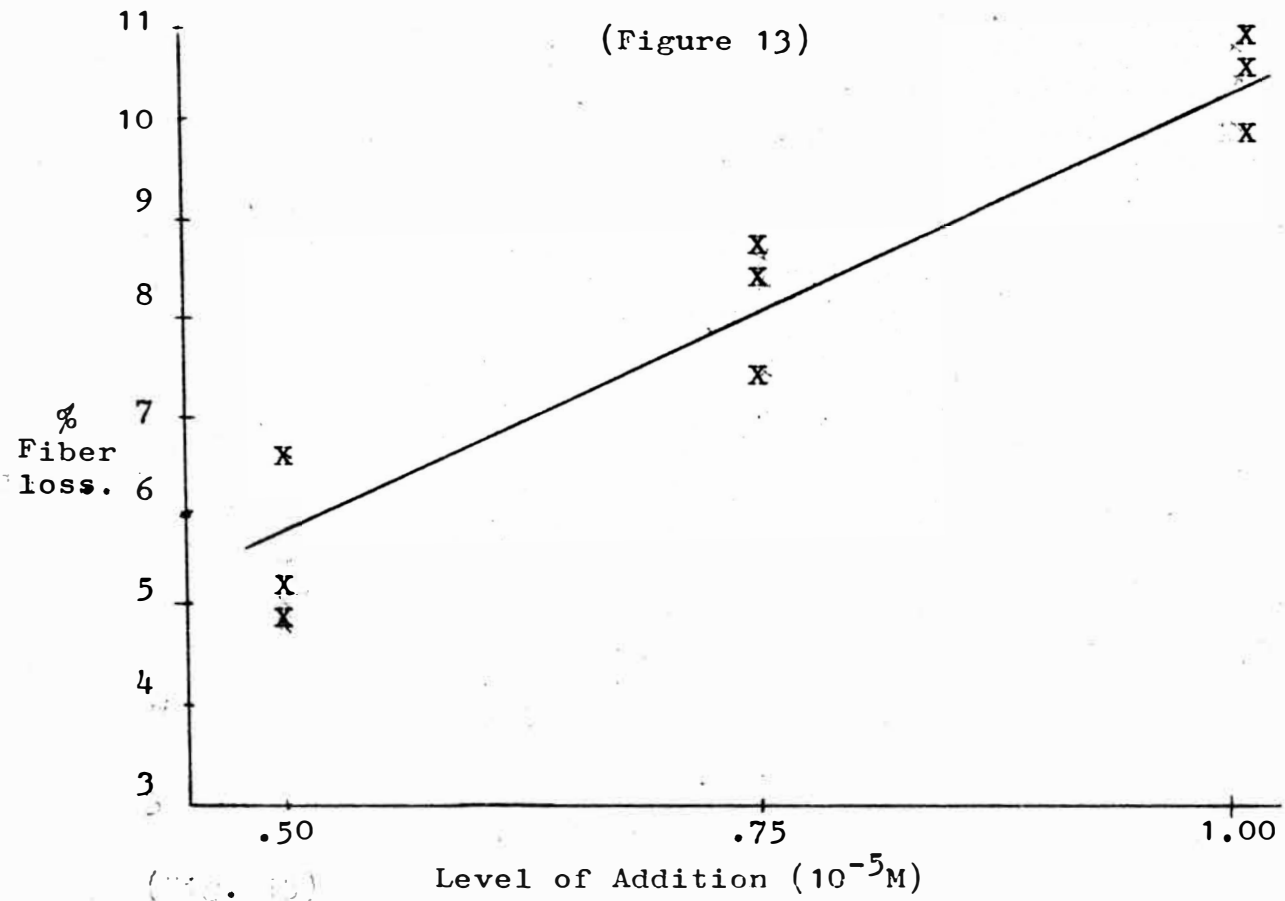
	$.5 \times 10^{-5}\text{M}$		$.75 \times 10^{-5}\text{M}$		$1.00 \times 10^{-5}\text{M}$	
RUNS	% Fiber loss	% Adh. Removal	% Fiber loss	% Adh. Removal	% Fiber loss	% Adh. Removal
#1	6.7	99.0	7.5	99.5	10.8	98.2
#2	5.1	99.3	8.4	99.0	10.0	99.5
#3	4.9	98.8	8.6	99.2	10.5	99.0
Avg.	5.6	99.0	8.2	99.2	10.4	98.9

	Coeff. of Deter.	Mult. Corr. Coeff.	Slope	
Over all pts.	.90840	.95310	.973333	$F_{\text{calc}} = .3773$
Avg. of pts.	.99769	.99884	.960000	F_{calc} is not greater than 5.1433.

