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Dispersion Properties of $BaTiO_3$ Tape-casting Slurries

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Abstract

The stability of suspensions suitable for the tape-casting of $BaTiO_3$ *has been studied. The quality of dispersions obtained in phosphate-ester-containing MEK:EtOH has been determined in the context of conductivity measurements to indicate the degree of dissociation of the ester and by adsorption measurements to indicate the nature of particle–dispersant interaction. Both electrostatic and steric contributions to stabilization are found.*

Es wurde die Stabilität von Suspensionen, die sich für den Bandguß von $BaTiO_3$ *eignen, untersucht. Die Qualität von Dispersionen, die aus einer Phosphat-Ester-haltigen MEK:Ethanol-Lösung gewonnen wurden, wurde mittels Leitfähigkeitsmessungen überprüft, um den Dissoziationsgrad des Esters zu bestimmen. Außerdem wurden Adsorptionsmessungen durchgeführt, um die Art der Wechselwirkung zwischen den Teilchen und der Dispersionslösung zu bestimmen. Sowohl elektrostatische als auch sterische Beiträge zur Stabilisierung konnten beobachtet werden.*

Cette étude porte sur la dispersion, par des esters phosphoriques, de suspensions de coulage en bande de $BaTiO_3$ *dans un solvant organique, MEK:EtOH. Les mécanismes de dispersion ont été étudiés par des mesures de conductivité indiquant le degré de dissociation des esters ainsi que par des mesures d'adsorption renseignant sur la nature des interactions particule–dispersant. Des contributions à la fois électrostatiques et stériques ont été mises en évidence.*

1 Introduction

Tape-casting is the most efficient and most reliable method to produce thin ceramic sheets.[1–6] In particular, tape-casting is used to prepare the $BaTiO_3$ dielectric sheets which are stacked for processing multilayer capacitors. Tape-casting slurries are composed of ceramic powders dispersed in a solvent. Common solvents are azeotropic mixtures such as 66:34 vol.% 2-butanone:ethanol (MEK:EtOH)[2,7,8] or 72:28 vol.% trichloroethylene:ethanol.[3–6] The solvent contains dispersant, binder and plasticizer additions. Dispersants favor the deagglomeration and stabilization of ceramic particles in the slurry. Steric hindrance generally explains the dispersion of powders in organic solvents with low dielectric constant, where little ionization is expected. However, mechanisms involved in non-aqueous media can be more complex, because steric hindrance and electrostatic repulsion can conjugate. Previous studies[9–12] have shown that special phosphate esters with a linear molecule, a high diester concentration, and a high hydrophilic:lipophilic balance (HLB) are effective dispersants for alumina and barium titanate slurries. Binders give pseudoplasticity and ensure the cohesion of green tapes after the solvent is evaporated. Polyvinyl butyral and acrylic resins are common binders.[1–4,6–8,13] Plasticizers improve the flexibility of green tapes. They partially break the bonds responsible for mechanical cohesion,[14] lower the viscosity and decrease the glass transition temperature (T_g).

A workable slurry for tape-casting should satisfy

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the following criteria: (i) high ceramic to non-ceramic ratio; (ii) low viscosity; (iii) high stability; and (iv) high homogeneity. The preparation of tape-casting slurries usually involves two stages: (i) deagglomeration of powders and dispersion in a solvent with the aid of dispersants; and (ii) homogenization with the aid of binders and plasticizers. The first stage of preparation strongly influences the characteristics of green tapes and, later, the properties of final products such as density and microstructure homogeneity. The present study deals with the dispersion of barium titanate powder in a MEK:EtOH solvent dispersed by a phosphate ester. Dispersion mechanisms were studied by rheology, adsorption, electrophoresis and conductivity methods.

