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Organotitanate dispersants for $BaTiO_3$ and Al_2O_3

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An alkoxytitanium carboxylate of a branched carboxylic acid was synthesized and its effectiveness as a dispersant for oxide powders determined. The amount of titanate required to produce stable dispersions in nonaqueous media corresponded to monomolecular layer coverage of the oxide particles by the titanate. Low-molecular-weight organotitanate dispersants should prove useful as substitutes for fish oil or polymers in ceramics processing.

1. Introduction

In several ceramics processing methods, a slip of ceramic particles and polymer in a solvent is cast and dried to a green body of particles bound together by the polymer. The degree of dispersion of the oxide powder in the solvent has a profound effect on the microstructure of the green body and its subsequent sinterability [1]. The degree of dispersion depends on the resistance of the particles to agglomeration and flocculation, determined by the balance between attractive (van der Waals) and repulsive forces between interacting particles. Repulsive forces between particles are due to the presence of surface charge and/or adsorbed organic layers.

In uncharged systems, adsorbed organic layers on the oxide surface cause the particles to be separated by a distance twice the adsorbed layer thickness, so the force of attraction between interacting particles is reduced. When the attractive force between particles is relatively large, interpenetration or compression of the adsorbed molecules may occur, resulting in a loss of configurational entropy per adsorbed molecule and a corresponding increase in the free energy of the system, leading to steric repulsion [2]. The magnitude of the steric repulsive force depends on the adsorbed molecules' surface coverage, their chemical nature and configuration, and the adsorbed layer thickness [2, 3].

The dispersant molecule can interact with the oxide surface by physisorption or by a chemical reaction that leads to a covalent linkage. Conventional dispersants like glyceryl trioleate, fish oil [4], and carboxylic acids [5] physically adsorb to the oxide surface by weak hydrogen bonds. Interaction with the oxide surface via covalent linkages, on the other hand, can be obtained by employing coupling agents [6–8]. The covalent link ensures that the dispersant is firmly anchored to the oxide particle so that other additives in the slurry (e.g., the binder and plasticizer) will not cause desorption of the dispersant.

Coupling agents are mainly of the form R_nMX_{4-n} ($M = $ Si or Ti, $n = 1$ to 3), and contain easily hydrolysable groups, R, whose removal *in situ* lead to substrate–O–M bonds. The X group remains stably bound to the metal, M. For example, when a dialkoxytitanium dicarboxylate, $(RO)_2Ti(OOCR')_2$, is added to an oxide powder, the alkoxy groups react with hydroxyls on the particle surface to form an organic monomolecular layer (Fig. 1). The hydrophilic oxide surface is thereby modified to become hydrophobic and organophilic [9]. The long hydrocarbon chains (R′) remain free and extend into the solution phase forming a steric barrier to particle flocculation.

The alkoxytitanium carboxylates are generally derived from straight-chain fatty acids [10]. It has been found, however, that branched carboxylic acids form more stable dispersions of oxide powders in nonaqueous media than straight-chain acids [11]. The branch in the long-chain ligand increases the dispersant's surface layer concentration and also reduces chain interpenetration when particles approach one another.

Di-isopropoxytitanium distearoyloxy stearate, a new alkoxytitanium carboxylate derived from the branched, long-chain carboxylic acid 12-stearoyloxy-

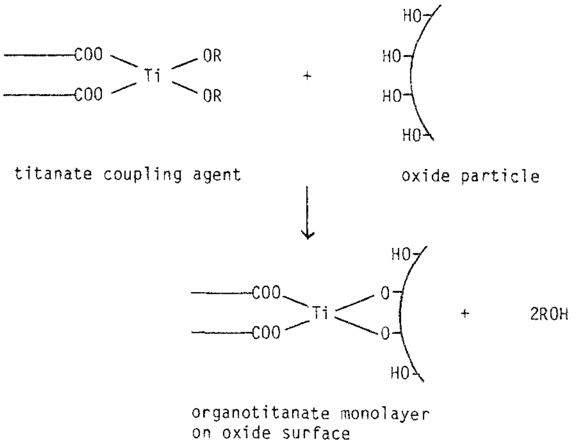

Figure 1 Reaction of an organotitanate coupling agent with an oxide particle surface.

