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ABSTRACT

Interfacial properties of toner are important characteristics for flotation. Specifically, the degree of hydrophobicity will influence whether a particle will be floated or not. A fundamental indication of the hydrophobicity is the contact angle.

The contact angles of various deinking liquors were measured against toner. A method to prepare samples for contact angle measurements was developed and validated by surface analysis. The analysis also showed the toner surface to be free of iron oxide, despite the significant iron oxide content of the toner. The contact angles decreased with increasing surfactant concentration when single surfactants were used. The combination of a fatty acid with calcium chloride maintained a high contact angle through the formation of soap flakes. The addition of a fatty acid with calcium chloride to the non-ionic surfactant resulted in higher contact angles than the non-ionic surfactant itself.

An optimal addition of non-ionic surfactant for maximum removal by flotation was observed. The optimal level represents the formation of a froth layer with a minimal decrease of the toner contact angle. Addition of a fatty acid collector along with the non-ionic surfactant led to decreased removal compared to the non-ionic surfactant alone, even though the contact angles for the combination were higher. The combination of fatty acid and calcium alone produced good results due to the formation of soap flakes which maintained the toner's hydrophobicity. Also, even though very little froth was formed in this case, a stable layer consisting of soap flakes, fibers, and toner formed, allowing the toner to be removed.

KEYWORDS
interfacial properties, toner, flotation, deinking, contact angles

INTRODUCTION

Deinking chemistry describes the role of chemistry and chemicals on deinking of waste paper (1, 2). Fundamentally, deinking chemistry can be broken down into two areas: interfacial properties of the components in the furnish and bleaching of the furnish. While the importance of interfacial properties has been widely stressed, the fundamentals of this aspect of deinking have been studied rarely in the published literature. It is the purpose of this work to address some fundamental aspects of flotation deinking of toner.

Flotation is a prime example of a process strongly influenced by interfacial properties. Flotation deinking of waste paper separates contaminants from paper fiber by selectively attaching the contaminant particles to air bubbles that float to the surface and are removed in a layer of froth. Flotation theory explains that for particles to be removed from a furnish, they must be more hydrophobic than the remainder of the furnish (3, 4). Flotation should be a very effective method to remove toner due to the hydrophobicity of the toner (5). In addition, the size distribution of the particles formed upon repulping predominantly falls within the reported size range for effective flotation (2). However, both mill operations and laboratory studies have shown that toner removal is limited. Since the interfacial properties of toner are favorable for flotation, it is believed that removal is limited due to modification of the interfacial properties during the process, the wide size distribution of toner particles and their plate-like shape, and the retention of hydrophilic fibers to toner after repulping (5-10). These characteristics may vary greatly, depending on the furnish and treatment of the furnish. This has hampered a fundamental understanding of flotation deinking. Since treatment through the addition of chemicals may adversely affect the interfacial properties, this paper will address the addition of surfactants on the interfacial properties of toner.

BACKGROUND AND THEORY

Several steps are involved in flotation, including the approach and attachment of bubble and particle, stabilization of the bubble-particle aggregate, transport of the bubble-particle aggregate to the slurry surface, and removal of the aggregate in a froth layer (4). The focus of this work is to investigate the stability of bubble-toner particle aggregates in various deinking solutions.

The stability of a bubble-particle aggregate can be described in terms of a balance of forces on the aggregate. Particles are stabilized by the capillary force along the contact perimeter which counteracts the forces that tend to pull the particle back into the liquid (4, 11). During and after stabilization, the bubble-particle aggregate rises to the surface, due to buoyancy forces. For effective flotation, aggregates must be strong enough to withstand the detaching forces including gravity, capillary pressure in the bubble, hydrodynamic forces, and inertial forces. Models show that a number of parameters affect the net force including the particle density, particle size, bubble size, contact angle, surface tension, and penetration distance of the particle into the air bubble (4, 11). In this work, we consider the effects of the contact angle and surface tension on the capillary force.

Figure 1 shows a model of bubble attachment to a planar solid surface. The planar solid surface represents a toner particle, although the actual toner particles may be smaller than the bubble. Additional models exist for the attachment of bubbles to spherical and prismatic particles, which may more closely describe the toner system (4, 11). However, this planar surface model shall suffice here. The capillary attachment force is given by (12, 13):

$$F_a = \pi d \gamma_{lv} \sin\theta \qquad (1)$$

Here F_a is the force of attachment (dynes); d is the diameter of the contact between the bubble and particle (cm); γ_{lv} is the liquid surface tension (dyne/cm); and θ is the contact angle measured through the liquid. Stratton has rewritten this equation in terms of the bubble diameter before attachment, D (12, 13). The simplified equation is valid for contact angles less than 60°:

$$F_a = \pi D \gamma_{lv} \sin^2\theta \qquad (2)$$

From experimental data, Stratton found a critical attachment force for the flotation of stickies and toner, above which there was little change in removal efficiency and below which there was a large decrease (12, 13). These equations show that the contact angle and surface tension should be kept high for a strong attachment force to facilitate flotation. To promote high contact angles, surfactants termed collectors are used. The collector makes particles sufficiently hydrophobic to be removed for the given flotation conditions by preferentially adsorbing with a proper orientation on the particle's surface (1, 2). In general, collectors should not be necessary for the flotation of already hydrophobic particles. Epple and Berg found that the contact angle of surfactant solutions against toner decreased with increased concentration, due to increased adsorption of surfactant on the toner surface (14). The contact angles were measured on fibers of toner that were drawn from a melt and not subjected to the conditions in the printing process. Ling found similar contact angle results for stickies, which were shown to be similar to toner in terms of their hydrophobicity (15). It is expected that the decrease in contact angle would adversely affect flotation due to a decrease in attachment force.

The contact angle, however, is not the only governing factor in flotation. Hornsby and Leja give a number of examples of fundamental studies that contradict a direct comparison between contact angles and actual flotability of particles (3). Snyder *et al.* found no relation between flotation results and contact angles for the flotation of eight different types of toner with three different collectors (5). The toner samples for contact angle measurements were made by the same method of Epple and Berg. Even though the variation of the contact angle against the different toners was small, the amount of toner removed varied greatly, indicating that other factors influenced flotation efficiency. It was proposed that the size and shape of the toner and the retention of fibers onto toner are important. In addition, all of these workers present the idea of the importance of maintaining the hydrophobicity of the contaminants while adding surfactants to generate a froth layer that is stable enough for flotation.

