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Extender Properties of Some Nigerian Clays

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Abstract

The extender properties of some Nigeria clays have been studied. The local clays were characterized using X-ray fluorescence and scanning electron microscope. The physico-chemical properties of the clays were evaluated using ASTM standards. The physico-chemical characterization of the local clays gave the following results: specific gravity (2.54 and 2.49), oil absorption (51.0 and 59.0 g/100g), refractive index (1.7 and 2.0) and pH (5.1 and 4.8) for Nsu and Ihitte-Uboma clays respectively. Compositional analysis showed that the clays consisted predominantly of silica (SiO_2) and aluminium oxide (Al_2O_3) in high proportions with the other constituents present in very small proportions. The clays were stable to heat and insoluble in toluene, methanol, ethanol, 2-propanol, chloroform and hydrochloric acidexcept for their slight solubility in acetic acid. The colour of the clays was not affected in cold or when heated except for slight colour change observed in the presence of hydrochloric acid when heated. The particle morphology of the clays indicated the presence of sub-angular platelet of varying sizes. The optimum calcination temperature of the clays was determined to be 850˚C for use in oil-based paints. The clays can be used in gloss paints, rubber and plastic composites and as an adsorbent with improved properties.

Keywords

Clay, Extender Pigments, Calcination Temperature, Titanium Dioxide, Characterization

1. Introduction

Clays has been used indispensably as extenders in architectural and industrial paints, and other industries such as in agriculture, in construction as a building material, in oil industry as drilling muds to protect the cutting bit while drilling, filtering and deodorizing agents in the refining of petroleum, in clarifying water and wine, in purifying sewage as an adsorbent, in textile and sugar industries to remove colour and other impurities, and in the paper, plastics, and rubber industries as fillers [1]. Titanium dioxide (TiO_2) is the most widely used prime pigment in coatings to ensure that appropriate service properties of paints are obtained due to the relatively high refractive index it possesses which is the main advantage for providing these properties [2] while calcined clays has the disadvantage of low hiding power. The combination of these individual pigment properties will help overcome their disadvantages.

However, TiO_2 requires long processing, including grinding, levigation, chemical treatments, etc. from ore to final stage resulting to significant loss of materials [3]. Thus, processed pigments like TiO_2 are expensive and are not indigenously available and this has led to increases in the cost of the resultant coating products.

Nowadays, calcined clays which are of low cost and environmentally friendly are considered alternatives to TiO_2 in paint making. The calcination of clays, generally at high temperatures has crucial effects on the morphology of clays which results to improved coating properties. The calcination of clays leads to the creation of air voids and this results to good crack and scrub resistance, low sheen, decreases in the specific gravity of clays and improvement in the hiding power of paints [4] [5]. Calcined clays are used in paints not only because of their high chemical resistance but also, the form and the charge distribution of their particles which have a positive impact on final coatings products. Furthermore, calcined clays affect paint thixotropy thereby ensuring better paint processing properties. The plate-like structure and aspect ratios of calcined clays give rise to reinforcing layer structure with improved properties. Fine calcined clay acts as a spacer for TiO_2 particles and this enhances scattering coefficient of TiO_2 pigments, with enhanced paint dry film opacity [6]. Calcined clays affect rheology, sedimentation and thixotropy and give better processing properties to coatings. Thus, the light scattering coefficient of the TiO_2 pigments is increased providing enhanced opacity, especially in dry paint films. The calcination process does not only cause dehydration but particles agglomeration.

Calcination of clays results to changes in the clay structure, physiochemical properties and composition of the clay minerals [7]. These concomitant changes can be varied from one clay mineral group to another and also, the particle size and heating regime. Raising the temperature to dehydration level leads to loss of adsorbed water thereby causing the alteration of the macro and micro-porosity of the clay minerals. This results to the collapse of interlayer spaces, and a reduction of cation exchange capacity (CEC). The partial loss of the adsorbed and hydration water can increase the hydrophilicity and surface acidity of the clay [8]. Additionally, calcination of clays results to stabilization of the clay to maintain important permanent properties. Initially, in the dehydration stage, the adsorbed and hydrated water and impurities attached to the clay particles are removed. This results in weight loss of the clay particles and an increased surface area, an indication of more sites for adsorption. Further heating leads to dehydroxylation and if heating is continued beyond dehydroxylation, the clay structure and the surface functional groups are altered [9].

