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Ultrasonic deagglomeration of Al_2O_3 and $BaTiO_3$ for tape casting

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Résumé. — L'agitation ultrasonore est une méthode très efficace de désagglomération et de dispersion de suspensions céramiques (alumine et titanate de baryum). Cette étude précise l'influence de paramètres tels que température, puissance et temps d'application des ultrasons sur l'efficacité de la désagglomération. En ajustant les paramètres, on peut obtenir grâce à des temps très courts du traitement par ultrasons (2-3 min) des suspensions stables et bien dispersées. L'influence du vieillissement des suspensions est également examinée.

Abstract. — Ultrasonic agitation is a very efficient method for deagglomeration and dispersion of ceramic slurries (alumina and barium titanate). The influence of parameters such as acoustic power, temperature, and treatment duration on the dispersion efficiency has been studied. For optimum conditions, very short times (2-3 min) of ultrasonic agitation are enough to obtain well dispersed, stable slurries. The role of aging of slurries has also been examined.

1. Introduction.

Ceramic slurries for tape-casting are composed of numerous components : ceramic powders, solvents, dispersants, binders, plasticizers, and other additives such as homogenizers and releasing agents. The preparation of slurries is commonly carried out in two stages, namely i) deagglomeration of powders and dispersion in the « solvent » (this improper term being the usual one) with the aid of dispersants, and ii) mixing with binders and plasticizers [1]. Deagglomeration of powders is necessary to obtain well-dispersed slurries and to avoid flocs. Deagglomeration and dispersion by ultrasonic agitation of sub-micrometer powders has been found much more effective than ball milling [2-4]. On the other hand, ultrasonic treatment is not specially efficient to mix the slurry components and can break the long-chain molecules of the binder [5]. Therefore, only the ultrasonic dispersion of ceramic slurries made with alumina and barium titanate powders was studied.

Ultrasonic vibrations induce pressure waves in the solvent and cavities can be produced when pressure is enough. At rather low pressures, the size of cavities oscillates around a constant value (stable cavitation) and bubbles develop and burst at the surface of the liquid (deaeration). At rather high pressures, the size of cavities oscillates around an increasing value (transient cavitation), then cavities collapse violently, which produces intense stresses able to break powder agglomerates into smaller aggregates [6]. The pressure-threshold value depends on the nature of liquid and frequency. For water at room temperature and a frequency of 20 kHz, this threshold is about 0.5 $W.cm^{-2}$.

At a given frequency, the main parameters which control the cavitation efficiency are ultrasonic power, treatment duration, and liquid characteristics. The liquid characteristics are sensitive to temperature.

2. Experimental.

One $BaTiO_3$ powder (APBG01, Rhône-Poulenc, France) and two Al_2O_3 powders (P152, Aluminium-Péchiney, France and A16SG, AlCoA, USA) were used. The slurries were prepared by mixing together (with a magnetic stirring bar) the powder with a phosphate-ester dispersant (C213-CECA, France) and a 66/34 vol% MEK/ethanol solvent. The solid content was 24 vol%.

The ultrasonic agitator (VC600, Sonics & Materials, USA) consisted of a generator, a piezoelectric transducer, and a probe with a titanium tip. Ultrasonic waves at a frequency of 20 kHz could be emitted at a power up to 600 W. The probe was immersed halfway below the surface of the slurry. Temperature of the slurry was regulated during the treatment either at 0 °C or at 20 °C, depending on the test. Slurries were generally treated using a « 50 % pulsed mode » where pulses were emitted during 50 % of the whole time. However, the study of the influence of temperature was conducted using a « 90 % pulsed mode ». An intermittent operation is more efficient than a continuous one, seemingly because it allows powder to rearrange after each ultrasonic burst.

The efficiency of ultrasonic dispersion was estimated from viscosity measurements for slurries without deflocculant and from agglomerate-size measurements for slurries with deflocculant. Viscosity was measured at various shear rates using a rotating-cylinder viscometer (Haake Rotovisco, RFA). An X-ray granulometer (Sedigraph 5000D, USA) working with the same MEK/ethanol mixture as that of the slurries was used to determine the particle-size distribution of powders. To avoid any change in the particle distribution, no additional dispersion technique was used during the sedimentation experiments.

3. Results and discussion.

3.1 SLURRIES WITHOUT DEFLOCCULANT. — Slurries of $BaTiO_3$ and Al_2O_3 (P152 grade) were treated at 20 °C for 3 min using various ultrasonic-power values.