The froth layer is important to carry the floated particles away from the surface and prevent them from re-entering the slurry. However, the mere presence of a froth layer is not necessarily sufficient, and one must consider the transport of particles in the froth (3). The froth layer should be stable enough to overflow the cell without releasing the attached hydrophobic particles while allowing the drainage of water that carries the hydrophilic particles. To create a stable froth, surfactants (typically non-ionic) termed frothers are added to the furnish. In addition, the frother may also promote the development of smaller bubbles and assist bubble attachment (3). In the case of flotation of hydrophobic particles, a frother should be the only necessary additive. Dorris and Sayegh found the addition of a small amount of non-ionic surfactant to work very well for the flotation of toner (16). It is believed that the surfactant played the role of a frother without significantly reducing the hydrophobicity of the toner.

The literature indicates the importance of physical characteristics of the toner particles to explain variability in flotation efficiencies. It is believed that the particles formed upon repulping are significantly different in terms of their size, shape, and the retention of fibers onto the particles. However, interfacial properties still play a key role: hydrophobicity must be maintained. This is an important consideration, especially in mixed furnishes in which higher surfactant additions may be necessary. In order to optimize deinking chemistry, we must understand the fundamental effects that the addition of surfactants have on the furnish. Surfactant development, for example, could be greatly facilitated if contact angles could be used for characterization. Flotation experiments are tedious and often difficult to interpret.

This work investigates the contact angle of model deinking solutions against toner and the effects that the solution composition have on the contact angle. Model toner surfaces for contact angle measurements are produced and compared with a real printed-toner surface. The removal of toner by flotation and the effects that the solution composition have on removal are also investigated and compared with the contact angle results.

EXPERIMENTAL METHODS

The toner used here is the Kodak Monocomponent 90 toner. This toner consists of a polyester resin (50-55 wt.%), an iron oxide pigment (35-40 wt.%), and salicylic acid chromium chelate as an additive.

Surface Tension and Contact Angles.

Samples for contact angle measurements were made by copying multiple layers of toner onto both sides of a transparency, then fusing the toner further by heating in an oven at 150°C for 30 minutes. This was necessary to smooth the toner surface for contact angle measurements. Figure 2 shows scanning electron micrographs of the improvement in the contour of the surface after heat treatment. Electron spectroscopy for chemical analysis (ESCA) was used to analyze the surface to determine if the heat treatment affected the chemical composition at the surface.

The surfactants used were Triton®X-100 (Aldrich) and sodium oleate (J.T. Baker, 'Baker Analyzed'). Triton®X-100 is a non-ionic surfactant used primarily as a frother. Sodium oleate is an anionic fatty acid which acts as a collector when used in conjunction with calcium ions. The goal was to see the effects of the individual surfactants and interactions between them. Various combinations were used with concentrations ranging from 0 to 200 mg/L in deionized water. Calcium chloride ($CaCl_2 \cdot 2H_2O$) was added to selected solutions at a concentration of 830 mg/L.

The surface tension of the model deinking liquors and the contact angles against the toner samples were measured using a Cahn Contact Angle Analyzer (DCA - 312). This analyzer uses the Wilhelmy plate method, which determines the contact angle based on the surface tension of the liquid, the perimeter of the sample, and the force exerted on the sample upon immersion in the liquid (17). This measurement gave the dynamic contact angle for the advance and retreat of the liquid across the solid. The contact angles from the advance and retreat are typically distinct from one another and referred to as advancing and receding contact angles. A difference in advancing and receding angles will arise if the surface is rough or chemically heterogeneous (17). It is uncertain which contact angle plays a more significant role in flotation. The receding angle likely affects the initial formation of the bubble - particle aggregate, during which the liquid recedes across the solid due to the displacement of liquid by the air bubble. The advancing angle will likely affect the attachment stability, as the detachment of a bubble involves the advancement of liquid across the solid. Here, we report the advancing contact angles. The observed trends are very similar for both advancing and receding angles.

The toner coated transparencies were cut into 2.0 cm x 3.0 cm sections for the contact angle measurements. The wetted perimeter was determined for each sample by multiplying the width of each sample by two, since the uncoated edge comprised less than 1% of the perimeter. The sample was then clipped in the stirrup and leveled. Before the sample was put into position, static charge on the toner was dispersed with a Cahn

Staticmaster ionizing unit. Reproducibility of the method was excellent with an accuracy of ±2° for repeated measurements on the same sample.

Flotation.

Samples for flotation were prepared by pulping of printed paper in a LaMort pulper. Conventional copier paper (alkaline based) was printed with a pattern of 'X's in the Kodak photocopier. The furnish for all the flotation runs was made in one batch, to eliminate any differences in flotation due to pulping conditions. The pulping was carried out for approximately 20 minutes at a consistency of 10.5%, a pH ranging from 8.5 to 9.0, and a temperature of 50°C. Tap water was used for pulping and flotation. Before flotation, the furnish was further disintegrated in a British disintegrator at 1.05% consistency for 10 minutes.

The flotation system consists of a 1135 cm^3 cylindrical plexiglass cell with a rubber disk (13.8 cm diameter) forming the bottom. Nitrogen is injected through perforations in the rubber disk to form the bubbles for flotation. Additional water is added to the cell with a buret to maintain a constant overflow. The froth is collected in an overflow trough.

The disintegrated furnish and concentrated surfactant solution were added to the flotation cell and mechanically agitated with a Lightnin' stirrer for 5 minutes. At this point, calcium chloride was added if it was required for the run, and the furnish was agitated for an additional 2 minutes. The pH was adjusted to 8.5 by the addition of 1 M sodium hydroxide or dilute sulfuric acid. The agitation was stopped after the furnish had been mixed for a total of 10 minutes after the initial addition of surfactant. Additional water was added to reach the full capacity of the cell, which gave a final consistency of 0.75%.

At this time, the water flow from the buret for overflow compensation was set to approximately 24 cm^3/min. and the nitrogen was set to a flow rate of 2400 cm^3/min. Typically foam started to form, and it was scraped away into the reject trough. Flotation was carried out for 10 minutes.

Handsheets for image analysis were made from the stock remaining in the cell. One gram handsheets were formed on a 15 cm Büchner funnel with a No. 1 coarseness filter. The handsheets were pressed once for 90 seconds at 50 psig, then dried in drying rings in a conditioned room at 50% relative humidity and 23°C.

Image Analysis.

Image analysis was used to determine the size distribution and area coverage of toner particles on the handsheets. The image analysis system included a MTI CCD72 camera, an IBM compatible PC with a Sharp GPB-1 card, and a stand to mount and illuminate the sample to be imaged and support the camera. The Sharp card contained functions to acquire an image from the camera, analyze the image to detect particles, and determine their dimensions. Software developed at IPST accumulated the number of particles within the imaged frame and the area of each particle. Then an effective diameter was calculated based on the area of each particle, assuming circular shape. The minimum detectable diameter was 10 microns.

