ON THE STRUCTURE OF INK-WATER EMULSIONS AS DERIVED FROM DIELECTRIC CONSTANT MEASUREMENTS

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Abstract: Some conclusions regarding the structure of ink/water emulsions were derived from static and dynamic dielectric constant measurements of real and synthetic black ink and dampening solution mixtures. Mixtures without carbon black were also evaluated.

Under static conditions, the results are consistent with carbon black dispersed as nonspherical agglomerates and dampening solution dispersed as a separate phase consisting of spherical particles.

When shear stress is applied to ink mixtures by forced flow through a tube, the dielectric constant increases significantly. The increase is greater when the dampening solution content is large. This may be explained by deformation of the water droplets by the flow field. The carbon black agglomerates remain unaffected at the shear rates used in these experiments.

Introduction

Ink-water interactions are central to the practice of conventional lithography; yet our understanding of the structure of the emulsions formed during the printing process is far from complete. The need to improve our understanding becomes even more important with the emergence of newer technologies such as keyless lithography. In a previous publication (Goldberg, 1986) we described how static dielectric constant measurements can be used to determine the concentration of water in mixtures of ink and dampening solution. In this paper we extend this work to the dependence of dielectric constant on the concentration of the various components of the emulsion, and on applied shear stress. From the results we

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are able to postulate a reasonable model for the microstructure of the emulsion.

Experimental

Materials. The ink used in the measurements was a well-established black lithographic newsprint ink. Synthetic ink mixtures were prepared from the ink components according to the ink formulation listed in Table 1. The ink vehicle was prepared first by mixing all the ingredients except pigment in the proportions given. Synthetic inks were made by blending the desired quantities of carbon black and vehicle and mixing with a high-speed stirring motor (Premier Mills Laboratory Dispersator Model 84). The resulting inks appeared to be well mixed and qualitatively were similar to the commercial ink.

Table 1

Composition of a Typical Black Lithographic Ink

Vehicle

Varnish = 50% (by weight)
Ink Oil = 30%
Solvent = 2%

Pigment

Carbon Black = 18%

The dampening solution was prepared by diluting Flint V-2020 concentrate with deionized water in the ratio 1:64. The concentration of phosphate in the dilute dampening solution, based on a colorimetric method of analysis (Quinlan, 1955; Riemann III, 1961), was determined to be approximately 150 µg phosphorus/ml, which would be equivalent to 840 µg K2HPO4/ml or about 0.08 percent phosphate salt.

Emulsions of ink and dampening solution were prepared by mixing the components manually. Uniform, stable emulsions of ink containing up to 50% dampening solution appeared to form readily by this method. Emulsions of vehicle and dampening solution did not form easily and required the use of a high speed stirrer. The emulsions prepared in this way had the appearance of yellow whipped cream but did not exhibit phase separation for several hours. A water phase could be observed, however, when the emulsion was kept overnight at laboratory temperature.

Suspensions containing iron powder and ink vehicle were prepared by manual mixing. Iron powder (HFQ grade from BASF Corp.) was synthesized commercially by thermal decomposition of iron pentacarbonyl. The diameters of the spherical particles ranged from 1 to 3 μm with a mean value of 1.2 μm. Both insulating and noninsulating Fe were used. Insulating Fe was made commercially by treating uninsulating particles with dilute phosphoric acid, which is believed to produce a thin layer of insulating iron oxide on the surface of the particles. The suspensions appeared to be reasonably stable; settling of the heavy powder particles did not become evident for about 1 hour. Measurements were carried out as quickly as possible to minimize the effects of settling.

Measurement Technique. The dielectric constant of ink-water emulsions was determined using the microwave cavity perturbation technique described in previous publications (Goldberg, 1981, 1986; Ho, 1973). Briefly, it involves measuring the shift in the resonance frequency and the power absorbed as a function of frequency in the region of the resonance frequency when samples contained in 3 mm quartz capillaries are inserted into the microwave cavity. Two cylindrical TM 010 mode cavities constructed of aluminum alloy pipe having internal diameters of 30.48 and 38.10 cm were used. The electric fields in the cavities are constant in the direction parallel to the cylindrical axis, and are maximum along the center of the sample tube.

The microwave cavity perturbation technique yields the complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' and ε'' are the real and imaginary parts of the complex dielectric constant, respectively. Both ε' and ε'' are functions of the microwave frequency. ε' is related to the nondissipative, out of phase capacitive current and refers to the ability of polar or polarizable molecules or particles to align with the alternating microwave field; at low frequencies ε' approaches the static or dc dielectric constant. ε'' is related to the conductance of the material, and is indicative of the absorption or dissipation of the electric field energy as heat. This term arises from induced electric currents in phase with the microwave electric field, and can result from the flow of electrons through a network of contiguous small particles, ionic conduction such as in aqueous solutions, or the motion of polar molecules in the oscillating electric field. ε' is calculated from the shift in the resonance frequency when the sample is inserted to the empty tube, and ε'' is calculated from the width of the absorption peaks at half power, according to Eqs. (1) and (2):

$$\delta = f_0 - f = A(\varepsilon' - 1) \tag{1}$$

and

$$\varepsilon'' = \frac{(\varepsilon' - 1) f_o}{2 Q_s \delta} \tag{2}$$

In these equations f_o is the resonance frequency of the cavity containing the empty sample tube, f is the resonance frequency of the cavity including the tube and the sample, A is a calibration constant related to the diameter of the cavity and the diameter of the sample tube, Q_s is the change in the Q-factor of the measuring system caused by introduction of the sample, and δ is the frequency shift defined by Eq. (1). The quantity Q_s is sometimes called the Q-factor of the sample. The value of A is determined for each sample tube by measuring δ with the tube filled with acetone or water, using $\varepsilon' = 20.9$ for acetone and $\varepsilon' = 74.4$ for water. The value of Q_s is determined from Eq. (3):

