

Performance of Local Clay-Titanium Dioxide Core-Shell Extender Pigments in Alkyd Paints

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Received 13 January 2016; accepted 15 February 2016; published 18 February 2016

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Abstract

The performance of local clay-titanium dioxide core-shell extender pigments in alkyd paints has been studied. The physico-mechanical properties of the prepared alkyd paints were evaluated according to ASTM measurements. The effects of various environmental and corrosive factors on the paints were also studied. The study showed that the alkyd paint samples formulated using the core-shell pigments generally had low specific gravity (1.30 - 1.38), an indication that more of the core-shell pigments can be incorporated into the alkyd paints with considerable cost savings. The dry film thicknesses of the paint samples falls within 0.24 - 0.39 mm, suggesting that the samples will perform well as anticorrosive coatings and their adhesion properties are generally good, showing that they can withstand abrasive and corrosive agents. The core-shell extender pigments formulated paint samples were observed to exhibit the best dust-free, tack-free, and through dry times compared to TiO₂ paint formulation. The formulated paint samples generally performed well on exposure to rain and sunlight as well as in distilled water, 2% Na₂CO₃, and 2% H₂SO₄ with only TiO₂ paint formulation exhibiting rust. The good paint performance characteristics obtainable with the core-shell extender pigments are enough evidence to justify their utilization in the surface coatings industry. The performances of these core-shell extender pigments in alkyd paints have shown that they combine the properties of both the clays and titanium dioxide, and have the potential to overcome their disadvantages.

Keywords

Clay, Titanium Dioxide, Extender Pigments, Nanoparticles, Core-Shell Pigments, Alkyd Paints

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1. Introduction

Extenders, which are sometimes referred to as extender pigments are an integral part of almost all coating formulations. Talc, mica, kaolin, and feldspar are widely used in coatings as extender pigments and they contribute significantly towards modifying various coating properties such as flow characteristics, settling tendency, abrasion resistance, etc. The pigment that is extended is titanium dioxide (TiO_2) which is a prime pigment widely used in coatings. These extenders separate the individual TiO_2 particles to enhance its opacifying effect.

Pigment extenders are also used to reduce the amount of relatively expensive TiO_2 required for a given level of opacification and whiteness. The use of extenders in coatings has the profound disadvantage of low hiding power while titanium dioxide is a photochemically active compound. TiO_2 not only contributes to the high cost of coating products, but also increases the rate of degradation of surface coatings [1]. Thus, paint formulators and technologists have begun to find technically and economically viable extenders for use in coatings, in order to bring down the cost of coatings to acceptable limit.

The use of functional fillers/extenders like core-shell extender pigments has shown promising prospects in the paint industry. The core-shell theory is a new way of obtaining high performance, and eco-friendly extender pigments that are cost-effective. In this theory, a cheap extender being the core is covered by a surface layer of very efficient and expensive pigment—the shell [2]. Core-shell particles are examples of nanostructured materials with functional properties such as composite materials where the morphology, microstructure and chemical composition are controlled to achieve various functional properties [3]. Synthesis of various kinds of core-shell particles were reported several decades ago [4]. The composite particles having silica core and titania shell are typically synthesized using techniques like layer-by-layer deposition [5]-[8], sol-gel synthesis [9]-[14], laser pyrolysis [15], heterocoagulation [16] and flame synthesis [17]. Most of these methods are difficult to replicate in commercial quantity because of the multiple steps, pH control, ingredients like surfactant polyelectrolytes and cutting-edge technologies required [3]. Many literature sources have revealed excellent report on the preparation of core-shell extender pigments [2] [18].

Ahmed and Selim [19] prepared new pigments by depositing a surface layer of an expensive ferrite anticorrosive pigment on a cheap kaolin extender. Paints prepared using the new hybrid pigments offered excellent corrosion protection to steel substrates. Similarly, a new pigment based on the solid-solid interaction of cobalt oxide with zinc oxide on surface of kaolin was prepared by Ahmed *et al.* [20]. They found that medium oil alkyd-based paints containing the pigments with higher concentration of zinc were best in protecting steel substrates. Ahmed and Selim [21] also prepared kaolin-phosphate (core-shell) pigments based on Egyptian kaolin ore and incorporated the pigments in medium oil alkyd resin. Their results showed that the pigments could successfully replace phosphate pigments with improved corrosion protection of the substrates tested.

In order to mitigate TiO_2 deficiency in coatings, and optimize paint formulations for the best cost-performance, the present study demonstrated the performance of a simple synthesized new extender pigment system using Nigerian local clay as core and titanium dioxide as shell in alkyd paints.

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. Analytical grade of titanium tetrachloride (TiCl_4), hydrochloric acid and ammonia solution from BDH Laboratory were used. The core-shell extender pigments were prepared using local clays of 0.150 mm particle size which was found to be the major size present in both clays.

