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## Prediction of Release Properties of Silicone Coated Paper Through Analysis of Coating Particle Size and Distribution

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Prediction of Release Properties of Silicone  
Coated Paper Through Analysis of Coating Particle Size and  
Distribution

By  
Kent Bartholomew

An Engineering Problem submitted  
in partial fulfillment of  
the course requirements for  
The Bachelor of Science Degree

Western Michigan University  
Kalamazoo, Michigan

December, 1989

## ABSTRACT

Silicone release coatings are gaining in popularity. The use of water-borne emulsions is seeing its way into the production of release coatings as well as pressure sensitive applications.

Thermoset silicone release coating systems consist of a reactive polymer, a crosslinker, and a catalyst. A condensation reaction takes place to form the low surface energy silicone film which is primarily what gives good release property.

It is believed that an emulsion's stability, and hence quality, can be related to the particle size and distribution.

It was the goal of this study to quantify the relationship between particle size/distribution and release properties of a silicone treated base sheet as the emulsion stability deteriorated. Some parameters that affect an emulsion's stability are temperature, pH, shear, and hardness of the water. The study was conducted by applying high shear over time keeping all the other parameters constant.

Over time, flocculation and coalescence of the particles indicated the emulsion stability to be deteriorating. This was evident by an increase in Kiel release values, percent flocs, average area of particles, and a decrease in coat weight and sub-adhesion.

These results confirmed the hypothesis that a correlation exists between particle size/distribution and that this can be used to predict release properties of silicone coated paper.

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## INTRODUCTION

The objectives of this study are: To develop a method by which the stability of a silicone emulsion can be determined using microscopy and image analysis, and to study the relationship between bath stability and release properties of a silicone treated sheet.

This problem attempts to quantify the relationship between particle size/distribution and release properties of a silicone treated base sheet as the emulsion stability deteriorates. This will be accomplished by the use of light microscopy and image analysis. It is proposed that a correlation will exist that can be used to predict (by particle size and distribution) release properties of a silicone coated base sheet which can be used for quality control of the final product.

## BACKGROUND DISCUSSION

### COLLOID CHEMISTRY

According to Hiemenz (1), any particle which has some linear dimension between 0.1 nm and 1  $\mu\text{m}$  is considered a colloid. Linear dimensions rather than particle weights or the number of atoms in a particle will define the colloidal size range. Colloid chemistry is interdisciplinary in many respects; its field of interest overlaps physics, biology, materials science, and several other disciplines. It is the particle dimension-not the chemical composition, sources of the sample, or physical state, that is of importance. It is evident that colloid chemistry is the science of both large molecules and finely subdivided multiphase systems.

Hiemenz (2) noted that either large molecules or finely subdivided bulk matter could be considered colloids inasmuch as both may consist of particles in the size range mentioned earlier. The difference between the two situations lies in the relationship between the colloidal particle and the medium in which it is dispersed.

The terms lyophilic and lyophobic are used to distinguish between one-phase and two-phase colloidal systems, respectively. These terms mean "solvent loving" and "solvent fearing". When water is the medium, the terms hydrophilic and hydrophobic are often used.

Hiemenz (3) states that two-phase dispersions will always spontaneously change into a smaller number of large particles,

given sufficient time. It should be noted that many solutions of macromolecules do not undergo spontaneous separation into two phases. The first is described as being "unstable" and the second as being "stable".

Two-phase colloids are thermodynamically unstable with respect to the coarsening process. It is important that we define this coarsening, specifically coalescence and flocculation. Coalescence is the process where two (or more) small particles fuse together to form a single larger particle. The central feature of coalescence is the fact that total surface area is reduced. Flocculation is the process where small particles clump together like a bunch of grapes (a floc) but do not fuse into a new particle. In flocculation there is no reduction of surface, although certain surface sites may be blocked at the points at which the smaller particles touch. When small particles coalesce, all evidence of the smaller particles is lost, only the new larger particle remains. With flocculation the small particles retain their identity: only their kinetic independence is lost. The floc moves as a single unit.

#### SILICONE EMULSIONS

According to Keiser (4) the European and US market for silicone-coated release liners is estimated between 475,000 and 525,000 tons. This estimate includes all silicone-coated release liners, not just those used in the pressure-sensitive adhesive markets. In addition to pressure-sensitive applications, release liners are used for processing candy and bakery goods,

interleaving unvulcanized rubber, packaging roofing tar, and releasing cast film and foams. In general, silicone release liner technology is similar for all of these end uses.

Fey and Wilson (5) state that thermoset silicone release coating systems consists of a reactive polymer, a crosslinker, and a catalyst. Two cure systems are available, one based on the condensation reaction and another on an addition reaction. The condensation system will be discussed in this paper.

The greater processing latitude of the condensation system is the result of refinements developed throughout its 25-year history. The condensation reaction takes place between a silanol-functional polymer and a silane-functional crosslinker in the presence of a catalyst (9) (see Appendix A). Moisture must be present for the reaction to take place at the normal rate. Normal atmospheric humidity is usually sufficient, except in dry climates or at low temperatures.

The reaction will take place at room temperature, so the catalyst must remain separate from the polymer system until it is ready for use. Heat accelerates the reaction, and the silicone cures to a nonmigration state within 20 to 30 seconds at 120 to 150 degrees centigrade (5).

The most commonly used catalyst is dibutyltin diacetate, although other dialkyltin esters may be used. They are not true catalysts. The esters hydrolyze during the reaction, eventually ending up as diorganotin oxides (5).

In a roll of coated substrate in the presence of heat, moisture, and pressure, the reaction can reverse direction. This



is more pronounced in the presence of excess tin catalyst. Fortunately, the extent of the positive, forward reaction is always greater than the reverse reaction (9) (see Appendix A).