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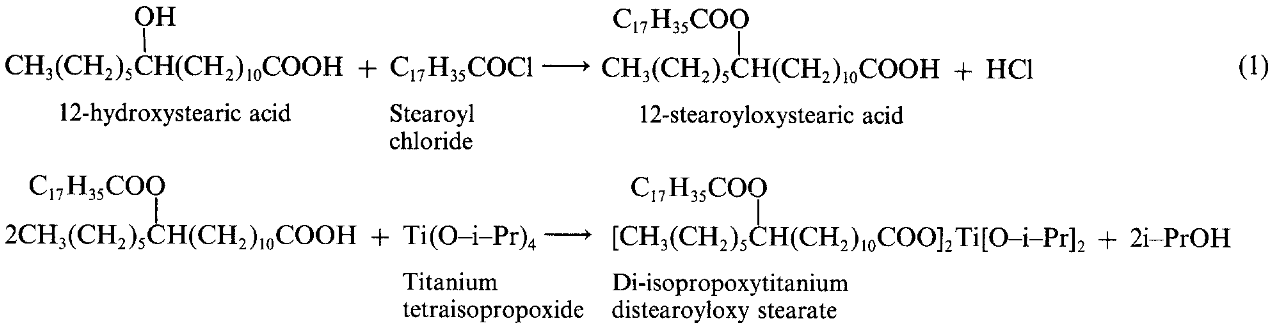
stearic acid, was therefore synthesized by the following two reactions:



$$CH_3(CH_2)_5\overset{\overset{OH}{|}}{C}H(CH_2)_{10}COOH + C_{17}H_{35}COCl \longrightarrow CH_3(CH_2)_5\overset{\overset{C_{17}H_{35}COO}{|}}{C}H(CH_2)_{10}COOH + HCl \quad (1)$$

12-hydroxystearic acid; Stearoyl chloride; 12-stearoyloxystearic acid

$$2CH_3(CH_2)_5\overset{\overset{C_{17}H_{35}COO}{|}}{C}H(CH_2)_{10}COOH + Ti(O\text{–}i\text{–}Pr)_4 \longrightarrow [CH_3(CH_2)_5\overset{\overset{C_{17}H_{35}COO}{|}}{C}H(CH_2)_{10}COO]_2Ti[O\text{–}i\text{–}Pr]_2 + 2i\text{–}PrOH$$

Titanium tetraisopropoxide; Di-isopropoxytitanium distearoyloxy stearate

To determine the effectiveness of the organotitanate as a dispersant, dispersion tests were conducted on different oxide powders in either hexane or toluene.

2. Experimental procedure

2.1. Materials preparation and synthesis

The following compounds used in this study were prepared as follows: 12-hydroxystearic acid (Alfa Products, Danvers, MA, USA; m.p. 82° C) was used as-received, stearoyl chloride (Aldrich Chemical Co., Milwaukee, WI, USA; b.p. 202° C/6 mm) and titanium tetraisopropoxide (Alfa; b.p. 58° C/1 mm) were purified by distilling under reduced pressure, and toluene and hexane (reagent grade) were dried over molecular sieves. The branched carboxylic acid was synthesized by heating 12-hydroxystearic acid with stearoyl chloride to 120° C and removing hydrogen chloride under reduced pressure [11].

The organotitanate was then synthesized by adding a solution of carboxylic acid (2 mol) in toluene to titanium tetraisopropoxide (1 mol) in the same solvent. The mixture was stirred under nitrogen, heated to 90° C, and held at that temperature for 1 h. The isopropanol : toluene azeotrope (b.p. 80.6° C) was removed by distillation; the residual solvent was removed *in vacuo*. The isopropanol (i-PrOH) content of the azeotrope was determined quantitatively using standard aqueous $K_2Cr_2O_7$ (in 12.5 vol % H_2SO_4) [12]. The product, a viscous brown liquid, was dried *in vacuo* and subjected to elemental analysis. Infrared (IR) and nuclear magnetic resonance (NMR) tests were also conducted.