2.2. Preparation of Core-Shell Extender Pigments [22]

Titanium tetrachloride (TiCl_4) was added in three different concentrations of 2, 4, and 6 cm³ to 100 cm³ hydrochloric (HCl) acid contained in three different 500 cm³ beakers. The Obowo or Ihitte-Uboma clay was then immersed in the three different solutions respectively, was gradually stirred and allowed for some time for the clay to settle, while the HCl formed an envelope on top of the settled clay. Ammonia solution was added to the impregnated clays in drops to adjust their pH till the extender pigments are completely precipitated. The paste formed was filtered through a Buchner funnel and washed with distilled water, dried, and calcined at 650°C. Three different concentrations of titanium dioxide, and consequently, of titanium, was expected to be deposited

on the clay surface.

2.3. Preparation of the Core-Shell Extender Pigmented Alkyd Paints

Alkyd paint samples were prepared using the prepared core-shell extender pigments and TiO₂. Paints prepared using TiO₂ were for reference purpose. Xylene was used as the solvent while a medium oil alkyd resin based on soya bean oil purchased from TonyKelv Nigeria Ltd., Onitsha, Nigeria was used in this study as the binder. The different alkyd paint formulations studied are shown in **Table 1**. Lead and Cobalt naphthanate with metal contents of 36% Pb and 12% Co were used as driers. Cobalt naphthanate was used for surface dry, while lead naphthanate drier was used for through dry.

2.4. Preparation of Paint-Drier Mixtures

A given quantity of the prepared paint sample was accurately weighed, 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 [23]. The amount of driers giving the above percentage of metals in the paint-drier mixtures was calculated as follows:

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

2.5. 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 D 1475-13), 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 D 609-00 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 leveled 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.

Table 1. Alkyd paint formulations with TiO₂, and core-shell extender pigments.

Ingredients	Formulations (wt%)						
	TiO ₂	OBC-TC2	OBC-TC4	OBC-TC6	IHC-TC2	IHC-TC4	IHC-TC6
	Commercial Kronox Titanium Dioxide	Core-Shell Extender Pigments from Obowo Clay Formulations			Core-Shell Extender Pigments from Ihitte-Uboma Clay Formulations		
Alkyd resin	37	37	37	37	37	37	37
TiO ₂	63	-	-	-	-	-	-
TiO ₂ /LCC (2)	-	63	-	-	63	-	-
TiO ₂ /LCC (4)	-	-	63	-	-	63	-
TiO ₂ /LCC (6)	-	-	-	63	-	-	63
Total	100	100	100	100	100	100	100
P/B ratio	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Solvent	12	12	12	12	12	12	12

Note: TiO₂/LCC (2), TiO₂/LCC (4), and TiO₂/LCC (6) are the three different core-shell extender pigments prepared for each local clay that contain 2, 4, and 6 cm³ of titanium tetrachloride.

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. Properties of the Prepared Core-Shell Extender Pigments

The X-ray fluorescence (XRF) determinations on the core-shell extender pigments presented in **Table 3** shows that two major constituents of the prepared extender pigments in order of abundance are silica, (SiO₂) and aluminum oxide (Al₂O₃). The titanium dioxide (TiO₂) content of the core-shell extender pigments are between 7.0 and 13.0 wt% while Weaver [24] reported that TiO₂ values in kaolin commonly range from 0.20% to 2.50%. The high TiO₂ content in the prepared core-shell extender pigments is an indication of the presence of titanium dioxide and consequently titanium deposited on the clays.

The particle morphology of the core-shell pigments obtained from scanning electron microscope (SEM) shown in **Figure 1** and **Figure 2** indicates that the Obowo and Ihitte-Uboma core-shell extender pigments are nodular (a rounded irregular shape) shaped structures of different sizes. It can be inferred that as titanium is deposited on the clay surfaces, new structures are formed which have the clays appearing as clouds in the background of the micrographs and this may be attributed to the purity and fine particle nature of the clays. Therefore, the combination of the clay and titanium dioxide structure possibly lead to the formation of core-shell structures of different plate sizes without any change in the plate shapes.

The properties of the core-shell extender pigments presented in **Table 4** shows that the prepared extender pigments are slightly alkaline having values ranging from 7.45 - 7.56. It is important to note that the pH of the prepared core-shell extender pigments were not much affected by progressive increase in titanium dioxide deposited on the pigments. The specific gravity of the core-shell extender pigments were found to increase with increase in titanium dioxide present in the pigments. From the present study, the core-shell extender pigments have lower specific gravity than titanium dioxide. Interestingly, lower specific gravity of pigments leads to a considerable cost saving in coatings [25].