$$Q_s^{-1} = Q^{-1} - Q_o^{-1}, \tag{3}$$

where Q and Q_o are the Q-factors of the cavity and coupling loop containing either the tube filled with sample or the empty tube. The Q-factor is calculated as the ratio of the resonance frequency to the bandwidth of the cavity resonance at the half-power point. Thus,

$$Q = f/\Delta f_{1/2} \tag{4a}$$

and

$$Q_o = f_o/(\Delta f_{1/2})_o \tag{4b}$$

As usual, the subscript o in Eq. (4b) refers to the cavity containing the empty tube.

Results

Four synthetic inks were made by mixing 6, 12, 18, and 24 weight percent of carbon black with ink vehicle. Emulsions were then prepared by mixing 10, 20, 30, 40, and 50 weight percent of dampening solution with each of these four synthetic inks. The dielectric constants ε' and ε'' of all of these mixtures as well as those of the ink vehicle were measured. The results for ε' are shown in Figure 1. In this figure the horizontal axis is the total volume fraction of additives (v); that is, carbon black (v_c) plus dampening solution (v_w). The solid lines illustrate the effect of increased dampening solution on fixed proportion mixtures of carbon black and ink vehicle, and the dotted lines represent the effect of adding a constant amount of dampening solution to inks containing increasing amounts of carbon black. Evidently the addition of carbon black causes a much greater increase in ε' than the addition of dampening solution.

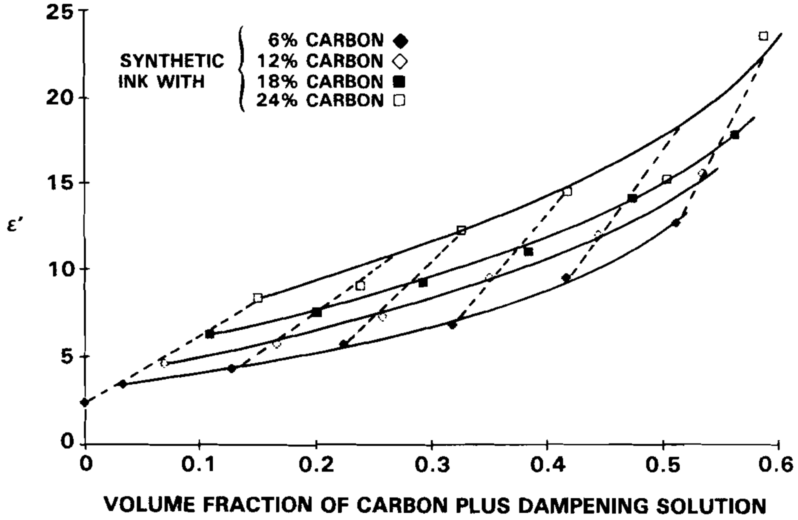

Figure 1. Dielectric constant as a function of carbon black and dampening solution contents.

The effect on ε' of adding pure water or dampening solution to the ink vehicle (no carbon black present) is shown in Figure 2. The curve for ε' when up to 23% water or10% dampening solution is added to the ink vehicle is essentially parallel to the solid line curves of Figure 1. However, when the volume fraction of dampening solution in the ink vehicle exceeds 10%, ε' increases more rapidly than it does with carbon black present.

Figure 3 shows values of ε" plotted against volume fraction of dampening solution for various amounts of carbon black content. In the presence of carbon black, ε" increases gradually with increasing concentration of dampening solution and with increasing concentration of carbon black. Both contribute to the value of ε" because they both tend to increase the electrical conductivity of the resulting emulsions. In the absence of carbon black, ε" remains nearly zero when pure water is added to the ink vehicle. However, when dampening solution is added to the ink vehicle, ε" increases very rapidly at concentrations above 10%, and values are much higher than those observed in the presence of carbon black.

The onset of rapid increase in both ε' and ε" occurs at the same concentration of dampening solution. The most obvious difference between pure water and dampening solution is the presence of ionized phosphate salts in the latter, with a consequent higher pH and higher conductivity. The sudden increase in ε' and ε" when

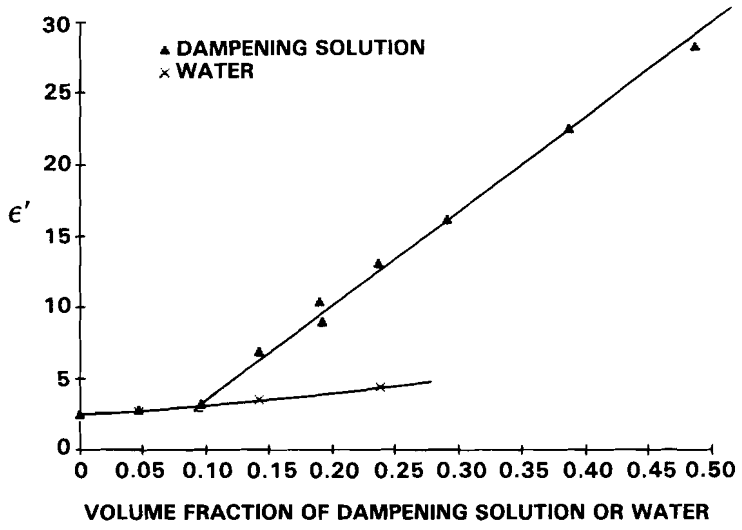

Figure 2. Dielectric constant of mixtures of dampening solution or water in ink vehicle.

