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Evaluating the Surface Coating Potentials of South-Eastern Nigeria Local Clays in Alkyd Paints

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Abstract: In the quest to develop sustainable materials for the coating industries, the surface coating potentials of two Nigerian local clays were evaluated in alkyd paints. The highly import-dependent coating industry in Nigeria gulps over ₦10b annually on materials that can be sourced locally, therefore, developing technically, and economically viable extenders for use in coatings, and thus, bringing down the cost of painting to acceptable limits in line with the sustainable development goals is very important. The local clays were analytically evaluated to study their chemical composition, structural morphology and physico-chemical properties. Alkyd paint samples were prepared using the clays, the clays containing varying amounts of TiO_2 pigment and xylene as solvent. Analysis on the local clays revealed that they are inorganic silty clays, moderately acidic, and containing over 32% grains of size < 0.150 mm. The major compositions of the clays are SiO_2 and Al_2O_3 in that order, with small amounts of TiO_2 and Fe_2O_3. Paint sample formulated using TiO_2 pigment only had the least viscosity value while the 100% Obowo clay formulated paint sample exhibited the highest viscosity value among the alkyd paint samples studied. The formulated paint samples shaded their colours on exposure to rain and sunlight, with only 100% Obowo clay paint formulation losing its adhesion after exposure. The alkyd paint dry film samples generally performed well in distilled water, 2% Na_2CO_3, and 2% H_2SO_4. The present study has demonstrated the utility of Obowo, and Ihitte-Uboma clays in formulating alkyd paints and shown they possess properties equivalent to the expensive imported extender pigments. The expectation is that these clays should find utilizations in the surface coatings industry which will help to reduce the over dependence on imported extender pigments. The clays are easy to process, stable and indigenously available.

Keywords: Kaolin, Clays, Alkyd Paints, Sustainable Development, Extender Pigments, Coatings

1. Introduction

In the current strive toward a sustainable future, renewable material resources are increasingly gaining attention and are being investigated for the development of future alternatives to conventional products. In this quest of sustainable materials for the coating industries, the potentials of two Nigerian local clays in alkyd paints are reported here. Local clays are known to be layered silicates and their unique mineral platelet structure has a thickness of one nanometer, although its dimensions in length and width can be measured in hundreds of nanometers, with a majority of platelets in 200–400 nm range after purification [1]. A single gram of clay contains over a million individual platelets. These clays are naturally abundant, renewable, cost effective and easy to process. For instance, According to the Nigerian Ministry of solid minerals development, Nigeria has large and economical deposits of kaolinite clay minerals with an estimated reserve reaching 3 billion tonnes in many localities [2]. There are at least 45 known deposits of kaolin in Nigeria with all states in the country having at least one deposit [3]. The major challenge has been the full characterization of these deposits to ascertain their grade, and their exploitation for national development via mineral processing [4]. In this regime of sustainable development, it is important to develop this local raw material for added value in line with the number 9 goal of the sustainable development goals (SDGs). This will ultimately generate employment for the local populace through the growth and development of small and medium enterprises (SMEs) that will engage in the mining and processing of the kaolinite clays thereby addressing SDGs 1 and 8. The paint industry in Nigeria is highly importing dependent as over 70% of the raw materials for the sector are imported. According to National Bureau of Statistics [5], Nigeria spent about ₦3.6b on the importation of paint pigment in 2008. This figure rose to ₦9.9b in 2011.

Pigments for paint formulations are submicron particles which must possess certain properties such as good opacifying strength (commonly called hiding power) and brightness. Other important features are excellent resistance to chemical attack, good thermal stability and resistance to UV degradation. Pigments from mineral sources offer opacity and brightness because they have the ability to scatter light. The degree to which minerals scatter light depends on their intrinsic index of refraction and also on the structure they form in the coating [6]. Titanium dioxide has high refractive index, strong absorption in the UV region of light spectrum and strong reflectance in the visible spectrum thereby giving it a very high light scattering properties which, when combined with its particle size creates an effective pigment for brightness and opacity [6]. Calcined kaolin also exhibit properties similar to titanium dioxide and therefore can be used as an alternative pigment to titanium dioxide. Calcined kaolin effectively scatters light due to its porous structure, hence when light encounters it, some of the light gets reflected off the planar surfaces, a portion of the light enters the structure and these rays upon reflection encounter other crystals in close proximity. This light then undergoes multiple internal reflections and diffractions giving excellent optical scatter [6].

Like all phyllosilicates, clay minerals are characterized by two-dimensional sheets of corner sharing SiO_4 tetrahedra and/or AlO_4 octahedra as shown if Figure 1. The sheet units have the chemical composition, $(Al,Si)_3O_4$. Each silica tetrahedron shares 3 of its vertex oxygen atoms with other tetrahedra forming a hexagonal array in two-dimensions. The fourth vertex is not shared with another tetrahedron, and all of the tetrahedra "point" in the same direction i.e. all of the unshared vertices are on the same side of the sheet [8].

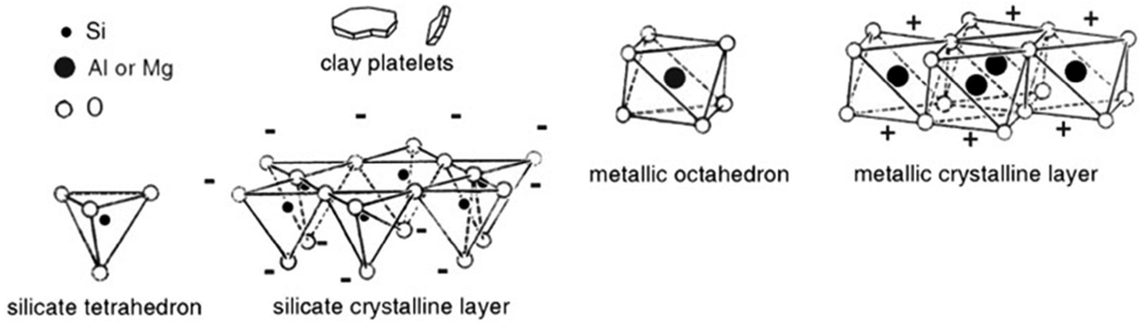

Figure 1. *Structure of clay mineral.*

The crystal structure of clay illustrated in Figure 2 shows that the tetrahedral sheets are always bonded to octahedral sheets formed from small cations, such as aluminium or magnesium, and coordinated by six oxygen atoms [7]. The unshared vertex from the tetrahedral sheet also form part of one side of the octahedral sheet but an additional oxygen atom is located above the gap in the tetrahedral sheet at the centre of the six tetrahedra. This oxygen atom is bonded to a hydrogen atom thereby forming an OH group in the clay structure. Clays can be categorized depending on the way the tetrahedral and octahedral sheets are packaged into layers. If there is only one tetrahedral and one octahedral group in each layer, the clay is known as a 1:1 clay. The alternative, known as a 2:1 clay, has two tetrahedral sheets with the unshared vertex of each sheet pointing towards each other and forming each side of the octahedral sheet.