The refractive indices of the prepared core-shell pigments determined using an Abbe's refractometer also presented in **Table 4** illustrates that the pigments have refractive index lower than that of TiO₂ pigment but higher than other extenders. It is important to note that all extenders have refractive index that fall in the range between, 1.45 and 1.65 [26]. Therefore, the core-shell extender pigments have shown a remarkable improvement in the refractive index of extenders and can be considered to impart opacity to polymer coatings. The refractive indices of the prepared core-shell extender pigments were found to increase with increase in titanium dioxide deposited on the extender pigments.

The core-shell extender pigments' oil absorption properties were determined using the spatula rub-out technique and results obtained are shown in **Table 4**. The various prepared core-shell extender pigments exhibited roughly the same oil absorption values, and which is higher than the oil absorption TiO₂ pigment. Less oil absorption indicates less resin demand without compromising other coating properties [27]. The oil absorption 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 [28].

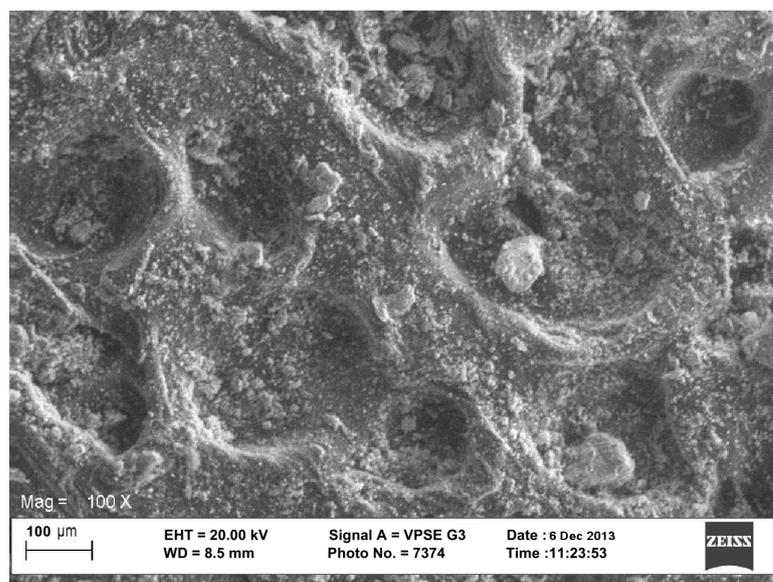
3.2. Specific Gravity

The specific gravity values of core-shell extender pigments and titanium dioxide (TiO₂) formulated alkyd paints are shown in **Table 5** and illustrated graphically in **Figure 3**. The table shows that the TiO₂ formulated alkyd paint has the highest specific gravity when compared to those formulated using the core-shell pigments. This is

Table 3. XRF analysis results of the prepared core-shell extender pigments.

Constituents (wt%)	OBC-TC2	OBC-TC4	OBC-TC6	IHC-TC2	IHC-TC4	IHC-TC6
SiO ₂	66.7	66.8	65.8	54.64	52.7	52.78
Al ₂ O ₃	19.8	17.3	17	27.83	25.7	25.56
TiO₂	7.22	9.94	11.3	7.18	10.8	12.54
K ₂ O	0.67	0.453	0.4	0.72	0.712	0.771
CaO	0.3	0.298	0.231	0.85	0.611	0.647
Fe ₂ O ₃	2.12	2.1	2.13	4.63	4.84	3.97
MgO	0.15	0.143	0.14	0.17	0.18	0.161
Na ₂ O	0.382	0.291	0.338	0.11	0.12	0.13
V ₂ O ₅	0.15	0.16	0.16	0.192	0.32	0.18
Cr ₂ O ₃	0.004	0.004	0.003	0.02	0.023	0.053
Ga ₂ O ₃	0	0	0	0.02	0.031	0.02
MnO	0.02	0.024	0.021	0.01	0.01	0.02
Sc ₂ O ₃	0	0	0	0.001	0.001	0.001
CuO	0.015	0.016	0.014	0.02	0.015	0.028
ZnO	0	0	0	0.008	0	0
Bi ₂ O ₃	0	0	0	0	0	0
L.O.I	2.4	2.4	2.41	3.58	3.86	3.12
Total	99.931	99.929	99.947	99.981	99.923	99.981

Abbreviations: OBC = Obowo clay core-shell pigment; TC = Titanium tetrachloride; IHC = Ihitte-uboma core-shell pigment; 2, 4, 6 = Quantity (cm³) of TC in OBC or IHC.

