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Original Article

Evaluation of sustainable eco-friendly paints based on Oguta clay for industrial applications

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ABSTRACT

Sustainable eco-friendly alkyd paints for industrial applications were prepared using treated Oguta clay as an extender and titanium dioxide (TiO_2) as the prime pigment. The clay which consisted mostly of silica (60.10%), aluminum oxide (24.56%), and iron (iii) oxide (5.71%) was calcined, sieved to 63, and 125 µm particle sizes, and treated with 1, 2, and 3 M HCl. The treated clays were subsequently incorporated into alkyd paints at 0–80 wt.% extender content. Paint characterization showed that the formulated paints exhibited satisfactory dust-free and through-dry times. Paint dry film thicknesses of the formulations were in the range, 0.10–0.36 mm, an indication that the paints will function as anti-corrosive paints for the protection of steel. The dry paint film hardness generally increased with clay content with the highest dry paint film hardness (5B) (12) obtained with 2 M HCl treated clays (63 and 125 µm) containing 80% clay. TiO_2-formulated paint exhibited the least dry paint film hardness (3B) (4). The adhesion of the paint films on mild steel panels was very satisfactory, an indication that the paints will protect painted surfaces adequately, and thus, function as anti-corrosive paints. The gloss (60°) of clays (63 µm) formulated paints containing 20–50 wt.% clays were high (70.0–79.0 GU), indicating that the paint would find utilization in the automobile industry. The formulated paints exhibited satisfactory performances in 2% NaCl, indicating their potential to function as anti-corrosive paints. While the performances of calcined clays formulated paints in 2% HCl were generally unsatisfactory, those of HCl-treated clays were generally good. All the formulated paints failed in 2% NH_3 solution; the same as calcined clays formulated paints in 2% Na_2CO_3. The performances of HCl-treated clays formulated paints were generally satisfactory in 2% Na_2CO_3. None of the formulated paints were chalked. The present study has highlighted the improved paint properties obtained with Oguta clay as a paint extender and it is expected that these performances should justify the utilization of Oguta clay in the coatings industry for the formulation of industrial paints.

Keywords: Alkyd paint, anti-corrosive paint, calcined clay, extender, film thickness, gloss, Oguta clay, through-dry time

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INTRODUCTION

Alkyd paints have achieved relevance in the surface coatings industry because of their desirable coating properties such as versatility, adhesion, and durability. They are widely used in interior and exterior applications, being long associated with the construction industries. Alkyd paints are produced using alkyd resins which are oil-modified polyesters, and the resins having oil contents that range from 30 to over 70% form excellent films that are capable of protecting painted surfaces against wear, weathering, and aging.[1] An important component of alkyd paint is titanium dioxide (TiO_2), a prime pigment which is used in paint systems where white pigment is desired. TiO_2 possesses a high refractive index that contributes to its efficiency in scattering visible white light, a property that imparts whiteness, brightness, and opacity when used in formulating paints. The report indicates that about 6.45 million tons of TiO_2 was consumed globally in 2020, and the paint and coatings industry accounted for 56% of this volume or 3.6 million tons.[2] The increasing TiO_2 consumption by the paint and coatings industry is greatly associated with growth in the global residential housing, commercial construction, and packaging markets. Although TiO_2 confers desirable properties to coatings, it is photo-chemically active which leads to degradation of painted surfaces.[3] On the other hand, TiO_2 which is of mineral origin requires long processing (grinding,

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chemical treatment, etc.) from ore to find a product with significant loss of materials. The pigment is not indigenously available, and the importation leads to the high cost of coatings products.

The coatings industry is embarking on a sustainable future by implementing goals leading to increased renewable content, improved production procedures, addressing customer expectations, and developing greener products. Thus, there are innovative researches to enhance the sustainability of alkyd paint formulations with the main aim of incorporating renewable materials in the form of economically fine-sized extenders that would partially replace TiO_2 and bring down the cost of coatings to acceptable limits. Coatings produced using different materials as extenders have been reported and included copper trailing waste,[4] fly ash,[5] silica waste fumes,[6] Egyptian dolomite,[7] calcite, talc, mica, barytes,[8,9] industrial waste clay,[10] *r*ice husk ash,[11] and granite quarry dust.[12]

