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UTILIZATION OF TREATED CLAYS IN FORMULATING ANTI – CORROSIVE PAINTS FOR PROTECTION OF STEEL

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ABSTRACT
Alkyd paints possessing anti – corrosive property on mild steel were prepared using Isiala Oparanadim clay as an extender. The clay which consisted mostly of inert oxides (SiO_2 and Al_2O_3) was calcined at 850°C, sieved to 75 µm particle size, treated with 3M, and 1M HCl and incorporated into alkyd paints at 0 to 80 wt.% extender contents. The surface -, and through – dry time of the formulated paint samples were satisfactory and followed the order: 3M HCl treated clay > 1M HCl treated clay > calcined clay. The paint samples exhibited good adhesion, paint dry film thickness and impact strength, and which contributed to the anti – corrosive property of the paints. While the performances of the formulated paint dry films in 2 % NaCl were good and which attested to their anti – corrosive property, the performances in 2% H_2SO_4 and 2% NH_3 varied depending on clay treatment. This study has highlighted the utility of treated Isiala Oparanadim clay in formulating anti – corrosive alkyd paints for the protection of steel in salty environment, a property which should justify the use of the clay in the surface coatings industry.
Keywords: extender, alkyd paint, calcined clay, Isiala Oparanadim, particle size, anti – corrosive property

INTRODUCTION
Paints are fluid materials which on application to surfaces produce coherent, solid films that are continuous. Paint can be applied for decorative, protective or for other purposes. Paints consist basically of four main components namely binder, solvent, pigment, and additives. Paint additives are incorporated into paints during manufacture to improve or modify certain paint properties [1]. These additives are added in small amount and can vary from 0.001 to 5%. Extenders, also referred to as extender pigments, are important paint additives that are part of, almost, all coating formulations contributing significantly to modifying various coatings properties such as gloss, settling tendency, flow characteristics, storage stability, exterior durability, brightness, and packing density [2]. Paint extenders differ from true paint pigments because they do not impart opacity to the coating and are transparent in the oil medium. Typical paint extender includes whiting (also called chalk), silica, barytes, mica, clay, and talc. Several engineering properties and aesthetics of a coating are optimized by proper selection and blending of suitable extenders; the technical demand on these extenders has grown appreciably.

Most paint extenders are of mineral origin that require long processing time which results to an appreciable loss of materials [3]. It has been reported that there is 75% yield in the processing of China clay, and 30 % for calcite [4]. These extenders, and several others used in coatings are expensive leading to increases in the cost of the resultant coating products. This has led to the search for economically viable extenders for use in paint production with the aim of reducing the cost of painting to acceptable limits. Thus, several materials have been investigated for possible use as extenders in coatings to replace the prime pigment partly or wholly, titanium dioxide (TiO_2) used in paint production. TiO_2 is the most widely used white pigment in the coatings industry. The pigment, however, is chemically active, and this has resulted to photocatalytic degradation of painted surfaces. The following materials have been investigated for possible use as paint extenders with various successes: fly ash [5], copper tailing waste [6], silica waste fume [7], Egyptian dolomite [8], industrial waste firebrick [9], and clay [10 - 14].

Clays, which are fine grained hydrated silicates of aluminum that approximate in composition to $Al_2O_3.2SiO_3.2H_2O$ are presently receiving attention from researchers as possible extenders for use in coatings. Clay minerals are easy to process, indigenously available, and are of low cost. Though, the physical properties of clays such as hardness, plasticity and cohesion can vary widely, the minerals have great affinity for water and the ability to exchange ions [15-16]. Usually white in colour, the colour of clays can vary from pink, orange to red due to the presence of iron oxide that gives clays distinct hue. The industrial utilization of clay minerals is associated with their reactivity and surface properties, and which depend mostly on clay surface modification. Generally, the surface modification of clays can be achieved by using a coupling agent, calcination, acid and alkali modifications, thermo - chemical treatment, and intercalation [17-18]. These surface modification processes alter the surface properties of clays such as functional groups present, and crystal structure to meet the industrial requirements of clays.