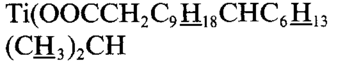
2.2. Elemental analysis

Predicted:

$$(i\text{-}PrO)_2Ti[OOC(CH_2)_{10}\overset{\overset{OOCC_{17}H_{35}}{|}}{C}H(CH_2)_5CH_3]_2$$ (72.18% C, 11.80% H, 3.69% Ti)

Found: 72.14% C, 12.00% H, 3.84% Ti

IR ν: 2930 cm^{-1}(s), 2860 cm^{-1}(s), 1730 cm^{-1}(s), 1550 cm^{-1}(s)

NMR $\delta(C_6D_6)$:		
5.1 multiplet	(1H)	$C\underline{H}OC{=}O$
5.0 septet	(1H)	$Me_2C\underline{H}$
2.2 double triplet	(4H)	$Ti[OOCC\underline{H}_2\text{–}]$; $C_{16}H_{33}C\underline{H}_2COO\text{–}$
1.3 singlet	(64H)	 $Ti(OOCCH_2C_9\underline{H}_{18}\overset{\overset{OOCCH_2C_{16}\underline{H}_{33}}{|}}{C}HC_6\underline{H}_{13}$
1.0 doublet	(6H)	$(C\underline{H}_3)_2CH$

Alkoxytitanium carboxylates are known to contain a small amount of ester, formed as a decomposition product [13]. The IR C=O absorption peak at 1730 cm^{-1} may include some contribution from the ester isopropyl-stearoyloxystearate, in addition to the mid-chain ester group. The peak at 1550 cm^{-1} has been attributed to absorption by the organotitanate carbonyl. No effort was made to separate any ester impurities from the organotitanate.

The oxide powders used in the dispersion tests ($BaTiO_3$ and Al_2O_3) are described in Table I. The powders were dried at 150° C under vacuum prior to use in the dispersion tests. Dispersion tests were carried out in 10-ml graduated cylinders: 4 g of the oxide powder were added to 10-ml solutions of the dispersant in hexane. The suspensions were ultrasonicated for 1/2 h to break up agglomerates, then tumbled overnight to ensure complete coating of the particles by the dispersant. The suspensions were then allowed to stand undisturbed for periods of up to 3 weeks before the precipitate volumes were measured. In these tests, isolated, noninteracting particles will precipitate to a high density, whereas agglomerated particles will form loosely packed sediments [14]. The observed sediment densities will therefore provide a qualitative estimate of the extent of flocculation.

Viscosity measurements were carried out on a Haake Rotovisco RV-100, electrophoretic measurements on a Pen-Kem System 3000, and thermogravimetric analysis on a Du Pont 900 thermal analyser. The treated powder was washed twice with pure solvent and dried under vacuum at 30° C before analysis.

3. Results and discussion

The percentage theoretical densities of $BaTiO_3$ and

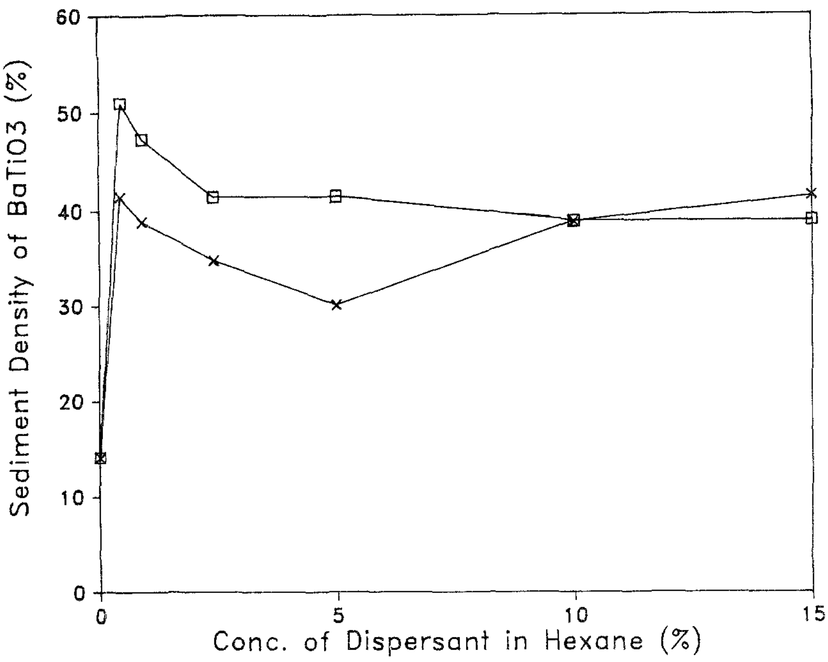


Figure 2 Effect of dispersant concentration on $BaTiO_3$ sediment density for organotitanate and carboxylic acid in hexane. (□) DITDSS, (x) SSA.

