Formulation of Anti-Corrosive Alkyd Paints Based on Umuahia Clay Extender

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Abstract
Umuahia clay was used as an extender to formulate alkyd paints possessing anti-corrosive property on mild steel. The clay which was sieved to 0.075 mm particle size was used within extender contents, 0 to 80.0 wt.%. Titanium dioxide prepared alkyd paint served as the reference paint while xylene was used as the solvent. Determinations on the properties of clay gave the following results: pH (6.50), specific gravity (2.10), oil absorption (36.0 g/100 g), and refractive index (1.63). The clay was stable to heat and the chemical media studied, and composed largely of silica (60.90 wt.%), alumina (24.63 wt.%) and titanium dioxide (3.50 wt.%). Other metallic oxides are present in negligible amounts. The formulated paints exhibited satisfactory surface -, and through-dry times, and the paint sample containing 80 wt.% clay had the best through-dry time of 216 min. The film thickness of the paint dry films were within 0.10 to 0.15 mm, an indication that the films will form barriers resistant to weathering. The formulated paint samples had good impact strength and the dry paint film hardness was observed to increase with increasing clay content. The paint samples containing 60, and 80.0 wt.% clay had maximum pencil hardness of 5H. The adhesion of the paint dry films to mild steel surfaces was generally good, and adhesion losses were in the range, 3.0 to 25.0 %. The paint dry films exhibited no blistering or severe paint defects on immersion in 3% NaCl except for slight colour changes which are suggestive of anti-corrosive property of the paints. The performance of the dry paint films in deionized water, and 3% Na_2CO_3, was generally satisfactory unlike the performance in 3% H_2SO_4 where some paint defects occurred. The present study has highlighted the utility of Umuahia clay in formulating paints for the protection of mild steel in salty environments, the property which is attributed to the presence of inert oxides of silica, alumina, and titanium dioxide in the clay.

Keywords: *Alkyd Paints, Umuahia Clay, Extender, Titanium Dioxide, Particle Size.*

I. INTRODUCTION

Clay is a common name for a number of fine grained earthly materials that are plastic and tenacious when moist, and permanently hard when fired or baked. Generally, clays are hydrated silicates of aluminium that approximate in composition to $Al_2O_3.2SiO_2.2H_20$ and which may contain impurities such as potassium, sodium, calcium, magnesium or iron in small quantities. They are one of the major minerals that are abundant on the earth's crust which are characterized by sheet silicate structures of composite layers stacked along the c – axis [1].

Clay minerals were envisaged to have been formed at different times in the geochemical cycle by the gradual weathering of rocks (usually silicates) by low concentrations of carbonic acid and other diluted solvents. Beside the weathering process, clay minerals are also formed by hydrothermal activity [2]. Clays appear in different colours ranging from dull grey to deep orange red depending on the soil content. The physical properties of clays such as hardness, cohesion, plasticity, and shrinkage under drying, can vary widely [3]. These common characteristics derive from their chemical composition, layered structure, and size. Generally, all clay minerals have great affinity for water and the ability to exchange ions[4].

Clays are used in a number of applications that depend on their qualities. They are utilized in the manufacture of industrial products such as paper, rubber, tiles, porcelains, white wares, and bricks. The clay, bentonite is used for cracking operations in the refineries [3], [5-6]. Fuller's earth is utilized in the processing of many minerals, and vegetable oils [7]. Recently, Rahim et al [8] used montmorillonite clay to enhance the thermal degradation property of polyacrylonitrile / nano composite filaments. It was also reported that fibres with increased concentration of montmorillonite clay exhibited higher crystalinity.

The use of clays as extenders in the formulation of paints is receiving attention from paint formulators and technologists who are searching for technically viable extenders that will partially or wholly replace titanium dioxide (TiO_2), the prime pigment used in surface coatings and thus, bring down the cost of paintings to acceptable limits. TiO_2, a white pigment with high refractive index is the most widely used pigment in paint formulations. However, the pigment is very expensive because of its mineral origin. Worse still, TiO_2 is chemically active leading to photocatalytic degradation of painted surfaces [9]. Most of the extenders such as talc, whiting, and barytes used in paint production are expensive due to their mineral origin, and they require long processing with significant loss of materials [10]. Coating extenders are cheaper than the primary pigments.

