DISPERSIONS OF BARIUM TITANATE
IN ORGANIC LIQUIDS

by

MARK V. PARISH

B.S., Alfred University

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Signature of Author ______________________
Department of Materials Science and Engineering
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Certified by ______________________
H. K. Bowen
Thesis Supervisor

Accepted by ______________________
Regis M. Pelloux
Chairman, Departmental Committee on Graduate Students

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ABSTRACT

The dispersibility of four commercial grade barium titanate ($BaTiO_3$) powders in 21 pure organic liquids with various functional groups, five alcohol-organic surfactant solutions, and water was investigated. Effects on sediment volumes were observed as a function of moisture, total mass, applied force, particle concentration, and particle size distribution. Dispersibility was attributed to the formation of an electrical double layer resulting from the surface-liquid interactions.

Sediments in the best dispersed systems were uniform and dense (up to 48.3% measured powder density), yet still displayed the ability to flow. Of the liquids tested, those with acid, alcohol, and aldehyde functional groups dispersed the $BaTiO_3$ powders better than esters, ethers, ketones, hydrocarbons, and water. Concentrations up to 30 vol% showed little effect on sediment densities. However, centrifugation resulted in more dense compacts. Powders with a narrow size distribution settled to very dense cakes with some close-packed ordering observed. Moisture significantly affected the sediment volumes of only the systems that did not disperse the powders well. Of the systems tested, benzaldehyde was the best pure organic liquid dispersing medium for the $BaTiO_3$ powders; a solution of p-hydroxybenzoic acid and ethyl alcohol was the best dispersing medium overall for the $BaTiO_3$ powders.

Thesis Supervisor: H. K. Bowen
Title: Ford Professor of Engineering

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I. INTRODUCTION

The sintering of powders is a major processing method for crystalline ceramics, and a large number of materials have been densified without liquid forming additives. This practice is advantageous for the dielectric industy in aiding the control of electronic properties of their ceramic products, such as $BaTiO_3$ multilayer capacitors, but involves care in handling. Mechanisms, models, and related aspects of sintering theory have been developed,[1] and it is widely appreciated that the microstructures which develop during sintering are determined also by the powder characteristics and the powder packing.[2] As a result, several powder synthesis techniques have been applied, improving the control of particle size, particle size distribution, and the powder composition.[3 4]

The problem of handling fine powders seems best solved when the powder is dispersed in a liquid medium. Historically, ceramists have not worked extensively on particle dispersion studies, but relevant research has been done by colloid chemists,[5] especially in the field of paint technology.[6] Recent work has demonstrated significant reductions of sintering time and temperature (1730°C to 1000°C) with a narrow particle size distribution and small size, and with a uniform, but not necessarily high, green density.[7] By combining the science of ceramics and the science of fine particles, it will be feasible to comprehend the basic principles in handling and controlling small particles and to produce green bodies with void sizes no larger than an average particle size. This may be possible through the utilization of a stable dispersion of a powder possessing more nearly ideal characteristics: small size ($< 1 \mu m$), equiaxed, monodispersed, non-agglomerated, and phase and compositionally pure.[8]

In the capacitor industry, for instance, major technological consequences are derivable from research results which establish the basic understanding for controlling the powder and powder packing:

(1) The microstructure of the dielectric can be reliably reproduced.

(2) There is a total elimination of warping and cracking in densified pieces.

(3) Thinner dielectric layers can be produced.

(4) Complex shapes can be reproducibly sintered to their final shape and better control of electrode and dielectric shrinkage is possible.

(5) Sintering aids are less likely to be required.

(6) Very fine grained microstructures are obtainable which may ultimately give improved dielectric and mechanical characteristics.

(7) The sintering time and temperature will be reduced and allow for silver or nickel electrodes.

Items (1) and (2) will help lower the rejection rate (which is often as high as 40%); (3) and (4) will help increase the capacitance per unit volume; (5) and (6) will improve control over the desired properties, and; (7) will not only allow substitution of less expensive metals for the electrode layers, but reduce production energy consumption.

The dielectric layers in a multilayer capacitor are on the order of 25 to 75 μm thick, but there will undoubtedly be a demand for capacitors with much thinner layers.[9] Consequently, the quality of the layers must be maintained or possibly improved as the layer thickness decreases. To maintain the electrical properties, dependability, and reproducibility, the ceramic layer must be several (5-10) grains thick with few, if any, voids. One can argue that the degree of dispersion in the slurry, and the particle size and size distribution all affect the final microstructure, which in turn, affects the electrical properties of the end product capacitor.[10-13] The importance of a well-dispersed, non-agglomerated powder is, therefore, especially critical to casting layers of several microns thickness.

Because of its high dielectric constant and temperature behavior characteristic,[1] [14] barium titanate has been widely employed in capacitor applications. In this research, initiated by S. Mizuta, et al.,[15] the fundamental dispersion properties of four commonly used commercial $BaTiO_3$ powders in a variety of pure organic liquids were investigated.

Clarification of the adsorption mechanism and/or interactions between an organic functional group and a $BaTiO_3$ solid is very useful to understanding multi-component systems, including polymer deflocculants. The general nature of $BaTiO_3$ dispersions and the effect of moisture were investigated using sediment volume and contact angle technqiues. Experiments of concentrated $BaTiO_3$ suspensions were performed as follows:

(1) Classification of the particles to obtain a narrow size distribution.

(2) Effects of (a) particle concentration, (b) particle size distribution, (c) the total mass of powder in the suspension,

(d) centrifugal settling on a sediment volume, and (e) moisture, were examined.

Several solution-$BaTiO_3$ systems were examined utilizing hydrogen bonding surfactants and solvents to investigate acid-base interactions at the solid-liquid interface.

II. LITERATURE REVIEW

II.1. Ceramic Powders

Since particulate materials consist of small units of solid matter that have specific physical characteristics, various names have been given to describe the small units (e.g., primary particle, grain, colloid, cluster, granule, floc, etc.). Many inconsistencies exist in the literature on the definitions and uses of these terms due, in part, to the preferences of the different disciplines. Onoda and Hench [2] have proposed the following terminology for the ceramics field.

Primary particles: A primary particle is a discrete, low-porosity unit, whether it is a single crystal, polycrystal, or a glass. Since the pores, if any, are isolated from each other, the primary particle is impervious to fluids.

Agglomerates: A small mass of primary particles bonded together by surface forces and/or solid bridges and having a network of interconnecting pores is termed an agglomerate. Agglomerates held together with surface forces (electrostatic, van der Walls' attractions, or liquid capillary forces) are readily disrupted by small external forces; these are termed weak agglomerates. Agglomerates with solid bridges which result from sintering, fusion, chemical reactions, or setting of a binder, may retain their identity under a wide variety of conditions and are termed solid or hard agglomerates.

Particles: A particle is a small mass that is free to move as an entity when the powder is dispersed by the breaking up of weak agglomerates; i.e., primary particles of solid agglomerates.

Flocs: A cluster of particles that form in a liquid suspension, held together by short-range interfacial forces or by organic flocculating agents is called a "floc".

Colloids: Colloids are dispersed particles (generally submicron) that are fine enough so that Brownian motion maintains them in suspension without settling.

II.2. Organic Liquids As Dispersion Media

Organic liquids can be classified with respect to their functional groups. The liquids of interest for this study belong to the following classes: saturated hydrocarbons, alcohols, ethers, and the carbonyl compounds of aldehydes, ketones, carboxylic acid and carboxylic acid esters. Molecular structures of these groups are represented in Table 1. Because the oxygen atom has two lone pairs of electrons (see Appendix), it is an electron density-rich species able to act as a base in a Lewis acid-base interaction[16] or in a hydrogen bond.[19] The hydrogen bond has been investigated extensively and a definite shift in the electron densities of two hydrogen bonded species has been found.[17]

These interactions have been redefined into a larger group of acid-base type interactions by Drago.[20] It is not clear, however, what degree of electron separation is necesssary to define an interaction in a hydrogen bond or in a donor-acceptor bond manner. Fowkes[21] proposed that since intermolecular attractions result from fairly independent phenomena (e.g., dispersion forces (d), dipole interactions (p), hydrogen bonds (h), etc.), the work of adhesion, W, may be separated as:

$$W = W(d) + W(p) + W(h) + \cdots \tag{1}$$

and surface tension, γ, as:

$$\gamma = \gamma(d) + \gamma(p) + \gamma(h) + \cdots \tag{2}$$

Because the work of adhesion of the hydrogen bond interactions was shown not to be a function of the geometric mean of the surface energies of the species involved (as was the case for the dispersion and dipole effects), Fowkes redefined these interactions as acid-base interactions to avoid confusion and proposed a new work of adhesion term for them. The results of these findings showed that for systems where hydrogen bonding and/or acid-base interactions are present, the dispersion force interactions are relatively negligible. When hydrogen bonding liquids are used to disperse fine oxide particles, the acid-base interactions dominate the adsorption process and thus, the stability and degree of dispersion.

Hydrogen bonding, or acid-base, capabilities of the classes of liquids in this study are as follows. Hydrocarbons have no functional group, yet the pi=bonded electrons in an aromatic ring are available for donation as a Lewis acid. Alcohols have an oxygen with an attached hydrogen which are Lewis base and acid atoms, respectively, only slightly hindered by the hydrophobic (-R-) section of the molecule. Therefore, alcohols are good hydrogen bonding molecules. Ethers have a singly bonded oxygen, but this Lewis base site is hindered on both sides by hydrophobic groups. Carbonyl groups have a doubly bonded oxygen, resulting in the oxygen's lone pairs being more accessible for bonding. Aldehydes, esters, and especially carboxylic acids can form resonance stabilized ionic species,[22] where the net negative molecule then behaves as a strong interacting base.

II.3 Dispersions

II.3.1. Aspects of Dispersions

Forming a dispersion may be thought of as the complete process by which a powder is incorporated into a liquid medium; the final product being made up of particles distributed throughout the medium. Three overlapping stages of dispersing a powder seem to exist: wetting, deagglomeration, and stabilization.[6] The first stage, wetting the powder, involves the substitution of the solid-vapor interface by a solid-liquid interface. The liquid must both wet the external surfaces and displace air and/or other contaminants (e.g., adsorbed water) from the internal surfaces between the particles and clusters. At equilibrium, wetting is describable in the interrelated terms of work, surface tension, and contact angle, θ. Three degrees of wetting exist, each listed here with their related work of interaction term, W, and contact angle range:

(i) Adhesional wetting, Wa, $90 < \theta < 180$

(ii) Immersional wetting, Wi, $0 < \theta < 90$

(iii) Spreading wetting, Ws, $\theta = 0$

Young's equation relates the equilibrium contact angle (θ), formed by a sessile liquid drop on a planar solid surface, with surface energies as:

$$\gamma(l/v)\cos\theta = \gamma(s/v) - \gamma(s/l) \tag{3}$$

where $\gamma(l/v)$, $\gamma(s/v)$, $\gamma(s/l)$ are the surface energies of liquid-vapor, solid-vapor, and solid-liquid interfaces, respectively. The total work, W(T), for the overall wetting process is given by:

$$W(T) = (Wa + Wi + Ws) \propto \left[\gamma(s/l) - \gamma(s/v) = -\gamma(l/v)\cos\theta\right]. \tag{4}$$

When θ equals zero, wetting is spontaneous (spreading wetting); any intermediate state may not be spontaneous. When $\theta > 0$, fine particles which are only partially submerged result, and are evident by flotation. However, gravity may exert sufficient force on a dense particle for the liquid to spread over the solid surface and bring about complete submersion. Equation (3) can be rearranged as

$$\cos\theta = \frac{\gamma(s/v) - \gamma(s/l)}{\gamma(l/v)} \tag{5}$$

For a $\theta < 90$, θ will decrease with a reduction in $\gamma(l/v)$ or $\gamma(s/l)$, hence improved wetting. Surface active molecules can adsorb on the solid surface and accomplish a reduction in both $\gamma(l/v)$ and $\gamma(s/l)$.

The second stage of dispersion involves a deagglomeration process. After a powder has been wetted with a liquid, the weak and solid agglomerates may need to be broken down by mechanical means to a required size. Weak agglomerates may require only mild agitation to disperse, where charge and surface tension effects are important. The penetration of liquid into channels between particles in a weak agglomerate may provide sufficient air pressure to bring about cluster disintegration.[23] Solid agglomerates require mechanical energy, such as ball milling, to destroy their bonds.[24] Both manufacturing history and storage conditions greatly affect the state of the powder and will determine the mechanical process needed for deagglomeration. The deagglomeration stage may be less important than the wetting and stabilization stages if the original powder is chosen unagglomerated with the desired particle size distribution before being dispersed.

After wetting and deagglomerating the powder, the dispersed system may need to be stabilized; the third stage of the dispersing process. A stable dispersion may be thought of as one which has no change in both the total number of particles and the particle size distribution over a period of time.[25] [26] Two ways in which the number of particles decrease when a solid is dispersed in a liquid are:[27]

(i) Sedimentation under gravity of larger dense particles which cannot remain suspended by thermal agitation, and

(ii) Flocculation when the particles come in contact with each other and adhere.

There are three major types of interactions involved when particles approach one another:

(i) London-van der Waals' forces of attraction,

(ii) Coulombic forces of attraction or repulsion associated with charged particles and their double layer, and

(iii) Repulsion due to solvation and adsorbed layers, e.g., adsorbed polymers.

Brownian motion causes particles to come into close contact with each other, and it is the attractive forces between the particles which cause them to remain in contact. Therefore, without any stabilizing influence, the kinetic phenomenon of flocculation is inevitable in a dispersion.[28]

Qualitatively, the discussion of stability can be carried out in terms of the height and the distance from the surface of energy barriers, and the effects of external influences on these factors. Quantitatively, the theory of interparticle energies and their combination to give total energies of interaction has been developed.[5] This led to the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory of the interaction of two charged particles, and to theories of steric stabilization by adsorbed polymeric species in systems where charge is less important to stability. The DLVO treatment expresses the interaction energy of two particles as the sum of an electrostatic repulsive term (which depends on the interfacial electrochemisty), and an attractive term. Electrostatic forces due to the interaction of the electric double layers surrounding the particles always lead to a repulsion between particles when the surface charges are of the same sign and of the same chemical nature. Specifically, this repulsion is due to the interaction of adsorbed ions at the particle surfaces, reduced by the space charges in the double layer. Several models have been developed to relate the surface and space charge densities to their field potentials. Equations for the surface and diffuse layer charge densities in terms of the surface potential were derived by describing the diffuse distribution of counter ions accumulated near a charged interface as a Boltzmann distribution.[29] This model was later refined by Stern and Grahame[30] who accounted for the unlikely approach of the counter ions to the surface closer than approximately the ionic radii of the adsorbed species.