According to Fey and Wilson (6) one of several important physical properties contributing to the release characteristics of the silicone polymer is its low surface energy, only 22 to 24 dyne/cm compared to a range of 30 to 50 dyne/cm for most organic adhesives. This differential helps prevent the two from bonding tightly by preventing the adhesive from intimately wetting the silicone surface. The result is enough adhesion to keep the adhesive in place, yet not enough to prevent easy parting of the silicone-adhesive interface.

### Water-Borne Systems

As stated by Fey and Wilson (7) aqueous emulsion silicone release coatings have been used mostly for non-pressure-sensitive applications. Some applications include releasing sticky products such as rubber or asphalt from containers and as sheets for sticky foods such as baked goods and candy. The development of faster, more stable cure systems and more shear stable water-based systems for coatings has led to some limited use in pressure-sensitive products. Some tapes, pressure-sensitive floor tiles and vinyl wall coverings have emulsion-coated release liners.

Emulsion-based release coatings are limited to low or medium molecular weight silicone polymers and are manufactured by mechanical emulsification or by emulsion polymerization. The

polymers, the catalysts and the range or release values attainable are more limited than with solvent-based systems. Typically, emulsion systems are cured for 30 to 40 seconds at 120 to 150 degrees centigrade.

Water borne silicone emulsions are used on a limited number of substrates. The most common being machine finished kraft for pressure sensitive applications. Bag kraft and parchment are coated for non-pressure-sensitive applications.

#### Emulsion Quality

According to Peters (8) it is believed that the stability of an emulsion, and hence its quality can be related to the particle size and distribution. The emulsion under study comes in two parts, one is the silicone polymer and catalyst, the other is the silicone polymer and crosslinker.

As stated by Peters (9) an emulsion is two phases of completely immiscible liquids; one is dispersed as finite droplets in the other. The oil droplets (discontinuous phase) are mixed with the water (continuous phase) and dispersed by mechanical shearing, making droplets. Silicone emulsions are of coarse colloid type with the average particle size being 2-3 microns. Polyvinylalcohol (PVA) is added as stearic stabilizer for the droplets. A surfactant is added to provide a negative charge which aids the emulsifying process and stability of the particles.

According to Clapp (10) an emulsion of finely dispersed particles when applied to a substrate and cured should result in

good release properties. If the stability of the emulsion decreases (coalescence/flocculation), the particle size becomes more coarse and the probability of the two different particles (polymer and crosslinker) reacting with one another is decreased. This could result in a loss in release properties.

Peters (8) stated that during the curing process, water is boiled off and a phase separation takes place. The silicone is crosslinked and tends to migrate toward the top of the coating since it is hydrophobic and the PVA migrates towards the paper interface since it is hydrophilic.

Peters (9) stated some parameters that should be controlled to insure that a well-dispersed emulsion will be applied to the substrate are; temperature, shear, pH and hardness of water. An increase in temperature reduces the surface tension of water allowing the particles to coalesce and cause polymerization in the emulsion. An increase in shear can be responsible for the catalyst and coating to prematurely coalesce. This increase in shear will accelerate the particles to the extent that their kinetic energy will surpass the negative potential and stearic stabilization existing between the particles and they will collide with one another. The hardness of the water will detract from the negative charge by the presence of positively charged calcium ions thus causing the emulsion to coagulate. Too high or low a pH disrupts the emulsion stability by upsetting the outer charge surrounding the particles or the chemical reactions.

The primary method of increasing the particle size and observing what effect this has on the release properties will be

to adjust the amount of shear in the emulsion to create coalescence and flocculation over a period of time. All other parameters will be kept as constant as possible.

#### PARTICLE SIZE DETERMINATION

According to Hiemenz (11) in an emulsion the dispersed particles are spheres of great polydispersity. The average particle size is at the upper end of the colloidal size range (on the order of micrometers) and the particles are usually visible in a light microscope. They can be described as "coarse emulsions" when we want to emphasize their size range. Because the particles are relatively large and polydisperse, coarse emulsions look white when examined visually. The fact that particles in the colloidal size range are not all identical in size also requires a statistical study.

As stated by Hiemenz (12) because of the particle sizes involved, the microscope is an instrument which is ideally suited for the study of some hydrophobic colloids. For a particle to be visible, there must be an acceptable difference between its refractive index and that of its surroundings. This requirement has nothing to do with particle size.

The first thing we tend to think of in connection with microscopes is the magnification they achieve. More important, however, is a quantity known as the resolving power, or limit of resolution, of the microscope. Magnification determines the size of an image, but the resolving power determines the amount of distinguishable detail. Enlargement with out detail is of little

value. Both the depth and area of the in-focus field decrease as the magnification is increased, so one pays a price for enlargement, even though the amount of perceptible detail is not affected much by the magnification.

## PRESENTATION OF PROBLEM

It is believed that over time the stability of a silicone emulsion deteriorates due to increased flocculation and coalescence. This deterioration of the emulsion results in the release properties of the coated sheet to degrade. The objective of this study is to develop a method by which the particle size and distribution of a silicone emulsion can be determined and to relate these to bath stability and release properties. Quantifying the relationship between particle size/distribution and release properties of a silicone treated base sheet as the emulsion stability deteriorates will be accomplished by the use of light microscopy and image analysis.

## EXPERIMENTAL

### DESIGN

This problem was approached by trying to keep the coat weight as constant as possible and choosing an upper limit of 150 for the Kiel release. Coat weight will effect release properties and a Kiel over 150 is deemed unsatisfactory for final release properties.

A silicone emulsion was prepared and subjected to constant shear, temperature, and pH. Samples were taken at designated time periods and photographed using a light microscope. Samples were also taken to determine the percent flocs. In addition draw downs were made for Kiel and Sub-Adhesion tests. Particle size and distribution were determined from the photographs using an image analyzer.