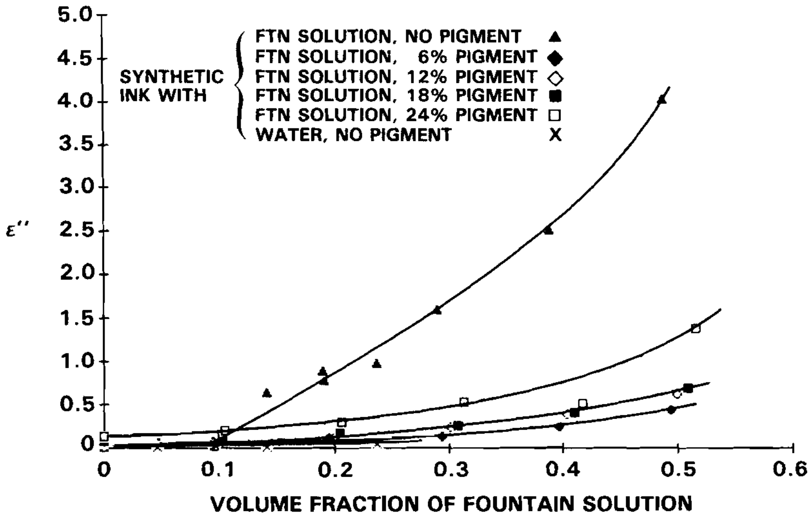

Figure 3. Loss factor ε" as a function of the volume fraction of dampening solution or water in synthetic ink.

carbon black is not present is consistent with incipient breakdown of the emulsion due to coalescence of the water droplets to form bulk water phase. Carbon black has a stabilizing effect and in its presence emulsion breakdown is not observed.

Effect of Salt Concentration. A series of "dampening solutions" was prepared by varying the volume ratio of water to V-2020 concentrate. The ratio of water to V-2020 ranged from zero (i.e., undiluted V-2020) to 64, a typical dilution ratio used during printing (2 oz/gal). We determined both ε' and ε" for mixtures containing 30% of each of these dampening solutions in the newsprint ink. The results are shown in Figure 4. The value of ε' is nearly independent of phosphate content so long as the concentration of phosphate in the dampening solution is less than about 20 mg/ml. The value of ε" increases slightly and gradually at low salt concentrations and levels out at about 1.3 as the concentration approaches 20 mg/ml. Above 20 mg/ml, both ε' and ε" increase very rapidly. These data illustrate that no unusual dielectric behavior occurs due to salt concentration except at values far above that used in the press.

Figure 5 shows microwave power absorption curves for three aqueous samples: pure water, dilute dampening solution (dilution factor 1:64), and a more concentrated dampening solution (dilution factor 1:16). Although the resonance frequency for the three samples is nearly the same, indicating similar values of ε' (as expected from Figure 4), the widths of the resonance peaks are vastly different. The effect of the salt is to increase the conductivity of the solution, and this results in a large increase in ε".

Figure 6 shows a similar set of curves when the three aqueous samples containing varying amounts of phosphate salt were mixed at 30% with the newsprint ink. In the presence of ink, the resonance frequencies are again virtually identical, corresponding to no effect on the value of ε'. However, in this case, the width of the resonance peaks increases only slightly, indicating a very small change in ε" and a corresponding small change in the conductivity. This is strong evidence for the existence of an interaction between dampening solution and carbon black.

The most obvious explanation for these observations is that in the absence of pigment the phosphate salt increases the electrical conductivity of the mixture, manifested as an increase in ε". In the presence of carbon black, the ionic mobility of the phosphate is reduced and ε" remains small. The salt is in fact removed from the water phase. The shapes of the curves in Figure 4 are reminiscent of a titration curve. They suggest that carbon black is very effective in adsorbing the phosphate salt, but that adsorption is limited to some upper value, which in this case is about 20 mg/ml, a value far above that which would be encountered in the printing process.

Suspensions of Iron Powder and Ink Vehicle. It is well known that the shape of the particles has an effect on the dielectric properties of suspensions (Voet, 1947). Carbon black pigment is known to exist

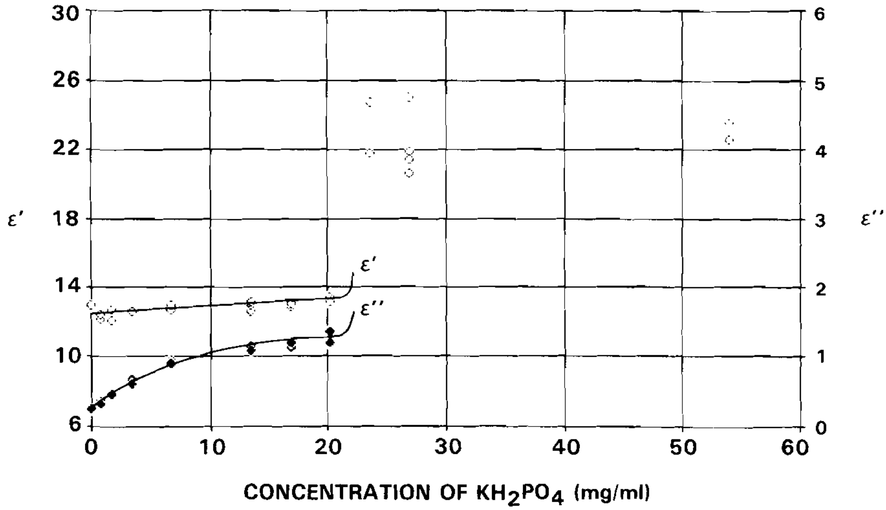

Figure 4. Dielectric effect of KH2PO4 concentration in dampening solution. Ink mixtures contain 30% dampening solution.