A minimum of viscosity was obtained at about 360 W for both $BaTiO_3$ and Al_2O_3 (Figs. 1 and 2). The increase in viscosity beyond a power threshold probably results from a ultrasonically-induced coagulation at high power levels, as mentioned by Aoky [7].

The range of available shear rates was limited to a ratio of two between the maximum rate and the minimum one. In this domain, the viscosity of barium-titanate slurries sonicated at 360 W remains constant whereas the viscosity of alumina slurries depends on the shear rate. These differences in the rheological behavior of the two slurries can be due to differences in the powder characteristics (size and shape distributions and nature of agglomerates) as well as to differences in the state of dispersion (degree of flocculation). Al_2O_3 particles are larger and have more intricate shapes than $BaTiO_3$ particles (Fig. 3). Attraction forces (e.g. Van der Waals) in $BaTiO_3$ and Al_2O_3 slurries are different due to differences in particle size distributions. Repulsion forces are different also due to differences in zeta potential values ($BaTiO_3$: 20 mV and Al_2O_3 : 40 mV in MEK/ethanol) and in particle size distributions.

The efficiency of ultrasonic treatments decreases when the solid content increases, which

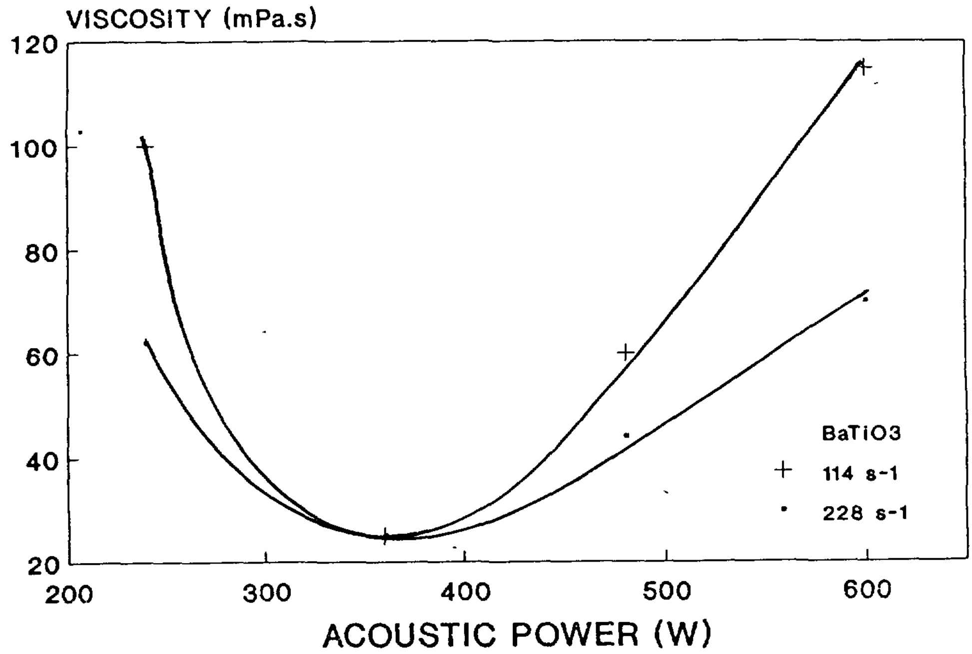


Fig. 1. — Viscosity *vs.* acoustic power for 24 vol% barium titanate slurries (20 °C-3 min).

