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Effects of TiO_2 Partial Substitution by Various Extenders on Architectural Interior Paints

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Abstract

The most commonly used pigment in paint formulations is titanium dioxide (TiO_2), which is a white particle with providing exceptional hiding power to the paint film owing to high refractive index. Since titanium dioxide is an expensive component, cost savings are realized through the reduction of titanium dioxide in architectural interior paint formulations. In this work, a partial substitution of TiO_2 up to 30 % was attempted with low particle size huntite, calcite and Neuburg siliceous earth. Increases in hiding power, whiteness and gloss values were achieved successfully by different amounts of huntite substitutions.

Key words: Neuburg siliceous earth, Architectural interior paints, Huntite, Titanium dioxide, Calcite

1. Introduction

Interior architectural paints are mainly used for the aesthetic appearance as well as protection of the surfaces inside the buildings. Architectural paints are generally composed of four basic components, namely binder, pigments and fillers, additives and dispersing medium. Each component within each category serves a function and the combination of the ingredients is responsible for creating the utility of the coating [1,2].

The pigment and filler particles within the coating are keys to achieving the ideal optical properties for the coating's intended purpose. Pigments can be categorized as being white, black and colored inorganic or organic. The most commonly used pigment is titanium dioxide (TiO_2), which is a white particle with providing exceptional hiding power to the paint film owing to high refractive index. Optimal particle size for rutile TiO_2 is between 200 and 300 nm. Besides, the distribution or arrangement of TiO_2 particles in the paint film also affects the resulting hiding power [3]. For instance, TiO_2 can be transparent when present in the form of large clusters of particles and its hiding power is reduced significantly when agglomerated due to reduced light scattering efficiency. Conversely, good particle dispersion increases the hiding efficiency of TiO_2 particles in the paint film. If the number of particles within a fixed volume increases beyond the certain limit, this creates a "crowding effect" within the system, which reduces the light

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scattering efficiency of each particle. Fillers with especially small particle size can be used to decrease this "crowding effect" by separating TiO_2 particles. In addition, certain small extender particles, such as flash calcined kaolin [4-6] contain entrapped air. When incorporated into a paint film, this entrapped air provides to hiding by the mechanism detailed above. It is noteworthy that this means of improving paint opacity is also accomplished by using hollow sphere polymer (HSP)-hiding technology [7,8]. Another consideration in the use of TiO_2 as an opacifying pigment in paints is cost. Since TiO_2 is an expensive component, cost savings are realized through the use of decreased amounts of TiO_2. Therefore, fillers can be added to the paint in order to increase its volume at a low cost. Various attempts have been patented to reduce the amount of TiO_2 as a hiding or opacifying pigment and therefore to decrease the cost of the paint compositions [9,10].

Fillers, also known as extenders, can come from a variety of materials and possess different shapes and sizes. The common ones are calcite, kaolin, talc, mica and aluminum silicates. In this work, the partial replacements of TiO_2 by different fillers, namely calcite, Neuburg siliceous and huntite extenders on architectural interior paint properties are investigated. The aim was to keep the hiding power of paint films without a significant loss of other performance properties. Different formulations have been designed and performance properties have been analyzed according to the international standards.

2. Materials and Method

2.1 Materials

All of the samples were technical grade and used without further purification. Aqueous copolymer dispersion based on vinyl acetate and ethylene as a binder was purchased from Celanese. The calcite, Neuburg siliceous earth and huntite extenders were obtained from Mikron'S, Hoffmann Minerals and Sibelco, respectively. The surfactants and Ti-Pure R 706 pigment were obtained from Coatex and Dupont, respectively. Thickener was obtained from Shin-Etsu. pH modifier and film forming agent were purchased from a local store and Dow Chemical Company, respectively. Defoamer was obtained from Evonik Endustries. Opaque polymer and biocide were purchased from Organik Kimya A.Ş. and Thor, respectively. The properties of TiO_2, extenders and other raw materials used in this work are given in Table 1 and 2, respectively.

