Bull. Mater. Sci., Vol. 8, No. 1, February 1986, pp. 1–11. © Printed in India.

Kinetics of electrophoretic deposition of β-alumina

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MS received 8 October 1984; revised 2 November 1985

Abstract. The equations describing electrophoretic deposition, proposed by Hamakar Avgustinik and coworkers, have been verified in the case of β-alumina suspended in isoamyl alcohol. The variation of electrophoretic yield with (i) concentration of suspension, (ii) extent of grinding the suspension, (iii) temperature of the suspension, and (iv) electrode separation was studied. The effect of addition of glycol monoethyl ether was also investigated. The effect of various parameters on the electrical conductivity of the suspension, which in turn influences the yield, was noted.

Keywords. Electrophoretic kinetics; electrophoretic deposition; beta alumina; concentration; temperature; electrode separation.

1. Introduction

The energy crisis has accelerated the pace of research on unconventional modes of energy generation and storage. Among the high energy density batteries, sodium-sulphur battery is a strong candidate (Robinson 1976). In this, liquid sodium and sulphur are separated by a solid-electrolyte, namely β-alumina ($Na_2O\,xAl_2O_3$) ceramic. Most of the cost and failures of these batteries are attributed to this electrolyte. Therefore, production of dense, mechanically sound, electrically conducting β-alumina in desired shapes (mostly one end closed tubes) is receiving active attention. Slip casting (Byckalo *et al* 1976), extrusion (Ford Annual Report 1975–76), isostatic pressing (Youngblood *et al* 1977) and electrophoresis (Fally *et al* 1973; Powers 1975; Kennedy and Foissy 1975; Powers *et al* 1981) are being explored for fabrication of these tubes, followed by sintering. Alternately, hot pressing may be employed.

1.1 *Electrophoresis*

Electrophoresis is an electrokinetic phenomenon in which the suspended charged particles move under the influence of an electric field. An electrical double layer is formed at the boundary between the solid and the surrounding liquid, since both the phases are electrically charged.

1.1a *Kinetics of electrophoretic deposition.* Hamaker (1940) showed that yield or amount of electrophoretic deposition, Y, in g,

$$Y = a \int \mu FCA \, dt. \tag{1}$$

Here, μ is the electrophoretic mobility, the velocity of a particle in a unit field of 1 V/cm; F is the electric field; C is the concentration of particles in g/cc; A is the electrode area, over which deposition is taking place; and t is the time. The coefficient a takes into account the possibility that not all particles which migrate to the electrode may deposit.

Avgustinik *et al* (1962) derived an expression for the electrophoretic yield, v_t, in g/cm,

$$v_t = \frac{F \zeta C t l \varepsilon}{3 \ln \frac{r_1}{r_2} \eta} \tag{2}$$

where ζ is the zeta potential; ε the dielectric constant of the medium; l the length of the cylinder; r_1, r_2 are the radii of inner and outer electrodes respectively; η is the viscosity of the medium; and F, C, and t are as defined in (1).

1.1b *Electrophoretic forming of β-alumina:* Tubes of β-alumina have been successfully fabricated by this technique by Fally *et al* (1973), Powers (1975), Kennedy and Foissy (1975, 1977) and Foissy and Robert (1982). Fally *et al* (1973) used polar and organic liquids such as nitromethane or trichloromethane as the vehicle for suspension. Their tubes were quite thick (200–2000 μm) and they needed isostatic pressing for removal from the electrode. Kennedy and Foissy (1975, 1977) and Foissy and Robert (1982) used dichloromethane as the medium with trichloro-acetic acid as additive. Kennedy and Foissy (1975) formed the tubes (3–4 cm long, 0·03 to 0·1 cm thick) on carbon electrodes and the tubes were removed by burning off the carbon rod. Powers (1975) evaluated various vehicles and found that vehicles which have dielectric constants in the range of 12 to 25 and specific conductance of 10^{-7} to 10^{-4} (ohm cm)$^{-1}$ are suitable. He used very smooth stainless steel electrodes and reported that the tubes came off easily from the mandrel after drying the deposits.