The present study reports the utilization of Oparanadin clay as an extender in formulating anti-corrosive alkyd paints for the protection of steel. The use of Oparanadim clay in formulating surface coatings has not been reported in the literature to our knowledge and presently, the clay has no industrial application despite its abundance. The locals used the clay to decorate the walls of houses and make drinking pots years ago and which had since been abandoned with the advent of modernity. The Oparanadim clay which was characterized for extender properties, calcined, sieved to 75µm particle size, and treated with hydrochloric was incorporated into alkyd paints at 0 to 80.0 wt.% extender content. The use of our indigenous clays in formulating emulsion, and oil - based paints has been receiving attention in our laboratory [19 - 22]. These studies are greatly in line with the local content policy statement of Federal Government of Nigeria with emphasis on developing local raw materials for industrial applications. There are rich clay deposits in Nigeria, and the mineral is estimated to represent more than 50% of the non - metallic earthy, and naturally occurring resources that occupy the country's sedimentary basins and on the basement. Despite their huge abundance, these clays are grossly underutilized, and the present study is an attempt to add value to their applications.

EXPERIMENTAL

Alkyd Resin

The alkyd resin was purchased from St. Austin Chemicals, Owerri, Nigeria. It is a medium oil length alkyd resin having acid number, 1.80 mg KOH/g. resin.

Clay Sample

The Isiala Oparanadin clay used as an extender was collected from Ahiazu Mbaise, lmo state, Nigeria. It was used at a particle size of 75 µm after treatment.

Metallic Driers

The cobalt and lead naphthenate driers were purchased from a Chemical store, Onitsha, Nigeria. They have metal contents of 12% Co, and 36% lead respectively. The lead drier was used for surface - drying of the applied paint film while cobalt drier was for through – drying.

Solvents and Reagents

The solvents and reagents used were of analytical grade and used without further purification.

Preparation of Clay Samples

The Isiala Oparanadim clay which was collected from the deposit was first sun dried, purified, crushed to fine powder, and calcined at 850^oC. The clay was later sieved to 75 µm sieve and stored in a tight lid container. Samples of the calcined clay was treated with 1M HCl, and 3M HCl as follows. 160 g of clay was measured into a beaker containing 1600 cm^3 of 1M HCl. The suspension was stirred for 1 h and allowed to stand for 48 h with occasional stirring. At the expiration of this period, it was filtered, and the residue was washed with distilled water and allowed to dry at 32^oC. The above procedure was repeated using 3M HCl. The acid treated clays were stored in tight lid containers for subsequent use.

Characterization of Treated Clays

Standard methods were used to characterize the treated clays as follows: pH (ASTM D 1208 – 96), specific gravity (ASTM D 153 – 84), refractive index (ASTM D 1208 – 96), oil absorption (ASTM D 281 – 12), and chemical composition (ASTM D 5381 – 94). The resistance to chemicals of the clay was determined as described previously [22]. The chemicals investigated were acetic acid, methanol, xylene, chloroform, ammonia solution, sodium hydroxide, sulphuric acid, and hydrochloric acid.

Preparation of Paint Samples

The paint samples were formulated using alkyd resin, TiO_2, xylene, calcined, and acid treated Isiala Oparanadim clays. The various paint formulations studied are as shown in Table 1. Lead naphthenate (0.12 g), and cobalt naphthenate (3.50 g) driers were used for through – dry, and surface - dry of the prepared paints respectively.