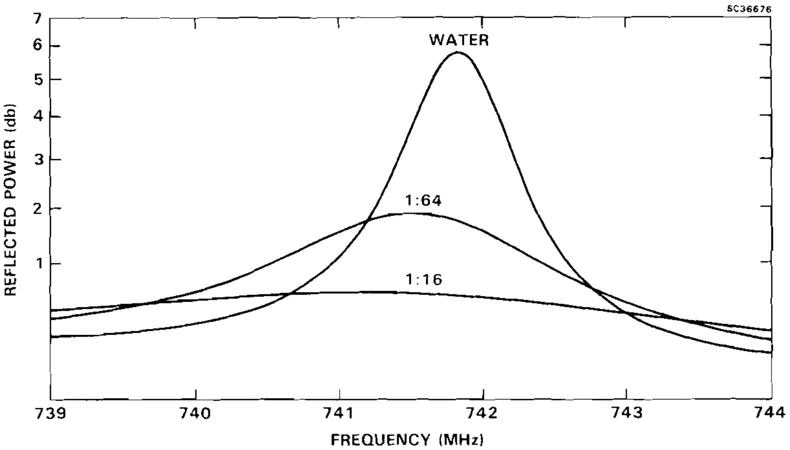

Figure 5. Cavity resonance curves for water and two concentrations of dampening solution.

as agglomerates of carbon particles with irregular, nonspherical geometry. To determine whether carbon black displays anomalous behavior, we prepared a series of mixtures in ink vehicle containing a known particle type, iron powder, and measured the resulting values of ε' and ε". Iron was chosen for this test because the iron powder was known from scanning electron microscopy (SEM) to consist of perfect spheres in the range of 1-3 μm diameter. The dielectric constant ε' of the iron suspensions is considerably smaller than that of the carbon black suspensions, as shown in Figure 7. The solid lines through the data points are theoretical lines and their significance will be discussed later.

Values of ε" for the iron suspensions are near zero because there is no electrical conduction between iron particles. Conversely, the increase in ε" when carbon black is in suspension (Figure 3) is probably due to ohmic dissipation of current between the carbon black particles. This suggests that the carbon particles are in loose contact throughout the entire matrix.

Effect of Shear. All the experiments described heretofore were carried out under static conditions. However, mixtures used on press are subjected to considerable shear stresses. To study the effect of shearing, we assembled a circulating system in which the fluid was pumped through the sample measuring tube of the microwave cavity. A positive displacement gear pump driven by a 1/3 HP motor was capable of moving the viscous ink samples through a 7 mm id Pyrex tube at a variable flow rate with maximum flow of about 2 liters/min. At maximum flow conditions, the linear velocity of the fluid at the center of the tube was estimated at 172 cm/s and the corresponding maximum shear rate was $172/0.35 = 488\ s^{-1}$. Rheological measurements of lithographic inks typically encompass shear rates of $0\text{-}3000\ s^{-1}$.

Figure 8 shows the dielectric constant behavior, ε', of the ink vehicle containing varying concentrations of emulsified dampening solution as a function of pump speed. Figure 9 similarly shows ε' of the newsprint ink. Measurements were always done in the sequence indicated by the arrowheads, starting with the ink at rest, increasing in steps to maximum speed, and then decreasing to zero speed.

Measurements of ε' using the synthetic ink mixtures at 6, 12, or 18% carbon black produce curves similar to those shown in Figures 8 and 9. The dielectric constant generally increases with increasing pump speed up to a maximum value, and the magnitude of the increase depends on the composition of the emulsion.

The overall effect of shear is summarized in Figure 10 with ε' plotted as a function of the emulsion composition expressed as the combined volume fractions of carbon black and water. The black symbols represent measurements of ε' at the lowest pump speed, and the white symbols show the highest values of ε'. Generally the highest ε' values were seen at the highest pump speeds. The length

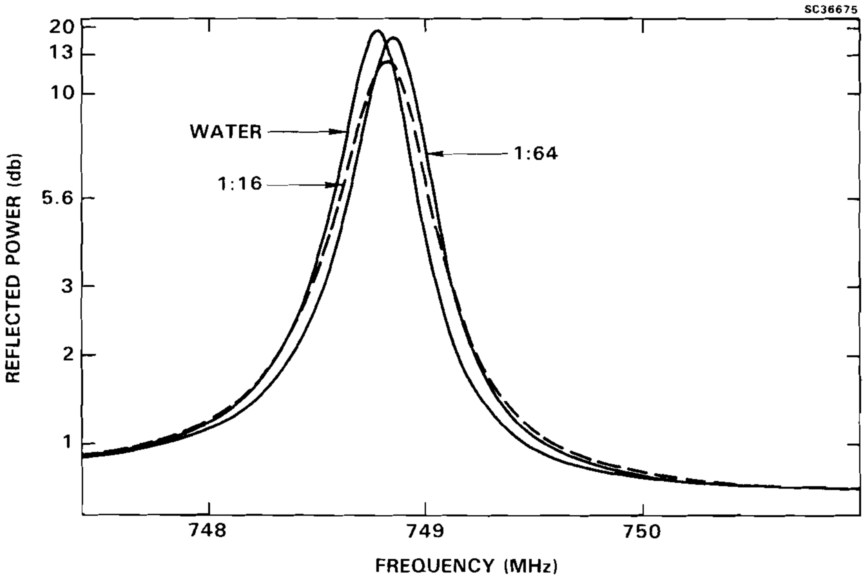

Figure 6. Cavity resonance curves for black ink containing 30% water or dampening solution at two different salt concentrations.

