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Oil-Related Deflocculants for Tape Casting Slips

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Abstract

The preparation of a stable, well-dispersed slip is a critical step in tape casting technology. The most widely used dispersants in non-aqueous slips behave as semisteric dispersants; they anchor to the particle surface but they have a relatively short chain. On the basis of chemical structure, other dispersants are proposed. Vegetable oils, such as linseed oil and castor oil, and other related substances, such as lecithin, have been tried for alumina slips. The dispersing mechanisms are discussed taking into account viscosity measurements of slips containing 50 wt% solids. Infrared spectroscopy has been used to study the adsorption mechanisms. Finally, the conductivity of the dispersants and the slips has been measured by complex impedance technique. An evaluation of the dispersing mechanism has been made. © 1996 Elsevier Science Limited.

Introduction

Stabilization of oxide ceramics in non-aqueous media has long been important in tape casting technology.[1–3] Stable and well-dispersed slips have been prepared using either surfactants[4] or polymeric stabilizers.[5] In general, it has been accepted that steric stabilization is the only effective mechanism in organic media, since typical dispersants anchor to the particle surface. However, steric stabilization requires another important condition: extent of the molecule, which must be long enough to avoid contact between particles. It is considered that a molecular weight of at least 10,000 is necessary to provide this kind of stabilization.

Most commercially available stabilizers for non-aqueous media have relatively low molecular weight. Some authors have called these dispersants semisteric stabilizers.[3] On the other hand, Fowkes *et al.*[6] have pointed out that, even in non-polar media, the particles are charged so that there is also some electrostatic contribution to the stabilization when polymers or semisteric stabilizers are present.

The aim of this work is to study the effect of oil-related dispersants on the rheological behaviour of Al_2O_3 slips. Some new dispersants are proposed in this work from a consideration of their chemical nature. Their behaviour is related to that of other usual dispersants, such as menhaden fish oil, glyceryl trioleate and phosphate esters. The stabilizing mechanisms are discussed in the light of the chemical nature, the rheology and the electrical response of the different dispersants.

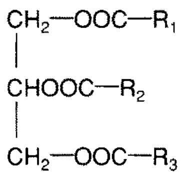
Theoretical Considerations

The most usual dispersants in tape casting formulations are phosphate esters and some glycerides, such as menhaden fish oil and its closest pure analogue, glyceryl trioleate.[7–9] The dispersing capability of these three substances has been studied in this work together with that of other oil-related substances, such as castor oil, linseed oil or lecithin. All these substances have some surface activity. They polymerize but the extent of the polymerization is not high enough to provide the required chain length for them to act as pure polymeric stabilizers.

Considering the charge of the surface-active part of the molecule, the surfactants can be classified in four different groups:

(1) Non-ionic surfactants.
(2) Anionic surfactants.
(3) Cationic surfactants.
(4) Zwitterionic surfactants, with both positive and negative charges.

From a structural point of view, oils consist basically of esters formed by reaction of glycerol with fatty acids. The efficiency of an oil as dispersant is related to its chain length, the presence of irregularities in the chain and the presence of unsaturation in the fatty acid (which is estimated by the iodine number). The general formula of glycerides is:

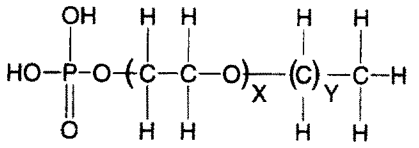


$$\begin{array}{l} CH_2\text{—}OOC\text{—}R_1 \\ | \\ CHOOC\text{—}R_2 \\ | \\ CH_2\text{—}OOC\text{—}R_3 \end{array}$$

where R_1, R_2 and R_3 are the chains of fatty acids.

