

# Surface Modification of Titanium Dioxide under Ultrasonic Treatment



Nikolay A. Bulychev

**Abstract:** The surface modification of titanium dioxide in aqueous dispersions of specially tailor-made periodic acrylic acid/isobutylene copolymers by ultrasonic treatment was studied. The pigment surface modification by the above copolymers was comparatively investigated regarding conventional adsorption as contrasted to an ultrasonic treatment assisted procedure. The course and efficiency of the polymer adsorption onto the pigment surface was quantified by electrokinetic sonic amplitude measurements. The higher efficiency of the pigment surface coating by the copolymers as achieved by ultrasonic treatment and is a consequence of ultrasonically induced pigment surface activation.

**Keywords:** surface modification, ultrasound, pigments, polymers.

## I. INTRODUCTION

The homogeneous dispersing of pigments is important in coatings formulations. For producing aqueous pigment dispersions, many approaches have been described in literature [1 - 3]. It was shown [4 - 6] that highly stable dispersions are obtained by ultrasonic treatment of pigment slurries in aqueous solutions of polymer surfactants. Recent studies [7, 8] by employing electrokinetic sonic amplitude (ESA) measurements have revealed that the origin of the improved stabilization of the pigment dispersion is due to first the generation of a finer dispersion of the pigment by the mechanical, i.e., ultrasonic treatment, and second the formation of a thicker layer of the polymeric additive around the pigment; the better encapsulation of the pigment by the stabilizer polymer is a consequence of the ultrasonically induced activation of the pigment surface. In this work, we report on the dispersing of TiO<sub>2</sub> in aqueous solutions of amphiphilic copolymers of well-defined structures by ultrasonic treatment. These copolymers are characterized by special sequences of hydrophilic and hydrophobic units which result in specific pigment-polymer interactions and stabilizing properties [9 - 10]. The effect of the ultrasonic treatment on the deposition of the stabilizer copolymer is discussed in the context of the various copolymer architectures.

## I. EXPERIMENTAL PART

### Materials

As solid material, the titanium dioxide rutile pigment Kronos 2310 (particle size 0.3 μm) has been chosen. The PiBA-PAA block copolymers of various well-defined structure, molecular weight and narrow polydispersity, were synthesized by controlled radical polymerization as described [3].

### Techniques

For the preparation of particle aqueous dispersions, particles were added to water as is or together with the polymer dissolved in THF and dispersing of particles was first achieved by a laboratory stirrer (700 rpm for 10 min). When ultrasonic treatment was applied, the system was further on treated with ultrasound (2 min) with an ultrasonic equipment Branson Sonifier B-12 (actual power of 1.5 W/cm<sup>2</sup>).

Colloidal stabilization of 1 % aqueous dispersions of TiO<sub>2</sub> was studied by sedimentation measurements. The particle-polymer interaction and the formation of polymer adsorption layer were studied by electrokinetic sonic amplitude (ESA) method as described earlier [7]. The particle size was measured by ESA [7]. Standard optical equipment was used for refractive index measurements.

## II. RESULTS AND DISCUSSION

Data recently reported in literature [11 - 16], showed that ultrasonification of aqueous dispersions of solid particles in the presence of surface active polymers leads to a significant rise of the stability of such dispersions in comparison to dispersions prepared without application of ultrasonic treatment. It was shown by IR-analysis that the firmness and stability of the adsorption layers of polymers were improved by the ultrasonic treatment. Parameters of polymer adsorption layers affected by the ultrasonic treatment were investigated [7]. However, the effect of the ultrasonic treatment on the particle-polymer interaction and polymer adsorption, especially for novel tailor-made amphiphilic copolymers is still not clear and needs further studies for the better understanding of the observed phenomena. First, sedimentation measurements for TiO<sub>2</sub> aqueous dispersions stabilized by a series of tailor-made amphiphilic copolymers containing PiBA and PAA segments in the presence and absence of ultrasonic treatment have been carried out. These data are presented in Table 1.