2 Experimental

2.1 Starting materials

Barium titanate was a high-purity grade (APBG01, Rhône-Poulenc, Paris, France), the main characteristics of which are given in Table 1. The solvent was a mixture of MEK and ethanol (Table 2). Three phosphate esters used as dispersants were compared (C210, C211 and C213, CECA, Paris, France). They were prepared by reaction between phosphoric acid and an ethoxylate. They were an equal mixture of monoester and diester, with some remains of the ethoxylate not combined with phosphoric acid. The typical chemical structure is shown in Fig. 1. The ethoxylate molecule contains both a polyoxyethylene group with hydrophilic behavior and an alkyl group with lipophilic behavior. The HLB values are 10, 11 and 13 for C210, C211 and C213, respectively.

2.2 Dispersion properties

As-received powders were poured into either pure solvent or phosphate-ester containing solvent. The powder content was usually 25 vol.% but the slurries used to characterize the rheological behavior had a powder content of 34 to 50 vol.%. As-received powders were vacuum dried at 120°C for 24 h. To study the influence of the water content in MEK:EtOH, the solvent was dried over 0·3 nm (3 Å) molecular sieve. To achieve dispersion and deagglomerate powders, suspensions were sonicated for 3 min at a power of 360 W cm^{-2}, then mixed for 48 h using a reciprocating shaker. A previous study[15] has shown that this treatment is very efficient to disperse and deagglomerate barium titanate slurries made with MEK:EtOH. X-ray granulometry (Sedigraph 5000D, Micromeritics, Norcross, GA, USA) shows a narrow particle size distribution, centered around 0·9 μm.

Table 1. Characteristics of APG01 BaTiO$_3$ powder

Density (g cm^{-3})	5·94
Mean grain size (μm)	0·88
Specific surface area (m^2 g^{-1})	2·1
Ba:Ti ratio	0·992
Mean purity (%)	>99·98

Table 2. Physical properties of solvents

	MEK *($CH_3CH_2COCH_3$)*	*Ethanol* *(C_2H_5OH)*
Dielectric constant (25°C)	18·5	24·3
Molecular weight	72·11	46·07
Density (25°C) (g cm^{-3})	0·805	0·78
Viscosity (25°C) (mPa s)	0·4	1·2
Boiling point (°C)	79·6	78·5

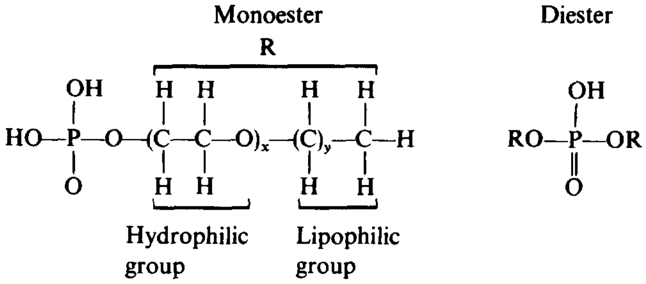

Fig. 1. Chemical structure of phosphate esters.

Adsorption isotherms were plotted to determine the quantity of polymeric phosphate ester adsorbed onto the surface of barium titanate particles. The slurries were centrifuged in polyethylene cells. The resulting supernatants were analyzed for residual phosphorus by an inductively coupled, argon plasma, atomic emission spectrometer (ICP/5000, Perkin-Elmer, Norwalk, CT, USA). The phosphate ester concentrations in the supernatants, and therefore the amounts of adsorbed dispersant, were calculated from the theoretical molecular weights.

Micro-electrophoresis measurements were performed with an automatic apparatus (Pen Kem 3000, Pen Kem, Bedford Hills, NY, USA), using dilute dispersions composed of a small quantity of barium titanate slurry and corresponding supernatants (10 μl liter^{-1}). The zeta potential (Z), defined as the potential at the shear plane (and directly related to the surface potential) was calculated using Helmholtz–Smoluchowski's equation:

$$Z = \Phi \cdot \mu / \varepsilon_r \cdot \varepsilon_0$$

where μ is the electrophoretic mobility, Φ the viscosity of the liquid medium, and $\varepsilon_r \cdot \varepsilon_0$ the dielectric constant of the medium.