Wibowo [10] studied the effects of calcination temperatures (350˚C - 650˚C) on the catalytical properties of basic clay and found that the basic clay calcined at 450˚C exhibited an optimum activity when used together with tetramethylammonium hydroxide (TMAOH). Ahmed [11] studied the differences in the performances of natural kaolin, thermally treated kaolin (calcined kaolin), and chemically treated kaolin in alkyd based paint in the protection of steel. The study showed that calcined kaolin performed better in the protection of steel than kaolin, while chemically treated kaolin varied in its performance according to the concentration of the modifier used. The result suggested that kaolin could be used as a reinforcing agent in making other polymer composites such as rubber, and plastic composites. Ewulonu [12] synthesized and characterized local clay-titanium dioxide core-shell extender pigment using simple chemical technique and found that they combined the properties of both the local clays and titanium dioxide. This study is aimed at understanding the impact of clay morphology and integrating the concept of calcination of local clays for cost effective paint formulation.

2. Materials and Method

2.1. Materials

The local clays used in this study were sourced from two different locations, Nsu in Ehime Mbano Local Government Area and Etiti in Ihitte-Uboma Local Government Area within the South-Eastern region of Nigeria.

2.2. Preparation of the Extender Pigments

The local clays (Nsu and Ihitte-Uboma clays) were hand dug from the deposit area and sundried. Impurities were removed from the clay before crushing. The crushed clay samples were calcined for three hours at the following temperatures 550, 650, 750, 850, and 950˚C respectively and stored for subsequent studies. The clay samples calcined at different temperatures were each sieved to 0.075 mm clay particle size and later, alkyd paint samples were formulated with each calcined clay sample, **Table 1**. Each of the prepared paint samples was subjected to a drying test, a very important factor driven by trends in modern architectural paints for end consumer which enabled the determination of the optimum calcination temperature of the clays.

2.3. Characterization of the Extender Pigments

The uncalcined clays and extender pigments (calcined clays) were analyzed for major oxides contents using Munipal 4 Energy Dispersive X-ray fluorescence spectrometer (EDXRF). A scanning electron microscope (SEM; JEOL JX 840), a microanalyzer electron probe was also used in this study to estimate the particle shapes of the clays and the extender pigments. The ASTM international standard was used to characterize the extender pigments for specific gravity (ASTM D153-84), oil absorption (ASTM D281-12), refractive index (ASTM D 1208-96), hydrogen ion concentration (ASTM D 1208-96), and chemical reactivity (ASTM D34-08).

Table 1. Formulation of Alkyd paints using local calcined clays.

Constituents [Wt. %]	Calcination Temperature, [˚C]				
	550	650	750	850	950
Calcined Clay	48.2	48.2	48.2	48.2	48.2
Alkyd Resin	147	147	147	147	147
Solvent	30	30	30	30	30
Total Binder	147	147	147	147	147
Total Pigment	48.2	48.2	48.2	48.2	48.2
P/B	0.32	0.32	0.32	0.32	0.32
Driers	3.2	3.2	3.2	3.2	3.2

*P/B = pigment to binder ratio.

3. Results and Discussion

3.1. Determination of the Optimum Calcination Temperature of the Clays

The results obtained the from the drying studies of paints formulated with the calcined clays presented in Table 2 show that both Nsu and Ihitte-Uboma clays formulated paints exhibited through-dry times of 210 and 201 min respectively for the formulations with local clays calcined at 850˚C. The surface-dry times of Nsu and Ihitte-Uboma clays formulated paints for clay calcined at 850˚C are 105, and 103 min respectively. Similarly, for the local clays calcined at 950˚C, the surface-dry times of the applied paint samples are 100 and 102 min respectively for Nsu and ihitte-uboma local clays. From energy consumption considerations, a very important factor in the processing industry, since the surface-dry times at 850˚C and 950˚C for the local clays are very similar, the temperature of 850˚C should represent the optimum calcination temperature for the local clays as the paints formulated with the clays calcined at 850˚C had good drying properties. It is important to note that trends in modern architectural paints is driven by two factors, namely, lower volatile organic compound (VOC) emission and, arguably, the most important is the end-consumers who are asking for long lasting, easier to use products that have quicker drying properties.

3.2. Particle Size Analysis

The particle size distribution (PSD) of the local clays was analyzed using the dry sieving method in accordance with ASTM D422-63. The results show that the greater portion of the clays were of particles less or equal to 0.30 mm and which were found to be the major particles present in the clays as shown in Figure 1. According to British Soil Classification System (BS 5930, 1981), both clays are classified as medium sand under coarse grain soil. Therefore 0.075 mm clay particle size was used in the characterization of the extender pigments and subsequent analysis.