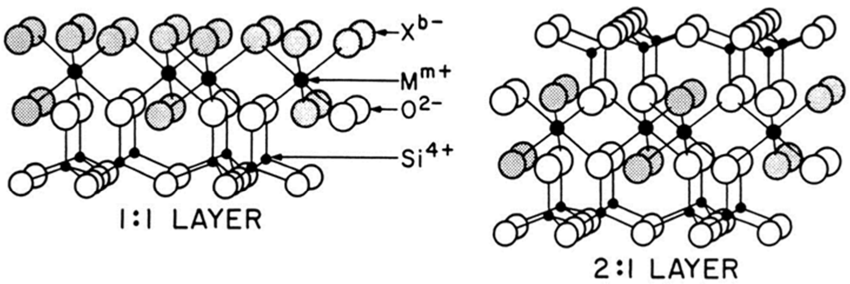

Figure 2. *Crystal structure of 1:1 and 2:1 layer type clay minerals, where X (shaded circles) is usually OH and M can be Al, Mg, Fe, [8].*

Each raw material in a coating formulation plays a significant role in deciding the performance of a coating system. Extenders, also referred to as extender pigments, are an integral part of almost all coating formulations, contributing significantly towards modifying various coating properties such as flow characteristics, gloss, abrasion resistance, setting tendency [9]. They differ from true pigments since they do not impart opacity to the coating, and are practically transparent in the oil medium. The selection and proper blending of suitable extenders in paint help to optimize several engineering properties and aesthetics of a coating. Extenders, in spite of their widespread use in almost all coatings and their elevation from "fillers" to "extenders" have received little attention from research scientists in the field of coating technology. Most of the extenders used in coatings are of mineral origin, and require long processing, including grinding, levigation, chemical treatments from one to final stage, resulting in significant loss of materials [10]. Available information indicates a yield of 75% in the processing of China clay and of 30% in the case of calcite [11]. Such extenders, and several other processed extenders are expensive leading to increase in cost of the resultant coating systems. Recently, paint formulators and technologists have begun to find technically, and economically viable extenders for use in coatings, and thus, bring down the cost of painting to acceptable limits. Some of the materials considered for extender purposes are reviewed below.

The use of red mud, a by–product of aluminum companies in protective coatings has been reported [12]. The utilization of fly ash, a waste by–product of thermal power stations, as an extender in water based coating formulations has also been reported [13]. However, there were certain disadvantages that limited the use of fly ash in water based coatings [14]. The major problems associated with such coatings are their greater tendency towards increasing corrosion of the substrate material owing to the presence of water. The addition of surfactants to reduce the higher surface tension of water led to the formation of films with poorer water resistance. Further investigation, on the possibility of using fly ash as extenders in solvent borne coatings for high performance industrial applications has been reported [11]. The extender properties of fly ash were assessed, and compared with those of conventional extenders. The coatings that were developed showed improved corrosion and abrasion resistance and better resistance to chemicals. Saxena and Dhjimole [15] characterized and utilized copper tailing waste as an extender in paints. The waste is a siliceous material containing aluminum oxide, iron oxide and sulphate in significant concentrations. The sieved waste was characterized for basic extender properties like oil absorption, specific gravity, etc. Results obtained indicated that the developed extender was environmentally clean, and cost effective.

Yousseff et al [16] studied the possible utilization of silica waste fumes as an extender in paints. Silica waste fume is a by-product produced in the manufacture of ferrosilicon. Results obtained from the various paint formulations showed that silica fume can replace satisfactorily the imported diatomaceous silica from the economic and environmental point of view. Ewulonu et al, [17] reported the characteristics of local clay-TiO_2 core-shell extender pigments. The performance of the core-shell extender pigments in alkyd paints showed that they combine the properties of both their precursors, and have the potential to overcome their disadvantages, e.g., low hiding power of clays and photochemical activity of titanium dioxide [18]. Anyiam and Igwe [19] used industrial waste firebrick as an extender to formulate alkyd paints. Results showed similarity in the values of specific gravity and film thicknesses obtained for the waste clay, and commercial whiting formulated alkyd paint samples. The waste clay extended paint samples exhibited good viscosity properties. The use of an indigenous clay (Kaolin) from Mbano in Imo State, Nigeria as an extender in alkyd paints was reported by Odozi et al [20]. The performance characteristics of the indigenous clays in alkyd paint were reported to be comparable, and even marginally better than that of the imported, and commercial China Clay. Igwe and Ezeamaku [21] studied the use of two local clays, Amankwo Afikpo and Okposi, present in large quantities in Afikpo and Okposi LGAs of Ebonyi State, Nigeria as extenders in alkyd paints, and found that the formulated alkyd paints had good chemical resistance, and no adverse effect on other coating properties was reported.

2. Materials and Methods

2.1. Materials

The local clays used were sourced from two different locations, Obowo and Ihitte-Uboma Local Government Areas within the South-Eastern region of Nigeria. Lead and cobalt naphthanate were used as driers in this study. They were purchased from A. Jokems Industries Nig. Ltd, Onitsha, Nigeria. Their metal contents are 36% Pb and 12% Co. driers. Cobalt naphthanate was used for surface dry, while lead naphthanate drier was used for through dry. Xylene was used as the solvent while medium oil alkyd resin based on soya bean oil purchased from A. Jokems Industries Nig. Ltd, Onitsha, Nigeria was used in this study as the binder.

2.2. Preparation of the Local Clays

The local clays were broken down into small lumps, dried under the sun and ground into small particle sizes before calcination at 650°C. The particle size distribution (PSD) of the clays were analysed using the dry sieving method in accordance with ASTM D422 – 63 before subsequent processes. The prepared calcined local clays were analyzed using Minipal 4 Energy Dispersive X-ray Fluorescence Spectrometer (EDXRF) to determine the different concentrations of major oxides present in them. A scanning electron microscope (SEM; JEOL JX 840), a micro-analyzer electron probe, was also used in this study to estimate the particle shapes of the extender pigments. American standard testing methods (ASTM) was used to evaluate the extender pigments for hydrogen ion concentration (ASTM D 1208-96), specific gravity (ASTM D 153-84), refractive index (ASTM D 1208-96), chemical reactivity (ASTM D 34-08) and oil absorption (ASTM D 281-12).