Table 1 Formulation of alkyd paint samples

	Ingredients (g)			
Sample Code	Alkyd Resin	Xylene	TiO_2	Clay
AT - 100/0	70	14.62	31.50	_
ATO - 80/20	70	14.60	25.20	6.30
ATO - 60/40	70	14,60	18.90	12.60
ATO - 50/50	70	14.60	15.75	15.75
ATO - 40/60	70	14.60	12.60	18.90
ATO - 20/80	70	14.60	6.30	25.26

AT = Paint sample without clay, ATO = Paint sample with clay

Evaluation of Properties of Prepared Paint Samples

The properties of prepared paint samples were evaluated using standard methods as follows. Specific gravity (ASTM D 1475 – 13), dry paint film thickness (ASTM D 1005 – 95), impact strength of dry paint film (ASTM D 2794 – 93), and dry paint film hardness (ASTM D 3363 –05). The applied paint film on mild steel panels was considered surface - dry when the finger, without pressure, was slightly run over the surface without picking up any paint on the finger. Similarly, the applied paint film on mild steel panels was considered through - dry when maximum pressure was applied, there was no loosening, detachment, wrinkling or evidence of paint film distortion.

Chemical Resistance of Dry Paint Films

Mild steel panels already coated with the prepared paint samples were allowed to dry to full hardness. The dry paint film was immersed one each into four beakers labelled A – D, and containing 2% H_2SO_4, 2% NH_3 solution, 2% Na_2CO_3, and 2% NaCl in that order. The panels were examined at regular time intervals for resistance to: (i) 2% H_2SO_4 (24 h), (i) 2% NH_3 solution (24 h), (i) 2% Na_2CO_3 (24 h), and (iv) 2% NaCl (24 h). The performance of the paint samples were rated according to the method of Muralidharan *et al*.[23] as follows: 0 – No change, 1 – Very slight effect (colour/ wrinkling), 2 – Light effect (wrinkling), 3 – Effect (blistering/peeling), and 4 – Definite effect (blistering/peeling).

RESULTS AND DISCUSSION

Chemical Composition of Isiala Oparanadim Clay

The chemical composition of Oparanadim clay determined using an Atomic Adsorption Spectrophotometer (2000 series Agilent Technology) is shown in Table 2. The results show an appreciable presence of silica (SiO_2), followed by aluminum oxide (Al_2O_3), iron (iii) oxide (Fe_2O_3), and titanium dioxide (TiO_2) in that order while the other oxides are present in very small proportions.

The presence of the unreactive oxides in the clay is indicative that paints formulated with the clays will function as anti - corrosive paints since the unreactive oxides will slow down the diffusion of corrosive species into the applied paint film thereby, slowing (delaying) the phenomenon of corrosion in the painted surfaces [4]. The metal oxide contents of the calcined clay are generally higher than those of hydrochloric acid treated clays except for aluminum oxide (Al_2O_3) contents where the reversed was observed. The Al_2O_3 content of the clays is in the order: Calcined clay < 1M HCl treated clay < 3M HCl treated clay. This observed order is attributed to the removal of metallic oxides during treatment with HCl [18]. The table shows that the percentage removal increases with the concentration of HCl.

pH Test

The pH of Isiala Oparanadim clay used in formulating alkyd paints was determined to be 7.66; an indication that the clay is slightly basic. The pH values of some extenders are: Okposi clay 7.46, fly ash 8.15, talc 9 – 9.50, and Okigwe - Mbano clay 6.0 [19].

Table 2 Chemical composition of Isiala Oparanadim clay.

Constituent (wt. %)	Calcined clay (850°C)	1M HCl treated clay	3M HCl treated clay
PbO	0.02	0.01	0.12
ZnO	0.31	0.24	0.21
CuO	0.05	0.03	0.02
Fe_2O_3	9.63	9.29	9.33
Mn_2O_3	0.02	0.01	0.01
MgO	0.29	0.05	0.01
N_2O	0.54	0.48	0.27
SiO_2	61.35	54.11	53.01
Al_2O_3	24.01	31.27	33.21
TiO_2	2.49	2.44	2.17
K_2O	0.53	0.42	0.44
CaO	0.70	0.63	0.53

Properties of Isiala Oparanadim Clay

The determined properties of Isiala Oparanadim clay are shown in Table 3.

