EFFECT OF PREMIXED TiO_2 AND CALCITE ON PAINT PRODUCTION

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Abstract

Nowadays, the search for new types of industrial minerals for use as pigment and extender in paint is considered as an important research area in surface chemistry applications. Since some functional minerals can improve both optical and mechanical quality of the paint, great research efforts are made to develop substitutes for relatively expensive pigment, TiO_2. Although it may possible to make direct replacement of TiO_2 by a synthetic opaque pigment, its feasibility has not been demonstrated. New trends prefer this replacement by performing some new particle preparation methods for paint. Efficiency of the replacement may require the use of natural extenders and pigments provided that some surface chemistry parameters including adsorption, electro-kinetics and rheology of the suspension are carefully adjusted.

In this study, naturally ground calcitewith 5 µm mean size and paint grade 0.3 µm mean size TiO_2 were premixed in an attritor in the absence and presence of varying amounts of sodium polyacrylate (NaPAA) as dispersant. The product obtained out of this interaction was fed as a composite material to the paint system. A direct relationship between the amount of NaPAA and opacity of the paint was found. Increasing the amount of NaPAA resulted in increased opacities and gloss values of the paint to a certain point above which both opacity and gloss started to decrease. The optimum amount of NaPAA was identified as 2.78 mg/g (NaPAA /pigment). Opacity and gloss value of the paint respectively increased by 0.56 % and 8 gloss units upon the addition of optimum amount of NaPAA during the premixing of calcite and TiO_2 in the attritor. Interestingly, if the same amount of NaPAA is added while the production of paint instead of premixing stage, no such increment in the paint quality was observed. Moreover, no change in paint quality was found without NaPAA addition to the premix in attritor. These results clearly show the effect of order of addition in which introduction of a surface active component to TiO_2 and calcite before the paint production significantly improved physical and chemical interactions.

Key words: Paint, TiO_2, Calcite, NaPAA

1. Introduction

In recent years, technological developments in various fields lead to enhance the existing conditions for any type of engineering product. Of these paint technologies have the biggest share where any kind of change in paint formulation results in windfall profits for paint manufacturers. Thus, depending on the characteristics of paints, these developments are also shaped where various inorganic minerals with different dosages are used in paint formulations. The addition ratios and the dosages of these minerals are also effective and improve some physical and mechanical properties of paints [1]. Besides many types of

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minerals, calcite and TiO_2 constitute the highest percentage in industrial paint recipes. However, due to the higher costs of TiO_2, recent studies are mainly focused on enhancing the dispersion conditions or alternative usages like coating calcite particles with TiO_2 or calcined kaolin instead of pure TiO_2while lowering the cost and resulted in more environmentally friendlypaints [2,3]. Therefore understanding of mechanisms during paint production may help producing paints with better quality and lowering the production costs. Thus, considering the different surface charges of these materials(Calcite, positive; TiO_2, negative), as mentioned in a previous publication [4], the main interaction mechanism can be regarded as heterocoagulation where the optimum size distribution of calcite resulted in better distribution of TiO_2 particles in paint medium [5,6]. The same mechanism is also valid for the coating of calcite surfaces with TiO_2, which then creates paints with calcite particles in similar characteristics like opacity, gloss as obtained for paint with the pure TiO_2. Thus, advanced analysis methods in terms of X-Ray Diffraction analysis and other scanning electron microscope (SEM) and transmission electron microscopy (TEM) resultsshowed these characteristics of particles [7].

Apart from the characteristics of these inorganic constituents in paint medium, the effect of other components like dispersants will also provide different point of views for gathering different assumptions to improve the quality of paints. As well known, the importance of dispersant type and amount resulted in stabilization of other inorganic components where any kind of destabilization will result in paints without adequate characteristics like opacity, gloss, etc. Therefore the optimization of these components becomes significant [8].

In this study, the effect of pre-mixing of TiO_2, calcite and NaPAA in attritor before the paint production on the quality of water borne paint was investigated. Standard paint tests such as opacity, gloss and viscosity measurements were performed for evaluation of the paints.

2. Materials and Methods

2.1. Properties of Raw Materials

Calcite (Turcarb 5K) used as inorganic filler material was received from Somgroup Company from Turkey. For coating and as a pigment, Titanium dioxide (CR-828) was received from Organic Chemical Company in Turkey. The typical properties of both TiO_2 pigment andcalcite filler were given in Table 1.