Al_2O_3 sediments for increasing dispersant concentrations in hexane are given in Figs 2 and 3. The organotitanate coupling agent yielded packing densities slightly higher than those obtained with the carboxylic acid. The organotitanate also produced sediments with high packing densities for TiO_2 and $SrTiO_3$ powders. The sediment densities obtained with either organotitanate or carboxylic acid in hexane were significantly higher than those obtained with fish oil in toluene, which under similar conditions gave a sediment density of only 37 wt % [15]. The solvent choice was important: when the solvent was changed from hexane to toluene, sediment densities for both organotitanate and carboxylic acid dispersions decreased by 5 and 13%, respectively. In hexane, as compared to toluene, the long hydrocarbon chains are relatively extended, producing a more effective steric barrier so that the equilibrium particle separation is greater.

Scanning electron micrographs of the top surfaces of sediments prepared from centrifuging $BaTiO_3$ dispersions in hexane with and without organotitanate are shown in Figs 4 and 5. From these micrographs it is evident that the organotitanate treatment yielded well-packed sediments. Viscosity measurements (Fig. 6) indicate that prior treatment of $BaTiO_3$ with organotitanate greatly reduced dispersion viscosity, as compared to untreated $BaTiO_3$. As shear rate was increased, deflocculation of the untreated particles led to a reduction in the effective volume of the dispersed phase and resulted in shear thinning. This effect was seen to a much smaller extent on the organotitanate-treated $BaTiO_3$: it is possible that in addition to stabilized particles, stabilized flocs were also present in the dispersion.

TABLE I $BaTiO_3$ and Al_2O_3 characterization

	$BaTiO_3$	Al_2O_3
Identification	HPB	XA 139
Supplier	Tam	Alcoa
Surface area[a] ($m^2\,g^{-1}$)	3.6	8.7
Density[b] ($g\,cm^{-3}$)	6.04	3.96
Particle size distribution[c] (μm)	0.4–2.5	0.1–3.0
Average particle size[c] (μm)	1.4	0.4

[a] Determined by BET method, N_2 (gas) adsorption.
[b] He(g), stereopycnometer.
[c] Sedigraph.

Thermogravimetric analysis of Al_2O_3 powders treated with organotitanate or carboxylic acid indicates that ~1 wt % dispersant was adsorbed on the oxide surface (Table II). This corresponds to a surface coverage of 0.53 molecules organotitanate per nm^2 of alumina surface. The molecular cross-sectional area of the carboxylic acid determined from an adsorption isotherm [11] was found to be $0.64\,nm^2$. Each organotitanate molecule has two carboxylic acid ligands, so assuming that the organotitanate molecules adopt a perpendicular orientation with the surface, the approximate chain packing area indicates that the organotitanate forms a monomolecular layer on the oxide surface.

To evaluate the extent of desorption, powders treated with organotitanate or carboxylic acid were soxhlet-extracted with ethyl acetate, a polar solvent, for 72 h (Table II). Afterwards, 97% of the organotitanate monolayer remained on the oxide surface, indicating that it is strongly linked [13], while only 10% of the organic acid withstood the treatment. It was therefore concluded that the carboxylic acid was primarily physisorbed to the oxide surface, though 10% had possibly reacted chemically with surface hydroxyls.

Maximum packing densities occurred above the estimated organotitanate concentration for monomolecular-layer coverage. Addition of excess organotitanate in hexane to Al_2O_3 powder resulted in the chemisorption of 1 wt % with respect to the oxide powder. However, a dispersion test of 0.6 wt % organotitanate in hexane, a concentration which should have produced monomolecular-layer coverage if all the dispersant in solution reacted with the oxide powder, yielded an agglomerated sediment, as

