

Effect of Polymeric Steric Stabilizers on the Settling of Alumina

G. H. ARMSTRONG,* L. JOHNSON, and A. A. PARKER†

Surface Technology Division, Aluminum Company of America, Alcoa Technical Center, Alcoa Center, Pennsylvania 15069-0001

SYNOPSIS

The effect of polymeric steric stabilizers on the dispersion stability of alumina was determined by settling experiments. The theoretical settling density was determined for alumina in a 90:10 wt% toluene-ethanol mixed solvent. Polymers evaluated were sulfonated polystyrenes, Shell's functionalized Kraton block polymers (styrene-hydrogenated diene), ICI's polymeric surfactants, homopolystyrene, a nonfunctionalized Kraton block polymer, and two Union Carbide Corporation silwet surfactants. The high-molecular-weight sulfonated polystyrene (60,000) containing a low level of sulfonation, functionalized Kraton block polymers, and one ICI polymeric surfactant were effective in improving the dispersion stability of the alumina. The percent of theoretical settling density for the "good" polymeric steric stabilizers ranged from 45 to 50%. The low-molecular-weight sulfonated polystyrene (10,000 MW), homopolystyrene, unfunctionalized Kraton block polymer, one ICI polymeric surfactant, and the silwet surfactants were ineffective in improving the dispersion stability of the alumina in the mixed solvent. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The ceramic industry makes a wide range of products, including decorative products, structure ceramics, and electronic packages. Many ceramic products are produced by mixing inorganic and glass powders in a vehicle consisting of a dispersion medium containing a polymeric binder, plasticizer, and dispersant to make a ceramic slurry. The slurry is cast into the desired shape, solvent dried out, remaining organics burned out, and finally the part is sintered. The dispersion medium should have enough solubility for the polymer, plasticizer, and dispersant to allow each to have adequate performance; this is often acquired by using a mixed solvent. The polymeric binder gives sufficient strength to the dried preform (green part) to allow handling. The dispersant prevents aggregation of particles, aiding processing and obtaining a denser green part.

The focus of this discussion is on nonaqueous

dispersions, where the dispersion stability of particles is generally considered to be by a steric stabilization mechanism. Steric stabilization refers to how a macromolecule assists in the dispersion of particulate material through a liquid and prevents it from undergoing coagulation.¹ Some inorganic powders in nonaqueous medium dispersions have been shown to be electrostatically stabilized. The stabilization of BaTiO₃ in methylethyl ketone-ethanol solvent by a phosphate ester was shown to be by an electrostatic mechanism.² The surface chemistry of the BaTiO₃ was involved in the process since the phosphate ester alone in the MEK-ethanol showed very low conductivity but increased dramatically when the BaTiO₃ was added. In another study, inelastic electron tunneling spectroscopy showed that a polyester polymer in acetone with alumina was cleaved to produce a carboxylate ($-\text{CO}_2^-$) anion and an alcohol.³ IR frequency characteristic of the carboxylate ion was also seen in spectra of a condensation polymer absorbed on surface-treated rutile.⁴ Koelmans and Overbeek showed that ionized surface-acting substances gave rise to stabilization of a number of powders in xylenes.⁵ The deflocculation of alumina in benzene by oleic acid was shown to be the result of surface charge on

* To whom correspondence should be addressed.

† Present address: Libbey Owens Ford Co., 1701 E. Broadway, Toledo, OH 43605.

the particles.⁶ Lee and Rives showed by electrophoretic deposition experiments with linolenic acid and a C₆₀ amine in both THF and toluene with alumina particles that a repulsive force existed in the suspensions, improving the stability of the dispersions.⁷ They proposed a stabilization mechanism with both electrostatic and steric components. It was seen in electrostatically stabilized dispersions of Fe₂O₃ in xylene with C₁₈, C₁₄, C₁₀, C₈, and C₆ fatty acids that greater dispersion stability was obtained with the longer chain acids, C₁₈ giving the greatest effect, suggesting a steric stabilizing component of the stabilization mechanism.⁵ These studies suggest that when low-molecular-weight molecules having strong basic or acidic groups are used to stabilize powders with opposite acid-base characteristics (some powders act both basic and acidic) in nonaqueous media, an electrostatic stabilization is important and can be present along with steric stabilization.