### PROCEDURES

#### Preliminary Tests

A) Testing was done and it was found that a zero Mayer rod would result in the required 0.5 lb./ream coat weight necessary for the experiments.

B) A preliminary test of release properties was performed on the emulsion and it was found that the Kiel release values exceeded the limit of 150 g/in. in three hours at constant shear, pH, and temperature. A value in excess of 150 is deemed unsatisfactory for final release properties. The Kiel release is a measurement of the force required to remove an adhesive tape from a surface

using an Instron tensile tester. The Subsequent Adhesion is a measurement of how well the silicone remains on the substrate after peeling the adhesive off. The higher the value the more silicone remains on the substrate. This value is obtained by the same methods for Kiel release except the adhesive removed from the substrate is then applied and removed from a metal plate.

#### Particle Size and Distribution and Floccs

A) The emulsion consisting of a Dow 1171 silicone and a Dow 1171A tin catalyst was prepared at a 14:1 ratio, respectively. The emulsion was subjected to constant shear using a Hamilton Beach blender. The pH was controlled at 7 using acetic acid if too high and sodium hydroxide if too low. The temperature was controlled at 75 F with the use of a water cooled coil. At one hour increments, a small amount of emulsion was removed, diluted 10:1, and photographed at 400x using an optical light microscope.

B) Drawdowns were made at one hour increments on 30# parchment and cured in a 250 F oven for 45 seconds. 20 hour Kiel release tests and Subsequent Adhesion (Sub-A) tests were performed and the results recorded.

C) Steps A and B were repeated on new emulsion and the Kiel and Sub-A values were averaged.

D) The mean particle area, total area, and distribution were measured from the photographs using an Omnicon 3600 image analyzer and the results for each time were averaged (see Appendix B for explanation of Image Analyzer procedure).

E) Two separate runs were performed on the emulsion under



previously stated conditions. The percentage of flocs was determined by passing the emulsion through a 325 mesh screen. The percentage of flocs was the percent by weight that was unable to pass through the screen. The values from both runs were averaged and recorded.

## PRESENTATION AND DISCUSSION OF RESULTS

Table I presents the statistical data from the image analysis of the emulsion at different times of shear and Figs. 1-6 show the relationship between shear time and the mean particle area.

The results in Table I and Figs 1-6 indicate that over time, the mean particle area increases. In addition to an increase in mean particle area over time, the total area and distribution (min./max.) increased as seen in Table I. The increase in the distribution can be attributed to increased flocculation and coalescence. When an emulsion starts to become unstable or starts to become more "coarse", both flocculation and coalescence tend to increase.

The increase in total area is contrary to the theory that as the particles increase in size through coalescence the total area decreases. This increase in total area was due primarily to the larger number of particles measured.

Table II and Figs 7-9 present the relationship between shear time and release properties, coat weight, and percent flocs respectively.

The results in Table II and Fig. 7 show that as the emulsion became more unstable over time, the Kiel release values increased.

It is proposed that as the amount of flocs and larger particles increased over the first hour (.25 to 1.25 hours) the curing process was hindered, thus the final release properties were degraded. The curing process relies on the intimate contact

Table I- Statistical Data on Particle Area (sq. mm.)

Time of Shear (hrs.)	.25	1.25	2.25	3.25
Count	861	1144	1726	887
Min:	3.84E-07	3.84E-07	3.84E-07	3.84E-07
Max.	2.92E-05	1.5E-03	9.91E-04	9.8E-03
Total:	1.63E-03	3.79E-03	8.44E-03	1.6E-02
Mean:	1.89E-06	3.31E-06	4.89E-06	1.8E-05
StDev:	2.93E-06	4.58E-05	4.49E-05	3.46E-04

Time of Shear (hrs.)	4.25
Count	918
Min:	3.84E-07
Max.	3.42E-02
Total:	4.22E-02
Mean:	4.59E-05
StDev:	1.14E-03

of individual particles to crosslink and form a uniform continuous film of silicone. If the particles applied to the sheet are larger in size, this might reduce the chances for intimate contact.

In addition it is felt that some cross-linking took place in the emulsion during shearing, which rendered that component less efficient when applied to the substrate and then cured.

Table II shows that between 1.25 hours and 4.25 hours of shear, the Kiel release values and percent flocs increased, while the coat weight decreased. The increase in Kiel values resulted mainly from the coat weight decrease which can be seen in Fig.8. The coat weight decrease was caused by the increase in percent flocs which can be seen in Fig. 9. As the percent of flocs increased, the application of the emulsion on the substrate became reduced in coat weight due to the removal of the silicone flocs with the Mayer rod. It is suggested that further studies be conducted to maintain the coat weight at a constant value by increasing the Mayer rod wire diameter.

Table II and Fig. 7 show that the sub-adhesion values decreased then increased over time. Between times 0.25 and 1.25 hours, the Sub-A value decreased. One possible reason for the decrease in value can be attributed to poor bonding of the silicone to the substrate during the curing process. After 2.25 hours, the increase in Sub-A can be attributed to low coat weight.