3.3. Property Evaluation of the Extender Pigments

The physical-characterization of the extender pigments are illustrated graphically in

Table 2. Drying properties of calcined local clays formulated alkyd paints.

Formulation Code	Calcination Temperature [˚C]	Paint Drying Properties (min)			
		Surface-Dry		Through-Dry	
		NC	IU	NC	IU
EP100	550	150	143	250	246
EP100	650	135	133	245	236
EP100	750	120	125	238	224
EP100	850	105	103	210	201
EP100	950	100	102	215	203

*NC = Nsu clay; IU = Ihitte-Uboma clay; EP = Extender pigment.

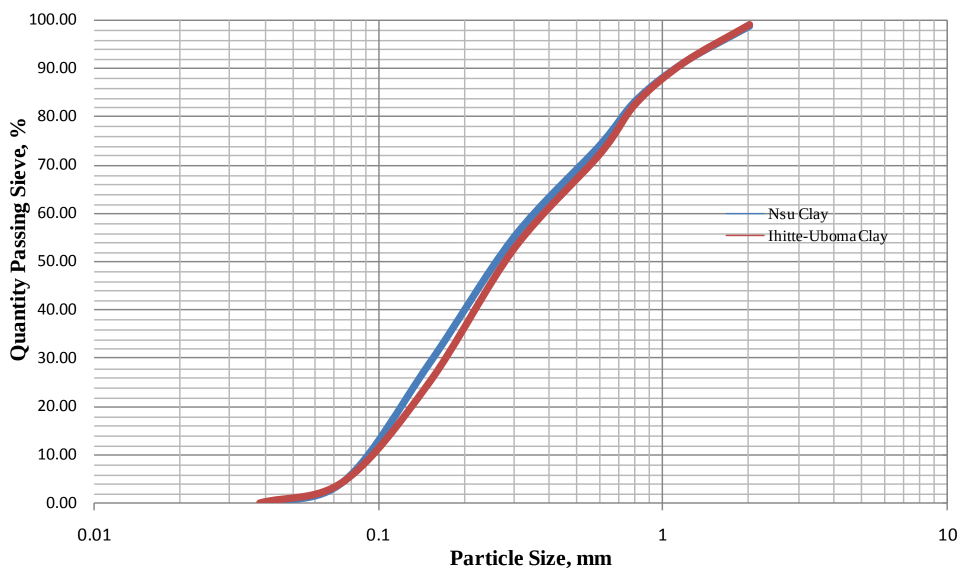


Figure 1. Particle size distribution of nsu and ihitte-uboma clay samples.

Figure 2. The local clays have the following physical properties: pH (5.1 and 4.8), oil absorption (59 and 51), refractive index (1.7 and 2.0) [13] and specific gravity (2.54 and 2.49) respectively for Nsu and Ihitte-Uboma clays. According to US Department of Agriculture on classification of soil pH both clays are strongly acidic in nature. Hare and Beck [14] had reported a pH that ranged from 4.5 - 7 for kaolin. The pH of some extenders are talc 9 - 9.5, commercial whiting 8.74, fly ash 8.15 [15] [16], and industrial waste clay 7.88 [17]. The oil absorption of extender pigments depends chiefly on the particle size, the surface area of the pigment, with lower particle sizes being associated with increased oil absorption. Oil absorption is the minimum quantity of oil required to convert a given mass of pigment to a coherent uniform paste [18]. The oil absorption value obtained in this study is in agreement with the result obtained by Odozi *et al.* [15] for Okigwe-Mbano clay (60.0). The high oil absorption recorded for the two local clays is an indication that more base resin may be required in the paint formulation. The oil absorption of some extenders are fly ash 19.0, China clay 30 - 60, barytes 10 - 14, and

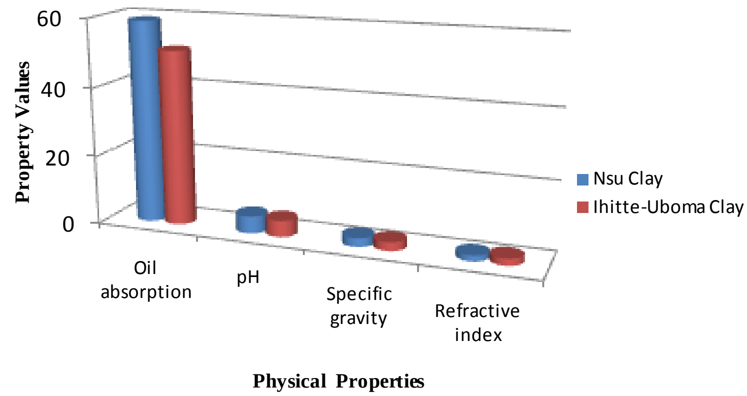


Figure 2. Physical characterization of extender pigment.