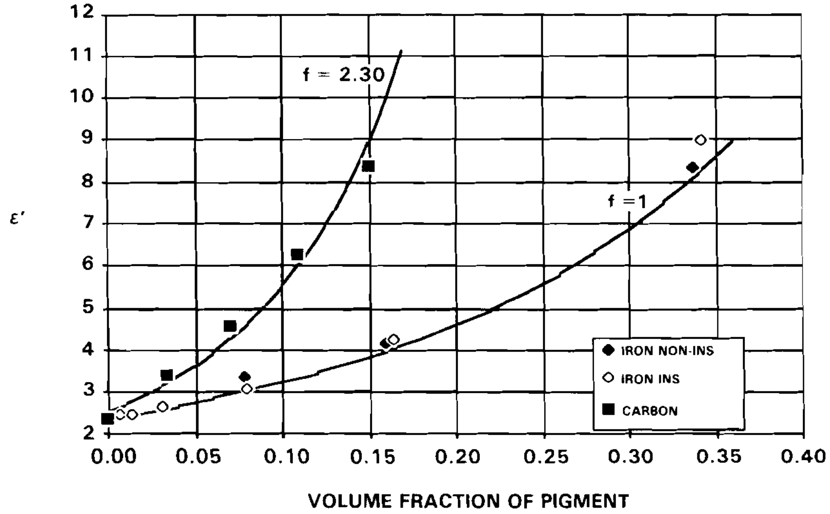

Figure 7. Dielectric constant of suspensions of iron and carbon black in the ink vehicle.

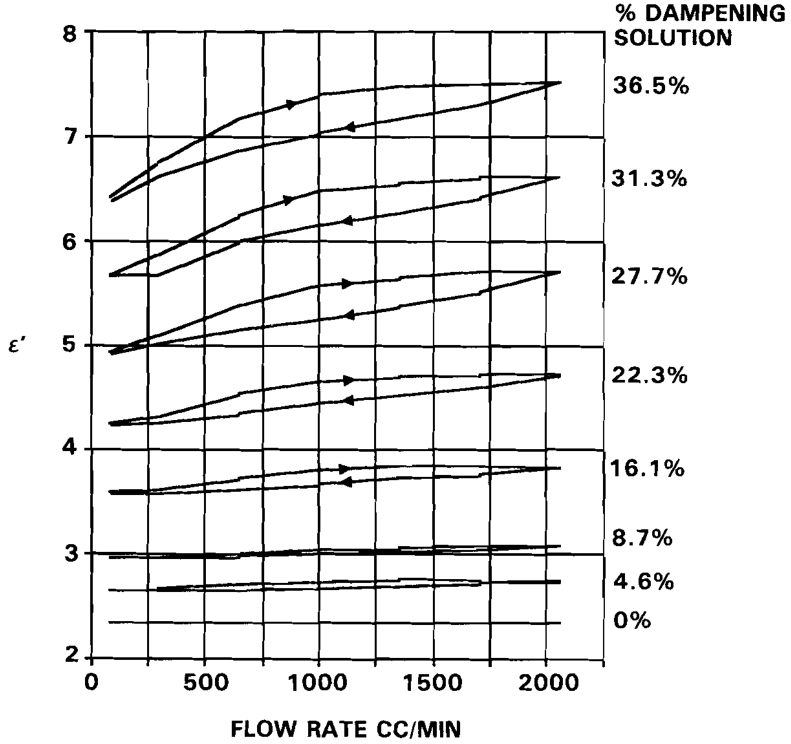

Figure 8. Effect of shear stress on the dielectric constant of mixtures of ink vehicle and dampening solution.

of the z-dimension lines represent the maximum change in dielectric constant caused by the change in pump speed (i.e., shear rate).

In the absence of water, the dielectric response of the ink vehicle and of the dry inks is nearly independent of shear rate, indicating no measurable change in the structure of the suspended materials. More importantly, in the presence of water the shear induced change of dielectric constant is greater with increasing concentrations of dampening solution than with increasing concentration of carbon black. Thus it appears that structurally the water phase is primarily affected in response to shearing conditions.

Effect of Temperature on Shearing Conditions. Figures 8 and 9 illustrate that for mixtures containing water, ε' increases significantly as shear rate is increased from zero, then levels off and/or goes through a maximum value. When the applied shear rate is decreased, ε' drops more or less linearly with pump speed. Consequently at the same pump speed, ε' is almost always higher