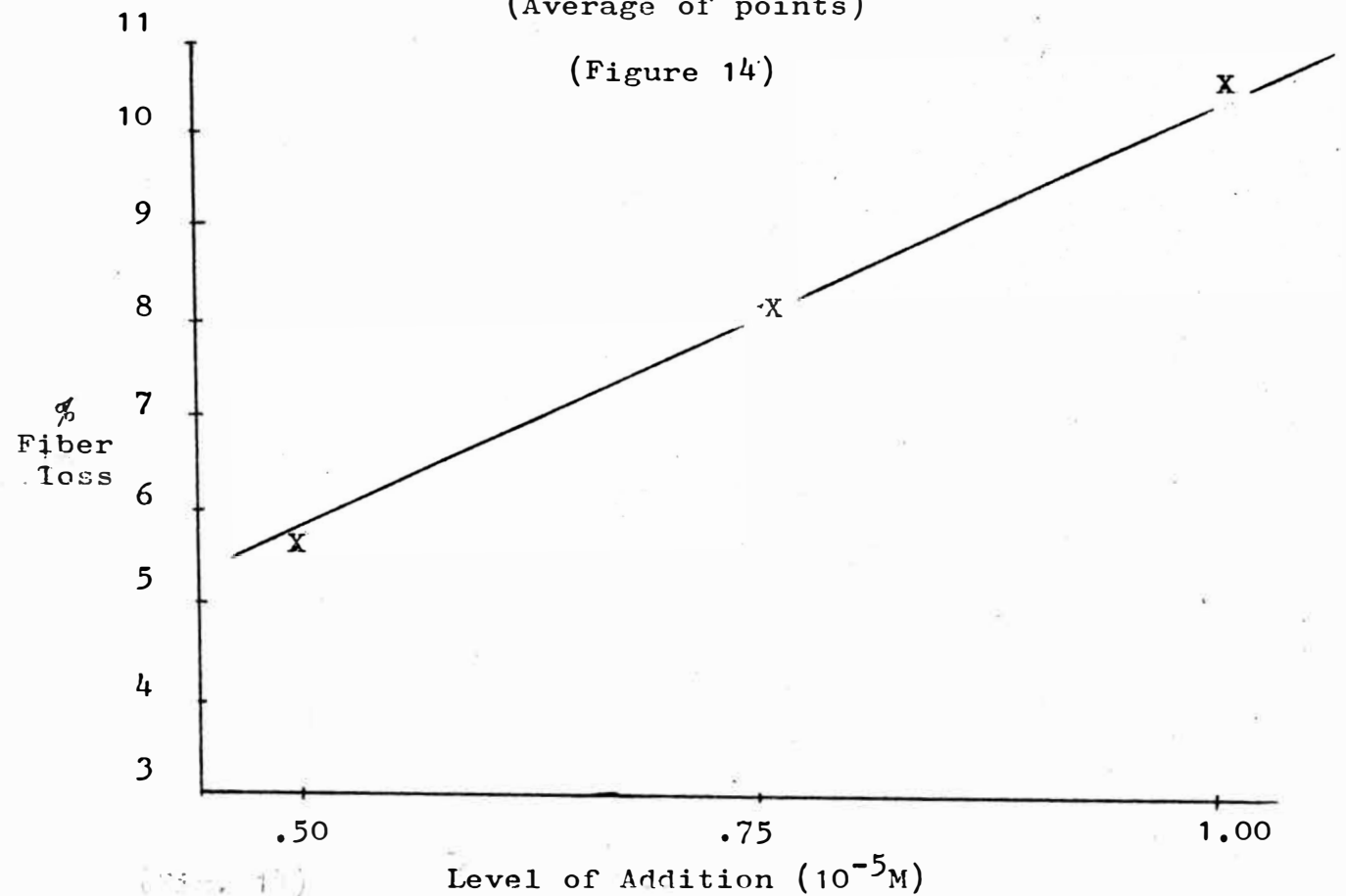
Discussion

Similar results were recieved for this surfactant

X-165 % Fiber loss vs. Level of Addition



X-165 % Fiber loss vs. Level of Addition
(Average of points)



as the other two (Figure 13 & 14). The only difference being a higher level of fiber loss.

General Discussion

No real difference in the % adhesive removal could be seen between each surfactant (99%+ removal). A linear regression was run on one of the surfactants, as mentioned, with a result of very little correlation.

Therefore no other regressions were run and the results were inferences obtained by comparing the raw data.

A general comparison of the surfactants showed that the slope of the N-100 was the smallest. The slopes on the X-114 and X-165 were larger and very close to being equal. Also, at the same level of addition the line for the X-165 correlated with a much higher fiber loss than the X-114.

CONCLUSIONS

In looking at the total picture, N-100 outperformed X-114 and X-165. N-100 had a smaller slope and therefore a smaller increase in fiber loss as the level of addition increased. Also it had the same amount of adhesive removal as the others while being added in a smaller amount. This could, in an industrial situation, have economic advantages depending on the cost of the surfactant.

The second best performer was X-114 which also had an excellent adhesive removal but a higher fiber loss.

Thirdly, the X-165 had the most fiber loss, even though it, as the others, had good adhesive removal.