They contribute little opacity to paint films and are used to cheapen paint products.

Presently, calcined clays which are of low cost and environmentally friendly are considered alternatives to TiO_2 in paint formulations. They impact a number of desirable properties to the paints. Similarly, fine calcined clays act as spacer to TiO_2 that enhances the scattering power of TiO_2 pigment with good paint dry film opacity [11]. The utilization of clays as extenders in paint formulations have been reported. Thus, an indigenous china clay obtained from Aghara Quarry, Mbano, Nigeria was used to formulate alkyd paints with improved coatings properties [12]. The paints exhibited good gloss, high scratch characteristics and obliterating value. Polsperse™ 10 (an ultrafine kaolin) was used to prepare alkyd – based paints that was capable of replacing up to 10 % of TiO_2 in the formulated paints with no loss of opacity, whiteness or gloss [13]. The incorporation of the clay also improved the sagging resistance of the formulated paints.

The utilization of calcined, and chemically treated Egyptian clay (kaolin) in the formulation of alkyd – based paints was reported by Ahmed [14]. Results showed that the calcined kaolin performed better than the untreated kaolin in the protection of steel while the corrosion protection performances of chemically treated kaolin varied depending on the concentration of modifier or dopant. Narayan and Raju [15] who prepared two latex paints based on a calcined clay reported that the clays can replace up to 20 % titanium dioxide in paint formulations without having any adverse effect on paint properties. Ferrite – kaolin hybrid pigments have been used to prepare solvent - based paints within pigment contents, 50 to 75 % [16]. The prepared paints exhibited good corrosion prevention property when applied on steel substrates.

In the present report, clay obtained from Ubakala, Umuahia, Nigeria was used as an extender to formulate alkyd paints that exhibited anti – corrosion properties when applied on mild steel surfaces. The clay which was calcined at 850°C, sieved to 0.075 mm particle size was used within extender contents, 0 to 80 wt %. TiO_2 formulated alkyd paint served as the reference paint while xylene was used as the solvent. This study was part of our on-going efforts in exploring the suitability of Nigerian clays in paint production. Our earlier reports on the suitability of some Nigerian clays in formulating paints were encouraging [17]-[20]. Nigeria has rich sources of clay, and it is estimated that clay minerals constitute over 50 % of the non – metallic, earthy, and naturally occurring resources that abound throughout the country's sedimentary basins and on the basement. The clays are grossly underutilized despite their vast potentials in agriculture and technology. Similarly, reported studies on clay deposits in Nigeria focused on their characterization with little emphasis on their industrial potentials [21].

II. MATERIALS AND METHODS

A. Materials

The following materials were used in this study.

1) Alkyd Resin:

This was a medium soyabean oil alkyd resin purchased from Jokems Indutries Ltd, Onitsha, Nigeria. It has an acid number of 2.30 mgKOH/gKOH.

2) Clay Sample:

The clay was collected from Ubakala, Umuahia, Nigeria and used as extender**.**

3) Metallic Driers:

Cobalt and lead naphthanates were used as driers and were purchased from a chemical store at Onitsha, Nigeria. The cobalt drier was used for surface drying of the prepared paints while lead naphthanate drier was for through drying of paints. Their metal contents are 36 % lead and 12 % cobalt respectively.

4) Solvents and Reagents:

The following analytic grade solvents and reagents were used in this study without purification: toluene (JHD), chloroform (JDH), methanol, xylene (BDH), sulphuric acid, hydrochloric acid (M&B), acetic acid (BDH), sodium hydroxide, ammonia, titanium dioxide (M&B), linseed oil, and stearic acid.

B. Methods

1) Preparation of Clay Extender:

The Umuahia clay extender was first sundried after which impurities were removed from it. It was later crushed using a motorized grinder, calcined for 6 h at 850°C, and sieved to 0.075 mm particle size. The sieved clay was stored in a tight lid container for further use.

2) Characterization of Clay Extender:

The prepared clay sample was characterized for the followings using standard methods: specific gravity (ASTM D 153-84), pH (ASTM D 1208-960), refractive index (ASTM D1208-96), oil absorption (ASTM D 281-12), and chemical composition (ASTM D 5381-94).

