The Use of Calcined Clay as Part Replacement of Titanium Dioxide in Latex Paint Formulations

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ABSTRACT: Titanium dioxide, TiO_2, being a prime pigment, has been used extensively in the paint industry. The growing demand and the increasing cost of TiO_2 has driven the attention of paint technologists to search for other alternatives. There has been continuous effort to replace part of the TiO_2 with a fine particle size extenders in paint formulations. A detailed study has been undertaken to replace TiO_2 pigment by various percentages of calcined clays in two latex paint formulations. Properties such as thixotropy, hiding power, light fastness, film brightness, scrub resistance, and weather resistance have been determined to establish the optimum use of calcined clays in the paint formulation. Thixotropy, one of the important properties of latex paints, has been studied with the help of thixotropic loop area method. The viscosity data has also been analyzed by Casson's equation. It has been found that the calcined clays can replace up to 20% TiO_2 in paint formulations without having any adverse effect on their properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1029–1036, 2000

Key words: titanium dioxide; calcined clay; latex paints; replacement; hiding power; thixotropic loop and light fastness

INTRODUCTION

Titanium dioxide, TiO_2, being a prime pigment and having good compatibility with other pigments, tinters and other additives has been used extensively in coating industry. The growing demand and increasing cost of TiO_2 has driven the attention of paint technologists to search for other alternatives.[1–3]

Inert pigments, having a low refractive index and being relatively inexpensive, are used as extenders or fillers in paints and allied industries. The judicious substitution of extender generally produces equivalent hiding, tinting strength, stains, and scrub resistance. The substitution of extenders not only helps to reduce the cost but also helps to improve the properties, such as the flow and rheological movement under stress, gloss, leveling after application, mechanical and impact resistance, hiding, reflectance, and brightness.[1,4–6] With the high price and short supply of TiO_2, extender pigments that maintain opacity or hiding properties at lower TiO_2 levels are more important than earlier. An extender like high oil absorption calcined clay may replace a part of titanium dioxide that demonstrates true internal hiding and sheen control in flat wall paints.

The influence of extenders on the properties of paints has been studied extensively. The incorporation of calcium carbonate and diatomaceous silica,[7,8] or a blend of micronized talc and dolomite[9,10] in TiO_2 pigmented paints results in good color uniformity, opacity, and washability. Similarly, the addition of finely ground extender to paints produces better dispersion, uniformity, color, hiding, gloss, and reflectance.[11–14] Cremer[15] found that the replacement of TiO_2 by Blanc fix up to a ratio of 7:3 did not affect the properties of paint formulation; whereas Nazrenko et al.[16] found that excessive

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loading of micronized extenders in TiO_2 pigmented paints has an adverse effect on the properties of paints. Raju and Yaseen[4] have studied the part replacement of TiO_2 by extender barytes in alkyd-based coatings exposed outdoors and indoors by measuring properties like scratch hardness, gloss retention, tensile strength, percent elongation, water vapor permeation, and water absorption. They have showed that paints pigmented solely with 30% PVC titanium dioxide can tolerate its replacement with a barytes extender to the extent of 10% PVC. Sathyanarayana et al.[2] have reported that properties like adhesion, scratch hardness, and tensile strength are not affected significantly in the case of unweathered alkyd coatings in which TiO_2 is partly replaced by zinc oxide, talc, barytes, and china clay to the extent of 30% by weight.

The wide use of kaolin pigments in a variety of architectural and industrial paints have been reported. Chemically, kaolin is a hydrated aluminum silicate formed from weathering and decomposition of feldspathic rock. Like many minerals, it occurs in the form of crystal lattice. Calcined clays have been produced by subjecting it to temperatures of approximately 1000°C. In this process, air voids are created within the particles of calcined clay. These clays specifically promote flow and leveling and contribute to dry hiding. It has been reported[1,17] that calcined/delaminated clays have high brightness and hiding and can replace a portion of titanium dioxide in some of the latex paints.

The rheological characteristics of latex paints play an important role in the assessment of application properties like flow, leveling, settling, sagging, brushability, film build, and stability. These are usually thickened by polymeric thickeners to achieve the desired rheological properties before, during, and after application. Thixotropy, a time-dependent, isothermal rheological property characterized by the reversible decrease of viscosity with shear, is caused by the existence of internal network structures, which are non-Newtonian in flow.[18] In some formulations, the presence of thixotropy is considered to be advantageous; and some times, it is built into the system deliberately[19,20] by using a suitable pigment, resin, solvent, or additive. This is because the lowering of viscosity at higher shear rates, as encountered in application process, facilitates the paint flow and ease of application; and the increase in viscosity after application helps in preventing the sagging of the paint.

