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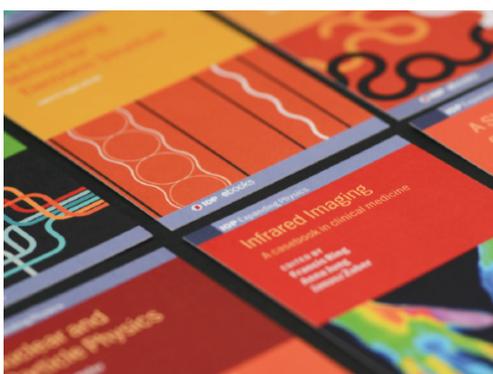
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Preparation, microstructure and electrorheological activity of nanosized modified titanium dioxide and titaniferous fillers

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Abstract. Nanodisperse powders of pure, superficially and structurally modified titanium dioxide as well as composition materials SiO₂-TiO₂ with different morphology are synthesized. Electrorheological properties of dispersions on their basis are investigated. It is established, that doping of TiO₂ by heterovalency replacement of the titanium with aluminum and chrome ions allows us to raise essentially electrorheological activity of dispersions in comparison with pure titanium dioxide.

1. Introduction

Micro- and nanosized poorly conducting, capable to be polarized in the electric field particles are used as a dispersed phase of electrorheological fluids (ERF). Among inorganic materials nanooxides of titanium, possessing high dielectric permeability, and of silicon, having low density, that provides sedimentation stability of ERF are a subject of active researches recently [1].

Investigating influence of microstructure (type of crystal structure, pore size, surface area) of pure TiO₂ on electrorheological properties of dispersions, Shang *et al.* [2] have arrived at a conclusion that TiO₂ particles of anatase structure show larger electrorheological (ER) activity in comparison with TiO₂ of rutile structure. However pure TiO₂ does not give a sufficient increase in viscosity in the electric field. Viscosity of the dispersion, containing 25 wt.% of filler, at the electric field intensity of 3.2 kV/mm and shear rate of 300 s⁻¹ increases only by 7 times. It results from the fact that the fast ionic or atomic polarization inherent crystalline TiO₂ does not provide the optimum dielectric and polarizing properties necessary for revealing high ER-activity.

Hao *et al.* [3] consider that the greatest contribution to electrorheological effect (ERE) is brought by the interfacial polarization caused by presence of a surface charge. Therefore, structural and surface modification of nanodisperse inorganic oxides by using reproducible methods of synthesis is a perspective way to increase the quantity of charge carriers, to intensify interfacial polarization, and, consequently, to create effective ERF fillers with high ER-activity [4].

2. Experimental

Nanodisperse pure titanium dioxide, and composition materials SiO₂ – TiO₂ with various morphology:

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co-precipitated powders and the materials having morphology core SiO_2 – shell TiO_2 , and also superficially and structurally modified titanium dioxide were synthesized and investigated. Co-precipitated materials SiO_2 – TiO_2 have been obtained by combined hydrolysis of silicon and titanium containing components. The materials with morphology core SiO_2 – shell TiO_2 , have been obtained by formation of titanium dioxide shell on nanodisperse microspheres of silicon dioxide by the mechanism of electrostatic interaction. As initial silicon and titanium containing components titanium and silicon alkoxides: titanium tetraisopropoxide (TTIP), tetraethoxysilane (TEOS), liquid glass (l. g.), titanium tetra- and trichlorides were used. Surface modification of TiO_2 was carried out by introduction of urea or sodium dodecyl sulfate (SDS) during the process of sol-gel synthesis. Cetyltrimethylammonium bromide (CTAB) was used as a template. TTIP was a source of titanium dioxide. Samples were dried at temperature 120 °C for 5 h. Structural modification of TiO_2 was carried out by doping with cations of aluminum, chrome, lanthanum, yttrium. Synthesis was realized at the presence of templates – dodecylamine (DDA) and triethanolamine (TEA). Samples were dried at 120 °C for 5 h and calcined at 600 °C for 3 h. Doping components and templates were introduced both into initial solutions of titanium containing components, and in colloidal solutions of titanium dioxide, obtained by peptization of freshly precipitated titanium dioxide from solutions of titanium tetrachloride in isopropyl alcohol. The obtained materials were tested by means of methods of the physical and chemical analysis: adsorptive and thermogravimetry, chemical and X-ray phase analysis methods.