Particle detection is based on contrast between the black toner particles and the white handsheet. To improve contrast, the handsheets were soaked in water for 5 minutes to make the fibers more translucent. The contrast is also affected by the black level and gain of the imaging system, the defined threshold level, and the light source (reflected or transmitted light). One set of optimum system parameters was used for all samples.

The bar graphs (Figures 6-8) represent the total counts for an analyzed field. A field consisted of an 11 x 11 grid of frames (0.2025 cm^2 each) located in the center of the handsheet. Visual inspection indicated the distribution of particles in the handsheets to be even.

RESULTS AND DISCUSSION

For contact angle measurements, a smooth surface was produced by heat treatment (see Figure 2). A surface analysis by ESCA showed no significant difference in the elemental surface composition of the smoothed heat treated vs. virgin samples (Table 1). In addition, there were no significant differences between different locations on the surface. This indicates that the contact angles measured on the smoothed toner surface will be meaningful for actual printed toner surfaces.

An interesting observation from the surface analysis is that iron was not detected on the surface of the toner, even though the toner contains 40-50% by weight of iron oxide. Iron was only detected several tenths of a micron below the surface. The lower surface energy polymer appears to spread over the iron oxide during heating above the polymer's glass transition temperature. This occurs similarly during printing and the heat treatment for smoothing of the surface. The presence of iron oxide on the surface of the toner would likely affect surface properties.

The advancing contact angles of various deinking solutions against toner are shown in Figures 3 to 5. The deinking solutions consisted of aqueous solutions of Triton®X-100, sodium oleate, and calcium chloride. The contact angles ranged from 110° to 0° depending on the concentration of surfactant and whether the contact angle was advancing or receding. The receding angles showed the same trends as the advancing angles and hysteresis typically ranged from 40° to 50°. This degree of hysteresis is expected due to surface heterogeneity. The surface tension was also measured and showed similar trends.

The high advancing contact angle (110°) against pure water shows that the toner surface is hydrophobic. This is similar to the results of Snyder *et al.* who prepared their samples from a toner melt (5). These values also resemble those of water against teflon and polypropylene (17). In general, the addition of a single surfactant decreases the contact angle. This is due to the increased adsorption of surfactant onto the toner surface, with its hydrophobic tail toward the surface and the hydrophilic head toward the solution. Therefore, particles become more hydrophilic and are expected to be less likely to be floated.

The addition of anionic and non-ionic surfactants simultaneously and the addition of calcium chloride was conducted to observe interactions. Figure 3 shows that the calcium chloride had little effect on the contact angle of solutions containing only the non-ionic Triton®X-100. However, when sodium oleate, an anionic fatty acid, is used in conjunction with calcium ions, hydrophobic soap flakes form. These soap flakes deposit on the toner and maintain the hydrophobic character of the toner surface. It is anticipated that this will promote flotation. The combination of the frother (Triton®X-100) and collector (sodium oleate) in the deinking liquor increased the contact angle from that with the frother alone (see Figures 4 and 5). The negative influence of the frother on the contact angle is partially counteracted by the collector, even without calcium present.

Since flotation theory explains that hydrophobic particles will preferentially be removed, based on these results one would expect a solution containing no surfactant to optimally remove toner. However, foam is necessary to carry the floated particles away. Considering both effects, an optimized solution should contain a minimal amount of surfactant to create a foam layer, yet without significantly decreasing the hydrophobicity of the toner particle. The attachment force should be maintained above a critical point. This should be able to be achieved by a minimal amount of Triton®X-100 or a combination of Triton®X-100 and sodium oleate with calcium.

The results of the flotation experiments are shown in Table 2. As expected, the runs without surfactant did not remove toner effectively, due to lack of foam. The best flotation results were obtained for the solution containing 50 mg/L of only Triton®X-100 (solution D), which generated foam, yet did not significantly reduce the contact angle. Figure 6 shows that when additional Triton®X-100 is used (100 mg/L, solution B), the flotation efficiency decreases. This is expected due to the reduction of the contact angle. A smaller amount of Triton®X-100 (10 mg/L, solution C) worked well, but not as good as the solution containing 50 mg/L. This was probably because there was not enough surfactant to maintain the foam over the entire flotation run. These results show that there appears to be a level of optimal addition of Triton®X-100. Both low and high levels of surfactant addition will be detrimental. Judicious application of surfactant and monitoring the effects of the surfactant (e.g., contact angles, surface tension) appear crucial.

The results for the solutions containing only sodium oleate are interesting because sodium oleate is a poor frother, and virtually no foam layer was formed at any level of addition. As shown in Figure 7, the toner removal was poor at lower concentrations (50 mg/L, solutions E and F) of sodium oleate even though the contact angle was quite favorable for flotation. However, at higher concentrations (200 mg/L, solutions G and H), removal was good, even though there was still no significant foam layer. In these runs, soap flakes formed and are believed to play a double role in flotation. First, the flakes maintained the toner particle's hydrophobicity so the toner would be floated to the surface. Secondly, while at the surface, an agglomeration of toner, soap flakes, and fiber formed, which stabilized the toner on the surface and allowed it to be removed. In other words, the soap produced a layer on the surface that replaced the functions of the foam. Unfortunately, this mechanism also contributes to high fiber loss, as observed visually. The higher addition of sodium oleate (solutions G and H) may be necessary to produce enough soap flakes.

These results indicate that calcium ions are present in sufficient amounts in the furnish itself. Soap flakes were observed to form in the run with no additional calcium (solution H). Also, the contact angles of this solution were very low which would be expected to lead to poor flotation. However, the flotation results were excellent, most likely promoted by soap flake formation and agglomeration.

The combination of surfactants had an adverse effect on flotation as can be seen in Figure 8. Solution D, with Triton®X-100 only, worked better than those with additional sodium oleate, solutions I, J, and K. These flotation results did not agree with the contact angle results for the combined surfactants which showed a higher contact angle than for Triton®X-100 itself.

Figure 8 also shows that a flotation run without calcium chloride (solution K) was comparable or even better than those with calcium chloride (solutions I and J). It is obvious here again that soap flakes form due to the presence of calcium in the furnish. It is interesting that the presence of additional calcium chloride had a deleterious effect on flotation when sodium oleate is present (solution I vs. K). The excess salt likely affects other mechanisms relevant to the flotation process, such as the zeta potential of the toner.

SUMMARY

This analysis of the interfacial properties of toner in deinking solutions gave quantitative values for the contact angles of solutions against the toner and a qualitative comparison of the contact angles with flotation efficiency.