When high-molecular-weight polymeric molecules having acidic or basic functional groups are used to stabilize dispersions, the predominant dispersing mechanism is most likely steric stabilization. The mechanism of interaction between the functional groups of small molecules and the particle surface should be similar to the anchoring mechanism for these functionalized macromolecules. A large number of copolymers containing functional groups have been used to stabilize inorganic powders in nonaqueous media. Poly(vinyl butyral)'s (PVB) hydroxyl and acetate groups are important sites for interaction with alumina.⁸ Poly(alkylmethacrylate) polymers improved the dispersion of alumina in heptane and paraffin oil. Poly(alkylmethacrylate)s can interact with the alumina by hydrogen bonding, as determined by DRIFT.⁹ A wide variety of polymers containing functional groups have been used to stabilize powders in nonaqueous media including PVB^{10,11} polyamides,¹² poly(methylmethacrylate-styrene) block polymers,¹³ and methacrylate copolymers.¹⁴ Copolymers of methylmethacrylate and small amounts of methacrylic acid (3.2% or less) gave very good dispersion of coated TiO₂ in MEK where the homopolymer was ineffective.¹⁴ Both polymers were effective dispersants for the powder in toluene.

In addition to the acid-base strength of polymer functional groups and the particles, the solvent also plays an important role. If the functional group is less acidic (or basic) than the solvent, the polymer will not absorb on the surface of particles, resulting in poor dispersion stability. The absorption of PMMA (basic) on silica (acidic) in various solvents illustrates the effect of solvents in dispersions.

PMMA is effectively absorbed from CCl₄, a neutral solvent, but is not absorbed from CHCl₂, an acidic solvent which dissolves the polymer too well for it to be taken from the solution. PMMA is poorly absorbed from THF and dioxane because these basic solvents preempt the acidic surface of silica so successfully that the basic polymer is excluded.¹⁵

Purely steric stabilization of powder can be obtained by chemically bonding the dispersant to the particle. Organoethoxysilanes (C₈, C₁₆, C₁₈) were covalently bonded to silica in hexane to give improved dispersion stability.¹⁶ The C₁₈ silane gave the best dispersion stability. Organoethoxysilanes [C₁₈H₃₇Si(OCH₃)₃ and C₁₈H₃₇(CH₃)₂Si(OCH₃)] showed little difference in effect on steric stability. High-molecular-weight polystyrene was grafted onto silica to obtain very good steric stabilization of the powder in toluene, whereas homopolystyrene was ineffective.¹⁷ These examples suggest that powders in nonaqueous dispersions can be stabilized by a purely steric mechanism and a wide range of dispersant molecular weights can be effective.

It seems clear from the information presented here that the surest way to stabilize inorganic powder in a nonaqueous medium is to chemically bond a polymer soluble in the medium to the particles. However, polymers with strong acid or base groups opposite in polarity to the particle generally work well by chemisorption to the particles. Polymers with weaker acidic (or basic) strength effectiveness depend to a large degree on the acidic or basic strength of the solvent. Homopolymers without functional groups such as polystyrene are least effective. Block polymers are more effective when one block has interacting functional groups, but can be effective in some cases without interacting functional groups with the proper choice of solvent.¹⁸

In this study, the primary focus was on the effect of an acidic group (—SO₃H) in polystyrene and Kraton block polymer poly(styrene-*b*-ethylenebutylene) on Al₂O₃ dispersed in toluene-ethanol dispersion medium. The dispersion stability of these polymers were compared to commercial dispersants with different functional groups having varied acid strengths.