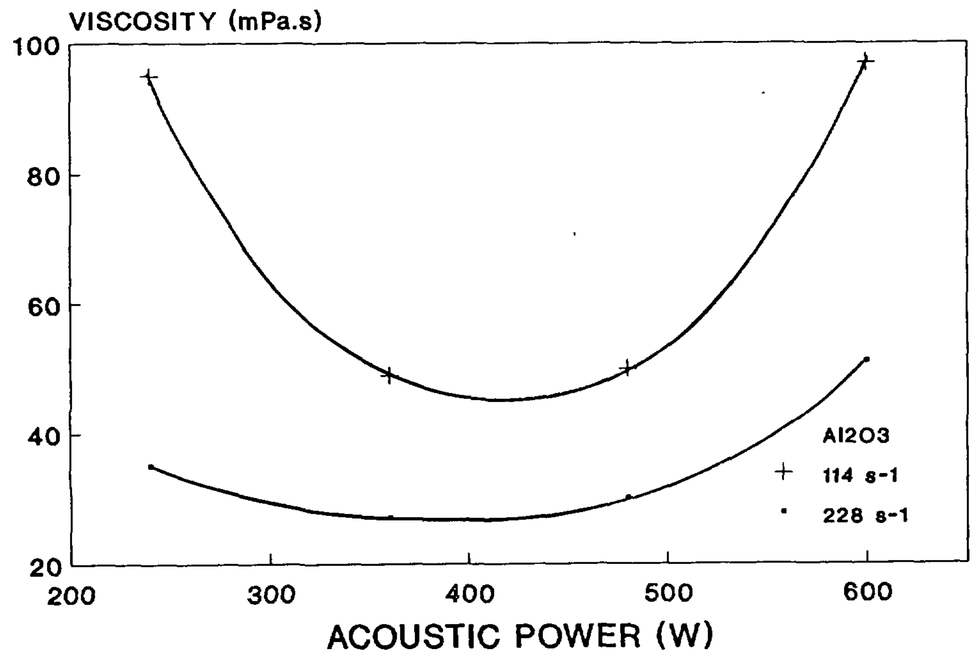
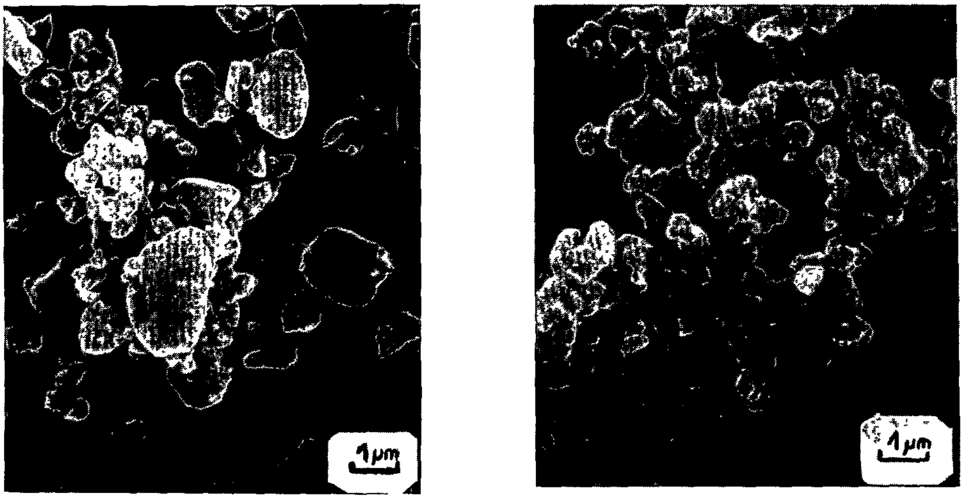


Fig. 2. — Viscosity *vs.* acoustic power for 24 vol% alumina slurries (20 °C-3 min).



a) b)

Fig. 3. — Scanning electron micrographs of (a) alumina (P152) and (b) barium titanate (APBG01) powders.

suggests that the cavitation mechanisms are disturbed by solid/liquid interface effects. This behavior is more pronounced in the case of the powders with the highest surface areas. The decrease in dispersion efficiency observed for high specific-area powders can also be associated with a greater amount of hard agglomerates and a higher reagglomeration rate of fine particles.

3.2 SLURRIES WITH DEFLOCCULANT. — Slurries of $BaTiO_3$ and A16SG Al_2O_3 were prepared with 1 and 0.6 wt% of dispersant, respectively.

3.2.1 *Influence of ultrasonic power.* — The slurries were treated at 0 °C for 4 min using various ultrasonic-power values. The equivalent diameters of particles at 10, 50, and 90 % cumulative weight are given in table I.

Table I. — *Equivalent spherical diameters of* $BaTiO_3$ *and* Al_2O_3 *particles* vs. *ultrasonic power* (0 °C-4 min).

Powder	Power (W)	d_{10}	d_{50} (µm)	d_{90}
$BaTiO_3$ (APBG01)	240	0.55	1.25	3.80
	360	0.55	0.90	1.60
	450	0.60	0.90	1.60
	540	0.80	1.05	1.70
Al_2O_3 (A16SG)	360	0.35	0.95	1.90
	450	0.25	0.70	1.50
	540	0.20	0.60	1.35

For $BaTiO_3$, the size of particles begins to decrease when the ultrasonic power increases, then reaches a minimum at the same power level (i.e. 360 W) as that where the minimum of viscosity measured for dispersant-free slurries occurs, and then increases again. The reagglomeration at high power levels is attributed to the ultrasonically-induced coagulation.

For Al_2O_3, the size of particles decreases monotoneously when the ultrasonic power increases to 540 W. However, this does not exclude the existence of a power threshold, and therefore of a minimum in the particle size, at a power higher than 540 W.