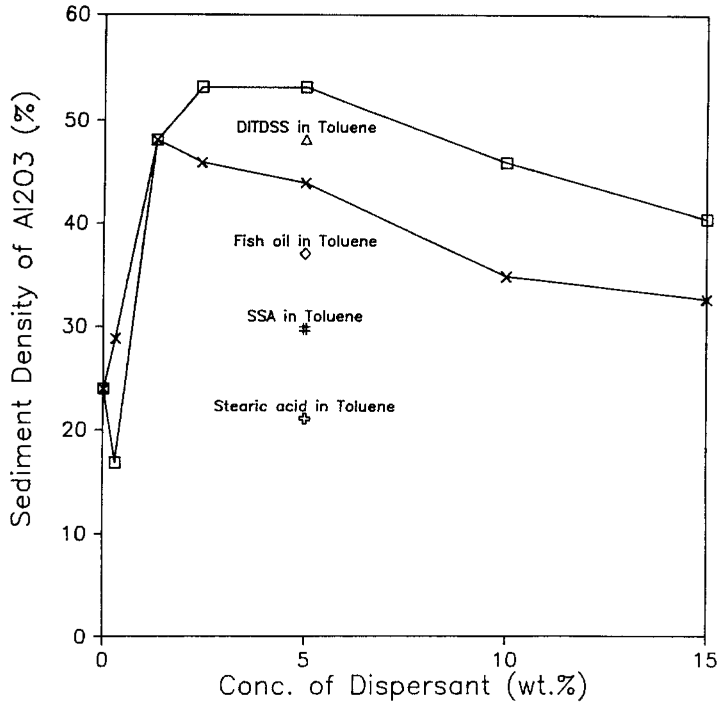


Figure 3 Effect of dispersant concentration on Al_2O_3 sediment density for organotitanate and carboxylic acid in hexane, and organotitanate, carboxylic acid, fish oil and stearic acid in toluene. (□) DITDSS in hexane, (x) SSA in hexane.

indicated by a low sediment density (Fig. 3). In practice, a minimum concentration of 1.3 wt % organotitanate in hexane was required to produce a stable dispersion, while an optimum concentration of 1.5 wt % yielded a sediment density of 53%. This probably occurs when each Al_2O_3 surface group capable of hydrogen bonding between particles is protected by an organotitanate molecule. With $BaTiO_3$ powder, even lower concentrations of organotitanate in hexane (0.5 to 1.0 wt %) yielded stable dispersions.

Using such small amounts of this low-molecular-weight dispersant should reduce problems associated with the burnout process. After burnout ~0.15 wt % TiO_2 will be deposited on the surface of the oxide powder. The consequent effects of this are uncertain, but may prove advantageous. The surface–O–Ti bond may bridge one particle to another, and the residual TiO_2 may act as a "cement" or a sintering aid.

To produce stable dispersions, therefore, an organotitanate dispersant with a molecular weight of 1300 is as effective as a polymeric stabilizer [16]. Polymers adsorb to thicknesses of around 1.5 nm^2 on particle surfaces [17]. Chain lengths measured from models indicate that the length of the branched carboxylic acid is ~4.0 nm [11] so the organotitanate would produce a steric barrier ~4.0 nm thick if present as a monomolecular layer on the particle surface. Electrophoretic measurements of $BaTiO_3$ powder treated with organotitanate in hexane showed the particles to be uncharged, indicating that electrostatic forces do not contribute to the dispersion stability. Based on minimum steric barrier thickness requirements for the stabilization of colloidal particles [18], the organotitanate chain length is surprisingly short.

4. Conclusions

For a given oxide powder in a given solvent, if the critical length of a stabilizing chain could be calculated it would then be possible to design organotitanate couplers with ligands of the appropriate

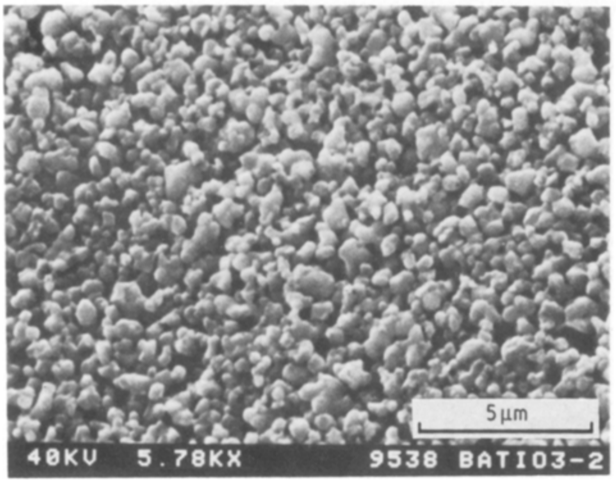


Figure 4 Scanning electron micrograph of the top surface of a well packed sediment resulting from centrifuging a dispersion of $BaTiO_3$ in 2.5% organotitanate in hexane.