2.3. Preparation of the Alkyd Paints

Alkyd paint samples were prepared using the prepared clays and various quantity of TiO_2 pigment as shown in Table 1. Paint samples were also prepared using only TiO_2 pigment to serve as the control. The paint-drier mixtures was also prepared by accurately weighing out a given quantity of the prepared paint sample and calculated amounts of lead naphthanate and cobalt naphthanate driers were added. The paint-drier mixture was mixed thoroughly using a glass rod. The amount of driers added represents 0.50 wt% lead (Pb), and 0.05 wt.% cobalt (Co) which are the amount of these metals normally used in the surface coatings industry [22]. The amount of driers giving the above percentage of metals in the paint-drier mixtures was calculated as shown in equation (1).

$$\text{Amount of drier required} = \frac{\text{Weight of resin in paint X\% of metal required}}{\text{\% of metal in drier}} \quad (1)$$

Table 1. *Alkyd paint formulations.*

Ingredients	Formulations (wt.%)								
	T100	**OB100–T0**	**OB50–T50**	**OB70–T30**	**OB30–T70**	**IH100–T0**	**IH50–T50**	**IH70–T30**	**IH30–T70**
	TiO_2	**Obowo Clay Formulations**				**Ihitte-Uboma Clay Formulations**			
Alkyd Resin	37	37	37	37	37	37	37	37	37
TiO_2 Pigment	63	-	31.5	18.9	44.1	-	31.5	18.9	44.1
Local Clay	-	63	31.5	44.1	18.9	63	31.5	44.1	18.9
Total	100	100	100	100	100	100	100	100	100
P/B ratio	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Solvent (Xylene)	12	12	12	12	12	12	12	12	12

2.4. Property Determination on Prepared Alkyd Paint Samples

The American standard testing methods (ASTM) was used to evaluate the prepared alkyd paint samples for viscosity (ASTM D 1200-10), specific gravity (ASTM D1475-13), adherence to surface (ASTM D 6677-07, 2012), settling and skinning tendencies (ASTM D 869-85). The settling tendencies of the samples were rated in accordance to the degree of settling on a scale that range from 10 to 0 (Table 2). Intermediate conditions were given appropriate odd numbers. The Nigerian Industrial Standard (NIS) procedure was used to study the mildew formation resistance (NIS 278: 1990), media resistance and chalking tendency (NIS 268: 1989) of the prepared alkyd paint samples. Mild steel panels were used as the coating surfaces for the casting of paint-drier mixtures. The panels were prepared according to ASTM D609-00 procedure, and were taped to 0.40 mm thickness for the casting of the paint-drier mixtures. The paint-drier wet film thickness was assumed the same as the thickness of the tape layer used. The paint-drier mixtures were cast immediately after their preparations on the taped-off portions of the mild steel panels; the wet paint-drier films were levelled off using a short glass rod. The coated plates were placed on a level surface and were allowed to dry at room temperature. Subsequently, the drying properties (surface (dust-free) dry, tack free dry and through dry) were studied. Then the dry film thickness was studied using digital micrometre screw gauge.

Table 2. *Ratings on degree of settling of paint samples.*

Rating	Description of Paint Conditions
10	Perfect suspension, no changes from original condition of paint.
8	A definite feel of settling and a slight deposit brought on spatula.
6	Definite cake of settled pigments, spatula drops through cake to bottom of the container under its own weight.
4	Spatula does not fall to bottom of container under its own weight. Difficult to move spatula through cake sidewise and slight edge resistance.
2	Definite edgewise resistance to movement of spatula.
0	Cake that cannot be reincorporated with the liquid to form smooth paint by stirring manually.

3. Results and Discussions

3.1. Particle Size Analysis

The particle size distribution (PSD) of the Obowo clay and Ihitte-Uboma clays were analysed using the dry sieving method in accordance with ASTM D422 – 63. The results show that in both clays, majority of the particles fall within 0.150 mm, while others are sparingly distributed between 4.75 mm to 0.063 mm as shown in Figure 3. Therefore, 0.150 mm particle size of the clays was used for the preparation of the alkyd paint samples and subsequent analysis. The results show that both clays contain over 32% of grains with size less than 0.150 mm. It is important to note that that grain size affects the hiding power of paints and the finer the pigment particle, the greater the hiding power of the paint. According to the British Soil Classification System, BS 5930 (1999) both clays can be classified as fine sand under coarse soils since the greater portion of the clays are less or equal to 0.150mm.

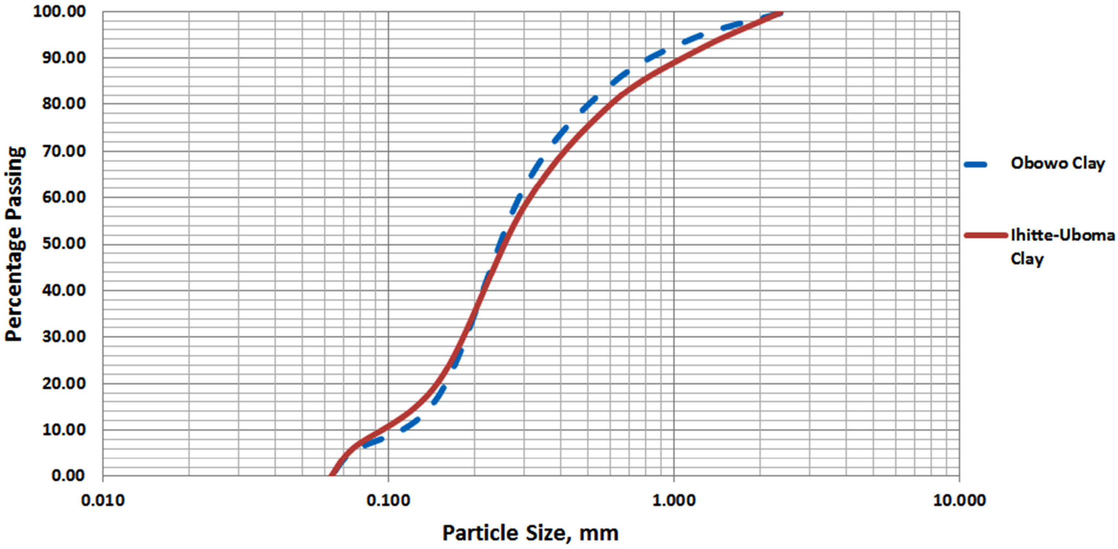

Figure 3. *Particle Size Distribution of Obowo and Ihitte-Uboma Clay Samples.*

3.2. Chemical Composition

The X-ray fluorescence (XRF) determinations on the local clays are presented in Table 3. The present study has shown that two major constituents of the local clays in order of abundance are silica, (SiO_2) and aluminium oxide (Al_2O_3). The SiO_2 and TiO_2 contents of Obowo clay were found to be higher than those present in Ihitte-Uboma clay, while the reverse holds for their Al_2O_3 contents. The high proportion of silica and alumina present in the local clays indicates that they are kaolinite clays. The high content of Fe_2O_3 observed in Ihitte-Uboma clay when compared to the one present in Obowo (OB) clay may be responsible for the reddish-brown colouration of the Ihitte-Uboma (IH) clay. In line with the reports of some researchers [23-25] both clays possess excellent composition for use as extender in paints.