Applicability of the DLVO theory to aqueous dispersions has been confirmed experimentally.[31] Applying DLVO theory to nonaqueous disperions has been attempted several times, and a number of cases have been explained by the theory.[32-34] Conversely, in many systems, stabilization cannot be explained so simply and other repulsive forces besides electrical repulsion have to be taken into account.[35] [36] This stabilization was shown to be a function of aliphatic chain length of adsorbed molecules, usually polymers, and was termed steric protection.[37] The DLVO theory does not include this steric effect of adsorbed polymers on stability which is completely different from the electrical charge effect. As a result, the total interaction energy may now be thought to be the sum of the attractive, electrical (dl), and steric energies.

The effect of adsorption of macromolecules differs in many respects from that of smaller molecules due to the difference in size and resultant flexibility of the larger polymer molecule. The configuration of the adsorbed polymer molecule depends upon the active site density on the solid surface, the number and position of adsorbable functional groups in the polymer molecule, the solvent-polymer competitive interactions, etc.[38] The extent of polymer adsorption from solution is determined by the balance of three interactions: polymer-solvent (solvation), polymer-solid (adsorption), and solvent-solid (wetting). This balance will be affected by any change in the polymer, solvent, or surface.

Two main effects are associated with polymer adsorption systems: (1) the effect of "solvent power" for polymers, and (2) competitive adsorption between solvents and the polymer for the surface of the adsorbent. The solvent power relates to how well a polymer molecule is solvated. In a good solvent, a polymer molecule is more solvated and, therefore, has a larger radius of gyration occupying more space than in a poor solvent, where it is more tightly coiled. Competitive adsorption arises when polymers approach the solid surface and the solvent molecules on the surface must be desorbed before the polymer functional group(s) can be adsorbed. The competition between the polymer molecule and the solvent molecule for the surface can be a predominant factor in the adsorption process.[39]

The adsorption isotherm for polymers has been described by the Langmuir equation for monolayer adsorption that is frequently applied to the adsorption of small molecules:[38]

$$\theta = \frac{K_1 K_2 C}{1 + K_1 C} \tag{6}$$

where θ is the fraction of surface covered, C is the equilibrium concentration of adsorbate, and K_1 and K_2 are constants. Further studies by Simha, Frisch, and Eirich (SFE) led to statistically derived, theoretical isotherms for polymer adsorption as a function of ν, the average number of adsorbable segments:[40]

$$\left[\frac{\theta \exp(2K_1\theta)}{1 - \theta}\right]^{\nu} = KC \tag{7}$$

where K_1 is now an interaction parameter and K is an effective adsorption isotherm. This equation was derived by assuming that the number of adsorbed segments is a function of the molecular weight and that only a few segments attach to the surface. The unattached segments are large loops whose size increases with molecular weight.

Most of the large number of theoretical isotherm equations, many of which are modified Langmuir and SEF equations, have not been confirmed experimentally.[38] Also, many of the experimental results for polymer adsorption fit the classical Langmuir isotherm, opening the question as to whether the theoretical isotherms derived from statistical mechanics can represent more precisely the real adsorption state of polymers at the interface than can the Langmuir model.

An important factor which governs the stability of a dispersion, particularly in a nonaqueous system, is the thickness of the adsorbed layer.[38] As two particles with adsorbed polymer layers approach each other, there is an interaction between the two layers upon contact. The energy change that occurs with this interaction quantitatively defines the degree of stabilization. If the Gibbs free energy change, ΔG, of the interaction (due to overlap of adsorbed layers) is negative, then flocculation will result; if ΔG is positive, stabilization will result. Under isothermal conditions, the stability is a function of the enthalpy change, ΔH, and the entropy change, ΔS, expressed as:

$$\Delta G = \Delta H - T\Delta S \quad . \tag{8}$$

Most of the proposed theories explaining a steric stabilization mechanism and estimating the energy change with the overlap of the adsorption layer may be classified as either entropic (based on statistics) or osmotic repulsion (based on statistical thermodynamics) stabilization. In the entropic stabilization theory, an impenetrable second surface which approaches the adsorbed layer is assumed. Upon compression of the polymer segments involved, there is a region of configurational entropy loss. This reduction in entropy increases ΔG, producing a net repulsion between the particles. The enthalpic interaction between the adsorbed molecules and the dispersion medium is neglected.[41] On the other hand, the osmotic repulsion theory assumes that the adsorbed layers of two particles overlap each other with no desorption upon collision. The contact of the polymer segments with the dispersion medium molecules is reduced as a result of the contact between the segments in the overlapped region producing an enthalpy of mixing term, ΔH_m. The increased segment concentration in the overlapped region results in a reduction in the configurational entropy of the adsorbed molecules, ΔS_m. In this case, the total free energy change due to the overlap of the adsorbed layers is a function of both an enthalpic change and an entropic change as in Equation 8.[42 43]

The results of an extensive study of the effect of the dispersion medium on dispersions by varying the temperature of the system was explained by Napper in terms of thermodynamics.[44-47] Equation 8 also expresses the change in the repulsive energy, ΔG_r, when two adsorbed layers interpenetrate each other. When ΔG_r is positive, stabilization can be attained as previously mentioned. By varying the temperature, Napper distinguished the contributions of the enthalpic and entropic terms as follows:

> If upon heating, a sterically stabilized dispersion flocculates, ΔG_r changes from positive to negative, and $\frac{\partial(\Delta G_r)}{\partial T}$ will be negative near the "critical flocculation temperature" (CFT). Since the standard thermodynamic relationship for the temperature dependence of ΔG_r is:
>
> $$\left[\frac{\partial(\Delta G_r)}{\partial T}\right]_p = -\Delta S_r \tag{9}$$

ΔS_r is positive. As a result, ΔG_r will be positive only when $\left|\frac{\Delta H_r}{T\Delta S_r}\right| > 1$; i.e., the contribution of the enthalpic term is greater than the entropic term, which represents enthalpic stabilization.

On the other hand, flocculation upon cooling implies a positive value for $\frac{\partial(\Delta G_r)}{\partial T}$ near the CFT, and a negative value for ΔS_r. If $\Delta H_r > 0$, then $\left|\frac{T\Delta S_r}{\Delta H_r}\right| > 1$, corresponding to entropic stabilization.

However, both ΔS_r and ΔH_r may be temperature dependent and this simple thermal criterion may not be definite. The signs of ΔS_r and ΔH_r are determined by measuring the temperature insensitive dilution parameters, γ and κ, respectively, where:

$$\Delta H_r \propto - \kappa \quad (10)$$

$$\Delta S_r \propto - \gamma \quad (11)$$

Though the capacitor industry relies on steric stabilization for its film production, functional group-surface interactions are still present in polymer systems. Therefore, no matter which type of stabilization is present, electrostatic or steric, the need to understand the interactions present between organic liquids and powder surfaces is necessary.

II.3.2. Assessment of Disperions

Technological properties of dispersions depend upon the degree of dispersion attained and the state of flocculation of the dispersion when applied to the systems of interest. It is necessary to label a dispersion with respect to these properties as "good" or "poor" dispersions. Not only must good and poor be defined as they pertain to a particular use for a dispersion, but the experimental procedure used to evaluate the degree of dispersion must be carefully developed. Sample preparation for microscopic inspection, for example, may change the interpretation of experimental results.

It has been shown that the state of dispersion, even of dispersions considered good, falls short of separation of all the primary particles.[48] Small clusters of particles may be present, apparently as the stable units, and Jeltmar has shown that such clusters would be of an equilibrium size range determined by the balance of all forces operating.[49] As a result, a good dispersion is frequently used to mean that a good dispersive product in relation to its purpose is obtained, rather than a maximum separation of all the particles. A good dispersion may settle into a densely packed cake, but the settled clusters may remain separate entities. That is, it is quite possible for a system to be unstable with respect to sedimentation, yet relatively stable (kinetically) with respect to flocculation. This settled cake can, therefore, be regarded as a stable, highly concentrated, good dispersion and may even flow with relative ease.

There are numerous methods used to study the properties of dispersions--from crude to elaborate techniques.[50-52] These measurements may relate primarily to either the degree of dispersion attained, or to the dispersion stability, or a combination of the two.

Great care is needed in analyzing the results of tests on the properties of dispersions.

Particle size analysis is also an important parameter to be investigated. These methods may be used to follow the changes in size distribution as a function of variables of interest.[53] Since these methods involve dilute systems, modifying the results to include concentrated systems may produce erroneous results. Size analysis by sedimentation methods gives results in weight size distribution, so that no problems of converting to number size distributions occur.

An important relation between rheological properties and behavior of dispersions has been presented by Fischer.[54] Rheological methods are widely used to characterize dispersions, to study their fundamental properites, and to assess their suitability for particular technological applications.[55]

II.3.3. Sedimentation Behavior

Sedimentation behavior is of considerable practical importance. A key relationship in understanding the rate of sedimentation is Stokes' law, a hydrodynamic relationship based on a balance of the drag forces and gravitational forces acting on a spherical particle:

$$\nu = \frac{2}{9}\,\frac{R^2(\rho_2 - \rho_1)g}{\eta} \tag{12}$$

where ν is the stationary state sedimentation velocity, R is the particle radius, ρ_1 and ρ_2 are the liquid and particle densities, respectively, g is the effective gravity, and η is the absolute viscosity of the liquid. Constant temperature and a dilute (-1 vol%) suspension are assumed. Note that the terminal velocity of a particle is proportional to the density difference and to the square of the particle size. A floc, therefore, will fall at a considerably greater rate than would a smaller individual particle. Since the effective density of the irregularly shaped floc will be less than that of a particle, a flocculated dispersion will settle to a volume per unit weight of solids larger than that of a deflocculated system. In the extreme case, a deflocculated system will have a slow rate of sedimentation and a low specific sediment volume, and it would be difficult to redisperse the well packed sediment. On the other hand, a flocculated system would have a rapid rate of sedimentation, show a high sediment volume, and the sediment would be soft and easily redispersable. Therefore, the behavior of sedimentation of a dispersion is dependent upon the dispersion stability and other factors. The sedimentation volumes of a number of pigments have been shown to be related to the dielectric constants of the suspending liquids;[6] lower sediment volumes result from dispersions using liquids with higher dielectric constants, consistent with DLVO theory. Sedimentation tests yield direct information of value concerning the technological uses of dispersions, giving information about the state of flocculation, and can be performed even with fairly concentrated systems.[6]

Studies can involve two separate, interrelated factors: The rate of sedimentation, and the sedimentation volume. Under Stokes' law conditions, the size of the flocculates can be measured. However, in more concentrated systems, measurements of sedimentation rates cannot be related directly to flocculate size. A completely flocculated system will settle very rapidly, leaving a clear liquid. The rate of descent of the top surface of the sediment is dependent upon the flow of the liquid through the packed bed. The composition of the sediment in this case is loosely packed and substantially uniform throughout its depth.

A polydispersed, deflocculated dispersion forms no clear top layer, even after considerable time. A dispersed layer of variable particle concentration, with no clearly defined upper boundry, settles into a dense sediment which is difficult to redisperse.

A similar behavior has been observed for monodispersed systems.[56] When all the particles are the same size though, they all fall at the same rate, showing planes of demarcation between the settled cake and the dispersed layers, and also between the upper, clear liquid layer and the dispersed layer; the dispersed layer is uniform in particle concentration. The sediment achieved will be one of close-packing, with the interparticle spacing slightly less than that of the secondary minimum distance predicted by the DLVO theory. In the DLVO theory, the secondary minimum distance is calculated for two isolated, interacting spheres, so it is expected that the interparticle spacing would be less than this amount under experimental conditions: i.e., many particle interactions. Opalescence due to ordering was observed in settled cakes of monodispersed SiO_2 particles.[4]

II.3.4. $BaTiO_3$ Dispersion Systems

Both aqueous and nonaqueous $BaTiO_3$ dispersion systems have been widely investigated. Aqueous systems generally utilize dispersing agents containing alkali and alkaline earth ions, both of which are to be avoided in the capacitor industry due to their effects on the end-product electronic properties. Only nonaqueous systems were considered in this research; the aqueous system was included for comparison only.

Dispersing media for $BaTiO_3$ powders previously reported are listed in Table 2. High viscosity and steric effects of organic polymers are utilized in nonaqueous systems for tape casting, while an electrostatic repulsive mechanism is used in aqueous solutions for size distribution studies. Highly concentrated suspensions have also been investigated for slip casting. With the exception of reference 64, the dispersion systems listed in Table 2 were used for sample preparation and casting studies; no correlation between the dispersing media and the dispersibility was presented.

Bzdawka and Haworth, though, studied the dispersibility of $BaTiO_3$ powder in both water and methylisobutylketone (MIBK) systems with several surfactants, using sedimentation volumes and light transmittance.[64] Their results of specific sediment volumes are listed in Table 3. These results show sediment volumes of MIBK systems equal to or greater than those of the water systems. The difference was attributed to the higher dielectric constant of water resulting in a more highly dispersed system. Water impurity increased the degree of flocculation in the MIBK systems. Also, the sediment volumes contained flocculates which prevented closer packing of the particles than existed in the dry state. Surface-active agents were found to prevent some flocculation in several instances (e.g., aqueous salt solutions and oleic acid in MIBK). No mention of the surface chemistry or adsorption mechanisms was given. The work presented in this thesis demonstrates the effect of various functional groups and dispersing media on the dispersibility of $BaTiO_3$ powders.

III. EXPERIMENTAL PROCEDURES

III.1. Characterization of Starting Materials

III.1.1. Powders

Four commercially available powders were used as representative $BaTiO_3$ raw materials: TAM-C (lot 448), TAM-COF (lot 29), Transelco 219-B (lot 79654), and Fuji Titanium BT-100PL (lot 9J06). Each powder had slight differences in physical and chemical characteristics, which may effect dispersion behavior. X-ray analysis, sedigraph particle size analysis, surface area measurements, scanning electron microscopy (SEM), density measurements, and chemical analysis were performed on each of the four powders. A Quantachrome Sorption System* was used to measure the surface area using a single point BET method with nitrogen gas. The particle density measurements were made with a gas pycnometer** using helium gas. Each powder was produced by a barium carbonate-titania calcination method.

A liquid classification method was adopted to obtain narrow-size distribution, TAM-COF powder. Narrow size ranges of 0.9-1.1 μm, 0.4-0.6 μm, and 0.1-0.2 μm were collected and confirmed by SEM observation and x-ray analysis.

III.1.2. Liquids

Several representative classes of organic liquids were investigated. These included aliphatic and aromatic hydrocarbons, alcohols, ketones, ethers, aldehydes, acids and esters. The grades and principal impurities of the 21 organic liquids are listed in Table 4. Table 5 lists some physical properties of each liquid: surface

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* Quantachrome Corp.