The conductivity of suspensions is sensitive to the ionic concentrations, which depend on phosphate ester dissociation and adsorption phenomena. Conductivity measurements were performed using an electronic conductance meter with platinum-coated electrodes (CD6NG, Tacussel, Paris, France).

The cell constant was determined with a 0·1 M KCl standard solution.

Rheology measurements (at 20°C) were performed using a rotating-cylinder viscometer (Rotovisco RV12, Haake, Karlsruhe, FRG). Viscosity measurements were done immediately after the ultrasonic treatment, to avoid reagglomeration. In the case of high solid concentrations (50 vol.%), viscosity measurement were done after a 3-h ball milling and a subsequent ultrasonic treatment for 3 min at $360\,W\,cm^{-2}$. The shear rate was continuously increased from 0 to $1000\,s^{-1}$ over a 1 min interval.

3 Results and Discussion

3.1 The phosphate ester–MEK:EtOH system

Figure 2 shows the electrical conductivity of the phosphate ester–MEK:EtOH system versus the phosphate ester HLB and Fig. 3 shows the same quantity versus the MEK:EtOH ratio, for two HLB values (10 and 13).

When its HLB increases, the displacement becomes more hydrophilic and its affinity with the solvent decreases. The dissociation of the dispersant is optimum for a solvent composition close to the azeotrope: 66MEK:34EtOH (in wt%). A concentration of $20\,g\,liter^{-1}$ allows the phosphate ester to be fully soluble, whatever its HLB.

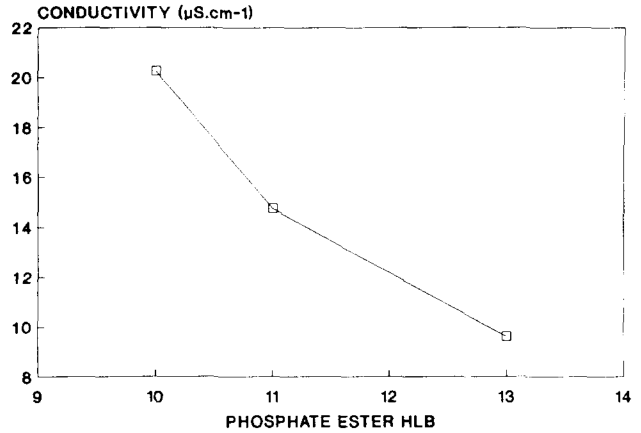

Fig. 2. Electrical conductivity of MEK:EtOH with $20\,g\,liter^{-1}$ of ester versus ester HLB.

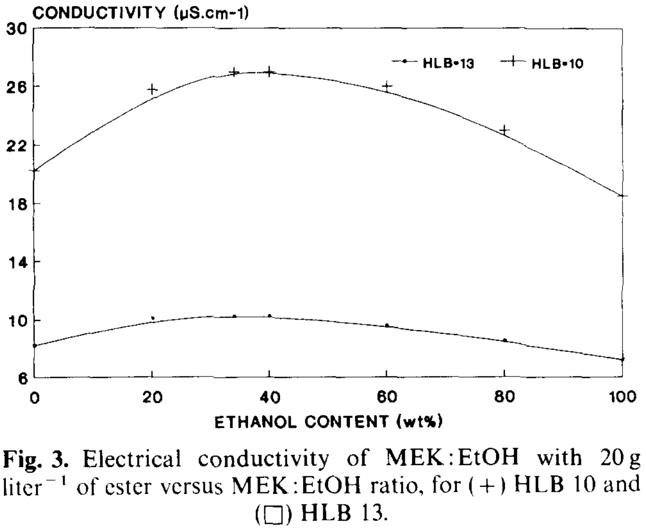

Fig. 3. Electrical conductivity of MEK:EtOH with 20 g $liter^{-1}$ of ester versus MEK:EtOH ratio, for (+) HLB 10 and (□) HLB 13.