Table 3 Physical Properties of Isiala Oparanadim Clay

Parameter	Value
pH	7.66
Oil absorption (g/100 g)	42.6
Specific gravity	1.06
Refractive index	1.63

Specific Gravity

The specific gravity of Isiala Oparanadim clay was determined to be 1.06. This study showed that the specific gravity of the clay is lower than that of titanium dioxide (4.26) which is the prime pigment used in paint formulations. The specific gravity values of some extenders are: China clay 2.6, whiting 2.7, talc 2.65, and mica 2.8 – 2.85 [19]. Low specific gravity of extenders is a desirable attribute in coatings formulations that lead to considerable cost savings. Generally, pigments that have low specific gravity exhibit low settling tendencies, and high tinting strengths in paints [24].

Refractive Index

The refractive index of Isiala Oparanadim clay was determined to be 1.63. This property has great influence on the scattering power of paints. The refractive index of Oparanadim clay is less than that of titanium dioxide which is 2.75. Generally, extenders do not enhance the opacity or colour of paint films. The refractive indices of some extenders are talc 1.40, barytes 1.64, and commercial whiting 1.58 [19]. The poor opacity exhibited in solvent paints by some extenders is attributed to their low refractive indices [24].

Oil Absorption

The oil absorption of Isiala Oparanadim clay was determined to be 42.60 g/100g clay. Less oil absorption by an extender indicates less resin demand without compromising other coating properties. The oil absorption by some extenders and pigments are barium sulphate (blanc fixe) 18.5, China clay 30, calcium carbonate 17.50, and talc 25 – 35[19].

Chemical Stability Tests
The effect of heat on the colour and solubility of Oparanadim clay was studied. It was observed that the clay was stable in hydrochloric acid, acetic acid, methanol, chloroform, and xylene. There was no colour change or solubility of the clay in the chemicals studied either in the cold or when heated. The stability of the clay is attributed to the large presence of the inert oxides silicon dioxide (SiO_2), and aluminium dioxide (Al_2O_3) in the clay which have high melting points (SiO_2, 1713^oC; Al_2O_3, 2054^oC) [25].

Properties of Prepared Paint Samples
Surface – Dry Time
The surface - dry times of the formulated alkyd paints of calcined, and hydrochloric acid treated clays are illustrated graphically in Figure 1 and were within 20 – 50 min. The surface – dry time of the paint sample without the extender pigment is 13 min. The surface - dry times increased with clay content up to 50 wt.% clay incorporation, and thereafter, decreased with clay content. The surface - dry times of the formulated paint samples satisfied the Nigerian Industrial Standards (NIS) requirement which stipulates that the surface - dry time of a gloss paint shall not exceed 6 h from the time of application. Thus, the incorporation of Isiala Oparanadim clay into alkyd paints did not adversely affect the paints surface - drying times. Generally, the calcined clay formulated paints exhibited higher surface - dry times than the acid treated clays. The observed order of surface - dry time of the paint samples is: Calcined clay > 1 M HCl treated clay > 3 M HCl treated clay. Acid treatment of the clay greatly reduced the surface - dry times of the formulated paint samples. The best surface - dry time of 15 min was recorded for 1 M HCl treated clay at 20 wt.% clay content, and which was very close to 13 min observed for the paint sample without clay.

Through – Dry Time
The through - dry times of the formulated paint samples are illustrated graphically in Figure 2. The figure shows that the paint sample formulated without clay has a through - dry time of 10 min. Figure 2 also shows that the dry - times of the paint samples increased up to 50 wt.% clay incorporation, and thereafter, decreased. The 3M HCl formulated paint samples exhibited the least through - dry times irrespective of the clay content considered. The surface - dry times of the formulated paint samples satisfied the NIS requirements that the through - dry of a gloss paint shall not exceed 24 h from the time of application. The least through - dry time of 225 min at 20 wt.% clay content was recorded 3M HCl treated clay.