The use of clay minerals as potential paint extenders is receiving attention in the literature. The mineral which approximates in composition to $Al_2O_3.2SiO_3.2H_2O$ is environmentally friendly and finds industrial utilizations due to its reactivity and surface properties which depend mostly on clay surface modifications. Surface modifications of clay can be achieved using various methods such as calcination, intercalation, chemical treatment, coupling agent, acid, and alkali modifications.[13,14] A number of efforts have highlighted the potential of clay minerals as paint extenders with improved properties.[15-21] Clay-formulated paints are non-toxic and volatile organic compounds free.[22]

The present study reports the utilization of Oguta clay in formulating alkyd paints for use in the automobile industry and the protection of steel. The use of Oguta clay in formulating alkyd paints has not been reported in the literature to our knowledge. The clay was calcined, sieved to two particle sizes (63 and 125 μm), treated with hydrochloric acid (1, 2, and 3 M), and incorporated into alkyd paints at 0–80% extender content. This study is part of our ongoing investigations aimed at adding industrial values to clay deposits which abound in many regions of Nigeria, and which are estimated to constitute over 50% of the non-metallic, earthly, and naturally occurring resources present in the country's sedimentary basins, and on the basement.[23] Despite the enormous potential of clay minerals, they are grossly underutilized in Nigeria, and few industries use them as raw materials for the production of ceramic wares. Documented studies on clay minerals in selected areas of Nigeria are mostly concerned with clay characterization with little emphasis on their industrial applications. Thus, the present study which emphasizes the development of local raw materials for industrial applications is in line with the main thrust of the economic reform program of the Nigerian government which is targeted at mobilizing national capability in converting the country's endowments into utility products, and services for the common man.[24]

MATERIALS AND METHODS

The following materials were used in this study:

i. Alkyd resin: This is a product of Chemical Industry Limited, Aba, Nigeria. It has an acid value of 0.5 mg KOH/g. resin
ii. Oguta clay: The processed clay was obtained from Oguta Lake, Oguta Local Government Area, Imo State, Nigeria. The clay was calcined, sieved to two particle sizes (63 and 125 μm), and treated with hydrochloric acid (1, 2, and 3 M)
iii. Cobalt and lead naphthanate driers: The driers were purchased from St. Austin's Chemicals, Wetheral Road, Owerri, Nigeria. Cobalt naphthanate with metal content, 12% Co. was used for dust-free drying of the applied paint films while lead naphthanate with metal content, 36% Pb was used for through-drying of the applied paint films.

The Oguta clay was analyzed for oxide composition using X-ray fluorescence. A series of alkyd paint samples were prepared using alkyd resin (binder), xylene (solvent), TiO_2 (prime pigment), calcined and HCl-treated clays (extenders), ethylene glycol (co-solvent), and acetone (thinner). Cobalt and lead naphthanate driers were used for dust-free, and through-dying of applied paint films. The following parameters of the prepared paint samples were investigated using methods as described previously: [18,21] dust-free, tack-free, and through-dry times, dry paint film thickness and hardness, adhesion of paint films on mild steel panels, resistance of dry paint films to 2% HCl, 2% NaCl, 2% NH_3, and 2% Na_2CO_3. The gloss (60°) of dry paint films was determined according to the ASTM D 3928 – 00 method. The chalking test was determined by rubbing the dry paint films with the finger to observe whether it chalked.

RESULTS AND DISCUSSION

Chemical Composition of Oguta Clay

Analysis of Oguta clay shows an appreciable presence of silicon oxide (60.10%), aluminum oxide (24.56%), iron (111), and oxide (5.71%). The quantity of TiO_2 present is 2.83%. Oguta clay is kaolinitic in nature. Treatment of Oguta clay with HCl decreased the quantities of aluminum oxide, iron oxide, and TiO_2, and the amounts decreased with increasing concentrations of the acid. The reverse trend was, however, observed for the presence of silicon dioxide.

Characterization of Alkyd Paint Samples

Drying times

The drying properties of the prepared paint samples are illustrated graphically in Figure 1. The drying properties investigated were dust-free and through-dry times.