3.2 The $BaTiO_3$–MEK:EtOH system

The electric charge on the surfaces of the dried $BaTiO_3$ particles is negative when measured in the as-received, hydrated solvent: the electrophoretic mobility is equal to $-0{\cdot}5\times10^{-8}\,m^2\,V^{-1}\,s^{1}$. After the water has been removed from the solvent using 0·3 nm (3 Å) molecular sieve, particle surfaces become positive: the electrophoretic mobility is equal to $+0{\cdot}5\times10^{-8}\,m^2\,V^{-1}\,s^{-1}$. The electrophoretic mobility of $BaTiO_3$ particles in a dehydrated solvent is sensitive to the drying temperature of the $BaTiO_3$ powder: it reaches its maximum for a drying temperature of about 50°C (Fig. 4). The vacuum heating of the powder eliminates the physisorbed water but does not eliminate the chemisorbed water, the removal of which requires a treatment at a temperature of about 500°C. The water which enters the azeotropic MEK:EtOH mixture preferentially covers the weakly basic surface of $BaTiO_3$ particles, which explains why their charge is negative. After the water has been removed from the solvent, the only possible interactions are those between MEK:EtOH and particles, which explains why their charge is positive. No explanation is proposed for the existence of a maximum in the electrophoretic mobility versus temperature curve.

3.3 The $BaTiO_3$–phosphate ester–MEK:EtOH system

Morris[16] has proposed an adsorption model for the $BaTiO_3$–phosphate ester–MEK:EtOH system. After the ester dissociation, the charged, resulting anionic dispersant adsorbs onto the particle surfaces and the linear carbon chains extend into the non-polar solvent, which provides steric stabilization. An electrostatic mechanism also occurs due to the

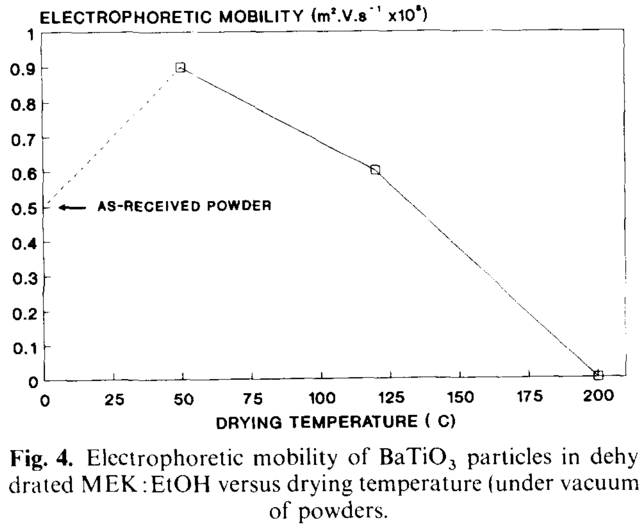

Fig. 4. Electrophoretic mobility of $BaTiO_3$ particles in dehydrated MEK:EtOH versus drying temperature (under vacuum) of powders.

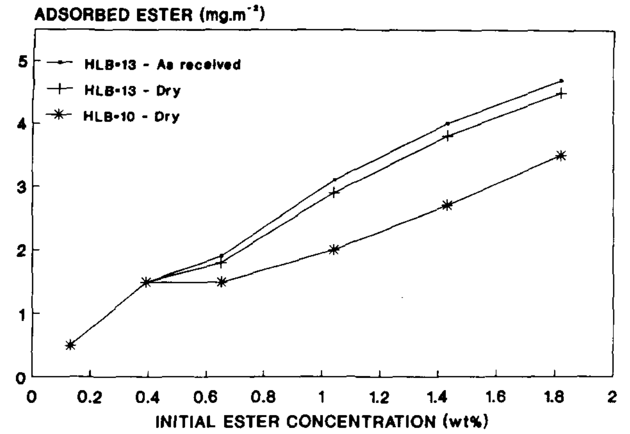

Fig. 5. Adsorption isotherms in MEK : EtOH of (□) as-received and (+) dried $BaTiO_3$ powders for C213-ester (HLB 13) and of (★) dried $BaTiO_3$ powders for C210-ester (HLB 10).