talc 25 - 35 [19]. Also other values reported include, calcium carbonate 6 - 30, talc 30 - 45, mica 50 - 70, and kaolin 25 - 50 [15]. The specific gravity values obtained compared to that reported by Hare and Beck [14] for 2.6. Generally, pigments having low specific gravity generally exhibit low settling tendencies, high oil absorptions, and high tinting strengths in paints [20]. The refractive indices of some extenders are: barytes (1.64), commercial whiting (1.58), and talc (1.40) [20]. Others are commercial whiting 1.65, mica 1.59, and kaolin 1.57 [19]. The refractive indices of extenders have great influence on the scattering power of paints. Generally, extenders do not enhance the true opacity or colour of the coating film. The low refractive indices of some extenders are responsible for the poor opacity exhibited in solvent paints [20]. The low specific gravity obtained in this study is an indication that the local clays can be used in high proportions without having any adverse effect in the bulk density of the formulated paint. The specific gravity of some conventional extender pigments are barytes (4.25 - 4.5), china clay (2.6), mica (2.8 - 2.85), talc (2.65), and whiting (2.7) [20].

3.4. Compositional Analysis

The X-ray fluorescence (XRF) determinations on the uncalcined and calcined (850˚C) local clays are presented in Table 3. These data are illustrated graphically in Figure 3. The result indicates the presence of silica (SiO_2) and aluminium oxide (Al_2O_3) in high proportions while the other constituents are present in very small proportions. The SiO_2 content of uncalcined and calcined Nsu clay was found to be lower than that of Ihitte-Uboma clay while the reverse was the case for Al_2O_3 and TiO_2 contents. The Nsu local clay was found to contain 57.52% SiO_2, 25.29% Al_2O_3, and 0.85% TiO_2 while Ihitte-Uboma local clay contained 63.09% SiO_2, 20.90% Al_2O_3, and 0.60% TiO_2 respectively. The high proportion of silica and aluminium oxide in the clays is indicative of the kaolinite nature of the clays and the basis for the type of clay to be used for the production of clay paint [21]. The oxide contents (SiO_2 and Al_2O_3) of the calcined clays were generally found to be higher than the uncalcined clays. The increase in the oxide contents with calcination at high temperature (850˚C) as observed in this study is an indication of more sites for adsorption. The oxide contents (SiO_2 and Al_2O_3) of some

Table 3. XRF analysis of nsu and ihitte-uboma local clays.

Constituents [wt. %]	Uncalcined clay		Calcined clay [850˚C]	
	Nsu	Ihitte-Uboma	Nsu	Ihitte-Uboma
SiO_2	57.52	63.09	62.87	64.88
Al_2O_3	25.29	20.90	28.75	24.82
TiO_2	0.85	0.60	2.10	1.48
K_2O	0.49	1.04	0.50	0.44
Na_2O	0.30	0.36	0.32	0.22
CaO	0.25	0.28	0.27	0.22
V_2O_5	0.23	0.26	0.24	0.22
Fe_2O_3	0.11	0.11	0.28	0.27
Cr_2O_3	0.08	0.08	0.09	0.08
CuO	0.02	0.02	0.2	0.02
MnO	0.02	0.03	0.2	0.02
SO_3	-	0.03	0.10	0.08
Se_2O_3	0.003	-	0.001	0.001
L.O.I	14.83	12.90	4.63	6.69
Total	99.99	100.06	100.35	99.44

