

Dispersions of oxide powders in organic liquids

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Thirteen oxide powders, all of which are important in the making of capacitors, were dispersed in nineteen pure organic liquids and water. The dispersions were characterized according to sediment volume results. Further experiments were performed to qualify the effects of moisture, particle concentration, and particle size distribution. Scanning electron micrographs of centrifuge casts of each powder in their best and worst dispersing medium were used to characterize further the dispersions. Results showed that alcohols and aldehydes were the best pure liquid dispersing mediums and hydrocarbons, ketones, and ethers were poor. The best results were obtained for a narrow-sized zirconia powder dispersed in methanol.

1. Introduction

It is the task of many ceramic process engineers in the electronics industry to manufacture devices which meet precise specifications. In the multilayer capacitor industry, these specifications (e.g. dielectric constant, loss tangent, temperature coefficient and breakdown voltage) are often not met due to faults in the dielectric microstructure such as voids and non-uniform grain size and inhomogeneities in the composition. At the same time, thinner dielectrics are desired in order to produce capacitors with higher energy storage per unit volume. To meet these requirements, improved processing methods are required. The purpose of this work was to study the dispersion of powders used to formulate capacitors in order to suggest ways in which reproducible, uniformly dense, unsintered compacts can be produced.

The degree of dispersion in a slurry is very important because compacts which are formed by various modes of slurry casting (e.g. doctor-blading) will have more uniform microstructures when the powder is well dispersed in the slurry. Sediment volume tests determine in a qualitative manner the degree of dispersiveness of metal oxide powders and incorporate into a single test many of the individual liquid–solid properties such as solvent

dielectric constant. To determine general features related to the functional groups on organic molecules, various classes of organics were studied. Since water is often present in these systems, the role of water in dispersions was also considered.

Some work has been reported on dispersions of BaTiO₃ powders by Mizuta *et al.* [1]. Therefore, the powders examined in this work were compounds which are additives to BaTiO₃ dielectric formulations. These common titanates, which are often mixed with BaTiO₃ to vary the dielectric characteristics and lower the temperature dependence of the dielectric constant, are SrTiO₃, CaTiO₃, and TiO₂. Zirconium-containing compounds like SrZrO₃, CaZrO₃ and ZrO₂ are commonly added in order to lower the temperature where the peak dielectric constant occurs. Bismuth oxide is added to BaTiO₃ to increase the temperature stability of the dielectric properties, and recently, rare earth oxides like Nd₂O₃ have been used to increase the temperature of the peak dielectric constant.

2. Background

2.1. Ceramic oxide dispersions

The fundamental aspects of dispersions have been documented by Parfitt [2]. Parfitt considered the

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overall process of dispersion as consisting of three stages: wetting the powder, breaking up the powder clusters, and particle stability against flocculation. The first stage, wetting the powder, is determined by the total surface-liquid interaction. Both the molecular structure of the liquid and the surface structure of the solid contribute to this interaction.

Most solid oxides (and all commercial oxides) have hydrated surfaces at room temperature [3]; these hydroxyls are either physisorbed or chemisorbed on the powder surface. The physisorbed water can easily be removed by heating the powder to between 100 and 200°C in a vacuum; the chemisorbed water cannot be removed without heating the oxide to 500°C or even higher. The concentration and configuration of the surface hydroxyls depends on the solid structure (lattice type) and the specific cations in the oxide.

The structure of the liquid is also important in a surface-liquid interaction. Basically, liquids adhere to oxide solids best through polar interactions. The most important of these interactions is the hydrogen bond. Fully discussed by Pimentel [4], a hydrogen bond is much stronger than a simple dipole interaction, and can be as strong as a weak covalent bond. Where simple organic liquids are considered, the type of functional group(s) in their molecular structure is one of the most important contributors to a hydrogen bond. For example, steric factors of the liquid molecule may be an important consideration; the liquid molecule can adsorb in such a way as to block another surface adsorption site.

There are many examples in the literature where interactions take place via surface hydroxyl groups and oxygens in liquids or between oxygens on the surface and hydroxyl groups in liquids [5]. It has often been noted that the interaction between a liquid and a solid decreases as the polarity of the liquid decreases [6], an indication that the liquid's inter-hydrogen bonding ability is also decreasing. For the liquids used in this research, both the polarity and the inter-hydrogen bonding nature of the liquid result from the presence of the heteroatom, oxygen.

Another type of interaction which exists between electrons in π -bonds and protons in surface hydroxyl groups has been noted in studies of the adsorption of benzene [7]. The nature of this interaction is weak and similar to that of a hydrogen bond; the electrons in a π -bond appear to donate

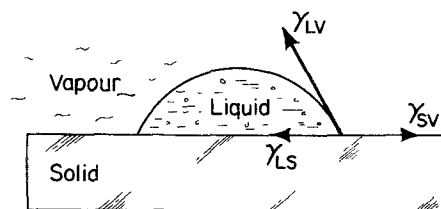


Figure 1 Contact angle of a drop of liquid on a flat dense solid surface.

electron density to an unshielded positive charge (hydrogen) [8].

The degree that a liquid wets a solid can be estimated by the contact angle formed between a drop of the liquid on a flat, dense, solid surface [9]. A contact angle of zero indicates complete wetting. The contact angle is related to the surface energies via Young's equation, easily derived from the schematic force balance shown in Fig. 1:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

where γ_{SV} , γ_{SL} , and γ_{LV} are the interfacial tensions between the solid and vapour phases, the solid and liquid phases, and the liquid and vapour phases, respectively. In most cases, liquids of low surface tension will wet high surface energy solids in order to lower the total surface free energy of the system.

Normally, powder contact angle measurements are estimated by drops on sintered or pressed pellets of the powders. Also, flotation of fine particles on a liquid surface may indicate non-wetting conditions, but lack of flotation of fine particles does not necessarily indicate wetting conditions (gravity may force a non-wetted particle into a liquid).

The second stage of forming a dispersion, breaking up the clusters, will expose new surfaces to the wetting liquid. Depending on the degree of agglomeration or aggregation, this may require just simple agitation like stirring or shaking, ultrasonification, or milling.

The third stage, stability of the dispersion to flocculation within required time limits, may incorporate several mechanisms. Powder particles wetted by liquids may still flocculate quickly due to London-van der Waals' attractive forces if no repulsive forces are present between the particles.