Table 3. *XRF analysis results of the local clays.*

Constituents (wt.%)	SiO_2	Al_2O_3	TiO_2	K_2O	CaO	Fe_2O_3	MgO	Na_2O	V_2O_5	Cr_2O_3	MnO	Sc_2O_3	CuO	ZnO	Bi_2O_3	L.O.I	Total
OB	67.08	21.6	2.98	0.75	0.254	2.58	0.16	0.39	0.16	0.03	0.02	0	0.012	0	0.05	3.91	99.976
IH	56.4	29.3	2.64	0.771	0.23	5.68	0.16	0.11	0.18	0.052	0.022	0.002	0.023	0.008	0	4.38	99.978

3.3. Pigment Morphology

The particle morphology of the local clays obtained from scanning electron microscope (SEM) is shown in Figures 4 and 5. The micrograph for Obowo clay (Figure 4) shows that the clay particles are hexagonal platelets with rounded edges, while the Ihitte-Uboma clay shows the presence of hexagonal platelets having sharp edges.

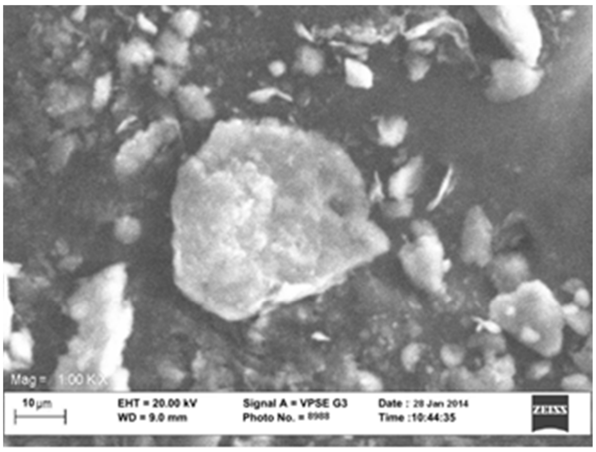

Figure 4. *SEM Micrograph of Obowo Clay.*

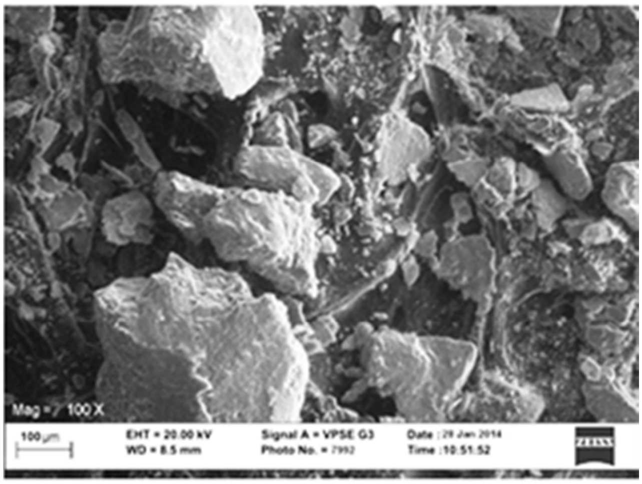

Figure 5. *SEM Micrograph of Ihitte-Uboma Clay.*

The particle shape of an extender pigment affects its packing efficiency, and the hiding power. The plates observed in the clay 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 paint films when used in paint formulations [26]. Plate-shaped particles also tend to overlap one another like tiles on roofs, thereby making it more difficult for water to penetrate the film, whereas rod-shaped particles can reinforce paint film, like iron bars in concrete, and they may tend to poke throughout the surface thereby reducing the gloss of the film. Such rough surfaces may help the next coat to stick more easily, and therefore, this type of pigment could be useful as an undercoat.

3.4. Extender Properties of the Clays

The extender properties of the local clays studied are given in Table 4. The pH of the local clays was determined to be 6.00 for Obowo clay (OB), and 5.68 for Ihitte-Uboma clay (IH). According to Soil Survey Division of US Department of Agriculture, [27], both the Ihitte-Uboma clay, and Obowo clay are moderately acidic. The pH of some extenders are talc, 9 – 9.5; fly ash, 8.15 [11]; Okigwe-Mbano clay, 6.0 [20]; Amankwo Afikpo, clay, 7.74; Okposi clay, 7.46 [21], and industrial waste clay, 7.88 [19]. It is interesting to note that the pH of the clays compared favourably with the pH of other extenders used in paint and also in line with the recommendations of Ghosh et al [23].

The specific gravity of the local clays presented in Table 4 shows that Obowo clay has a specific gravity 2.48 while that of Ihitte-Uboma is 2.58. The specific gravity of some conventional extender pigments have been reported to be: China clay, 2.60; barytes, 4.50; gypsum, 2.34; talc, 2.65 – 2.85, and quartz, 2.80 [28]. Similarly, Nelson [29] reported the following specific gravity values for these extenders and pigments; kaolin clay, 2.58; calcium carbonate, 2.55; rutile titanium dioxide, 4.2. From the present study, it is evident that the local clays have specific gravity within the same range as conventional extenders. The specific gravity of pigments are related to their extent of sedimentation and granulation in paint [30, 31]. Lower specific gravity of pigments leads to a considerable cost saving [32].

Table 4. *Extender Properties of the Local Clays.*

Sample	pH	Specific Gravity	Refractive Index	Oil Absorption g/100 g
OB	*6.00*	*2.48*	*1.44*	*35*
IH	*5.68*	*2.58*	*1.51*	*32*

The refractive indices of the calcined local clays determined using an Abbe's refractometer is also presented in Table 4. Obowo clay has a refractive index of 1.44 while that of Ihitte-Uboma clay is 1.51. It is important to note that all extenders have refractive index that fall in the range between, 1.45 and 1.65 [11]. This is not markedly different from the values found in most dry polymer films (1.45 – 1.7), and so, extenders give neither opacity nor much colour when they are added to clear coatings. The refractive indices of some extenders are calcium carbonate (whiting), 1.58; talc, 1.59 – 1.64; China Clay, 1.56 [11]. Thus, the refractive indices of the local clays compared favourably with those of the other commercially important extenders used in coatings. Titanium dioxide is normally used to impact opacity to coatings because its refractive index nears 2.75, which is higher when compared to those of the local clays and polymer films.

The calcined local clays' oil absorption properties were determined using the spatula rub-out technique and the results obtained are shown in Table 4. The oil absorption value of Obowo clay is determined to be 35 g/100g clay, while that of Ihitte-Uboma clay is 32 g/100 g clay. The oil absorption of some extenders and pigments are talc, 25-35, and fly ash 19 [32]. Schoff [33] and Koleske [22] also reported the following oil absorption values: china clay, 30; amorphous silica, 29; lampblack, 51; red iron oxide, 20; barium sulphate (blanc fixe), 15; calcium carbonate, 17.5; zinc oxide, 19.5; titanox (rutile), 18.5; titanox (anatase), 22; barytes 10-20; carbon black (medium), 124; Okigwe – Mbano clay, 60 [20].