Paints are usually formulated with a high order of opacity or hiding power, as well as with good optical properties, appearance, film brightness, and fastness to light because they have to cover the surface and look more attractive.

The objective of the present article is to emphasize the use of calcined clay as part replacement of TiO_2 in paint formulations and to demonstrate the effect derived from it on the rheological, optical, mechanical, and weathering properties in paint formulations.

MATERIALS

The main constituents used in preparing the paint formulations are as follows.

1. Commercial acrylic and vinyl acetate emulsions.
2. High-whiteness calcined clays, Himacot, and Himafil, products of M/s English Indian Clays Ltd. (EICL), Thiruvananthapuram, and their pigmentary properties are given in Table A.I in the Appendix.
3. Other material like TiO_2, talc, calcium carbonate, and additives are of commercial grade.

DETAILS OF PAINT FORMULATIONS

For the present work, two different paint formulations, A and B, based on acrylic and vinyl acetate emulsion, respectively, have been used. The pigment volume concentration (PVC), pigment-to-binder ratio (P/B), and percent replacement of TiO_2 by calcined clay is given in Table I. In all paint formulations, an attempt has been made to use materials, which are widely used in the paint industry. In both formulations, code nos.2 and 3 represent the part replacement by Himafil and code No.4 is Himacot, respectively.

PREPARATION OF PAINTS

Paints were prepared in high-speed mixer, and their percentage solids have been fixed for each set of paints by diluting with water. The pH has been adjusted to 9–10, and the fineness of dispersion of each paint formulation was 6^+.

VISCOSITY MEASUREMENTS

The viscosity was measured employing a Brookfield RVT viscometer in ascending order of speeds

Table I Pigment Volume Concentration and Pigment-to-Binder Ratio of Paint Formulations

Formulation No.	Replacement (%)	Pigment[b] A: PVC P/B	Pigment B: PVC P/B
1	0	65 (5.02 : 1)	70 (7.3 : 1)
2	15	65 (5.02 : 1)	70 (7.3 : 1)
3	20	65 (5.02 : 1)	70 (7.3 : 1)
4	20H[a]	65 (5.02 : 1)	70 (7.3 : 1)

[a] Himacot.
[b] The pigment-to-binder ratio is in parentheses.

of the spindle (0.5 to 50 rpm), followed by the descending order (50 to 0.5 rpm).

Casson's equation,[21] which is based primarily on hydrodynamics and some kinetic arguments, defines the rheology of dispersions better than that of solution.

$$\tau^{1/2} = \tau_o^{1/2} + \eta_\infty^{1/2} \cdot \gamma^{1/2}$$

$$\eta^{1/2} = \eta_\infty^{1/2} + (\tau_o/\gamma)^{1/2}$$

Here, τ_o is the yield stress, and η and η_∞ are the apparent and infinite shear rate viscosity, respectively.

RESULTS AND DISCUSSION

Rheological Properties

Shear stress was calculated from the dial reading data, and shear rates were determined using the

