The Preparation and Properties of Titanium Dioxide Pigments with Acidic Surfaces

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ABSTRACT

Titanium dioxide pigments used in commercial polymers are generally coated with a neutral, alumina/silica gel-coat to improve the pigment physical properties and also to reduce the chemical activity of the titania surface. Production of an acidic alumina/silica coating on titania pigments gives them a chemical activity similar to that previously found in dry clays. This activity is sufficient to increase greatly the bonding of basic organic materials to the pigment surfaces. The enhanced bonding can lead to materials with highly organophilic surfaces. The property changes in polymer composites brought about by these acidic pigments are discussed.

INTRODUCTION

In recent papers [1-5] we have shown that the chemical activity of a number of inorganic fillers—previously considered to be inert—can

have a considerable effect on the polymer composite properties. Of particular interest in this work was the high acidity of kaolin and other aluminum silicate mineral fillers at low moisture levels ($<1\%$). The reasons for this development of acidity are discussed in Ref. 1-5. By way of contrast, the structurally related magnesium silicates (e.g., talc) show little or no surface acidity [2].

In some polymer composites a pigment or filler with an acidic surface should offer advantages over a neutral material; for example, where the acidity would destroy species responsible for polymer decomposition. However, in selecting pigments and fillers for composites, factors such as the particle size and shape, particle size distribution, and refractive index, as well as price, are usually considered first and the surface chemistry is controlled by expensive additives. In extreme cases the filler cannot be used (e.g., some clays are unsuitable for PVC). Therefore, it would often be desirable to select a pigment or filler for its physical characteristics and to control the surface chemistry by suitable coating procedures.

The formation of neutral, organophilic coatings by modification of a mineral surface with magnesium silicate is described in the following paper. This paper describes methods of producing an acidic surface on titania to give pigments with new and useful properties [6].

DISCUSSION

The titanium dioxide pigments normally used in polymeric coatings and composites are surface modified with 1 to 10% silica/alumina gel coatings [7], emphasis being placed on the desireability of 1) essentially neutral surfaces [8] and 2) a minimum level of photochemical activity of the coated pigment [9]. Earlier results [2, 10] indicated that even after drying silica/alumina-coated titanias contain only a small number of sites of low acidity, and more extensive tests on commercial pigment samples from many sources confirm this (Table 1).

Preparation of Acidic Titanias

Titania pigments with highly acidic coatings were prepared by washing alumina/silica-coated pigments with aqueous acids as described in the experimental section. The major factors important to the development of this acidic surface are the pH used in the process and amount of alumina on the pigment surface. The optimum pH lies between 3 and 5 but depends partly on the time and temperature of treatment. In general, the higher the amount of alumina and the lower the treatment pH, the greater the number of acid sites produced and the higher their strength. However, below pH 3 some of the alumina

on the surface is removed, especially if the treatment is carried out at elevated temperatures or for long times. The type of acid used made no noticeable difference to acidity even when organic acids such as formic and acetic acid were applied (see Table 2).

Higher acidities and more active sites [2] were produced by drying at higher temperatures than the normal 125°C. These very active sites were quickly neutralized on exposure to atmospheric moisture or to other bases. All of the acidity was lost on prolonged exposure to the atmosphere or very active bases, but could generally be recovered by drying. The most acidic pigments produced had acid sites with $pK_a <$ -5.6 and a total acidity (measured by titration with amine to $pK_a > 4$) of 0.04 meq/1 g (of amine); these results are comparable to those obtained with dry clays [2].

The acidity of these pigments after prolonged drying at high temperatures and their formation even when organic acids were used shows that the acidity is due to changes in the aluminum-silicate coating and not to adsorbed acid. Acid treatment of uncoated rutile or anatase did not give pigments with acidic surfaces; thus clearly demonstrating the necessity of having an alumina/silica coating.

Properties of the Acidic Pigments

Polymerization

The acidity of these dry pigments is such that they have been used to initiate cationic polymerization of suitable monomers. The results of these experiments are described in a following paper [11].

Neutralization

As found previously for acidic clay minerals [4], the acidity of the titania can be neutralized with organic bases to provide strongly bonded organophilic surfaces on the mineral. The neutralization effects produced depend on the basicity of the added organic material, its concentration, and the length of its nonpolar section. Amines are by far the most effective bases although the pigments sometimes develop unwelcome tones, probably because of impurities or oxidation products in the amines. Alcohols, though less strongly basic, can often be substituted for the amines to overcome this problem.