** Quantachrome Stereopycnometer, Model No. SPY-2, Quantachrome Corp.

tension, dielectric constant, boiling point, viscosity, density, and water solubility.[71-73]

To understand the wetting phenomenon and its effect on powder dispersions, it is important to know the surface energy at the interface between the solid and the dispersing liquid.[74] By measuring the contact angle of the liquids, a relative scale of the surface energies may be obtained. The contact angles of the liquids were measured on a sintered $BaTiO_3$ substrate (TAM-COF) powder, die-pressed at 6 kpsi and sintered at 1460°C for 15 hours). A Rame-Hart Contact Angle Goniometer was used to meausre the angle formed when a 0.2 ml droplet was placed on the $BaTiO_3$ substrate surface using a syringe at 23°C in air.

III.2. The Sediment Volume Experiment

Sediment volume measurements were used to observe the general characteristics of the dispersions for each $BaTiO_3$ powder in the 21 pure organic liquids and water. The use of the sedimentation volume to evaluate the degree of dispersibility is not an absolute measurement, but since sediment volumes are inversely proportional to the degree of dispersibility, sediment volumes can be used to demonstrate relative degrees of dispersibility.

The sediment volumes were determined in the following manner. A sample of $BaTiO_3$ powder (2.0 g) was placed into a dry 10 ml glass-stoppered graduated cylinder. Sufficient liquid was added to a total volume of 10 ml, corresponding to a particle concentration of 3.3 vol% $BaTiO_3$. The cylinder was agitated by hand until the particles were thoroughly dispersed. Flotation of fine particles and turbidity of supernatant were noted after three days. The volume of the settled particles was measured after standing for 14 days. The sediment volume experiments were also performed for dried powders and dewatered (dried) liquids. The dispersion of powders is often related to the surface chemistry of the particles. The surface may have intrinsic characteristics, or more often characteristics dependent upon the processing history; surface adsorbed contaminants are of particular concern. Therefore, the effect of water, both adsorbed on the powders and contained in the liquids, was suspected to greatly influence the dispersion properties of $BaTiO_3$. The original four powders were dried in a vacuum of about 0.1 mmHg (13.3 N/m^2) at 120°C for 18 hrs; the weight loss upon drying the powders was 0.2 wt%. Each liquid was dried by placing 15.0 grams of molecular sieve* in 30.0 ml of liquid for three days.

A series of sediment volume experiments were used to investigate the effect of concentration, mass, particle size distribution, and gravity on the sediment density. The state of a $BaTiO_3$ dispersion should be kept nonagglomerated, especially under production conditions, if a liquid is to be considered a good dispersing medium for film casting.

Preliminary experiments suggested that the total mass of particles present may affect the sediment volume. For this reason, the concentration experiments were performed with a constant mass of particles, i.e., higher particle concentrations were achieved by using

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* Union Carbide Corp., Linde Division, 3A Molecular Sieves, No. MS-1015

smaller amounts of liquid while maintaining the mass of particles constant.

For each experiment in this series, a 25 ml graduated cylinder was used for mixing the liquid (benzaldehyde) and the powder (TAM-COF). The quantities used are listed in Table 6. The cylinder was shaken vigorously by hand until the powder and liquid were thoroughly mixed, and then placed in an ultrasonic bath for 30 minutes. The suspension was allowed to stand undisturbed for two weeks. After this time, almost all particles had settled out and the sediment volume was measured directly.

When the effect of mass on the sediment density was investigated, the particle concentration was held constant at 30 vol%, while the total volume of suspension was varied. The effect of a narrow size distribution on the sediment density was investigated by using particles in the 0.9-1.1 μm size range.

The effect of increased gravitational forces on the sediment density for 10, 20, and 30 vol% particle concentrations was investigated. The total suspension volume was fixed at 15 ml. A centrifuge tube was used for this test rather than a graduated cylinder. Centrifugal sedimentation was made at 12,000 rpm (17,000 g) for 10 minutes. This corresponds to all particles with a radius of 0.06 μm and larger having settled.

A sample of an as-received, 30 vol% $BaTiO_3$/benzaldehyde dispersion was mixed in a centrifuge tube and placed in an ultrasonic bath for 30 minutes. After centrifugally settling at 12,000 rpm (17,000 g) for 10 minutes, the supernatant was removed. The sediment was then dried at

90°C under a vacuum of 0.1 mmHg (13.3 N/m^3) for one day, then was observed using an SEM. This experiment was repeated using a narrow-sized (0.1-0.2 μm) $BaTiO_3$ powder.

III.3. The Effect of Hydrogen-Bonding Organics

After the preceding results were tabulated and the trends noted (see discussion), five more organic molecules (listed in Table 7) were tested to investigate possible mechanisms involved with the adsorption and stability of the dispersions. The moelcules were chosen based on their hydrogen bonding and Lewis acid-base characteristics, which proved to work well in the pure organic liquid tests, i.e., combinations of alcohol, acid, aldehyde, and aromatic ring groups.

Since these organics are solids at room temperature, they had to be dissolved in a solvent. An alcohol (ethanol) was chosen as the solvent because of its compatibility with the organics as well as its own good dispersing qualities. In general, hydrogen bonding between alcohols and a conjugate base (the organic solids in this case) is an energetically favorable component of the solvation process, i.e., alcohol is a good medium for acid dissociation.[75] Concentrations dissolved are also listed in Table 7. Sediment volume tests were performed with the solutions and TAM-COF $BaTiO_3$, using the same method as the pure organic liquid sediment volume experiments.

IV. RESULTS AND DISCUSSION

IV.1. Starting Materials

IV.1.1. Powder Characteristics

Barium titanate is usually manufactured from equimolar $BaCO_3$ and TiO_2 (rutile) mixtures heated in air or CO_2.[76] Phases of $BaTiO_3$, Ba_2TiO_4, $BaTi_3O_7$, Ba_4TiO_9, $BaCO_2$ and TiO_2 have been reported to exist in the end product.[77] The percent of each phase present is a function of temperature and soak time. The phases found in each particle are also expected to be a functin of distance from the center of the particle. Other methods include precipitation techniques of alkoxides and oxalate reactions.[78] These methods yield extremely pure, stoichiometric $BaTiO_3$ after calcination. Of course, many forms of $BaTiO_3$ powders are produced with a wide range of particle sizes and shapes, size distributions, purities, stoichiometries and surface properties; dispersions may be highly dependent upon these factors.

Chemical analyses of each of the four powders are listed in Table 8. Note that the TAM-COF and Transelco 219-3 are reported to be titanium deficient and that the TAM-C and Fuji BT-100PL, titanium excessive. The x-ray analyses indicated slight differences in peak heights (orientation), however, there was no indication of impurities, second phases, or hydrated constituents. The sedigraph particle size analyses are shown in Figure 1, and compared to the BET results in Table 9. TAM-C was the coarsest powder; the other three were similar to each other. Scanning electron micrographs are shown in Figure 2. Note the high degree of agglomeration that is typical of ceramic powders. The measured density of each powder is listed in Table 9.

An SEM photomicrograph of a sample from the 0.4-0.6 μm classified powder is shown in Figure 3. Note that the particle size is close to that predicted, estimated by Stokes' Law. The high degree of agglomeration is due to the drying, collecting, and sampling procedure.

A closer look at Figure 3 shows a significant percentage of particles less than 0.4 μm. This is due to the classification method as explained: If all the particles began their descent in a column of liquid at the exact same time and height, Stokes' Law would predict that after some time, t, the particles would order themselves from smallest to largest with respect to distance from the initial height. Classification could be executed by "slicing" horizontal layers of this column. It is more practical to begin with a homogeneous dispersed system, though, and not one with nonagglomerated powder resting on top of the liquid surface. Smaller particles will certainly settle from low heights as the desired, larger size particles settle from the top to the bottom of the dispersion.

IV.1.2. Liquid Characteristics

The results of the contact angle measurements are listed in Table 10. Measurable contact angles were found for n-octanol, benzyl alcohol, ethylene glycol, furfuryl alcohol, n-octanal, n-octanoic acid, oleic acid, and water. A zero contact angle, spreading wetting, was found for the remaining liquids. The contact angles given for ethylene glycol and furfuryl alcohol are equilibirum values measured after 20 minutes. The instantaneous, nonequilibrium contact angles are given in parenthesis. The effect is present when contaminants in the vaopr phase and/or on the surface are adsorbed at the liquid interfaces and possibly dissolve into the liquid phase.

Also listed in Table 10, is the observation of flotation of the fine particles, a result of immersional wetting. All four powders showed flotation with the same liquids. The minimum surface energy condition for a particle at the interface of two phases is a form of Young's equation,

$$\cos\theta = \frac{\gamma_{(s/v)} - \gamma_{(s/l)}}{\gamma(l/v)} \qquad (5)$$

This equation applies only to specific conditions: the vapor phase should include the vapor of the liquid with an inert vapor only, the temperature of the whole system must remain constant, no vibration should be present, and the solid must be perfectly planar, smooth, and chemically homogeneous. However, the $BaTiO_3$ substrate surface was both microscopically rough and heterogeneous, the measurement was made exposed to the atmosphere, and the sintered surface may not exactly resemble the powder surface; i.e., the accuracy of the measurements is limited. Still, the contact angle data showed a good correlation with the flotation observations, indicating the wetability of the liquids on $BaTiO_3$. The values of the contact angles and their relation to the interfacial surface energies indicate relevant dependencies. Note that Young's equation (Eq. 5) indicates that an increase in $\gamma(l/v)$ gives a larger contact angle (θ) resulting in poor wetting, unless the interfacial surface tension, $\gamma(s/l)$, is decreased. In other words, high surface tension tends to cause flotation, but it is not the determining factor. It is easily understandable that most of the high surface tension liquids showed measurable contact angles. The exceptionally good wetting and zero contact angle of benzaldehyde on $BaTiO_3$, in spite of its high surface tension, could be attributed to the extremely small interfacial energy. This low interfacial energy is due to the strong interaction between benzaldehyde's functional group and the $BaTiO_3$ surface.

IV.2. Sediment Volume Experiments

IV.2.1. The Effect of Moisture

Experimental results with evaluations on the effect of moisture and the state of the dispersions are presented in two formats. The direct results of the sediment volume tests and their corresponding sediment densities are listed in Table 11. To show the dramatic differences upon drying and the relative degrees of dispersion between different functional groups, these results are also presented graphically in Figures 4a-4d.

With respect to the effect of moisture, the suspensions which showed significant changes in sediment height (> 10%) upon drying were labeled unstable dispersions; the suspensions with slight or no changes in sediment height were labeled stable. Turbidity of the supernatant and flotation were also noted. Generally, for the undried systems, relatively well dispersed systems were obtained for the alcohols, the aldehydes, propionic acid and butyl butyrate. The same applied to the dried systems with the addition of isopentyl ether and 2-heptanone. Systems with insignificant changes in the sediment densities upon drying (i.e., stable systems) generally included the alcohols and aldehydes, propionic acid, n-octanoic acid, and water.

A small amount (~ 2 ml) of extremely agglomerated particles was found at the bottom of the cylinders for all the tests involving the Fuji powder, perhaps due to particles with a surface phase different than the other powders and undetectable through the x-ray analysis.

The results given in Table 11 suggest three objectionable features of the sediment volume experiment:

(1) The dispersibility might be dependent on the extent of drying, or the amount of water still remaining on the particle surface and in the liquid. Since the drying conditions of the powders (120°C, 18 hrs.) corresponds only to the elimination of physically adsorbed water, chemically adsorbed water may still be on the particle surface. Also, the difference in water solubility of each liquid before or even after the dehydrating procedures.

(2) Drying not only includes the elimination of moisture from the surface of an individual particle, but may also allow the agglomerates to fall apart into smaller agglomerates. Thus, the hand shaking method of agitation may not be the ideal procedure to break up the agglomerates in all size ranges.

(3) Drying the liquid with molecular sieve may rsult in contamination of the liquid. This may lead to sediment volume results not dependent on the original pure organic liquid structure, but on a contaminant which may be present in the liquid.

In spite of these experimental drawbacks, the general trends of the sediment volume results were quite distinct. The presence of water was found undesirable for hydrocarbons, ethers, ketones, and ethyl acetate, while insignificant or significantly favorable for the other systems.

The mechanism involving the effect of water on a hydrophilic solid based on the spreading coefficient of the liquids against water (S_w) was reviewed by E. K. Fischer.[54] For a given hydrophilic solid, a low sediment volume, or dispersion, results from a relatively high S_w liquid. Similarly, a high sediment volume, or flocculation, results from a relatively low S_w liquid. The facts related to this mechanism have been reported for glass spheres,[79] asphalt,[80] ZnO, ZnS, and TiO_2[81] systems. The S_w values for some of the liquids in the present work are listed in Table 4 for comparison.[54 72]

This theory is apparently applicable to the results obtained in the n-hexane, toluene, methanol, isopropanol, n-octanol, and benzyl alcohol systems, though found unacceptable as the dominating mechanism because of the following inconsistencies:

(1) The sediment volume with acetone is very high in spite of its high S_w value of 48.

(2) Despite the relatively low S_w (< 34), the sediment volume of the undried benzaldehyde system is the smallest.

(3) Considering the flotation of fine particles, the measureable contact angle, and the fairly high sediment volume for water, the affinity between $BaTiO_3$ and water is not large enough. In other words, the spreading coefficient of water on $BaTiO_3$ is considered to be less hydrophilic.

Therefore, the S_w value is not the determining factor of the moisture effect, and a more complex situation exists.

Thus, the competitive adsorption mechanism between water and a liquid onto a $BaTiO_3$ surface should be considered.[83] In this case, the preferential adsorption of liquids is reported to be greatly dependent on both the polarity of the liquid and whether the solid surface is hydrophilic or hydrophobic.[84] In addition, more extensive and detailed studies have revealed further complications in the multicomponent system. For a TiO_2 dispersion in heptanol, as reported by F. J. Micale, et al., a slight amount of water corresponding to less than a monolayer coverage of each particle was observed to be favorable for the deagglomeration of positively charged TiO_2 particles.[85] That is, a positive zeta potential increased with an adsorption of water. Another research study shows that a monolayer of water is undesirable in Al_2O_3 dispersions in C_3, C_4, and C_5 alcohols, since it reverses the zeta potential from negative to positive, enhancing flocculation.[86]

In summary, an evaluation of the state of the dispersions with respect to moisture reveals the following results:

(1) Unstable, poorly dispersed systems for the hydrocarbons, ethers, ketones, and ethyl acetate.

(2) Stable, poorly dispersed systems for water.

(3) Unstable, well dispersed systems for furfuryl alcohol, acetic acid, oleic acid and butyl butyrate.