3.2.2 *Influence of temperature.* — Slurries were sonicated for 4 min at 0 °C and 20 °C, using a « 90 % pulse mode » to enhance thermal effects. Power was 360 W for $BaTiO_3$ and 540 W for Al_2O_3. Al_2O_3 slurries were better deagglomerated at 0 °C than at 20 °C, whereas there is no significative difference for $BaTiO_3$ slurries (Tab. II).

Temperature modifies many parameters, for instance the surface tension, gas solubility, vapor pressure, and viscosity of solvent. Information on these parameters are summarized in table III, from Sirotyuk [8].

Table II. — *Equivalent spherical diameters of* $BaTiO_3$ *and* Al_2O_3 *particles* vs. *temperature* (4 min-$BaTiO_3$: 360 W, Al_2O_3 : 540 W).

Powder	Temperature (°C)		(μm)	
$BaTiO_3$ (APBG01)	0 20	0.55 0.60	0.90 0.90	1.60 1.60
Al_2O_3 (A16SG)	0 20	0.20 0.35	0.60 0.95	1.35 2.00

Table III. — *Change in liquid parameters and in cavitation efficiency with an increase in temperature.*

	Liquid parameters	Cavitation efficiency
Surface tension	decrease	decrease
Gas solubility	decrease	increase
Vapor pressure	increase	decrease
Viscosity	decrease	increase

Surface tension : Laplace's law states that the difference of pressure between a liquid and a gas inside a cavity increases with surface tension. High surface-tension liquids (e.g. water) yield a higher cavitation-efficiency than low surface-tension liquids (e.g. organic solvents).

Gas solubility : Gases are often less soluble in water than in organic solvents. Therefore, the pressure inside a cavitation bubble is lower — and the fall of pressure at the collapse is higher — for water than for organic solvents. This indicates that water is a better medium for ultrasonic deagglomeration than organic solvents.

Vapor pressure : Bebchuk [9] has shown that the highest efficiency is obtained at temperatures where vapor pressure is in the range from 5×10^3 to 10^4 Pa, whatever the nature of the liquid.

Solvent viscosity : An increase in solvent viscosity produces a loss of mechanical energy during collapse, therefore decreases the cavitation efficiency.

To sum up, temperature plays a role on numerous parameters, in particular when the solvent is concerned. It is therefore difficult to determine which parameter is the most effective to control cavitation efficiency. Bebchuck [10] has found that this efficiency is maximum at a temperature of 0 °C-20 °C for organic liquids and of about 50 °C for water.

3.2.3 *Influence of treatment time.* — The slurries were treated at 20 °C for various durations at a ultrasonic power of 360 W for $BaTiO_3$ and 540 W for Al_2O_3. The particle size reaches a plateau after 2 min of treatment for $BaTiO_3$ and 3 min for Al_2O_3.

3.2.4 *Influence of aging.* — The influence of aging was studied on slurries of $BaTiO_3$ at 0 °C. Aging was carried out by a slow rotation in jar to avoid breaking agglomerates by another mechanical action.

Aging does not play a significant role when the optimum conditions (360 W-2 min) are chosen but it is beneficial when other conditions are used. For instance, table IV shows that 4 days of aging allows a $BaTiO_3$ slurry treated for 2 min at 540 W to reach a particle-size state similar to the « optimum » one, obtained with a power of 360 W. It is assumed that interparticle bonding is not the same for initial agglomerates and for agglomerates reformed during ultrasonic exposure [7]. In the second case, the action of dispersant can be sufficient to break reformed agglomerates.

Table IV. — *Equivalent spherical diameters of* $BaTiO_3$ *particles* vs. *treatment and aging time* (540 W-0 °C).

Treatment time (min)	Aging time (day)	d_{10}	d_{50} (μm)	d_{90}
2	0	1.00	1.40	2.10
	2	0.70	1.15	1.90
	4	0.55	0.90	1.60
3	0	0.70	1.00	1.75
	2	0.55	0.90	1.60
4	0	0.80	1.05	1.70
	2	0.55	0.90	1.60

4. Conclusion.

Deagglomeration is an important stage in the preparation of tape-casting slurries, especially when thin tapes (e.g. for multilayer capacitors) are produced.

Ultrasonic dispersion acts through the collapse of cavities formed in the liquid. The resulting stresses can break agglomerates. The ultrasonic efficiency depends on many factors, such as acoustic power, treatment duration, and solvent characteristics, in particular surface tension, gas solubility, vapor pressure, and viscosity. The solvent parameters depend on temperature. This study has demonstrated that alumina and barium-titanate slurries can be dispersed very efficiently, as far as the process parameters are optimised.

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