**Figure 1.** SEM micrograph of IHITTE-UBOMA core-shell pigment.

to be expected since TiO₂ pigment has the highest specific gravity value compared to the core-shell pigments used in this study [22]. The alkyd paints formulated using the core-shell pigments exhibited low values of specific gravity. Obviously, more of the core-shell pigments can be incorporated into the alkyd paints with considerable cost saving when compared to the incorporation of TiO₂ in alkyd paint. Specific gravity of paints is used to determine the coverage of paint products on a substrate, that is, the volume occupied by a known weight of paint product [29].

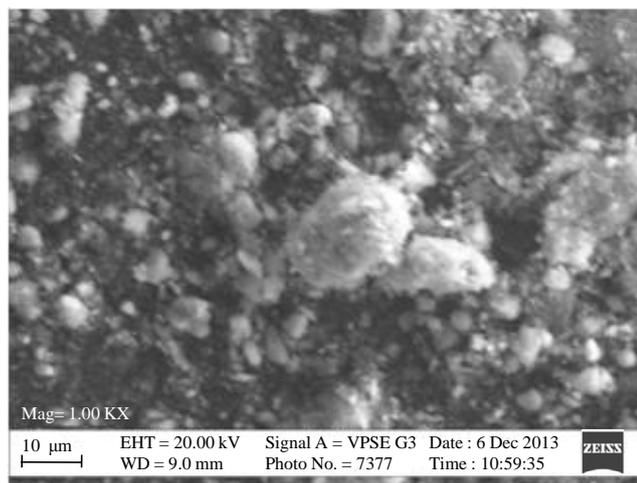


Figure 2. SEM micrograph of Obowo core-shell pigment.

Table 4. Properties of the core-shell extender pigments.

Sample	pH	Specific Gravity g/cm ³	Refractive Index	Oil Absorption g/100g
KRONOS 2190 TiO ₂	7.5 - 8.0	4.1	2.55	18
OBC-TC2	7.56	2.87	1.88	25
OBC-TC4	7.55	3.05	1.93	25
OBC-TC6	7.56	3.08	1.96	24
IHC-TC2	7.45	2.92	1.91	24
IHC-TC4	7.46	3.07	1.93	25
IHC-TC6	7.46	3.10	1.95	25

Table 5. Coating properties of prepared core-shell extender pigmented paints.

Formulation Code	Specific Gravity	Viscosity (poise)	Dry Film Thickness (mm)	Drying Time (Min)			Settling Test	Adherence Test (%)
				Dust Free	Tack Free	Through Dry		
TiO ₂	1.55	16.61	0.24	71	99	150	9	4
OBC-TC2	1.30	58.13	0.30	30	40	88	6	1
OBC-TC4	1.35	57.53	0.27	32	49	88	7	2
OBC-TC6	1.35	36.61	0.26	40	58	92	7	8.5
IHC-TC2	1.35	56.57	0.30	17	28	38	5	1
IHC-TC4	1.35	54.88	0.30	19	30	43	5	1.5
IHC-TC6	1.38	34.50	0.29	22	31	44	6	1

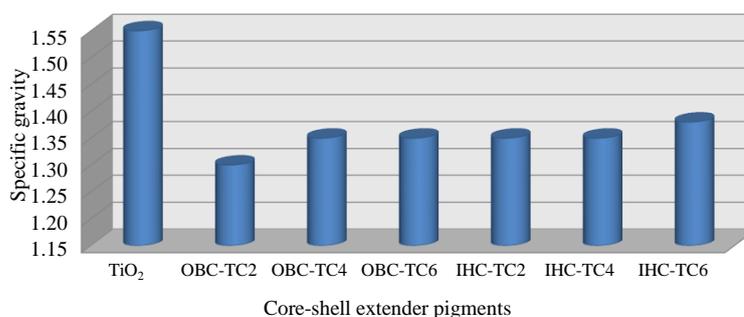


Figure 3. Effect of core-shell extender pigments on the specific gravity of alkyd paint formulations.

The study shows that alkyd paints formulated using Ihitte-Uboma core-shell extender pigments prepared using 2 cm³, and 4 cm³ of TiCl₄, as well as Obowo core-shell extender pigments prepared using 4 cm³ and 6 cm³ TiCl₄ exhibited the same specific gravity (1.35) in paints. The alkyd paint formulated using Obowo core-shell pigments that was prepared using 2 cm³ TiCl₄ exhibited the least specific gravity in the prepared paints.

3.3. Viscosity of Alkyd Paint Samples

The viscosity values of the formulated alkyd paint samples are presented in **Table 5** and illustrated graphically in **Figure 4**. Titanium dioxide (TiO₂) formulated alkyd paint exhibited the least viscosity value among the alkyd paints studied. The present study has shown that the viscosity of alkyd paints prepared using the core-shell extender pigments was observed to decrease as the quantity of TiO₂ they contain increased, and vice-versa. The range of viscosities observed for the paint samples makes them suitable for application by spray or brush. Tiwari and Saxena [26] 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 [30]. Viscosity affects the application and flow properties of a coating and is generally adjusted to the intended application [31] [32]. According to the Nigerian Industrial Standard NIS 268:1989, the minimum viscosity for gloss paint shall be 22 centipoise.