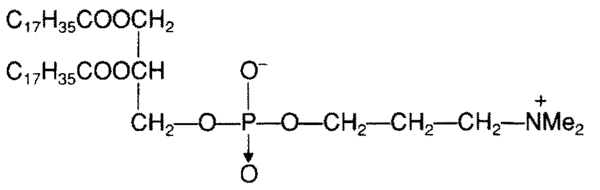
The efficiency of oil-related compounds as dispersants is related to their composition. Since there is always a major fatty acid in the composition,[10–11] it is possible to select an oil by taking into account the characteristics of the main fatty acid.[12] Table 1 shows the major component and the percentages of saturated and unsaturated fatty acids in different oils. It has been demonstrated that the first two oils in this series cannot produce well-dispersed Al_2O_3 slips. A high percentage of polyunsaturated fatty acids is required to provide stabilization. For this reason, linseed and castor oils have been proposed by the present authors as non-ionic dispersants for ceramics.[12,13] Menhaden fish oil and glyceryl trioleate have been also studied for comparison purposes, since they have been described extensively in the literature.

Phosphate esters can be considered anionic surfactants with the following structure:



$$HO\text{—}\underset{\overset{\|}{O}}{\overset{OH}{\overset{|}{P}}}\text{—}O\text{—}\left(\underset{H}{\overset{H}{C}}\text{—}\underset{H}{\overset{H}{C}}\text{—}O\right)_X\text{—}(C)_Y\text{—}\underset{H}{\overset{H}{C}}\text{—}H$$

Lecithin is proposed in this work as a zwitterionic surfactant. In this case both positive and negative charges are present in the molecule, which has the following general formula:



$$\begin{array}{l} C_{17}H_{35}COOCH_2 \\ \quad\quad\quad\quad\;| \\ C_{17}H_{35}COOCH \quad\quad O^- \\ \quad\quad\quad\quad\;| \quad\quad\quad\;\; | \\ \quad\quad\quad\;\; CH_2\text{—}O\text{—}P\text{—}O\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}\overset{+}{N}Me_2 \\ \quad\quad\quad\quad\quad\quad\quad\quad\;\downarrow \\ \quad\quad\quad\quad\quad\quad\quad\quad\;O \end{array}$$

Lecithin is obtained from soybean oil. The crude oil contains relatively large amounts of phosphatides, chiefly lecithin. Before it is marketed, the phosphatide content is greatly reduced by water washing.[14]

Experimental

An α-Al_2O_3 powder (Alcoa A16SG, USA) has been selected for this study. This powder has a mean particle size of 0·5 μm and a specific surface area of 8 m^2/g.

Different solvents were tried as dispersing media, including polar and non-polar liquids. The non-polar solvents such as toluene do not produce well-dispersed slips. The best dispersability was achieved using an azeotropic mixture of methylethylketone (MEK) and ethanol (EtOH) and this mixture was selected for further experiments.

The following substances were used as dispersants: glyceryl trioleate (GTO), menhaden fish oil (MFO), linseed oil and castor oil (non-ionic), phosphate ester (anionic) and lecithin (zwitterionic).

Alumina slips have been prepared in MEK/EtOH with solid loadings of 50 wt%. Stabilization has been achieved by adding a concentration of 1 wt% (relative to solids) of the mentioned surfactants.

The slips were ball-milled for 2 h in an alumina jar with alumina balls. A controlled excess of solvent was added to sustain the solid content of the slip during the measurements.

The characterization of the dispersants themselves and the dispersed alumina slips has been performed using three main techniques: (1) viscosimetry, (2) Fourier transform infrared spectroscopy (FTIR) and (3) complex impedance spectroscopy.

The apparent viscosity was measured with a rotational viscometer (Haake Rotovisco RV20) at a constant temperature of *c.* 25°C. Adsorption of the dispersants onto the Al_2O_3 surface was detected by FTIR (Perkin-Elmer FTIR, USA). The slips were dried in an oven at temperatures not higher than 50°C. FTIR measurements were performed for the starting powder, solvent, pure dispersants and also for the centrifuged and air dried powders treated with the dispersants. For liquid samples KRS-5 crystals were used. A drop of liquid is put on one crystal and then covered by the other crystal. For solid samples, $\approx$0·8 mg of sample was mixed with 300 mg of KBr.