For determination of ER-activity of samples, dispersions on the basis of the obtained powders with weight concentration of 5 % in transformer oil are tested by means of the measuring cell consisting of two coaxial cylinders.

3. Results and discussion

Some conditions of synthesis and properties of obtained fillers are tabulated below. Pure titanium dioxide and nanocomposition materials SiO_2 – TiO_2 have the developed specific surface area. Dispersity of fillers, their phase structure and surface properties depend on preparation conditions and processing temperature. Samples after drying at 120°C represent amorphous materials characterized by appreciable hydrophilicity. Calcination of them at temperatures between 200–1000°C is accompanied by the processes of dehydration (weight losses at calcination in the range of temperatures 200–1000°C are 15 – 25% and they are caused by removal of physically adsorbed, coordinated bound water and surface hydroxyl groups), crystallization of titanium dioxide, considerable reduction of a specific surface area.

It is established that doping of titanium dioxide with compounds of Cr, Al, La, Y within 5–10 mol. %, and also introduction of templates slows down crystallization process of titanium dioxide at heat treatment and allows to receive nanocrystal product with a crystallite size $d = 10\text{--}15$ nm and a specific surface area $S = 80\text{--}150$ m²/g. Titanium dioxide obtained in similar conditions and not containing doping additions, has $d = 45\text{--}50$ nm and $S = 30\text{--}50$ m²/g.

According to the chemical nature and technology of production, the samples 1 – 4 of the table 1 concern to containing water materials, and samples 5 – 11 on a basis of nanodisperse doped titanium dioxide concern to waterless fillers.

The fillers, containing partially physically adsorbed and coordinated bound water (samples 1 – 4), have shown appreciable electrorheological activity (figure 1a). However, some of them (samples 1 and 4), as seen in figure 1b, have rather high conduction current densities 20–35 $\mu\text{A}/\text{cm}^2$. The sample of titanium dioxide modified by urea, obtained by template synthesis (figure 1a, curve 3), showing appreciable ER-activity, has a rather low values of density of conduction currents 0.01–2.5 $\mu\text{A}/\text{cm}^2$ (figure 1b, curve 3), in spite of the fact that heat treatment of this sample was carried out at 120°C. The ERF on the basis of the titanium dioxide sample modified with DDS (the sample 4 of the table 1), has shown ER-activity, comparable with the activity of the sample 3. However, heat treatment of water containing samples at temperature 200°C results in full loss of ER-activity because of the removal of physically adsorbed and, probably, coordinated bound water which is an activator of ERE in this case.