Table 1. Typical Properties of $TiO_2$and Calcite

	TiO_2, %	**Calcite, %**
Density, g/cm^3	4.1	2.7
Mean size, microns	0.3	5.0
Natural pH	7.5	9

For paint production, apart from pigment and filler, various components like binder, anti-foam, conditioner, pH adjuster, wetting and dispersant agents wereused. Copolymer form of styrene butyl acrylate (Orgal PST 50A) was used as a binderwhich was obtained from

Organic Chemical Company, while other constituents like antifoam, conditioner, pH adjuster, wetting and dispersing agents were obtained from AkçalıPaint Company. Additionally,sodium polyacrylate (NaPAA)used as dispersant in paint recipes was obtained from Sigma-Aldrich in powderform and sodium salt of polyacrylic acid (PAA). It was dissolved by tap water before usage in coating experiments.

2.2. Paint production and characterization

Paint production involves 3 main steps; mixing of some additives in water, pigment paste production (mill base) and gentle mixing of all ingredients (letdown). The details of the production was given in our previous publication [6]. Viscosity, opacity, gloss, pH and density of the paints were measured in order to characterize the paints. Sheen Mixer was used for paint production while BrookfieldKrebs Viscometer, Sheen Tri-Glossmaster, Sheen opacitymeter, liquid pycnometer and standard pH meter were used for characterization of the paints. More details of the characterizations of paints were also given in elsewhere[6]. Two paint references were formulated in order to observe the effect of pre-mixing of TiO_2 and calcite with NaPAA on paint properties especially on opacity and gloss values. In Reference 1, a commercial dispersant was used while it was substituted by NaPAA in Reference 2. These reference paint were preparedfollowing the regular process and TiO_2 and calcite were added without any pre-mixing stage.

2.3. Coating of calcite surfaces with TiO_2 before the paint production

Union Process SD-1 Model laboratory type attritor was used for coatingCalcite surfaces with TiO_2. For these experiments, zirconium oxide balls (5 mm in size) were used and the optimum rotational speed was determined experimentally as 410 rpm.In these tests, the amount of calcite and TiO_2 were kept constant as the same as in Reference paints.
NaPAA is generally used as a dispersant in paint mixtures. However, it can also be useful for the physical and chemical interactions between calcite and TiO_2 particles during wet coating processes. In this regard, different amounts of NaPAA were used in order to investigate its effects on coating and by the way paint characteristics. For this aim, different amounts as 0.2, 0.5, 1 and 1.5 g. of NaPAA in a 360 g of mixture (120 TiO_2 + 240 Calcite) were used. This mixture produced in the attritor were used as pigmentin the paint. Commercial dispersant “Dispex” which is generally used as dispersant in regular paint production was not added during these tests. However, another reference, Reference 3, was formulated including both dispex and 1 g of NaPAA in the pre-mixed of TiO_2 and calcite. All the paint recipes are presented in Table 2. TiO_2, calcite and NaPAA were pre-mixed in the attritor for Reference 3 and A series of paints while there is no any pre-treatment of materials in Reference 1 and 2. A0.2, A0.5, A1 and A1.5 represent the paint recipes in which 0.2, 0.5, 1 and 1.5 g of NaPAA was added.

Table 2. Paint recipes.

	Regular production			TiO_2 and calcite were pre-mixed in attritorwith existing of NaPAA			
	Quantity, %						
Material	Reference 1	Reference 2	Reference 3	A0.2	A0.5	A1	A1.5
Water	29.15	29.35	29.05	29.43	29.05	29.05	29.05
Antifreeze	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Biocide	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Thickener	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Dispersant	0.3	-	0.3	-	-	-	-
NaPAA	-	0.1	0.1	0.02	0.05	0.1	0.1
Wetting Agent	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Defomaer	0.6	0.6	0.6	0.6	0.6	0.6	0.6
pH adjuster	0.05	0.05	0.05	0.05	0.05	0.05	0.05
TiO_2	12.0	12.0	12.0	12.0	12.0	12.0	12.0
Calcite	24.0	24.0	24.0	24.0	24.0	24.0	24.0
Binder	28.0	28.0	28.0	28.0	28.0	28.0	28.0
Coalescent	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Butyl Glycol	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Anti settling agent	0.3	0.3	0.3	0.3	0.3	0.3	0.3
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0

3. Results

Opacity and gloss values of paints and the effect of NaPAA addition during coating process on opacity and gloss values are shown in Figure 1. Increasing the dispersant amount result in better size distribution in paint matrix that gloss value which is strongly influenced by the particle size distribution in paints showed an increasing trend.