The source of repulsive forces between particles results from the presence of surface charges (the electrostatic mechanism) or large molecules adsorbed to the particle surface (the steric barrier mechanism). Surface charges, existing due to

adsorbed ions or dipoles, create an electric potential around each particle which extends into the dispersant and whose magnitude decreases exponentially with distance according to the Debye–Huckel approximation [10].

The coulombic forces between the surfaces keep the particles from flocculation if the surface charge is large enough, and if the potential extends out far enough. The liquid–surface interactions and the liquid’s dielectric properties both influence these conditions. Liquids which adhere well to the surface create larger and more extensive potential fields, because the degree of dipole (or ion) orientation is high. In these systems, the repulsive forces between particles will be large and stable dispersions will occur.

The electrostatic theory is most often applied to aqueous systems where ions adsorb on the surface. However, Parfitt *et al.* [10] have extended the theory to non-aqueous systems such as pure organics. This extension applies to the organic liquids used to disperse ceramic powders in this research. Non-aqueous dispersion systems are often stabilized by adsorbing large macromolecules on the surfaces of the particles [11]. Part of the molecule is soluble in the non-aqueous medium and therefore extends out away from the particle surface. This orientation forms a steric barrier to keep the particles from coming into contact with each other, preventing flocculation. This mechanism was applied in the toluene–fish oil systems in this work.

2.2. Sediment volume tests

A simple and reliable test of whether a certain liquid or solution will disperse a powder is to mix the powder in the liquid and observe the sedimentation behaviour. A series of these experiments with selected liquids and several different powders can be very valuable in providing an understanding of the physical and chemical forces which play a role in a powder dispersion. Although there is debate on the quantitative value of a sediment volume experiment [2], there are many examples in the literature in which valuable information is extracted from this type of experiment.

The work done in this paper is a continuation of sediment volume work performed by Mizuta *et al.* [1]. Their work examined the dispersion properties of BaTiO₃ powder systems based on sediment volume experiments. They found that the sediment volume was adversely affected by

water and that generally the best sediment volumes were obtained with hydrogen bonding liquids.

In a flocculated system, particles fall rapidly and a loosely packed sediment is obtained. However, in a well dispersed system, particles settle into a tightly packed sediment. Therefore, the sediment height is inversely related to the dispersiveness of the liquid and the more dispersed the system is, the smaller the sediment volume will be.

3. Experimental details

3.1. Characterization of Powders

The powders and liquids used in this study are listed in Table I. Each was of commercial grade with levels of impurities not more than 1 to 2% according to the suppliers’ analyses. X-ray diffraction experiments were performed on each powder. The diffraction patterns were made with a standard diffractometer scanning from 20° to 90° at 4° min⁻¹. The patterns were used to identify the compounds and any second phases in the powders.

The density of the powders was measured using a Quantachrome stereo pycnometer (Quantachrome Corp, Model No. SPY-2). Three readings were made on each powder and an average density was used in this report. The variation in the readings, $\Delta\rho/\rho_{avg}$, was less than 1%.

The particle size distribution of each powder was obtained using a Sedigraph (Micromeritics model 5000D). Each powder was mixed in isopropanol or methanol (whichever was the better dispersant), and dispersed using an ultra-sonic bath (Mettler model ME 11).

Finally, the amount of moisture on the surface of the powder and the temperature at which the water desorbed were obtained using thermal gravimetric analysis. The powders were heated from room temperature to 1000° C at 2° C min⁻¹ in air. (Measurements were made by Orton Laboratories, Columbus, OH, USA).

3.2. Sediment volume tests

The powders and liquids used in these experiments are listed in Table I. The purpose of these experiments was to determine the degree of dispersiveness of the powders with several pure organic liquids, to ascertain the stability of the dispersions with respect to water, and to understand the dispersion process. A mass of each powder needed to produce 10 ml of a 4 vol% dispersion was weighed into a

TABLE I Experimental powders and organic liquids

Powders		
TiO ₂ (TAM)	ZrO ₂ (TAM)	Bi ₂ O ₃ (Tranelco)
TiO ₂ (Tranelco)	SrZrO ₃ (Tranelco)	Nd ₂ O ₃ (Molycorp)
TiO ₂ (N. J. Zinc)	CaZrO ₃ (TAM)	SiO ₂ (Newton Potters)*
SrTiO ₃	CaZrO ₃ (Tranelco)	
Liquids		
Hydrocarbons: n-Hexanes ^b Toluene ^a	Alcohols: Methyl alcohol ^b Isopropyl alcohol ^a	Aldehydes: Octanal ^d Benzaldehyde ^a
Ethers: Isoprenyl ether ^a Tetrahydrofuran ^a	Octanol ^a Benzyl alcohol ^a Ethylene glycol ^e	Acids: Propionic acid ^b Octanoic acid ^e
Ketones: Acetone ^b Heptanone ^d	Furfuryl alcohol ^d	Esters: Ethyl acetate ^c n-Butyl n-butyrate ^f

^aBaker Analysed Reagent Grade.

^bFisher Scientific Certified.

^cMallinckrodt Analytical Reagent.

^dAldrich Chemical.

^eKodak (665).

^fCity Chemical Corporation of NY.

*"Supersil" powder was classified to less than 5 μm .

clean 10 ml graduated cylinder. Each cylinder was then filled with one of the pure liquids for each test. The cylinders were vigorously agitated by hand for approximately 30 sec and then allowed to settle for 14 days without being disturbed.

In a second set of cylinders, dry liquids and dry powders were used. The liquids were dried by placing ~ 10 g of a 0.3 nm molecular sieve (Union Carbide Linde potassium zeolite) in 50 ml of each liquid for 3 days. The powders were dried in a vacuum oven (~ 0.1 mm Hg) at 120° C for 18h. The mixing and settling experiments using dried liquids and powders were performed in a glove box. The air in the glove box was passed through a column of Drierite at 5 ft³ h⁻¹ yielding an atmosphere of less than 100 ppm water.

After 14 days, the sediment volume in each cylinder was recorded along with flotation or other changes in the colour or consistency of the liquid.

Two other experiments were performed using the same sediment volume procedure. The first of these was a test of the amount of water required to no longer maintain a good dispersion. In this test, the volume of water in isopropanol was varied from 0 to 100% (in 10% intervals) in a dispersion with 4 vol % BaTiO₃, TAM COF.