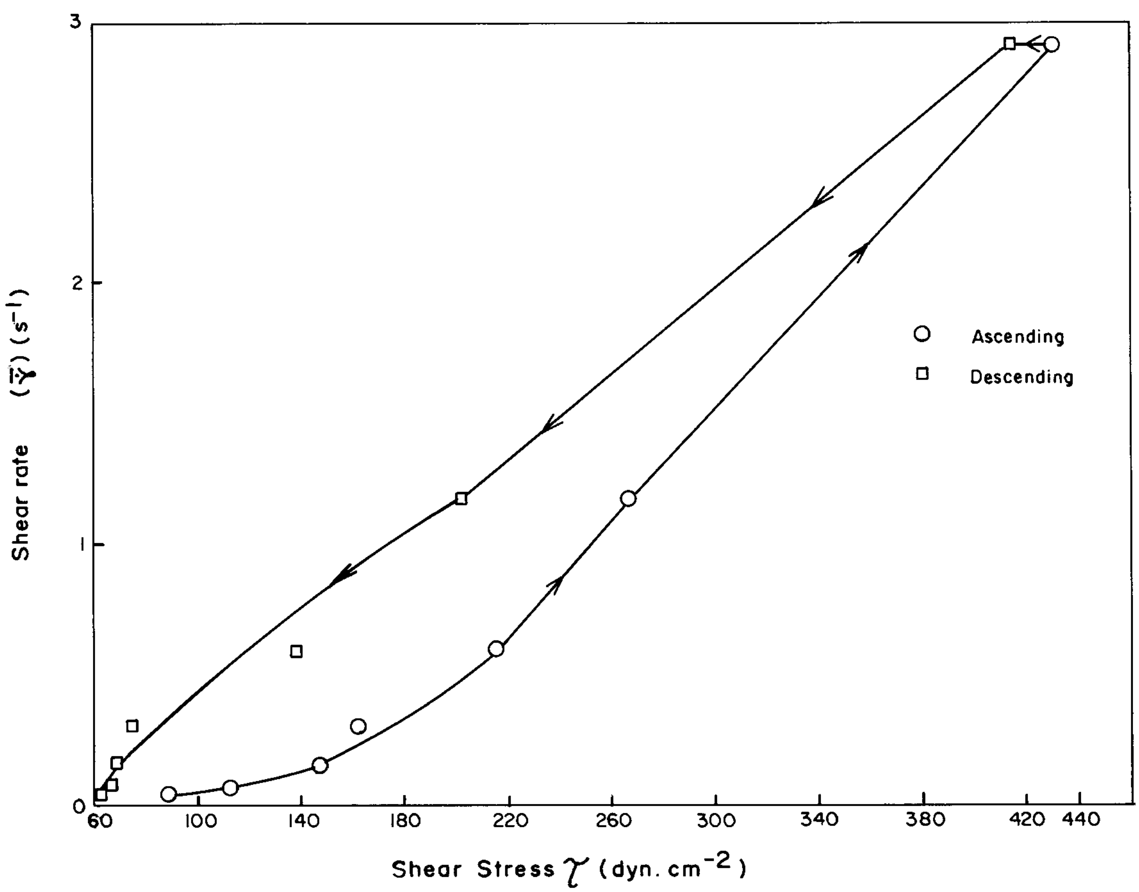

Figure 1 Thixotropic loop of paint formulation 3A.

Table II Representative Data for the Calculation of Thixotropic Loop of Paints

Speed of Spindle (rpm)	Shear Rate (s^{-1})	Shear Stress (τ)		Difference in Shear Stress ($\Delta\tau$)	Area Factor (A)	Thixotropic Area ($\Delta\tau \times A$)
		Ascending	Descending			
0.5	0.02904	87.7462	62.9961	24.7500	0.0147	0.3638
1.0	0.05808	112.4951	66.4967	45.9984	0.0294	1.3357
2.5	0.14515	146.2437	67.4967	78.7466	0.05808	4.5736
5.0	0.2904	161.9930	74.2468	87.7462	0.14515	12.7363
10.0	0.5806	215.2257	138.7291	76.4966	0.2904	22.2146
20.0	1.1612	267.7385	201.2410	66.4975	0.5806	38.6100
50.0	2.9031	431.1715	413.1723	17.9992	1.1612	20.9006
				Total thixotropic area		100.7340

rotational speeds of the spindle as per the method described elsewhere.[22] The results were analyzed using standard equations, and findings are reported in terms of the thixotropic nature of paints, sag resistance, and brushability.

Thixotropic Nature of Paints

The degree of thixotropy in various paints was estimated quantitatively using the thixotropic loop method.[23] The plot of shear rate versus shear stress yields characteristic thixotropic loop, the area of which may be measured with a planimeter. A simpler and quicker method with acceptable accuracy of measurements involves a calculation of the trapezoidal and triangular segments of the loop.

A representative shear rate versus shear stress plot of paint 3 of formulation A (code no. 3A) is shown in Figure 1. The area of the thixotropic loop was calculated from the plots and the procedure of Shackelford and Glaser[24] and also by others.[21,25] The representative data of Figure 1 for the calculation of the thixotropic loop area are reported in Table II. The total thixotropic loop area of each paint is reported in Table III. The values of thixotropic loop area decreases with an increase of calcined clay content in the paints. This shows that the increase of calcined clay content hinders the building up of internal network structures in the paint formulation. Interparticulate forces presumably hold the structure, and it reacts elastically to a small stress. This also shown that calcined clay has good dispersing ability due to its fine particle size, which, in turn, increases the surface area of pigments. This property can be used to adjust the required thixotropy in paints. In comparing the values of the thixotropic loop of paint A and paint B, it is observed that areas of thixotropic loop are more in paint A than in paint B. This may be due to better interaction of pigment, stability, and pseudoplastic behavior at a low shear rate of acrylic emulsion.