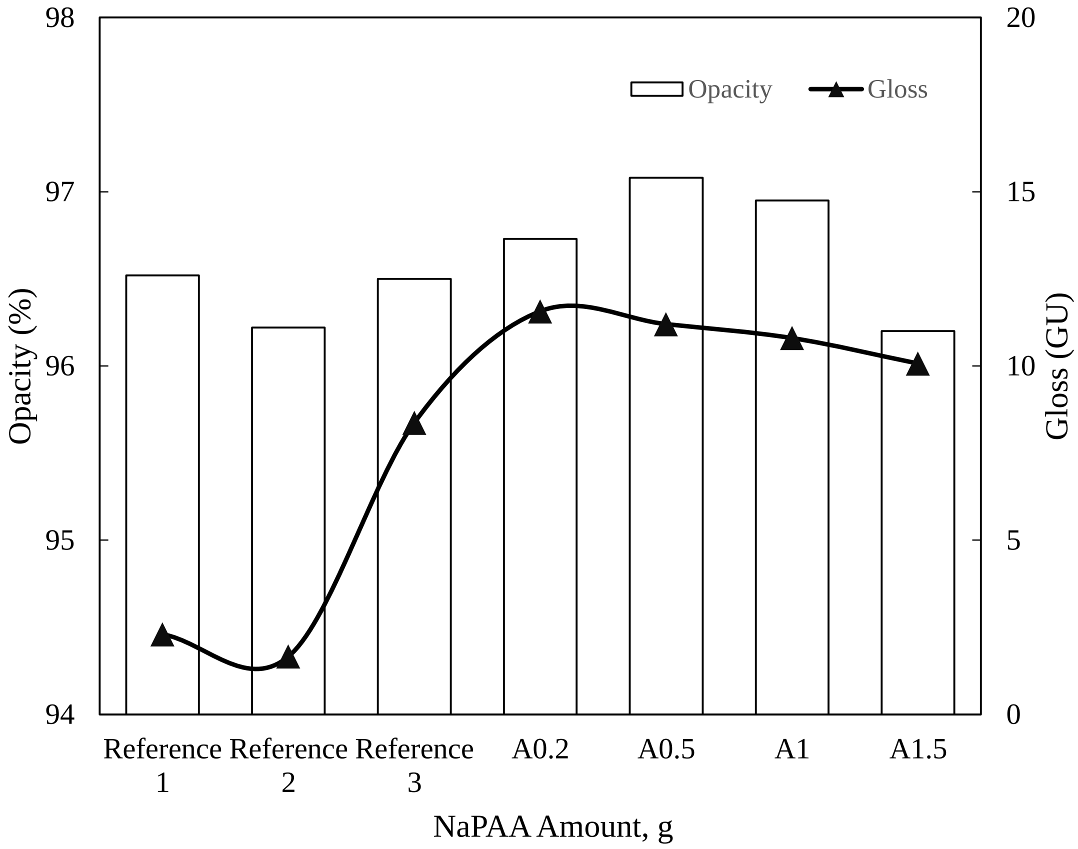

Figure 1. The opacity and gloss variation of paints as a function of NaPAA addition ratio.

In Figure 1, it can be clearly seen that pre-mixing of TiO_2 and calcite with NaPAA in attritor improve the both opacity and gloss value of paints. This is probably because of the better stabilization of particle dispersion in paint medium thanks to the steric stabilization effect of NaPAA.

Thus, increasing amounts of NaPAA resulted in higher opacity and gloss values to a certain addition amount as 0.5 g and decreased in further additions in particular for opacity. Moreover, it is worth to note that the opacity and gloss values obtained after the addition of 0.5 g NaPAAshowed a bit higher value like 0.56 % opacity and 8.9 gloss unit respectively compared to values for Reference 1. It is also higher than Reference 2 that shows the importance of pre-treatment of particles before the addition of them in paint.A series of paints also have higher quality than Reference 3 that shows detrimental effect of higher amount of dispersants (Dispex+NaPAA). This detrimental effect is also true for A1.5.