The sediment volume experiment was also used to test the ability of a large complex polyester

(free of all elements except carbon, hydrogen and oxygen) to disperse ceramic powders. Both 3 and 4 wt % solutions of Menhaden fish oil in toluene were used to disperse SrTiO₃ (Tranelco), TiO₂ (TAM), TiO₂ (Tranelco), CaZrO₃ (TAM), SrZrO₃ (Tranelco), and ZrO₂ (TAM) powders. The sediment heights of these dispersions were also measured after 14 days.

3.3. Effect of concentration and mass

Using a similar experiment to the sediment volume test, the effect of mass and concentration on the sediment volume was tested for each powder. To check the concentration effect, a 25 ml graduated cylinder was filled with 5, 10, 15, and 20 vol % powder by varying the volume of liquid to adjust the concentration. To check the mass effect, a 20 vol % suspension was prepared in three 25 ml graduates with the total mass doubled and tripled in two of the cylinders. In all cases, the dispersions were prepared in either isopropanol or methanol. Each mixture was dispersed in the ultra-sonic bath for 30 min and the sediment heights were measured after 14 days.

3.4. Preparing ZrO₂ powder with a narrow size distribution

Zirconia powder with a narrow size distribution

was prepared, using a Stokes's settling technique [12]. According to Stokes's law, particles of the same size will fall with the same velocity in a dispersion, if the particles do not interact with each other. Using this rate, a dispersion of ZrO_2 was allowed to settle until all particles $0.6\ \mu m$ and larger had settled from the dispersion. The supernatant was poured off and all the $0.4\ \mu m$ and larger particles were allowed to settle. Again, the supernatant was poured off and the sediment was saved. This sediment contained mostly particles of 0.4 to $0.6\ \mu m$ diameter. The sizing procedure was repeated on this 0.6 to $0.4\ \mu m$ ZrO_2 powder to further decrease the occurrence of particles outside this range.

3.5. Scanning electron micrographs of centrifugally cast powders

In order to compare the sediment from a good dispersing medium and a poor dispersing medium, centrifuge casts of 15 vol% dispersions were prepared. A 15 vol% powder dispersion based on 10 g of powder and the appropriate volume of liquid was prepared in a 50 ml centrifuge tube by inserting an ultra-sonic microtip probe (Ultrasonics, Inc, Model 220F, 70 W) into the mixture for 30 sec. Each tube was centrifuged for 10 min at 12 000 rpm (15 000 g) and the supernatant was poured off. The resulting casts were dried in air and examined in a scanning electron microscope (SEM) for particle packing uniformity and particle size distribution. SEM micrographs were also made of as-received powders in order to examine the degree of agglomeration and the particle size distribution. Finally, centrifuge casts of the narrow-sized ZrO_2 were examined in the SEM to see how particle size distribution affects packing. These centrifuge casts were prepared in the same manner as the other casts.

4. Results and discussion

4.1. Characterization of liquids

The liquids which were used are listed in Table I and, based on their functional groups, were divided into seven classes. The selection of each liquid was to emphasize the importance of the functional group. For example, toluene, benzyl alcohol and benzaldehyde are structurally similar but their different functional groups lead to very different physical and chemical properties.

The seven classes of liquids which were used do not cover the entire spectrum of organics. Amines

are an important class of organics which was not examined, but the organics which were tested are commonly used and do cover a spectrum of types. That is, a variation in properties like degree of hydrogen bonding, dielectric constant, surface tension, and polarity were represented.

Physical property data (boiling point, viscosity, surface tension, and dielectric constant) are given in Table II. It was assumed that the solubility of the oxide powders in the liquids is negligible. Hydrogen bonding capability ranged from none (the hexanes) to very good (the alcohols and acids).

4.2. Characterization of powders

X-ray diffraction patterns of each powder showed that all of the powders contained only the pure compound and no impurities within the detection limits ($\sim 5\%$) of the diffractometer. Also, diffraction peaks were not shifted by a measureable amount, indicating that no appreciable solutes were present. The measured density of all the powders along with the reported single crystal density is given in Table III. These measurements show that Bi_2O_3 may be non-stoichiometric or contains impurities because the measured density is higher than the single crystal density. This difference in chemistry would be reflected in its dispersion properties if the extra metal cations segregate to the surface of the powder.

Particle size measurements of each powder, given in Figs. 2 and 3, demonstrate that the distributions were typical of commercial powders and were not bimodal or narrow sized. The 50% particle size was $3.5\ \mu m$ for most of the powders.

The amount of moisture present in the bulk powders based on the results of thermogravimetric analysis (TGA) is given in Table IV. Although this is not a measure of the number of surface hydroxyl groups, it is an indication of their presence. The range of 0.22 to 2.06 wt% indicates ~ 2 to 20 monolayers for the typical particle size of $\sim 3.5\ \mu m$.

4.3. Sediment volume results

4.3.1. As-received powders and pure undried liquids

The sediment volume results for the as-received powders and pure undried liquids are given in Figs. 4 and 5. These results represent the particle packing density as a percentage of powder density. A value of 74% particle density corresponds to a perfect closed-packed structure of monosized hard spheres. However, the commercial powders used in this

TABLE II Physical properties of liquids*

Liquid	Dielectric constant†	Vapour-liquid surface Tension‡ (mN m ⁻¹)	Boiling point ¹⁶ (° C)	Viscosity† (cP)
1. n-Hexane	1.89 a	18.4 a	69.0	0.326 a
2. Toluene	2.4 a	28.5 a	110.6	0.590 a
3. Isopentyl ether	2.82 a	22.85 (21.7° C)	173.2	0.4 a
4. Tetrahydrofuran	7.85 a	27.4	67	0.53 a
5. Acetone	20.7 a	25.1 a	56.2	0.316 c
6. 2-Heptanone	9.77 (22° C)	26.7 a	151.5	0.766 c
7. Methanol	32.6 c	22.5 a	65.0	0.597 a
8. Isopropanol	18.3 c	21.3 a	82.4	2.86 d
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. Ethylene glycol	38.7 a	48.4 a	197.5	20.5 a
12. Furfuryl alcohol	—	38 a	171	4.62 a
13. n-Octanal	13 a	—	163.4	—
14. Benzaldehyde	16.8 a	38.5 a	178.1	1.315 c
15. Propionic acid	3.3 e	26.7 a	141.0	1.10 a
16. n-Octanoic acid	2.45 a	28.0 a	239.3	4.63 (30° C)
17. Ethyl acetate	6.15 a	23.52 a	77.06	0.416 c
18. Butyl butyrate	5 a	23.72 a	164.8	0.977
19. Water	78.5 a	72.75 a	100.0	1.002 a

*Temperature (° C) at which measurement was made: a = 20° C, b = 17° C, c = 25° C, d = 15° C, e = 10° C.