A method of contact angle measurement was developed to determine the contact angles of deinking liquors against printed and smoothed toner surfaces. Surface analysis showed that treatment of the samples for contact angle measurement did not affect the surface composition. Despite a high concentration of iron oxide, no iron was found in as-printed and smoothed toner surfaces. Contact angles for single surfactant solutions behaved as expected, in general decreasing with increasing surfactant concentration. The combination of sodium oleate and calcium maintained the hydrophobicity, due to the formation of soap flakes. The addition of sodium oleate, with or without calcium, increased the contact angle from that of Triton®X-100 alone.

Results of flotation with the non-ionic surfactant Triton®X-100 support the idea of an optimal level of surfactant addition. Enough surfactant should be added to create a foam layer, yet not to decrease the hydrophobicity significantly. Addition of a collector with the non-ionic surfactant resulted in less toner removal. The sodium oleate and calcium system shows more complex behavior due to formation of soap flakes and lack of foam. This system may still be effective due to formation of a surface layer of soap flakes, toner particles, and fiber.

The influence of the zeta potential on similar model toner surfaces will be reported in the future.

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FIGURE 1: **Bubble attachment and contact angle (θ) against a solid surface. High contact angle indicates hydrophobicity.**

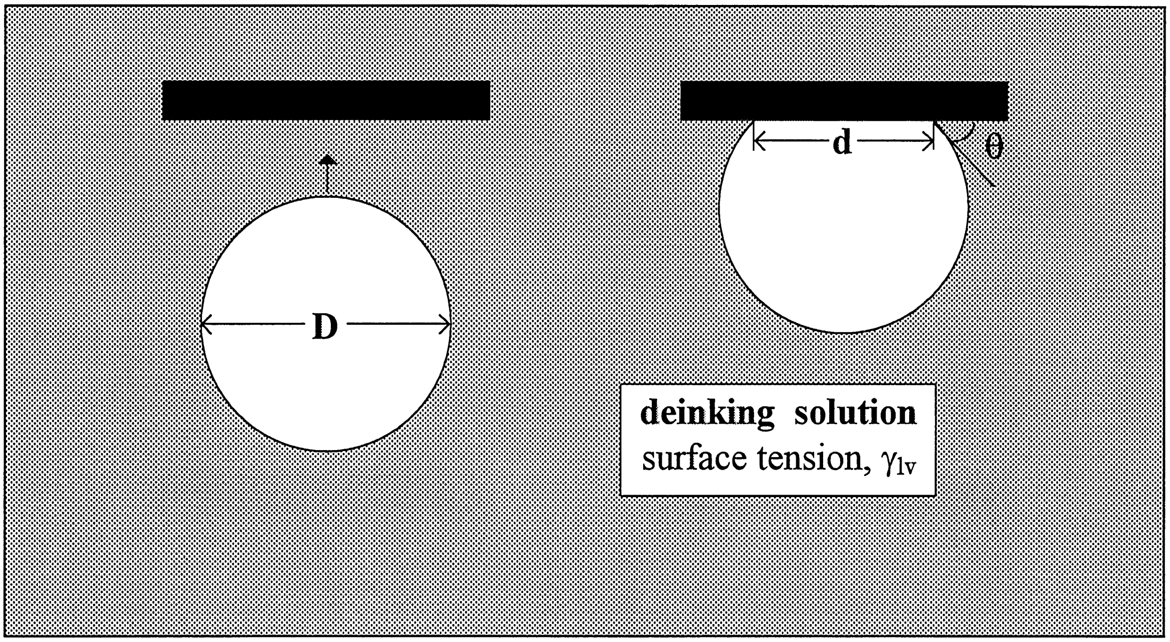

FIGURE 2: **Scanning electron microscope images of virgin and smoothed heat treated toner surfaces.**

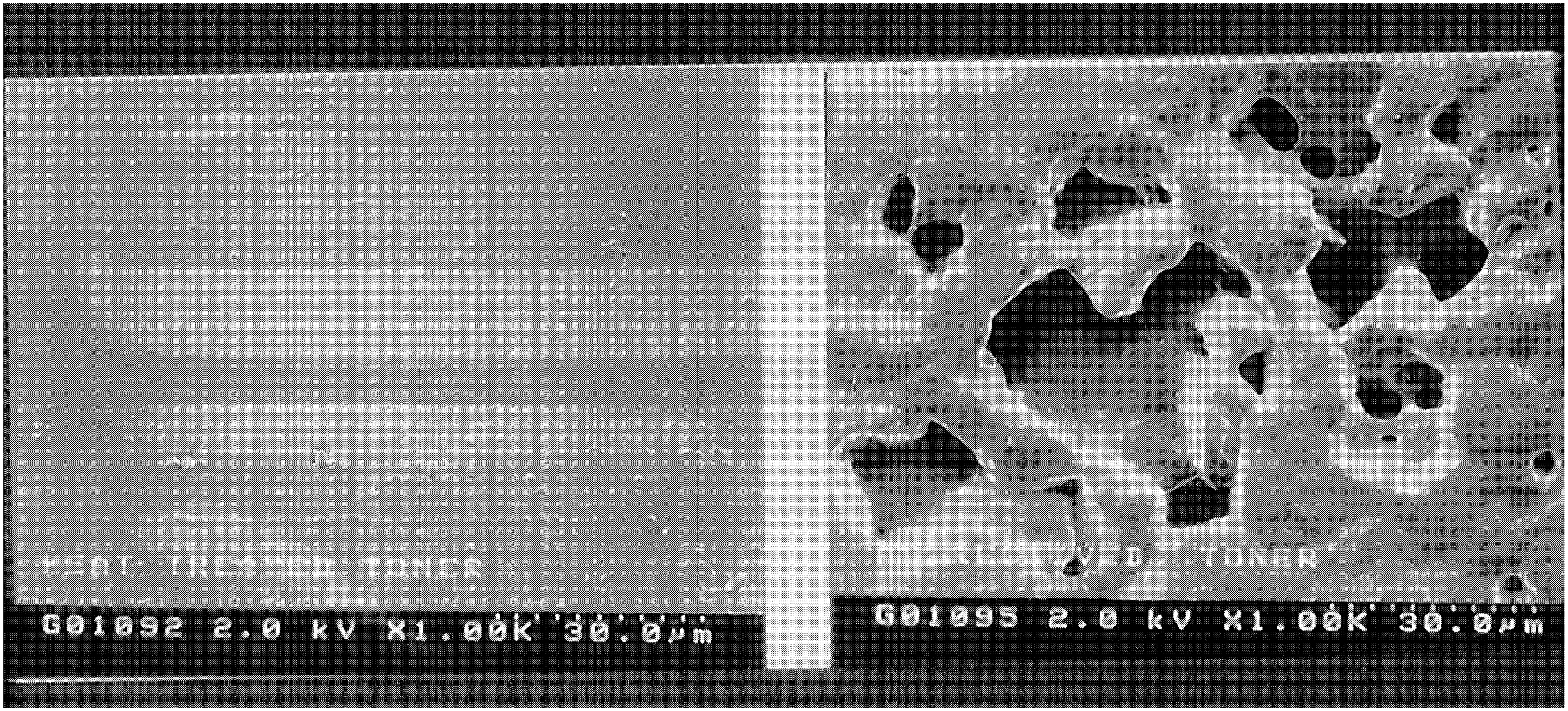

FIGURE 3: **Advancing contact angle of single surfactant solutions against toner, with and without calcium chloride. Refer to Table 2 for key to letters.**