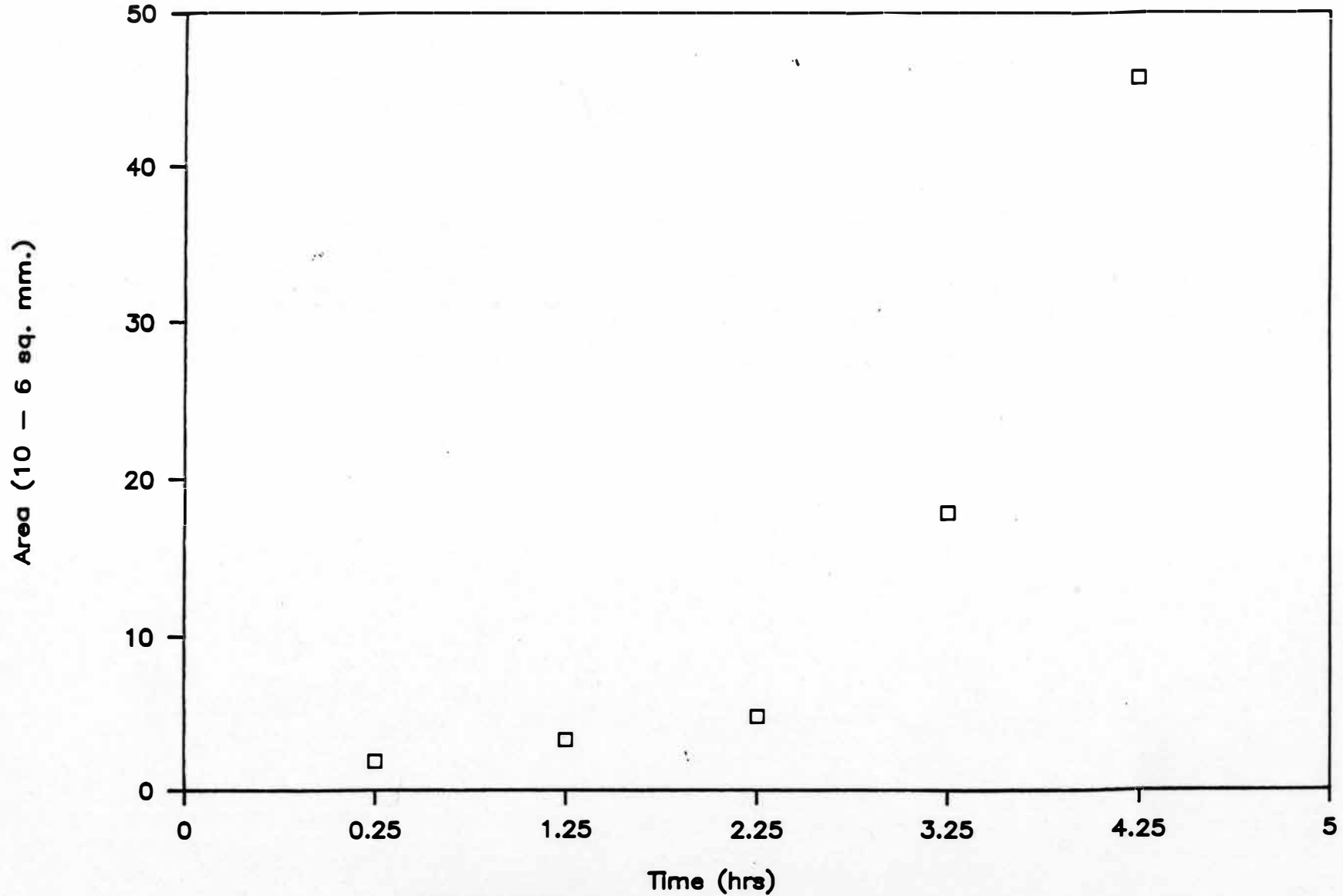


Fig. 1 - Relationship between mean particle area and shear time.

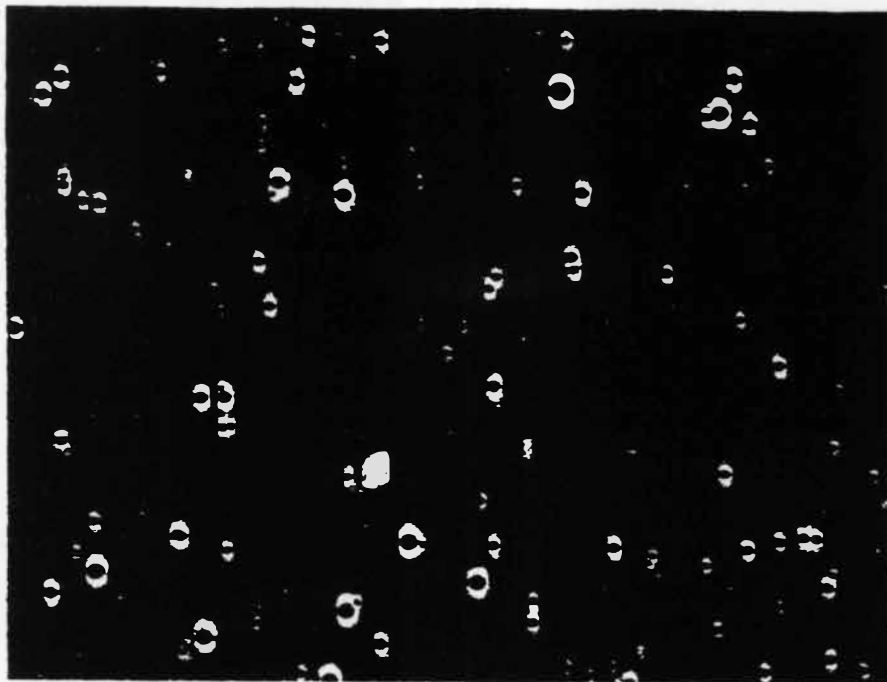


Fig. 2 - Photograph from light microscope (400x) of silicone particles after .25 hours of shear.