†“Handbook of Chemistry and Physics”, 55th edition, edited by R. C. Weast (CRC Press, Cleveland, OH, 1974).

‡J. J. Jasper, *J. Phys. Chem. Ref. Data* 1 (1972) 84.

work contain a distribution of particle sizes which could be packed to densities higher than 74%, if the small particles in the distribution fill the voids between the larger close-packed particles.

Hexane and toluene are hydrocarbons and can form no hydrogen bonds. There is evidence which suggests that the π -bonds of a benzene ring as in toluene are able to accept electrons and act as a Lewis acid. Therefore, an acid/base interaction can exist between toluene and a lone pair of electrons on a hydroxyl group on the surface of a powder. On the other hand, toluene has about 1½ times the surface tension of hexane. As a result, the difference in sediment volumes between hexane

and toluene systems was small. The large sediment volume is indicative that both flocculated the powders. Ethers are able to form weak hydrogen bonds, with tetrahydrofuran more able than isopentyl ether. Overall, these ethers dispersed the powders about the same, or slightly better than the hydrocarbons; tetrahydrofuran was slightly better than isopentyl ether. Ketones also form only weak hydrogen bonds. As a group, the ketones dispersed the powders slightly better than the hydrocarbons and ethers.

Generally, the alcohols had much lower sediment volumes than the previous three classes, which may be directly related to their good hydrogen

TABLE III Reported single crystal and measured density of several metal oxide powders

Powder	Single crystal density (g cm ⁻³)	Measured density (g cm ⁻³)
TiO ₂ (TAM)	4.26*	4.24
TiO ₂ (Transelco)	4.26*	4.17
TiO ₂ (N.J. Zinc)	4.26*	4.22
SrTiO ₃ (Transelco)	5.12	5.05
ZrO ₂ (TAM)	5.6 *	5.74
SrZrO ₃ (Transelco)	5.12	5.25
CaZrO ₃ (TAM)	4.78*	4.27
CaZrO ₃ (Transelco)	4.78*	4.60
Bi ₂ O ₃ (Transelco)	8.9 *	9.34
Nd ₂ O ₃ (Molycorp)	7.24	6.88
SiO ₂ (Newton Potters)	2.635–2.660*	2.64

*“Handbook of Chemistry and Physics” 55th edn, edited by R. C. Weast (CRC Press, Cleveland, OH, 1974).

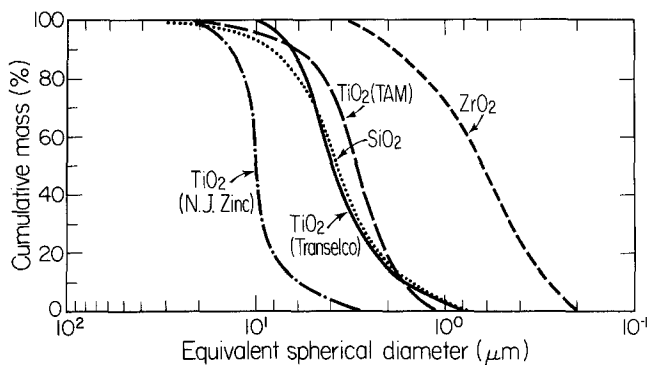


Figure 2 The Sedigraph particle size distributions of the TiO_2 , ZrO_2 and SiO_2 powders.

bonding ability. The difference in sediment heights among the alcohols can be explained by their different physical properties and the different structures of the metal oxide surfaces. For example, the high dielectric constant of methanol reflects the polarity of the molecule. The more polar the molecule, the stronger the hydrogen bonds it may form and the higher the surface charge that may develop. Therefore, methanol should be a good dispersant. However, methanol will also hydrogen bond to itself, and therefore, the dispersing ability will depend on the structure of the surface; whichever alcohol best matches the positions of hydrogen bonding sites on the surface will probably interact the most strongly and disperse the best. This fact was reflected in the different sediment volumes for ZrO_2 and TiO_2 (Transelco) in isopropanol and methanol, as seen in Fig. 4; i.e., it is assumed that ZrO_2 and TiO_2 (Transelco) were dispersed differently by methanol and isopropanol partly because the surface structures may be different. In another example, the chain length did not have a significant effect on the dispersing ability in these liquids. However, the high viscosity of octanol, due to its chain length, may have enhanced the dispersiveness of the heavier compounds by slowing their settling rate.

Though benzaldehyde and octanal may be considered to form relatively weak hydrogen bonds as compared to alcohols, the results in Figs. 4 and 5 indicate that the aldehydes worked as well as the alcohols; in several cases, benzaldehyde was the best dispersing medium studied. This contradiction is best explained by the decomposition of aldehydes like benzaldehyde and octanal into their corresponding acids [13]. Therefore, the dispersing capacity of benzaldehyde and octanal must be analysed in terms of a three-component system. Acids are extremely good hydrogen bond formers and interact with the surface of the powders, aiding the dispersion process. Benzaldehyde (or benzoic acid) probably worked better than octanal because of the resonance stabilization possible.

Propionic acid and octanoic acid are very good hydrogen bond formers, yet the pure acids did not disperse the oxide powders too well. A problem develops with these acids since the hydrogen-bonded layer formed has a higher surface tension than the pure acid and the pure acid may not wet the surface product formed. This phenomenon has been observed in other systems [9]. In this study, this phenomenon was indicated by the flotation of particles on the surface of the liquid. In general, the carboxylic acids dispersed the powders slightly

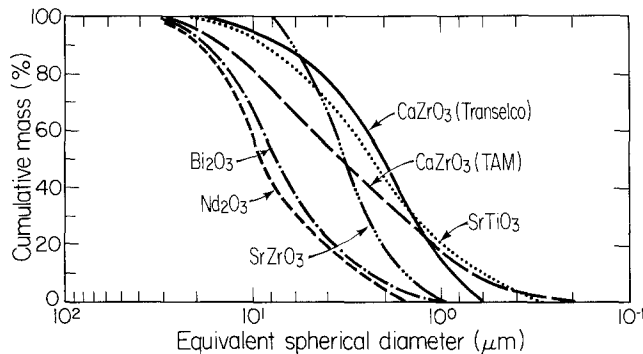


Figure 3 The Sedigraph particle size distributions of the SrTiO_3 , SrZrO_3 , CaZrO_3 , Bi_2O_3 and Nd_2O_3 powders.