For many applications of inorganic fillers and pigments the normally hydrophylic/organophobic surface has to be modified to become organophilic. In most of the presently used systems for modifying titania, only relatively weak bonding occurs between the surface and an amine so hydrophilic organics such as triethanolamine are often used. Compared with nonacidic material, acidic pigments provide strong binding forces for simple organic bases so that long-chain amines or alcohols can be strongly attached, yielding very organophilic materials.

TABLE 1. Acidity of Commercial

Manufacturer	Grade	Maximum acidity as given by pK_a range
Tioxide Australia	R-SM	>4.0
	R-SM2	"
	R-CR	"
	R-CR2	"
	R-CR3	"
	R-CR6	"
	R-CR10	"
	R-CR21	"
	R-HD	3.3 to 4.0
	R-PP5	>4.0
	R-XL	2.8 to 3.3
	A-E	>4.0
	A-LF	"
	A-PP2	"
Tioxide International	R-HD2	"
	R-TC2	"
	R-TC5	"
	R-TC6	"
	R-SM3	"
	R-FC	"
American Potash	Tronox CR-800	"
	CR-801	"
Bayer	R-FD1	"
	R-FD2	"
	R-KB1	"
	R-KB2	"
	R-KB3	"
	R-UF	"
Dupont	R-500	>4.0
	R-900	"
	R-901	"
	R-902	"
	R-960	"

[a]Pigments dried at >120°C for 2 hr before testing by methods used

Titanium Dioxide Pigments[a]

Manufacturer	Grade		Maximum acidity as given by pK_a range
Ishihara	R-780		>4.0
	R-820		"
	R-830		"
Laporte (Australia)	A-G		"
	A-RG		"
	A-RH.20		"
	A-RH.200		"
Laporte (United Kingdom)	Tiona WDB		"
	RG2		"
	RP		"
	RE-30		"
	RH-42		"
	RO-60		"
	RO-676		"
National Lead	Titanox	CL	"
		CLNC	"
		RA-67	"
		RA-51	3.3 to 4.0
		RA-47	>4.0
		RA-44	2.8 to 3.3
New Jersey Zinc	R-760		>4.0
	R-770		"
Titangesellschaft	Kronos	R	"
		RN-45	"
		RN-57	"
		RN-58	"
		RN-59	"
		RN-61	"
Thann et Mulhouse	RL-17		"

in Ref. 2.

TABLE 2. Acidity of Dry Alumino-Silica Coated Titanias

Pigment No.	Acid wash[a] pH	% Al_2O_3 After washing	%SiO_2	pKa range of strongest sites	Total acidity[b] to pKa -3.0 (meq amine/g)	Total acidity[b] to pKa 4.0
No. 1	Nil	2.51	0.32	>4.0	Nil	Nil
	3.5	"	"	-3.0 to -5.6	0.005	0.015
No. 2	Nil	3.45	8.30	2.8 to 3.3	Nil	0.005
	5.5	"	"	1.5 to -3.3	Nil	0.010
	4.5c	"	"	-3.0 to -5.6	0.020	0.025
	3.5	"	"	-3.0 to -5.6	0.020	0.025
	3.5d	"	"	-3.0 to -5.6	0.025	0.030
	2.5	"	"	-5.6 to -8.2	0.030	0.035
	1.5	2.5	8.19	-3.0 to -5.6	0.020	0.025
No. 3	3.5d	0.58	3.80	-3.0 to -5.6	0.010	0.015
No. 4	3.5d	2.21	0.09	-3.0 to -5.6	0.020	0.025

aDilute sulfuric acid washed and then dried at 125°C for 2 hr before testing.
bAcidity determination methods described in Refs. 2 and 12.
cDilute acetic acid used instead of sulfuric acid.
dDried at 250°C for 1 hr before testing.

TABLE 3. Viscosity of Treated Titania Dispersions (30% w/w in Paraffin Oil)[a]

Treatment of titania (No. 2)	Yield stress (dyne cm^{-2})	η_∞ (poise)
Undried	1420	2.72
Dried	806	2.25
Treated with 0.5% w/w heptanol when dry	225	2.25
Acidified[b] at pH 3.5, dried	221	2.51
Acidified,[b] dried, treated with 0.5% w/w heptanol	63	2.52
Acidified,[b] dried, treated with 0.5% w/w decylamine	58	2.54
Acidified,[b] dried, coated with 2.9% polyisoprene	15	2.34
Acidified,[b] dried, coated with 4.1% piperylene	<1	2.34
Silane treated titania (commercial)	120	2.25

[a]Measured in Ondina oil 33 at 23°C using a Haake Rotovisco viscometer at a series of shear rates. The resulting flow curves were fitted to Casson's equation, and the yield stress and viscosity at infinite shear rate were calculated [4].
[b]Acidified at pH 3.5.