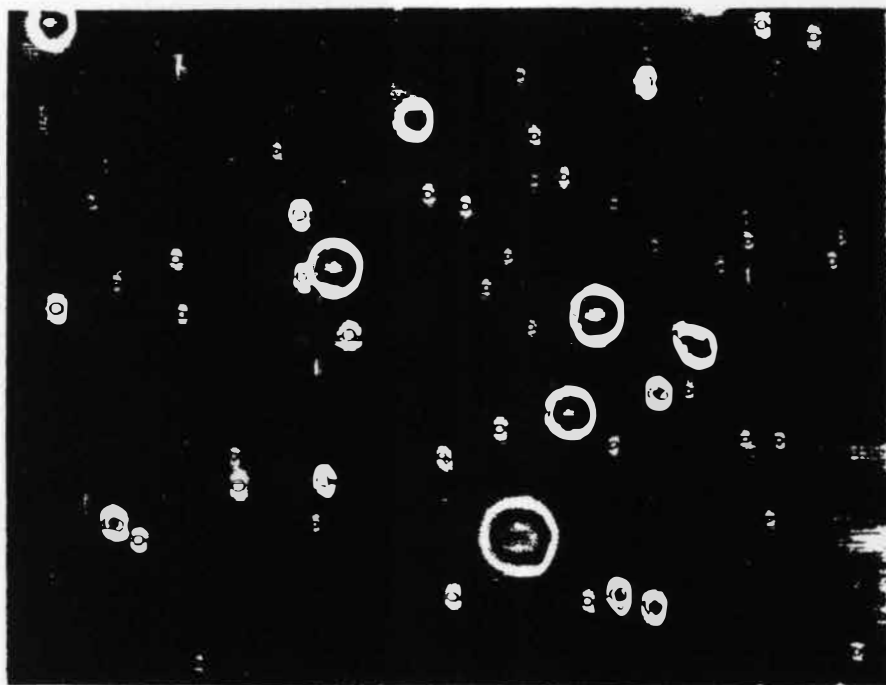


Fig. 3 - Photograph from light microscope (400x) of silicone particles after 1.25 hours of shear.

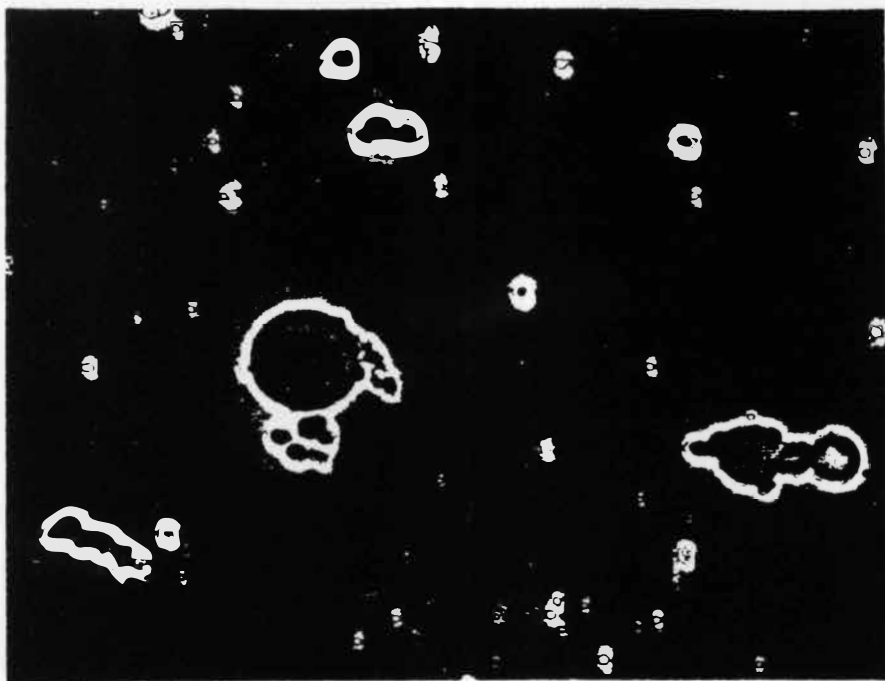


Fig. 4 - Photograph from light microscope (400x) of silicone particles after 2.25 hours of shear.

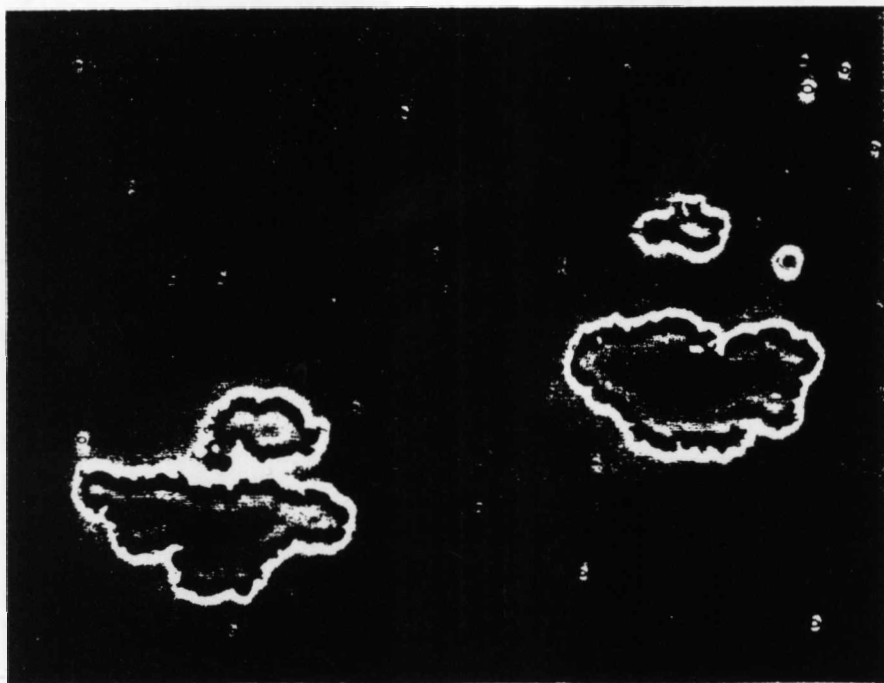


Fig. 5 - Photograph from light microscope (400x) of silicone particles after 3.25 hours of shear.