From the above, it may be noted that some of the variables governing the kinetics of electrophoretic deposition of beta alumina have been examined qualitatively, but there was hardly any quantitative data even in the case of the variables explored. The purpose of the present work is, therefore, to study the effect of various parameters on the rate of electrophoretic deposition of beta alumina in non-aqueous media in quantitative terms. The variables chosen are:

(i) selection of vehicle (benzyl vs iso-amyl alcohol) on the basis of yield rate, conductivity, viscosity, and boiling point;
(ii) effect of concentration, grinding (particle size) and temperature on viscosity, conductivity and specific yield;
(iii) effect of addition of ethylene glycol on conductivity and yield;
(iv) role of electrode separation and mandrel material (graphite and stainless steel) in electrophoretic deposition.

2. Experimental

The three major steps involved in this work are (1) preparation of β-alumina powder; (2) preparation of suspension; and (3) electrophoretic deposition.

2.1 *Powder preparation*

Alumina (Alcoa A-2) was heated to 1000°C and preserved in an oven at 110°C. Sodium carbonate (BDH), which is hygroscopic, was also stored in the oven at 110°C. 1:5 mol of Na_2O and Al_2O_3 were mixed in acetone in an alumina ball jar. The liquid was dried and the cake was calcined in platinum crucibles at 1250°C for 4 to 5 hours. Then the furnace was cooled to 800°C in 2 hrs and the crucibles were taken out of the furnace, air-cooled (Baral 1977) and stored till usage in an oven at 350°C to prevent rehydration (Foissy and Robert 1982; Powers *et al* 1981).

The calcine contains β and β'' alumina, the latter being preferable to β-alumina as a solid electrolyte. The relative amount of β-alumina is given by a factor (Youngblood *et al* 1977)

$$f(\beta) = \frac{I_{(\beta)}}{I_{(\beta)} + I_{(\beta'')}}, \tag{3}$$

which was calculated by using the integrated intensities of the x-ray diffraction characteristic lines at $2\theta = 44{\cdot}3°$ and 46° of β and β''-alumina, respectively.

The $f(\beta)$ of the calcine in the present work was found to be 0·33, showing more of β'' alumina. However, for convenience, the powder is referred as β-alumina here.

A small amount of powder was stirred well in dichloromethane with two drops of trichloroacetic acid to increase stability (Kennedy and Foissy 1975, 1977). It was dispersed on a glass slide and dried before studying under NU2 Carl Zeiss-Jena microscope for particle size distribution. The particles of the calcined powder were 0·8 to 6 μm in size with an average of 2 μm. The powder density was 3·19 g/cm^3, whereas the theoretical density of β and β'' are 3·24 and 3·27 g/cm^3, respectively.

2.2 *Preparation of suspension*

Generally, 100 g of powder and 200 cc of vehicle were taken in an alumina ball jar, ground for 5½ hrs and transferred to the electrophoretic cell.

2.3 *Electrophoretic deposition*

Two types of cells were used (figure 1). To prevent settling, the beaker was rotated for 1 minute before every deposition. The perforations in the tubular counter electrode (figure 1a) and its off-centre position in the beaker enhanced the stirring action. In the second case, figure 1b, the counter electrode itself was the container for the suspension, which was stirred before pouring into the container.

2.4 *Computation of concentration and conductivity of the suspension and area of coated mandrel*

A method was devised to calculate the concentration of the suspension for each deposition (Krishna Rao 1978). It was computed on the basis of geometry of the cell (figure 2), which is self-explanatory. The volume of the suspension in the can