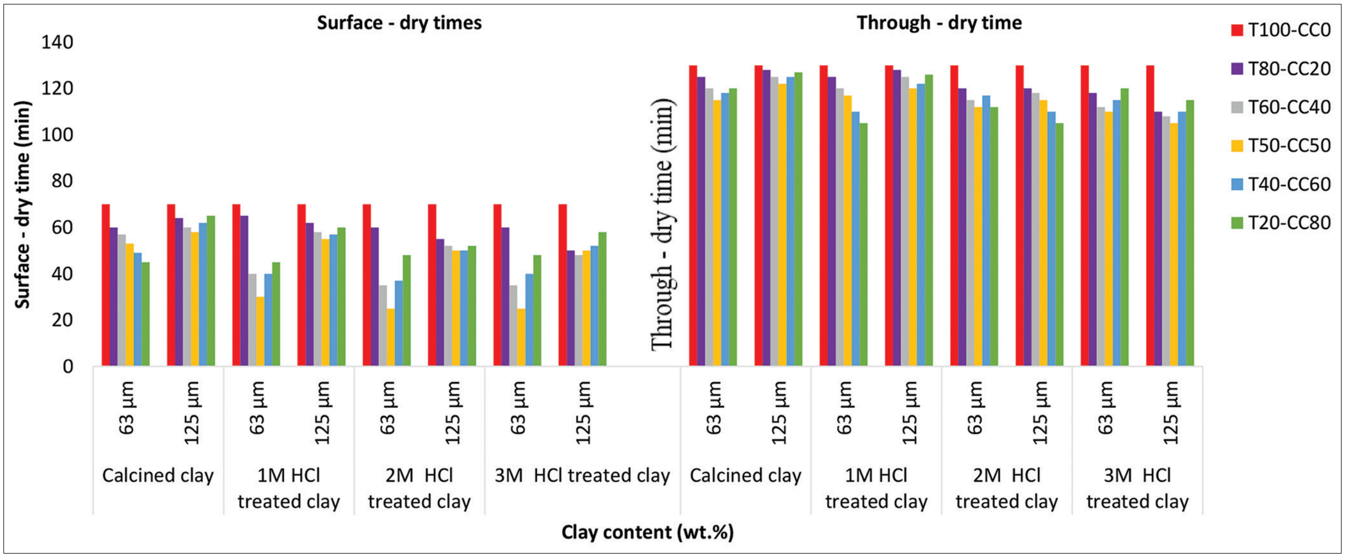

Figure 1: Effect of clay content and particle size on the dry times of prepared paint samples

Dust-free dry times

Figure 1 shows that TiO_2-formulated paint exhibited higher dust-free dry time (70 min) than those clay-formulated paints irrespective of clay content, acid treatment, or particle size. Thus, the alkyd paint samples formulated using Oguta clay exhibited better dust-free dry times than the one formulated using TiO_2 as shown in Figure 1. The paint sample formulated with 80% TiO_2 and 20% clay exhibited the highest dust-free dry times among the clay-formulated paints, irrespective of clay particle size. The dust-free dry times of calcined clay (63 µm) and 2 M HCl-treated clay (125 µm) generally decreased with clay content. The paint samples formulated with clay of particle size, 125 µm generally exhibited higher dust-free dry times than those formulated with clay of particle size, 63 µm. The HCl (2 and 3 M) treated clay (63 µm) formulated paints exhibited the same dust-free dry times at 20, 40, and 50 wt.%. The incorporation of Oguta clay into the formulated paints did not have an adverse effect on the dust-free dry times of the paints, and they satisfied the National Industrial Standards[25] requirements which stipulate that the dust-free dry time of gloss paint shall not exceed 6 h from the time of application. The least dust-fee dry time of 25 min was exhibited by 2, and 3 M HCl treated clay (63 µm) at clay content, 50 wt.%.