Table III Area of Thixotropic Loop of Paints

Formulation No.	Area of Thixotropic Loop			
	1	2	3	4
A	151.971	138.553	100.734	117.250
B	27.560	19.890	16.760	16.720

Analysis of Data Using Casson's Equation

The shear dependence of paints has been analyzed by using Casson's equation. The data has been plotted as $\eta^{1/2}$ versus $1/\gamma^{1/2}$, and representative plots for paint formulation A are shown in Figure 2. The yield stress obtained from the slopes of these plots is the measure of sag resistance, and the infinite shear rate viscosity is a measure of brushability.

Since leveling and sagging occur at very low rates of shear[20] of the order of 0.1 to 0.5 s^{-1}, the low shear rate region has been taken into account for the present purpose. At high shear rates, the latex emulsion paints are mechanically broken down rapidly; therefore, no attempt was made to run thixotropic loops. The slope and intercept of these plots have been calculated, and the values are reported in Table IV. According to Patton, yield stress is directly related to the maximum film thickness that might be applied without sagging. In general, if one requires a thicker film with good sag resistance, it can be achieved by increasing the yield value of the coating. Results of yield stress values in Table IV show that this value is influenced by the content of calcined clay in the paint formulation. These values decrease with increasing calcined clay content in the case of acrylic emulsion paints; however some anomalous behavior is observed in the case of vinyl

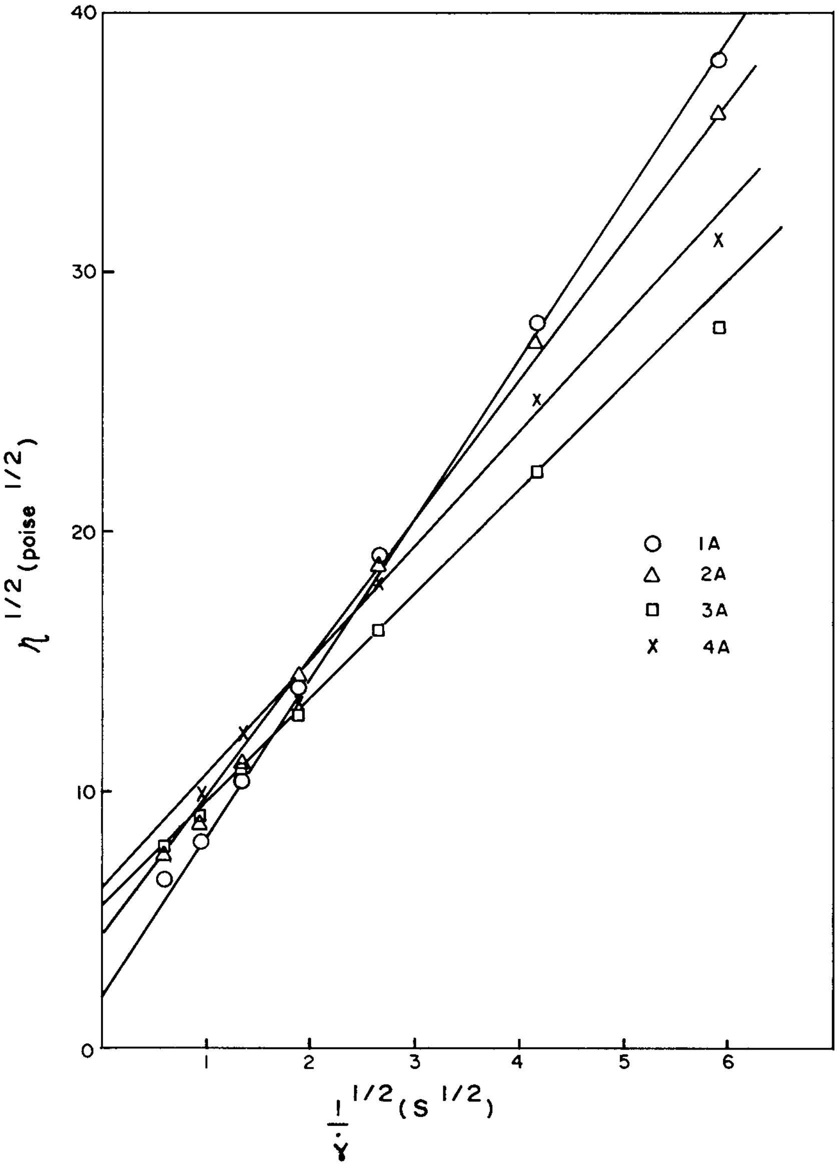

Figure 2 Casson's plots of formulation A.

emulsion paints. One thing that can be inferred from here is that to obtain better sag resistance of the paint formulations, the optimum use of calcined clay is 20%.