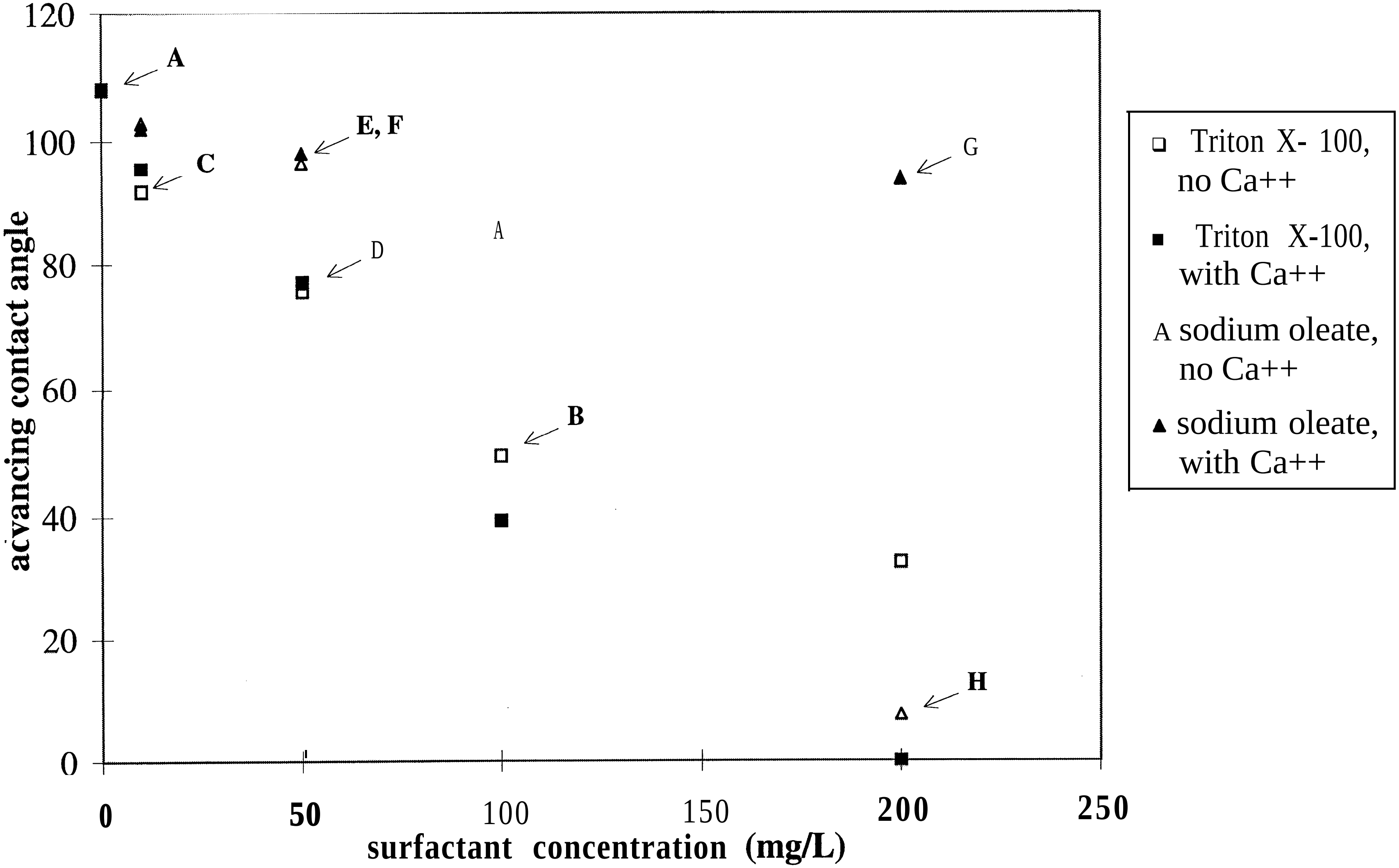

FIGURE **4: Advancing contact angle of mixed surfactant solutions against toner, with no calcium chloride. Refer to Table 2 for key to letters.**