Through-dry times

The through-dry times of the prepared paint samples as illustrated in Figure 1 show that TiO_2-formulated paint had a through-dry time of 130 min, which was higher than those of Oguta clay-formulated paints that lie between 110 and 128 min. Oguta paint samples prepared with calcined clay (125 µm) (20 wt.%) and 1M HCl treated clay (125 µm) (20 wt.%) exhibited the highest paint through-dry time of 128 min. Conversely, Oguta paint samples prepared with 2 M HCl treated clay (125 µm) (80 wt.%), 3 M HCl treated clay (125 µm) (50 wt.%), and 1 M HCl treated clay (63 µm) (80 wt.%) exhibited the best through-dry time of 105 min. The through-dry times of 2 M HCl treated clay (125 µm) formulated paints generally decreased with clay content. The through-dry times of calcined clay (125 µm) and 1 M HCl treated clay (125 µm) formulated paint samples were generally greater than those of calcined (63 µm) and 1 M HCl treated clay (63 µm) formulated paints. The 3 M HCl treated clay (63 µm) formulated paint samples generally exhibited higher through-dry times than those of 3 M HCl treated clay (125 µm) paints of any clay content considered. The drying times of the formulated paint samples satisfied the national industrial standard[25] requirements for a gloss paint which stipulates that the through-dry time shall not exceed 24 h from the time of application.

Dry paint film thickness

Data obtained on the thicknesses of the dry paint films are illustrated in Figure 2. TiO_2-formulated paint exhibited dry paint film-thickness of 0.11 mm which happened to be the film thickness of 1M HCl-treated clay (125 µm) paint at extender content, 20 wt.%.

The paint dry film thickness of the formulated paints did not show any relationship with clay content. The film thickness of calcined clay (125 µm) formulated paints was generally greater than those of calcined clay of particle size, 63 µm. Furthermore, the dry paint film thicknesses of 1 M HCl treated clay (125 µm) formulated paints was generally greater than those of particle size, 63 µm. The paints formulated with calcined clay (63 µm), and 3 M HCl treated clay (63 µm) exhibited the least dry paint film thickness of 0.10 mm at clay content, 40 wt.%.

The thicknesses of the paint films generally lie between 0.10 and 0.36 mm. The film thickness of a paint directly affects

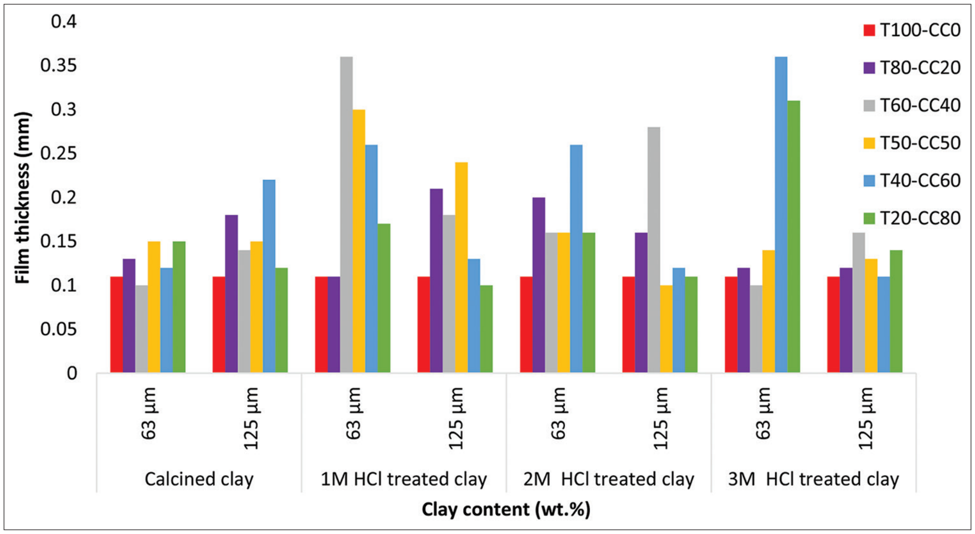

Figure 2: Effect of clay content and particle size on the thickness of prepared paint samples

its durability. According to Tan Tian Aik,[26] a film thickness of more than 20 μm performs well as a barrier resistant to weathering. This indicates that the clay-formulated paints in this study can function as anti-corrosive paints.

Adherence to surfaces of dry paint films

Data on the loss of adhesion of paint dry films on mild steel surfaces are illustrated in Figure 3. The TiO_2-formulated paint exhibited an adhesion loss of 8.33% on mild steel surfaces. Some clay paint formulations also exhibited an adhesion loss of 8.33%.