EXPERIMENTAL

Materials

Polystyrene (10,000 MW) was purchased from Pressure Chemical Company and 60,000 MW polystyrene (G1C7) was obtained from Amoco Chemical

Company. Block polymers were obtained from Shell Chemical Company: G-1726MX, styrene/ethylene-butylene block copolymers with 70% diblock, 40,000 MW; WRC-801, styrene/ethylene-butylene diblock copolymer containing succinic anhydride grafted to the polymer backbone, 20,000 MW; 6511-3, same as WRC-801, except 45,000 MW. Polymeric dispersants were obtained from ICI Specialty Chemicals: Hypermer KDI (IR analysis showed this sample to be a condensation polyester with an amide group present), 1500 MW; Hypermer KD2 [IR and nuclear magnetic resonance (NMR) analysis showed this polymer to be a propyleneoxide-ethyleneoxide copolymer, with an amine group], 1500 MW. Silwet surfactants were obtained from Union Carbide Corporation: surfactant L-7500 (polypropylene oxide, butoxy terminated), 3000 MW; surfactant L-7604 (polyethyleneoxide hydroxy terminated), 4000 MW. Reagent grade 1,2-dichloroethane, tetrahydrofuran (THF), *n*-hexane, toluene, and ethanol were purchased from Fisher Scientific. Silver sulfate and fuming H₂SO₄ were purchased from Aldrich. The alumina was XA-4000 Alcoa alpha alumina, approximately 5 μm average particle size, 0.8 m²/g surface area, and 3.98 g/cm³ density.

Sulfonation of Polystyrene and Polystyrene-Ethylene-Butylene Block Polymer

One hundred grams of 1,2-dichloroethane was added to a four-neck round-bottom reaction flask equipped with a stirrer, nitrogen purge, and heating mantle. Fuming sulfuric acid (6–18 g) was slowly added to this flask while stirring. Next the silver sulfate was added and allowed to mix for 20 min. A solution containing polymer (10–30 g) dissolved in 200 mL 1,2-dichloroethane was added slowly from a dropping funnel dropwise into the reaction flask. The reaction mixture was then stirred at a given temperature for a prescribed time (Table I). The reaction mixtures were transferred to a separatory funnel and washed two or three times with deionized water and then (except samples 7 and 8 of Table I) precipitated in ethanol. These samples were redissolved in 1,2-dichloroethane, washed with water, and reprecipitated in ethanol. These samples were redissolved in 1,2-dichloroethane, washed with water, and reprecipitated in ethanol. Samples 7 and 8 would not precipitate in ethanol and were precipitated in hexane. They were redissolved in 1,2-dichloroethane and washed with water. The water-dichloroethane-polymer mixtures were stripped of most of the dichloroethane and water until they precipitated in a small amount of water. These were filtered and

Table I Sulfonation of Polystyrene and Polystyrene/Ethylene-Butylene Block Polymer (Kraton G1726MX)

Sample No.	Polymer	Grams Polymer ^a	Grams H ₂ SO ₄	Reaction Temp. (°C)	Reaction Time (h)	mL NaOH, 0.05N	Polymer Reprecipitated ^b (mL NaOH)	μmol SO ₃ H/g	SO ₃ H/10,000 MW
5	Polystyrene 60K	30	18.2	50	10	2.0	0.6	0.030	0.3
6	Polystyrene 60K	30	9.1	50	10	2.1	0.6	0.030	0.3
7	Polystyrene 10K	20	12	50	6	—	10.2 ^c	0.51	5.0
8	Polystyrene 10K	20	6	50	3	—	1.7 ^c	0.085	0.85
9	Kraton G1726MX 40K	20	7.1	50	19	5.7	2.0	0.1	1.0
10	Kraton G1726MX 40K	20	14.1	50	19	12.8	2.6	0.13	1.3

^a In all cases the polymer was dissolved in 200 mL 1,2-dichloroethane, 0.03 g of silver sulfate was used as catalyst, and 100 mL 1,2-dichloroethane was added directly to the reaction vessel at the beginning of the reaction.

^b All samples (except 7 and 8) were redissolved in 1,2-dichloroethane and reprecipitated in ethanol.

