Magnesium-Silicate Coated Minerals as Polymer Fillers and Pigments

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ABSTRACT

The chemical reactivity of many fillers and pigments used in commercial polymer formulations often causes detrimental polymer-filler interactions unless compensating additives are applied during compounding. A method of reducing these interactions by forming stable, inert magnesium-silicate gel-coatings on the surface of the mineral fillers is described. Various methods of measuring this reduction in chemical activity are discussed. Considerable changes in rheological properties of the mineral dispersions in paraffin oil and water are observed.

INTRODUCTION

Previous work [1-5] has shown that many of the "inert" mineral fillers used in plastics become quite reactive chemically under the

normal processing conditions. This is particularly so with aluminum-silicate minerals, such as kaolin [5], or with minerals which have activated alumina/silica coatings [6]. In contrast, the magnesium-silicate minerals, for example talc, are generally neutral and have little chemical effect in filled plastics. Talc is also distinguished from the aluminum silicates by its hydrophobic/organophilic character.

Most pigments or fillers are selected for properties other than their surface chemistry (e.g., particle size, shape and size distribution) but often it would be desirable to retain these properties while modifying the surface chemistry. In order to control the chemical activity of fillers and to improve their performance in plastics, we explored the possibilities of forming talc-like, magnesium-silicate, gel-coatings on various active fillers and pigments [7].

DISCUSSION

The formation of inorganic gel coatings is a common industrial process for modifying the properties of commercial pigments. For example, alumina/silica coatings are normally used on titanium dioxide pigments to improve their physical properties in organic media and also to moderate the photochemical activity of the under-lying titanium dioxide [8]. For use in nonpolar organic media such as hydrocarbon polymers, fillers and pigments can be further improved by treatment with organic compounds having polar groups (to bond to the inorganic mineral surface) attached to long-chain hydrocarbon sections (for polymer compatability). These materials have a number of disadvantages, which include instability at high temperatures, rather weak bonds between the filler surface and the organic compound, as well as relatively high cost. Hence a cheap, stable, inorganic coating which would give organophilic properties is of considerable interest.

Methods of Forming Magnesium-Silicate Coatings

The coatings were formed by the addition of sodium metasilicate solutions to mineral dispersions which contained a soluble magnesium salt; generally magnesium sulfate. Addition of the magnesium sulfate to a dispersion of the mineral in sodium silicate solution was equally satisfactory, although pH adjustment tended to be more complex. For coating clay the latter method was preferred because sodium silicate lowers the suspension viscosity and gives easier processing. In the absence of suspended minerals the reaction produces a white gelatinous precipitate of hydrated magnesium silicate [9]. The

standard techniques for gel coating used in the production of titanium dioxide pigment can be used to improve the consistency and stability of the coating, these include vigorous stirring and adjustment of temperature, pH, and time of deposition.

Good coatings, containing almost all the magnesium and silicate ions used, could be obtained provided the final pH in the slurry (before filtration and washing) was between 8.5 and 11. Below pH 8.5 a considerable quantity of the magnesium redissolves and silica-rich coatings are obtained (Table 1). This solubility of the magnesium ion decreases greatly on heat treatment of the coated mineral. Other variables, such as temperature changes during re-action, speed of filtering, and type of washing method, also affect the coating, as shown by changes in the rheological characteristics of the pigment dispersions.

The coating procedure is not restricted to titania; a number of other minerals (Table 2) were similarly coated. The standard coat-ing method eventually adopted gave a final coating of approximately 4% magnesium silicate. The ratios of starting materials used, although not stoichiometric, gave a final solution of pH 10 and a coating which contained approximately stoichiometric quantities of magnesia and silica. Heavier coatings could be readily applied to all minerals; however, the standard (4%) coating generally gave the optimum balance between properties and cost.

The coated material was washed with distilled water to free it of excess soluble ions and dried. The drying procedure is also an important variable as magnesium-silicate coatings continue to lose water at temperatures up to $700°C$ and beyond. Thermogravimetric analysis (Fig. 1) shows that this is a characteristic of freshly precipitated, hydrated magnesium silicate, whereas precipitated aluminium silicate loses essentially all its water by $\sim 125°$. The effect of drying on the properties of the coated mineral will be dis-cussed in the following sections.