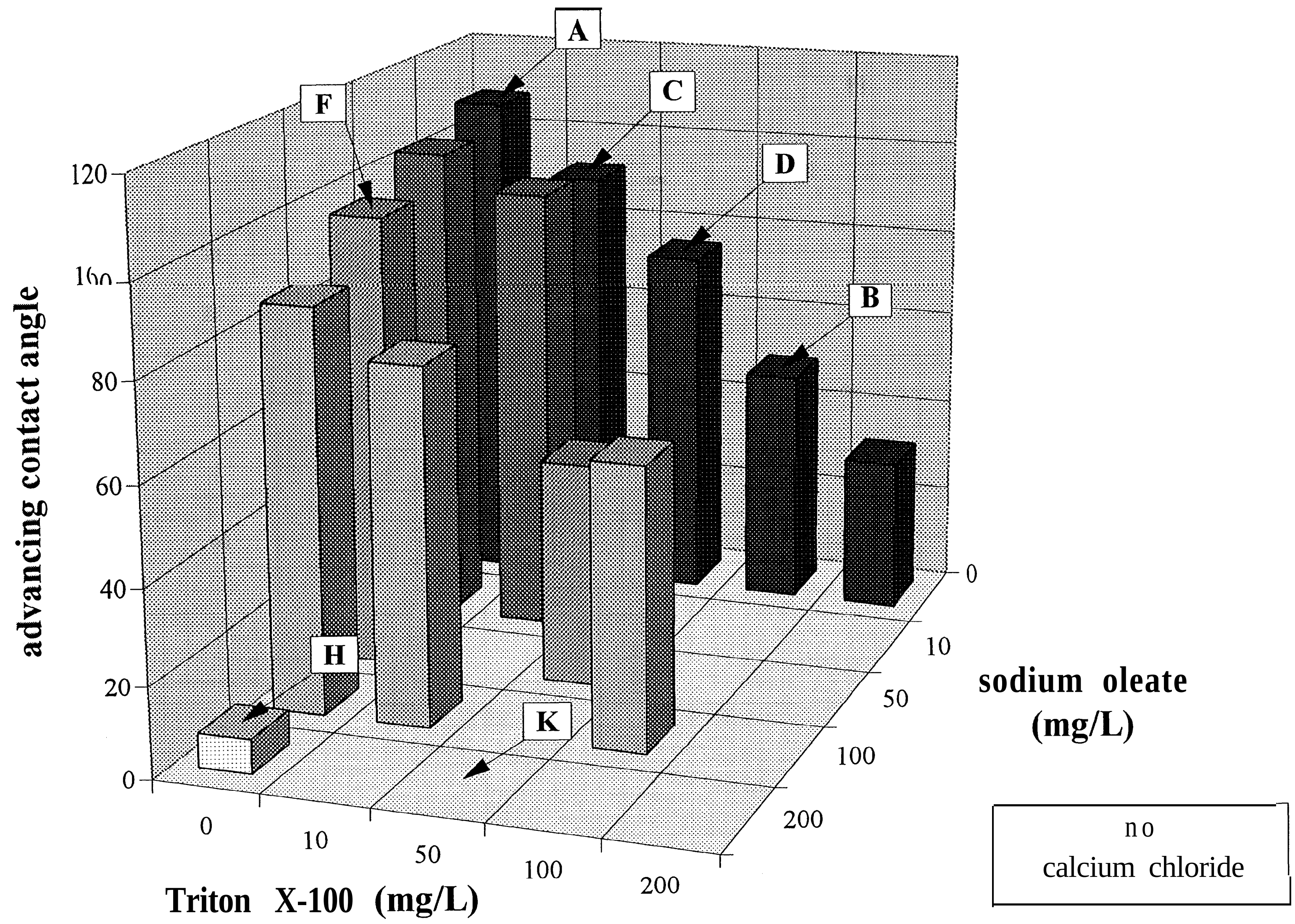

FIGURE 5: **Advancing contact angle of mixed surfactant solutions against toner, with calcium chloride. Refer to Table 2 for key to letters.**

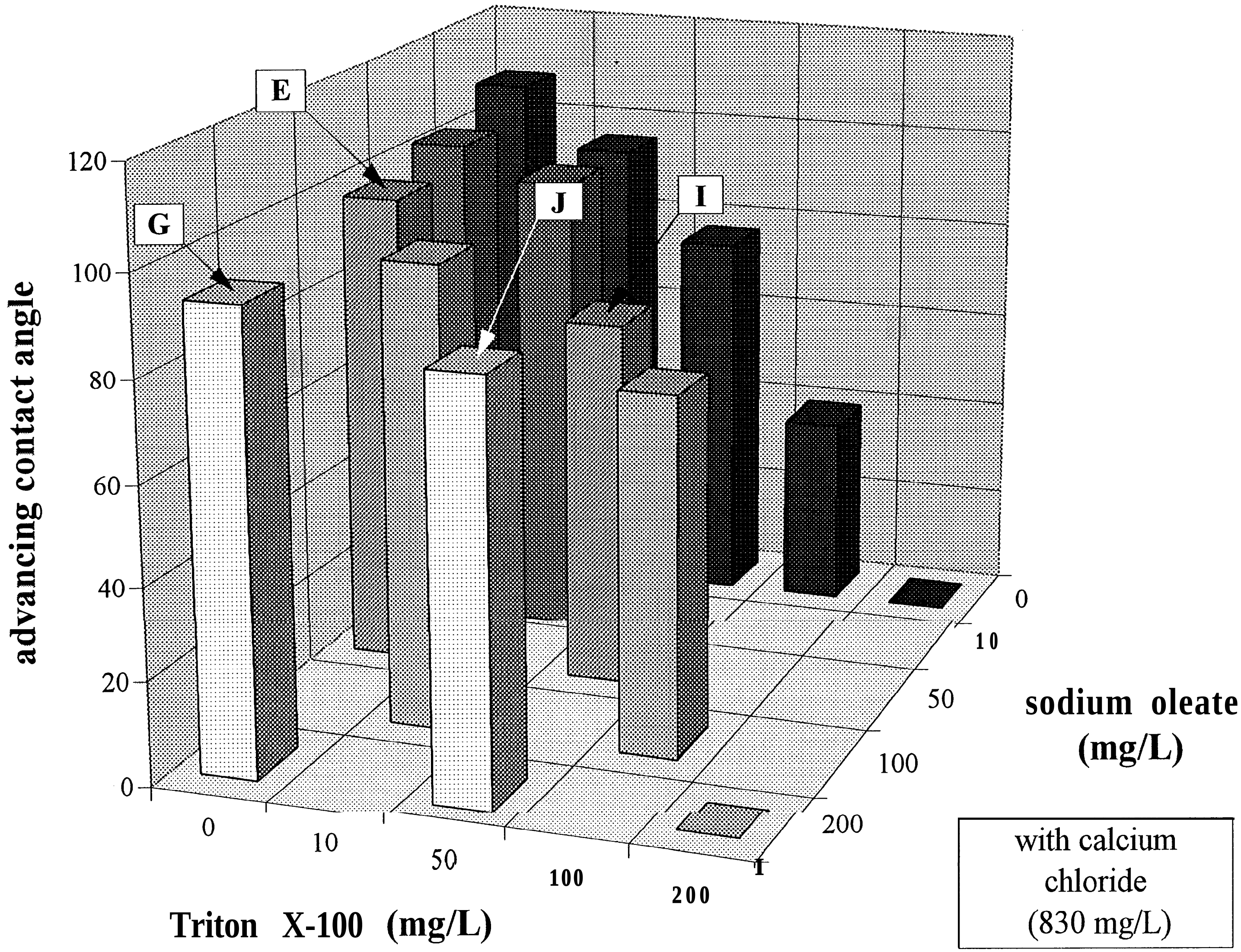

FIGURE 6: **Particle distribution for remaining toner after flotation of toner printed paper in Triton X-100 solutions.**