^c Would not precipitate in ethanol, were precipitated in hexane, had too much H₂SO₄ impurity to be titrated. Were redissolved in dichloroethane and washed with water in separatory funnel and stripped of dichloroethane and some of the water on a rotovap; then filtered and dried.

washed on filter paper with copious amounts of water. Polymers precipitated in ethanol were dried at 60°C for 24 h. Samples 6 and 7 were dried at 80°C for 48 h to remove water.

The amount of sulfonation was determined by dissolving 1 g of sulfonated polymer in 50 mL of THF and titrated with 0.05 N sodium hydroxide using phenolphthalein red indicator. Experimental data is given in Table I.

Settling Studies

Settling experiments were performed at 25°C in 10-mL graduated cylinders. Slurries for all settling experiments were prepared by mixing 15 g of Al₂O₃ with 20 g of premixed solution of polymer in solvent. The polymer (or dispersant) is expressed as weight percent (w/o of solvent). Most settling experiments were performed in 90:10 toluene-ethanol mixed solvent. Some settling experiments were carried out in other toluene-ethanol ratios to assess the effectiveness of some dispersants in a range of solvent polarities. The slurries were mixed in a shaker bath for 24 h at 25°C, and aliquots of the slurries were weighed into the graduated cylinders. Final equilibrated sediment volumes were converted to percentage of theoretical density by taking the measured sediment density (g/mL with experimental error determined to be ±2%) divided by the density

of Al₂O₃. Equilibrium densities were typically reached after 24 h. These data are given in Tables II and III. Select polymers (or dispersants) were evaluated with decreasing amounts of polymer (from 2.5 wt % of solvent to 0.15%) to determine critical concentration of dispersant needed to effect stability of the dispersion. These data are shown in Figures 1-4.

RESULTS AND DISCUSSION

The stabilization of fine particles in dispersion media requires either an electrostatic or steric mechanism to overcome polar and van der Waals forces to prevent agglomeration of the particles. In a polymer dispersion, where the density of the dispersed polymer is close to that of dispersion medium, good dispersion is indicated by nonsettling, relative low viscosity and good filterability of the dispersion through small-mesh screens. Most small inorganic powders have much higher densities than the dispersion media and tend to settle even in the presence of "good" dispersants. The "goodness" of a dispersant with an inorganic powder is determined by its effects on the settling time, settling density (some workers use settling height), and viscosity. The lower settling heights (higher settling densities) are indications of good dispersion stability. In practical applications,

Table II Results of Settling Experiments^a: Comparing Dispersant at 1.5 % Dispersant in Solvent and 43 % Al₂O₃ in the Slurry

Polymer (Dispersant)	Settling, Percent Theoretical Density	Dispersant	Settling, Percent Theoretical
No dispersant	39	Hypermer KD1	58
60K homopolystyrene	39	Hypermer KD2	38
60K sulfonated polystyrene (Table I, sample 5)	48	Kraton WRC-801	44
60K sulfonated polystyrene (Table I, sample 6)	50	Kraton 6511-3	47
60K sulfonated polystyrene (Table I, sample 6) sodium salt	47	UCC L-7500	37
10K sulfonated polystyrene (Table I, sample 7)	40	UCC L-7604	34
10K sulfonated polystyrene (Table I, sample 8)	23		
Kraton G1726MX	31		
Sulfonated Kraton G1720MX (Table I, sample 9)	52		
Sulfonated Kraton G1720MX (Table I, sample 10)	52		

^a All settling experiments were done in 90 : 10 toluene-ethanol solvents.

Table III Results of Settling Experiment: Effect of Solvent Composition (Toluene–Ethanol Ratio) 1.5 % Dispersant in Solvent and 43 % Al₂O₃ in Slurry

Polymer	Toluene–Ethanol Ratio ^a						
	100	98 : 2	95 : 5	90 : 10	80 : 20	70 : 30	55 : 45
60K sulfonated polystyrene (Table I, sample 6)	Insoluble	22	41	50	19	25	Insoluble
Sulfonated Kraton G1726MX (Table I, sample 9)	—	45	—	52	—	—	Insoluble ^b
Hypermer KD1	—	—	50	58	48	—	43

^a All results reported in this table are % theoretical density.