An impedance analyzer Hewlett-Packard HP 4192 A was used to characterize the dielectric and electrical properties of all the dispersants studied and the slips. For a precise measurement of the dielectric constant a guard ring electrode inside a hermetic sample holder was employed.

Results and Discussion

Characterization of the dispersants

The rheological flow curves of the dispersants used in this work are plotted in Fig. 1. In the case of oils the viscosity is directly related to the iodine value, that is, the number of unsaturations in the chain of the main fatty acid constituting the oil. As reported in a previous work[12] the apparent viscosity decreases in the sense: coconut oil (main

Table 1. Typical compositions of different oils

Oil	*Major fatty acid*	*Saturated (%)*	*Monounsaturated (%)*	*Polyunsaturated (%)*
Coconut	Lauric 0 C=C	90–92	5–8	0–2
Olive	Oleic 1 C=C	9–20	65–85	16·5–45
Soybean	Linoleic 2 C=C	11–20	15–30	55–65
Linseed	Linolenic 3 C=C	7–15	15–26	55–80
Menhaden	>3 C=C	30–50	25–30	20–45
Castor	Ricinoleic 1 C=C, 1 OH	2–4	86–96	4–7

component: lauric acid, saturated) higher than olive oil (main component: oleic acid, with one double bond) higher than soybean oil (main component: linolenic acid, with two double bonds) higher than linseed oil (main component: linolenic acid, with three double bonds). The exception is castor oil, whose major component is ricinoleic acid, with one double bond and one functional group (OH). In this case, the presence of hydroxyl-substituted groups strongly increases the viscosity due to hydrogen bonding. Lecithin is a solid product which is directly dissolved during mixing. The phosphate ester presents a high viscosity due to the polymerization of the molecule.

The infrared spectra of the dispersants considered in this work are plotted in Fig. 2. The most characteristic peaks for oils are located at the following wavelengths: 1654 cm^{-1}, due to carbon–carbon double bond; 1764 cm^{-1}, due to carbonyl adsorption. The zone between 3020 and 2850 cm^{-1} presents three peaks corresponding to the stretching vibrations of C–H (located at 3020 cm^{-1} for the =C–H group and at 2960 cm^{-1} for the –C–H one) and to the COO–H interactions of the fatty acids.

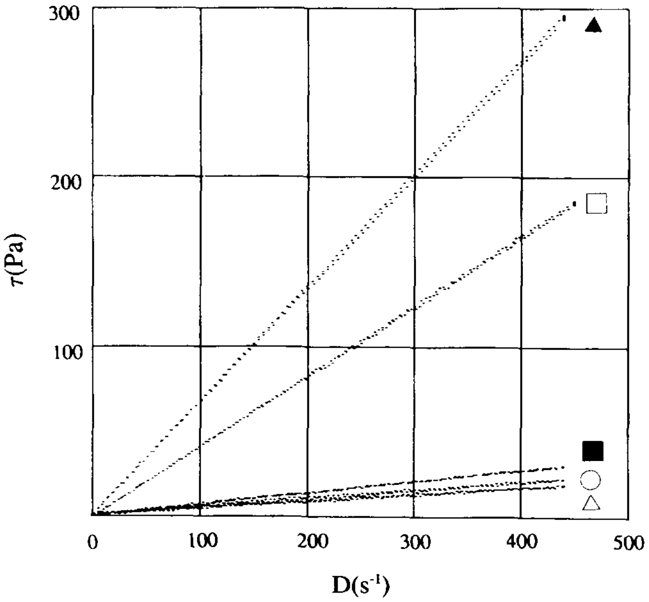


Fig. 1. Flow curves of the liquid deflocculants: (△) MFO, (■) GTO, (○) linseed oil, (▲) castor oil, (□) phosphate ester.