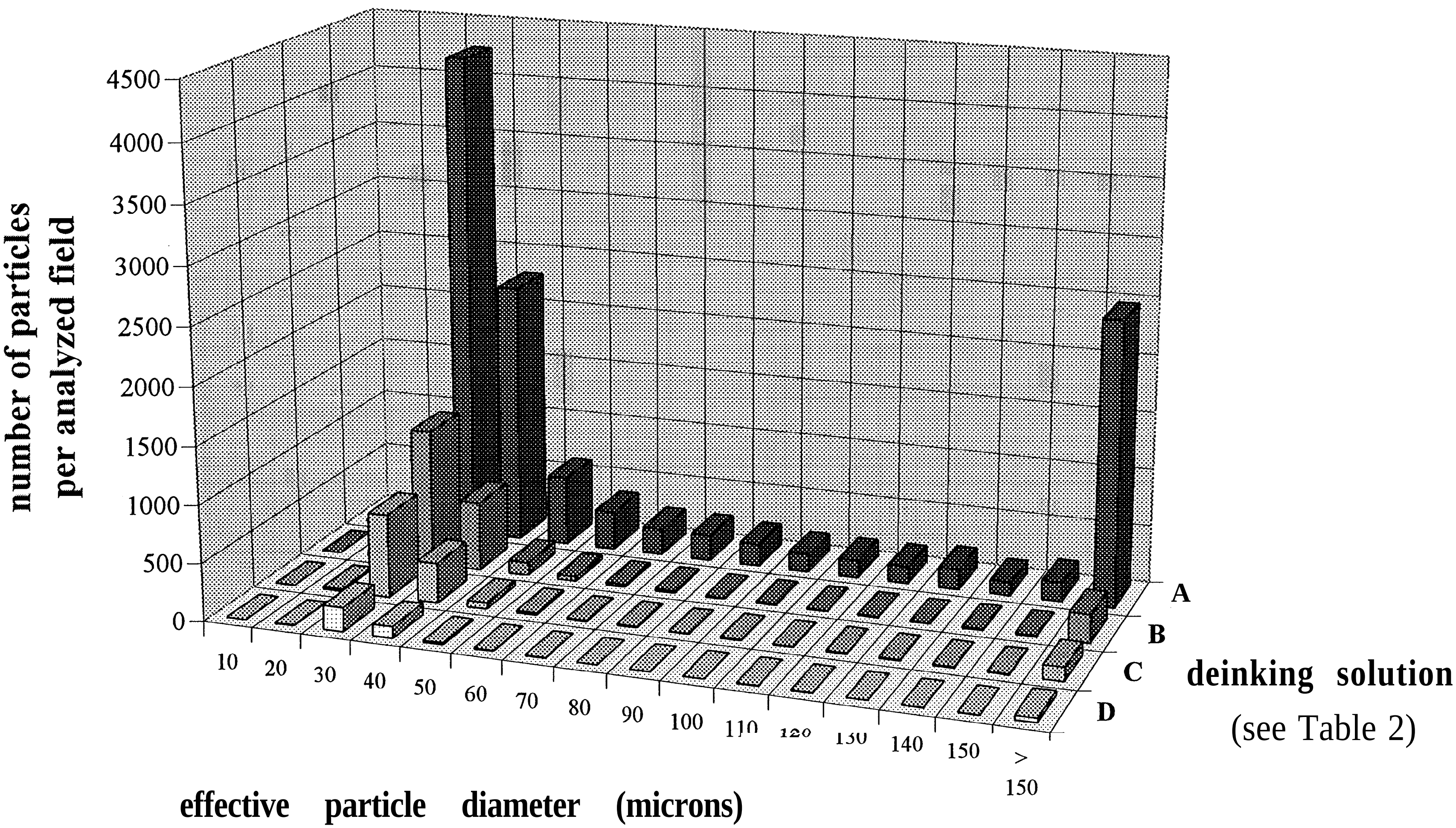

FIGURE 7: **Particle distribution for remaining toner after flotation of toner printed paper in sodium oleate solutions.**