The resistance to chemicals of the prepared clay sample was determined as follows :

1 g of sieved clay was placed in a 50 cm^3 beaker and 10 cm^3 of test chemical was poured into the beaker. The beaker containing the clay was gently heated while noting the solubility and colour of the sample in the cold, and when heated. The resistance to chemicals was performed in the following chemicals: toluene, chloroform, hydrochloric acid, sodium hydroxide, and ammonia solution.

3) Preparation of Extended Alkyd Paint Samples:

The paint samples were prepared using titanium dioxide (TiO_2), medium soyabean oil alkyd resin, and xylene. The various alkyd paint sample formulations studied are shown in Table 1.

Table 1. Formulations for Alkyd Paint Samples.

S/N	Sample Code	Ingredients (g)			
		Alkyd resin	Clay	TiO_2	Xylene
1	AT-100	66	0.00	29.70	11.90
2	ATU-80/20	66	5.90	23.80	11.90
3	ATU-60/40	66	11.90	17.80	11.90
4	ATU-50/50	66	14.90	14.80	11.90
5	ATU-40/60	66	17.80	11.90	11.90
6	ATU-20/80	66	23.80	5.90	11.90

Amount of lead drier used = 0.11g
Amount of cobalt drier used = 3.30g
Pigment/Binder Ratio = 0.45
Note:
AT = Paint sample containing 100% TiO_2.
ATU = Paint sample formulated using TiO_2 and Umuahia clay.

4) Characterization of Alkyd Paint Samples:

The prepared paint samples were characterized for dry paint film thickness (ASTM D 1005-95), dry paint film hardness (ASTM D 3363-05), and impact resistance of dry paint films (ASTM D 2794-93) using standard methods. The prepared paint samples were also characterized for the surface - dry time and the through – dry time.

The dry paint film on mild steel panel was considered surface dry when the finger, without pressure, was slightly run over the wet paint surface without picking up any paint on the finger.

The paint was considered through-dry when with maximum pressure, there was no loosening, detachment, wrinkling or other evidence of distortion of the paint film after being pressed maximally with the finger.

The adhesion of dry paint films on mild steel panels, and media resistance of dry paint films on 3% H_2SO_4, 3% NaCl, 3% Na_2CO_3, and deionized water were determined using the ASTM D 6677-07, 2012, and NIS 268: 1989 methods respectively.

III. RESULTS AND DISCUSSION

A. Characteristics of Umuahia Clay

The Umuahia clay used in formulating the alkyd paints has the following properties:

1) *pH:*

The clay has a pH of 6.50, an indication that it is moderately acidic. The pH of some paint extenders are Okposi clay, 7.45[18], Okigwe - Mbano clay, 6.0[12] and fly ash, 8.15[22].

2) *Specific Gravity:*

Umuahia clay has a specific gravity of 2.10 while titanium dioxide used as a reference pigment in this study has a specific gravity of 4.20. The specific gravity of an extender pigment affects the oil absorption and settling tendency of the extender pigment. The lower the specific gravity, the lower will be the settling tendency in paints, and the higher is the oil absorption [23]. The specific gravity of some convectional extender pigments are: China clay (2.60), whiting (2.70), barytes (4.25 - 4.50)[23], and calcium carbonate (2.55)[24]. Pigments with low specific gravity generally lead to considerable cost savings in coatings.

3) Refractive Index:

The refractive index of Umuahia clay determined using an Abbe's refractometer is 1.63. The refractive index of an extender pigment affects the refractive index of paint. Generally, extenders do not give opacity or colour when added to paints. The refractive index of extender pigments are in the range 1.45-1.65. The refractive index of titanium dioxide (2.75) used in this study is higher than that of Umuahia clay. Many extenders used in coatings have lower refractive indices compared to titanium dioxide, and this accounts for the poor opacity observed in solvent paints formulated with these extenders [23].

4) Oil Absorption:

The oil absorption of Umuahia clay is determined to be 36.0g/100g. The titanium dioxide has an oil absorption value of 18.5g/100g, a value which is lower than that of Umuahia clay. The lower the oil absorption of an extender pigment, the less the resin demand without compromising other coating properties [25]. The oil absorption of a coating pigment depends on the size and shape of the pigment particles which on the other hand affects other coating properties such as film durability, and flow characteristics [10].