$$V = \pi \frac{D^2}{4}(H + h + p - L) - \pi \frac{D_x^2}{4} H. \tag{4}$$

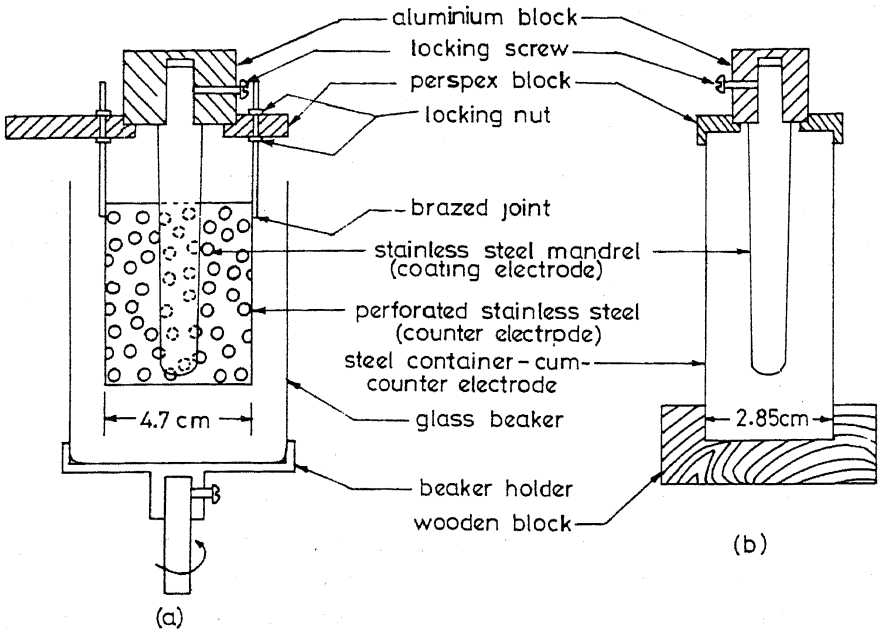

Figure 1. Cells for electrophoresis.

Concentration of the suspension (g of powder per 100 cc suspension) =

$$\frac{\text{amount of solid in the suspension}}{\text{volume of the suspension}} \times 100 \tag{5}$$

The amount of solid in the suspension was calculated as follows. The amount deposited in each deposition stage was measured, and after all the depositions, the remaining suspension in the can was dried at 350°C and weighed. The total amount of solid in the suspension was computed by adding the weight of the dried suspension and amount deposited. Thus, the amount of powder in the suspension at any stage of deposition could be computed and, thereby, the concentration of suspension as well.

The area of deposition (A) of the electrode (figure 2) is calculated as follows:

$$\tan\theta = \frac{H/2}{(D_x - d_e)/2} = \frac{L}{(d_s - d_e)/2}, \tag{6}$$

$$D_x = \frac{(d_s - d_e)\,H}{2L} + d_e, \tag{7}$$

$$A = \pi D_x H + \frac{\pi}{4} d_e^2 . \tag{8}$$

The conductivity of the suspension (σ) was measured using the I–V characteristics using the equation

$$\sigma = (\text{current} \times \text{electrode separation})/(\text{voltage} \times \text{surface area of the mandrel, } A, \text{ dipped in the suspension}). \tag{9}$$

These results were in good accordance with the value measured with a General Radio impedance bridge (GR 1608) at a frequency of 1 kHz.

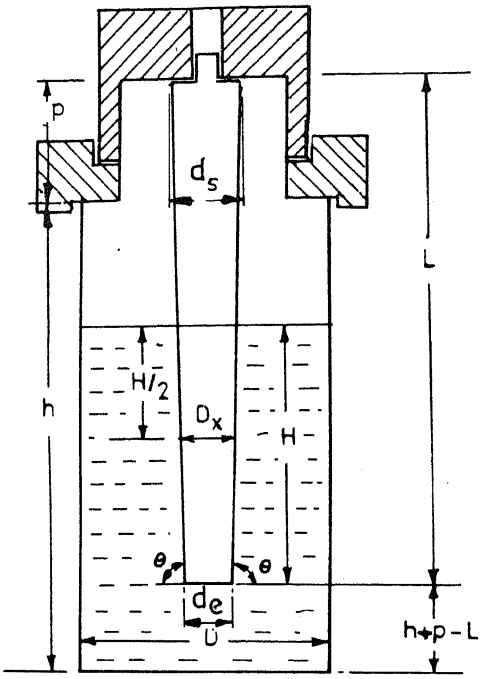

Figure 2. Geometry of the cell and the mandrel.

Table 1. Characteristics of β-alumina suspensions

Vehicle and (boiling point)	Viscosity millipoise	Dielectric constant	pH	Conductivity	Specific yield rate ($\times 10^4$ g/cm^2 min V)
Benzyl alcohol (205)	(55·82) at 20°C	(13·0)	(5·25) 9·0	(0·926) 20·46	4·6
Iso-amyl alcohol (130)	(4·811) at 15°C	(14·7)	(6·0) 8·0	(2·256) 9·09	4·25

The charge on particles was positive; the numbers in brackets refer to the properties of the vehicle.