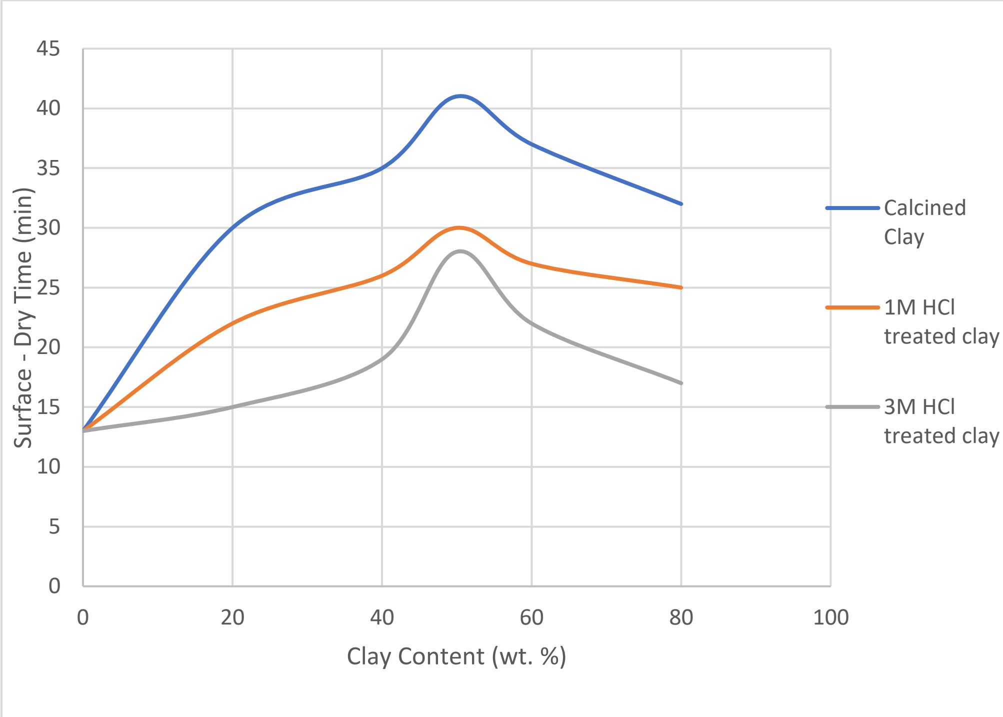

Figure 1 Effect of clay content on surface - dry time of formulated paint samples