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\* Correspondence Author

Nikolay\*, P.N. Lebedev Physical Institute, 119991, Leninsky pr-t, 53, Moscow, Russia,

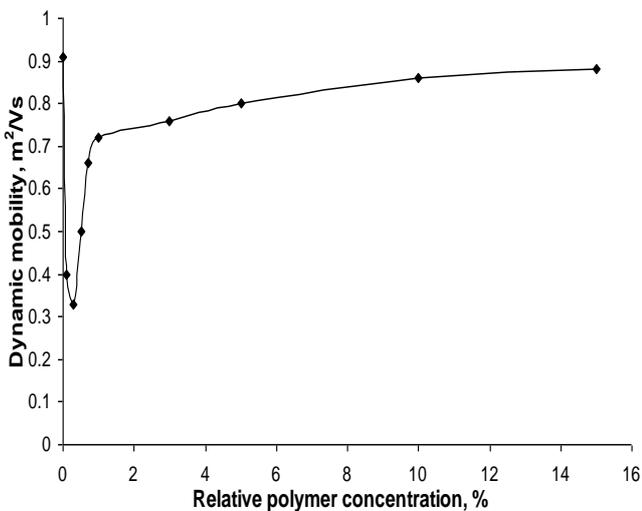
A. Bulychev, Moscow Aviation Institute, 125993, Volokolamskoe shosse, 4, Moscow, Russia

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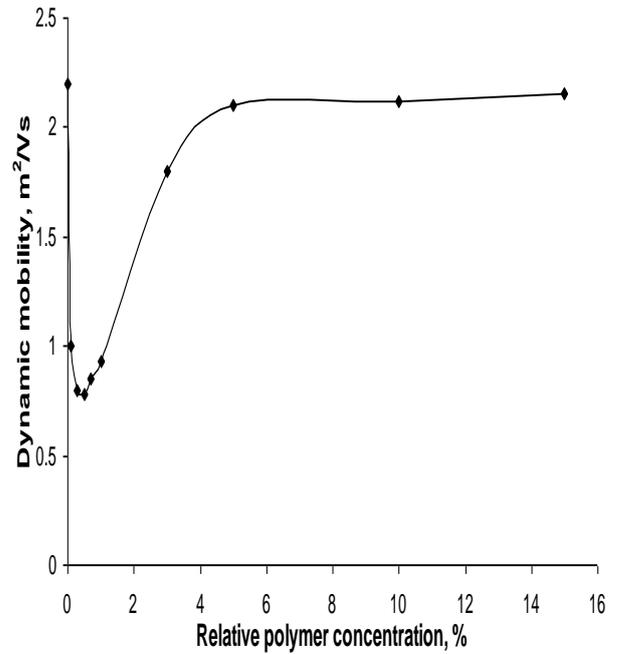
**Table 1: Stability of TiO<sub>2</sub> aqueous suspensions modified by PiBA-PAA block copolymers.**

Polymer	Suspension stability (half-time of the sedimentation, days)	
	Without mechanical treatment	After ultrasonic treatment
PiBA <sub>72</sub>	0.2	4
PAA <sub>28</sub>	2	10
PiBA <sub>53</sub> – PAA <sub>49</sub>	2	14
PiBA <sub>53</sub> – PAA <sub>26</sub>	0.1	1
PiBA <sub>17</sub> – PAA <sub>97</sub>	3	30
PAA <sub>17</sub> – PiBA <sub>72</sub> – PAA <sub>17</sub>	0.3	7

First, as one can see from Table 1, all explored copolymers allow to obtain particle dispersions even in the absence of ultrasonic action while recent data on the application of PMVE containing block copolymers showed the impossibility to obtain dispersions without mechanical treatment [3]. It could be ascribed to that fact that THF used as a solvent of polymer in this study is known to create micelles with water and so provide the transport of the polymer to the pigment surface. Second it is evident that, irrespective of the composition of the copolymer, the ultrasonic treatment substantially enhances the dispersion stability as reflected from the comparison of the sedimentation times for the non-treated and treated systems. The data also infer that an optimal copolymer structure exists with regard to the block length ratio; this is in accordance with previously discussed constitutional effects [3]. Third, there is a pronounced effect of the particle surface nature on the polymer structure acting as the best stabilizer: for hydrophilic TiO<sub>2</sub> dispersions, PiBA<sub>17</sub> – PAA<sub>97</sub> with long PAA block showed good stabilization. ESA investigations of aqueous dispersions of TiO<sub>2</sub>, stabilized by block copolymers of PiBA-PAA, allow to give quantitative data regarding the process of polymer adsorption as reflected both from the dependence of the value of dynamic mobility  $\mu$  on the relative polymer concentration [7] as shown in Fig. 1 and 2, and from the comparison of this dependency for systems without and with ultrasonic treatment.