However, many clay formulations (both calcined and HCl treated) exhibited no adhesion loss thereby, attesting to their good quality. For example, paints containing 2 M HCl treated clay (125 μm) (40–80 wt.% clay content) and 3 M HCl treated clay (125 μm) (40–80 wt.%) clay content exhibited no adhesion loss on mild steel panels. The maximum paint dry film removal in this study was 8.33% recorded for some calcined and HCl-treated paint formulations.

For a coating to perform satisfactorily, it must adhere to the substrate on which it is applied. The standard maximum adhesion loss for gloss paint is generally considered to be 20–30%. However, this can vary depending on the specific paint formulation, substrate, and environmental conditions.

According to Nigerian industrial standards,[25] a gloss paint shall not exhibit more than 50% adhesion loss. Thus, all the formulated paints satisfied the NIS requirement on adhesion loss. This further attests to the good quality of the prepared paints.

Adhesion according to ASTM D 907 (2012)[27] 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, etc. The results obtained from this study suggest that alkyd paints should perform well as industrial paints.

Chalking of paint films

The chalking test carried out on the formulated paint samples indicated that none of the paint samples were chalked. A good paint should not chalk. This result indicates that the Oguta clay performed well in paints just like the paints prepared using TiO_2 pigment.

Hardness of dry paint films

The hardness of paint dry films is illustrated in Figure 4. TiO_2-formulated paints exhibited a paint dry film hardness of 3B (4). The hardness of formulated paints generally increased with increasing clay content. The 1 M HCl treated clays (63 and 125 μm) formulated paint samples generally had the same film hardness at any clay content considered. The calcined clay (125 μm) formulated paint containing 20 wt.% clay exhibited the least film hardness of B (6) whereas 2 M HCl treated clays (63 and 125 μm) formulated paints containing 80 wt.% clay exhibited the highest paint hardness of 5H (12). The incorporation of treated clays generally increased the hardness of the paints. The hardness of a paint dry film gives indications of the effectiveness of the binder molecules, pigment/extender particles, and additives in attracting one another. A higher degree of pigmentation gives strength and stiffness to paint films.[28] This is because the pigment particles can act as loading bearing part of the film thereby, restricting movement within the film.

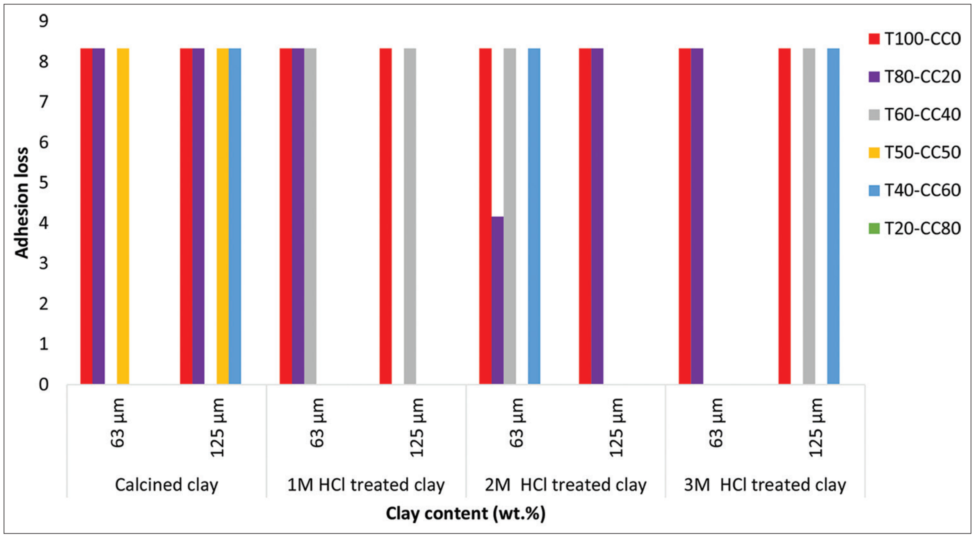

Figure 3: Effect of clay content and particle size on the adherence to surfaces of prepared paint samples