^b All Kraton polymers (G1726 MX, WRC-801, and 6511-3) were insoluble in 55 : 45 toluene–ethanol ratio solvent.

generally the inorganic powders are formulated with other components, including a polymer binder and high loading of particles at relatively high viscosities, and are used immediately after formulation or re-dispersed before use, which minimizes settling during processing. Shown schematically in Figure 5 are representations of a stabilized inorganic powder dispersion, a nonstabilized inorganic powder, and a stabilized polymer dispersion. Figure 5(a) shows schematically the nonaggregated low height (high settling density) of a stabilized dispersion, whereas Figure 5(b) shows how the nonstabilized aggregated particles give high settling volume (low settling density).

Sulfonated Polystyrene Dispersants

Fine particles dispersed in nonaqueous media are generally considered to be steric stabilized, although there are examples where an electrostatic mecha-

nism is important. In this study, steric stabilization should be the predominant mechanism since the dispersants are high-molecular-weight molecules. In steric stabilization, the polymer coating on the particle forms a barrier, preventing close approach of particles, and presumably allows the inorganic particle to roll past each without agglomeration to give good settling. In Table II, we see that the percent theoretical density for Al₂O₃ in the solvent alone is 39%, and when homopolystyrene is added, it remains unchanged. Two 60,000 MW sulfonated polystyrenes prepared with different amounts of H₂SO₄ but having the same —SO₃H content markedly improve the dispersion stability. The percent theoretical densities are 48 and 50%. The sodium salt of one of these polymers gave essentially the same results, 47% theoretical density. Since ionization of organic acids on the surface of powders give —CO₂⁻, presumably this happens with —SO₃H to give —SO₃⁻. One would then expect to get the same

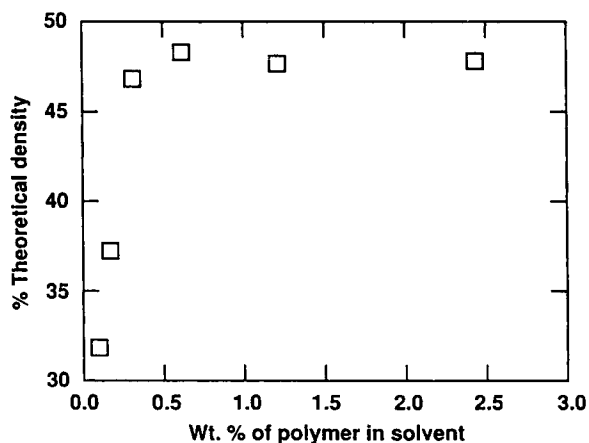


Figure 1 Effect of sulfonated polystyrene (Table I, sample 6) on settling density of Al₂O₃ in 90:10 toluene–ethanol.

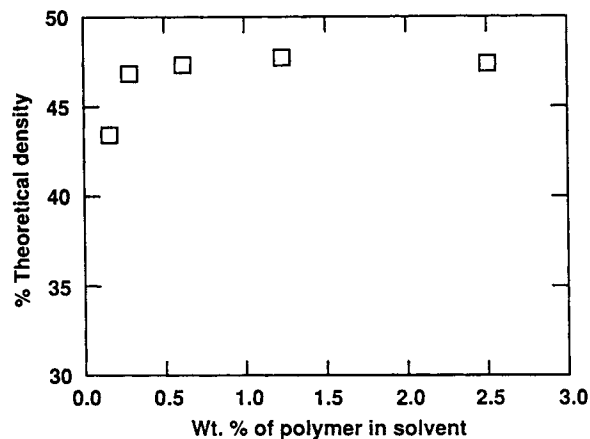


Figure 2 Effect of sulfonated Kraton G1726MX on settling density of Al₂O₃ in 90:10 toluene–ethanol.