Fig. 6 - Photograph from light microscope (400x) of silicone particles after 4.25 hours of shear.



Table II - Results of Kiel Release Values , Subsequent Adhesion Coat Weight, and Percent Floccs.

Time (Hrs.)	Kiel (g/in)	Subsequent Adhesion (g/in)	Coat Wgt. lbs/ream	Percent Floccs
0.25	29	565	0.53	0
1.25	43.5	470	0.54	2.6
2.25	135	345	0.34	9.9
3.25	313	585	0.11	62.7
4.25	320	633	0.004	79.5

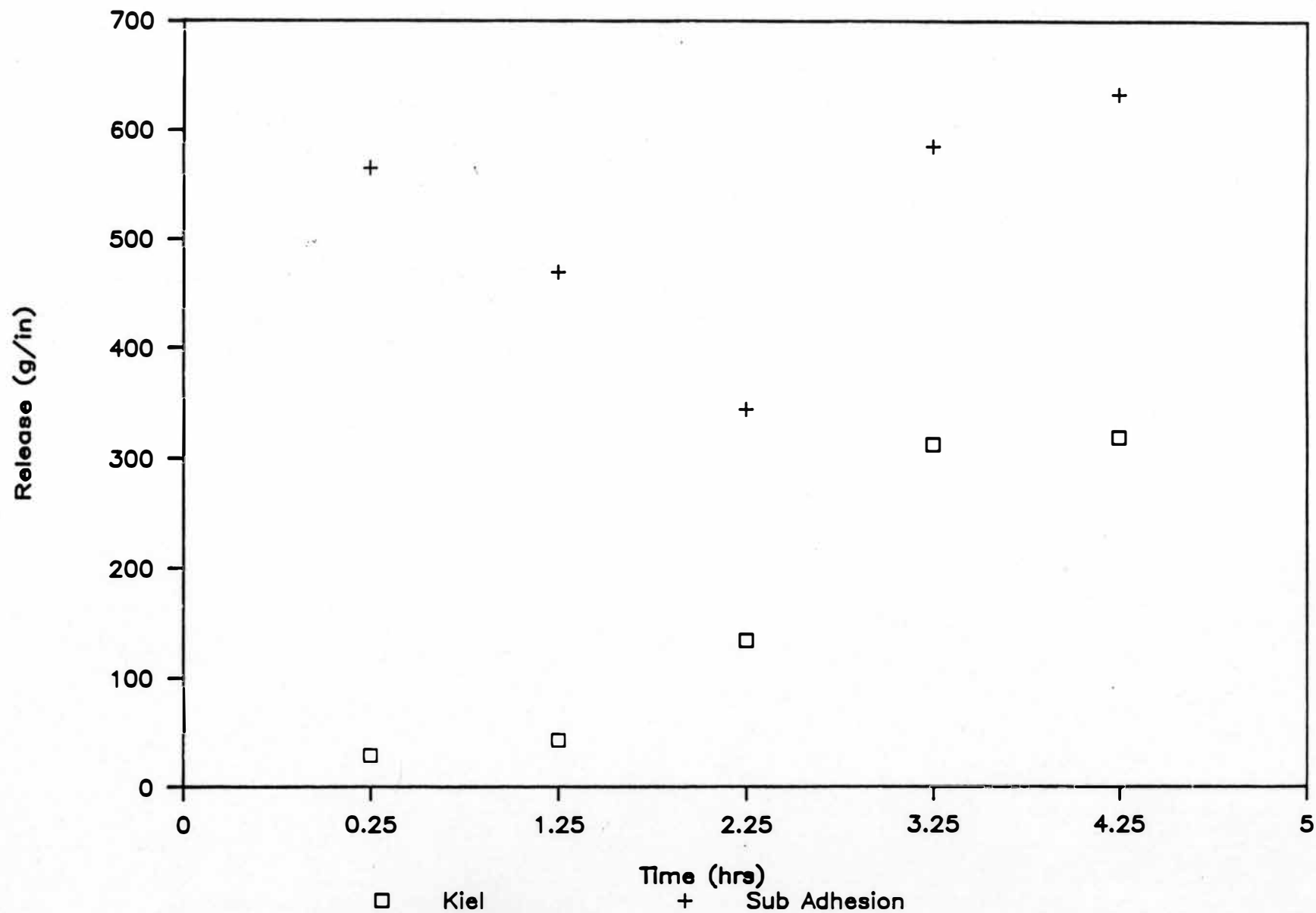


Fig. 7 - Relationship between release values and shear time.