3. Results and discussion

3.1 *Evaluation of vehicles*

Powers (1975) has shown that satisfactory deposits of β-alumina can be obtained only with vehicles in a limited range of dielectric constants (12–25). Lower zeta potential liquids (Kennedy and Foissy 1977) and higher voltage (Powers 1975) were suggested for good electrophoretic deposition of β-alumina. Higher voltages decrease the time required to get a required thickness of deposit and this minimizes the problem of the suspension stability. Also the amount of dripping from the mandrel decreases. To use higher voltages, low conductivity suspensions have to be used, otherwise bubbling of the deposit occurs. Also, it was reported (Troelstra 1951) that the yield is inversely proportional to conductivity of the suspension. Two types of alcohols viz benzyl and isoamyl alcohols were evaluated. From table 1, it may be noted that, with β-alumina

powder addition to the vehicle, both the pH and conductivity of the suspension increased. Even though the specific yield was almost equal with benzyl and iso-amyl alcohols, the former was not preferred as it has higher viscosity, boiling point (b.p.) and also higher conductivity of the suspension. Because of higher b.p., drying of the deposit was more difficult and because of high viscosity of the vehicle, deformation of the deposit during drying was possible. These results are consistent with the earlier reports on MgO (Krishna Rao and Subbarao 1979). Therefore, iso-amyl alcohol was chosen for further studies.

3.2 *Concentration*

The effect of concentration of the suspension (g of powder/100 cc suspension) on the amount of material sticking to the mandrel (g/cm^2), conductivity of suspension and specific yield (g/cm^2) at 100 V/1 min were studied (figure 3).

To start with, higher concentration (about 80 g/100 cc) suspension was prepared. The concentration decreased as successive depositions were made from the same suspension. As the concentration decreased from 76 to 28 g/100 cc suspension, the conductivity increased from 14 to 24 $\mu\mho\,cm^{-1}$. This may be because of the accumulation of leached out ions in the suspension (Foissy and Robert 1982) with successive depositions. This was not the case with MgO system (Krishna Rao and Subbarao 1979) where there may not be any leaching of ions. The amount of powder (suspension) sticking to the mandrel when it is dipped in the suspension, is a function of viscosity of the suspension and the viscosity increases drastically at higher concentra-