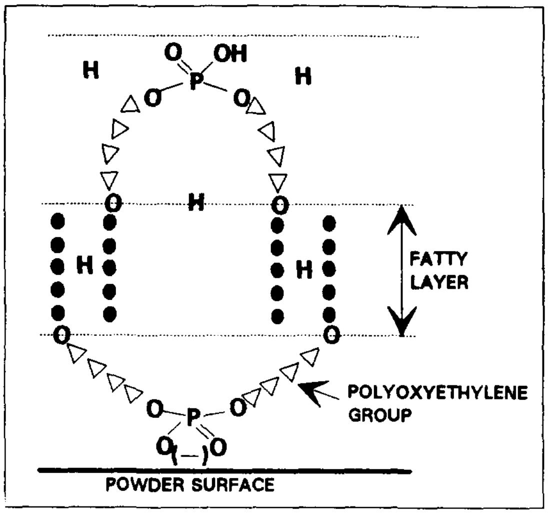

Fig. 6. Schematic of a double layer of phosphate ester molecules adsorbed onto $BATiO_3$ particle surfaces.

liberation of hydronium ions by dissociation, which provides electrostatic stabilization.

Figure 5 compares the adsorption of phosphate esters on dried and as-received $BaTiO_3$ powders, for two values of HLB (10 and 13). Adsorption is higher for HLB = 13. This shows that an increase in HLB allows phosphate esters to have a better affinity with the charged surface of particles. Moreover, a small lipophile chain (high HLB) may increase the surface accessibility. The adsorption isotherms are rather similar for the as-received and dried powders.

The adsorption of the two phosphate esters is complete as long as the concentration of powder is below a threshold of about 0·4 wt%, which corresponds to 1·8 mg (i.e. 3 μmol) of adsorbed phosphate ester per m^2 of powder. This means that all the dispersant is adsorbed onto the surfaces of the powder particles and that there is no dispersant in the solution. Above the threshold, the adsorption continues to proceed but a part of the dispersant remains in solution. The authors did not observe the presence of a significant plateau, as commonly mentioned in the literature. It is difficult to analyze the evolution of phosphate ester adsorption, maybe due to the presence of residues of phosphoric acid and non-reacted ethoxylate, which can disturb interactions.

Using the value of 0·7 mg m^{-2} of adsorbed phosphate ester given by Mikeska & Cannon,[17] it is possible to propose a double-layer configuration of adsorbed phosphate ester molecules, as shown in Fig. 6. The hydrophilic head of the molecule strongly adsorbs onto the powder surface and its non-polar tail freely extends into the solvent. When the phosphate ester concentration increases a second layer is formed, by orientation of a polar head into the solvent. This double layer contains one inner, non-polar, 'fatty' region.

The double layer establishment may be disturbed by the conformation of the polymeric chains at the surface of particles. The present adsorption isotherms are similar to those obtained by Eirich,[18] who proposed a model consisting of a monolayer adsorption, followed by an overlapping of polymeric chains, which increases the 'density' of the layer.

Figure 7 compares electrophoretic mobility of as-received and dried $BaTiO_3$ powders versus ester concentration, for two phosphate esters (HLB 10 and 13).

The surface charge is reversed when phosphate ester is mixed with solvent. As discussed in Section 3.2, $BaTiO_3$ particles are negatively charged when dispersed in pure, as-received MEK : EtOH, which is due to the presence of water residues in the solvent. In contrast, they are positively charged when dispersed in an ester-containing solvent. This can be explained by the dissociation of phosphate ester, as