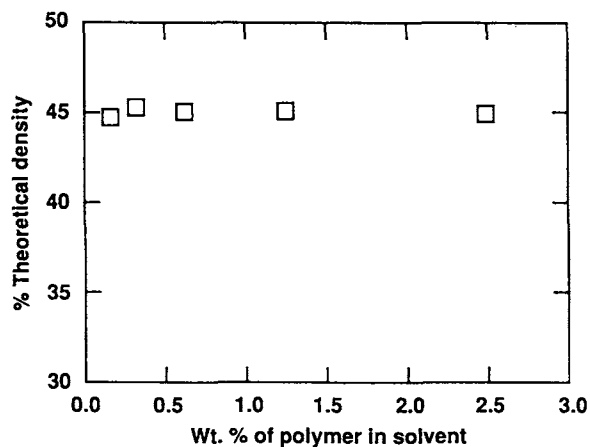


Figure 3 Effect of succinic anhydride grafted block polymer (Kraton 6511-3) on settling density of Al_2O_3 in 90:10 toluene-ethanol.

results with both sulfonated polymer and the sodium salt of the polymer, which already has the $-\text{SO}_3^-$ ion.

The low-molecular-weight sulfonated polystyrenes (Table I, samples 7 and 8) were not effective in stabilizing Al_2O_3 particles in the 90:10 toluene-ethanol mixture. The theoretical density settlings were 40 and 23%, respectively. Since low-molecular-weight (C_{18}) acids and silanes have been effective in stabilizing inorganic particles in nonaqueous media, the molecular weight (10,000) of the polymers is not likely to be the reason for these poor results. These polymers have higher degrees of sulfonation, as evidenced from titrations with NaOH (Table I) and the fact that they could not be precipitated in ethanol. The multiple $-\text{SO}_3\text{H}$ groups on the polymer possibly caused bridging and agglomeration of Al_2O_3 to give poor settling or extreme anchoring with low solubility and, thus, no steric barrier.

The effect of the toluene-ethanol ratio on a sulfonated polystyrene dispersant (Table I, sample 6) is shown in Table III. The solvent was varied from 100% toluene to 55:45 toluene-ethanol ratio. The polymer was insoluble in 100% toluene and 55:45 ratio solvent mixture but soluble in 95:15 and 80:20 solvent ratios. However, the sulfonated polymer was only effective in the 90:10 toluene-ethanol ratio, giving 50% theoretical settling density. Since in all cases in which the sulfonated polymer was soluble, we expected the $-\text{SO}_3\text{H}$ group to anchor to Al_2O_3 particles because of its high acidity, its ineffectiveness in toluene-ethanol ratios other than 90:10 suggests an unfavorable configuration of the polymer chain in solution. This argument is more plausible

in the solvent mixture that has high ethanol content where chains are less extended, but the poor result with high toluene content is less clear. Further study is needed to elucidate this finding.

The effect of the concentration of sulfonate polymer (Table I, sample 6) is shown in Figure 1. The concentration of the polymer was reduced by one-half successively in 90:10 toluene-ethanol from 2.5 wt % of the solvent to 0.08%. Good dispersion stability is seen at $\sim 0.3\%$ sulfonated polymer.

Functionalized Kraton Block Polymers

The Kraton block polymers G1726MX were sulfonated with two concentrations of H_2SO_4 but had essentially the same low level of sulfonation (Table I). Both of these polymers gave 52% theoretical density in 90:10 toluene-ethanol solvent, where the unsulfonated G1726MX was ineffective as a dispersant. This sulfonated polymer was also tested in 98:2 solvent mixture and gave a 45% theoretical settling density, suggesting that it might be a somewhat more versatile dispersant than the sulfonated polystyrene. The effect of polymer concentration is shown in Figure 2. We see that this polymer is effective at ~ 0.2 wt % in 90:10 toluene-ethanol solvent. Kraton block polymers WRC-801 (20K MW) and 6511-3 (45K MW) contain 2-3% grafted succinic anhydride. The anhydride groups are probably converted to acid by adventitious moisture. Both polymers improved Al_2O_3 stability in 90:10 toluene-ethanol solvent, giving 44 and 47% theoretical settling density, respectively. We can see from Figure 3 that Kraton 6511-3 is effective at ~ 0.2 wt % dispersant in 90:10