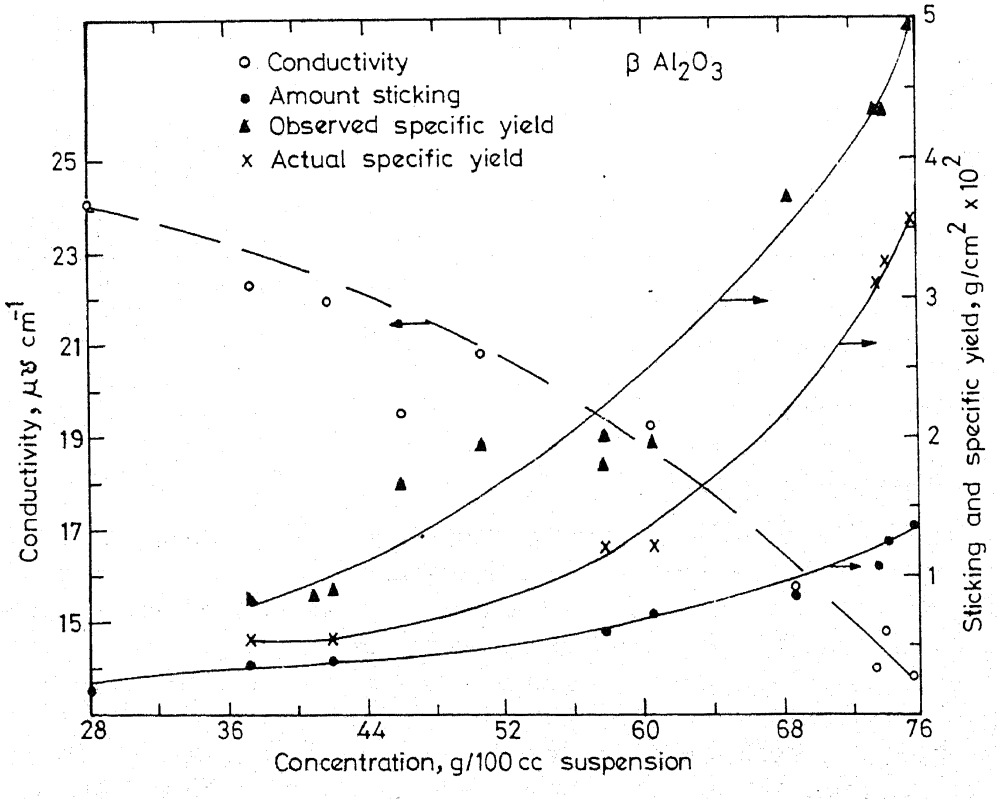

Figure 3. Variation of conductivity of suspension, amount sticking and specific yield with concentration of the suspension.

tions (Krishna Rao and Subbarao 1979). In the present study, the observed and actual (observed minus the amount sticking to mandrel) specific yields increased drastically with concentration (figure 3). Similar type of behaviour was observed by Krishna Rao and Subbarao (1979) and Andrews *et al* (1969). This nonlinear behaviour was not in accordance with equations (1) and (2), and may be due to the following: (1) The coefficient *a* in (1) appears to increase with the concentration of the suspension (Hamaker 1940), i.e., all the particles reaching the electrode may not be depositing at low concentrations; (2) The probability that the moving particles may drag other particles with them and thus raise the yield rate, as suggested by Avgustinik *et al* (1962). This dragging effect may be more pronounced at higher concentrations. The linear behaviour observed by Powers (1975) appears to be due to the limited range of concentrations studied.

3.3 *Grinding*

One hundred grams of the powder in 200 cc iso-amyl alcohol was ground for zero, 1½ and 7 hours successively. Electrophoresis was carried out with cell 1 (figure 1a) at 25 V for different durations of deposition. The results (figure 4) show that (i) the specific yield increases with deposition time in accordance with (1) and (2), (ii) the curves do not

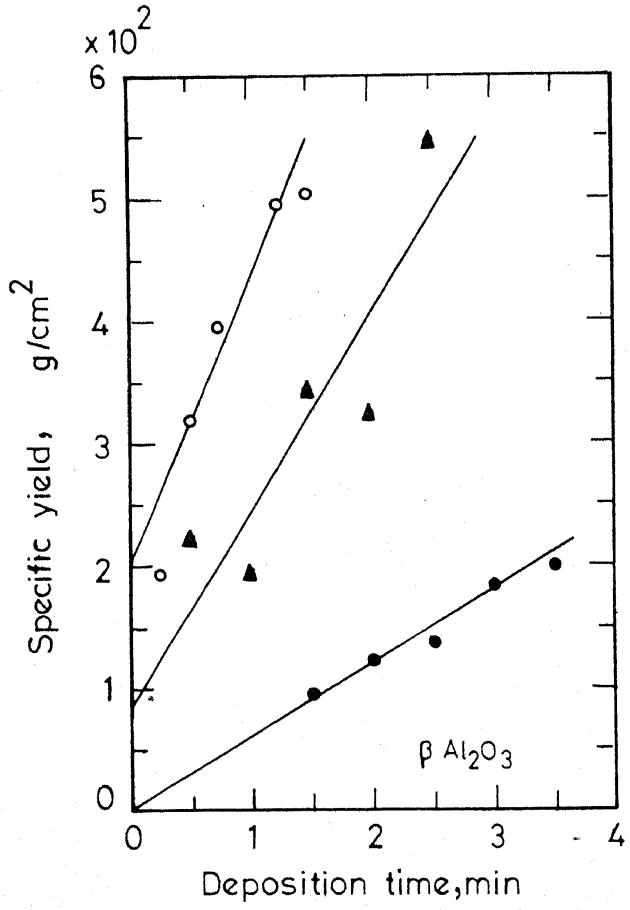

Figure 4. Variation of specific yield with deposition time (voltage = 25 V). The grinding time was 0 (solid circle) 1·5 (solid triangle) and 8·5 hr (circle) and the slopes ($\times 10^4$ g/cm^2 V_{min}) were 2·4, 6·4 and 8·8, respectively.

pass through the origin, confirming the physically observed fact that the amount of material sticking to the mandrel soon after insertion into the suspension (and in the absence of an applied voltage) increases with fineness of particle size (i.e. larger grinding) and greater viscosity (see figure 3 also), and (iii) the change in yield rate is not linear with grinding time. Similar results were obtained at higher applied voltages also. Based on these results, grinding for $5\frac{1}{2}$ hours was employed for further experiments.