3.4. 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** and illustrated graphically in **Figure 5**. From the figure, it is evident that TiO₂ formulated paint exhibited the least paint dry film thickness (0.24 mm). Though the thickness of the

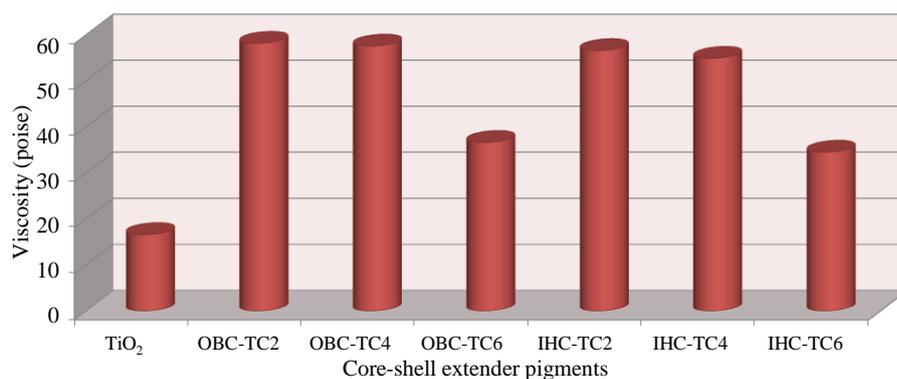


Figure 4. Effect of core-shell extender pigments on the viscosity of alkyd paint formulations.

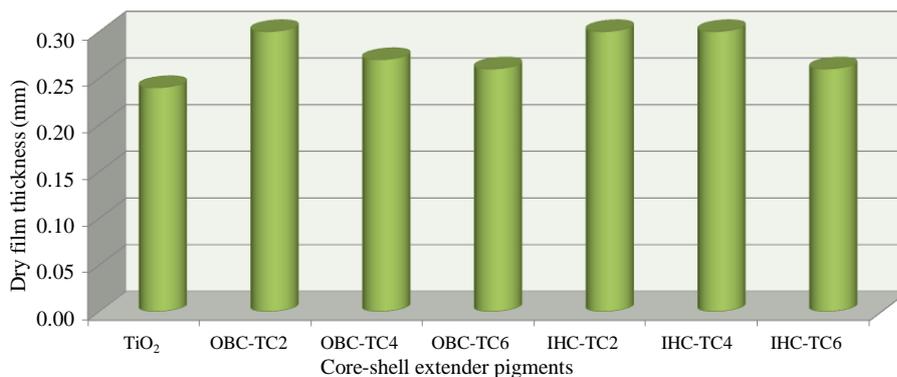


Figure 5. Effect of core-shell extender pigments on the dry film thickness of alkyd paint formulations.

alkyd paint films formulated using the core-shell extender pigments were generally observed to decrease with increase in TiO_2 content, the Ihitte-Uboma core-shell extender pigments formulated paint samples exhibited the highest film thickness.

According to Tan Tian Aik, [33], 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. Drying Studies on Paint Film Samples

The drying properties of the prepared paint samples given in Table 5 are illustrated graphically in Figure 6. The drying properties investigated are dust-free dry, tack-free dry, and through-dry.

3.5.1. Dust-Free Dry Times

The alkyd paint samples formulated using the Ihitte-Uboma core-shell pigments exhibited the best dust-free drying times than Obowo core-shell pigments and TiO_2 in the formulated paint samples. The paint samples formulated with Obowo, and Ihitte-Uboma core-shell pigments exhibited good dust-free drying times which were found to increase with increase in the quantity of TiCl_4 used in preparing the pigments. It is important to note that the higher the quantity of TiCl_4 used in preparing the pigments, the higher the quantity of TiO_2 deposited on the extender pigments [22]. In essence, high TiO_2 content was observed to increase the dust-free drying times of the formulated alkyd paints; with TiO_2 formulated paint having the highest dust-free drying time.

3.5.2. Tack-Free Dry Times

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 TiO_2 had the highest tack-free drying time of 99 minutes, while the paint samples of Obowo core-shell pigment formed with 6 cm^3 of TiCl_4 followed with a tack-free drying time of 58 minutes. Like was noted for the dust-free drying times of the prepared paint samples, the tack-free drying times of the core-shell extender pigments formulated alkyd paints of Obowo, and Ihitte-Uboma clays exhibited drying times that increased with increase in TiO_2 incorporated into the clays. The core-shell pigments of Ihitte-Uboma clay prepared using 2 cm^3 of TiCl_4 exhibited the least drying times in the formulated paint samples. The alkyd paint samples of the core-shell extender pigments were observed to exhibit lower tack-free drying times than TiO_2 formulated paint. The tack-free dry times of the formulated alkyd paint samples with core-shell extender pigments are generally good. 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.