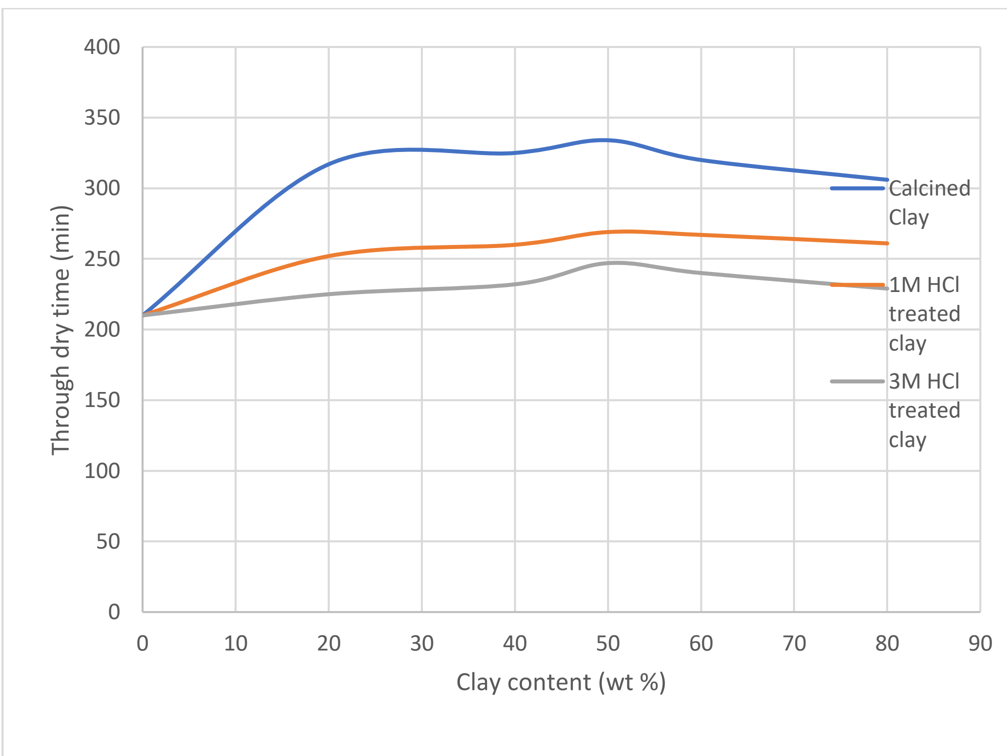

Figure 2 Effect of clay content on through - dry time of formulated paint samples

Thickness of Dry Paint Films

The variation of the prepared dry paint film thicknesses with clay content, and treatments are illustrated in Figure 3. The TiO_2 formulated paint sample had a dry paint film thickness of 1.25 mm. The dry paint film thicknesses of the paint samples ranged from 0.70 – 1.40 mm. Generally, a film thickness of more than 20 µm performs well as a barrier resistant to weathering [4]. The film thicknesses obtained in this study are in this range, and which is an indication that the formulated paints will function as anti - corrosive paints. Paint samples containing 50 wt. % 1M HCl treated clay exhibited the highest film thickness of 1.41 mm while the sample containing 40 wt. % calcined clay had the least film thickness of 0.70 mm. There is no general order of variation of paint film thicknesses of the treated clays with clay contents.

Hardness of Dry Paint Films

The hardness of the formulated paint samples with clay content is shown Table 4. Paint samples containing 60, and 80 wt. % calcined clay, and 80 wt.% 1M HCl treated clay had maximum dry film hardness of 5H, followed by 3M HCl treated clay containing 80, and 40 wt. % clays which had pencil hardness of 4H. The least film hardness of 2B was recorded for TiO_2 formulated paint without clay. The hardness of paint films for the calcined clay generally increased with clay content. The formulated paint samples had good hardness property, an indication that the paint films will protect the painted substrate from mechanical damage, and subsequently, prevent corrosion of the substrate from environmental damage.