Depending on the suspension system (Fally *et al* 1973; Powers 1975; Kennedy and Foissy 1975, 1977), the grinding of the suspension influences the charge, zeta potential and mobility of particles. In the present system, the yield and conductivity of the suspension have gone up. According to Troelstra (1951), higher conductivity should decrease the yield. However, in the present case, the higher conductivity may be due to increased charge on the particles, which can lead to increase of the mobility (Kennedy and Foissy 1977) and therefore the yield.

3.4 *Temperature*

The suspension with the can and mandrel (figure 1b) was heated to 70°C in an oven, stirred and taken out. Before every deposition at 100 V for 1 min, the temperature was noted after stirring. The depositions were carried out as the suspension cooled. The variation in concentration of suspension was not much during this series of experiments.

It was observed that with temperature, the yield increased linearly (figure 5), which is consistent with the behaviour observed in the case of alumina in ethanol (Michaels

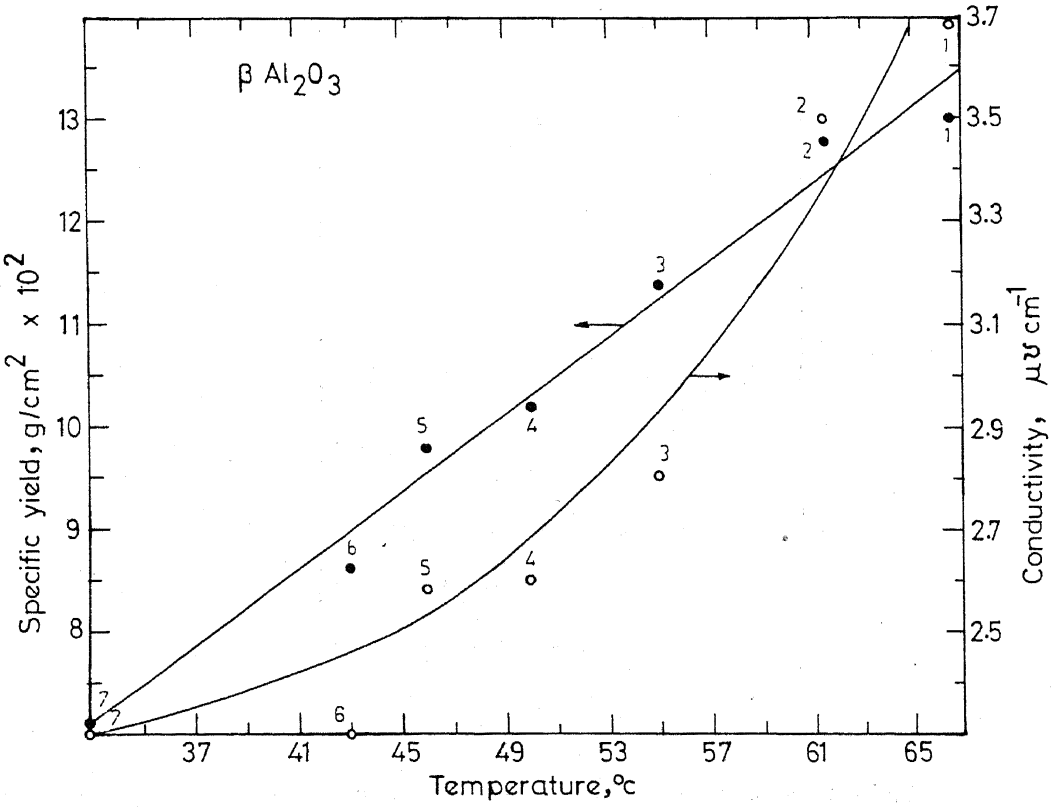

Figure 5. Variation of specific yield and conductivity of the suspension with temperature.

1958). With temperature, the ionic mobility and conductivity increase and the viscosity of the suspension decreases and thereby increases the yield ((1) and (2)).

