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Stabilization mechanism of main paint pigments

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ABSTRACT

Different types of minerals in varying amounts are used in paint formulations depending on the paint characteristic. While titanium dioxide (TiO_2) is used as a main pigment to improve the paint properties, some minerals such as calcite and calcined kaolin are used as a filler to decrease the cost of the paint, and in some cases as a substitute for TiO_2. An important criterion for developing paint formula, especially for architectural ones, is to load maximum amounts of mineral pigments or fillers as much as possible to satisfy the rheology of the paint. Appropriate type and amount of dispersants is crucial at this stage to get the proper flowability at high amount of pigment and fillers.

Polyacrylic acid sodium salt (NaPAA), a well-known dispersant, is generally used as a commercial dispersant in various paint formulations. Interaction of NaPAA with a group of minerals as single or mixture will be rather different. In the case of paint, as a variety of minerals and reagents are available in a mixture, in order to improve the paint formulation, this complex system should be revealed step by step. In the present study, the interaction of single minerals, titanium dioxide (TiO_2), calcined kaolin (C.Kaolin), ground calcite (GCC) and their mixtures as TiO_2 + GCC, TiO_2 + C.Kaolin and TiO_2 + GCC + C.Kaolin in the presence of NaPAA was investigated in terms of adsorption, rheology, and electrokinetic phenomena. The results showed that adsorption plateau, zeta potential and viscosity values of the mixtures were very close to the arithmetic mean of the individual minerals of the mixtures. The most attractive mineral ingredient for NaPAA was TiO_2, followed by GCC and C.Kaolin. The mixture of minerals behaved differently at the same dosage of NaPAA compared to the single minerals. It is thus important to adjust the minerals mixtures and dispersant type and dosage to closely tune the paint properties. This study clearly revealed that it is more viable to adjust the desired paint properties using a mixture of minerals of different surface properties than a single mineral.

1. Introduction

A typical paint is a mixture of pigment particles, polymers, polyelectrolytes, and surfactants with complex colloidal properties. While surfactants are usually used to control the flocculation and wetting properties, polymers are used to control rheological properties [1].

The interaction of surface active materials in paint media can be both physical and chemical in nature. Knowledge of adsorption properties of polyelectrolytes and surfactants onto particles is crucial to reveal their interactions. Any interaction of such ingredients in a mixed form is more complex than a single system as it probably involves synergistic effect among chemical additives and/or particles. It is well known that adsorption mechanism of a polymer used as a dispersant on an inorganic mineral can be affected both positively and negatively by another polymer or a surfactant that would be present in the media [2]. Santhiya et al. [3] showed that adsorption isotherms of PAA on Al_2O_3 below pH 7 exhibited Langmuir type isotherms whereas the compatibility of the Langmuir model decreased at pH = 7-9. They also concluded that adsorption of PAA on Al_2O_3 remained the same in the presence of PVA while the adsorption density of PVA on Al_2O_3 decreased with PAA in the same medium [3].

Bing et al. [4] showed that stabilization of TiO_2 particles was positively affected by a mixture of two different polymers (NaPAA and N-Polyethylene glycol) due to their synergetic effect. Sequence of addition of polymers was also found important for stabilization; it was better to add NaPAA first, and then polyethylene glycol [4]. Portet-Koltalo et al. Portet-Koltalo et al. [5] found that while adsorption of nonylethylene glycol *n*-dodecyl ether ($C_{12}E_9$) on silica surface at low concentration induced the adsorption of sodium dodecylsulfate (SDS), mixed surfactant aggregates at higher concentration desorbed from the surface.

Although adsorption and interaction studies of polymers and surface active agents on a single particle have been largely performed, interaction of the same species with a mixture of more than one type of particles is rare in literature. It should be noted that mixture of mineral

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particles are very common in a variety of applications such as paint, plastics and paper. Li and Tripp [6] investigated adsorption mechanism of NaPAA and poly (dialkyl dimethyl ammonium) chloride on a mixture of TiO_2 and SiO_2 by IR spectroscopy. No transition of NaPAA from TiO_2 to SiO_2 surfaces after adsorption of NaPAA onto TiO_2 surface was noted.

The contribution of individual and mixture of particles using sedimentation, viscosity, and liquid-limit tests was shown by Palomino et al. [7]. Kaolinite, calcium carbonate, and kaolinite-calcium carbonate mixtures were used to exemplify the interparticle interactions and identify the role of mineral surface-fluid effects, particle geometry, relative particle size, and solids content. While electrostatic interactions acted as the effective mechanism at low solids for the kaolinite-calcium carbonate mixture, the effect of specific surface area was shown to govern the high solids contents [7].

Although competitive adsorption of different surfactants or polymers was investigated, understanding of adsorption of polymers or surfactant onto different mineral particles used in paint formulations is still not well advanced to reveal the complex interactions in paint media. In this study, the adsorption of NaPAA onto TiO_2, GCC and C.Kaolin, commonly used pigments and extenders particles in waterborne paints, was systematically studied. Suspensions of each individual particle and their mixture were compared in the light of adsorption, viscosity and zeta potential measurements. To our knowledge, there is no specific study that identifies the properties of mixed mineral suspensions in the presence of NaPAA as a dispersant in paint related systems.

2. Experimental

2.1. Materials and methods

Three different kinds of minerals, TiO_2, GCC and C.kaolin generally used in paint as pigment and filler, were selected to investigate their interaction mechanism with NaPAA both in individual and mixed forms.