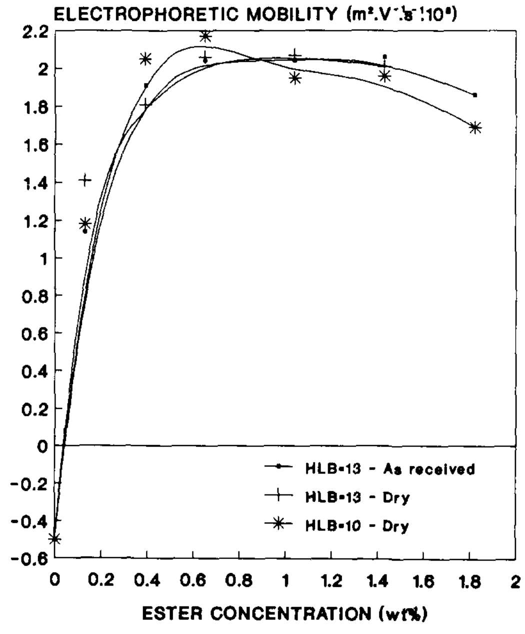

Fig. 7. Electrophoretic mobility in MEK : EtOH of (□) as-received and (+) dried $BaTiO_3$ powders for C213-ester (HLB 13) and of (★) dried $BaTiO_3$ powders for C210-ester (HLB 10) versus ester concentration.

proposed by Morris,[16] who suggested that liberated hydronium ions are adsorbed onto the particle surfaces.

The electrophoretic mobility versus dispersant concentration relationship is quite similar for the as-received and dried powders.

For a HLB of 10, electrophoretic mobility reaches its maximum when the concentration of powder is of about 0·6 wt% and decreases beyond this. For a HLB of 13, high mobilities are obtained. The ester: powder ratio ranges from 0·6 to 1·4 wt% and in this domain the calculated value of the zeta potential exceeds 70 mV, which demonstrates that the electrostatic contribution to stabilization is high. The decrease in the zeta potential, for high concentrations of phosphate ester, may be related to the increase in ion concentration shown in Fig. 8, hence to a decrease in the double layer thickness. The decrease of the electrophoretic mobility, at a lower ester concentration (about 0·6 wt%), using a phosphate ester with a HLB of 10 is in agreement with the higher ionization of the low-HLB dispersant in MEK:EtOH solvent (Fig. 3).

Figure 8 shows that a little ionization of phosphate ester (HLB = 13) is achieved in the low dielectric constant MEK:EtOH azeotrope ($\varepsilon_r = 20{\cdot}5$). However, a higher ionization is obtained with the addition of powder. The conductivity of slurry is lower than that of supernatant, due to insulating properties of barium titanate. Fowkes *et al.*[19] have suggested that ionization in organic media may occur through surface phenomena. The dispersant adsorbs, as a neutral molecule, onto particle surfaces, then dissociates and creates charged surfaces. The ionization of the phosphate ester molecule can be possible in places close to polar particle surfaces, which results in an electrostatic barrier. For dispersant concentrations higher than 1 wt%, the evolution of conductivity becomes linear, with a slope close to that of the solvent–ester system.

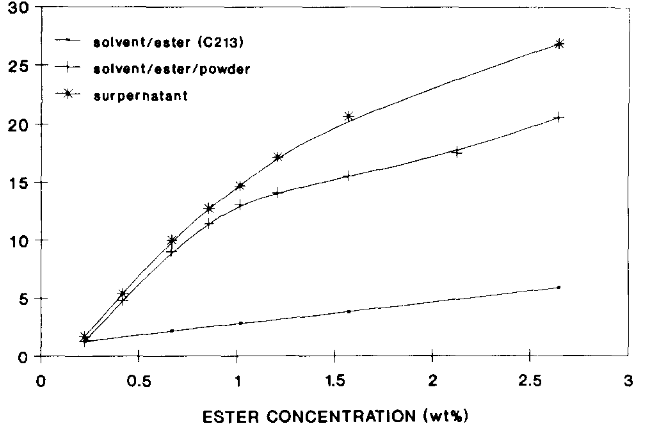

Fig. 8. Electrical conductivity of (★) supernatant and of MEK:EtOH with (☐) C213-ester with (+) $BaTiO_3$ and C213-ester systems versus ester concentration.