3.5 *Additives*

The concentration of additives such as water, trichloro-acetic acid, and benzoic acid influences the charge on particle, mobility, stability of suspension (Fally *et al* 1973; Powers 1975; Kennedy and Foissy 1975, 1977; Foissy and Robert 1982; Powers *et al* 1981; Andrews *et al* 1969), depending on the vehicle used for dispersing the powder. A limited study was carried out in the present system with ethyl glycol monoethyl ether additions on electrophoretic yield.

Addition of 0·5 cc of this additive to 50 cc of the ground suspension increased the specific yield by 8·3 times and the conductivity of suspension by about 2·5 times (figure 6). There was no bubbling even at 100 V. The increased conductivity could be due to the increased charge on the particles as is reported in other systems (Fally *et al* 1973; Powers 1975; Kennedy and Foissy 1975, 1977; Foissy and Robert 1982). The specific yield and the conductivity of the suspension varied linearly with the concentration of the suspension, thus verifying (1) and (2) and consistent with the behaviour reported in figure 3. It was observed that adding ethyl glycol to the ground suspension gave more specific yield than making the addition before grinding. This aspect requires further study.

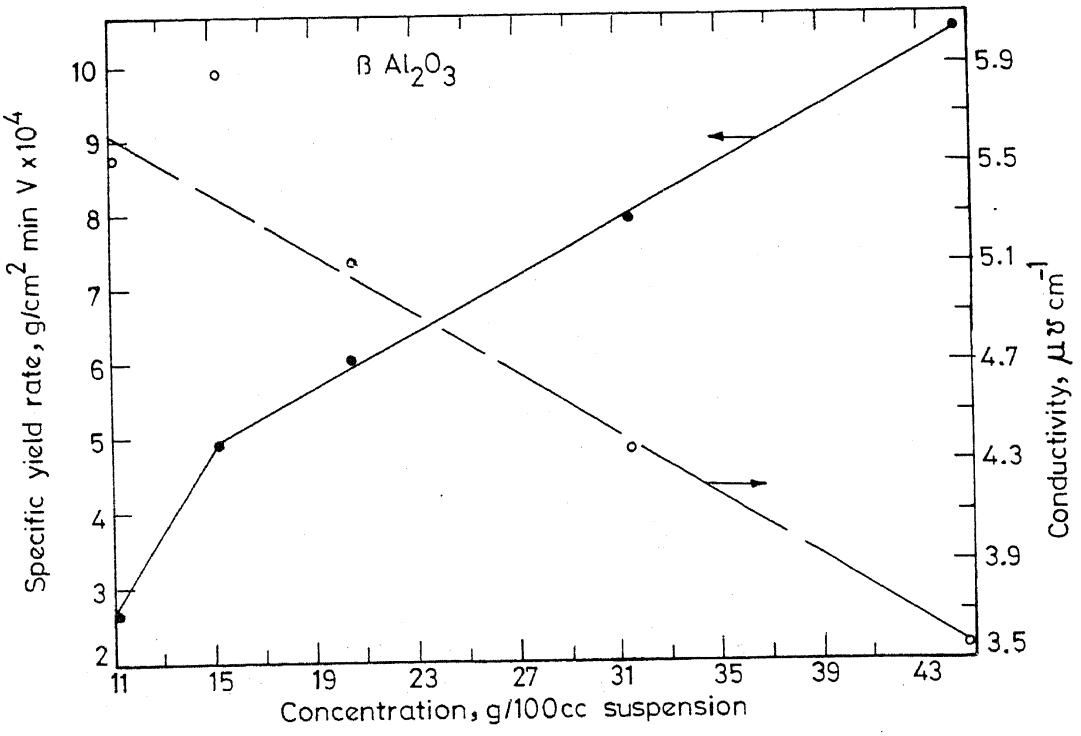

Figure 6. Variation of specific yield rate and conductivity of the suspension with concentration of the suspension containing ethylene glycol.

3.6 *Electrode separation*

The effect of electrode separation on specific yield was studied by using two types of mandrels, viz steel and graphite and steel counter electrodes of different sizes (table 2).

Experimental yield ratio M and the computed yield ratio N, from (2) were noted in table 3. The M/N ratio should be 1, but the experimental values varied from 1·05 to 1·13, which is within the experimental error (Malage 1979; Krishna Rao 1978). v_g/v_s is also in agreement with (2), which shows that the yield rate is independent of the mandrel material (graphite or steel).