5) Chemical Composition:

X-ray fluorescence (XRF) analysis of Umuahia clay shows an appreciable presence of silicon oxide (SiO_2) (60.90wt.%) in the clay, followed by aluminium oxide (Al_2O_3) (24.63 wt.%), and titanium oxide (TiO_2) (3.50 wt.%) in that order. The quantities of potassium oxide (K_2O) and iron(iii)oxide (Fe_2O_3) are 0.83, and 2.58 wt.% respectively, with other oxides present in minute quantities. According to Raheem and Olowu [26], a large presence of SiO_2 and Al_2O_3in an extender indicates the kaolinite nature of the extender pigment and which will form the basis fir its utilization in paint making. The presence of unreactive oxides in the clay shows that paints formulated with it will function as an anti-corrosive paint since the unreactive oxides will slow down the diffusion of reactive species into the painted surface, and thus, prevent corrosion of the painted metallic surface.

6) Resistance to Chemicals:

The present study shows that Umuahia clay was generally stable in the chemicals studied either in the cold or when heated since it did not change colour or dissolve in the chemical media. However, there was slight solubility and colour change of the clay in sulphuric acid when heated, thus discouraging the use of paints formulated with Umuahia clay in sulphuric acid prone environment. The appreciable quantities of SiO_2 (60.90 wt.%) and Al_2O_3 (24.63 wt.%) in the clay may be responsible for the stability of the clay in the chemical media studied since these two components have high melting points (SiO_2, 1713^oC; Al_2O_3, 2054^oC), and are insoluble in water, and mineral acids [27]. The good resistance of Umuahia clay to the chemicals studied also indicates that paints formulated with it will be good weather resistance in the environment of these chemicals. The dissolution of an extender pigment in its solvent on application to a surface causes the solvent to migrate to the surface, which on evaporating leaves the crystals (particles) of the extender on the paint surface in the form of powder. This phenomenon is responsible for the chalking observed with poorly formulated paint.

B. Performance Evaluation of Prepared Paint Samples

1) Surface Dry Times:

The surface dry times of the paint samples illustrated graphically in Fig. 1 shows that the dry times increased with increasing clay content, up to 50 wt.% clay incorporation, and thereafter, decreased with clay content, and were in the range, 10 - 20 min. The paint sample containing 80 wt.% clay, and TiO_2 formulated paint had the same surface dry time of 10 min. Thus, the incorporation of high amount of clay into alkyd paints produced good surface drying properties. The addition of Umuahia clay into the alkyd paints did not adversely affect the paint's surface dry times because according to Nigeria Industrial Standards, (NIS)[28], the surface dry times of a gloss paint shall not exceed 6 h from the time of application.

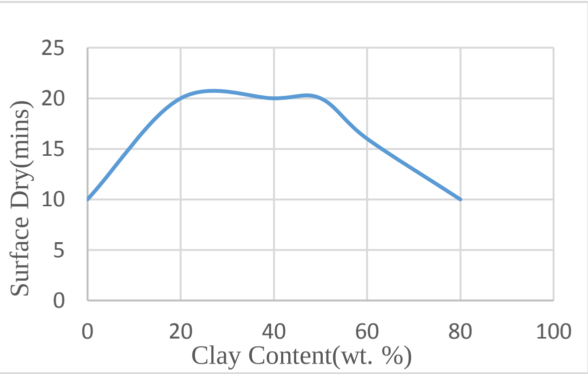

Fig. 1: Effect of Clay Content on Surface Dry Times of Formulated Alkyd Paints.

2) Through Dry Times:

Fig. 2 shows that the incorporation of Umuahia clay into the alkyd paint samples increased the through dry times of the paints, up to 40 wt.% clay incorporation, and later decreased with further clay incorporation into the paints. TiO_2 formulated paint sample had a through dry time of 270 min. The Umuahia clay formulated paint containing 80 wt.% clay had the best through dry time of 216 min. The formulated paint samples had good through dry times since according to Nigeria Industrial Standards (NIS, 1989), the through dry time of a good gloss paint shall not exceed 24 h from the time of application.