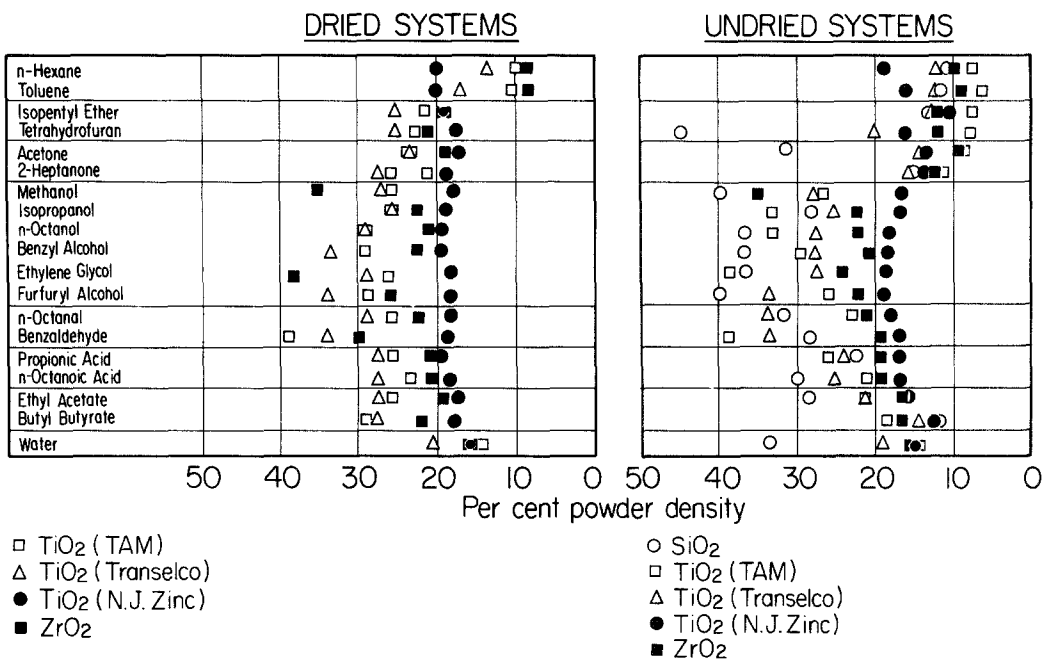


Figure 4 The sediment volume results for the dried and undried systems of the TiO₂, ZrO₂ and SiO₂ powders.

less well than alcohols, but much better than the ketones, ethers and hydrocarbons.

Ethyl acetate and butyl butyrate will form relatively weak hydrogen bonds, yet these two liquids only work slightly less well than the alcohols and much better than the hydrocarbons, ethers, and ketones. Like the aldehydes, ester dispersions must be treated as three component systems. Because esters are made by combining an acid and an alcohol, there is always an equilibrium amount of both the acid and the alcohol in the ester [8]. This small amount of acid and alcohol will probably

interact with the surfaces of the powders and enhance the dispersion process.

Distilled water with a pH of 5 was used in these experiments and was found to be a poor dispersing agent even though it is capable of forming very strong hydrogen bonds and an electrical charge. Water has a very high surface tension which led to flotation (non-wetting) in these systems. The effect of water on dispersions is discussed further in the next section.

In the above presentation of settling data, the powders were assumed to have similar surface properties. Generally, this is true. However, the physical properties and surface properties of each powder can change the dispersion results greatly. This fact is demonstrated for the TiO₂ powders, all rutile but from different sources. The large particle size TiO₂ (N. J. Zinc) resulted in difficulty in making a good dispersion using any of the liquids. The sediment densities for this powder are consistently much lower than finer TiO₂ (TAM and Transelco). Overall, TiO₂ (TAM) is dispersed slightly better in the liquids than TiO₂ (Transelco).

It is also interesting to observe the difference between powders with different crystal structures. For example, note the difference in sediment densities between ZrO₂ with the fluorite structure and TiO₂ (Transelco) with the rutile structure. The variation in their structures implies different

TABLE IV The amount of water present in several commercial oxide powders as measured by thermogravimetric analysis*

Powder	Moisture content (wt %)
TiO ₂ (TAM)	0.36
TiO ₂ (Transelco)	0.43
TiO ₂ (N.J. Zinc)	0.54
SrTiO ₃ (Transelco)	0.88
ZrO ₂ (TAM)	0.68
SrZrO ₃ (Transelco)	1.16
CaZrO ₃ (TAM)	2.06
CaZrO ₃ (Transelco)	0.83
Bi ₂ O ₃ (Transelco)	0.22
Nd ₂ O ₃ (Molycorp)	0.46

*Measurements were made at Orton Laboratories. The powders were heated from 25 to 1000° C at 2° C min⁻¹ in air.

surface structures and surface chemistries so that the spacing between the attached hydroxyls will vary; the fluorite structure is more open and the hydroxyls will be spaced further apart. The differences in their sediment volumes can only be explained by the dissimilar surface structures and the powder density differences.

4.3.2. Dried powders and dried liquids – effect of water

Sediment volume results for the dried liquids and powders are given in Figs. 4 and 5. Hydrocarbons, ethers, and ketones were able to disperse the powders much better when the amount of water was minimized in the systems. It is obvious that the vacuum drying procedure used in this study did not eliminate all the water present on the surface of the powders, but did eliminate much of the physically adsorbed water leaving only chemisorbed hydroxyl groups. It has been noted that loosely bonded molecules of water adversely affect adhesion [3]. From a molecular level, it seems that hydrocarbons, ethers and ketones cannot displace the water molecules and the particles flocculate. On the other hand, the other liquids generally are not greatly affected by water. In these liquids, it appears that the organics can displace some of the surface water and interact with the surface.