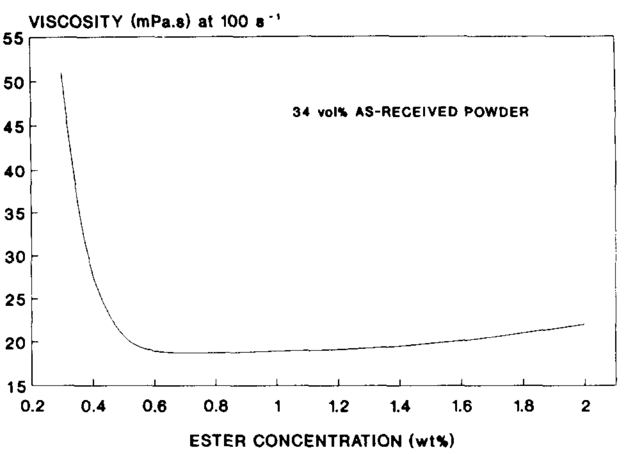

Fig. 9. Apparent viscosity of suspensions with 34 vol.% of as-received powder versus C123-ester concentration.

It can be assumed that the ionization of ester molecules on particle surfaces is no longer possible because polymer adsorption and ionization are now controlled by the solvent. The zeta potential reaches its maximum for a dispersant concentration of about 1 wt% and decreases beyond this.

The rheological behavior of slurries was studied as a function of $BaTiO_3$ concentration, drying state of powder, and shear rate.

Figure 9 shows the apparent viscosity of a 34 vol.% $BaTiO_3$ slurry versus its ester (C213) concentration. In the range of the shear rates which were tested (0 to 1000 s^{-1}), slurry viscosity does not depend on shear rate. A comparison of the curve with those of electrophoretic mobility (Fig. 7) and adsorption (Fig. 5) shows that the zeta potential and the degree of dispersion reach their maximum at the same concentration of phosphate ester (0·6 wt%), which demonstrates the existence of a high contribution of an electrostatic mechanism to the system stabilization. Then, both the zeta potential and the dispersion state decrease (and therefore viscosity increases) while adsorption increases continuously as the phosphate ester concentration increases beyond the value for which there is full adsorption (about 0·4 wt%). The increase in viscosity seems to be only associated with the decrease in the zeta potential.

Figure 10 shows the apparent viscosity of a 50 vol.% $BaTiO_3$ slurry versus shear rate, for various ester concentrations. The rheological behavior becomes pseudoplastic at high ester concentrations. For low shear rates ($< 130\,s^{-1}$), the best dispersion is achieved for a dispersant concentration of 0·45 wt%, whereas for high shear rates ($> 130\,s^{-1}$) a concentration of 0·24 wt% is enough to give optimum dispersion. This latter concentration does not correspond to the maximum in zeta potential. It can be assumed that the electrostatic contribution to stabilization decreases as the powder concentration increases and that the rhe-

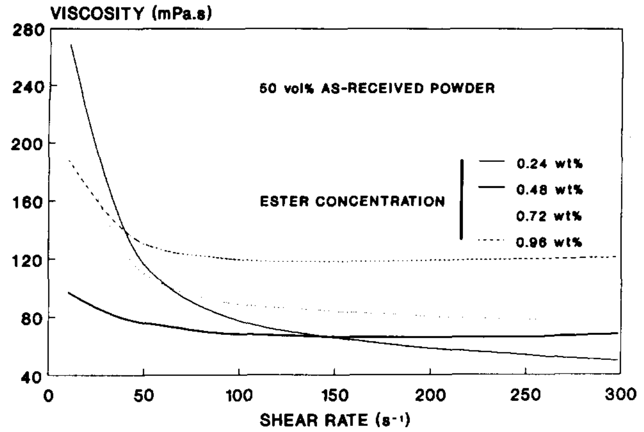

Fig. 10. Apparent viscosity of suspensions with 50 vol.% of as-received powder versus shear rate, for various C213-ester concentrations. ———, 0·24 wt%; ———, 0·48 wt%; ·····, 0·72 wt%; ----, 0·96 wt%.

ological behavior depends more and more on steric hindrance.