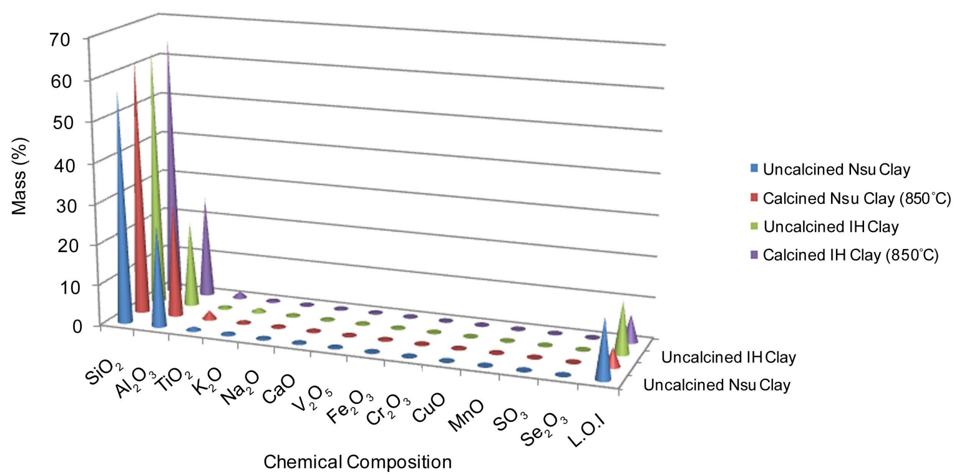


Figure 3. Chemical composition of nsu and ihitte-uboma clays.

Nigerian clays are Obowo clay 67.08%, 21.6% and Ihitte-Uboma clay 56.4%, 29.3% [12], Ibere clay 52.06%, 27.87% and Oboroclay 60.21%, 19.05% [22], Mayo-Belwa clay 59.8%, 7.08% [23], Omankwo Afikpo clay 87.13%, 6.70%; Okposi clay 53.04%, 19.70% [19]. The presence of the unreacted oxides in the clays in indicative that paint formulated with the clays will function as anti-corrosive paints since the unreactive oxides will slow down the diffusion of corrosive species thereby delaying the phenomenon of corrosion in painted surface [14].

3.5. Chemical Reactivity

The effects of heat on the solubility and colour stability of the local clays was studied and was shown in Table 4 and Table 5. The results show that Nsu and Ihitte-Uboma clays were not soluble in methanol, toluene, Ethanol, chloroform, 2-propanol and hydrochloric acid except for the slight solubility of the clays observed in acetic acid.

Generally, the colour of the clays were not affected in the media investigated either in the cold or when heated. However, Nsu and ihitte-Uboma clays exhibited slight colour change in the presence of hydrochloric acid on heating. Therefore, paints formulated with these clays may not be suitable for use in hydrochloric prone environment. The same recommendation applies for the clays in acetic acid (CH_3COOH) prone environments.

3.6. Morphological Analysis

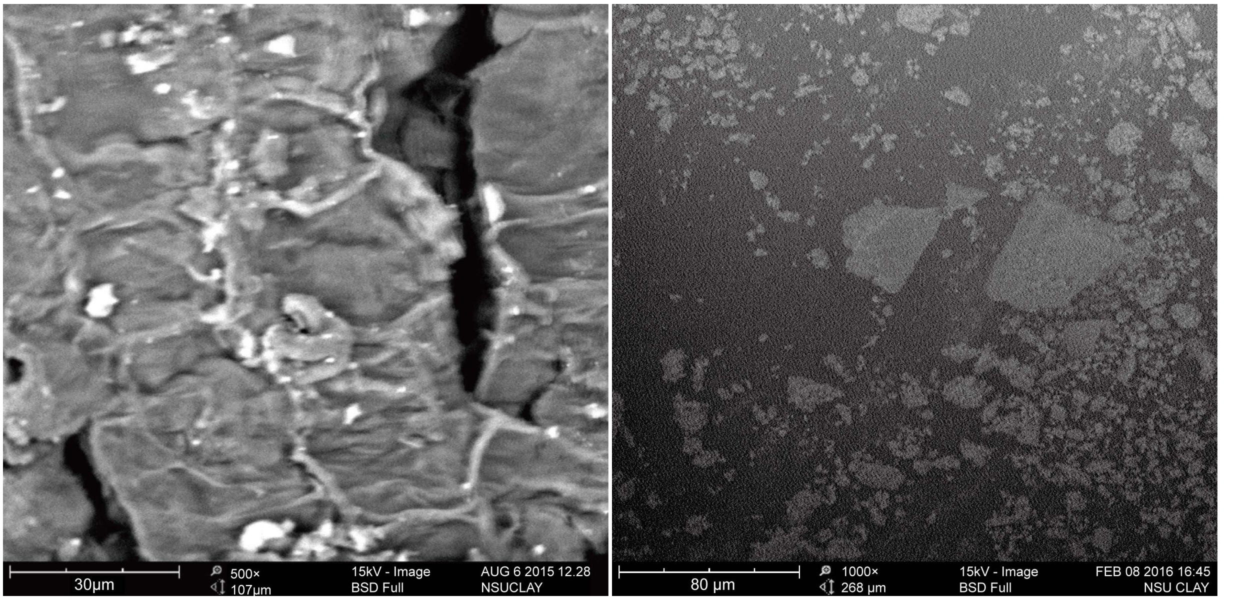
The morphology of the clays obtained from scanning electron microscope (SEM) are shown in Figure 4 and Figure 5. The SEM micrograph of uncalcined Nsu clay (Figure 4(a)) shows alternate structures with grains of metallic impurities imbedded in the matrix base in chains of irregular structures. Also, seen in the figure are some dark sec-

Table 4. Effect of chemical media on reactivity of nsu clay.