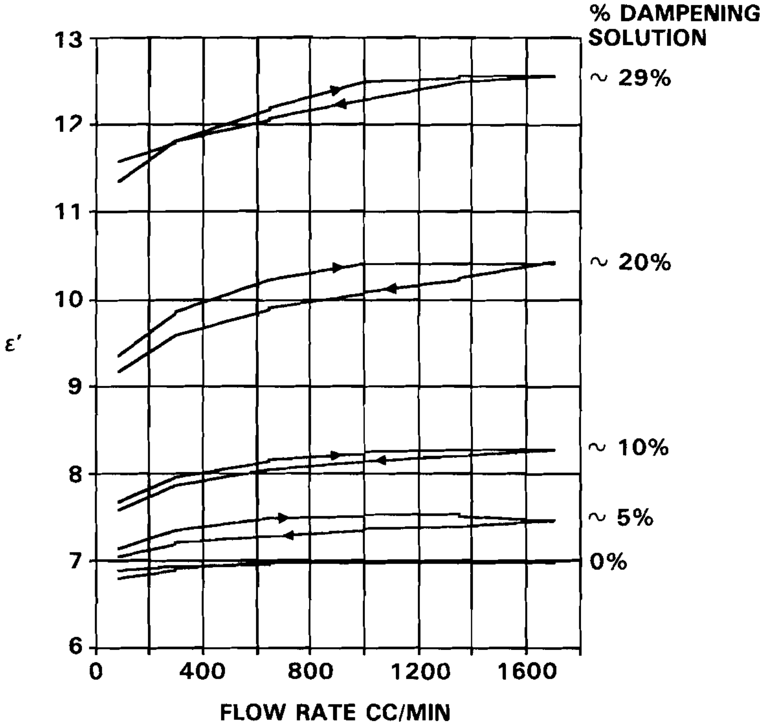

Figure 9. Effect of shear stress on the dielectric constant of mixtures of newsprint black ink and dampening solution.

when the shear rate is increasing than when the shear rate is decreasing. This result may be related to changes in the fluid temperature. Considerable heat is generated at the pump, particularly at the higher speeds because of ink emulsion's resistance to flow. Despite the use of a cooling water jacket surrounding the flow tube, the ink temperature increases slowly with time, no doubt due to the high heat capacity of the system and the corresponding slow response time to external cooling. Generally, the temperature of the fluid "on the way down" was 3-5°C higher than "on the way up." We have previously noted that at constant flow the dielectric constant decreases with increasing temperature. The observed differences in ε' at any given speed correlate well with these measured temperature differences.

Discussion

Model for Ink-Water Mixtures. Dielectric constant measurements provide a useful tool for investigating the internal structure of complex heterogeneous systems. Voet has shown in a series of

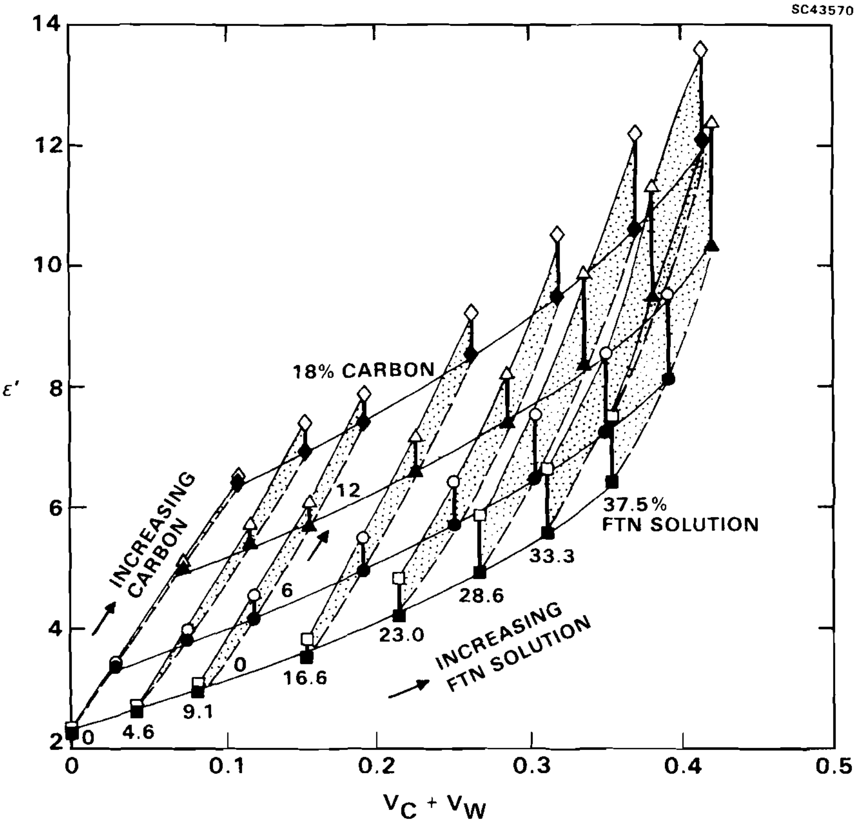

Figure 10. Effect of pump speed on the dielectric constant of ink mixtures.

articles (1947, 1953, 1957) that the dielectric constant of a liquid containing a suspension of particles is affected by the particle concentration, their shape, and their state of aggregation. He noted that suspensions of nonspherical particles have a greater dielectric constant than suspensions of spherical particles at the same concentration. Consequently, deviation from spherical shape has the same effect on ε' values as an increase in the volume of the dispersed phase.

The dependence of dielectric constant on concentration for an assembly of spherical particles suspended in a homogeneous medium is described by the well-documented equation derived by Bruggeman (1935):

$$\frac{\varepsilon_2-\varepsilon}{\varepsilon_2-\varepsilon_1}\left(\frac{\varepsilon_1}{\varepsilon}\right)^{1/3} = 1 - v_2 \qquad (5)$$

where ε is the dielectric constant of the suspension, ε_1 is the dielectric constant of the vehicle, ε_2 is the dielectric constant of the particles, and v_2 is the volume fraction of the particles.

For systems in which ε_2 is very large compared with ε and ε_1, such as with suspensions containing metals or carbon black, Bruggeman's equation becomes independent of ε_2 and reduces to:

$$\varepsilon = \varepsilon_1/(1-v_2)^3 \qquad (6)$$

For small values of v_2, that is, dilute suspensions, Eq. (6) can be written in the approximate form,

$$\varepsilon = \varepsilon_1(1+3v_2), \qquad (7)$$

where terms greater than first order in the mathematical expansion of Eq. (6) are neglected.