3.4 Influence of the drying state of powder

Several authors[9,13,20-22] have mentioned the influence of water on the adsorption of dispersing agents and the stabilization of suspensions.

Figure 11 compares the apparent viscosity of 50 vol.% $BaTiO_3$ slurries made either with as-received or dried powders versus shear rate, for a 0·72 wt% ester (C213) concentration. Dried powders lead to a higher viscosity than as-received powders. Drying powders at 120°C for 24 h under vacuum affects neither the adsorption of phosphate ester nor the electrophoretic mobility of $BaTiO_3$ particles, whereas the rheological behavior depends on the drying state of powder. The same amount of phosphate ester is adsorbed onto as-received and dried powders, and the electrical double layer is not affected by drying powders. The difference in dispersion may be due to the conformational state of the phosphate ester molecules on the particle surfaces.

A pseudoplastic–dilatent transition occurs for a shear rate of about 200–300 s^{-1}. This transition may be due to the interpenetration of phosphate ester layers surrounding particles at high shear rates.

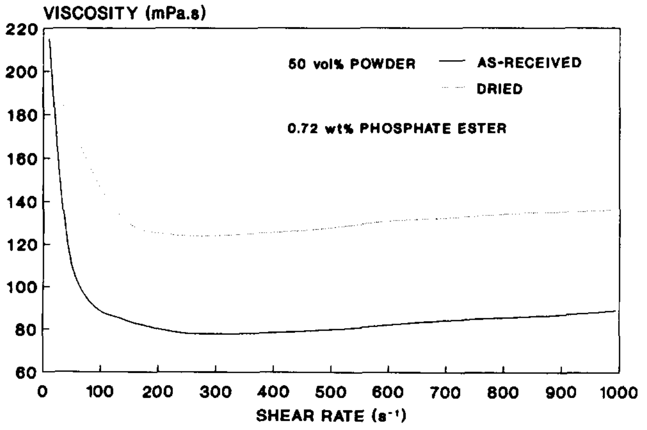

Fig. 11. Apparent viscosity of suspensions with 50 vol.% of (———) as-received and (·····) dried powder versus shear rate, for 0·72 wt% of C213-ester.

4 Conclusion

The dispersion properties of $BaTiO_3$ in phosphate-ester-containing MEK:EtOH depends on the ionic concentration of slurry, in relation to the phosphate ester dissociation. Conductivity measurements have indicated that dissociation is a function of the phosphate ester HLB and MEK:EtOH ratio. The highest degree of dispersion (i.e. the lowest viscosity) is achieved when using the azeotrope composition of MEK:EtOH mixture, dispersed by a phosphate ester with a HLB of 13, at a concentration of about 0·6 wt%.

Adsorption of phosphate ester is improved when HLB is high, which is due to a better affinity of hydrophilic molecules for the charged surfaces of particles. The adsorption isotherms do not exhibit a well-defined plateau. Adsorption is total up to a phosphate ester concentration of about 0·4 wt%, then there is a continuous increase in adsorption as the phosphate ester concentration continues to increase. According to Eirich's results,[18] it can be suggested that the phosphate ester polymer adsorbs in packed arrangements onto particle surfaces.

Conductivity measurements indicate that the dissociation of phosphate ester is enhanced when the powder concentration increases, which suggests that ionization is induced by surface phenomena.

The degree of dispersion of 34 vol.% powder slurries, determined by rheological measurements, is in agreement with the electrophoretic mobility data, which suggests a high electrostatic contribution to stabilization. However, at high powder concentrations (50 vol.%), which correspond to a dense packing of particles, the electrostatic contribution decreases and the steric contribution becomes necessary to prevent agglomeration.

The electrophoretic mobility of $BaTiO_3$ particles and the adsorption of phosphate ester do not depend on the drying state of powders, but the degree of dispersion of dried powders is lower than that of as-received (hydrated) powders. The conformational state of the phosphate ester molecules adsorbed onto the particle surfaces may be affected by the drying of powders.

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