Something which was not measured in this experiment was the degree of contamination of

TABLE V Sediment volume results of isopropanol water mixtures and BaTiO₃ (TAM COF)

Water (wt %)	Isopropanol (wt %)	Sediment volume (cm ³ g ⁻¹)
100.0	0	1.15 (Flotation)
90.4	9.6	1.20 (Flotation)
80.0	20	1.25 (Flotation)
70.1	29.9	1.30
60.7	39.3	1.35
49.9	50.1	1.40
40.3	59.7	1.45
29.9	70.1	1.45
19.8	80.2	1.50
10.0	90.0	1.70
0	100.0	0.65

the liquids. Using molecular sieves to dry the liquids probably does not alter the molecular make-up of the liquid, but it may contaminate the liquid enough to change interfacial properties. The molecular sieves did slightly contaminate a few of the systems because a colour change was observed in the liquids.

To examine the effect of water, isopropanol and water were mixed in various ratios and used to disperse BaTiO₃ powder. The results of this experiment are given in Table V. According to the above results, between 0 and 10% water adversely affects the system, but as more water is added (greater than 10%) the sediment volume stabilizes and decreases. An activity diagram for the water/ isopropanol system shows a positive deviation from ideality (as

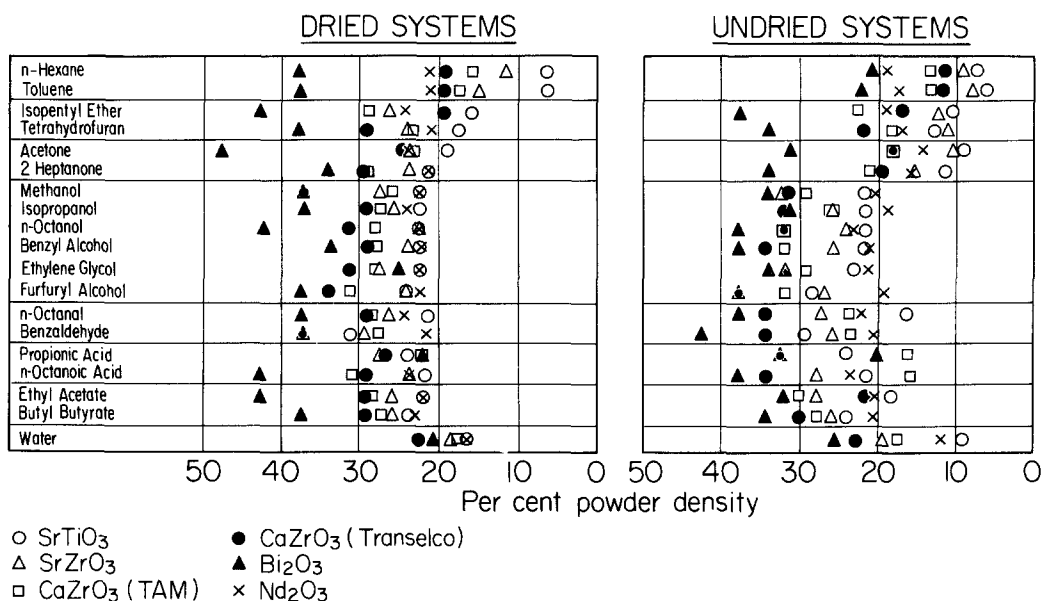


Figure 5 The sediment volume results for the dried and undried systems of the SrTiO₃, SrZrO₃, CaZrO₃, Bi₂O₃ and Nd₂O₃ powders.

TABLE VI Mass and concentration effects on sediment density

Powder	Mass effect (20 vol % powder)*:			Concentration effect (constant mass)†:			
	sediment density (% powder density)			sediment density (% powder density)			
	1 x	2 x	3 x	5%	10%	15%	20%
TiO ₂ (TAM)	46.0	49.9	52.2	47.9	47.9	47.9	47.9
TiO ₂ (Tran selco)	26.1	28.9	30.7	27.3	26.1	27.3	26.1
TiO ₃ (N.J. Zinc)	18.3	20.6	21.1	18.9	16.9	16.4	18.3
SrTiO ₂ (Tran selco)	40.1	42.3	43.1	41.3	40.4	40.3	40.1
ZrO ₂ (TAM)	35.0	35.7	36.4	43.6	41.5	41.5	35.0
SrZrO ₃ (Tran selco)	36.8	37.5	38.2	38.2	39.0	34.8	36.8
CaZrO ₃ (TAM)	35.0	36.7	36.7	36.7	35.5	35.0	35.0
CaZrO ₃ (Tran selco)	36.8	37.5	38.2	38.2	39.0	34.8	36.8
Bi ₂ O ₃	56.2	56.2	56.2	56.2	51.1	53.5	56.2
Nd ₂ O ₃	27.1	26.6	30.3	23.8	26.1	26.2	27.1

*As the mass of each sediment volume system was increased by two times and three times the total mass, the sediment densities consistently increased a small, but significant amount.

†As the solids concentration of each system was increased from 5 to 20%, the sediment densities remained roughly the same.

water is added to isopropanol) indicating a dissociation of water and isopropanol molecules which would be responsible for causing the water to segregate at the surface [14]. When more than 10% water is added, the alcohol can interact with the surface, enhancing the dispersing ability of the mixture. At these concentrations, the amount of water has little effect. Finally, when there is not enough alcohol to cover the surface completely, the powder is no longer wetted and floats.

The above discussion is a very qualitative and an over-simplified version of what goes on at a surface. In fact, the role of water at interfaces is very complex. Since water is a polar molecule, it can affect the surface charge by how it adsorbs. If the oxygen adsorbs, then the outer hydrogens will

cause the powder surface to have a net positive charge. If the hydrogens adsorb, then there will be a net negative charge due to the exposed oxygens. The position of the adsorbed molecule is directly related to the acidity or basicity of the solid surface. This phenomenon was not clearly defined and was not measured in these systems. In either situation, different molecules which compete for the same adsorption sites make the system more complex.