3.5.3. Through Dry Times

The through dry times of the formulated paint samples illustrated in Figure 6 shows that TiO_2 formulated paint

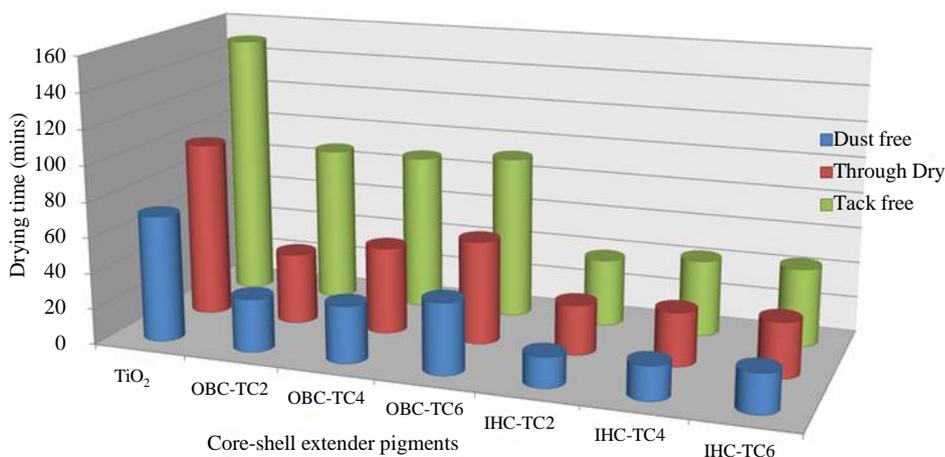


Figure 6. Effect of core-shell extender pigments on the adherence of alkyd paint formulations.

sample exhibited the highest through dry time (150 minutes). All the core-shell extender pigment formulated alkyd paints of Obowo, and Ihitte-Uboma clays generally had through dry times that increased with increase in TiO_2 content. The through dry times of Obowo core-shell extender pigments were generally greater than the through dry times of Ihitte-Uboma core-shell pigments formulated alkyd paints.

Generally, the core-shell extender pigments formulated alkyd paints of Obowo, and Ihitte-Uboma clays exhibited the best dust-free, tack-free, and through dry times when compared to the TiO_2 paint formulation. According to the Nigerian Industrial Standard, NIS 268:1989, the through dry time of gloss paint shall not exceed 24 hours.

3.6. Chalking Test on Paint Film Sample

The chalking tests carried out on the formulated paint samples indicated that none of the paint samples showed any sign of chalking. A good paint should not chalk. The results of the above test showed that the core-shell extender pigments performed equally well in coatings just like the paint prepared using the conventional TiO_2 pigment.

3.7. 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** and illustrated graphically in **Figure 7**. The settling tests shows that paints formulated using the core-shell extender pigments from both local clays showed moderate settling tendencies when compared to the formulation containing TiO_2 pigment which almost showed no settling tendency. However, the settling tendencies of the core-shell extender pigment formulated alkyd paints were observed to be independent on TiO_2 content though at the highest TiO_2 content of the core-shell pigments, they showed an improved settling tendency.

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. The properties of the binder also influence the settling tendencies. It is probable to reason that the difference in settling tendency observed for the core-shell extender pigments 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 core-shell pigments were reported [22] to have specific gravity that was lower than that of TiO_2 . The proportional difference between the specific gravities of these extender pigments and the binder may have led to the slight settling noticed in the core-shell extender pigments based paint formulations. 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. TiO_2 pigments were reported [22] to have oil absorption value that was lower than those of the core-shell pigments. This could have also contributed to the various levels of settling observed in the paint samples.