OPTICAL PROPERTIES

Four films of different thicknesses of each paint were applied on Sheen Black and White hiding

Table IV Slope and Intercept Data Derived from the Plots of Casson's Equation

	1		2		3		4	
Formulation	$\tau^{1/2}$	$\eta_\infty^{1/2}$	$\tau^{1/2}$	$\eta_\infty^{1/2}$	$\tau^{1/2}$	$\eta_\infty^{1/2}$	$\tau^{1/2}$	$\eta_\infty^{1/2}$
A	6.02	2.00	5.45	4.60	4.40	5.40	4.00	6.20
B	2.51	5.70	3.40	5.04	4.84	4.16	4.81	3.39

Table V Hiding Power Values (M^2/l)

	Hiding Power Values (M^2/l)			
Formulation No.	1	2	3	4
A	8.62	8.51	8.42	8.60
B	6.45	6.22	6.10	6.39

power charts by using an automatic applicator and were allowed to dry at room temperature for 96 h. These films were used for measuring reflectance values by using a reflectometer. The dry film thickness of 80 μm of all the films provided the maximum contrast ratio. The reflectance, *L, a* and *b,* whiteness and yellowness index values were measured by using a Macbeth Eye computerized spectrophotometer.

Hiding Power

Kubelka–Munke Method

The procedure for determining the hiding power of paints is based on the Kubelka–Munk two-constant theory of light scattering. Mitton and Jacobsen[26] have explained this technique, mentioned above. The measured CIE tristimulus values Y divided by 100 has been taken into consideration for the determination of R, R_B and R_∞. These values were substituted for the determination of hiding power. The advantage of this technique is an accurate calculation of hiding power at reflectivity levels lower than actually prepared, which enables one to compare the hiding contribution of calcined clays in paints. The hiding power values are reported in Table V.

The hiding power of paints (A and B) by using calcined clays as part replacement of TiO_2 (code nos.2–4) shows fairly close values as compared to TiO_2 (code no.1) formulation. This may be due to fine particle size, high oil absorption, platy character, and air voids within the particles of calcined clays. Its fine particle size provides large surface area, which, in turn, gives better scattering efficiency. Its platy character and spherical voids within its particles also contributes to the hiding power of paints because of internal reflection. Its high oil absorption, coupled with a large surface area, causes effective PVC to move into higher range, which, in turn, contributes to dry hiding. The hiding power of all the paints of formulation A is more than those of paint B, it may be due to better dispersing ability of acrylic as compared to vinyl acetate emulsion.

For many years, it has been postulated that fine particle size extenders can act as diluents or spacers to enhance the light-scattering ability of TiO_2. This spacer theory suggests that coarse extenders crowd TiO_2 particles together, reducing the ideal spacing at which the pigment affect maximum light scattering. The fine particle size extenders can act as diluents or spacers to enhance the light-scattering ability of TiO_2. It may prove disadvantageous if the TiO_2 concentration is increased in the formulation, due to the crowding effect and the inability of the fine particle size extenders to efficiently separate the TiO_2 particles. It has been reported that at high TiO_2 concentration, a slight reduction in the scattering efficiency of the paints in which fine particle size extenders like calcium carbonate and sodium aluminum silicate have been used.[1,27–29] This is one of the reasons for taking high PVC matt paint formulation with low TiO_2 loading for the present work.

Fastness to Light

Fastness to light is measured in terms of whiteness and yellowness indices and *L, a,* and *b* values of paint formulations containing TiO_2 pigments and of those in which calcined clays replace a part

Table VI(a) Yellowness Index (YI) and Whiteness Index (WI) of Paint Coating (formulations A and B) Films Before and After Exposure to Carbon Arc Lamp

		A				B			
Property		1	2	3	4	1	2	3	4
YI	UE[a]	3.48	3.08	2.80	3.20	5.51	5.29	5.10	5.4
YI	E	3.55	3.08	2.92	3.09	75.6	5.31	5.17	5.09
WI	UE	83.7	82.8	82.0	83.0	75.6	74.5	74.0	75.2
WI	E	82.6	81.4	80.3	81.9	75.6	73.8	73.1	75.0

[a] UE indicates unexposed films; E indicates exposed films.