A measure of organophilicity of these coated pigments is their rheology in mineral oil dispersions (detailed studies of the rheology of minerals in organic fluids and the methods used have been published elsewhere [4]). Table 3 gives a comparison of the effects of added bases on the yield stress of acidic and nonacidic titania dispersions in mineral oil. The low initial yield stress of the acidic pigment without any base present may be due to repulsion of similarly charged particles.

Like kaolin [4], the viscosity improvement for titania dispersions in mineral oil reaches an optimum value with simple amines or alcohols containing more than about seven carbon atoms in the chain. The viscosity of paraffin oil dispersions of such amine-coated, acidic titanias is considerably lower than that of similar dispersions of a commercial silicone-treated titania which is recommended for use in nonpolar polymers. Higher loadings of base give lower yield stresses, but the improvement levels off at about 3% w/w of base. The table

also shows the effect of various other treatments on the rheology of titania dispersions. Polymer-coated acidic pigments have the best rheology in paraffin oil, but some of their pigmentary properties are still unsatisfactory [11].

The organically treated acidic pigments do not pick up significant amounts of water on standing, so the properties of their dispersions do not change with pigment ageing, unlike dispersions of uncoated pigments. An indication of the importance of water adsorption is seen in the difference in yield stress of the first two pigment samples in Table 3.

For composites or coatings where pigment-polymer interaction is desirable, the acidic pigments should interact with basic groups in suitable polymers. Recent results with acidic clay minerals and new basic polymers used as binders in the paper coating area [13] suggested that similar improved binding might also be obtained with acidic titanias. That the acidic titanias react as predicted can be demonstrated by the ready flocculation of their aqueous dispersions by small amounts of basic polymer emulsions (e.g., Gentac Latex). Larger amounts of these emulsions cause redispersion as the individual titania particles are encapsulated by strongly bonded polymer which remains attached when the titania is removed from the water and dried. No such flocculation changes were observed with the nonacidified titania dispersions, and very little of the latex was absorbed on the surface. The difference in polymer binding was highlighted when the treated materials were redispersed in paraffin oil (30% solids); the yield stress using the coated acidified pigment was 112 dyne cm^{-2} compared to 635 dyne cm^{-2} for the coated, nonacidified titania.

Photochemical Effects and Peroxide Decomposition

The photochemical effects of titanium dioxide pigments are extremely important in the coatings industry as they have a direct bearing on the durability of such coatings. From considerable study of the surface photochemistry of titanium dioxide in organic systems, mechanisms of photochemical decomposition have been proposed [14-17]. However, it is generally believed that in the best of the pigments the titania surface is completely covered [18] with an alumina/silica layer, the structure of which is unknown. This layer also contains minor but important constituents, such as zinc oxide (added as a rutilizing catalyst), which add to the surface complexity.

Of the tests used in industry to measure photochemical activity and to relate this to durability [17, 19, 20], we have used the simplified method of Poisson et al. [21], which consists of a straight comparison of the colors produced by irradiation of a mixture of titania, linseed oil, and leuco base. This system is believed to parallel the decomposition

TABLE 4. Photochemical Activity of Treated Titania Pigments

Pigment used	Color rating[a]		Weatherbility[d]	% Zinc[e]
	LMG[b]	LCV[c]		
Uncoated rutile	1	2	Poor	0.92
Alumino/silicate coated titania 1	6	7	Very good	0.88
Alumino/silicate coated titania 2	7	5	Good	0.71
Uncoated rutile acid washed	10	10	Extremely poor	0.49
Titania 1 acid washed	8	8	Very poor	0.60
Titania 1 acid washed, coated with 0.1% Decylamine	0	0	Poor	0.60
Titania 1 double coated then acid washed	3	2	Very good	0.79

[a]Arbitrary rating of color intensity from 0 to 10; 0 being no color and 10 the most intense color developed.
[b]LMG is Leuco malachite green.
[c]LCV is Leuco crystal violet.
[d]Assessment of tensile properties after exposure of high density polyethene panels in a weatherometer with a dew cycle for 100 hr.
[e]Determined by atomic absorption spectrometry.

of paint systems where titania pigment accelerates the oxidation of susceptable organic bonds. In the case of the test, the final product is a colored dye which by its intensity gives an idea of the photochemical activity of the pigment. Our results with various commercial pigments and with acidified pigments are shown in the first two columns of Table 4.