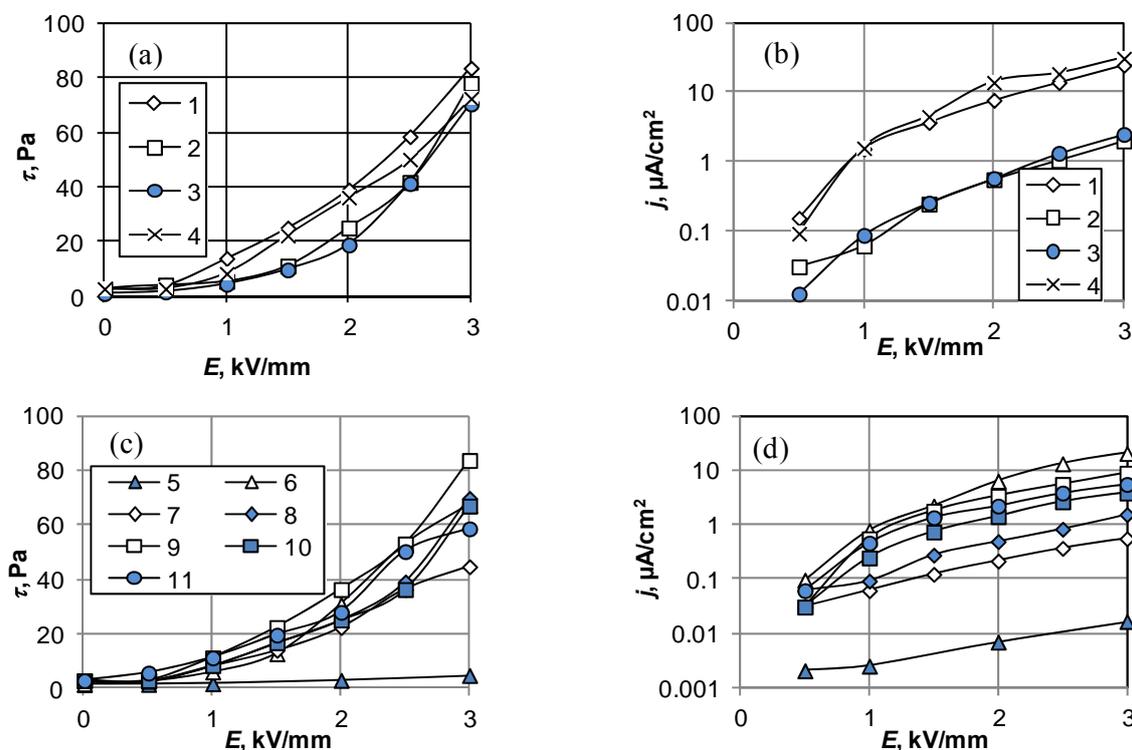


Figure 1. Dependence of shear stress (a, c) and conduction current density (b, d) of ER fluids on the electric field intensity (shear rate is 32 s^{-1} for samples 2, 5, 6; 17.2 s^{-1} for the rest of samples); filler concentration is 5 wt. %; numbers of samples correspond to numbers in the Table 1.

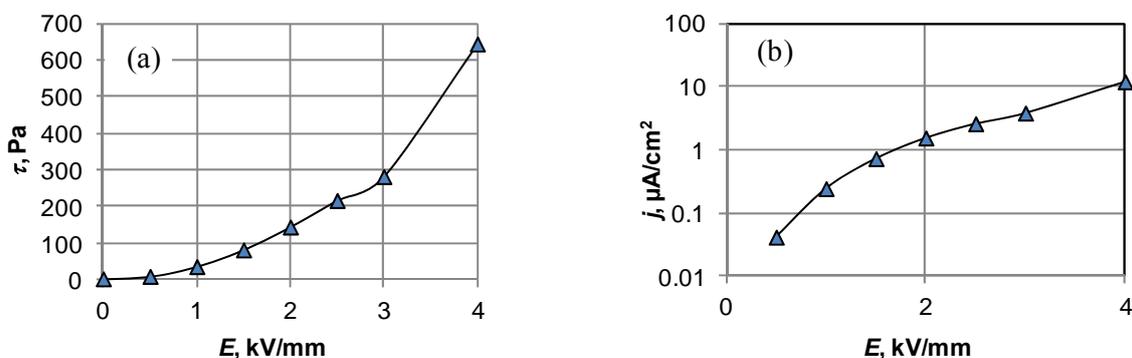


Figure 2. Dependence of shear stress (a) and conduction current density (b) of ERF with 30 wt. % (sample 8) on the electric field intensity (shear rate is 17.2 s^{-1}).

The samples doped with aluminum and chromium (6, 8, and 9), having the developed specific surface area $120\text{--}135 \text{ m}^2/\text{g}$, were the best among waterless fillers. Increase of shear stress τ of ERF on the basis of these fillers reach 30–40 times at $E = 3 \text{ kV}/\text{mm}$ at current density of $7\text{--}21 \mu\text{A}/\text{cm}^2$ while pure mesoporous titanium dioxide (the sample 5) has shown increase only by 3.5 times.