Oil absorption of an extender/pigment gives directly an idea of the amount of base resin required. Less oil absorption indicates less resin demand without compromising other coating properties [34]. Oil absorption property depends mainly on the physical structure (i.e. size and shape of the extender particles), which also affects several other coating properties including flow characteristics, setting tendency, film durability [10]. It is important to note that the particle size of both local clays used for the determination of oil absorption value were the same as described in section 3.1. Thus, the difference in the oil absorption values could be attributed mainly to their particle shape and nature of the particles surface.

The effects of heat on the solubility and colour of the local clays were studied and it was observed that the clay samples are not soluble in petroleum spirit, n-hexane, toluene, chloroform, methanol, ethanol, acetic acid, ammonia solution, sodium hydroxide and hydrochloric acid, except for sulphuric acid where all the samples dissolved. Similarly, heat, generally has no effect on the colour of the local clays in the various chemical media studied except for Ihitte-Uboma clay which was found to bleach in the presence of hydrochloric acid. This latter observation may be attributed to the removal of iron oxide which stained the clay [35]. Eze et al [35] reported that treatment of kaolinite in dilute hydrochloric acid cleaned the clay minerals by removing iron oxides and other metallic compounds from the surface of the clay. The present study has shown that the local clays should be stable in the surrounding environment of use devoid of the presence of hydrochloric acid. The mineral whiting ($CaCO_3$) has been reported to be soluble in dilute mineral while TiO_2 does not dissolve in dilute mineral acids, but dissolves slowly in hot concentrated sulphuric acid [36, 37]. The extender talc has been reported to be partially soluble in diluted hydrochloric acid whereas, the extender barites and quartz are chemically inert [11].

3.5. Performance of the Local Clays in Alkyd Paint Formulations

3.5.1. Specific Gravity

The specific gravity values of Obowo, and Ihitte-Uboma clays and titanium dioxide (TiO_2) pigment formulated alkyd paints are shown in Table 5. The table shows that the TiO_2 formulated alkyd paint has the highest specific gravity when compared to those formulated using the local clays or local clays substituted in parts with TiO_2 pigment. This is to be expected since TiO_2 pigment has the highest specific gravity value when compared to both clays. Specific gravity of paint is used to determine the coverage of paint products on a substrate, that is, the volume occupied by a known weight of paint product [38]. The study further shows that paints prepared using Obowo clay containing 50% TiO_2 pigment and Ihitte-Uboma clay containing 70% TiO_2 pigment exhibited the same specific gravity (1.48). Paints of Ihitte-Uboma clay containing 30% TiO_2 exhibited better specific gravity (1.38) when compared to other samples containing TiO_2 pigment. It can then be inferred that 70% of Ihitte-Uboma clay in paints can lead to considerable cost reduction. The specific gravity of the alkyd paints formulated using the Obowo, and Ihitte-Uboma clays compared favourably to paints prepared using Amankwo Afikpo clay (1.32 to 1.37), and Okposi clay (1.42 to 1.36) [21].

Table 5. *Coating Properties of Paint Samples.*

Formulation Code	Specific Gravity	Viscosity (Pa.s)	Dry Film Thickness (mm)	Drying Time (Min)			Settling Test	Loss of Adherence Test (%)
				Dust Free	*Tack Free*	*Through Dry*		
T100	1.55	1.661	0.24	71	99	150	9	4
OB100 – T0	1.40	5.980	0.39	42	60	71	4	20
OB70 – T30	1.40	5.891	0.34	30	54	109	8	3
OB50 – T50	1.48	1.709	0.30	15	27	82	8	6
OB30 – T70	1.50	2.493	0.27	54	76	121	8	6
IH100 – T0	1.35	5.740	0.39	45	60	70	4	2
IH70 – T30	1.38	4.848	0.33	29	42	91	6	1.5
IH50 – T50	1.43	3.277	0.27	24	37	40	6	2
IH30 – T70	1.48	38.15	0.31	55	76	122	6	1

3.5.2. Viscosity of Alkyd Paint Samples

The viscosity values of the formulated alkyd paint samples are presented in Table 5. Titanium dioxide (TiO_2) formulated alkyd paint exhibited the least viscosity value among the alkyd paints studied. The range of viscosities observed for the paint samples makes them suitable for application by spray or brush. Tiwari and Saxena [11] who studied fly ash extended coatings obtained viscosities that ranged between 2.0 and 2.58 Pa.s, and noted that the formations were suitable for application by brush or spray. The interaction of various constituents in any coating system determines its viscosity [39]. Viscosity affects the application and flow properties of a coating and is generally adjusted to the intended application [40, 19]. According to the Nigerian Industrial Standard NIS 268: 1989, the minimum viscosity for gloss paint shall be 0.22 Pa.s.

3.5.3. Dry Paint Film Thickness

The thickness of a coating is of importance since it profoundly affects the other properties of coatings such as the extent of protection of a substrate by the applied paint. The data obtained on the thickness of the dried paint films in this study are presented in Table 5. From the table, it is evident that TiO_2 formulated paint exhibited the least paint dry film thickness (0.24 mm). The Obowo and Ihitte-Uboma formulated paint samples exhibited the highest film thickness (0.39 mm). For the Obowo formulated alkyd paint samples, the thickness of dry paint film was observed to decrease as the amount of TiO_2 pigment incorporated increased. The Ihitte-Uboma clay formulated paint samples did not exhibit any clear cut order of the variation of dry paint film thickness with TiO_2 pigment content. According Tan Tian Aik, [41], weight loss due to weathering is proportional to film thickness up to 20 μm, above which the rate of weight loss becomes indifferent of the thickness. Thus, a film thickness of more than 20 μm performs well as a barrier resistant to weathering. The results obtained in this study on the film thickness of the samples studied are in the desired range to be considered for corrosion protection.

3.5.4. Drying Studies on Paint Film Samples

The drying properties of the prepared paint samples are presented in Table 5. The alkyd paint samples formulated using the Obowo clay, Ihitte-Uboma clay, and TiO_2 pigment had dust-free drying times of 42, 45, and 71 minutes respectively. Thus, the local clays exhibited better dust-free drying times than TiO_2 in the formulated paint samples. The paint samples prepared using Obowo, and Ihitte-Uboma clays that were substituted with 70% TiO_2 exhibited the highest dust-free drying times when compared to paint formulations of these clays that were substituted with 30, and 50% TiO_2. In essence, high TiO_2 content was observed to increase the dust-free drying times of the Obowo, and Ihitte-Uboma formulated alkyd paints; with TiO_2 formulated paint having the highest dust-free drying time. The dust free drying time of 15 minutes exhibited by Obowo clay paint sample substituted with 50% TiO_2 is outstanding.