Voet found experimentally that for suspensions of spherical particles, Eq. (7) applies closely. For many of his systems, Voet found a linear dependence of ε on v_2, but the slope was higher than that predicted by Eq. (7). Voet ascribed this result to deviations of the suspended particles from spherical shape, and therefore modified Eq. (7) by introducing an empirical form factor f as follows:

$$\varepsilon = \varepsilon_1(1+3fv_2), \qquad (8)$$

where $f = 1$ for spherical particles and $f > 1$ for nonspherical particles. Although no quantitative relationship between the magnitude of f and the shape of the particle was given, in general, the larger the value of f, the greater the deviation from sphericity. Voet's values of f ranged from 1.0 for iron to 12.6 for copper.

Our example of a known spherical particle suspension is that of iron with the ink vehicle. The solid line from iron in Figure 7 was calculated using Eq. (6) and our measured dielectric constant of the ink vehicle. Agreement between the observed and calculated values is excellent up to 34% iron particles. With carbon black in the ink vehicle, deviation of the ε values from the Bruggeman equation with $f = 1$ is large, corresponding to the known deviation of the suspended carbon black pigment from sphericity.

With Voet's results in mind, the static results shown in Figure 1 can be understood. The large increase in dielectric constant when carbon black is added to the ink vehicle occurs because the carbon black exists as agglomerated, nonspherical clusters. The smaller increase in dielectric constant with the addition of dampening solution implies that the latter is present as essentially spherical droplets suspended in the pigmented medium.

To test this suspension model, we compared our experimental ink results with predictions based on the Bruggeman equation as modified by Voet. In Figure 7 the dielectric constants of the carbon black suspensions are in good agreement with a curve calculated using Eq. (6), except that the concentration v_2 is replaced by the product fv_2, using $f = 2.3$, chosen to optimize agreement. The calculated curve is not too sensitive to the value of f for concentrations below 0.1, and the range of f producing reasonable overall agreement is approximately 2.1 to 2.5. Comparing with Voet's results, such relatively low values of f imply only modest deviation from sphericity. By way of comparison, the f value determined by Voet (1947) for carbon black in several oily liquids under shear at volume fractions below about 0.1 was 3.9*.

In Figure 11 the dielectric constant values observed under static conditions for 0, 6 and 18% carbon black in oil containing varying amounts of dampening solution are compared with curves from two theoretical equations frequently quoted in the literature to describe the dielectric constant of dilute suspensions of spherical particles. They are the Bruggeman equation (Eq. (6)) and the Maxwell-Wagner equation (van Beek, 1967) shown in Eq. (9):

$$\varepsilon = \varepsilon_1 \frac{2\varepsilon_1+\varepsilon_2+ 2v_2(\varepsilon_2-\varepsilon_1)}{2\varepsilon_1+\varepsilon_2- v_2(\varepsilon_2-\varepsilon_1)} \tag{9}$$

where the symbols have the same meaning as in the Bruggeman equation. In our calculations we used the known dielectric constant of pure water for ε_2 and the measured dielectric constant of the ink vehicle-carbon black mixtures for ε_1.

The results shown in Figure 11 demonstrate that both theoretical models represent the observed dielectric constants reasonably well for volume fractions of water or dampening solution up to about 20%, less well at higher concentrations.

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*Voet calculated the value $f = 3.9$ for the system under shear using the linear fit denoted by Eq. (8). A better comparison with our data is obtained if we take Voet's nonlinear data for the system at rest and fit the results to the modified Eq. (6). We find the optimum fit by choosing $f = 3.0$ rather than 3.9.

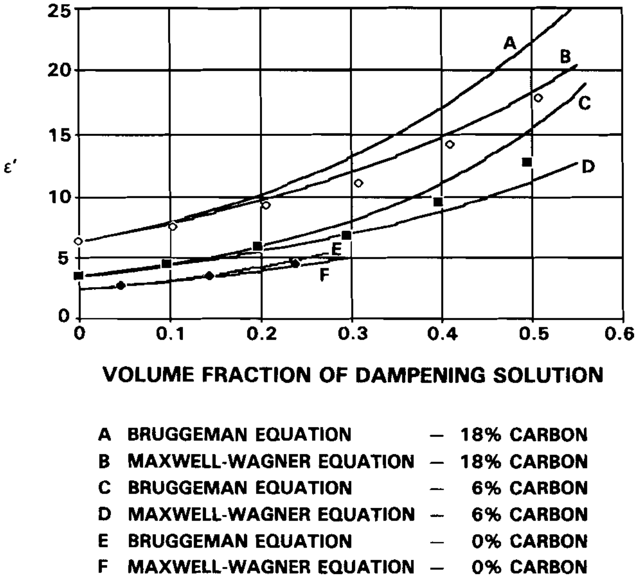

Figure 11. Dielectric constant of synthetic ink containing 0%, 6%, and 18% carbon black.

Effect of Shear on the Structure of the Ink-Water Emulsions. The data summarized in Figure 10 clearly show significant increases in dielectric constant of ink-water emulsions when subjected to shearing stress. This result contrasts with that of Voet who found higher values for systems at rest. Voet proposed that shear stress applied to emulsions initially at rest breaks up nonspherical agglomerates, resulting in a decrease in the dielectric constant. The results of our experiments differ from Voet's and require a different explanation.