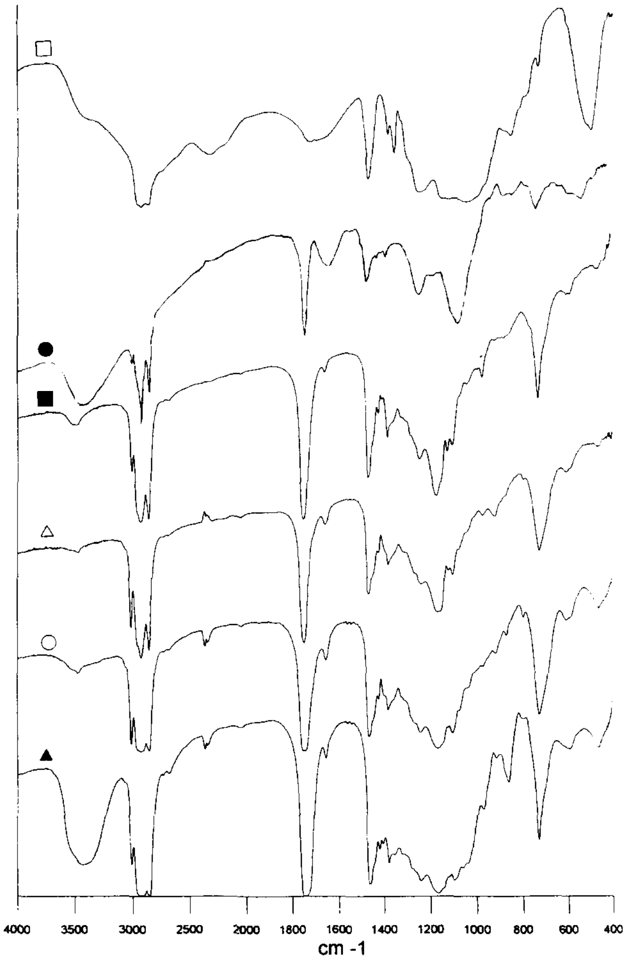


Fig. 2. Infrared spectra of the studied deflocculants: (△) MFO, (■) GTO, (○) linseed oil, (▲) castor oil, (□) phosphate ester and (●) lecithin.

At 3436 cm^{-1} a strong peak appears in the castor oil as a consequence of the hydroxyl group constituting the ricinoleic acid. Peaks at 2363 cm^{-1} and 1630 cm^{-1} are due to CO_2 contamination and to the KBr used for solid sample preparation, respectively. In the case of phosphate ester, the C–H interactions can be seen, as well as the C–O ether signal, located at 1150–1085 cm^{-1}. The P–O bands of the phosphate group appear also in this zone. In the case of lecithin, the characteristic peaks of glycerides also appear. In this case a strong band is observed at 3400 cm^{-1} due to the KBr used for solid sampling, which overlaps the NMe_3 group.

An electrical characterization of the dispersants has been made using the complex impedance technique. In this technique the conductivity is obtained from the representation of the real and the imaginary components Z' and Z''. When the substance has a measurable conductivity, a clear semicircle appears in the complex plane representation. The oils, non-charged surfactants, do not present this behaviour. The charged surfactants, lecithin and phosphate esters, present a perfectly developed and single arc, as shown in Fig. 3. The conductivity values are $1{\cdot}7 \times 10^{-6}$ S/cm for phosphate ester and $2{\cdot}1 \times 10^{-5}$ S/cm for lecithin. The solvent conductivity is 3×10^{-6} S/cm, the dielectric constant being 19·6 at 10^6 Hz.

Characterization of the slips

Figure 4 shows the rheological flow curves of the Al_2O_3 slips dispersed with 1 wt% of each of the dispersants considered. In all cases the solid loading was maintained constant at 50 wt%. For oils, the viscosity decreases when the unsaturation degree of the oil increases. Castor oil gives a very low viscosity. However, the lowest viscosity values are obtained when using charged surfactants, the minimum corresponding to phosphate ester, in fact the most commonly used dispersant in tape casting. GTO and MFO give very high viscosity to the slip, making it difficult to obtain a well-dispersed slip. Vegetable oils with high iodine value provide slips with viscosities much lower than in the case of MFO and GTO. This is probably related to the presence of a high concentration of saturated fatty acids in the composition of these glycerides, as can be observed in Table 1.