(4) Stable, well dispersed systems for the remaining alcohols, aldehydes and acids.

Benzaldehyde was found to be the best overall dispersing pure organic liquid in this experiment.

IV.2.2. The Effects of Concentration, Mass, Gravity, and Distribution

Results of the sediment volume experiments testing concentration, mass, gravity and distribution effects are presented in Table 12 and Figure 5. Sediment densities which were approximately 40% of the measured particle density (MPD) of TAM-COF $BaTiO_3$ did not vary significantly with particle concentratin in the range of 5-30 vol%, when the total mass of the particles was kept contstant at 7.5 g (denoted ○ in Figure 5). As the total mass of particles was increased from 7.5 to 22.5 g, the sediment density was raised from 42% up to 54% of MPD at 30 vol% particle concentration (denoted ●, in Figure 5). The sediment of 7.5 g (30 vol%) narrow-sized particles (0.9-1.1 μm) denoted □ in Figure 5, (46% of MPD) was denser than that of the sediment of the original size-distributed particles. In the case of centrifugal settling, much higher densities in the range of 50-70% of MPD were found (denoted ▲ in Figure 5). Based on these results, the following three observations can be made:

(1) Sediment densities changed only slightly with concentration from 5 to 30 vol%, i.e., no flocculation was found with an increase in particle concentration. Thus, the $BaTiO_3$ dispersion in benzaldehyde is considered independent of particle concentration in this range. However, at higher concentrations, this independence will be contingent on the particle-particle replusive interaction forces.

(2) A wide particle-size distribution was considered to be undesirable for the dense and homogeneous packing of particles in a sediment. A poly-dispersed system is

favorable only when finer particles uniformly fill the voids of close packed larger particles. However, such an ideal configuration was not present with the powders in this experiment. Therefore, a wide size distribution was found to give rise to heterogeneous packing resulting in a lower sediment density.

(3) Sediment density was found to be a function of both the total mass of particles and gravity, namely, forces applied onto the particles. As a result, the liquid should be extracted from the spaces between the settling particles in the final stage of sedimentation. If each of the individual particles was deposited out of an extremely dilute suspension onto the bottom of a cylinder with a very slow settling rate, one by one, no effect of mass or gravity would be observed. But in actuality, as particles simultaneously start to settle down with various velocities corresponding to their sizes, the suspension gradually becomes highly concentrated in the lower regions of a vessel with a fairly dilute supernatant above. When such a settling-concentrating process takes place, other forces are required to produce a more densely packed settled cake, since the capacity of a vessel is limited. Therefore, an increase in the total mass of the particles and/or the gravitational force is considered to enhance the "squeezing" of the highly concentrated layer of the suspension.

IV.2.3. Observations of the Sediment

SEM photomicrigraphs of the centrifugally settled particles are presented in Figure 6, showing the top surface of the as-received TAM-

COF powder, and in Figure 7, for the 0.1-0.2 μm narrow-sized distributed powder. Even though the as-received powders seem well packed for a ceramic green body, extremely dense and uniform packing of particles is observed for the sediment of the narrow-sized distributed particles. No voids larger than the particle size are present and several areas show ideal close packing of spheres. This is further evidence that benzaldehyde disperses $BaTiO_3$ well. Also, due to the greater degree of ordering/packing, there is an increase in the particle-particle contacts. Not only does this improve the strength of a green piece, but allows a decrease in the amount of binder necessary for a tape-cast, slurry formulation.

IV.3. Surface-Liquid Interactions

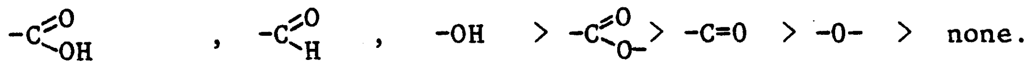
For the preparation of a stable suspension, some polarization of the solid-liquid interface is required according to the general principles of colloidal suspensions.[87] Thus, the dielectric constant (ε) of the liquid is assumed to be related to the stability of a suspension; i.e., a high ε is favorable for a stable suspension, while a low ε tends to give rise to flocculation. Relations between ε and the state of the dispersions are presented in Table 13. No strong correlation are found; e.g., propionic acid, n-octanoic acid, and butyl butyrate show dispersions in spite of their low ε. Thus, the dielectric constant is considered a less important factor in the stability of commercial grade, $BaTiO_3$ powder dispersions.

On the other hand, a significant correlation exists between hydrogen bonding and the state of $BaTiO_3$ dispersions as shown in Table 14. Two exceptions are water and butyl butyrate. Butyl butyrate is an ester of butanoic acid and butanol, minus water. Since the presence of both of these molecules is inevitable in butyl butyrate, and based on the behavior of the other acids and alcohols tested, both would "aid" in dispersing $BaTiO_3$. Since there seemed to have been a competitive interaction between water and many of the organics for the surface, water may have been expected to disperse $BaTiO_3$ better than it had. However, even though distilled water was used, it was not deionized. Ions are known to have a marked effect on the particle-particle interactions, possibly producing a poor dispersion. In addition, the surface of the $BaTiO_3$ may have contained an extremely hydrophobic adsorbed species with which only certain organic liquids could interact favorably. Aqueous systems were not investigated in this research.

Since nonstoichiometric, Ba-excessive $BaTiO_3$ powders (Ba/Ti > 1) are reported to dissolve slightly in acetic acid,[88] some $BaTiO_3$ dissolution is assumed present in the acids and even in the aldehydes or alchols. However, note that similar results were present for both the Ba-rich powders (TAM-COF and Transelco 219-3), and also the Ti-rich powders (TAM-C and Fuji BT100PL).

Overall, the intensity of the interactions between organic functional groups and a $BaTiO_3$ surface can be expressed as:

Carboxylic Acid, Aldehyde, Alcohol >Ester >Ketone >Ether >Hydrocarbon



$$-\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow\!\!\!\nearrow\mathrm{O}}{\searrow\mathrm{OH}} \;,\; -\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow\!\!\!\nearrow\mathrm{O}}{\searrow\mathrm{H}} \;,\; -\mathrm{OH} > -\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow\!\!\!\nearrow\mathrm{O}}{\searrow\mathrm{O}-} > -\mathrm{C}=\mathrm{O} > -\mathrm{O}- > \text{none.}$$

The functional groups having greater interactions (or adsorptions) with a $BaTiO_3$ surface are found to be less sensitive to the presence of water.

If the $BaTiO_3$ surface can be regarded as alkaline, the adsorption of electron accepting liquids onto the surface may be regarded as an acid-base reaction. Likewise, if the $BaTiO_3$ surface is regarded as acidic, electron donating liquids may adsorb on the surface with a similar type of acid-base reaction. As explained in section II.2., acids, aldehydes, and alcohols may behave as both a Lewis base or a Lewis acid depending upon their position and their associated/dissociated form. If these molecules preferentially adsorb onto a $BaTiO_3$ surface, the effect of water is expected to be slight. Although the exact mechanism of an acid-base and/or hydrogen bonding adsorption has not been determined in this study, the importance of electron donating capability is presented.

The five additional organic structures listed in Table 7, were tested to further investigate this acid-base type adsorption at the $BaTiO_3$ surface. Each solution dispersed the $BaTiO_3$ powder well, and though benzoic acid was excellent in dispersing the powder, p-hydroxybenzoic acid performed the best, producing a sediment of 48.3% MPD (see Table 15). The combination of the alcohol and acid functional groups directly attached to an aromatic ring in the para position, combined with the alcohol solvent, proved to have extremely favorable liquid-surface interactions. The exact adsorption mechanism of these molecules on the surface of the TAM-COF $BaTiO_3$ powder is not known, but a possible mechanism of adsorption and the development of a double layer can be used to explain the results. Surface charge is developed by ionization of the amphoteric $BaTiO_3$ surface sites through the reactions with the organic molecules and their dissociated constituents. Organic molecules with functional groups of higher polarity or molecules which more easily form their conjugate bases (i.e., the more stabilized a molecule is in its ionic form) interact more favorably with the surface to develop the ion-counter ion double layer. The charge formation resulting from such reactions, stabilizes the dispersion, allowing it to settle into a dense compact.

V. CONCLUSIONS

Stable, well dispersed commercial grade $BaTiO_3$ dispersions are possible in media containing only pure organic liquids; no alkali/alkaline earth or polymeric surfactants were used. Of the liquids used, ones with acid, alcohol, and aldehyde functional groups disperse the $BaTiO_3$ powders better than esters, ethers, ketones, and hydrocarbons. These conclusions are based on sediment volume tests, wetting behavior, and SEM observations of the settled cakes. Moisture has little effect on the systems that worked well, and a significant effect on the other systems. Sediment volumes decreased with an increase in the mass or an applied gravitational force to the system. Particle concentrations between 5 and 30 vol% has little effect on the sediment density. Sediments of the best dispersed systems are uniform and dense, yet display the ability to flow, i.e., plastic behavior.

Dispersibility in the examined systems is attributed to the formation of an electrical double layer resulting from the surface-liquid interactions. These interactions are defined by the powder surface characteristics and the functional group of the liquid molecule; they range from polar effects to hydrogen bonding to dissociation/association reactions and acid-base reations.

Of the pure organic liquids tested, benzaldehyde disperses $BaTiO_3$ powders best. A solution of p-hydroxybenzoic acid and ethanol disperses commercial $BaTiO_3$ powders better than any of the liquid systems tested.

VI. FUTURE RESEARCH

The importance of a well-dispersed, non-agglomerated powder is especially critical to casting layers of several microns thickness. In industry, tape casting is a major method utilized to produce thin, green sheets of a dielectric ceramic on which electrodes are screen printed.[89] These layers are then laminated and cosintered.[90] The liquid medium not only has to disperse the powder well, but provide the necessary rheological properties of the slurry during casting; the cast layer must dry to a workable product to enable the successful manufacture of the component.

Major constituents usually included in the liquid vehicle forming the casting slurry are the solvent, deflocculant, binder, and plasticizer.[91] Each of these has to be volatile upon heating and leave no residue behind. There are two principal types of solvents used in slip preparations, aqueous and nonaqueous. Requirements for the solvent not only include that it be volatile at a low temperature, but that it be effective in dissolving or dispersing the other slurry components (qualities found more often in organic systems). Preferred characteristics for the solvent include a low viscosity, non-flammability, reclaimability, and should not dissolve or chemically react with the dispersed powder.[61 92] When a combination of solvents is used, azeotropic mixtures should be chosen to avoid preferential volatilization.

The dispersant, or deflocculant, must be used to prevent the particles from flocculating. However, another constituent of the liquid medium (the solvent for example) may disperse the particles well, avoiding the use of the deflocculant.

After the powder has been dispersed, film-forming binders and plasticizers are added. The function of the binder is to provide strength to the green film after the solvent evaporates during a subsequent drying operation. The binder is chosen to enable the film to have good handling, machining, and storage characteristics . A proper binder will not contribute to the formation of cracks, pinholes, and defects in the unfired or fired film. In addition, the binder should be compatible with the surface on which the film is cast. Plasticizers are added to most binders to lower viscosity, improving the flexibility and workability of the green film. The plasticizer has to be soluble in the solvent, but should not phase separate from the binder. Occasionally, plasticizers are present in amounts greater than the binder itself. In aqueous systems, wetting agents promote both the slip spreading during casting (preventing pinhole formation) and the formation of uniform slip viscosity.

The present film technology of casting formulations is based predominantly on empirical reasoning with little understanding of the fundamental behavior involving the specific constituents beyond a few general objectives. Nonaqueous slurry formations dominate in industry; more research is needed to optimize the performance of aqueous systems. Though the risk of certain constituents hydrating and slower drying rates hinder its use, aqueous systems are attractive when considering cost and environmental aspects. Some previously employed $BaTiO_3$ systems have been included in Table 2.

The primary objective of the proposed research is to apply the dispersion characteristics demonstrated in this thesis toward understanding and improving the dispersed-slurry systems used by the multilayer capacitor industry. This work will necessitate the understanding of the interactions and the mechanisms involved in a casting slurry; a suitable liquid medium will be developed based on these understandings. Further studies will include the development of an appropriate thin layer process, determination of optimum powder properties needed for this process, and characterizing the resulting multilayer ceramic in the green state.

The following procedures and techniques to be utilized for each of these steps is explained:

(i) The adsorption mechanism and behavior of several binders will be investigated and their extent of stabilization in a $BaTiO_3$ system will be determined. A qualitative, infrared (IR) analysis will indicate how the binder molecules are oriented on the particle surfaces. Thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and scanning electron microscopy (SEM) will aid in investigating the behavior and state of the binder-particle interactions. Several presently employed binder $BaTiO_3$ powder systems will be investigated. The TGA and DTA along with an evolved gas analysis will aid in the investigation of decomposition of the organic constituents. If equiaxed, monosized particles are cast in a perfect array, open channels exist throughout the entire cast layer. These channels allow the important removal of the organic molecules from the structure completely upon heating, leaving no residual carbon behind.

Problems which may be encountered include blockage of this interconnected pore structure by the formation of organic "skin" buildup. As the particles begin to sinter, carbon becomes trapped in the structure creating an unfavorable situation.[93] If the organics involved were to decompose at a low enough temperature into small, volatile molecules which easily desorb, this problem may be avoided. This situation becomes more important as the particle size distribution deviates from the ideal equiaxed, monosized case. Although available narrow-size distributed particles form areas of ordered arrays, some areas will not be ordered and the uniform, interconnected pore structure may not exist; i.e., passage of the organic molecule through the pore channels may be too constricted or blocked for large macro-molecules but not for smaller ones.

(ii) Based upon the previous liquids investigated and the desired properties of the solvent, a lower alcohol (methanol, ethanol, or propanol) seems to be the most appropriate choice. Based on the information found in element (i) above, it may be possible to develop a solvent-binder medium for $BaTiO_3$ powders avoiding dispersants, plasticizers, or other additives. A possible molecular structure may be extended upon the p-hydroxybenzoic molecule which proved to work well as a dispersant for $BaTiO_3$. Selection of a system will depend on availability, dispersibility (indicated by sediment volume tests and SEM observation), and decomposition behavior (revealed by TGA and DTA data). It is important that upon drying, enough strength is provided by the binder to the cast layer for workability. It is for this reason that polymer-binder systems are chosen; i.e., polymer binders provide the dried (laminated) layers with enough flexibility so they can be punched, cut, pushed, and handled without cracking or damaging the green component. However, unlike substrates, capacitors only need to be produced in simple shapes (rectangular). Therefore, less binder may be required due to the reduction in handling. Since narrow-size distributed particles can be utilized [see element (iv)], a greater degree of ordering is achieved, as demonstrated in this thesis. As a result, particle-particle contact is increased and less binder should be necessary to provide the required strength. Also, it may be possible to use smaller macro-molecules than the presently employed, extremely large (molecular weights of 10^4-10^5 g/mol) polymer molecules. Smaller molecules may be kinetically and thermodynamically favorable over larger macro-molecules since they may decompose, desorb and depart from the green structure at a lower temperture with less problems than macro-molecules.