4.3.3. As-received powders in toluene and Menhaden fish oil mixtures

The results for the powders dispersed in the Menhaden fish oil mixtures are given in Fig. 6. These results showed that polymeric mixtures

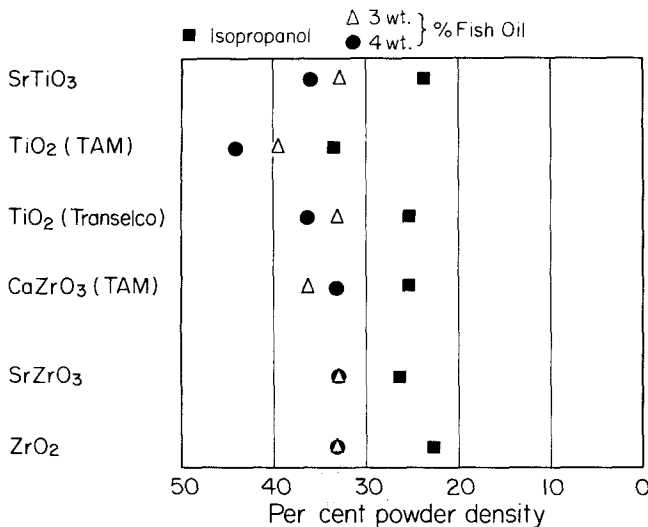


Figure 6 Sediment volume results for various powders in a toluene/Menhaden fish oil mixture and in pure isopropanol.

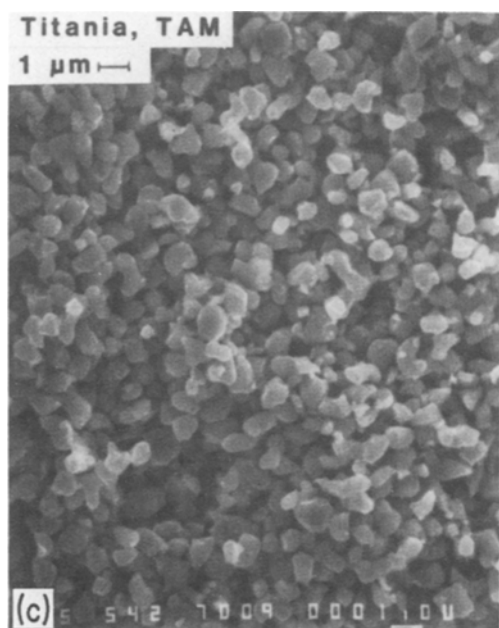
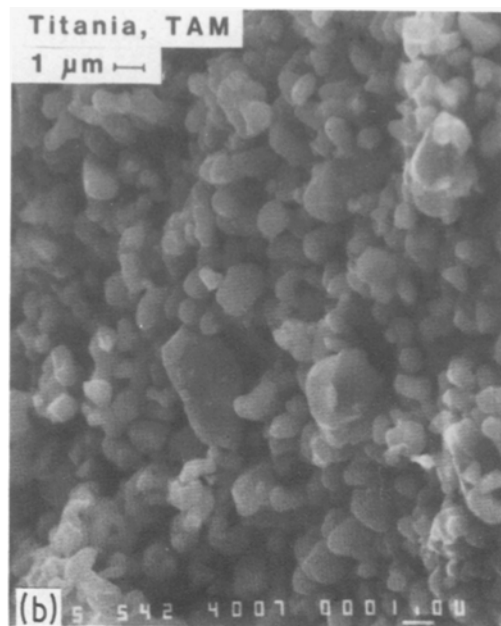
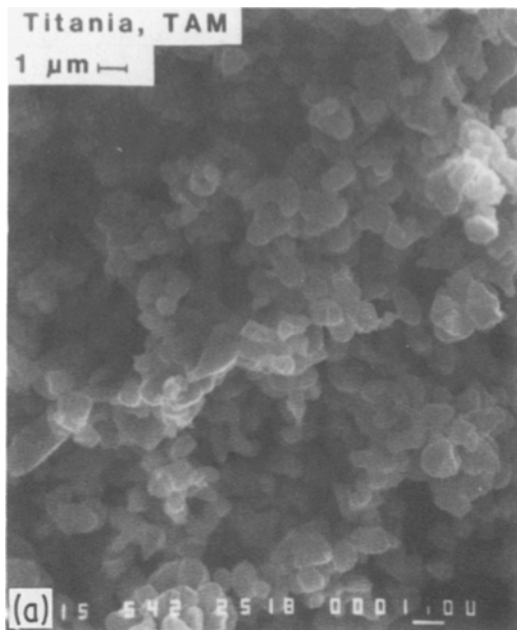


Figure 7 Scanning electron micrographs of the TiO_2 , TAM powder. (a) As-received; (b) dispersed in hexane; (c) dispersed in isopropanol.

4.3.4. Effect of mass and concentration changes on sediment volume

The results of the mass and concentration experiments are shown in Table VI. These results showed that in almost all the cases, larger masses decrease the sediment volume but changes for the indicated concentrations had little or no effect on sediment volumes. The mass effect can be explained by gravitational forces. The additional forces on the particles which helped them pack to denser compacts were provided by the added mass. The negligible change in sediment volumes for concentrations from 5 to 20 vol% indicate no large changes in particle interactions.

4.4. Scanning electron micrographs

The scanning electron micrographs provided a visual way of observing the packing in sediments and therefore, supporting the dispersion results. The micrographs for two good example systems are shown in Figs. 7 and 8 (TiO_2 , TAM, and CaZrO_3 , Transelco). Each powder compact was examined (a) as-received and undispersed, (b) from a poor dispersion (hexane), and (c) from a good dispersion (alcohol). There was little difference between the as-received powder compacts and the compacts from the powders dispersed

dispersed the oxide powders slightly better than the best pure liquids. The 4% mixture worked only slightly better than the 3% mixture, possibly indicating total surface coverage of the particles with fish oil. This fact has been substantiated by other researchers [15]. These results indicate that pure organics can replace some polymeric dispersant systems in industrial applications.