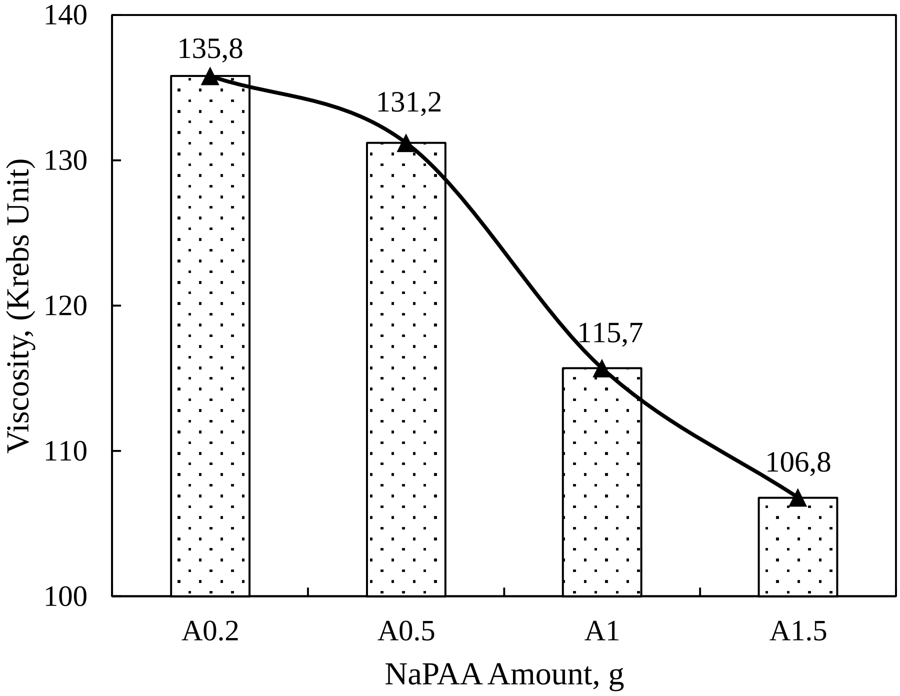

Figure 2. The variations on viscosity of paints upon addition of NaPAA during coating processes.

Following the paint production, the qualificiations of paints were also evaluated by the differences on their viscosity values. Viscosity is one of the most important parameter to be mentioned for qualifying the paint quality.The variations on paint viscosity upon NaPAA addition was shown in Figure 2. It is clear from these results that upon addition of NaPAA, a proportional decrease was obtained on viscosity.

Thus, evaluation of paints were carried out by considering the effects of different parameters such as viscosity, opacity, gloss, size distribution etc. These tests were also performed for the characterization of our samples after the addition of NaPAA during coating processes. Although A0.5 has the highest opacity and gloss values, optimum paint recipe was found as A1 considering all the parameters. As it was shown in Figure 1, the addition of 1 g NaPAA (0.1 % based on 1 kg of paint and 2.78 mg/g based on 360 g of mineral mixture) significantly increased the opacity value to 96.95 % while mixture of Dispex decreased this value to 96.5 %. From these results, it can be clearly understood that the amount of dispersant (or dispersant mixtures) is significantly effective that less or above an optimum addition results in decreases for opacity and other characteristics of paint. Similar trend was also obtained for the gloss values where increasing the amount of NaPAA to 1 g causes a remarkable increase and like for opacity values, addition of higher amount caused a negative trend for gloss values. These results are all in accordance with our previous results that any kind of increase or over amounts of dispersant in matrix would provide dispersion of particles to some extent however during the ongoing process of paint production, an agglomeration will occur in matrix which will reversely affect both the gloss and opacity values.

Conclusions

In this study, the effects of NaPAA addition during pre-mixing of filler and pigment materials were investigated in detail considering addition ratio and properties of paints such as opacity, gloss value and viscosity. In addition, reference paints were prepared with well-known paint recipes in order to make a reliable evaluation for our paint products.

The results of these tests revealed that 1 g NaPAA addition can be accepted as the optimum addition ratio based on its higher opacity and gloss values and its viscosity value (115.7 KU) which was the closest one to the reference paints (111.7-119.4 KU).

Thus, pre-treatment of pigments with NaPAA improves the paint quality that opacity values for paints increased to 96.95 % which was 0.73 % higher than Reference 2. In addition, a significant increase was also obtained for gloss parameter that the value increased to 10.8 upon 1 g NaPAA usage while this value was 1.68 for Reference 2 with the same amount of NaPAA without pre-treatment.

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