An applied paint film is considered tack-free (TF) when the finger with a slight pressure did not leave any mark, and the surface not sticky. The paint sample prepared using only TiO_2 pigment had the highest tack-free drying time of 99 minutes, while the paint samples of Obowo, and Ihitte-Uboma clays exhibited the same tack-free drying times of 60 minutes. The latter clays also exhibited similar dust-free drying times. Both the Obowo and Ihitte-Uboma clays substituted with 70% TiO_2 pigments exhibited higher and the same drying times of 76 minutes in the formulated alkyd paints. No general order on the tack-free drying times of TiO_2 substituted local clays could be observed in the prepared paint samples. According to Nigerian Industrial Standard, NIS 268: 1989, the surface dry time of gloss paint shall not exceed 6 hours from the time of application.

The through dry times of the formulated paint samples presented in Table 5 shows that TiO_2 pigment formulated paint sample exhibited the highest through dry time of 150 minutes. Both the Obowo and Ihitte-Uboma clay formulated paint samples exhibited similar through dry times of 71 and 72 minutes respectively. The order in the variations of through dry times of both the Obowo, and Ihitte-Uboma clay substituted with varying amounts of TiO_2 in the formulated paint samples is 70% TiO_2 > 30% TiO_2 > 50% TiO_2 content. In essence, the local clays containing 70% TiO_2 pigment exhibited the highest through dry times in the prepared alkyd paints than the paint samples having local clay substituted with 30, and 50% TiO_2 pigment. All the formulated paint samples based on the local clays, and clays replaced in parts by TiO_2 pigment exhibited good drying properties. According to the Nigerian Industrial Standard, NIS 268: 1989, the through dry time of gloss paint shall not exceed 24 hours.

3.5.5. Skinning and Settling Tests

The formulated paint samples exhibited no sign of skin formation after eight months of storage. Various degrees of settling were observed in the samples after eight months of storage as shown in Table 5. Paint samples prepared using the Obowo clay containing varying amounts of TiO_2 pigment have fairly good settling tendencies when compared to paint samples prepared using 100% Obowo clay, 100% Ihitte-Uboma clay, and Ihitte-Uboma clay containing varying amounts of TiO_2 pigment. Generally, some properties of pigments affect their settling tendencies. These include particle size, particle shape, specific gravity, and the activity which includes such properties as basicity, wettability, flocculating, dispersing and gel forming tendencies [42]. The properties of the binder also influence the settling tendencies. It is probable to reason that the difference in settling tendency observed for the local clays, and TiO_2 formulated paint samples may be due to the difference in their particle structure.

Furthermore, specific gravity is known to be related to the sedimentation and granulation of paints and affects the rate at which solid particles settle in liquids. The proportional difference between the specific gravities of these extender pigments and the binder may have led to the slight cake formed by the local clays. Oil absorption of pigments also relates to its settling tendencies. Pigments with high oil absorption will tend to absorb the paint vehicle and form coat after an extended period of storage [43, 14]. TiO_2 pigments were noted to have oil absorption value that was lower than those of the local clays. This could have also contributed to the various levels of settling observed in the paint samples.

3.5.6. Adherence to Surface of Paint Films

Data on the adhesion properties of the prepared paint samples are shown in Table 5. The table shows that all the alkyd paint samples exhibited good adhesion properties. According to Nigerian Industrial Standard, NIS 268: 1989, gloss paint should not exhibit more than 50% removal of the dried paint film. The paint samples prepared using the Ihitte-Uboma clay containing 30 – 70% TiO_2 exhibited particularly good adhesion properties. Obowo clay formulated paint sample exhibited the highest% adhesion loss of dry paint film (20%). Majority of the prepared paint samples exhibited % adhesion loss in the range, 1 – 10. Adhesion according to ASTM D907 [2012] is defined as the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action or both. For the most part, organic coatings are removed in service by abrasion, chipping, coins, and other instruments, picking away at exposed edges, corrosion of the substrate, impact or impingement by stones.

3.5.7. Mildew Formation and Light Fastness of Dry Paint Film Samples

All the formulated alkyd paint samples did not show any sign of mildew formation after seven months of exposure to rain and sunlight. This is an indication that the local clay formulated paint samples performed equally well in coatings just like the TiO_2 pigment formulated paint samples. On the other hand, the alkyd paint formulated samples shaded their colour after seven months of exposure to rain and sunlight. The paint formulations containing only TiO_2 pigment and local clays substituted in part with 70% TiO_2 pigment exhibited slight rust while all the other paint formulations resisted rust as shown in Figure 6. The 100% Obowo clay based paint formulation exhibited poor outdoor performance as it was found peeling off the substrate after the exposure. This is an indication that paint formulations containing local clays substituted with lower quantity of TiO_2 pigment can withstand environmental challenges, and therefore can be used in corrosive environment.