Chemical media	Solubility test		Colour change	
	Cold	Hot	Cold	Hot
Hydrochloric acid	Nil	Nil	Nil	Very slight
Methanol	Nil	Nil	Nil	Nil
Toluene	Nil	Nil	Nil	Nil
Ethanol	Nil	Nil	Nil	Nil
2-propanol	Nil	Nil	Nil	Nil
Chloroform	Nil	Nil	Nil	Nil
Acetic acid	Dissolves slightly	Dissolves slightly	Nil	Nil

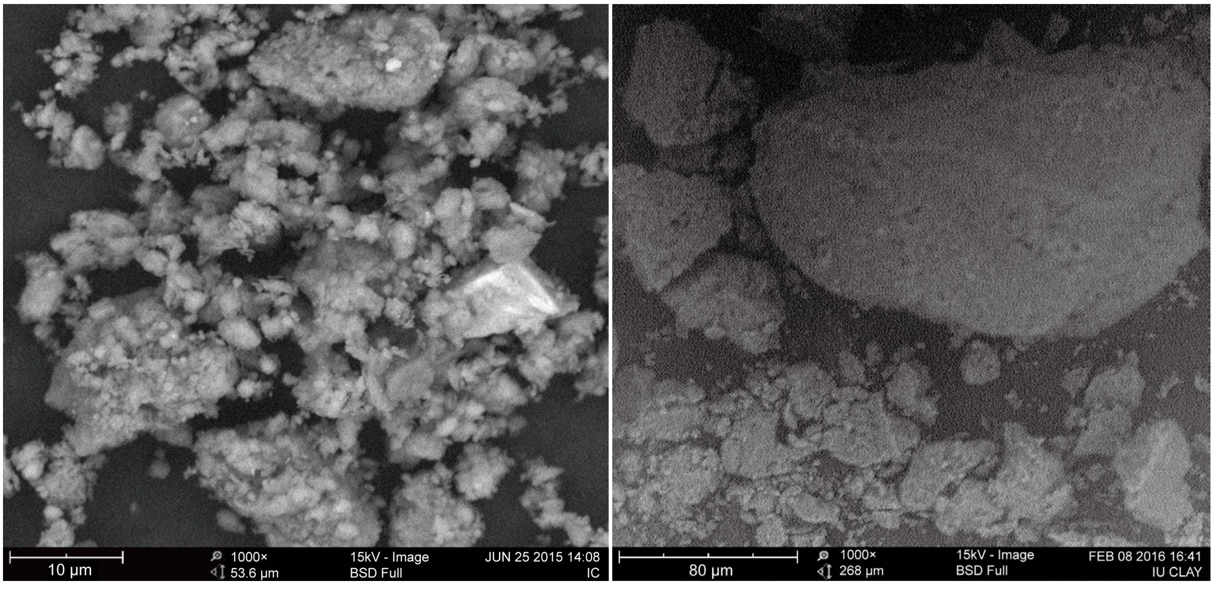
Table 5. Effect of chemical media on reactivity of ihitte-uboma clay.

Chemical media	Solubility test		Colour change	
	Cold	Hot	Cold	Hot
Hydrochloric acid	Nil	Nil	Nil	Very slight
Methanol	Nil	Nil	Nil	Nil
Toluene	Nil	Nil	Nil	Nil
Ethanol	Nil	Nil	Nil	Nil
2-propanol	Nil	Nil	Nil	Nil
Chloroform	Nil	Nil	Nil	Nil
Acetic acid	Dissolves slightly	Dissolves slightly	Nil	Nil



(a) (b)

Figure 4. (a) SEM micrograph of uncalcinednsu clay, (b) SEM micrograph of calcined nsu clay.



(a) (b)

Figure 5. (a) SEM micrograph of uncalcinedihitte-uboma clay, (b) SEM micrograph of calcined ihitte-uboma clay.

tions indicating the presence of carbonaceous materials or cracks within the clay morphology. The SEM micrograph of calcined Nsu clay Figure 4(b) shows the presence of sub-angular platelet with sharp edges of varying sizes. From the SEM analysis studied, the calcined Nsu clay was determined to contain a total of 67 particles (Table 6). The SEM micrograph of uncalcined Ihitte-Ubomaclay in Figure 5(a) shows the presence of uniform texture having more distribution of metal oxides in the matrix in the form of regular shapes rather than elongated chains (of irregular shapes) as present in uncal-

Table 6. Particle properties of nsu clay 1 image with a total of 67 particles.