Electron microscopic investigations of magnesium-silicate coated titania pigments indicated that the surface coating was similar (although slightly thicker and less dense) to those obtained on com-mercial alumina/silica-coated pigments at similar loading levels.

TABLE 1. Composition of the Coating Obtained on Titania vs Final pH[a]

pH	% MgO	% SiO$_2$
7.1	0.38	1.65
8.1	0.74	1.78
10.0	1.25	1.87

[a]By standard method described in Experimental Section.

TABLE 2. Composition of the Coating Obtained on Various Minerals

Mineral (500 g)	Wt of magnesium sulfate used (g)	Wt of sodium silicate used (g)	% MgO[a]	%SiO$_2$[a]
Clay	40	40	1.34	b
	80	80	2.60	b
Rutile	40	40	1.32	1.98
	85	106	3.06	5.25
Anatase	40	40	1.34	2.34
Calcium carbonate	40	40	1.37	2.18
Mica	40	40	1.55	b

[a]Determined by atomic absorption spectroscopy; for minerals containing magnesium and silica, the composition of the coating was obtained, where practicable, by difference.
[b]Not attempted because the mineral base contains large amounts of silica.
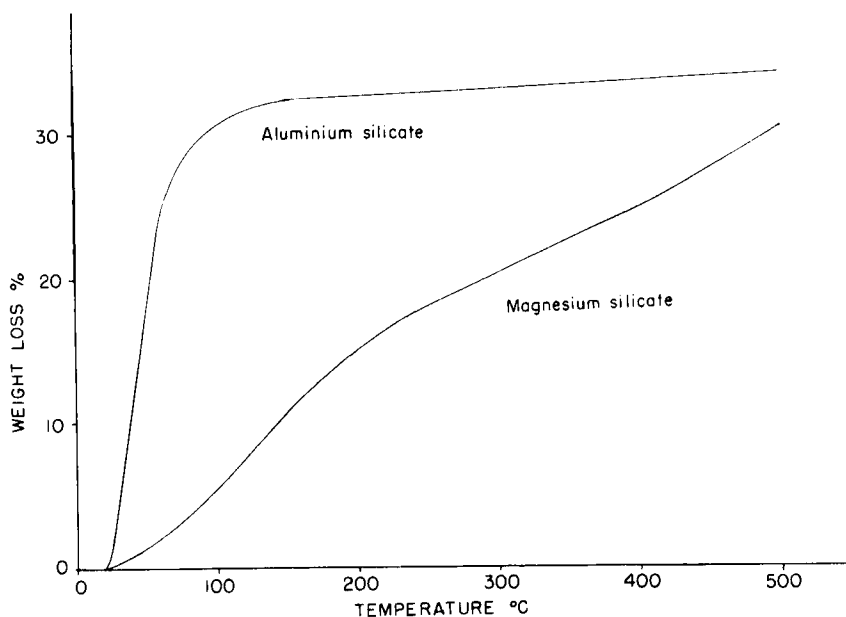

FIG. 1. Thermogravimetric analysis of freshly precipitated silicates (air, 2.5°C/min).

Properties of Magnesium-Silicate Coated Minerals

Rheology

In Organic Media. One of the major benefits of talc as a filler in organic polymers is its organophilic behavior without the need for additional coatings or additives, a property which the magnesium-silicate coatings on other minerals were designed to duplicate. The rheological properties of dispersions of these coated minerals in various organic media were therefore used to determine the changes in organophilicity produced by different coatings. The results reported here are mainly concerned with the uses of paraffin oil as the dispersing media. This was chosen as a guide to filler behavior in nonpolar polymers [4]. Yield stress values for dispersions in paraffin oil have been shown [4] to be a good measure of the organophilicity of the dispersed minerals. Table 3 shows the reduction in yield stress resulting from the increased organophilicity

TABLE 3. Flow Curve Parameters for 30% Mineral Dispersions in Paraffin Oil (23°C)

Mineral	Yield stress (τ_0, dyne cm^{-2})	Viscosity at infinite shear rate (η_∞, poise)
Kaolin	529	2.65
Kaolin[a] (magnesium-silicate coated)	166	2.25
Rutile (uncoated)	>3000	
Rutile (commercial, alumino-silicate coated $\simeq$ 4%)	1850	2.25
Rutile[a] (magnesium-silicate coated	572	2.20
Anatase (uncoated)	990	1.84
Anatase[a] (magnesium-silicate coated)	154	2.13
Calcium carbonate (whiting)	150	2.31
Calcium[a] carbonate (magnesium-silicate coated)	83	2.37
Barium sulfate	170	2.10
Barium sulfate[a] (magnesium-silicate coated)	64	1.88
Talc	144	2.56

[a]Coated with the general standard magnesium-silicate coating, $\simeq$ 4%.

of various minerals after being coated with ~4% magnesium silicate.