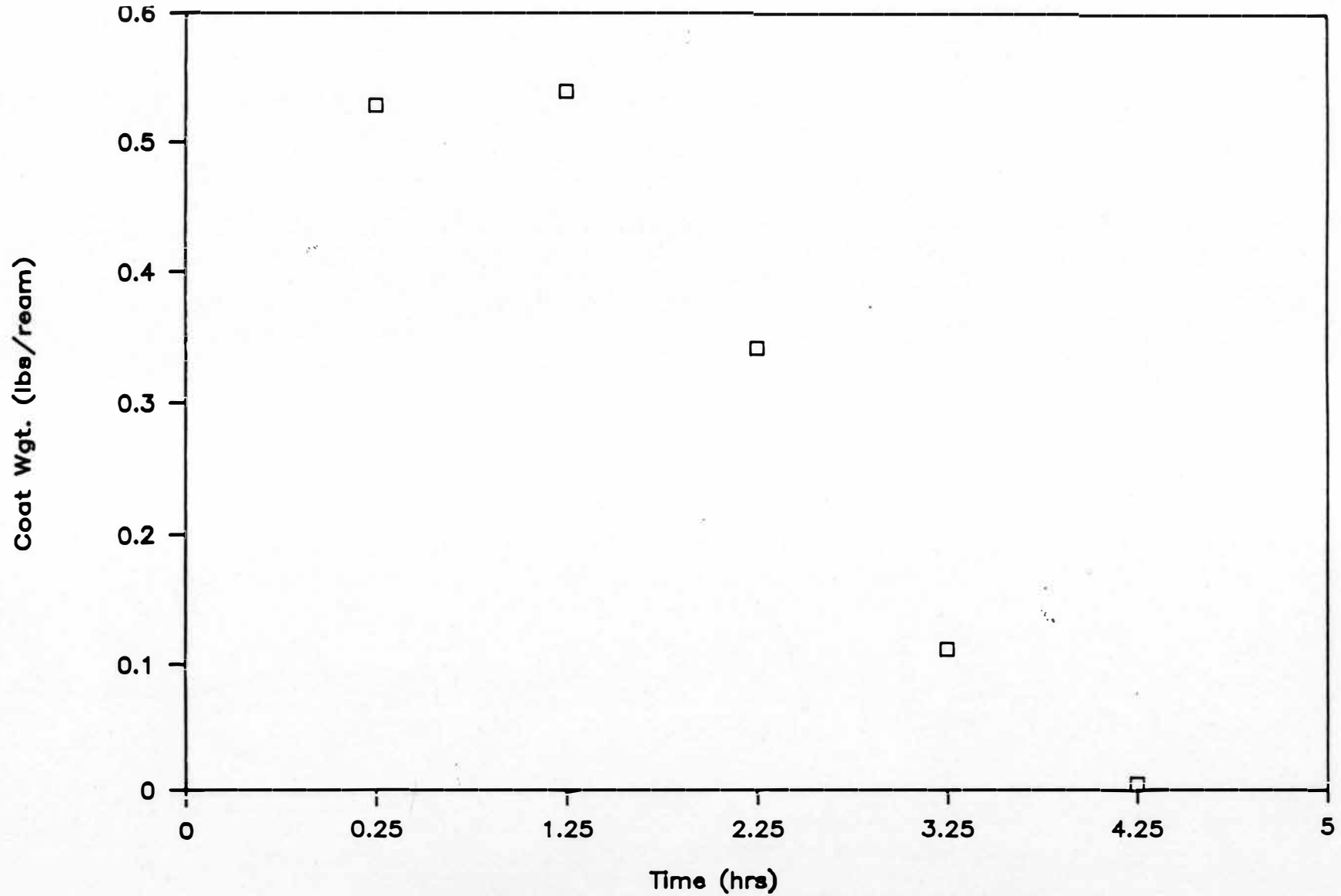


Fig. 8 - Relationship between coat weight and shear time.

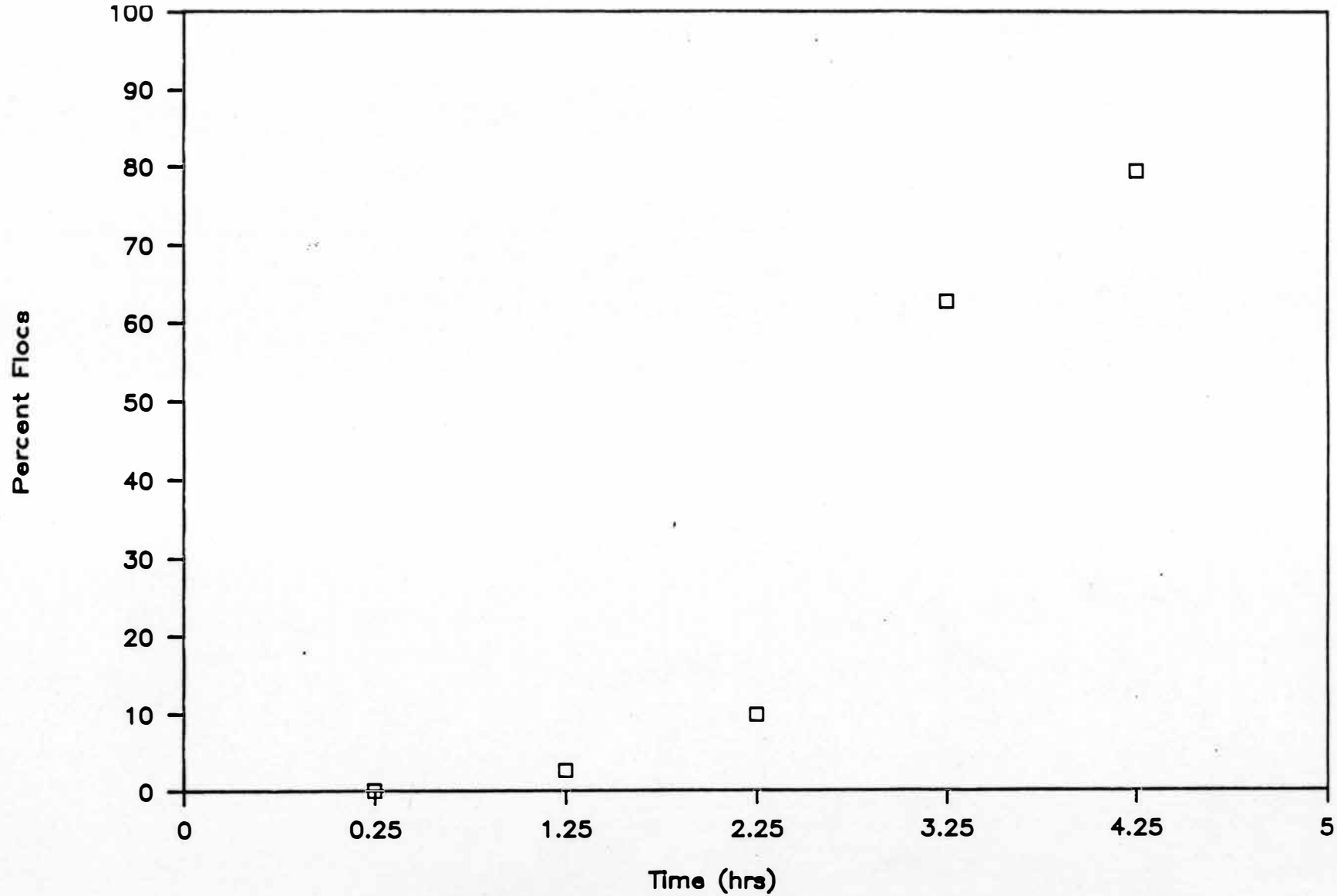


Fig. 9 - Relationship between percent flocs and shear time.