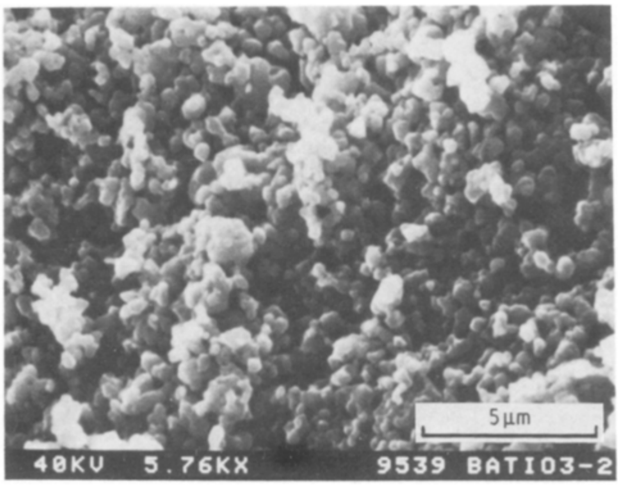


Figure 5 Scanning electron micrograph of the top surface of a poorly packed sediment resulting from centrifuging a dispersion of $BaTiO_3$ in pure hexane.

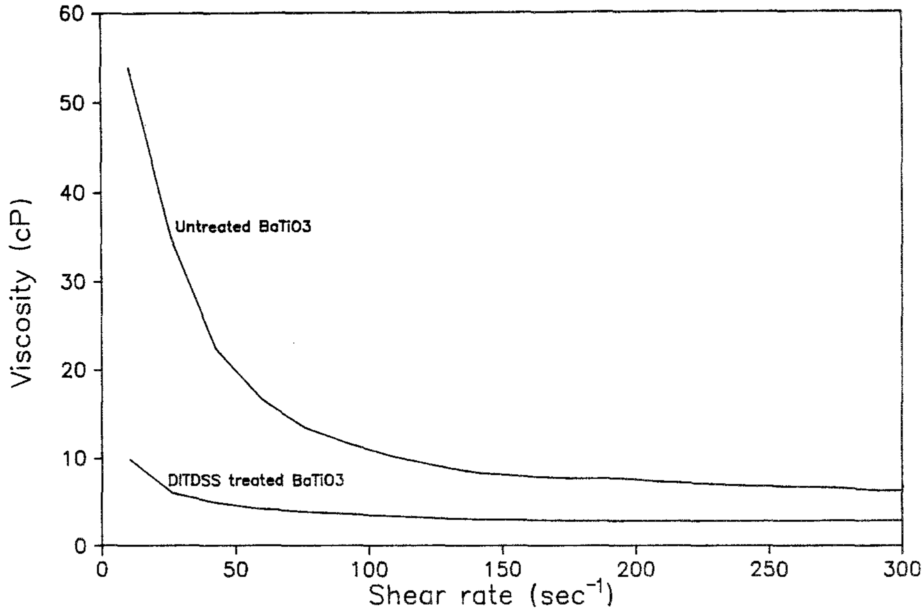


Figure 6 Rheological behaviour of $BaTiO_3$ in dodecane with and without organititanate treatment. (Partical size 0.2 to 0.4 μm; volume fraction 0.1; at 20° .C.)

length. The size of the dispersant molecule could therefore be minimized, which would in turn minimize problems associated with the subsequent burnout process. The long-chain ligands could also be modified for use in different solvent systems. These organotitanates could therefore be tailored to meet the demands of different powder-solvent systems, and prove to be versatile dispersants in ceramics processing.

Acknowledgements

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TABLE II Reduction in adsorbed dispersant upon treatment with ethyl acetate

Dispersant	Powder	Concentration of dispersant adsorbed on powder (wt %)	Surface coverage (molecules nm^{-2} of alumina surface)	Reduction[a] (%)
Organotitanate	Al_2O_3	1.01	0.53	3
Carboxylic acid	Al_2O_3	1.05	1.20	90

[a] After soxhlet extraction with ethyl acetate for 72 h.