In addition, adsorption isotherms will be measured and IR spectroscopy will be employed to investigate the adsorption mechanisms involved and the degree of adsorption. The effects of temperature and moisture will be examined.

(iii) Though the doctor-blade technique is industrially popular for film production, a process similar to silk screening will be employed in this research. Both the conductive and dielectric layers will be alternately screen printed on a suitable base. Ihochi referred to this process as a screened multilayer ceramic (SMC) process.[94] Important factors which must be considered with multilayer screen printing include:

(1) screenability of pastes
(2) pinhole freedom in the screened dielectric, and
(3) surface flatness.

Screening the dielectric layer is very critical, as the uniformity of the layer thickness determines the capacitance between the metallized layers. The screenability controls the packing density of the product. A highly viscous slurry may improve the printed pattern resolution, but uniformity may be lost due to insufficient flow needed to seal pinholes. These opposed requirements of printability and pinhole freedom will have to be considered during the preceding slurry formation steps. Print resolution will be important, but not critical in this application since the capacitor will be sectioned from a larger cast piece. Further, surface flatness has to be maintained at each printing stage. If mechanical leveling is necesssary, the method chosen must be carefully controlled so as to maintain uniformity of the green density. Density variations lead to warping or deformation of the piece during firing. Finally, both the screen and substrate with which the layers are to be cast will be chosen to be compatible with the slurry system developed above.

(iv) The optimum properties of the $BaTiO_3$ powder will be defined by the limitations of the thin film process. Characterization will include x-ray analysis, sedigraph particle size analysis, multi-point BET surface area measurements, SEM observation, gas pycnometer density measurements, and chemical analysis. A goal of a five micron dielectric layer thickness has been chosen which necessitates an average particle size in the 0.1-0.5 μm range; this will maintain a several grain thickness layer in the sintered product. For reasons mentioned in (ii), fractionated, narrow-size distributed, commercially available $BaTiO_3$ powder will be used, though equiaxed, monosized precipitated $BaTiO_3$ powder will be substituted pending availability. The increase in the degree of ordering also helps control the shrinkage, cracking, and warping problems experienced in the capacitor industry.

(v) Characterization of the green-state multilayer capacitor will include density, tensile properties, laminated bond strength, permeability, and compressive properties as defined by R. A. Grandner and R. W. Nufer.[95]

APPENDIX

1. Bonding in Organic Liquids

To more completely understand the adsorption mechanisms and bonding characteristics of these organic molecules, it is important to review the shapes of organic molecules and their electron distributions. The molecular orbital model is a means of describing these chemical bonds with quantum-mechanical reasoning. First, consider atomic orbitals; the region of space near the small, massive nucleus in which there is a high probability of finding an electron. Classically, the solution to the Schroedinger wave equation results in a description of the shapes of orbitals, the energies of the electrons in their orbitals, and the electrons' spin angular momentum. Shapes of electron orbitals of interest in this study include the spherical 1s and 2s orbitals, and the ellipsoid-like orbitals of the $2p_x$, $2p_y$, and $2p_z$ orbitals which lie on three mutually perpendicular axes and contain a node at the origin (nucleus). By using the Pauli exclusion principle (no more than two electrons per orbital), the electronic structure of the three atoms of interest can be presented as: hydrogen, H, one electron, $1s^1$; carbon, C, six electrons, $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$, and; oxygen, O, eight electrons, $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$.

The process of bond formation between two atoms may involve the hybridization of the atomic orbitals in one or both atoms, and the combination of atomic and/or hybrid orbitals to form molecular orbitals. Favorable energetics of bond formation require maximum orbital overlap and a maximum number of bonds consistent with electrostatic and steric forces. Hybridization (the combination of the outer shell-bonding orbitals, specifically the 2s and 2p orbitals of C and O, to form symmetric, energetically degenerate spin hybrid orbitals) provides the maximum bonding interaction and minimum energy for the molecule. The most commonly encountered hybridizations, and those important in this study are sp^3 and sp^2. The three 2p orbitals combine with the 2s orbital to form sp^3 hybrid lobes, each oriented toward a corner of a tetrahedron (109°). The combination of two 2p orbitals and a 2s orbital form an sp^2 hybridization. The sp^2 orbitals consist of three lobes, 180° apart in a common plane perpendicular to the remaining p orbital. When two orbitals of two separate atoms form a bond such that the electron density is along the axis connecting the nucleus of each atom, the bond is termed a sigma (σ) bond. The p orbital not involved in the sp^2 hybridization may bond to a similar p orbital in the other atom, forming a pi (π) bond encircling the σ bond along its axes to produce a double bond. A maximum of four, single σ bonds form with sp^3 hybridization; three σ bonds and a π bond (two single bonds and one double bond) form with sp^2 hybridization.

As noted above, carbon has four electrons in its outer shell, thus it can form four bonds when sp^3 hybridized, or a double bond and two single bonds when sp^2 hybridized. Oxygen, on the other hand, has six electrons in its outer shell. In the tetrahedral sp^3 configuration, oxygen will form two single bonds and have two pairs of non-bonding electrons (lone pairs). When sp^2 hybridized, oxygen forms a double bond with two lone pairs.

The polarity of these bonds determines the Lewis acid-base (electron acceptor-electron donor) behavior.[16] The attractive interaction between a Lewis acid and a Lewis base can range from dipole-dipole weak attractions to slightly stronger hydrogen bonds and even to dissociation-association electrostatic interactions.[17] Situations of interest in this research are as follows: The C-H bond is very nonpolar, except when an electronegative atom (such as a singly bonded oxygen, or, even more electronegative doubly bonded oxygen) is also bonded to the carbon, in which the hydrogen behaves acidic.[18] The O-H bond is very polar and forms an acidic region at the hydrogen site, and a basic region at the oxygen lone pair area. This O-H group often forms hydrogen bonds. When oxygen is singly bonded to two carbon atoms, a low-polarity situation is present. Even though the oxygen has two lone pairs as a potential base site, the two attached carbon chains hinder any interaction with an acidic site. When an oxygen atom and a carbon atom are doubly bonded to each other, the pair is referred to as a carbonyl group. The lone pairs on the oxygen interact as a strong Lewis base in this very polar group. One other Lewis donor, though weak, is the aromatic ring (a six carbon ring of three pairs of resonating single and double bonds, represented as  or ), in which its π bonding electrons are available for donation.[18] The aromatic ring can also stabilize a charge of an attached dissociated functional group by resonance.

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TABLE 1

CLASSES OF ORGANIC COMPOUNDS

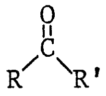
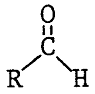
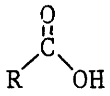
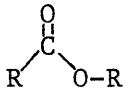
CLASS	FUNCTIONAL GROUP
Hydrocarbon (-R)	none
Alcohols	R-OH
Ethers	R-O-R'
Ketones	
Aldehydes	
Carboxylic Acids	
Esters	

TABLE 2

Dispersions of $BaTiO_3$

	Solvent Basis (Vehicle Basis)	Dispersing Agent or Binders	Comments	Ref
Nonaqueous	polycarbonate and polysulfone polymers		tape casting	57
	camphor and naphthalene		high viscosity sublimation	58
	xylene and/or amyl acetate	polyethylene glycols, lecithin, polyisooctylphenyl ether, butylmethacrylate	high viscosity tape casting	59
	tetrahydrofuran	polystyrene	tape casting	60
	toluene	diethyl oxylate, lecithin, staybelite, albalyn, ethocel type 50, diethyl oxalate, ethyl cellulose		61 62
	toluene	vinyl chloride copolymer, triethylene glycol, methoxypolyethylene glycol	tape casting	63
	MIBK Water	various commercial surfactants,oleic acid	dispersion studies	64
Aqueous	water	sodium pyrophosphate sodium borate triethylam monium dodecylsulfate	photosedimentation, particle size analysis	65 66
	water	sodium phosphate	particle size analysis	67
Slurry	water	tannic acid, ammonium	slip casting	68
	polyvinyl alcohol	glycerol, triethylamine, tannic acid	slip casting	69
	water	sodium pyrophosphate	slip casting	70
	toluene and polyvinyl butyral	alkyl ether, polyethylene-glycol	tape casting	9

TABLE 3

Specific Sediment Volumes (cm^3/gm) of $BaTiO_3$
From Ref. 64

Surfactant	Solvent			
	Water	MIBK	MIBK + 1% Water	Dry
none	0.94	1.07	0.90	0.77
Triton X-45*	0.97	0.83		
Triton X-102*	0.98	0.92		
Tamol 731+	0.47	1.52		
Tamol 8509+	0.47	1.57		
Darvan C‡	0.47	1.67		
Tween 209†	0.93	0.93		
Oleic Acid	1.33	0.57		

* Alkylaryl polyether alcohol
\+ Sodium salt of polymeric caroboxylic acid
‡ Ammonium salt of a polyelectrolyte
† Polyoxyethylene sorbgitan monolaurate

TABLE 4

Grades and Impurities of the Organic Liquids Used

No.	Liquid	Supplier	Grade	Main Impurities
1	Hexanes	Fisher	Certified	Sulfur Compound, 0.002%
2	Toluene	J. T. Baker	A. R.	Sulfur Compound, 0.002%
3	Di-ethyl Ether	Malinckrodt	Reagent	H_2O, 0.01%, CH_3COOH, 0.001%
4	Isopentyl Ether	J. T. Baker	Baker	-
5	Acetone	Mallinckrodt	Analytical	CH_3OH, 0.01%, $(CH_3)_2CHOH$, 0.005%, H_2O, 0.3%
6	2-Heptanone	Aldrich	-	-
7	Methanol	Mallinckrodt	Absolute	$(CH_3)_2CO$, 0.001% CH_3COOH, 0.0018%
8	Ethanol	US Ind. Chem.	Reagent	-
9	n-Octanol	Fisher	Certified	$C_7H_{15}COOH$, 0.01%
10	Benzyl Alcohol	Mallinckrodt	Analytical	C_6H_5CHO, 0.2%
11	Isopropanol	Fisher	Certified	H_2O, 0.1%
12	Ethylene Glycol	Fisher	Certified	CH_3COOH, 0.004% H_2O, 0.2%
13	Furfuryl Alcohol	Matheson Colman & Bell (MC&B)	-	-
14	n-Octanal	Aldrich	-	-
15	Benzaldehyde	J. T. Baker	A. R.	-
16	Acetic Acid	Mallinckrodt	Glacial(ACS)	$(Ch_3CO)_2O$, 0.0002%
17	Propionic Acid	Fisher	Certified	H_2O, 0.1%
18	n-Octanoic Acid	Eastman	-	-
19	Oleic Acid	Atomergic Chem. Corp.	Reagent	-
20	Ethyl Acetate	Mallinckrodt	Analytical	CH_3COOH, 0.002% H_2O, 0.02%
21	Butyl Butyrate	City Chemical Corp. (NY)	-	-

TABLE 5
Physical Properties of the Liquids*

Liquid	Dielectric Constant≠	Vapor-Liquid Surface Tension≠≠ (mN/m)	Boiling Point≠ (°C)	Viscosity≠ (cPoise)
1 Hexanes	1.89 a	18.4 a	69.0	0.326 a
2 Toluene	2.4 b	28.5 a	110.6	0.590 a
3 Di-ethyl Ether	4.335 a	-	34.6	0.222 b
4 Isopentyl Ether	2.82 a	22.85 c	173.2	-
5 Acetone	20.7 b	25.1 a	56.2	0.316 b
6 2-Heptanone	9.77 c	26.7 a	151.5	-
7 Methanol	32.6 b	22.5 a	64.6	0.597 a
8 Ethanol	24.30 b	22.39 a	78.5	1.200 a
9 n-Octanol	10.3 a	27.5 a	194.5	10.6 d
10 Benzyl Alcohol	13.1 a	35.5 a	205.4	5.8 a
11 Isopropanol	18.3 b	21.3 a	82.4	2.86 d
12 Ethylene Glycol	38.7 a	48.4 a	197.5	20.5 a
13 Furfuryl Alcohol	-	38.0 a	171	4.402 f
14 n-Octanal	-	-	163.4	-
15 Benzaldehyde	17.8 a	38.5 a	178.1	1.315 c
16 Acetic Acid	6.15 a	27.59 a	118	1.155 b
17 Propionic Acid	3.30 e	26.7 a	141.0	1.18 a
18 n-Octanoic Acid	-	28.0 a	239.3	4.63 f
19 Oleic Acid	2.46 a	-	286.0	25.6 f
20 Ethyl Acetate	6.15 a	23.52 a	77.06	.416 b
21 Butyl Butyrate	-	25.72 a	164.8	.977 b
22 Water	78.5 a	72.75 a	100.0	1.002 a

* Temperature (°C) at which measurement was made: a = 20°, b = 22°, c = 22° d = 15°, e = 10°, f = 30°.

≠ Handbook of Chemistry and Physics, ed. R.C. Weast, CRC Press, Cleveland, 1974, (55th ed.), REf. 72.

≠≠Jasper, J.J., "The Surface Tension of Pure Liquid Compounds", J. Phys. Chem. Ref. Data, 1, 84-1010 (1972), Ref. 71.

TABLE 5 (continued)
Physical Properties of the Liquids

Liquid		Density* (g/cm^3)	Hydrogen Bonding ‡	Spreading Coefficient Against H_2O (S_v)	Solubility to H_2O
1	Hexanes	0.688	n	3	insoluble
2	Toluene	0.865	n	7	insoluble
3	Di-ethyl Ether	0.706	ed	-	slightly
4	Isopentyl Ether	-	ed	-	insoluble
5	Acetone	0.791	ed	49	∞
6	2-Heptanone	0.820	ed	50	soluble
7	Methanol	0.791	ea,ed	51	∞
8	Ethanol	0.789	ea,ed	-	∞
9	n-Octanol	-	ea,ed	37	insoluble
10	Benzyl Alcohol	1.045	ea,ed	33	soluble
11	Isopropanol	0.785	ea,ed	51	∞
12	Ethylene Glycol	1.114	ea,ed	-	∞
13	Furfuryl Alcohol	1.128	ea,ed	-	∞
14	n-Octanal	0.821	ed	-	slightly
15	Benzaldehyde	1.043	ed	<34	slightly
16	Acetic Acid	1.049	ea,ed	-	soluble
17	Propionic Acid	0.993	ea,ed	-	∞
18	n-Octanoic Acid	0.110	ea,ed	-	slightly
19	Oleic Acid	0.895	ea,ed	-	slightly
20	Ethyl Acetate	0.898	ed	-	soluble
21	Butyl Butyrate	0.869	ed	-	slightly
22	Water	1.00	ea,ed	-	∞

* densities at 25°C
‡ ea = electron acceptor, ed = electron donor,
n = neither, inert

From Refs. 47, 48, 50.