It can then be concluded that an increase in the length of the hydrophobic chain on a nonionic surfactant can decrease the rate at which fibers will be lost when the oxyethylene group is varied in size and level of addition. It should be kept in mind that these results came from one type of adhesive. Whether all adhesives will react the same is not known.

SUGGESTION FOR FURTHER WORK

First of all it would be good to investigate anionic surfactants if the structural formulas and molecular weights can be found. Long hydrophobic groups either branched or linear, should be used as long as it is soluble in water. Also a study could be performed to find the difference in nonionic polyoxyethylenated alkylphenols and polyoxyethylenated straight chain alcohols. This would be a very interesting study since it would compare the performance of two different types of long chain hydrophobic groups on the % fiber loss and adhesive removal. These surfactants could also be compared as to how a varying size hydrophilic group effects the performance.

The effect of various temperatures and pH's could be studied in relation to how they effect adsorption of the surfactant on the adhesive. Finally the effect of lowering the level of surfactant addition to the point where there is a large drop in the % adhesive removal could be studied. This would show the point at which the performance of each surfactant becomes significant. This perhaps may be a good means of comparing surfactants.

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APPENDIX 1. DETAILED PROCEDURE

- 1) Use coating roll bar to make draw downs of adhesive on basestock paper. The adhesive is melted in a beaker under a hood for good ventilation.
- 2) Find the approximate weight of a 1" X 2" strip of base stock and use this as a tare weight .
- 3) Cut the base stock with the adhesive into 1" X 2" strips and weigh. Record the amount of adhesive on the strip. (The weight should be in the range of .102 - .1275 grams of adhesive since this would give a .2 - .25% range of adhesive in the cell based on 51 grams of pulp).
- 4) Disperse the strip in Waring blender for 30 seconds at high speed.
- 5) Place the beaten adhesive into 17 liters of .3% consistency pulp (50/50 H.W. & S.W. beaten to 500 freeness) with about 35 ml of NaSilicate. (use medium agitation).
- 6) Make 4 or 5 (3 gram) handsheets on the Noble & Wood handsheet machine to insure good replication. Dry the sheets on a hotplate between 2 blotter papers.
- 7) The specks in the sheet can be counted by making a grid of 64 in.^2 and counting the specks in each square.

Thus a total amount of specks for each sheet can be found.

8) Do various strips at different adhesive weights (.102 - .1275 gr) to find how many specks in a sheet correlate to each weight used.

9) Surfactant is added to the .3% pulp along with the NaSilicate under mild agitation. This is placed into the cell along with the beaten strip of adhesive also, under mild agitation to insure a good mixing.

10) The cell is run for 12 minutes with little or no make-up water added so that no residual fiber or adhesive will be lost simply because it overflowed the froth exit. (To be quantitative, just the froth should be skimmed off the top of the water so that the results show the actual amount of fiber and adhesive floated).

11) Collect the rejected froth in a bucket during the flotation. Filter through a Buchner funnel and dry the pad. Weigh the pad and compare the weight of fibers to the original amount of fiber in the system. (Subtract .1 gr from the pad to approximately account for the amount of adhesive in the pad).

12) The stock left after flotation, is removed and 3 or 4 (3gram) handsheets are made on the Noble & Wood.

13) The sheets are dried on a hot plate as before and the specks in each sheet are counted.

14) By comparing the amount of specks in a sheet to a standard base sheet which had approximately the same weight adhesive in it, a % adhesive removal can be found.

The formula used to calculate amount of surfactant added:

= level of addition

$$\frac{\# \times 10^{-5} \text{ mol}}{\text{Liter}} \times \frac{\text{gr}}{\text{mol}} = \frac{\text{gr added}}{\text{Liter}}$$

$$\frac{\text{grams}}{\text{liter}} \times \frac{\text{gals}}{\text{lb}} \times \frac{11\text{b}}{454 \text{ gr}} \times \frac{3.785 \text{ liters}}{\text{gal}} \times \frac{1000 \text{ cm}^3}{\text{liter}} = \frac{\text{cm}^3 \text{ added}}{\text{liter}}$$

Amounts of Surfactant Used.

Level
of.
Add.

N-100

.2X10 ⁻⁵ M	.4X5 ⁻⁵ M	.6X15 ⁻⁵ M
.0012 cm ³ /lit	.0025 cm ³ /lit	.0036 cm ³ /lit
1.3 ppm	2.6 ppm	3.8 ppm

Level
of
Add.

X-114

.75X10 ⁻⁵ M	1.0X10 ⁻⁵ M	1.25X10 ⁻⁵ M
.0038 cm ³ /lit	.0051 cm ³ /lit	.0063 cm ³ /lit
4.0 ppm	5.3 ppm	6.7 ppm

Level
of
Add.

X-165

.5X10 ⁻⁵ M	.75X10 ⁻⁵ M	1.0X10 ⁻⁵ M
.0042 cm ³ /lit	.0063 cm ³ /lit	.0084 cm ³ /lit
4.6 ppm	6.8 ppm	9.1 ppm