Property weighted by volume			Property weighted by count		
Property	**Median**	**Average**	**Property**	**Median**	**Average**
Circle equivalent diameter	27.6 μm	29.25 μm	Circle equivalent diameter	19 μm	21.7 μm
Major axis	34.7 μm	38.9 μm	Major axis	26.5 μm	28.2 μm
Minor axis	21 μm	22.7 μm	Minor axis	15 μm	16.9 μm
Circumference	124 μm	134 μm	Circumference	83.1 μm	95.8 μm
Convex hull	106 μm	113 μm	Convex hull	72.7 μm	82.5 μm
Circumscribed circle diameter	41.7 μm	44.9 μm	Circumscribed circle diameter	30.1 μm	32.7 μm
Area	599 μm^2	756 μm^2	Area	283 μm^2	405 μm^2
Volume by area	1.1E+04 μm^3	1.78E+04 μm^3	Volume by area	3.5E+03 μm^3	7.13E+03 μm^3
Pixel count	2184	2755	Pixel count	1032	1476
Aspect ratio	0.627	0.606	Aspect ratio	0.603	0.614
Circularity	0.507	0.509	Circularity	0.536	0.541
Convexity	0.868	0.855	Convexity	0.886	0.876
Elongation	0.369	0.399	Elongation	0.397	0.386
Grayscale	87.2	98.7	Grayscale	99.9	106

cined Nsu clay. Figure 5(b) is the SEM micrograph of calcined Ihitte-Uboma clay showing the presence of sub-angular platelet with rounded edges of different sizes. The clay was determined to contain a total 53 particles from SEM analysis (Table 7). The particle properties of the clays presented in Table 6 and Table 7 are illustrated graphically in Figure 6 and Figure 7. The figures indicated that the surface area of both clays increased with increases in volume. The particle shape of an extender affects its parking efficiency and the hiding power Ewulonu *et al.* [12]. The angular-shaped particles observed in this study will contribute to increased paint viscosity due to their low particle-to-particle distance which will restrict the movement of the molecules when used in paint formulation. The plates observed in this study will not only exert reinforcing effects but also reduce the clay's water and gas permeability. This has the applicability to imparting good anticorrosive properties and special appearances to paints when used in paint formulations. The low aspect ratio (length to diameter ratio) and elongation observed in this study provides a reinforcing layer structure of the clays and has other advantages on the applied paint film durability such as high gloss, high opacity, increased hardness and consequently improved abrasion (crack and scrub) resistance when used in paint formulations.

4. Conclusion

The two Nigerian local clays, Nsu and Ihitte-Uboma clays have been analyzed to be inorganic clays, acidic, and composed mainly of silica (SiO_2), and aluminium oxide

Table 7. Particle properties of ihitte-ubomaclay 1 image with a total of 53 particles.

Property weighted by volume			Property weighted by count		
Property	Median	Average	Property	Median	Average
Circle equivalent diameter	29.3 μm	30.3 μm	Circle equivalent diameter	21.2 μm	22.6 μm
Major axis	38 μm	41.5 μm	Major axis	26.3 μm	29.6 μm
Minor axis	22.5 μm	23.3 μm	Minor axis	16.5 μm	17.6 μm
Circumference	132 μm	146.6 μm	Circumference	92.1 μm	99.5 μm
Convex hull	112 μm	121μm	Convex hull	80.8 μm	86.7 μm
Circumscribed circle diameter	43.6 μm	48.3 μm	Circumscribed circle diameter	31.7 μm	34.5 μm
Area	675 μm^2	829 μm^2	Area	352 μm^2	443 μm^2
Volume by area	1.32E+04 μm^3	2.06E+04 μm^3	Volume by area	4.97E+03 μm^3	8.16E+03 μm^3
Pixel count	2459	3020	Pixel count	1284	1612
Aspect ratio	0.581	0.591	Aspect ratio	0.596	0.622
Circularity	0.467	0.485	Circularity	0.541	0.553
Convexity	0.849	0.849	Convexity	0.903	0.891
Elongation	0.417	0.409	Elongation	0.404	0.378
Grayscale	109	115	Grayscale	114	119