Because the yield stress depends markedly on such factors as particle size and size distribution, identical mineral samples were used for coating and test comparison. The viscosity at infinite shear rate (η_∞) is mainly a measure of particle size and concentration; large reductions in η_∞ usually indicate particle agglomeration. This does not appear to occur in these coated samples.

Besides these gross changes in the surface properties of the minerals, smaller changes due to processing variables were also studied by the same techniques. Postheating of the coatings considerably altered the properties of the minerals. Table 4 shows the effect of heat treatment on the yield stress of coated titania. Many other properties of titania pigments were improved after heating to ~250°C, but further heating resulted only in degradation of the properties. Properties which showed this type of improvement were the dry brightness, tint strength, and opacity in plastics. The sharp change in η_∞ for coated titania heated at 700°C was due to the formation of hard agglomerates. This and degradation of the surface coating may also be responsible for the increase in yield stress with higher temperatures.

The washing process was critical when coating clay minerals

TABLE 4. Effect of Heat Ageing on a Coated Titania. Rheology of 30% Dispersions in Paraffin Oil

Mineral treatment[a]	Yield stress (dyne cm^{-2})	Viscosity at infinite shear rate (η_∞, poise)
Uncoated/untreated	>3000	–
Coated titania[b]		
100°C/24 hr	1590	2.56
200°C/3 hr	1380	2.43
300°C/1 hr	1150	2.76
400°C/1 hr	1210	2.57
500°C/1 hr	1235	2.53
700°C/1 hr	2110	1.25

[a]After heat treatment the materials were reequilibrated at 23°C and 60% RH.

[b]Coated with the general standard magnesium-silicate coating, $\simeq$ 4%.

because the presence of residual adsorbed ions has a marked effect
on rheological properties of clay surfaces [10]. For this reason small
changes in the rheological properties caused by processing changes
during coating were not considered reliable indicators of property
changes in this mineral. For example, heat treatment of coated
clay only caused significant changes and general property degradation
above 500° C.

In organic media more polar than paraffin (polyester solution,
linseed oil, polymethyl methacrylate, and alkyd resin) the viscosity
of magnesium-silicate coated minerals was again lower than that
of uncoated minerals. The improvements here were significant
but of a lower order than those in the nonpolar paraffin oil.

In Aqueous Media. Aqueous dispersions of minerals which
have been coated with magnesium silicate might be expected to show
less favorable rheological behavior than dispersions of uncoated
minerals. However, as shown in Table 5, the reverse is true. In
the cases tested, the reductions in viscosity and yield stress were
so great that it was not possible to carry out the determinations at
the same mineral concentrations. With kaolin almost the same
reductions in viscosity can be brought about by the addition of 1%
or greater of sodium silicate [10] but such dispersions are
pseudoplastic whereas those of the magnesium silicate-coated
materials are not noticeably shear sensitive.

TABLE 5. Flow Curve Parameters for Mineral Dispersions in Water

Mineral	Mineral concentra-tion (%)	Yield stress (dyne cm^{-2})	Viscosity at in-finite shear rate (η_∞, poise)
Anatase	40	1114	0.16
Commercial aluminosilicate coated anatase	50	319	0.04
Magnesium-silicate coated anatase[a]	55	220	0.04
Kaolin	50	1926	0.16
Kaolin with 1% sodium silicate	65	782	0.01
Magnesium-silicate coated kaolin[b]	65	164	0.09

[a]The mineral concentration was varied in 5% steps to get measur-able viscosities.

[b]Coated with the general standard magnesium-silicate coating, ≃ 4%.