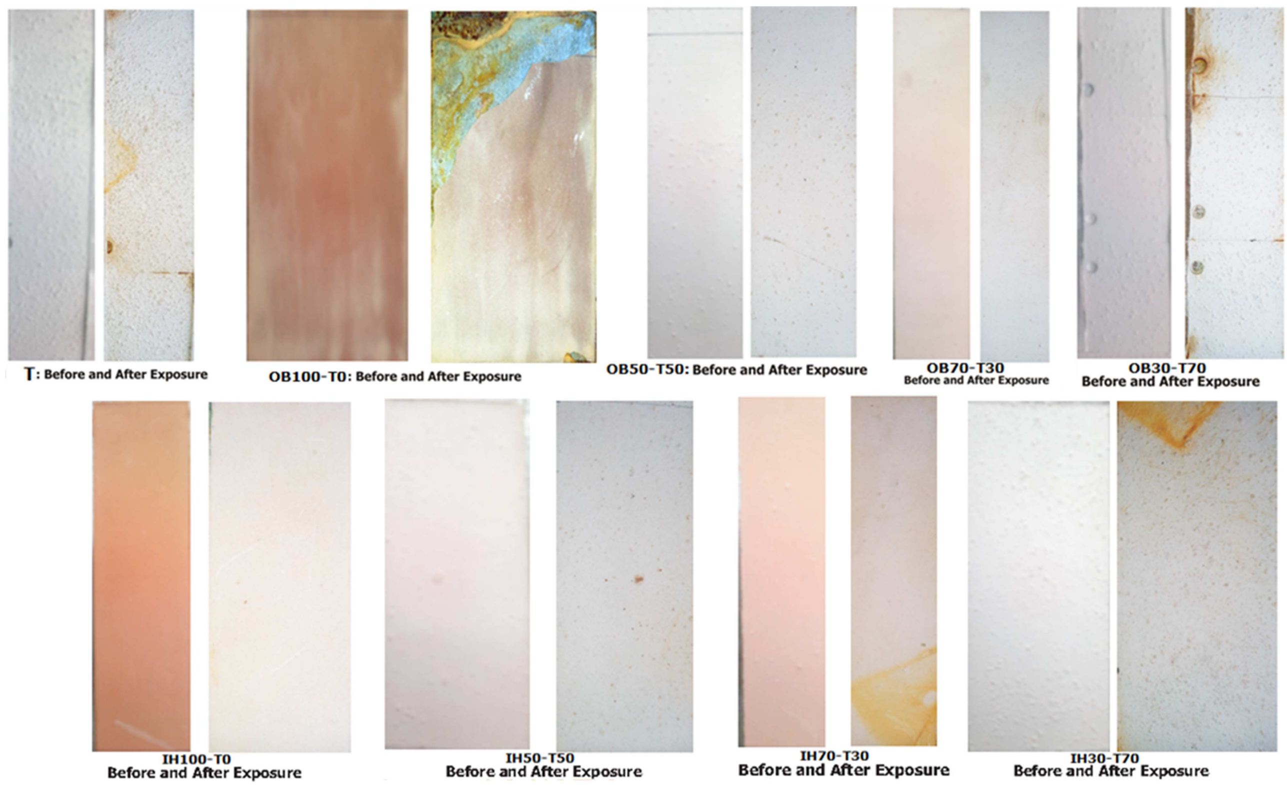

Figure 6. *Pictures of the formulated paint samples before and after exposure to rain and sunlight.*

3.5.8. Media Resistance Test on Paint Film Samples

The visual changes that occurred on the formulated paint films after immersion in 2% NaCl, 2% H_2SO_4, and 2% Na_2CO_3 and distilled water for 24 hours are presented in Table 6. The performance of the paint samples shown in Table 6 were rated according to the method of Muralidharan et al, [44] as follows: 0 – No change; 1 – Very slight effect; 2 – Effect; 3 – Light effect; 4 – Definite effect; 5 – Bad effect.

From the table, it is evident that all the formulated paint samples performed satisfactorily in 2% Na_2CO_3 and distilled water with the exception of TiO_2 formulated paint sample. The paint samples also performed well in 2% sulphuric acid. The performance in 2% NaCl was good; except for slight salt effect on paint samples formulated containing only TiO_2 pigment and Obowo clay containing varying amounts of TiO_2 pigment. The good performance of the local clay based paints in acidic as well as 2% Na_2CO_3 could be attributed to the presence of inert oxides they contain. It is important to note that water in one way or the other is the common enemy to most materials of construction. The absorption of water by paint films can lead to loss of components from the film, and subsequent deterioration of paint films but the prepared paint samples performed very well in the presence of distilled water. The slight chemical reactivity of paint samples formulated using Obowo clay containing varying amounts of TiO_2 in NaCl solution should restrict the paints applications where high durability against corrosive environment is required.

Table 6. *Media Resistance of Prepared Paint Samples.*

Formulation Code	2% NaCl	2% H_2SO_4	2% Na_2CO_3	Distilled Water
T100	3	3	1	0
OB100 – T0	1	1	1	0
OB70 – T30	3	1	0	0
OB50 – T50	3	1	0	0
OB30 – T70	3	2	1	1
IH100 – T0	2	1	1	0
IH70 – T30	2	0	0	0
IH50 – T50	2	0	0	0
IH30 – T70	2	0	0	0

4. Conclusion

Alkyd paint samples have been prepared using Obowo, and Ihitte-Uboma clays, and the local clays containing varying amounts of TiO_2 pigment. Analysis on the local clays revealed that they are inorganic silty clays, moderately acidic, and containing over 32% grains of size < 0.150 mm. The major compositions of the clays are SiO_2 and Al_2O_3 in that order, with small amount of TiO_2 and then Fe_2O_3 found to be higher in Ihitte-Uboma clay contributing to its reddish-brown colouration. The local clays were found to be stable to heat and insoluble in the chemical media examined, except for their solubility in sulphuric acid.

The film thicknesses of the paint samples formulated were found to be in the range that places the paint samples as anti-corrosive paints. The local clay formulated paint samples were observed to exhibit the best dust-free, tack-free, and through dry times. The alkyd dry film samples exhibited no chalking tendency and mildew formation and generally performed well in distilled water, 2% Na_2CO_3, and 2% H_2SO_4. The present study has demonstrated the utility of Obowo, and Ihitte-Uboma clays in formulating alkyd paints. The expectation is that these clays should find utilizations in the surface coatings industry which will help to reduce the over dependence on imported extender pigments, thereby saving the country the scare resource, spent on importation. The local clays are easy to process, stable and indigenously available.

References

[1] Patel, H (2006). Nanoclays for polymer nanocomposites, paints, inks, greases and cosmetics formulations, drug delivery vehicle and wastewater treatment. Bulletin of Material Science, v. 29, n. 2, p. 133–145.

[2] Edomwonyi-Otu LC, Aderemi BO, Ahmed AS, Coville NJ, Maaza M (2013). Influence of thermal treatment on kankara kaolinite. Opticon 1 826 (15): 5, DOI: http://dx.doi.org/10.5334/opt.bc.

[3] Badmus BS, Olatinsu OB (2009). Geophysical evaluation and chemical analysis of kaolin clay deposit of Lakiri village, southwestern Nigeria. Intl. J. Phys. Sci. 4 (10): 592-606.

[4] Onyemaobi, O. O.; Mark, U. (2009). Assessment of the Industrial Potentials of Some Nigerian Kaolinitic Clay Deposits. International Research Journal in Engineering Science & Technology, v. 6, n. 1, p. 77-84.

[5] NFTS (2008, 2009, 2010 and 2011). Nigerian Foreign Trade Summary Report. A publication of the National Bureau of Statistics, Plot 762 Independence Avenue, Central Business Area, Abuja-Nigeria.

[6] Imerys P (2013). Calcined clays in light weight coatings technical guides. Retrieved September 19, 2013, from http://www.imeryspaper.com/Technical_Guide_Calcined_Clay_in_LWC_pdf

[7] Sposito, G., Skiper, N. T. Sutton, R. Park, S. H. Soper, A. K and Greathouse. J. A. (1999). Surface geochemistry of the clay minerals. Proceedings of National Academy of Science, USA, 96: 3358–3364.

[8] Brigatti, M. F., Galan, E. and Theng, B. K. G (2006). Structures and mineralogy of clay minerals. In, F. Bergaya, B. K. G. Theng, and G. Lagaly (eds.), Handbook of Clay Science 5, 19-86. Elsevier, Netherlands.