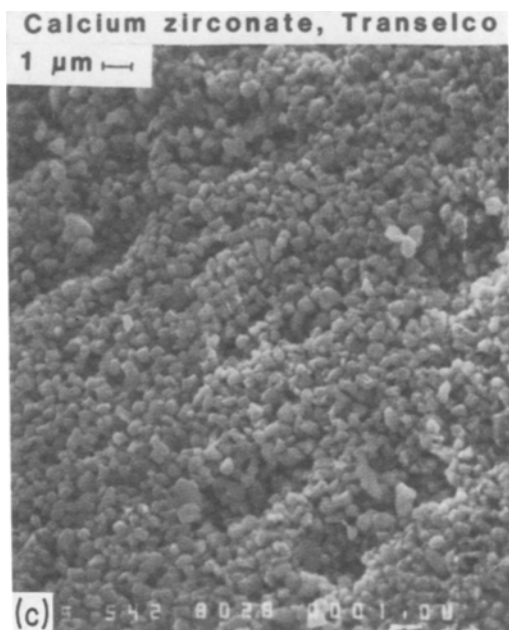
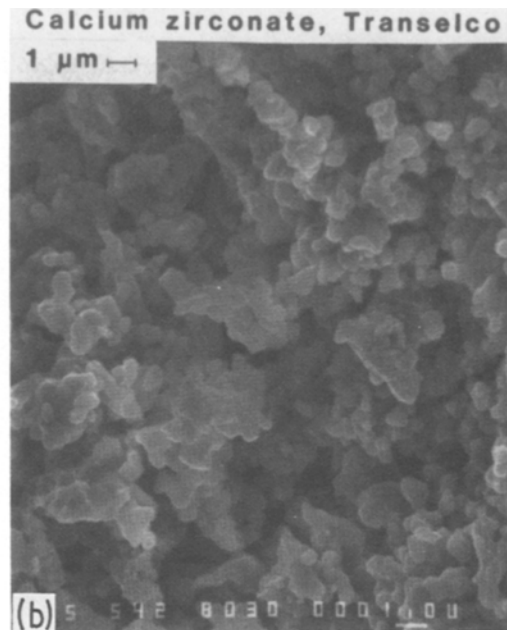
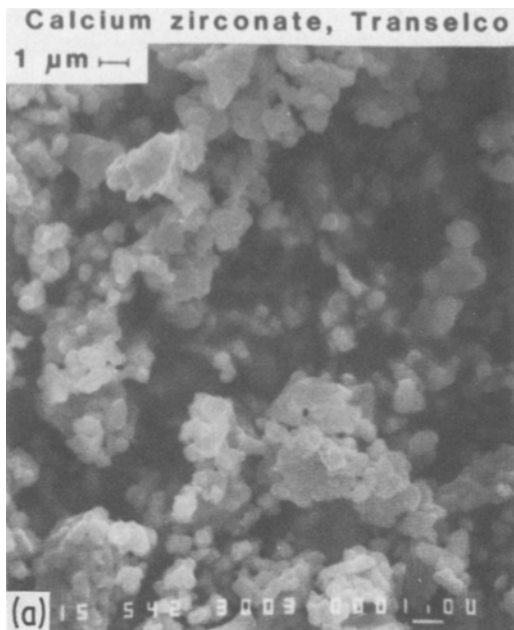


Figure 8 Scanning electron micrographs of the CaZrO_3 , Transelco powder. (a) As-received; (b) dispersed in hexane; (c) dispersed in isopropanol.

along in the processing sequence [16]. This micrograph also demonstrates the ability of using Stokes's settling to classify particles [12], since most of the particles shown are of sizes between the expected 0.4 and 0.6 μm .

5. Conclusions

The fundamental properties of capacitor oxide powder dispersions in several classes of pure organic liquids, one polyester solution, and water were examined by sediment volume tests and SEM observations of centrifuged compacts. Hydrogen bonding capabilities of the dispersion medium were found to be an important factor in determining the degree of dispersion; the good hydrogen bonding liquids dispersed the oxide powders much better than the poor or non-hydrogen bonding liquids.

The effect of water in a dispersion system was found to be unfavourable for the hydrocarbons, ethers, ketones and esters; its effect was insignificant for alcohols, aldehydes and acids. Pure alcohols disperse metal oxide powders almost as well as a typical polymeric-type dispersant, fish oil. It may therefore be possible to "clean up" a tape casting slurry formulation by eliminating unnecessary (and usually difficult to remove) ingredients by carefully selecting a more simple dispersion system.

in hexane. However, the compacts from the powders which were dispersed in isopropanol or methanol were packed better; there were fewer number of large voids and loosely packed agglomerates.

The scanning electron micrograph of the mono-sized ZrO_2 , shown in Fig. 9, demonstrates the extremely good packing obtained when the particles are of similar size. The packing approaches close-packed spheres in some regions. This would aid in controlling sintering mechanisms further

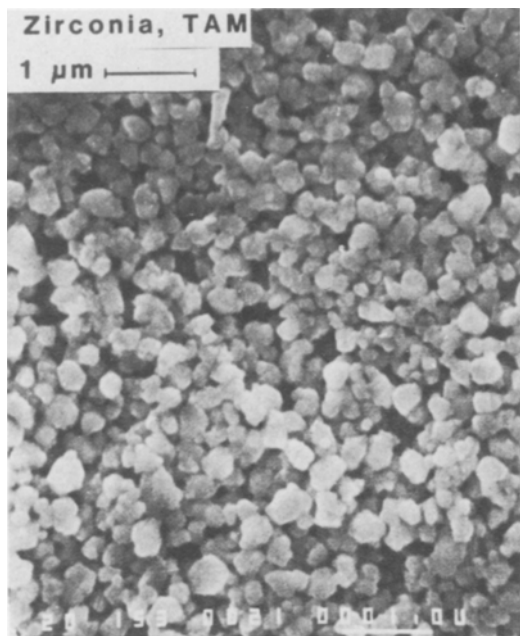


Figure 9 Scanning electron micrograph of the narrow-sized ZrO_2 powder.

Tightly packed sediments with few voids are obtainable when powders are well dispersed and especially when the powders have a narrow size distribution. This effect would aid subsequent processing steps such as sintering. In good dispersions, moderate changes in the total mass or particle concentrations do not adversely affect the sediment volume results (i.e., the degree of dispersion attainable).

These results are found to be in good agreement with previous studies [1]. The emphasis of this work was to characterize the effect of the organic functional groups when present in dispersion systems for some oxide powders. This report may help form a basis to develop new slurry formulations for the tape casting methods used in the capacitor industry.

Acknowledgement

The authors would like to thank Mrs L. van Uitert

for preparing the manuscript and Dr R. L. Pober for his helpful comments. The authors are grateful to the Multilayer Ceramic Chip Consortium of companies for supporting this research.

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Received 9 April

and accepted 10 May 1984