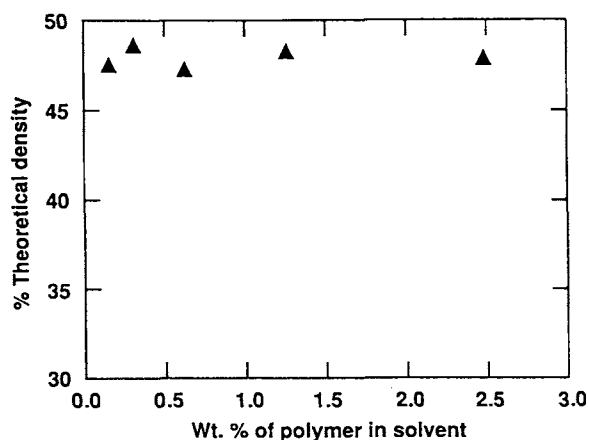


Figure 4 Effect of polymeric surfactant (Hypermer KD1) on settling density of Al_2O_3 in 90:10 toluene-ethanol.

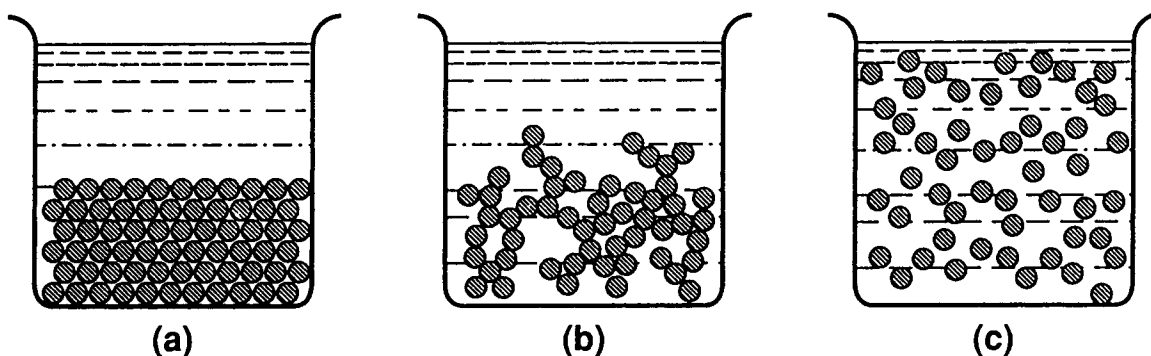


Figure 5 Schematic diagram showing (a) stabilized inorganic powder, (b) an unstabilized inorganic powder, and (c) a stabilized polymer dispersion.

toluene-ethanol solvent. It seems reasonable to expect that the same anchoring mechanism is involved with these polymers as for the sulfonate polymer, since their acidic character is significantly higher than ethanol, and they should preempt ethanol for base sites on Al_2O_3 .

Polar Polymeric Dispersant

Hypermer KD1 (from ICI), a condensation polyester with an amide group, was effective in stabilizing Al_2O_3 in 90:10 toluene-ethanol solvent. KD2, poly(ethyleneoxide-co-propyleneoxide) with an amine group was ineffective in the same solvent (Table II). There are two factors governing the effectiveness of dispersants, the effectiveness of the anchoring group and the solubility of the polymer. KD1 is less polar than KD2, since we know the polyethyleneoxide is water soluble. Both groups have basic anchors; KD1 amide and KD2 amine are more basic than ethanol and should anchor to the amphoteric Al_2O_3 . While more study is needed to explain the difference in effect of these dispersants, the solubility of polymers seems to be the main factor. Hypermer KD1 was effective in stabilizing Al_2O_3 in 95:5, 90:10, and 80:20 toluene-ethanol (Table II), suggesting that this dispersant can be used in solvents with a wide range of polarities. It is shown in Figure 4 that KD1 is effective at ~ 0.1 wt % of dispersant.