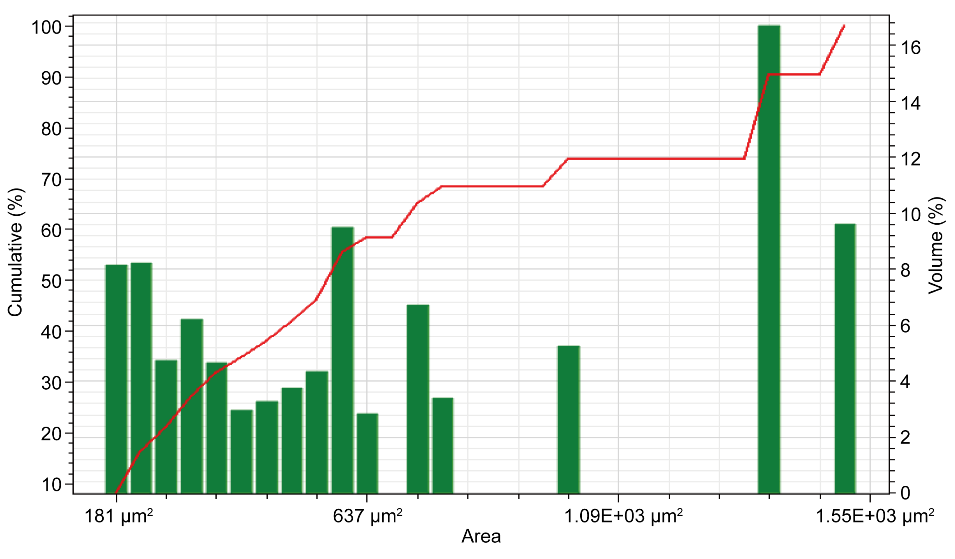


Figure 6. Particle properties of calcined Nsu clay.

(Al_2O_3) in higher proportions with the other constituents present in small proportions. The oxides were seen to increase with increased calcination temperature which indicated improved adsorption property of the clays. The low specific gravities of the clays are indicative that more of the extender pigments can be incorporated in paints without adverse effect on the resultant paint product. The high refractive index of the clays in-

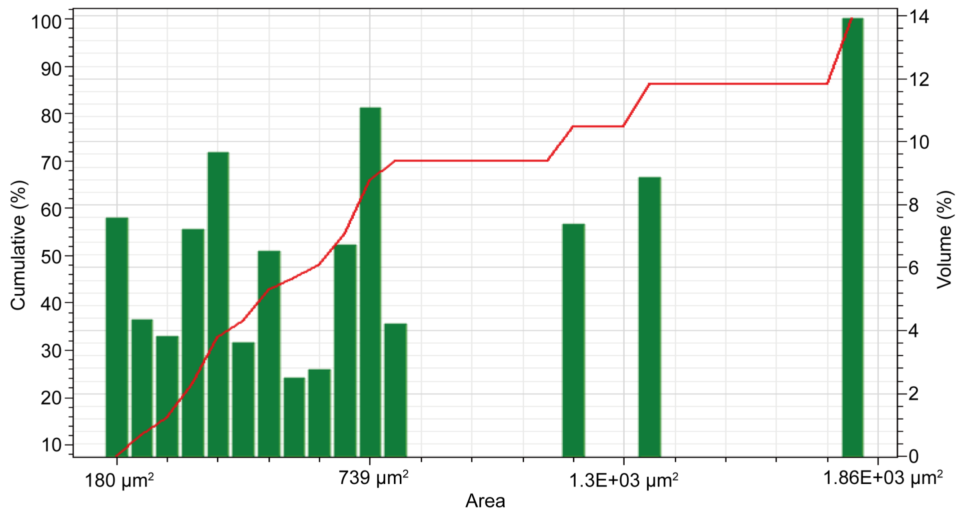


Figure 7. Particle properties of calcined ihitte-uboma clay.

dicates improved gloss property of the clays and hence can be used in gloss paints. The high oil absorption of Nsu and Ihitte-Uboma clays indicates more resin demand without compromising other coating properties. The clays were stable to heat and insoluble in the chemical media studied except for their slight solubility in acetic acid and slight colour change with hydrochloric acid when heated. The optimum calcination temperature of Nsu and Ihitte-Uboma clays was determined to be 850˚C for use in oil-based paints. The clays are indigenously available and easy to process with little loss of material. It is expected that the clays, Nsu and Ihitte-Uboma clays should find utilization in the surface coatings industry as this will reduce the cost and dependence on imported extender pigments and also overcome the disadvantage of paint film degradation caused by titanium dioxide.

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