Table 1. The properties of TiO_2, Calcite, Neuburg Siliceous Earth and Huntite

Property	**TiO_2**	**Calcite**	**Neuburg Siliceous Earth**	**Huntite**
Specific Gravity, g/cm^3	4.1	2.7	2.7	2.7
Mean Particle Size (d_{50}), μm	0.2	1.25	2.0	3.0
Oil Absorption, ml/100 g	18.0	30.0	55.0	57.0
Refractive Index	2.7	1.59	1.55	1.64

Table 2. The properties of other raw materials

Component Name	Property
Thickener	Hydroxyethyl-cellulose
pH Modifier	NaOH
Dispersing Agent	Ammonium polyacrylate (40 %)
Defoamer	Mineral oil-based
Film Forming Agent	Dipropyleneglycol n-butyl ether
In-can Preservative	CIT/MIT combination
Binder	VAE emulsion (53%, MFFT 0°C, T_g 12 °C)
Opaque Polymer	Hollow polymer emulsion (30 %)

2.2 Preparation of Paints

The paints were prepared in a 2-liter conventional paint disperser (Dissolver Dispermat CN) with a blade of 70 mm. Water, surfactant, first portion of thickener and pH modifier were loaded to the disperser and mixed at 750 rpm for 5 minutes to obtain the initial mixture. Then, dispersant, defoamer, pigment, extenders and the second portion of thickener were added to the initial mixture and dispersed at 3000 rpm for 10 to 15 minutes to obtain a grind below 40 µm. Finally, in the let-down stage; several additives including binder, film forming agent, biocide and defoamer were added into the grind and mixed at 750 rpm for 5 minutes. The compositions of the prepared paints in which TiO_2 was partially substituted by different amounts of calcite, Neuburg siliceous earth and huntite are given in Tables 3 and 4.

Table 3. Paint Formulations with Different Amounts of TiO_2 and Calcite

	Amount (wt.%)		
Component	**1**	**2**	**3**
Water	22,95	22,95	22,95
Thickener	0,70	0,70	0,70
pH Modifier	0,10	0,10	0,10
Dispersing Agent	0,80	0,80	0,80
Defoamer	0,75	0,75	0,75
Film Forming Agent	0,80	0,80	0,80
In-can Preservative	0,40	0,40	0,40
Binder	29,00	29,00	29,00
Opaque Polymer	5,50	5,50	5,50
Titanium Dioxide	**23,00**	**20,00**	**17,00**
Calcite	**16,00**	**19,00**	**22,00**

Table 4. Paint Formulations with Different Amounts of TiO_2, Neuburg Siliceous Earth and Huntite

	Amount (wt.%)			
Component	**1**	**4 and 7***	**5 and 8***	**6 and 9***
Water	22,95	22,95	22,95	22,95
Thickener	0,70	0,70	0,70	0,70
pH Modifier	0,10	0,10	0,10	0,10
Dispersing Agent	0,80	0,80	0,80	0,80
Defoamer	0,75	0,75	0,75	0,75
Film Forming Agent	0,80	0,80	0,80	0,80
In-can Preservative	0,40	0,40	0,40	0,40
Binder	29,00	29,00	29,00	29,00
Opaque Polymer	5,50	5,50	5,50	5,50
Titanium Dioxide	**23,00**	**20,00**	**18,00**	**16,00**
Calcite	16,00	16,00	16,00	16,00
Neuburg Siliceous Earth/Huntite	**-**	**3,00**	**5,00**	**7,00**

*4-5-6 with three different amounts of Neuburg siliceous earth and 7-8-9 with three different amounts of Huntite

2.3 Tests and Measurements

The paint film samples were prepared on glass plates for gloss and on black and white cards (Leneta) for hiding power measurements ($7m^2/L$). Specular gloss tests (200 µm wet film thickness samples) have been performed according to EN ISO 2813. Hiding power of the samples have been measured based on EN ISO 6504-3. For wet scrub resistance measurements, paints were applied on a plastic foil and after 28 days of drying the samples went a scrubbing procedure. The classification was made according to EN 13300 by measuring the amount of the missing dry layer of paint on a test board.

3. Results

The paints were prepared by partial substitutions of TiO_2 by different amounts of three different extenders. A standard paint, having 47% pigment volume concentration (PVC) with satisfactory performance properties was chosen as a base paint and TiO_2 substitutions were carried out 3-6 wt.% for calcite and 1-7 wt.% for Neuburg siliceous earth and huntite. The performance results of the prepared paints are given in Tables 5-7.