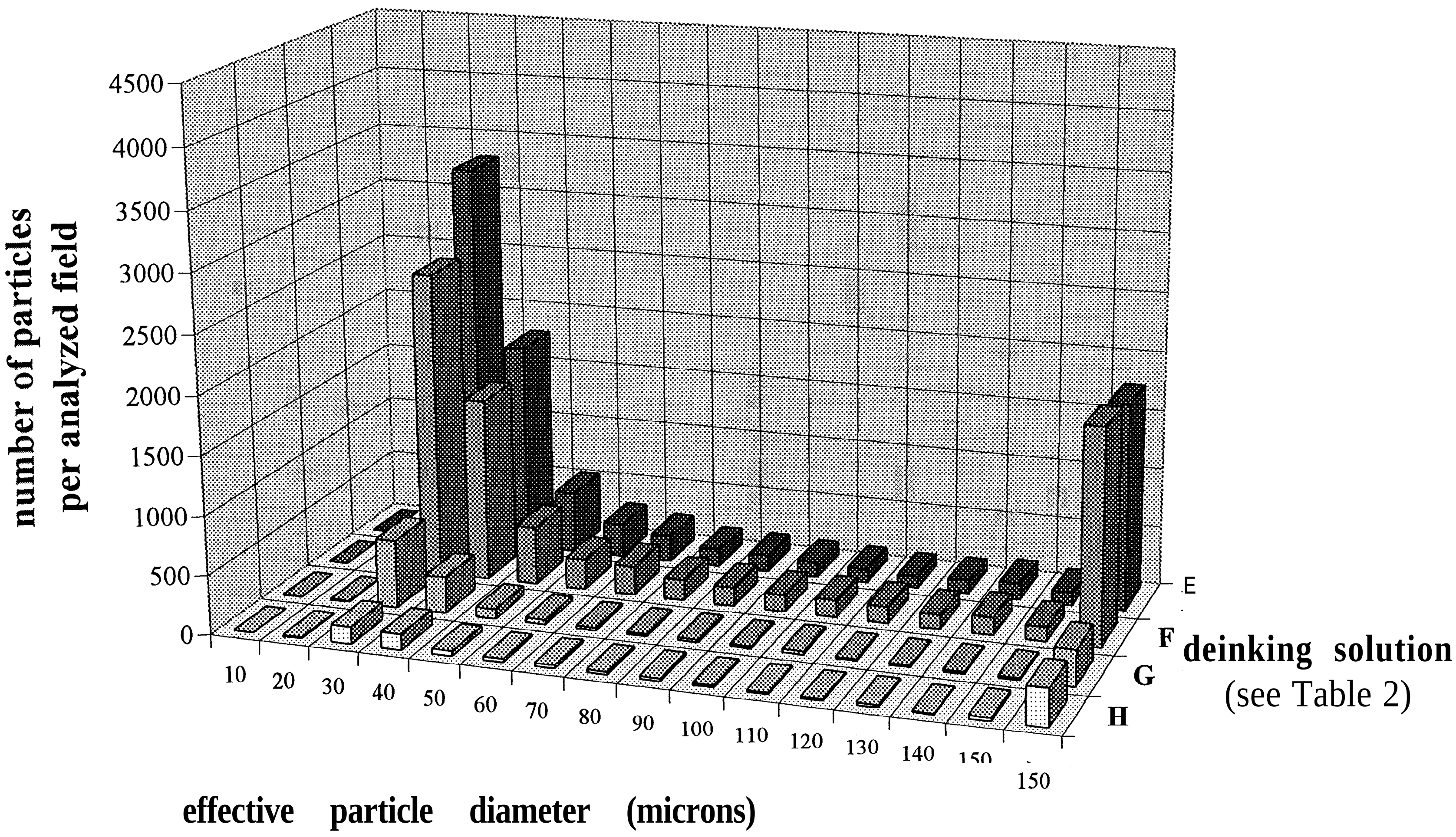

FIGURE **8: Particle distribution for remaining toner after flotation of toner printed paper in mixed surfactant solutions.**

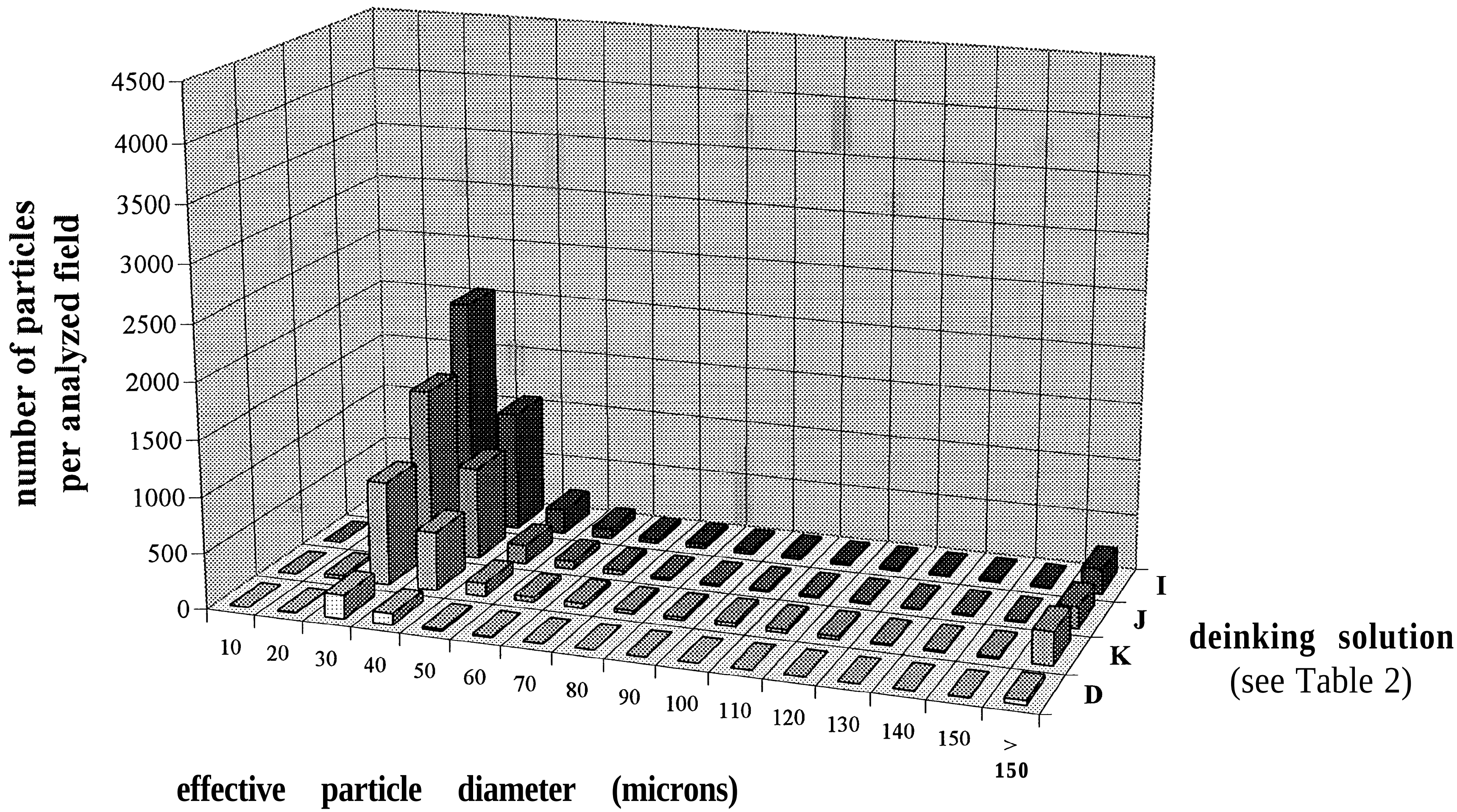

Table 1. Elemental Composition (atomic percent) of the Surface of Toner Samples.

Sample	Oxygen	Carbon	Silicon	Iron
virgin A	20	68	12	n/d
virgin B	20	63	17	n/d
virgin C	20	67	13	n/d
virgin D	18	74	9	n/d
heat treated A	20	68	13	n/d
heat treated B	23	56	21	n/d
heat treated C	21	59	19	n/d
heat treated D	21	65	14	n/d

n/d = not detected

Table 2. Flotation Results for Toner Printed Paper in Surfactant Solutions.

Flotation Run	Surfactant: Triton X-100 (mg/L)	Surfactant: sodium oleate (mg/L)	$CaCl_2$ (mg/L)	Flotation Results	Contact Angles	Foam	Figures: contact angles	Figures: flotation
A	0	0	0	poor	+++	-	3, 4	6
B	100	0	0	good	-	↑↑↑	3, 4	6
C	10	0	0	very good	++	↑	3, 4	6
D	50	0	0	excellent	+	↑↑	3, 4	6, 8
E	0	50	830	poor	++	→	3, 5	7
F	0	50	0	fair	++	→	3, 4	7
G	0	200	830	very good	++	→	3, 5	7
H	0	200	0	excellent	--	→	3, 4	7
I	50	200	830	fair	++	↑	5	8
J	50	50	830	good	+	↑↑	5	8
K	50	200	0	very good	--	↑↑	4	8

To find contact angles: use composition, refer to Figures 3-5.
To find flotation particle count: refer to Figures 6-8.
Contact Angles: +++ highly hydrophobic, superior flotation expected;
-- highly hydrophilic, poor flotation expected.
Foam: ↑↑↑ excessive foam; → very slight foam, no stability; - no foam.