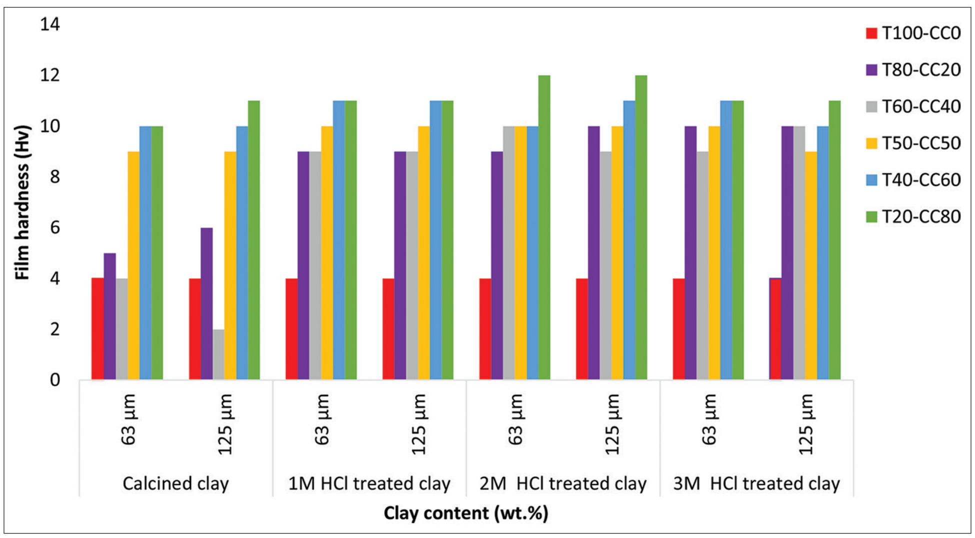

Figure 4: Effect of clay content and particle size on the film hardness of prepared paint samples

Dry paint film gloss

Data on the gloss of formulated paint samples are illustrated in Figure 5. At 60° gloss measurement, TiO_2-formulated paint had a gloss of 79.81 GU, the highest gloss obtained in this study. This value indicates that the TiO_2-formulated paint is of high gloss. The gloss of the clay-formulated paints decreased with increasing clay content and particle size. Thus, at any clay content considered, the gloss decreased with an increase in particle size. The gloss of the clay formulated paints at clay (63 µm) contents, 20–50 wt.% lie between 74.0 and 79.0 GU. These are high gloss paints that have a high refractive appearance, stain resistance, and durability. The latter paints should find utility in the automobile industry. The gloss of 60 wt.% clay (125 µm) formulated paints lie between 53 and 72 GU, at clay contents, 20–50 wt.%. The gloss of HCl-treated clays (125 µm) formulated paints was only of high gloss at clay content, 20 wt.%. The gloss of calcined clay (63 µm) (60 wt.%) and HCl-treated clays (63 µm) at clay contents (40–60 wt.%) were glossy. These paints should be easier to clean than lower gloss paints and can be used in kitchens, bathrooms, and cabinets exposed to fingerprints. All the formulated paints at 80 wt.% clay contents were eggshells and are ideal for areas with traffic such as dining rooms or a kid's room.

Chemical resistance of dry paint films

The clay-formulated paint samples exhibited satisfactory performance in 2% NaCl with the exception of TiO_2-formulated paint which exhibited slight color change. The paint samples also performed generally well in 2% Na_2CO_3 except those formulated with calcined clay, and 2 M HCl treated clay containing 80 wt.% clay which displayed adverse effects ranging from color change to peeling off. In distilled water,