In magnesium silicate-coated clays the surface charge is probably blocked by an inert layer of insoluble gel, so that particle interaction is lowered and viscosity decreased. With uncoated clays the addition of sodium silicate is known to produce multiple layers of sodium ions on the electrical double-layer and this, in the presence of excess electrolyte, decreases the viscosity of the dispersion at high shear rates or in dilute solutions. However, at low shear rates this provides a weak gel structure which accounts for the pseudoplastic phenomenon [10]. Addition of sodium silicate to dispersions of the coated clays improves the viscosity further but does not cause pseudoplasticity. Other minerals have less highly charged surfaces so the effect of the coating is not as marked.

Surface Chemistry of Coated Pigments

The above results show that magnesium-silicate coatings render the mineral surface more organophilic, but this type of coating should also render minerals with high chemical activity relatively inert. Clay minerals, such as kaolin, can be very acidic when dry [1-5], and uncoated titania has high photochemical activity in organic media [11]. Changes in these properties were studied for the magnesium-silicate coated minerals.

Acidity

As seen in Table 6, Hammett indicators show that the acidity of magnesium-silicate coated kaolin is drastically reduced compared to that of the uncoated material. Another indication of acidity in clay minerals is their ability to decompose organic peroxides. Dry kaolin decomposes cumene hydroperoxide rapidly and exothermally but after coating with magnesium silicate little or no decomposition of the peroxide takes place. This effect could be of considerable economic importance in such areas as the curing of rubber and polyesters, and the decomposition of polyvinyl chloride and polyethylene during processing.

Photochemical Activity

Numerous tests have been used to measure the photochemical activity of titania pigments in organic media [12, 13]. One of the simplest to use is that of Poisson et al. [14] which relies on the forma-tion of a colored dye from certain leuco bases on the interaction with pigment and sunlight. Magnesium-silicate coated titanias promoted less oxidation of the leuco bases [6] to the colored dyes than commercial alumina/silica-coated titanias or uncoated titania. The test was useful in assessing the quality of the coating as incomplete surface coverage of the active sites on the titania surface gave pigments with greater dye color formation than did good coatings.

TABLE 6. Acidity Changes in Coated Kaolin[a]

Property	Uncoated kaolin	Magnesium silicate[b] coated kaolin
Maximum acidity[c] (pK_a of strongest acid site)	<-8.2	4.0 to 3.3
Total acidity[d] $< $ pK_a 4.0	0.04 mmole/g	<0.005 mmole/g
% Decomposition of CHP[e] in 24 hr	57	0

[a]Dried at 125°C for 2 hr.
[b]Containing 1.52% MgO.
[c]Using Hammett indicators [15].
[d]Titration with n-butylamine [2].
[e]Cumene hydroperoxide. The conditions used were the same as in Refs. 5 and 6.

TABLE 7. Gelation Times of Mineral Filled (20%) Polyester Resin (25°C)

Filler	Treatment		Gelation time (min)
Kaolin A	None		930
	Magnesium-silicate coated	(2.45% MgO)	165
		(1.38% MgO)	265
Kaolin B	None		770
	Magnesium-silicate coated	(0.93% MgO)	140
	1% Octylamine		130
	Magnesium-silicate coated heated to 300°C/1 hr	(0.93% MgO)	330
Anatase	None		321
	Magnesium-silicate coated	(1.34% MgO)	168
Rutile	None		321
	Commercial aluminium-silicate coated	(2.51% Al_2O_3)	210
	Commercial silane-coated titania		141
	Magnesium-silicate coated	(1.39% MgO)	132
Calcium carbonate (whiting)	None		129
	Magnesium-silicate coated	(1.74% MgO)	123
		(1.50% MgO)	137

Gelation of Polyesters

The effects of magnesium-silicate coated minerals on the gelation behavior of a commercial polyester were also studied in a system comprising polyester resin, 20% filler, a peroxide initiator (0.25% cumene hydroperoxide) and a cocatalyst (0.01 mole % cobalt naphthenate). Table 7 shows the effect of magnesium-silicate coating is greatest on the very reactive minerals such as clay and anatase, and less on rutile and calcium carbonate. A comparison between magnesium-silicate coated kaolin and an amine-neutralized sample of the same clay indicates that the coatings are comparable in reducing the activity of the kaolin acidic sites. Some of this protection appears to be lost as the coating is heated to high temperatures but similar conditions would eliminate organic coatings.