4. Conclusion

The experimental results on the electrophoretic yield of β-alumina suspended in iso-amyl alcohol are in quantitative agreement with (1) and (2) in terms of (i) a linear

Table 2. Electrophoretic yield with different electrodes

	Mandrel		Counter electrode		
Set	Type	Radius (cm)	Type	Radius (cm)	Yield
(a)	Steel	0·43	Steel can	1·72	v_x
	Steel	0·43	Steel can	1·42	v_y
	Steel	0·43	Steel can	0·93	v_z
(b)	Steel	0·42	Steel can	1·42	v_c
	Steel	0·42	Perforated steel can	2·35	v_p
(c)	Steel	0·42	Steel can	1·42	v_s
	Graphite	0·37	Steel can	1·42	v_g

Table 3. Effect of electrode separation on electrophoretic yield

	Electrophoretic yield ratio			
Set	Ratio	Expt. M	Computed N	M/N
(a)	$\frac{v_x}{v_y}$	0·93	0·86	1·08
	$\frac{v_y}{v_z}$	0·68	0·65	1·05
	$\frac{v_x}{v_z}$	0·63	0·56	1·13
(b)	$\frac{v_p}{v_c}$	0·75	0·71	1·05
(c)	$\frac{v_g}{v_s}$	0·99	0·92	1·07

variation with time and (ii) inverse dependence of ln (r_1/r_2) where r_1 and r_2 are the radii of the inner and outer electrode (irrespective of the electrode material, viz steel or graphite). However, the nonlinear dependence of yield on concentration is not consistent with these equations and may be due to the very wide concentration range (28 to 76 g of solid/100 cc of suspension) covered.

Other interesting results obtained are (i) the yield rate increasing with grinding duration of the suspension, though not proportionately, (ii) the yield increased linearly with temperature in the range 33 to 66°C and (iii) addition of 1% ethyl glycol monoethyl ether increases the yield substantially.

References

Andrews J H, Collins A H, Cornish D C and Drass J 1969 *Proc. Br. Ceram. Soc.* **12** 211
Avgustinik A I, Vigdergamz V S and Zherravlev G I 1962 *Zh. Priklad Khim.* **35** 2175
Baral D 1977 *β-β″ alumina electrolytes preparation, characterization and electrophoretic forming of tubes*, M. Tech. Thesis, I.I.T, Kanpur
Byckalo W, Rosenblath G, Lam J and Nicholson P S 1976 *Am. Ceram. Soc. Bull.* **55** 286
Fally J, Lasne C, Lazennec Y, Le Cars Y and Margotin P 1973 *J. Electrochem. Soc.* **120** 1296
Foissy A and Robert G 1982 *Am. Ceram. Soc. Bull.* **61** 251
Ford Annual Report 1975–76 *Research on electrodes and electrolytes for the Ford sodium-sulphur battery*, under contract No. NSF-C805
Hamaker H C 1940 *Trans. Faraday Soc.* **36** 279
Kennedy J H and Foissy A 1975 *J. Electrochem. Soc.* **122** 482
Kennedy J H and Foissy A 1977 *J. Am. Ceram. Soc.* **60** 33
Krishna Rao D U 1978 *Electrophoretic deposition of magnesia, and β-alumina*, M. Tech. Thesis, I.I.T, Kanpur
Krishna Rao D U and Subbarao E C 1979 *Am. Ceram. Soc. Bull.* **58** 467
Malage A B 1979 *Factors affecting electrophoretic deposition of β-β″ alumina tubes*, M. Tech Thesis, I.I.T, Kanpur
Michaels A S 1958 in *Ceramics fabrication processes* (ed.) W D Kingery (New York: John Wiley) p. 24
Powers R W 1975 *J. Electrochem. Soc.* **112** 490
Powers R W, Mitoff S P, King R N and Bielawski J C 1981 in *Fast ion transport in solids* (eds) J B Bates and G C Farrington (Amsterdam: North Holland) p. 287
Robinson A L 1976 *Science* **192** 541
Troelstra S A 1951 *Phillips Tech. Rev.* **12** 293
Youngblood G E, Cannon W R, Ramussen J R and Gordon R S 1977 *Am. Ceram. Soc. Bull.* **56** 206