TiO_2 (Tronox CR823) is a commercial pigment used in paint applications. Production of paint grade TiO_2 is accomplished by chloride process by the manufacturer. Zirconia and alumina coatings are also applied on TiO_2 surface to create more durable pigments in paint medium. The TiO_2 content, oil absorption and refractive index of the pigment were 95%, 19 mL/100 g and 2.7, respectively.

GCC (N95) and C.Kaolin (Microbrite® C80/95 C1) were obtained from Som Group Inc. and Microns Inc. in Turkey, respectively. GCC is a natural ground calcium carbonate without any surface treatment. Its d_{50}, d_{80} particle size and specific surface area (BET) were found as 0.9 µm, 3.0 µm and 1.71 m^2/g, respectively. All the particles used in the study are free of impurities and of paint quality.

Natural pH of C.Kaolin is 6.4 and its isoelectric point (iep) is 3.8 as presented in Table 1. Kaolin is an anisotropic mineral and thus shows different zeta potential at its face and edge [8]. The specific surface area, d_{50} and d_{80} sizes of C.Kaolin are 10.76 m^2/g, 1 and 2 µm, respectively. Some properties of TiO_2, GCC and C.Kaolin minerals are presented in Table 1.

Sodium polyacrylate or sodium polyacrylic acid (NaPAA) (2100 g/mol) were purchased from Sigma-Aldrich as powder. Hyamine 1622 and sodium citrate used for the quantitative determination of NaPAA were also purchased from Sigma-Aldrich. Distilled water with a specific conductance of 1.4 µmho/cm was used in all experiments.

Single and mixed mineral suspensions were prepared at 30% wt. for the adsorption, zeta potential and viscosity measurements. In mixed particles systems, each mineral were mixed in equal proportion on the basis of weight. Temperature controlled vibratory incubator was used for mixing and shaking of the samples.

Adsorption density of NaPAA on various mineral particles was determined using the supernatant of mineral suspensions [9]. For this purpose, calibration line (R^2 of 0.999) was constructed at 500 nm wavelength using T80 + UV/VIS spectrometer (PG Instruments Ltd). Viscosity of the samples was measured using Brookfield DVII + viscometer and the yield stress of the suspensions was calculated from the Casson flow model using Rhocalc V3.1-1 software.

The zeta potential of the samples was measured using Zeta Meter 3.0 + . Specific surface area of the particles was measured by BET method using "Monosorb" instrument. Particle size distribution of the samples was determined by Mastersizer 2000 (Malvern Instruments Ltd.).

Paint production and its detailed analysis are given elsewhere [10,11]. Paint recipe used in the study is presented in Table 2. The effect of mineral type and its amount on opacity and gloss values of the paints was revealed through 22 different paint recipes. The only difference in these recipes is the amount of TiO_2, C.Kaolin and GCC and their total amount was fixed as 36.6% of the total paint.

3. Results and discussion

As shown in Fig. 1, the natural pH of GCC is 9.3 that is very close to its iep of 9.2. The zeta potential values of GCC vary in the range of + 20 mV and −20 mV at pH 7.5–11.

Changes in yield stress values against pH of the suspension are also shown in Fig. 1. Yield stress is the stress value in which a material starts to be deformed. It can also show the dispersion stage of a suspension. If the yield stress is high, particles are probably in an agglomerated form. Lower yield stress values indicate that suspension contains better dispersed particles. Interestingly, the maximum yield stress values of TiO_2 and C.Kaolin coincided with their iep. Conversely, GCC exhibited an opposite trend. Normally, particles tend to aggregate at the iep and the yield stress values increase. However, this is not the case for GCC in this study and thus its mechanism deserves a comprehensive investigation.

Zeta potentials and viscosities of suspensions were simultaneously measured for characterization of the system at natural pH values, 30% solids by wt. and 25 ^{O}C temperature for single minerals and their mixtures (TiO_2, GCC, C.Kaolin, TiO_2 + GCC, TiO_2 + C.Kaolin and TiO_2 + GCC + C.Kaolin). Adsorption isotherms in the presence of NaPAA were constructed under the same conditions.

In Fig. 2, while TiO_2 exhibited the maximum adsorption densities, the mixture of TiO_2 + C.Kaolin yielded the lowest plateau in adsorption densities. The adsorbed amount of C.Kaolin could not be obtained because of low level adsorption of NaPAA and inconsistent data obtained in different experiments, it can be concluded that the lowest affinity of NaPAA adsorption was found for C.Kaolin followed by GCC based on the adsorption of NaPAA onto TiO_2 and TiO_2+C.Kaolin. Adsorption of NaPAA on oxide minerals is mainly governed by electrostatic interaction forces between COO- group of NaPAA and surface sites of solid

Table 1
General properties of TiO_2, GCC and C.Kaolin.

Material	Supplier	Specific Gravity, g/cm^3	Particle size, µm		Specific Surface Area, m^2/g	Refractive index	Natural pH	iep
			d_{50}	d_{80}				
TiO_2	Tronox	4.10	0.20	0.95	18.14	2.70	7.5	7.7
C.Kaolin	Microns	2.64	1.00	2.00	10.76	1.56	6.4	3.8
GCC	Som Group	2.70	0.90	3.00	1.71	1.58	9.3	9.2