Table VI(b) *L, a,* and *b* Values of Paint Coating (formulations A and B) Films Before and After Exposure to A Carbon Arc Lamp

Property		A				B			
		1	2	3	4	1	2	3	4
L	UE[a]	94.2	95.5	94.7	94.1	92.6	92.5	93.1	93.2
L	E	94.2	95.0	94.7	94.1	93.0	93.1	93.0	93.2
a	UE	−0.35	−0.50	−0.35	−0.21	0.06	0.10	−0.01	0.01
a	E	−0.37	−0.44	−0.36	−0.25	0.02	−0.03	0.00	0.00
b	UE	1.73	1.61	1.40	1.53	2.57	2.94	2.48	2.44
b	E	1.77	1.57	1.46	1.48	2.34	2.50	2.41	2.40

[a] UE indicates unexposed films; E indicates exposed films.

of TiO_2. The results have been tabulated in Table VI(a) and Table VI(b).

The yellowness index, whiteness index, and *L, a,* and *b* values have not changed much by the replacement of $Ti0_2$ with calcined clays in formulations A and B, which are based on acrylic and vinyl acetate emulsions on exposure. This may be due to these binders are more stable to oxidative degradation on exposure to a carbon arc lamp.

Film Brightness

The CIE tristimulus value *Y* is considered as film brightness. The results have been reported in Table VII. The results indicate that there is not much difference in film brightness by calcined clay replacement with titanium dioxide.

Scrub Resistance

Scrubbability is always required for latex paints. It is directly related to washability and stain removal, which is duly required for interior latex paints. This test has been carried out with a wet abrasion tester. The paints of 80 μm were applied on a primed glass panel and dried for 96 h. These panels were soaked in water for 30 min, followed by an additional 5 min of soaking in 0.5% soap solution and were used for a scrub resistance test. The test panel was mounted firmly on the plate, the soap-filled brush was placed in a position, and the motor was started. The addition of soap solution drops over the panel is arranged at a fixed rate of 12 drops per min.[30,31] This test continued up to 2000 cycles. All the coated panels have passed the test.

HUMIDITY AND ACCELERATED WEATHERING PROPERTIES

The paints are subjected to rain and changing weather conditions so that the paint coatings are exposed to 100% relative humidity at 42–48°C cycles. The accelerated weathering studies have been done by using a Ci-65 ATLAS Weather-*o*-meter. The exposed films were tested for defects like chalking, checking, and blistering, and all the films have passed these tests.

CONCLUSION

Earlier workers have found that some optical and physical properties of paints are improved when part of the TiO_2 pigment of the paint is replaced by extender. The rheological, optical, mechanical, and weathering properties of the paints prepared by part replacement of TiO_2 with calcined clays have been studied. The values of area of thixotropic loop shows that these extender pigments do affect the

Table VII Tristimulus (Y) Values of Paint Films

Property	Substrate	A				B			
		1	2	3	4	1	2	3	4
Y	Black	87.5	90.0	87.8	86.7	83.4	83.2	82.3	84.1
Y	White	88.7	91.1	89.7	88.5	85.8	85.5	86.7	86.9

thixotropic loop, which can be adjusted to the required value with the appropriate content of calcined clay. The sag resistance and brushability of paints also can be controlled with optimum use of calcined clay. Hiding power values show that the replacement up to 20% of TiO_2 with calcined clay is possible with fairly close and acceptable values. Optical properties, that is, the light fastness, film brightness, and reflectivity values obtained, are also within a comparable range. The good scrubbability of the paint formulations prepared by using calcined clay is attributed to the reinforcing effect of its platy character. In humidity and accelerated Weather-*o*-meter tests, no change has been observed as compared to the original paint formulation. According to results obtained, it can be concluded that the calcined clay extender may replace up to 20% TiO_2 in paints formulation without having any adverse effect on their properties, where the reduction in cost is main criterion.

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APPENDIX

Table A.I Pigmentary Properties

Properties/Size	Himalfil	Himacot
Optical Properties:		
Brightness (ISO)	90.1	92.1
Yellowness	1.62	1.31
Whiteness	85.5	88.7
L	95.6	96.7
a	0.12	0.12
b	1.09	0.92
Color (appearance)	white	white
Refractive index	1.62	1.62
Specific gravity	2.63	2.6
Particle size (%):		
+10 μm	3	0
−2 μm	70	85
Median particle size	0.83	0.723
Particle shape	platelet	platelet
Oil absorption (g/100 g)	58	62
pH	5.6	5.8

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