Table 5. Performance Properties of Calcite

	Paint Number		
	1	**2**	**3**
Titanium Dioxide (%)	**23,00**	**20,00**	**17,00**
Calcite (%)	**16,00**	**19,00**	**22,00**
Viscosity (mPa.s)	324	330	340
Density (g/ml)	1,42	1,40	1,37
Dry Hiding Power (%)	98,9	98,6	98,5
Whiteness (%)	85,8	86,6	86,8
Gloss (60°)	2,2	2,2	2,2
Gloss (85°)	11,9	11,3	10,8
Scrub Resistance (µm)	3,9	3,8	3,8

Table 6. Performance Properties of Neuburg Siliceous Earth

	Paint Number			
	1	**4**	**5**	**6**
Titanium Dioxide (%)	**23,00**	**20,00**	**18,00**	**16,00**
Calcite (%)	16,00	16,00	16,00	16,00
Neuburg Siliceous Earth (%)	**-**	**3,00**	**5,00**	**7,00**
Viscosity (mPa.s)	324	380	385	290
Density (g/ml)	1,42	1,40	1,38	1,37
Dry Hiding Power (%)	98,9	99,1	98,9	98,9
Whiteness (%)	85,8	84,40	84,3	84,4
Gloss (60°)	2,2	2,2	2,2	2,2
Gloss (85°)	11,9	12,1	12,3	12,4
Scrub Resistance (µm)	3,9	3,4	3,2	3,2

Table 7. Performance Properties of Huntite

	Paint Number			
Component	**1**	**7**	**8**	**9**
Titanium Dioxide (%)	**23,00**	**20,00**	**18,00**	**16,00**
Calcite (%)	16,00	16,00	16,00	16,00
Huntite (%)	**-**	**3,00**	**5,00**	**7,00**
Viscosity (mPa.s)	324	345	350	430
Density (g/ml)	1,42	1,41	1,40	1,38
Dry Hiding Power (%)	98,9	98,9	98,9	99,1
Whiteness (%)	85,8	87,5	87,6	87,8
Gloss (60°)	2,2	2,5	2,5	2,5
Gloss (85°)	11,9	14,6	16,1	17,5
Scrub Resistance (µm)	3,9	3,9	4,2	4,3

4. Discussion

The substitution of TiO_2 by calcite caused to decrease hiding power of the paints from 98.90 to 98.50 (6 wt.% substitution) while the whiteness of the paints was increased slightly, as shown in Table 5. Also, stable gloss and scrub resistance performance was obtained.

In the case of Neuburg siliceous earth, while the low amount of substitution (3 wt.%) increases the hiding power, probably owing to decreasing of the "crowding effect", higher amounts caused a slight decrease in hiding power, which is still the same as that of the base paint (Table 6). Moreover, slight decreases in whiteness and scrub resistance were also observed.

Huntite substitution provided the best performance results in terms of hiding power and whiteness. Also, gloss values at both 60 and 85 significantly increased as shown in Table 7. However, due to high oil absorption of huntite mineral as in the case of Neuburg siliceous earth (Table 1), the scrub resistance decreased as expected.

Conclusions

The results indicate that up to 30 % substitution of TiO_2 by huntite extender increased hiding power, whiteness and gloss values and moderate contributions were also obtained with low particle size Neuburg siliceous earth. Another significant contribution of these substitutions is the reduction of density as expected, which provides further financial advantages.

References

[1] Ciullo PA (Ed). Industrial Minerals and Their Uses. A Handbook & Formulary. Westwood New Jersey. Noyes Publication; 1996.
[2] Vaziri Hassas B, Ozhan K, Boylu F, Celik MS. Calcined Kaolin and Calcite as a Pigment and Substitute for TiO_2 in Water Based Paints, IV Balkan Mineral Processing Congress 2011; 1: 461-464.
[3] Diebold, M. A Monte Carlo Determination of the Effectiveness of Nanoparticles as Spacers for Optimizing TiO2 Opacity J. Coat Tech Res 2011; 8: 541-52.
[4] Dietz PF. Spacing for Better Effects. Eur. Coat. J. 2003; 7: 14–19.
[5] Dietz PF. The Effect of Fine-Particle-Size Extenders and Entrapped Air on TiO_2 in Emulsion Paint. Paint Coat. 2003; 9: 28–37.
[6] Gittins D, Gadson M, Skuse D. Mineral Blends for Low Titania Coatings 2010; WO 2010/143068 A1.
[7] Stieg FB. Ending the ‘Crowding/Spacing Theory Debate. J. Coat. Technol. 1987; 59: 96–97.
[8] Mussard I. 25 Years of Hollow-Sphere Hiding Technology. Paint Coat. Ind. 2005; 21(9): 96–100.
[9] William DE, William CF, Meredith AM. Process for controlling adsorption of polymeric latex on titanium dioxide 1995; US5385960 A.
[10] Dandreaux G, Brewer A, Jardel C, Ogorzalek P, Luz C, Sheerin R. Additives for improved hiding and paint compositions containing same 2016; WO2016073345 A1.