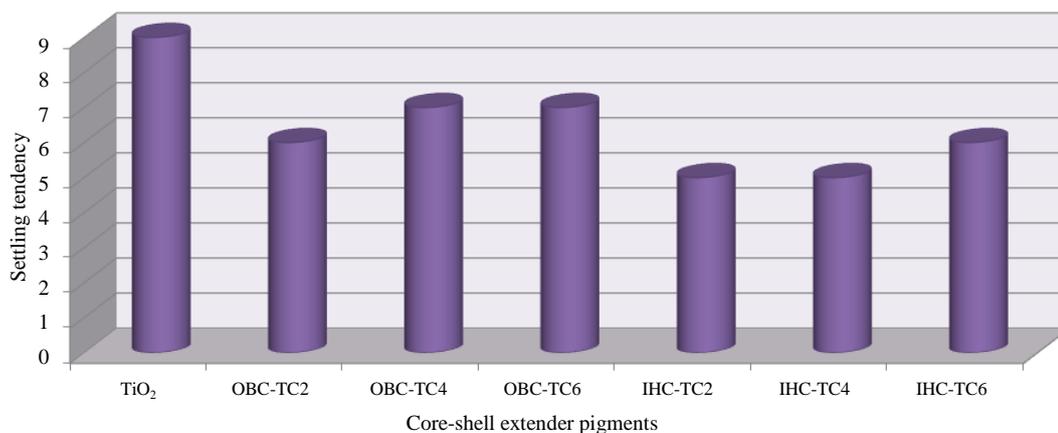


Figure 7. Effect of core-shell extender pigments on the settling tendency of alkyd paint formulations.

3.8. Adherence to Surface of Paint Films

Data on the adhesion properties of the prepared paint samples are shown in **Table 5**, and illustrated graphically in **Figure 8**. The figure 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 core-shell extender pigments of Ihitte-Uboma clay, core-shell extender pigments of Obowo clay (with the exception of the pigment containing $6 \text{ cm}^3 \text{ TiCl}_4$), exhibited particularly good adhesion properties. For the paint samples formulated using the Obowo core-shell extender pigments, the % adhesion loss of paint dry film was observed to increase with increase in TiO_2 content. Alkyd paints formulated with Obowo clay core-shell extender pigment prepared using $6 \text{ cm}^3 \text{ TiCl}_4$ exhibited the highest % adhesion loss of dry paint film (8.5%) followed by the TiO_2 pigment formulated paint sample. All the prepared paint samples exhibited % adhesion loss in the range, 1 - 10. Adhesion according to ASTM D 907 (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, etc.

3.9. 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 core-shell extender pigments performed equally well in coatings just like the TiO_2 formulated paint samples. On the other hand, the alkyd paint formulated samples shaded their color after seven months of exposure to rain and sunlight. The paint formulations containing TiO_2 exhibited slight rust while all the core-shell extender pigment based paint formulations resisted rust as shown in **Figure 9**. This is an indication that the core-shell extender pigment formulations can withstand environmental challenges, and therefore can be used in corrosive environment.

3.10. 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 **Figure 10** were rated according to the method of Muralidharan [34] as follows: 0—No change; 1—Very slight effect; 2—Effect; 3—Light effect; 4—Definite effect; 5—Bad effect.

From **Table 6**, 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 using TiO_2 . The good performance of the core-shell pigments based paints in acidic as well as 2% Na_2CO_3 could be attributed to the presence of inert oxides they contain [22] [26].

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

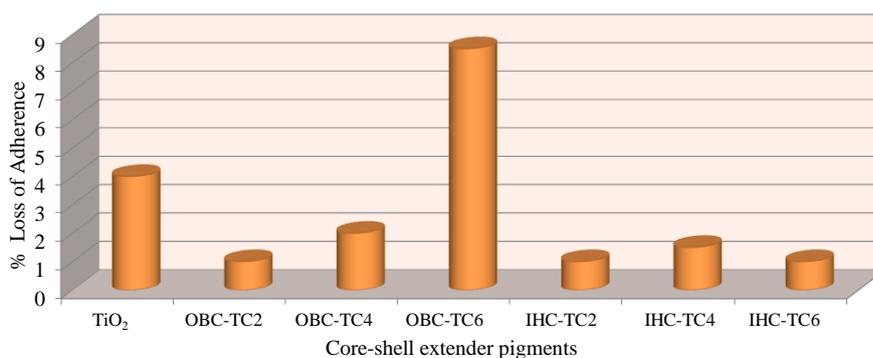


Figure 8. Effect of core-shell extender pigments on the % loss of adherence of alkyd paint formulations.

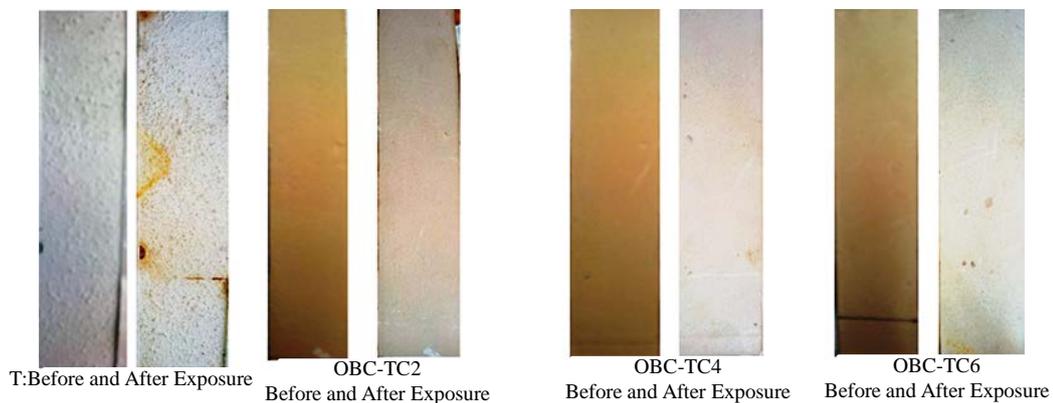


Figure 9. Pictures of environmental tests on paint film samples.