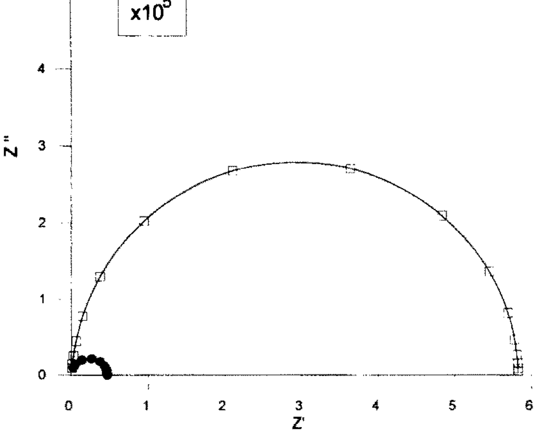


Fig. 3. Conductivity arcs of (□) phosphate ester and (●) lecithin.

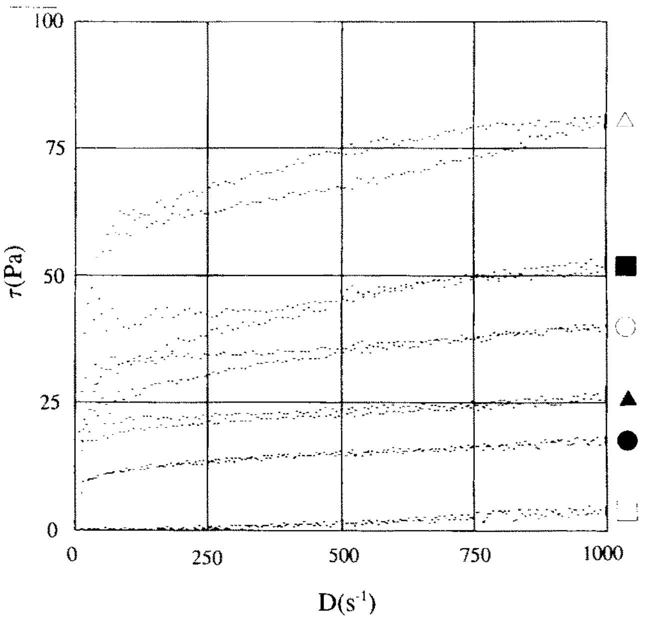


Fig. 4. Flow curves of Al_2O_3 slips dispersed with 1 wt% of the different deflocculants: (△) MFO, (■) GTO, (○) linseed oil, (▲) castor oil, (□) phosphate ester and (●) lecithin.

The adsorption of the dispersants onto the Al_2O_3 surface has been detected by FTIR on centrifuged and dried surfactant-treated powders. The FTIR spectra of the oil-treated aluminas are shown in Fig. 5. At low frequencies (<1200 cm^{-1}), a very strong band appears due to the intense vibration of condensed and isolated hexacoordinated AlO_6 groups. In this zone it is not possible to identify any characteristic peak. In the oil-treated aluminas, the high intensity peaks of the oils also appear. In all cases the carbonyl adsorption appears at 1746 cm^{-1}. The peak does not shift from that of the oil alone and hence the adsorption does not take place through the bulk of the carbonyl group. The same behaviour has been observed for GTO. The peaks between 3020 cm^{-1} and 2850 cm^{-1} corresponding to C–H and COO–H interactions in the oils appear also in the oil-treated alumina spectra, as well as a broad peak located at 3436 cm^{-1} due to the KBr employed in the preparation of solid samples.