Considering positive characteristics – high ER-activity and low values of current density of the sample TiO_2 doped by aluminum (the sample 8), the fluid containing 30 wt. % of filler in mineral oil is prepared on its basis. In figure 2 dependences of shear stress and current density on the electric field intensity are presented. In the electric field of intensity of 3 kV/mm shear stress increases more than by 2 orders. At that, values of current density do not exceed $12 \mu\text{A}/\text{cm}^2$ (at the electric field intensity of 4 kV/mm). In the range of E up to 3 kV/mm, the dependence $j(E)$ practically coincides with the

dependence for the sample doped with lanthanum (10), which has a smaller dispersed phase concentration of 5 wt. % (figure 1d). The samples doped with chrome and yttrium (6 and 11) give even larger values j (at 5 wt. %). Therefore it is necessary to expect, that current density for these samples at a bigger concentration of a dispersed phase will be essentially higher and will not allow to reach high ER-activity. Thus, aluminum seems to be the most perspective doping element among the investigated metals.

Table 1. Samples of fillers and their properties.

No.	Chemical nature and morphology	Parent substances	Treatment conditions		Template	S (m ² /g)
			T (°C)	Time (h)		
1	Co-precipitated composite SiO ₂ – TiO ₂	L. g., TiCl ₃	120	5	–	355
2	Core SiO ₂ – shell TiO ₂	L. g., TiCl ₄	120	5	–	206
3	TiO ₂ + urea + TEA	TTIP, urea, TEA, NaOH	120	5	CTAB	300
4	TiO ₂ + DDS	TTIP, CH ₃ COOH	120	5	DDS	160
5	TiO ₂	TTIP, TEA	120 450	5 3	CTAB	37
6	TiO ₂ + Cr	TTIP, CrCl ₃ , TEA, NaOH	450	3.5	CTAB	135
7	TiO ₂ + Al Ti/Al=90:10	sol TiO ₂ , Al(NO ₃) ₃	150 600	5 3	DDA	79
8	TiO ₂ + Al Ti/Al=93:7	sol TiO ₂ , Al(NO ₃) ₃	150 600	5 3	DDA	120
9	TiO ₂ + Al Ti/Al=94:6	sol TiO ₂ , Al(NO ₃) ₃	150 600	5 3	DDA	130
10	TiO ₂ + La Ti/La=94:6	sol TiO ₂ , La(NO ₃) ₃	150 600	5 3	DDA	112
11	TiO ₂ + Y Ti/Y=94:6	sol TiO ₂ , Y(NO ₃) ₃	150 600	5 3	DDA	142

Note: TiO₂ content (wt. %) in the samples: 1 – 32.0; 2 – 7.0; the rest samples – 82–90

4. Conclusion

Thus, it is established that structural modification of titanium dioxide (production of the mesostructured product in the presence of urea), and also doping TiO₂ by heterovalent replacement of the titanium with ions of some transition and rare-earth elements allows to raise essentially ER-activity of dispersions on its basis in comparison with pure TiO₂. For promotion of titanium dioxide as effective filler of industrial ERF it is necessary to continue investigations in wider interval of structures, temperatures, to optimize the production technology of such fillers by using the available initial reagents of the inorganic nature.

References

- [1] Zhao X P and Yin J B 2006 *J. Ind. Eng. Chem* **12** (2) 184–98
- [2] Shang Y, Ma S, Li J, Li M, Wang J and Zhang S 2006 *J. Materials Science & Technology* **22** (4) 572–6
- [3] Hao T, Kawai A and Ikazaki F 1998 *Langmuir* **14** (5) 1256–62
- [4] Wu Q, Zhao B Y, Fang C and Hu K A 2005 *Eur. Phys. J. E* **17** 63–7