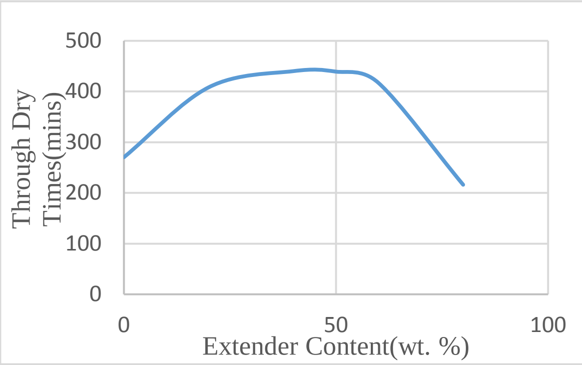

Fig. 2: Effect of Clay Content on Through Dry Times of Formulated Alkyd Paints.

3) Dry Paint Film Thickness:

The film thickness of the prepared paint samples illustrated in Fig. 3 shows that there was no definite order of variations of paint film thickness with clay content. The TiO_2 formulated paint, and paint samples containing 40, 60, and 80 wt.% clay had the same film thickness of 0.15 mm. Paint samples containing 20, and 50 wt.% clay had the best film thickness of 0.10 mm. The film thickness of a coating affects its durability, and paint film thickness of more than 20 µm is reported to perform well as a barrier resistant to weathering [22]. Therefore, the film thicknesses obtained in this study that were in the range, 0.10 - 0.15 mm indicate that Umuahia clay formulated paint samples will function as anti-corrossive paints

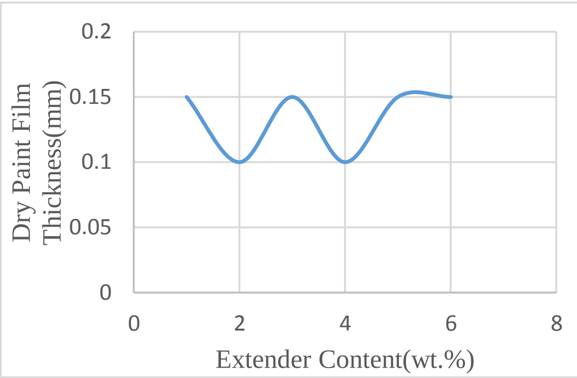

Fig. 3: Effect of Clay Content on Dry Paint Film Thickness of Formulated Alkyd Paints.

4) Dry Paint Film Impact Strength:

Coatings generally are expected to be resistant to impact damage during their service life. The impact strength of the paint films determined using Charpy impact tester showed that the formulated paint samples passed the impact test attesting to their good quality.

5) Dry Film Hardness:

The hardness of Umuahia clay formulated paint dry films were observed to increase with increasing clay content. The TiO_2 formulated paint sample exhibited the least paint dry film hardness (6B). The paint samples containing 60, and 80 wt. % clay had maximum pencil hardness of 5H. This study shows that the formulated paint samples exhibited good hardness property indicating the effectiveness of the binder molecules, and pigment particles in attracting one another.

6) Adhesion of Paint Films to Substrate:

According to ASTM D 907(2012), adhesion is the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action or both. Data on the adhesion of the paint films to mild steel panels illustrated in Fig. 4 showed no definite order of variation of paint film's adhesion with clay content. TiO_2 formulated paint, and paint sample containing 50 wt. % clay had an adhesion loss of 6.25%. The introduction of 20 wt. % clay into the alkyd paint increased the paint film adhesion loss to 25.0 %, after which decreases in paint film adhesion losses were observed with increasing clay content. The prepared paint samples had good adhesion property because a gloss paint shall not exhibit more than 50 % removal of the dried paint film [28]. Factors such as chipping, abrasion, coins and other instruments, corrosion of the substrate, impact by stones, and picking away at exposed edges are responsible for removal of paint films in service.