The systems studied by Voet were for the most part suspensions of non-deformable solid particles in oil. Suspended water particles are expected to be deformable, and it is reasonable to assume that under shear the water droplets readily form ellipsoids, each with its major axis aligned in the direction of flow, which is also the direction of the applied electric field. Theoretically this should increase the dielectric constant (Sillars, 1937) as we have seen experimentally. Other studies measuring capacitance under shear (Voet, 1947; 1957; Bondi, 1953; Forster, 1951) have used a rotating cylinder in a cup arrangement. In these experiments the applied electric field is perpendicular to the flow. In these rotating cylindrical capacitors, the deformable spheroids will be aligned perpendicular to the electric field, resulting in a dielectric constant decrease with increased shear rate (Altshuller, 1954). This effect was in fact observed by Voet for dispersions of 0.5 normal sodium hydroxide in mineral oil. On the other hand, if instead the shear field breaks up suspended agglomerates, the dielectric constant should decrease in both arrangements. In our experiments with carbon black/oil/water mixtures, we observe an increase, not a decrease in dielectric constant. This suggests that our shear rates, which are lower than those in Voet's experiments by factors of 2-10, merely distort the spherical water particles but are not strong enough to disrupt or break up the carbon black agglomerates.

Effect of Particle Shape on the Dielectric Constant. The general equation for the dielectric constant of an assembly of spheroids characterized by major axes a and b, one of which is aligned with the electric field is given by Eq. (10) (Sillars, 1937):

$$\varepsilon = \varepsilon_1 \frac{\varepsilon_1 + [A(1-v_2) + v_2](\varepsilon_2-\varepsilon_1)}{\varepsilon_1 + A(1-v_2)(\varepsilon_2-\varepsilon_1)} \tag{10}$$

where ε_1 and ε_2 are the dielectric constants of the vehicle and the droplets, respectively, v_2 is the volume fraction of the droplets, and A is the depolarizing factor along the a axis. For prolate spheroids (a > b) the quantity A is given by:

$$A = \frac{-1}{\alpha^2-1} + \frac{\alpha}{(\alpha^2-1)^{3/2}} \ln[\alpha+(\alpha^2-1)^{1/2}] \tag{11}$$

where $\alpha = a/b$. For spheres, $a/b = 1$, $A = 1/3$, and Eq. (10) reduces to the Maxwell-Wagner equation (Eq. (9)). We can calculate ε for estimated values of α and A and compare the results with the values observed for mixtures of vehicle and dampening solution both at rest and at maximum shear. The value $A = 0.22$ representing spheroids with axial ratio $a/b = 1.6$ was found empirically to optimize agreement with experimental observation. The agreement is remarkably good, as shown in Table 2.

A theoretical shape analysis of deformable droplets suspended in a liquid under shear (Taylor, 1934) indicates that the eccentricity of a drop (defined as (a-b)/(a+b)) is directly proportional to the velocity gradient, the diameter of the drop, the viscosity of the dispersing fluid, and inversely proportional to the interfacial tension between the continuous and dispersed phases. Since viscosity is the most sensitive quantity with respect to changes in temperature, we would expect the eccentricity to decrease with increasing temperature (decrease in viscosity), resulting in a decrease in ε, which agrees with our observations. It should be noted that under static conditions the dielectric constant is not a strong function of temperature

(Goldberg, 1986). This is consistent with absence of deformation in the absence of shear.

Table 2

Comparison of Observed and Calculated Dielectric Constants for Mixtures of Ink Vehicle and Fountain Solution at Rest and Under Shear

	At rest: A = 1/3; a/b = 1		Max. Shear: A = 0.22; a/b = 1.6	
v2	ε(exp)	ε(calc)	ε(exp)	ε(calc)
0.000	2.34	2.34	2.35	2.34
0.044	2.66	2.63	2.75	2.77
0.084	2.96	2.92	3.08	3.18
0.154	3.58	3.49	3.85	3.99
0.215	4.21	4.05	4.72	4.79
0.267	4.93	4.60	5.71	5.57
0.313	5.53	5.14	6.60	6.33
0.354	6.21	5.68	7.52	7.09

We do not know from separate observations whether an axial ratio of 1.6 is reasonable. Experimental observations of ellipsoidal droplets in a fluid under shear have been reported by Bartok (1959) and Torza (1972). Since the systems studied by Bartok and Torza are very different from those studied here, a comparison is difficult to make. However, photomicrographs published by Bartok of droplets of cyclohexanol phthalate suspended in corn syrup under shear stress clearly show deformations in which the axial ratios are in excess of 1.6.

Summary and Conclusions. Our experiments allow postulating a tentative model for the ink-water emulsion system studied here:

1. Carbon-black particles in ink at rest are present as nonspherical clusters. Based on the results of Voet, carbon black clusters partially break up under strong shear. The presence of the clusters manifests itself in a higher ink dielectric constant than would be predicted for individually suspended spherical particles.

2. Dampening solution added to the ink is present in the form of individual spherical droplets suspended in the oil vehicle portion of the ink. The dampening solution droplets are readily deformed when the ink is in motion.

3. The data suggest that water droplets are freely suspended in the ink oil, but we cannot state whether they are also attached to the carbon black clusters. Carbon black stabilizes the oil/water emulsion.

4. Phosphate salts originally dissolved in the added dampening solution become strongly adsorbed on the surface of the carbon black particles at all practical concentrations. Consequently there is little difference in the electrical properties of ink mixtures containing water or dampening solution. It is not clear from our measurements how the water droplet elongation or the properties of the phosphate salts affect the printing process. It is conceivable that the adsorbed salts help stabilize the ink/water emulsion.

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