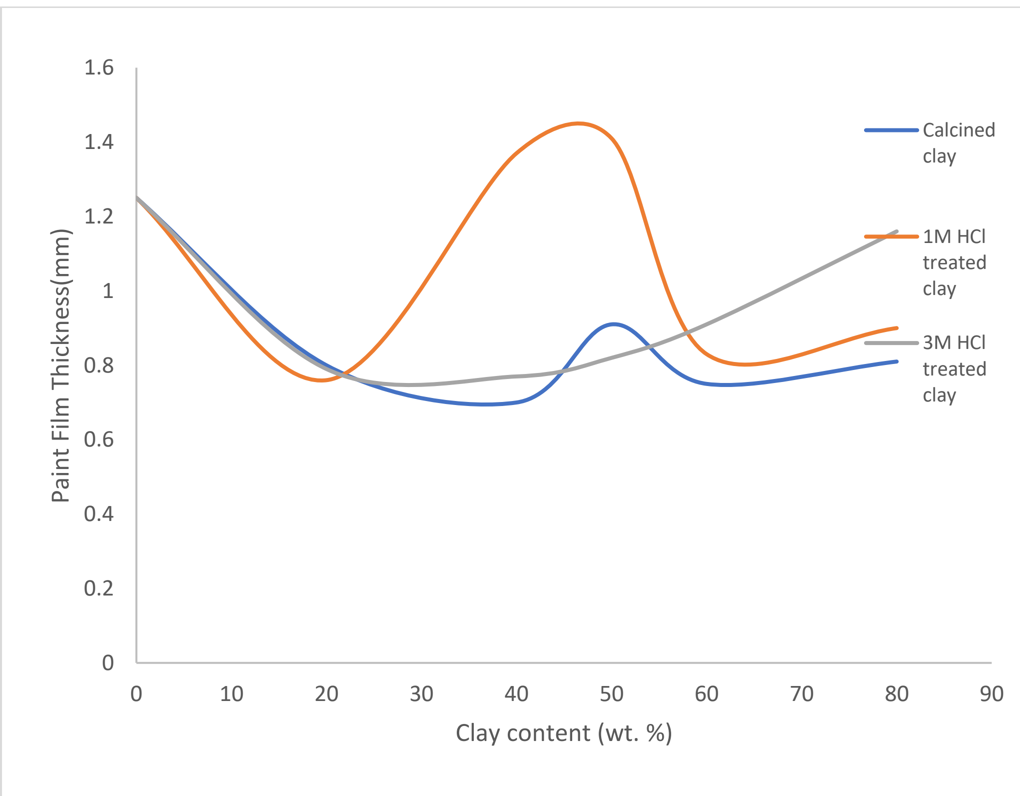

Figure 3 Effect of clay content on dry paint film thickness.

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Table 4 Pencil hardness of dry paint films

Formulation	Pencil Hardness		
	Calcined clay	1M HCl treated clay	3M HCl treated clay
100/0	2B	2B	2B
80/20	H	2H	H
60/40	3H	H	4H
50/50	3H	3H	B
40/60	5H	3H	2H
20/80	5H	5H	4H

Adherence to Surface of Paint Films

The dry paint films exhibited good adherence properties to mild steel surfaces as evident from Figure 4. According to Nigerian Industrial Standards (NIS), an oil (gloss) paint shall not exhibit more than 50 % removal of the dried paint film. The TiO_2 formulated paint had 1.88 % removal of paint dry film. The paint sample containing 50 wt.% calcined clay, and 40 wt.% 1M HCl treated clay exhibited the least dry paint film removal of 5.0 % while 50 wt.% 3M HCl treated clay had the highest dry paint film removal of 30.0%. The differences observed in the adhesion properties of the treated clays formulated paints on mild steel could be attributed to the cumulative effects of changes in surface properties and compositions occasioned by the different clay treatments. Thus, calcination of clays improves their dispersion which will greatly improve the adhesion properties of the formulated paints. Generally, the good adherence property recorded for the paint samples is an indication that the paint samples should function as anti-corrosive paints.