Calvert *et al.*[8] studied the efficiency of menhaden fish oil and glyceryl trioleate as dispersants

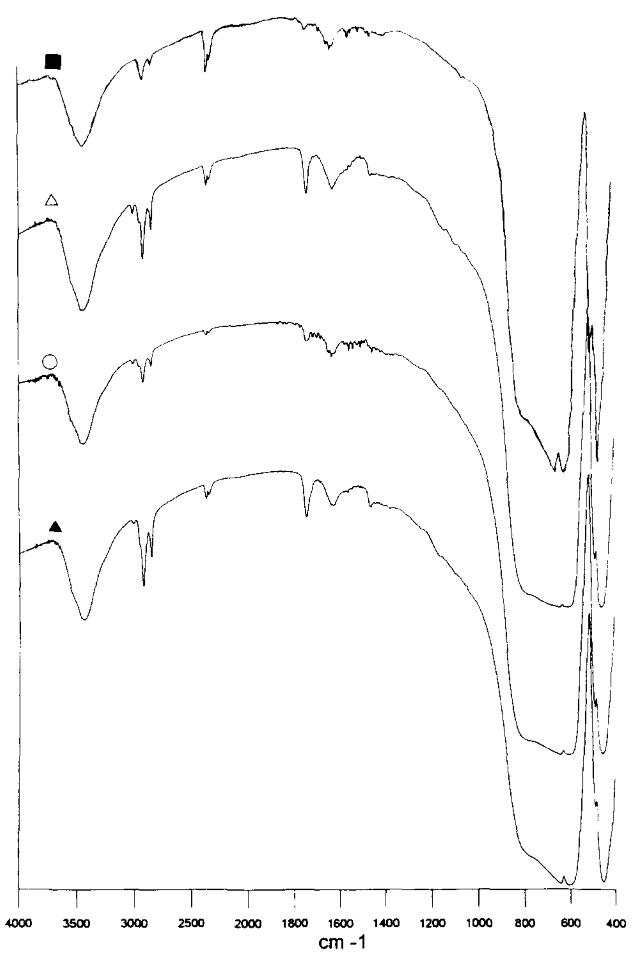


Fig. 5. Infrared spectra of dried Al_2O_3 powders treated with the oil-related deflocculants: ( ) MFO, (■) GTO, (○) linseed oil, (▲) castor oil.

for Al_2O_3. They concluded that GTO ester groups interact strongly with the powder surface, whereas in the fish oil most ester groups are not attached directly to the surface. They observed that a peak shift of the carbonyl group takes place in the case of GTO. This peak shift does not occur in the case of MFO. However, this shift occurs after a lengthy oxidation process. In the present work, fresh slips were always used and hence there is no time for the oxidation phenomena observed by those authors. As a consequence, no shift in the peaks has been observed for any of the dispersants studied in this work. In good agreement with the authors mentioned, it has been also demonstrated that non-oxidized GTO and MFO at a concentration of 1 wt% are not efficient dispersants for Al_2O_3 slips. On the other hand, the vegetable oils considered here are much more efficient. This is related to the composition of the oils. MFO has polyunsaturated fatty acids with molecules containing up to six unsaturations. However, there is also a high percentage of saturated fatty acids (30–50 wt%) and monounsaturated acids (25–30 wt%), which can produce a competitive adsorption among the fatty acids. This relatively high concentration of saturated acids strongly reduces the potential surface activity of MFO. In the case of linseed oil, the percentage of linolenic acid with three double bonds is 55–80 wt% and only a concentration of 7–15% of saturated fatty acids is present in the composition.

In the case of charged surfactants, the dispersing capability is produced by the dissociation of the ester, in which hydronium (H_3O^+) ions are liberated into the solvent.[2,7] The particles become positively charged and attract anionic phosphate ester molecules. Infrared spectroscopy of the phosphate-ester-treated alumina shows the presence of the C–H stretching vibrations. The broad, strong bands due to Al_2O_3 overlap the possible interactions due to the phosphate group. In the case of lecithin, the interaction of phosphate group cannot be seen for the same reason and the NMe_3 group is also covered by the KBr.