Two dispersants which had neither a strong acid nor a basic group were evaluated. Union Carbide L-7500 [3000 MW butoxy-terminated poly(propylene oxide)] and L-7604 (4000 MW hydroxy-terminated poly(ethylene oxide)) were both ineffective as dispersants. Neither of these dispersants had strong enough acidic or basic groups to effect anchoring on

the Al_2O_3 particles in the 90:10 toluene-ethanol solvent. This finding is in general agreement with our previous studies,¹⁹ which have shown that primary mono-alcohols and diols are inefficient for anchoring to the Al_2O_3 particle surface.

CONCLUSION

A variety of polymers can be used effectively for dispersing Al_2O_3 in toluene-ethanol solvent provided a strong acidic or basic group is present to anchor the polymer to the Al_2O_3 particles. It was shown that the sulfonate, succinic anhydride (probably hydrolyzed to the acid form), and amide groups were effective. One dispersant with an amine group was ineffective, probably not because of the amine group's ineffectiveness, but because of the low solubility of the polymer. Both hydrocarbon polymers [(polystyrene and poly(styrene-*b*-ethylenebutylene)] and a polar polymer (polyester) were effective soluble parts of dispersants. Polymers which did not contain strong acidic or basic anchors like L-7500, L-7604, and homopolystyrene were ineffective as dispersants. This study suggests that dispersants can be designed for specific systems by choosing the appropriate anchoring functional group (strong acidic or basic) for the particle and a soluble polymer for the dispersion medium.

REFERENCES

1. D. H. Napper, *Proc. Roy. Aust. Chem. Inst.*, **38**(11), 327 (1971).
2. W. R. Cannon, R. Becker, and K. R. Mikeska, *Adv. Ceram.*, **26**, 525 (1989).

3. J. Comyn, C. C. Horley, R. G. Pritchard, and R. R. Mallik, *Adhesion* (London) **11**, 38 (1987).
4. V. T. Crowl and M. A. Malati, *Discuss. Faraday Soc.*, **42**, 301 (1966).
5. H. Koelmans and J. T. G. Overbeek, *Discuss. Faraday Soc.*, **18**, 52 (1964).
6. A. E. Lewis, *J. Am. Ceram. Soc.*, **44**(5), 233 (1961).
7. B. I. Lee and J. P. Rives, *Colloids and Surfaces*, **56**, 24 (1991).
8. K. E. Howard, C. D. E. Lakeman, and D. A. Payne, *J. Am. Ceram. Soc.*, **73**(8), 2543 (1990).
9. T. K. Yin and I. A. Aksay, *Ceram. Trans I (Ceram. Powder Sci. 2 Pt. B)*, 654 (1988).
10. Y. H. Kim, S. R. Park, and K. Y. Kim, *J. Korean Ceram. Soc.*, **23**, 41 (1986).
11. M. D. Sacks and G. W. Scheffele, *Adv. Ceram.*, **19**, 175 (1986).
12. T. Sato, *J. Appl. Polym. Sci.*, **15**, 1053 (1971).
13. H. Lee, R. Pober, and P. Calvert, *J. Colloid Interface Sci.*, **110**(1), 144 (1986).
14. G. J. Howard and C. C. Ma, *J. Coating Tech.*, **51**, 47 (1979).
15. F. M. Fowkes and M. A. Mostafa, *Ind. Eng. Chem., Prod. Res. Dev.*, **17**, 1 (1978).
16. J. R. Fox, P. C. Kokoropoulos, G. H. Wiseman, and H. K. Bowen, *J. Mat. Sci.*, **22**, 4528 (1987).
17. R. Laible and K. Hamann, *Adv. Colloid Interface Sci.*, **13**, 65 (1980).
18. C. E. Molau and E. H. Richardson, *Adv. Chem. Ser.*, **99**, 379 (1971).
19. A. A. Parker, M. Y. Tsai, G. Biresaw, T. Stanzione, G. H. Armstrong, and J. J. Marcinko, *Mat. Res. Symp. Proc.*, **249**, 273 (1992).

Received May 8, 1992

Accepted November 21, 1993