**Fig. 1: Dependence of the value of dynamic mobility of 1 wt.-% TiO<sub>2</sub> on the relative concentration of PiBA<sub>17</sub> – PAA<sub>97</sub> in aqueous dispersion after ultrasonic treatment.**



**Fig. 2: Dependence of the value of dynamic mobility of 1 wt.-% TiO<sub>2</sub> on the relative concentration of PiBA<sub>17</sub> – PAA<sub>97</sub> in aqueous dispersion after ultrasonic treatment.**

As it can be seen from the comparison of Fig. 1 and 2, ultrasonification has a pronounced influence on the behavior of the particle-polymer dispersion. Before ultrasonic action, the formation of the polymer adsorption layer on the particle surface is reached at 1 wt.-% PiBA<sub>17</sub> – PAA<sub>97</sub> in relation to the particle concentration (saturation concentration as indicated by the unchanged dynamic mobility with further increase of polymer concentration). In the conditions of ultrasonic action, first feature is that the starting dynamic mobility of the pristine TiO<sub>2</sub> is significantly higher, and the saturation of polymer adsorption is reached at only about 5 %. Further portions of polymer do not affect the dynamic mobility. The decrease of the dynamic mobility upon addition of small portions of a polymer is in concordance with the data obtained for PS-PAA block copolymers.

Obviously the ultrasonic action not only increases the pigment surface by creating a more fine dispersion but activates the particle surface as well, consequently leading to definitely higher polymer adsorption comparing to the non-treated samples.

In order to get quantitative information regarding the polymer adsorption as revealed from the ESA data, and to correlate the amount of polymer adsorbed with the dispersing conditions, calculations of the area of the pristine pigment particle surface and of the particle coated with polymer were done for both the systems without and with ultrasonic treatment and related to the amount of adsorbed polymer.

**Table 2: Effect of ultrasonic treatment on the particle diameter  $d_{part}$ , and effect of ultrasonic treatment on the increase of the particle surface area ( $S_{tot}$ ) as well as on the saturation concentration (SC) of added amphipolar copolymer as expressed by the corresponding  $S_{tot}$  and SC ratio; the indexes 1 and 2 refer to the non-treated (1) and ultrasonically treated (2) sample.**

System	Averaged particle diameter $d_{part}$ in $\mu\text{m}$ .		Ratio between particle surface area with and without ultrasonic treatment $S_{tot2} / S_{tot1}$	Ratio between saturation concentration with and without ultrasonic treatment $SC_2 / SC_1$
	Without ultrasonic treatment	After ultrasonic treatment		
TiO <sub>2</sub> + PiBA <sub>17</sub> – PAA <sub>97</sub>	1,2	0,6	2	5

The comparison of the experimentally measured diameter  $d_{part}$  of the polymer coated particles which were obtained by application of ultrasonification (column 3 in Table 2) and without ultrasonification (column 2 in Table 2) shows that smaller particles resulted from the ultrasonification; this was to be expected since ultrasonic treatment is known to cause a breaking of agglomerates/aggregates present in pigment slurries.

The thicknesses of the adsorbed polymer layer as obtained for the TiO<sub>2</sub> pigment dispersions under conditions of ultrasonic treatment in comparison to the systems without ultrasonic treatment are compiled in Table 3. The thicker adsorption layers observed for the ultrasonically treated systems confirm that an activation of the pigment surface occurs by the action of ultrasonic power.

**Table 3: Thicknesses  $d$  of the adsorption layer of the amphipolar copolymer on TiO<sub>2</sub> and CuPc surface for ultrasonically treated and non-treated dispersions as calculated using the saturation concentration value obtained by the ESA measurements (see Table 2).**

System	Thickness $d$ of the adsorption layer without ultrasonic treatment, nm.	Thickness $d$ of the adsorption layer after ultrasonic treatment, nm.	Ratio between the thicknesses of treated and non-treated samples
TiO <sub>2</sub> + PiBA <sub>17</sub> – PAA <sub>97</sub>	5,5	13,6	3,2

**CONCLUSIONS**

A general conclusion that can be drawn from the data obtained is that the increasing of the thickness of the polymer adsorption layers upon ultrasonic treatment is confirmed from both the information obtained from the ESA measurements and from the calculations of the particle surface.

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