To ascertain whether the use of acidic titanias would improve polyethylene durability by causing heterolytic decomposition of peroxides and hydroperoxides produced by oxidation, the above results were compared with those from an accelerated weathering test (Maar Weatherometer) using high-density polyethylene panels containing 2 and 10% titanium dioxide. No difference between the levels of titania was noticed except a general increase in weathering at the higher level.

The correlation between weathering tests and photochemical activity in Table 4 was generally poor. However, for the early acid-washed titania pigments, which gave extremely brittle panels, it was shown that the acidification step had removed a considerable proportion of the surface zinc. Acid treatment of uncoated rutile removes only zinc and does not give an acidic surface; the poor performance of polymers containing this product shows the great influence of zinc on photochemical activity and durability. Loss of zinc during acid treatment could be partly overcome by using a double coating of alumina/silica to protect the zinc during acidification. This type of acidic pigment appeared to have improved photochemical activity and the durability in polyethylene expected. Durability studies in other types of polymer are also being carried out, and these would be expected to give widely different results depending on the major decomposition mechanisms in these polymers.

From previous work with clay minerals [5] it was predicted that pigments with acidic surfaces would catalyze the nonradical breakdown of peroxides. However, the effects, measured by the methods used in our earlier work, were smaller than expected (Table 5), and again it appears that other factors in the surface coating are influencing the results.

Minerals other than titanium dioxide have also been coated with acidified alumina/silica coatings. These include talc and barium sulfate, and they have been found to behave in a similar way to the treated titanium dioxide pigments. Detailed information on these materials will be reported in subsequent publications.

Conclusions

Novel titanium dioxide pigments with activated alumina/silica coatings can be produced by the methods described above. Their chemical properties are similar to those of acidic clay minerals in

TABLE 5. The Effect of Acidic Titanias on the Rate of Breakdown of Cumene Hydroperoxide[a] at 50°C

Titania[b]	% Remaining after 24 hr
Uncoated titania	95
Coated titania No. 1 unacidified	88.5
acidified	87
Coated titania No. 2 unacidified	67.5
acidified	59

[a]Concentration used = 0.4 mmole peroxide/g titania in 10 ml benzene.
[b]Dried at 125°C for 2 hr.

that they catalyze the cationic polymerization of hydrocarbon
monomers and the heterolytic breakdown of organic peroxides. How-
ever, the interactions of acidic titania pigments with organic polymeric
media are complicated by changes to the photochemically active surface
of the pigment. Because of these aspects the acidic pigments should
have properties complimentary to the magnesium silicate coated pig-
ment, which have chemically inert coatings [22]. Acidic pigments on
further modification with monomeric or polymeric organic amines or
hydrocarbon monomers can produce organophilic minerals with
strongly bonded organic layers on the surfaces.

EXPERIMENTAL

Materials

The pigments used were commercially available titania pigments
donated by Tioxide Australia Pty. Ltd., Burnie, Tasmania. The un-
coated Rutile was RSM; titania 1, RCR-6; titania 2, RXL; titania 3,
RCR; titania 4 and 5 were experimentally coated RSM; silane-treated
titania, RPP-5; uncoated anatase, A-E; and anatase 1, APP-2. The
paraffin oil used was Ondina 33 supplied by Shell Petroleum Co., and
Gentac Latex was supplied by General Tyre and Rubber Co.
All the monomers and amines were AR quality, further purified
and thoroughly dried by standard methods. The indicators were those
described by Benesi [12] and were recrystallized to have melting
points corresponding to those reported in the literature, as were
Leuco crystal violet and malachite green.

Acidity Titration Procedure

The titration procedure was similar to that used by Benesi [23]
except for the minor modifications reported in a previous paper [3].

Preparation of Acidic Pigments

The following standard procedure was adopted for the preparation
of acidic pigments. The alumina/silica coated titania (1 kg) was well
dispersed by vigorous stirring in dilute sulfuric acid (4l, pH, 3.5) and
allowed to settle for 1 hr before filtering. The pigment was washed
with distilled water to remove excess acid and while still damp washed
with AR acetone (organic impurities in the solvent can react with the
acidic surface) to prevent agglomeration. The titania was then dried
for 24 hr at 130°C and stored in sealed containers.

Paraffin Oil Rheological Tests

The flow properties were measured with a Haake Rotovisco using the procedure and calculations described in detail in a previous publication [4].

Reaction with Leuco Bases

The leuco dyes were dissolved in linseed oil and the dry titania pigments were tested by the procedure of Poisson et al. [21]. The color developed after 1 hr exposure to glass-filtered sunlight was compared with that of a set of arbitrary standards, starting with no color as 0 and ending with the color developed by acid-washed un-coated rutile as 10.

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