TABLE 6
Sediment Volume Test Parameters

Experiment*	Particle Concentration vol%	Volume of Suspension (ml)	Volume of Liquid (ml)	Weight* of Particles (g)
Concentration Effect	5	25.0	23.75	7.5
	10	12.5	11.25	7.5
	20	6.25	5.0	7.5
	30	4.17	2.92	7.5
Mass Effect	30	4.17	2.92	7.5
	30	8.33	5.83	15.0
	30	12.5	8.75	22.5
Gravity Effect	5	15.0	14.25	4.5
	10	15.0	13.5	9.0
	20	15.0	12.0	18.0
	30	15.0	10.5	27.0
Distribution Effect**	30	4.17	2.92	7.5

* 6.0 g/cc was considered the density of $BaTiO_3$

** narrow-sized particles of 0.9 - 1.1 μm

TABLE 7
Hydrogen-Bonding Organics

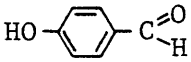
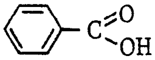
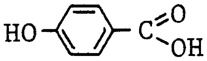
Name	Structure	Concentration in Ethanol, wt%
p-Hydroquinone		26
p-Hydroxybenzaldehyde		13
n-Nitrobenzaldehyde		3.3
Benzoic acid		56
p-Hydroxybenzoic Acid		32

TABLE 8
Chemical Analysis* of the Powders Used

	TAM-C Lot 448	TAM-COF Lot 29	Transelco (219-3) Lot 79654	Fuji BT-100PL 9J-06
SrO	1.00	0.71	0.35	1.46
Na_2O	0.006	0.02	0.10	0.079
SiO_2	0.1	0.05	0.02	<0.2
P_2O_5	0.007	0.05	0.06	
Al_2O_3	0.12	0.13	0.18	<0.2
CaO			0.08	
Fe_2O_3	0.005		0.007	
K_2O			0.007	
ZrO_2			0.007	
Nd_2O_5			0.20	
SO_3	0.23	0.19	0.22	
CO_2	0.17	0.46		
BaO	63.73	64.80	64.38	
TiO_2	34.57	33.30	33.52	
Ig loss	0.18	0.53	0.64	0.387
(Sr + Ba)/Ti	0.976	1.030	1.006	0.983

* by supplier, wt%

TABLE 9
Powder Characteristics

	Particle Size (μm) at 50% cut*	% Particles less than 0.7 μm*	B.E.T. Surface Area (m^2/g)	Density (g/cm^3)
TAM-C (lot 448)	2.2	5	1.5	5.90
TAM-COF (lot 27)	1.4	18	2.1	5.92
Transelco 219-3 (lot 79654)	1.15	20	2.3	5.85
Fuji Titanium BT 100PL (lot 9)	1.3	15	1.6	5.80

* from Sedigraph, Fig. 1.

TABLE 10
Contact Angle and Flotation Results

	Liquid	Contact Angle (°)	Flotation of Fines
1	n-Hexane	0	no
2	Toluene	0	no
3	Di-ethyl Ether	0	no
4	Isopentyl Ether	0	no
5	Acetone	0	no
6	2-Heptanone	0	no
7	Methanol	0	no
8	Ethanol	0	no
9	n-Octanol	15	yes
10	Benzyl Alcohol	22	yes
11	Isopropanol	0	no
12	Ethylene Glycol	18 (52)*	yes
13	Furfuryl Alcohol	6 (24)*	yes
14	n-Octanal	27	yes
15	Benzaldehyde	0	no
16	Acetic Acid	0	no
17	Propionic Acid	0	no
18	n-Octanoic Acid	31	yes
19	Oleic Acid	27	yes
20	Ethyl Acetate	0	no
21	Butyl Butyrate	0	no
22	Water	22	yes

* The contact angles given for ethylene glycol and furfuryl alcohol are equilibrium values measured after 20 min. The instantaneous contact angle is given in parenthesis.

TABLE 11
Sediment Volume Tests Results: The Effect of Moisture, %MPD

Liquids	TAM-COF		TAM-C		Fuji		Transelco	
	U*	D^{+}	U*	D^{+}	U*	D^{+}	U*	D^{+}
Hexanes	5.4	7.0	6.8	10.6	8.4	8.4	6.8	7.8
Toluene	5.7	8.2	7.4	8.3	7.0	7.5	8.1	8.3
Isopentyl Ether	9.9	22.5	12.1	28.2	14.4	24.6	13.1	22.8
Ethyl Ether	9.1	19.3	9.5	15.4	9.1	16.4	10.4	15.6
Acetone	7.3	18.8	10.9	24.2	8.0	19.2	9.5	19.0
2-Heptanone	14.1	22.5	18.8	26.1	11.9	20.3	14.9	21.4
Methanol	24.1	24.1	28.2	30.8	34.5	28.7	22.8	22.8
Ethanol	24.1	25.0	26.1	26.1	28.8	28.8	2.14	21.4
n-Octanol (f)	22.5	21.1	28.2	26.1	21.6	20.3	22.8	22.8
Benzyl Alcohol (f)	26.0	26.0	26.1	28.2	21.6	24.6	24.4	21.4
Isopropanol	24.1	24.1	26.1	28.2	20.3	20.3	22.8	22.8
Ethylene Glycol	28.2	26.0	30.8	30.8	26.5	23.0	24.4	22.8
2-Furfuryl Alcohol	33.8	28.2	30.8	26.1	26.5	21.6	31.1	24.4
n-Octanal (f)	21.1	24.2	24.2	24.2	20.3	21.6	24.4	24.4
Benzaldehyde	33.8	33.8	42.4	42.4	26.5	28.7	28.5	21.4
Acetic Acid	27.0	24.1	26.7	24.2	26.6	22.9	24.4	25.3
Propionic Acid	26.0	26.0	26.1	26.1	26.5	24.6	24.4	26.3
n-Octanoic Acid (f)	22.5	2111	22.6	22.6	24.6	19.2	24.4	22.8
Oleic Acid (f)	21.1	24.1	26.1	23.4	18.1	20.3	24.4	23.4
Ethy Acetate	14.7	21.1	13.0	22.6	11.9	17.2	14.9	20.1
Butyl Butyrate	28.2	24.1	24.2	24.2	28.7	21.6	26.3	21.4
Water (f)	14.1	14.1	16.9	16.9	12.3	12.8	16.3	15.5

* u = undried
\+ D = dried
(f) flotation

TABLE 12
Sediment Volume Test Results: The Effect of Concentration, Mass, Applied Force, and Particle Size Distribution

Experiment	Particle Concentration vol%	Sedimentaion Volume (cm^3)	Sediment Density (g/cm^3)	% MPD TAM COF ($5.92\ g.cm^3$)
Concentration Effect	5	3.2	2.3	8.9
	10	3.05	2.45	41.4
	20	3.0	2.5	42.2
	30	3.0	2.5	42.2
Mass Effect	30	3.0	2.5	42.2
	30	5.2	2.9	49.0
	30	7.0	3.2	54.1
Gravity Effect	5	1.55	2.9	49.0
	10	2.3	3.9	65.9
	20	4.4	4.1	69.3
	30	6.4	4.2	70.9
Distribution Effect*	30	2.8	2.7	45.6

* Narrow sized particles of 0.9 - 1.1 μm.

TABLE 13

The Relation Between the Dielectric Constant (ε) and $BaTiO_3$ Dispersions

	Flocculation	Unstable Dispersion	Stable Dispersion
$\varepsilon < 8$	Hexanes Toluene Di-ethyl Ether	Isopentyl Ether Ethyl Acetate Oleic Acid	Acetic Acid Propionic Acid Butyl Butyrate n-Octanoic Acid
$8 < \varepsilon < 15$		2-Heptanone	n-Octanol Benzyl Alcohol
$15 < \varepsilon$	Water	Acetone	Methanol Ethanol Isopropanol Benzaldehyde Ethylene Glycol

TABLE 14

The Relation Between Hydrogen Bonding Liquids and $BaTiO_3$ Dispersions

	Flocculation	Unstable Dispersion	Stable Dispersion
Non-hydrogen Bonding	Hexanes Di-ethyl Ether	Isopentyl Ether Ethyl Acetate 2-Heptanone Acetone	Butyl Butyrate
Hydrogen Bonding	Water	Furfuryl Alcohol Oleic Acid	Methanol Isoproponal n-Octanol Benzyl Alcohol Acetic Acid Ethylene Glycol n-Octanal Benzaldehyde Propionic Acid n-Octanoic Acid

TABLE 15
Sediment Volume Tests Results: The Effect of Hydrogen-Bonding Organics

	Supernatant	Sediment Volume (cm^3)	Sediment Density (g/cm^3)	%MPD TAM COF
p-Hydroquinone	c	1.3	1.54	26.0
p-Hydroxybenzaldehyde	c	1.4	1.43	24.1
n-Nitrobenzaldehyde	c	1.55	1.29	27.8
Benzoic acid	m	0.75	2.67	45.0
p-Hydroxybenzoic Acid	m	0.7	2.86	48.3

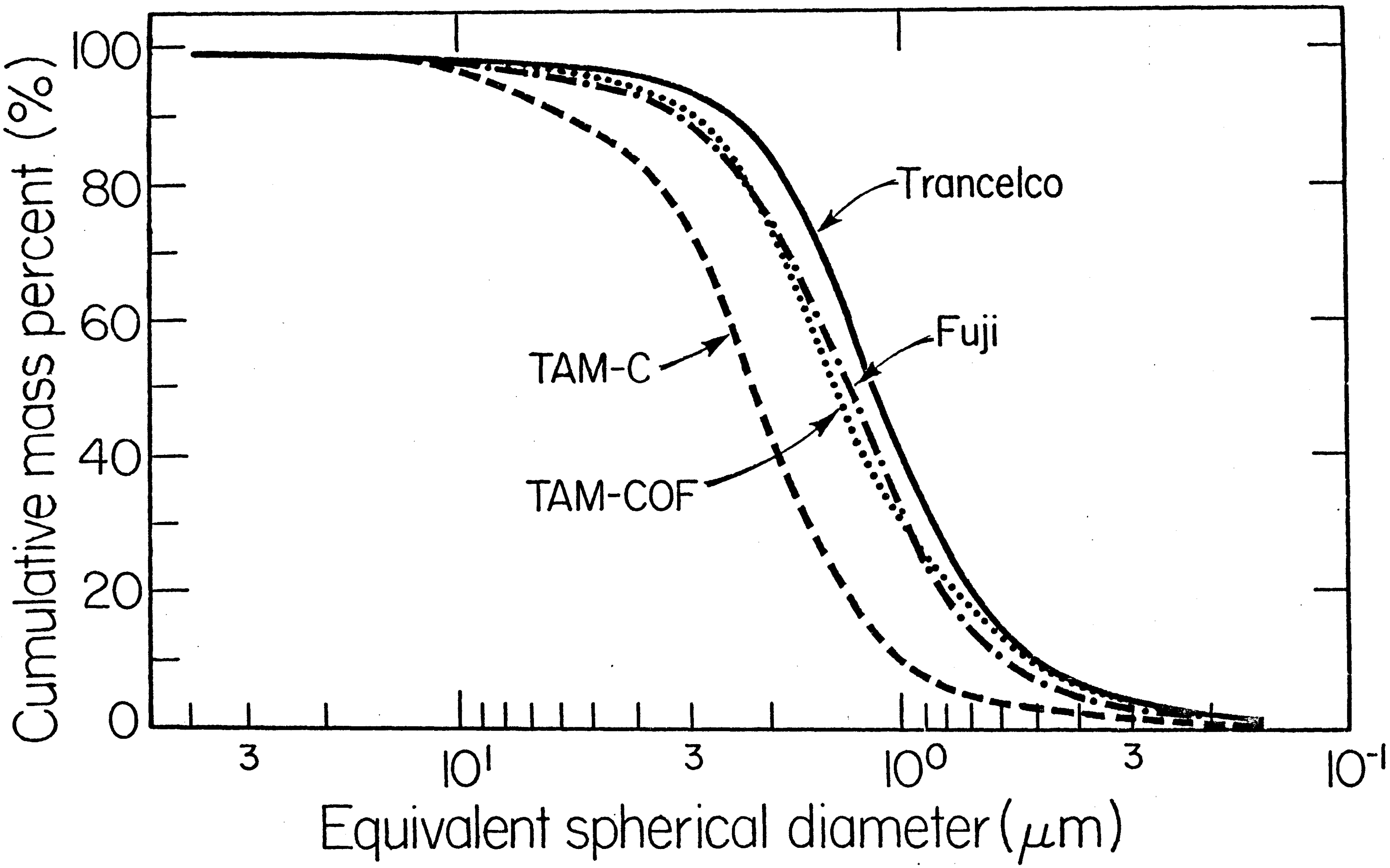
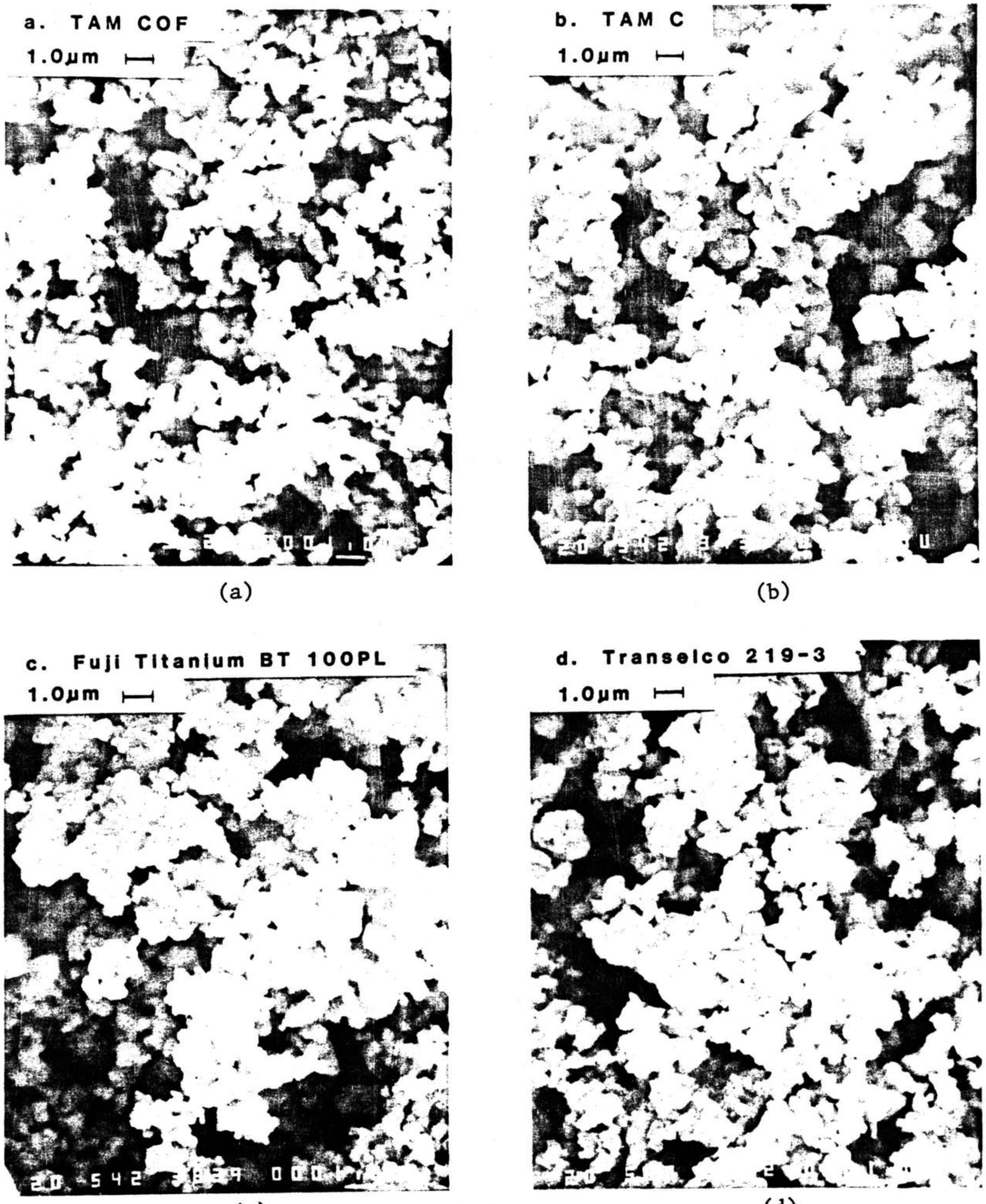