Table 6. Media resistance of prepared paint samples.

Formulation Code	2% NaCl	2% H ₂ SO ₄	2% Na ₂ CO ₃	Distilled Water
TiO ₂	3	3	1	0
OBC-TC2	2	1	1	0
OBC-TC4	1	0	0	0
OBC-TC6	1	0	0	0
IHC-TC2	1	0	0	0
IHC-TC4	1	0	0	0
IHC-TC6	1	0	0	0

0—No change; 1—Very slight effect; 2—Effect; 3—Light effect; 4—Definite effect; 5—Bad effect.

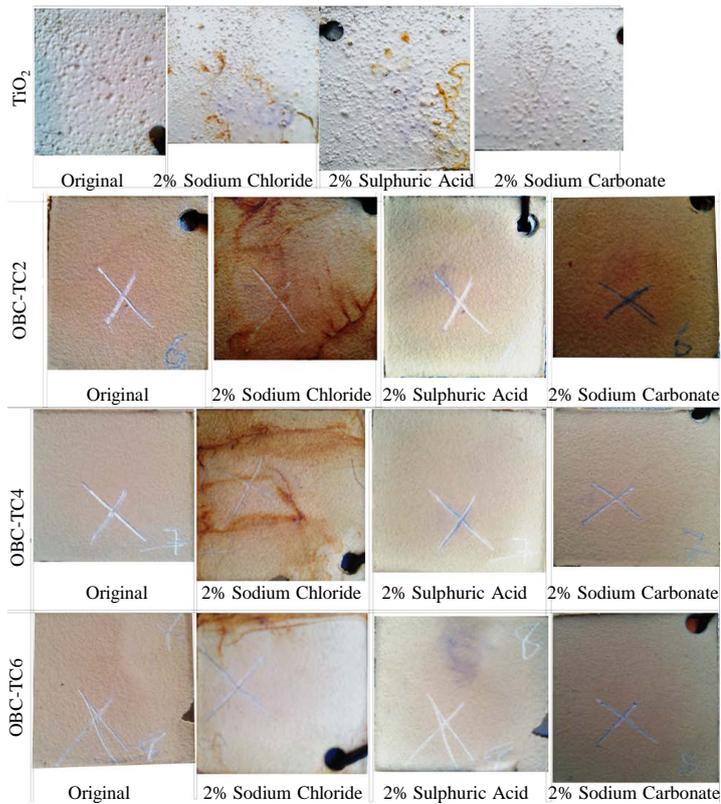


Figure 10. Pictures of media resistance test on paint film samples.

of paint films. The stability of paint samples formulated using the core-shell pigments in NaCl solution means that the paints can be applied where high durability against corrosive environment is required.

4. Conclusions

Alkyd paint samples have been prepared using core-shell extender pigments prepared from Obowo, and Ihitte-Uboma local clays. Paint samples formulated using TiO₂ served as the reference paint and had the least viscosity value among the alkyd paint samples studied. The alkyd paint samples formulated using the core-shell pigments generally had low specific gravity, an indication that more of the core-shell pigments can be incorporated into the alkyd paints with considerable cost savings. The film thicknesses of the paint samples are in the range that places the paint samples as anticorrosive paints. The core-shell extender pigment formulated paint samples were observed to exhibit the best dust-free, tack-free, and through dry times. The adhesion properties of the paint samples are generally good which shows that they can withstand abrasive and corrosive agents. The core-shell extender pigments formulated paint samples exhibited moderate settling tendencies.

The alkyd dry film samples exhibited no chalking tendency, and mildew formation. The formulated paint samples shaded their colours on exposure to rain and sunlight, with only TiO₂ paint formulation exhibiting rust. The formulated paint samples generally performed well in distilled water, 2% Na₂CO₃, and 2% H₂SO₄. The present study has demonstrated the utility of core-shell extender pigments from Obowo, and Ihitte-Uboma clays in formulating alkyd paints. The expectation is that this core-shell extender pigments should find utilizations in the surface coatings industry which will help to reduce the over dependence on imported extender pigments, thereby saving scarce resource, spent on importation.

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