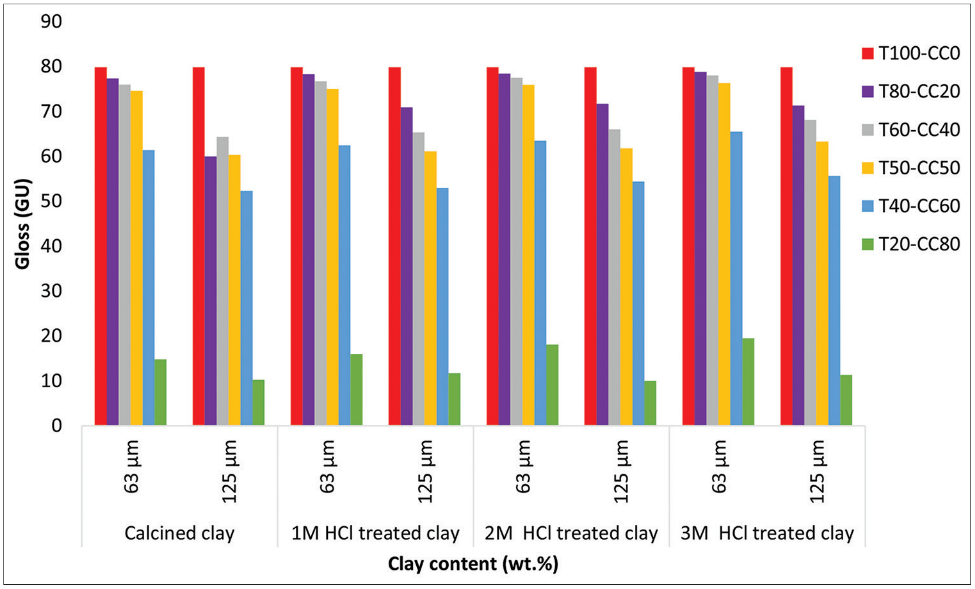

Figure 5: Effect of clay content and particle size on the gloss (60°) of prepared paint samples

paints formulated with 1 M, and 2 M HCl treated clays (125 µm) exhibited good performances whereas those of calcined clay and 3 M HCl treated clay (125 µm) generally performed poorly showing signs of peeling off and wrinkling. The calcined clay-formulated paints and 3 M HCl-treated clay-formulated paints generally performed poorly in 2% Na_2CO_3 solution. Similarly, all the formulated paint samples performed poorly in 2% NH_3 solution. However, they exhibited varying performances in 2% HCl ranging from slightly good to very good. Some paint formulations of calcined clay and 3 M HCl treated clay were adversely affected in 2% HCl.

The satisfactory performances of the paint samples in 2% NaCl with no observable film defects indicate that the paint will function as an anti-corrosive paint for the protection of steel in a salty environment. The presence of the unreactive oxides in the clay will slow the diffusion of corrosive species into the film substrate thereby, slowing down the corrosion of mild steel. The poor performances in 2% NH_3 indicate that the formulated paint samples will not be used in an ammonia-prone environment.

CONCLUSION

Eco-friendly alkyd paints based on treated Oguta clays were successfully prepared with improved properties. The paints exhibited satisfactory air-drying properties, and dry paint film thicknesses generally lie between 0.10 and 0.36 mm, a range of paint film thickness can confer anti-corrosive properties to coatings. The adhesion of the dry paint films on mild steel panels was generally satisfactory. The paint samples generally exhibited higher paint hardness than TiO_2-formulated paint (3B) (4). The gloss of the clay (63 µm) formulated paints at clay contents, 20–50 wt.%, and the HCl-treated clays (125 µm) prepared paints containing 20wt.% clay exhibited high gloss. The chemical resistances of the formulated paints were generally good in 2% NaCl. The 2 and 3 M HCl treated clays formulated paints performed well in distilled water whereas the performances in 2% HCl varied depending on the formulations. The formulated paints generally performed poorly in 2% NH_3 as did calcine clay-prepared paints in 2% Na_2CO_3. The present study has demonstrated the industrial potential of treated Oguta clay as an extender in formulating anti-corrosive, and automotive paints, which will justify its usage in the coatings industry.

REFERENCES

1. Dizman C, Cerrahoglu Kaçakgil E. Alkyd resins produced from bio-based resources for more sustainable and environmentally friendly coating applications. Turk J Chem 2022;47:1-23.
2. Recent and Current Developments in the Titanium Dioxide Market. Available from: https://www.european-coatings.com [Last accessed on 2024 Aug 04].
3. Paint and Coating Industry Magazine (PCI, 2015). A Comprehensive Understanding of TiO_2 Pigment Durability. Available from: https://www.pcimag.com/articles [Last accessed on 2024 Aug 05].
4. Dhimole LK, Saxena M. Utilization and Value Addition of Copper Tailing as an Extender for Development of Paints. Uttar Pradesh: Regional Research Laboratory, CSIR; 2005.
5. Tiwari S, Saxena M. Use of fly ash in high performance industrial coatings. Br Corros J 1999;34:184-91.
6. Youssef EA, Nivin M, Abd El-Ghaffar MA. Characterization and evaluation of silica fume as an extender pigment for surface coating applications. Pigment Resin Technol 2015;27:88-98.
7. Youssef EA. Characterization, surface modification, and evaluation of Egyptian dolomite ore as an extender pigment for