Figure 1. Sedigraph particle size analyses of the powders.



(a) (b)

(c) (d)

Figure 2. SEM photomicrographs of the powders:
(a) TAM-COF, (b) TAM-C, (c) Fuji Titanium BT-100PL,
(d) Transelco 219-B

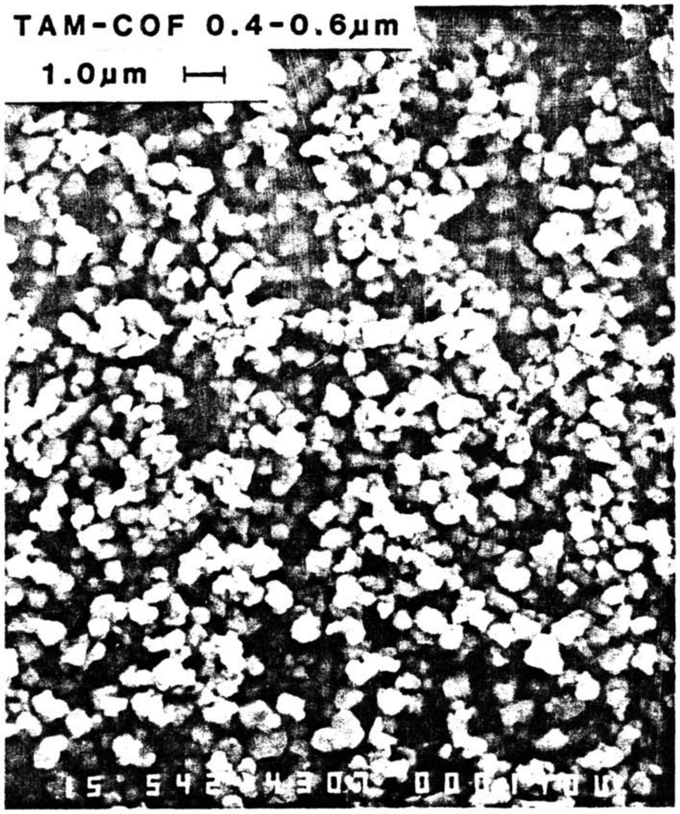


Figure 3. SEM photomicrograph of the 4.0-6. 0µm classified powder.