[9] Woodridge, R. (1991). Principles of paint formulation, Blackie Academic & Professional, New York.

[10] Morgans, W. M. (1990). Outlines of paint technology. Edward Arnold, London.

[11] Tiwari, S. and Saxena, M. (1999). Use of fly ash in high performance industrial coatings. British Corrosion Journal, 34 (3), 184-191.

[12] Vassiliou, P. and Argyropoulos, T. (2005). Red mud as anticorrosive pigment for metal protective organic coatings. 5th international exhibition and conference on environment (HELECO 2005), Athens, Greece.

[13] Gogte, B. B. and Agrawal, A. (1994). Fly ash based coatings. Paintindia XLIV (10), 51-56

[14] Wicks, Z. W., Jones, F. N., Pappas, S. P., Wicks, D. A. (2007). Organic coatings: Science and Technology 3rd ed. John Wiley and sons Inc., New Jersey, USA.

[15] Saxena, M. and Dhimole, L. K (2005). Utilization and value addition of copper tailing as an extender for development of paints. Journal of Hazardous Materials, 129 (1-3), 50-57.

[16] Youssef, E. A. M. (2002). Characterization, surface modification, and evaluation of Egyptian dolomite ore as an extender pigment for paint. Journal of Pigment and Resin Technology, 31 (4), 226-233.

[17] Ewulonu, C. M., Igwe, I. O. and Onyeagoro, G. N. (2016a). Synthesis and characterization of local clay–titanium dioxide core–shell extender pigments. Journal of Coatings Technology and Research, 13 (4). http://dx.doi.org/10.1007/s11998-016-9786-4.

[18] Ewulonu, C. M., Igwe, I. O. and Onyeagoro, G. N. (2016b). Performance of local clay-titanium dioxide core-shell extender pigments in alkyd Paints. Advances in Nanoparticles, 5, 90-102. http://dx.doi.org/10.4236/anp.2016.51011.

[19] Anyiam, C. K. and Igwe, I. O. (2012). Studies on the use of an industrial waste clay in alkyd paint formulations. International Journal of Academic Research, 4 (2).

[20] Odozi, T. O., Dore, R. and Onu, C. O. (1986). Paint extenders based upon an indigenous clay. Journal of Nigeria Society of Chemical Engineers, 5 (2), 34-40.

[21] Igwe, I. O. and Ezeamaku, L. U. (2010). The use of some local clays in alkyd paint formulations. Malaysian Polymer Journal, 5 (1), 81-94.

[22] Koleske, J. V. (1995). Driers and Metailc Soaps. In, J. V. Koleske (ed.), Paint and coating testing manual: Fourteenth edition of the Gardner-Sward Handbook. ASTM, Philadelphia, USA.

[23] Ghosh S, Warrier KGK, Damodaran AD (1990). Thermally treated kaolin as an extender pigment. J. Mater. Sci. Letts. 9 (1): 1046-1048.

[24] Murray, H. H., 2007. Applied Clay Mineralogy: Occurrences, Processing and Applications of Kaolins, Bentonites and common clays. Developments in Clay Science, vol. 2, Elsevier, Amsterdam.

[25] Mesbah H, Wilson MA, Carter MA (2011). The role of the kaolinite-mullite reaction sequence in moisture mass gain in fired kaolinite. Retrieved August 13, 2013, from http://www.scientific.net/ATS.68.38.pdf

[26] Lambourne, R. (1999). Paint composition and applications – a general introduction. In, R. Lambourne and T. A. Strivens (eds.), Paint and surface coatings theory and practice second edition. Woodhead publishing Ltd, Cambridge, England, 1-18.

[27] Soil Survey Division Staff (1993). Soil survey manual 1993: Chapter 3, selected chemical properties. Soil conservation service. USA department of agriculture handbook. Retrieved 2011-03-12 from (http://soils.usda.gov/technical/manual/contents/chapter3.html).

[28] Mendham, J. Denneg, R. C. Barnes, T. D. and Thomas, M., (2000). Vogel's Textbook of Quantitative Inorganic Analysis, Sixth Edition. 15, 584-615.

[29] Nelson, K. L. (2007). Enhanced performance and functionality of titanium dioxide papermaking pigments with controlled morphology and surface coating. Georgia Institute of Technology, ProQuest, USA.

[30] NPCS Board of Consultants & Engineers (2009). Surface Coating Technology Handbook. Asia pacific business press Inc., New Gian, Delhi.

[31] MacEvoy, B. (2005). The material attributes of paints. Paints. Retrieved November 02, 2014 from http://www.handprint.com/HP/WCL/pigmt3.html

[32] Imerys (June 2009). Saving TiO_2 in semi-gloss emulsion paints with supreme. Imerys world minerals publication, www.imerys-perfmins.com.

[33] Schoff, C. K. (2009). Coating clinic. JCT Coatings Technology. Pennsylvania, USA.

[34] Wang, B., Michael Greene, M. and Singh, R. K. (2010). Natural amorphous silica filler products. World minerals, Inc. US Patent, WO2010104831 A1.

[35] Eze, K. A., Nwadiogbu, J. O. and Nwankwere, E. T. (2012). Effect of acid treatments on the physicochemical properties of kaolin clay. Archives of Applied Science Research, 4 (2), 792-794.

[36] Osabor, V. N., Okafor, P. C., Ibe, K. A. and Ayi, A. A. (2009). Characterization of clays in Odukpani, South Eastern, Nigeria. African Journal of Pure and Applied Chemistry, 3 (5), 079-085.

[37] Talabi, A. O., Ademilua, O. L. and Akinola, O. O. (2012). Compositional Features and Industrial Application of Ikere Kaolinite, Southwestern Nigeria. Research Journal in Engineering and Applied Sciences 1 (5), 327-333.

[38] Henton, L. E. (1981). Determination of volume solids of paints and coatings. Engineering experiment station, Georgia Institute of Technology, USA.

[39] Nylen, P. and Suderland, E. (1965). Modern surface coatings. Interscience, London.

[40] Payne, H. F. (1954). Organic coating technology: volume 1, oils, resins, varnishes, and polymers. Chapman & Hall, New York – London.

[41] Tan Tian Aik, D. (1995). Durability and TiO_2 pigments. 1995 Paintindia Annual, 84-93.

[42] Murray, H. H. (1991). Overview — clay mineral applications. Applied clay science, 5 (5-6), 379-395.

[43] Guy, A. (2004). The science and art of paint formulation. In, The chemistry and physics of coatings 2nd ed. Marrion, A. R. (ed.), The Royal Society of Chemistry, Northampton, UK.

[44] Muralidharan, N. M., Unnikrishnan, K. G., Unnikrishnan, M. and Nair, C. S. B. (1981). Utilization of rubber seed oil and karinnota oil for the preparation of air drying oil modified alkyd resin. Paintindia, 31 (5), 5-9.