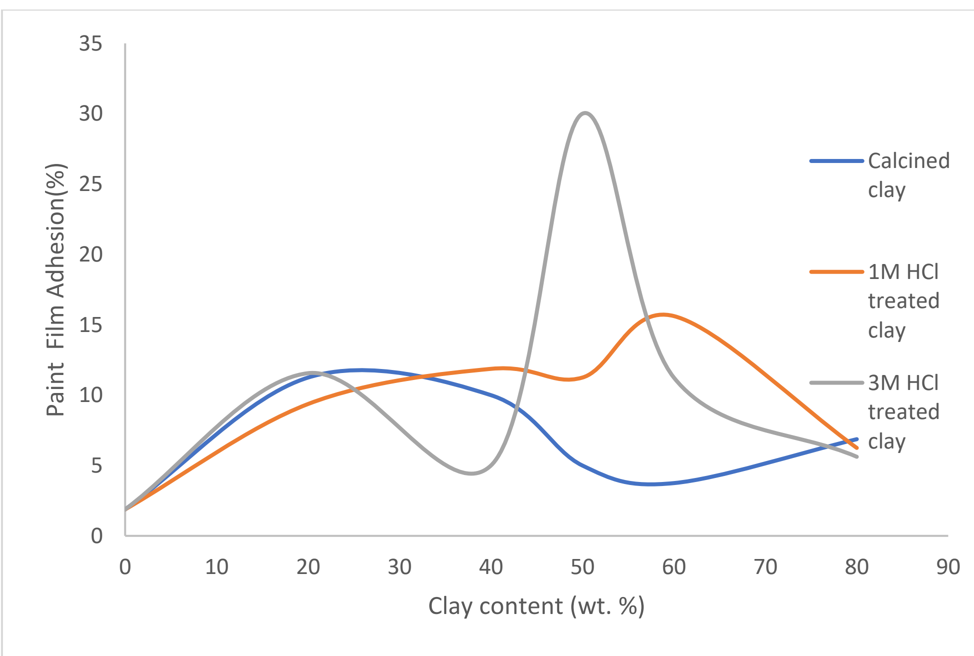

Figure 4 Effect of clay content on adhesion of formulated paint samples

Impact Strength of Dry Paint Films

The impact strength of the formulated paint samples was determined using Charpy Impact Tester. All the formulated paint samples passed the impact test. This attests to the good quality of the paints

Chemical Resistance of Paint Films Dry

The resistance of the dry paint films to 2% NaCl, 2% NH_3, 2% H_2SO_4, and 2% Na_2CO_3 are shown in Table 5. No blistering or other film defect was observed on immersion of the dry paint films in NaCl. This indicates that the formulated paint samples will function as anti-corrosive paints for the protection of steel in salty environments. It occurs because of the presence of unreactive metallic oxides in the clay samples which will slow down the diffusion of corrosive species into the film substrate thereby, slowing down the corrosion of mild steel.

Table 5 Chemical resistance of dry paint films

Formulation	Resistance to chemicals		
	NaCl		
	Calcined clay	1M HCl treated clay	3M HCl treated clay
100/0	0	0	0
80/20	0	0	0
60/40	0	0	0
50/50	0	0	0
40/60	0	0	0
20/80	0	0	0
	Na_2CO_3		
100/0	0	0	0
80/20	2	3	3
60/40	2	4	4
50/50	2	4	4
40/60	2	3	3
20/80	1	3	4
	H_2SO_4		
100/0	0	1	1
80/20	0	0	0
60/40	0	0	0
50/50	0	1	0
40/60	0	1	0
20/80	0	1	0
	NH_3		
100/0	1	1	1
80/20	0	3	4
60/40	4	2	3
50/50	3	3	4
40/60	2	1	2
20/80	1	4	1

From Table 5, the paint dry films also performed well on immersion in 2% H_2SO_4. The performances in 2% Na_2CO_3 and 2% NH_3 were not generally good except for slight wrinkling or colour change observed for some formulations. From Table 3.3, it is apparent that calcined clay formulated paints exhibited fairly better resistance to 2% Na_2CO_3, 2% NH_3 and 2% H_2SO_4 than HCl treated clay formulated paints.

CONCLUSION

Calcined and hydrochloric acid treated Isiala Oparanadim clays have been used to prepare alkyd paints possessing anti – corrosive property on mild steel.

(i) The surface -, and through - dry times of the formulated alkyd paints were within acceptable limits. The HCl formulated paints exhibited better dry times than the others.
(ii) The film thickness, hardness, impact strength, and adhesion properties of the paint dry films were generally good and contributed to the observed anti – corrosive properties of the paint samples on mild steel.
(iii) The paint dry films exhibited no blistering or any other defects on immersion in 2% NaCl; an indication of the anti - corrosive nature of the paints on application in salty environments.
(iv) The performances of the dry paint films were generally good in 2% H_2SO_4. However, the calcined clays formulated paints exhibited fairly better resistance to 2% Na_2CO_3, 2% NH_3, and H_2SO_4 than the HCl formulated paints.

The present study has highlighted the utility of Isiala Oparanadim clay in formulating anti-corrosive alkyd paints for the protection of steel. The clay, which is stable to heat, chemicals, easy to process, and indigenously available will greatly provide a cheap source of paint extender, and economic empowerment for the rural populace where the clay deposit is located.

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