### CONCLUSIONS

It can be concluded that as the time of shear increased, the increase in flocculation and coalescence increased the mean particle area , distribution, and the total particle area (due mainly to an increase in the number of particles measured).

As the flocculation and coalescence of the particles increased in the early stages, the curing of the silicone was probably reduced resulting in the Kiel release values to increase. The increase in Kiel values in the later stages was caused by reduced coat weight due to an increase in percent flocs.

The Subsequent adhesion values decreased in the early stages probably due to poor cure and increased in the later stages due to low coat weight resulting from an increase in percent flocs.

It can be concluded that there existed a correlation between particle size/distribution and that this can be used to predict release properties of silicone coated papers.

## LITERATURE CITED

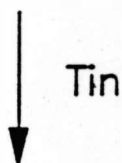
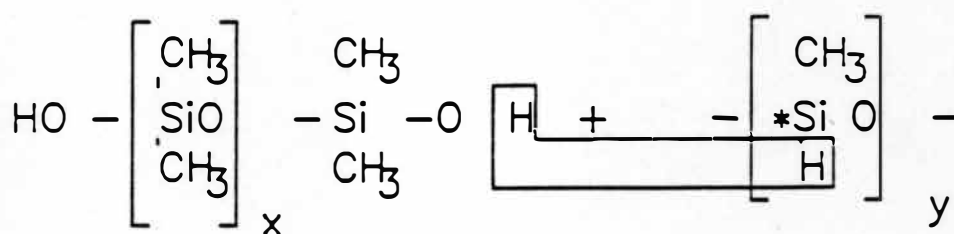
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## APPENDIX A

### Condensation Reaction Chemistry

## Chemistry

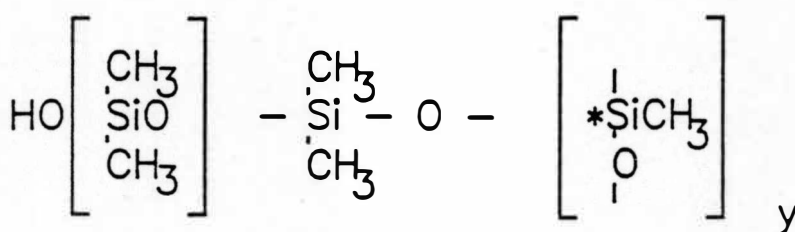
TIN CATALYZED PRODUCTS  
 SILANOL CONDENSATION CURING CHEMISTRY (9)



Crosslinked  
Polymer  
(Rubber)

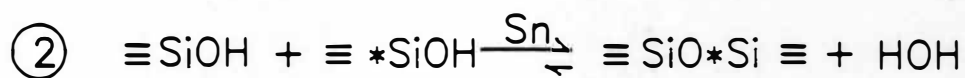
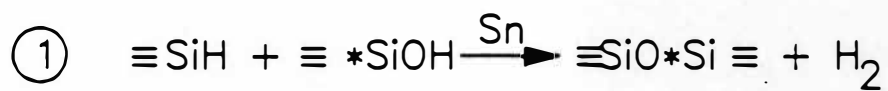
+

H<sub>2</sub>





## PRIMARY REACTIONS (9)



a)  $\xrightarrow{\text{Sn}}$  post cure

b)  $\xleftarrow{\text{Sn}}$  leads to cleavage of  $\equiv\text{SiO*Si}$  and blocking

## APPENDIX B

### Use of Omnicon 3600 Image Analysis System

## USE OF THE OMNICON 3600 IMAGE ANALYSIS SYSTEM (13)

The Omnicon uses a black and white video camera to make the gray level images that are needed for the measurements. This camera uses various lenses. The lenses used with the camera are for macroscopic samples (i.e. stickies in a handsheet) that do not require a great deal of magnification to produce a usable image. A good rule of thumb is if the smallest known particle can be seen unaided then lenses should be used. Since the photographs of the silicone emulsion were taken at 400x, which were visible to the naked eye, lenses were used.

The lighting used was from overhead lamps which were effective for the camera/lens setup. The light sources were adjusted to give the best contrast to produce the gray level image.

The program used for this analysis was the Omnicon Image Analysis which contains all the properties for measuring particles or fiber groups. Measurements such as total area, particle count, minimum size and maximum size are done with this program.

After the correct program was selected and the system was allowed to warm up, the shading corrector was adjusted to read 100% by repositioning the lighting and adjusting the aperture on the camera. This procedure produced a very distinctive image of the silicone particles.

Calibration was performed on the Macro Viewer Chart. This chart consist of a series of circles of known diameter. A circle of 6.246 mm diameter was chosen as this best fitted the size of the particles on the photographs to be measured. Because the photographs were taken at 400x, the 6.246 value was divided by 400 to arrive at a value representative of true particle size of the silicone emulsion. This value was entered into the image analyzer as a reference.

From the main menu, area was chosen as the measurement and the statistical results were printed out. Area was chosen to take into account any flocculation that was present as the analyzer has difficulty in distinguishing between two or more particles in contact with one another. Statistics such as count, average particle area, min./max. particle area, total area of particles, and standard deviation were used to compile the results in Table I.