The magnesium-silicate coatings reduce the activity of titanium dioxide to the level of the least active commercial material (in this formulation). With calcium carbonate the changes are insignificant as expected for a material which is relatively inert in this type of system. In practice use of these coated minerals may permit a reduction in the number or amount of additives normally needed when particular fillers are used in resin systems.

Miscellaneous Tests

The magnesium-silicate coated minerals were noticeably easier to process as fillers in polyethylene. The composites formed with coated kaolin were light-cream colored unlike the grey tone obtained with uncoated clay, especially at higher (40%) clay concentrations. These color differences were partly due to initial decomposition of the polyethylene by the uncoated clay, and partly to masking, by the white magnesium-silicate layer, of the color caused by clay impurities. Similarly in polyvinyl chloride (rigid and plasticized), the reduced acidity of magnesium-silicate coated clays gave less polymer decomposition. Hence there exists the possibility of reduction in the stabilizers used and formulation costs.

In polyethylene and polyvinyl chloride, mechanical properties such as tensile and impact strength were unaffected as would be expected for a coating which does not interact chemically with the matrix polymer [16].

Magnesium-silicate coated titania pigments were tested for pigmentary properties such as reflectivity, tint strength, color, and opacity in plastics. Some of the coated materials were equivalent to good commercial aluminum-silicate coated pigments and much better than the uncoated minerals. Tests in a carbon-arc weatherometer showed that magnesium-silicate coated minerals equalled aluminum-silicate coated rutile pigments in durability properties in filled polyethylene panels.

Studies of the properties of other magnesium-silicate coated minerals are continuing.

EXPERIMENTAL

Materials

The pigments used were commercially available titania pigments donated by Tioxide Australia Pty. Ltd., Burnie, Tasmania. The uncoated rutile was RSM; rutile 1, RCR-6; uncoated anatase, A-E; and anatase 1, APP-2. The kaolin used was Rodda 37 from Steetley Australasia Pty. Ltd., Melbourne, and the calcium carbonate filler was Whiting 25 from the same supplier, as was the barium sulfate filler BA-10. The reagents used were all obtained from BDH Ltd. as Analar reagents, and the paraffin oil was Ondina 33 supplied by Shell Petroleum Co.

The indicators were those described by Benesi [15] and were recrystallized to have melting points corresponding to those reported in the literature. Leuco crystal violet and malachite green were recrystallized to the melting points reported in the literature.

The polyester used was a commercial resin, Crystic RP-433 from Monsanto Australia, Melbourne, with 0.01 mole % cobalt naphthenate accelerator to which was added 0.25% cumene hydroperoxide initiator at the start of a gelation test.

Coating Procedure

The following standard procedure was generally used: The mineral filler (500 g) was suspended in water (3 liters at 70°C) and stirred vigorously as a solution of magnesium sulfate heptahydrate (40 g in 200 ml of water) was added over 20 min. Sodium metasilicate pentahydrate solution (40 g in 200 ml of water) was added slowly (20 min) to the well-stirred suspension and after further stirring (while cooling for 1 hr) the solution was allowed to stand for 2 hr before being filtered. For other types of coatings where the final pH was considerably higher than 10, the pH was adjusted to 9 to 10 before filtering by the addition of dilute sulfuric acid. The coated mineral was washed with slightly basic (pH 8, ammonia) water, and dried at 125°C overnight and then at ~250°C for 1 hr. With titania an acetone wash was carried out after the water wash as this prevented the formation of hard agglomerates on drying. On standing in unsealed containers, the minerals absorbed small quantities of water which could be readily removed on drying at 125°C for 2 hr.

Analysis of Coating Constituents

The composition of magnesium-silicate coatings was determined by atomic absorption spectroscopy, using a Varian-Techtron AA5 instrument, and the methods described by Nesbitt [17], with minor modifications.

Evaluation of Coated Minerals

The flow properties of mineral dispersions in paraffin and linseed oil [4], the acidity measurements [2], and the reactions of the minerals with leuco dyes [6] were studied as previously described.

Gelation Times

The gelation times were measured on a standard Tecam GT3 gelation timer from Techne, Cambridge, England. The polyester mixtures contained 20% by weight of the pigment which was mixed into the resin before the peroxide initiator addition. The tests were carried out in a thermostated bath kept at 30° C.

ACKNOWLEDGMENTS

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