From the conductivity measurements it has been proved that some conductivity is always present even when oils are used as dispersants. The corresponding conductivity arcs are plotted in Fig. 6 for different dispersants. Conductivity must accordingly be taken into account also for ceramic slips in non-aqueous media. The conductivity (σ) and the dielectric constant (ϵ') at 10^6 Hz for the different slips are shown in Table 2, as well as those corresponding to the dispersants themselves. As can be observed, GTO provides to the slip a conductivity value slightly higher than that of the solvent. This dispersant has been demonstrated to be non-effective for ceramic slips. Linseed oil provides an enhanced conductivity and MFO and castor oil double the conductivity. The highest conductivity values are obtained for charged surfactants, as expected. These are, in fact, the most effective dispersants among all the substances

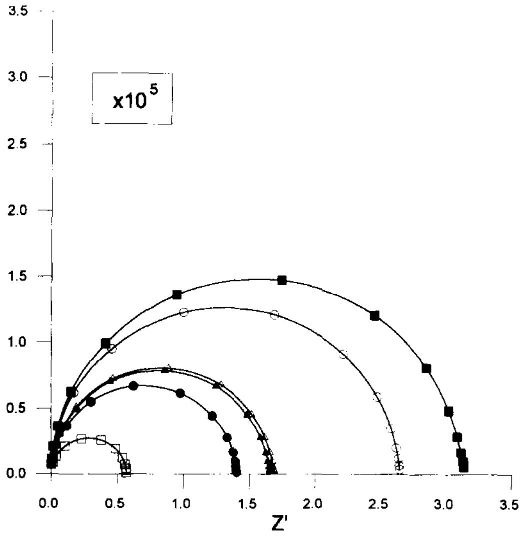


Fig. 6. Conductivity arcs of Al_2O_3 slips containing 1 wt% of the following deflocculants: ( ) MFO, (■) GTO, (○) linseed oil, (▲) castor oil, (□) phosphate ester and (●) lecithin.

Table 2. Dielectric constant and conductivity of dispersed slips

Dispersant	ϵ *(at* 10^6 *Hz)*		σ *(*$\times 10^{-6}$ *S* cm^{-1}*)*	
	Slip	*Alone*	*Slip*	*Alone*
GTO	23·3	8·4	3·2	–
MFO	26·6	6·2	5·9	–
Linseed	23·1	8·0	3·8	–
Castor	27·6	13·3	6·0	–
Lecithin	21·5	20·0	7·1	21·0
Phosphate ester	18·6	19·2	17·5	1·7

studied here. The unexpected high conductivity of slips dispersed with MFO must be related to the cross-linked structure of this oil, much more efficient than GTO, as reported by Calvert *et al.*[8] who proposed that most ester groups of this oil are not really attached to the surface. In all cases an important increase of the dielectric constant can be seen for oils whereas in the case of charged surfactants no variation can be seen with respect to the slips. Further work is now in progress to elucidate the dielectric contribution of the different components.

Since in a non-polar liquid such as toluene it is not possible to obtain well-dispersed slips with the oil-related dispersants, all these data indicate that conductivity is clearly related to the dispersing power. This suggests that, as according to Fowkes *et al.*,[6] the electrostatic stabilization mechanism has some significance in the dispersion of ceramic slips in non-aqueous media.

Conclusions

Phosphate ester is the most efficient dispersant for tape casting of ceramics when compared with other traditional dispersants such as MFO and GTO. In keeping with their chemical structure, other oil-related substances have been successfully used as dispersants. The effectiveness of an oil as dispersant is related to the irregularities of the major fatty acids, mainly double bonds and functional groups. Linseed and castor oils are much more efficient than other oils, such as MFO and GTO. Lecithin, considered as a zwitterionic surfactant, has also been used successfully. In fact, the two charged surfactants studied here give the lowest viscosity in the slips. IR spectra show that oils do not anchor to the particles through the bulk of the carbonyl groups. On the other hand, the general variation of the dielectric constant and the conductivity of the slips when compared to those of the solvent and the dispersants allows us to suggest that the modifications in the electric charge in the slips could be due to some electrostatic interaction, as clearly observed in the case of phosphate ester. However, the solvent properties provide the most clear contribution, although some variations take place. Further work is now in progress to elucidate the effect of all the other components of the system.

Acknowledgements

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