paint. J Pigment Resin Technol 2002;31:226-33.
8. Inci M, Karademir D, Ülkü S, Turgut H, Turgut G. Effects of partial substitution of titanium dioxide (TiO_2) with different extenders on architectural interior paint properties. J Coat Technol Res 2017;14:153-60.
9. Farzaneh A, Mohammadi M, Yazdani E, Falahati M. Effects of different types and concentrations of mineral extenders on main properties of long oil alkyd paint with titanium dioxide pigment. Prog Org Coat 2019;134:316-24.
10. Anyiam C, Igwe IO. Studies on the use of an industrial waste clay in alkyd paint formulations. Int J Acad Res 2012;4:306-13.
11. Igwebike-Ossi CD. Pigment extender properties of rice husk as in emulsion paint. IJIRSET 2015;4:6824-9.
12. Igwe IO, Acha FN, Agwu GI, Ifeacho VC, Okonkwo SN, Ekwueme CC, *et al*. Utilization of granite quarry dust extender in formulating anti-corrosive paints for the protection of steel. AJST 2021;5:631-7.
13. Ding S, Zhang L, Xu B, Liu Q. Review and prospect of surface modification of kaolin. Adv Mater Res 2012;430-2:1382-5.
14. Eze KA, Nwadiogbu JO, Nwankwere ET. Effect of acid treatments on the physicochemical properties of kaolin clay. Arch Appl Sci Res 2012;4:792-4.
15. Odozi TO, Dore R, Onu CO. Paint extenders based upon an indigenous clay. J Niger Soc Chem Eng 1986;5:34-40.
16. Narayan R, Raju KV. The use of calcined clay as part replacement of titanium dioxide in latex paint formulations. J Appl Polym Sci 2000;77:1029-36.
17. Igwe IO, Osuoha G, Nwapa C. Characterization and utilization of Eziulo clay as an extender in emulsion paint formulations. J Miner Mater Sci Eng 2017;5:174-84.
18. Igwe IO, Acha FN, Anyaegbu GO, Agwu GI, Ifeacho VC, Esinwoke WC, *et al*. Formulation of anti-corrosive alkyd paints based on Umuahia clay extender. SSRG Int J Polym Text Eng 2020;7:25-30.
19. Igwe IO, Ezeamaku LU. The use of local clay in alkyd paint formulations. Malay Polym J 2010;5:81-4.
20. Ahmed NM. Comparative study on the role of Kaolin, calcined kaolin and chemically treated kaolin in alkyd-based paints for protection of steel. Pigment Resin Technol 2013;42:3-14.
21. Igwe IO, Anyanwu AC, Maduagwu SC, Iwuanorue JA, Udoh NM, Oragwu IP. Utilization of treated clays in formulating anti-corrosive paints for protection of steel. JPST 2022;7:1-12.
22. Raheem AA, Olowu OA. Production of household paints using clay minerals. Int J Eng Res Appl 2013;3:85-93.
23. Oluwafemi SA. Documentation, Application, and Utilization of Clay Minerals. London: IntechOpen Science. Available from: http://dx.doi.org/10.5772 [Last accessed on 2015 Feb 03].
24. National Planning Commission. National Economic Empowerment and Development Strategy (NEEDS). Abuja, Nigeria: National Planning Commission; 2004. p. 144.
25. Nigerian Industrial Standards. Standard for Paints and Varnishes Part 3. Lagos: Nigerian Industrial Standards; 1989.
26. Tan Tian Aik D. Durability and TiO_2 pigments. Paintindia Annu 1995;44:84-93.
27. ASTM D 907 - 12a. Standard Terminology of Adhesives. West Conshohocken, PA: ASTM International; 2012.
28. Tsoukleri G, Parthenios J, Papagelis L, Jalil R, Ferrari A, Geim A, *et al*. Subjecting a graphene monolayer to tension and compression. Small 2009;5:2397-402.