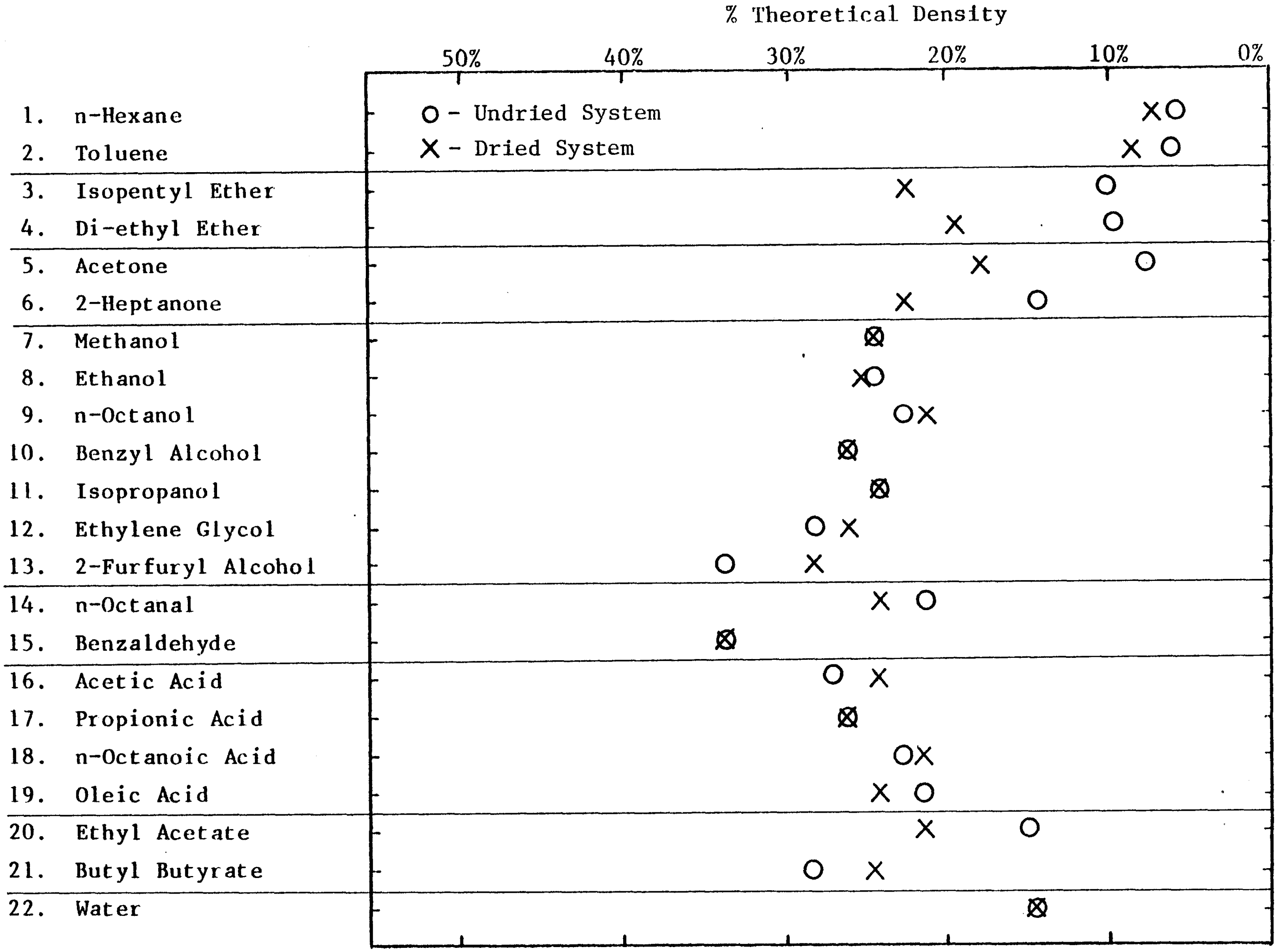


Figure 4a. The effect of moisture on the sediment volume: TAM-COF

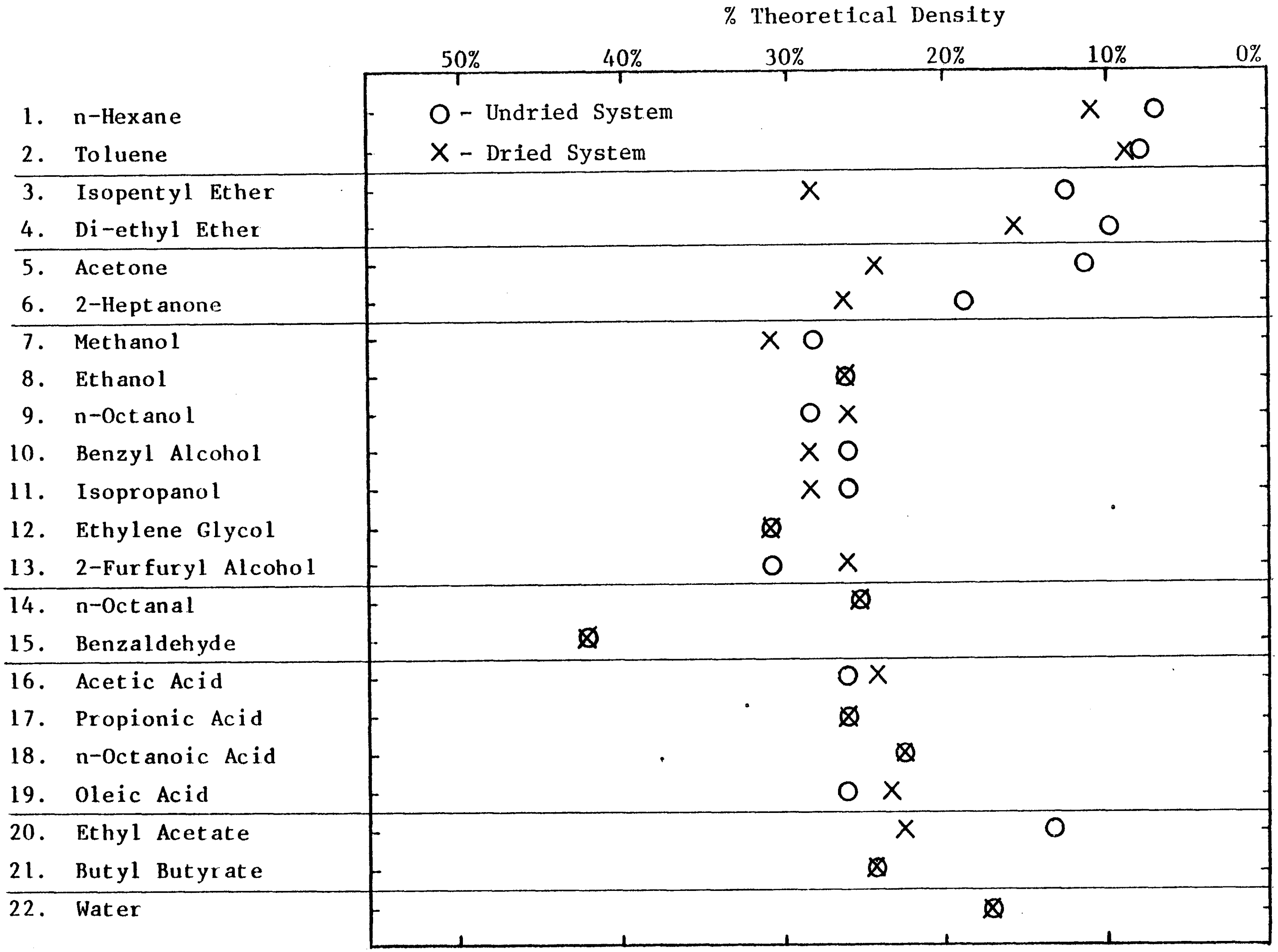


Figure 4b. The effect of moisture on the sediment volume: TAM-C

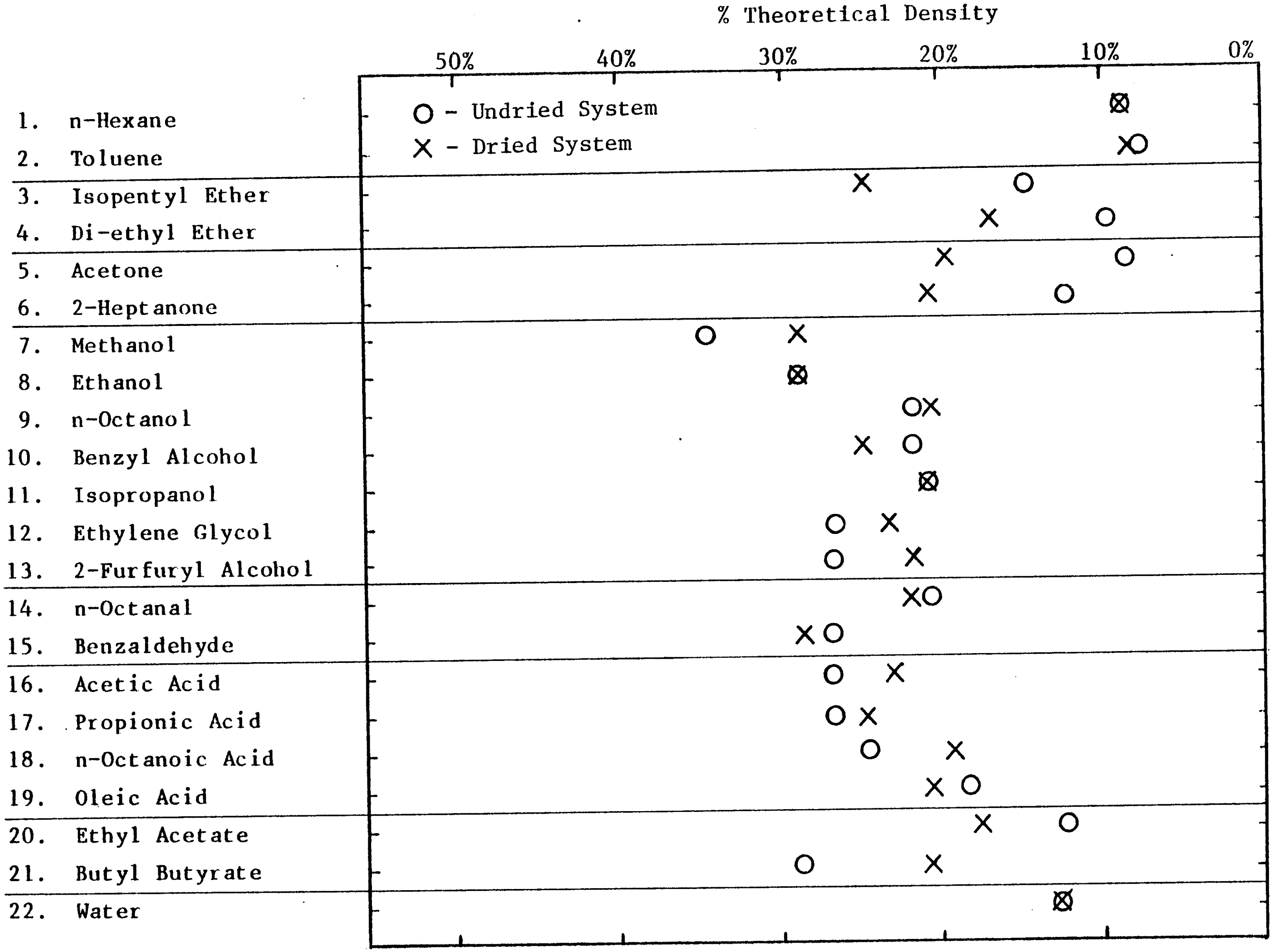


Figure 4c. The effect of moisture on the sediment volume:
Fuji Titanium BT-100PL

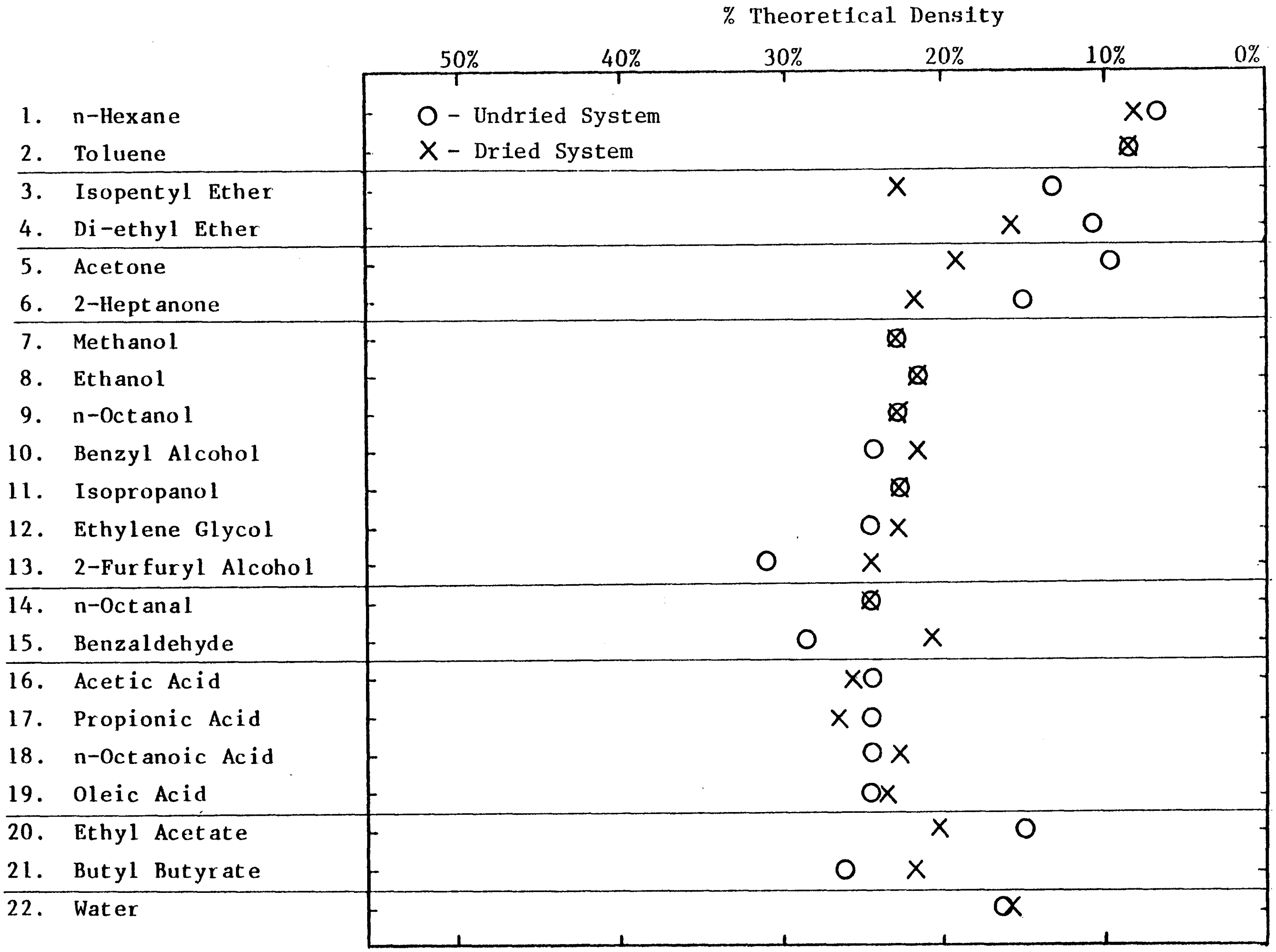


Figure 4d. The effect of moisture on the sediment volume: Transelco 219-B

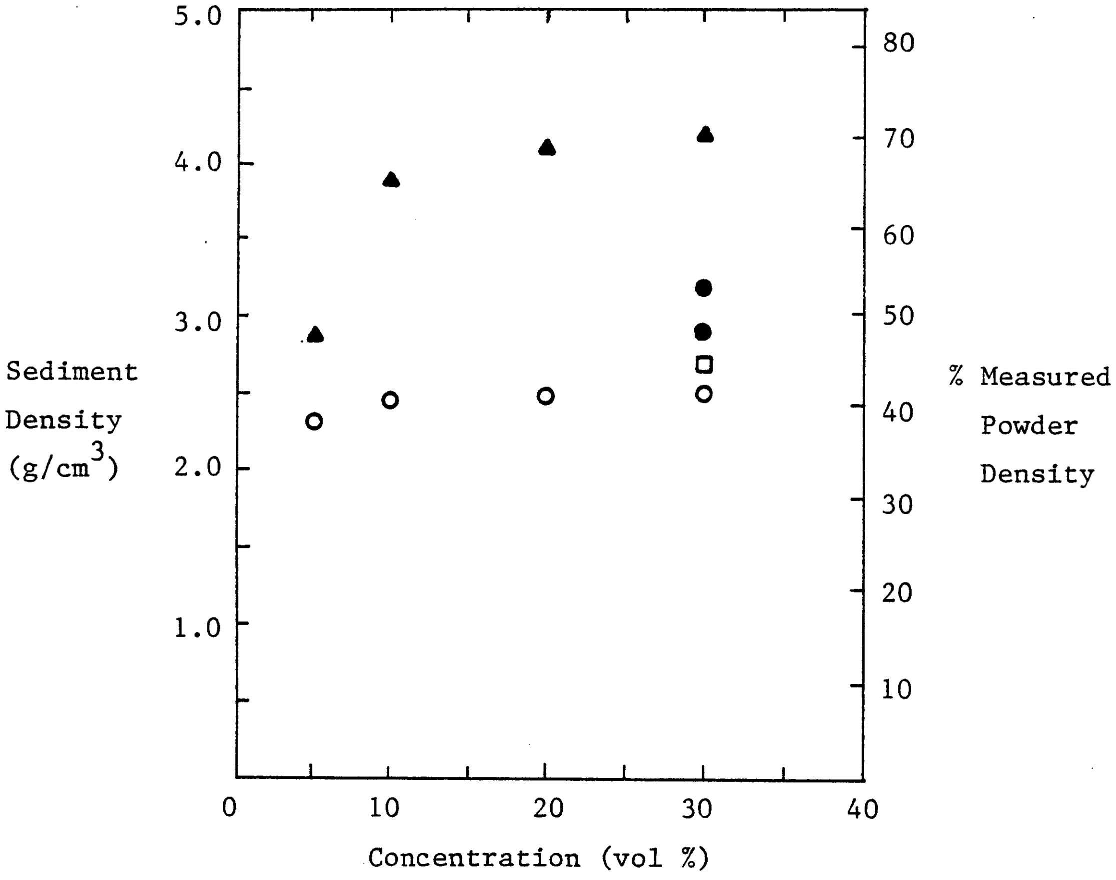


Figure 5. The effect of concentration, mass, applied force, and particle size distribution on the sediment volume of TAM-COF/benzaldehyde systems.

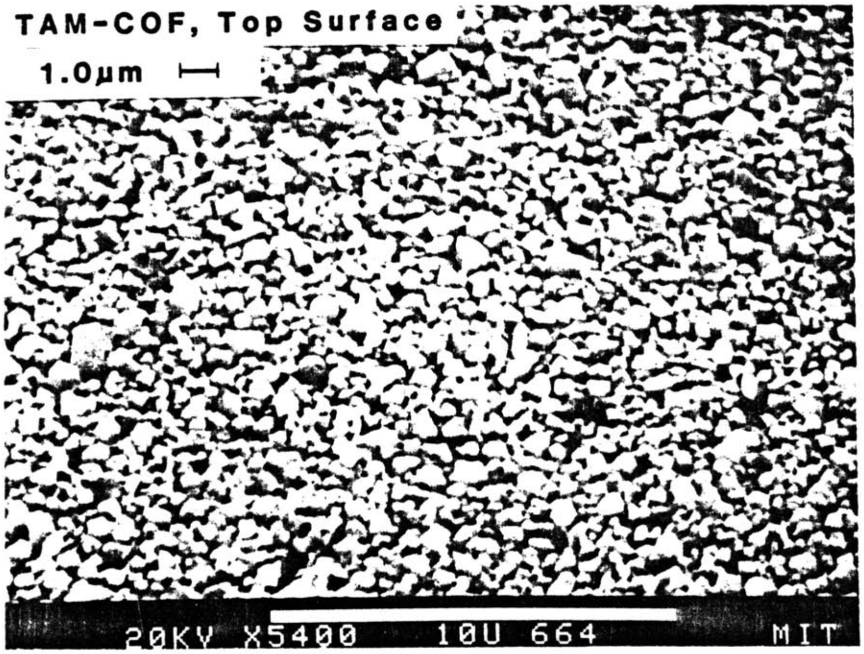
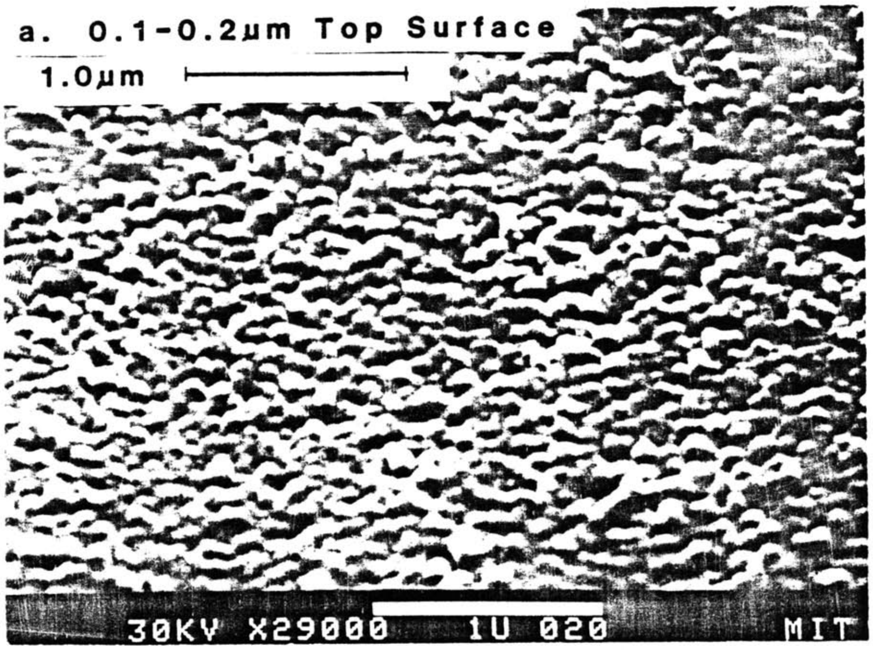
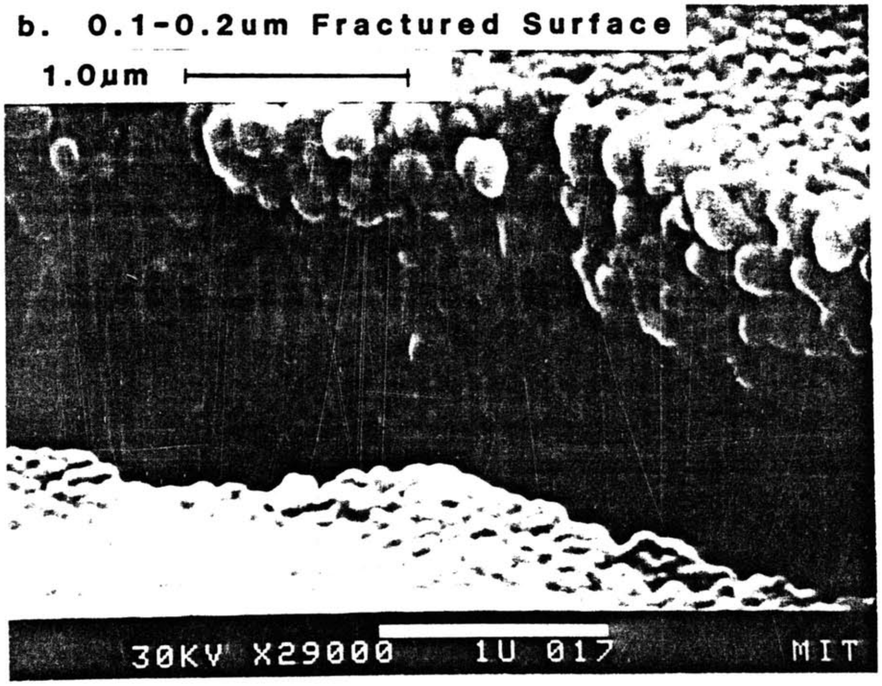


Figure 6. SEM photomicrograph of a centrifugal cast from a TAM-COF/benzaldehyde system: Top surface.



(a)



(b)

Figure 7. SEM photomicrographs of a centrifugal cast from a fractionated (0.1-0.2μm) TAM-COF/benzaldehyde system: (a) Top surface, (b) Fractured surface.