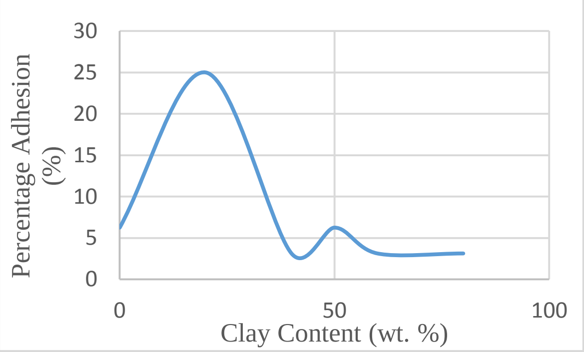

Fig. 4: Effect of Clay Content on Adhesion Property of Formulated Alkyd Paints.

7) Resistance of Paint Dry Films to Chemicals:

The resistance of the dry paint film samples to chemicals (3% NaCl, 3% Na_2CO_3, 3% H_2SO_4, and distilled water were observed visually at regular intervals within the period of immersion and the results are given in Table 2. In the NaCl immersion test, no blistering or other film defects was noticed on the paint films containing Umuahia clay, except for the very slight colour change noticed in the formulations. This results shows that Umuahia clay will have good corrosion protection for mild steel in a salty environment. This occurs because the presence of unreactive oxides of Si, Al, Fe, and others in the clay will slow down the diffusion of corrosive species into the film substrate thereby delaying the corrosion of mild steel. Thus, the incorporated clay in the paints provides a barrier between the metal substrate and the advancing corrosive species. It has been reported that silica and alumina are used to coat TiO_2 pigment to improve its durability in coatings [22]. From Table 2, the formulated paint samples performed well in distilled water, and fairly well in Na_2CO_3 but generally poorly in H_2SO_4 except for the fairly good performance of the paint samples containing 40, and 50 wt.% clay. The good performances of the paints in NaCl attest to their anti-corrosive property. The formulated paint samples, however, are not recommended to be used in H_2SO_4 prone environment except for the samples containing 40, and 50 wt.% clay.

Table 2. Resistance of Dry Paint Films to Chemicals.

Sample Code	Resistance to: 3% H_2SO_4	3% Na_2CO_3	3% NaCl	Distilled water
AT – 100	4	1	2	1
ATU –80/20	4	1	1	0
ATU –60/40	2	1	1	1
ATU –50/50	2	1	0	0
ATU –60/40	4	2	0	0
ATU –80/20	4	1	1	1

NOTE:
0 = No effects
1 = Very slight effect (colour/wrinkling)
2 = Slight effect (wrinkling)
3 = Effect (blistering/peeling)
4 = Bad effect (blistering/peel)

IV. CONCLUSIONS

Umuahia clay which was stable to heat and chemicals consisted mostly of the inert oxides of silica, alumina, and titanium dioxide was utilized successfully to formulate alkyd paints having anti-corrosive property. The clay was sieved to 0.075 mm particle size and incorporated into the formulated paints at extender contents, 0 to 80 wt.%. Results showed that the formulated paints exhibited good surface -, and through - dry times, and the best dry time was achieved on incorporation of 80 wt.% clay into the paints. TiO_2 formulated paint had the same surface dry time (10 min) as the paint containing 80 wt.% clay while the paint containing 80 wt.% clay exhibited better through – dry time (216 min) than the TiO_2 formulated paint (270 min). The film thicknesses of the paints were in the range, 0.10 to 0.15 mm, suggesting that the paints will function as anti-corrosive paints. While the TiO_2 formulated paint had pencil hardness of 6B, the Umuahia clay formulated paint samples containing 60, and 80 wt. % clay had the maximum pencil hardness of 5H. This latter hardness property is necessary for efficient protection of painted steel surfaces. The formulated paint sample dry films exhibited good adhesion to mild steel surfaces, and were generally resistant to serious film defects on immersion in 3% NaCl, and deionized water, an indication of anticorrosion property of the formulated paints. The paint dry films also performed well on immersion in 3% Na_2CO_3 but some formulations failed in 3% H_2SO_4. The present study has demonstrated the utility of Umuahia clay in formulating alkyd paints possessing anti-corrosive property. The use of the clay which is stable to heat and chemicals, easy to process, and locally available will greatly provide a cheap source of coatings extender to the paint industry, and source of economic empowerment for the rural populace where the clay deposits are located.

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