Study on Pigment-Extender Effect of Some Nigerian Clays and Calcium Carbonate in Emulsion Paint

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Abstract:

This work investigated the pigment-extender effect of Aningene clay, Nwangene clay and calcium trioxocarbonate(iv) in emulsion paint. The clay samples were prepared by washing, sedimentation, drying, grinding and sieving. The clay particles obtained were calcined at 750 °C. The calcined and uncalcined clay were used to formulate emulsion paint. Physical and performance properties of the produced paint were determined. The compositional and morphological analyses were also carried out on the calcined clays via X-ray fluorescence and scanning electron microscopy. The XRF showed that the Aningene clay and Nwangene clay contained silica (SiO_2) and aluminum oxide (Al_2O_3) percentages of 43.02%, 66.20% and 23.92%, 27.50% respectively. The Aningene clay also contained 6.08% of iron oxide (Fe_2O_3), the rest of the constituents is in small quantities for both clays. The SEM micrograph of the calcined clays showed that the clay particles are 50 *um* in size. The physical tests showed that the pH and specific gravities of the clay formulated paint were lower than that of the calcium trioxocarbonate (IV) formulated paint. While the viscosities were also higher than that of the calcium trioxocarbonate (IV) formulated paint. The performance tests showed that the opacity and spread rate of the clay formulated paints were lower than calcium carbonate formulated paint. Also, none of the clay formulated paints chalked on drying. The Aningene clay formulated paint gave better paint property than the Nwangene clay formulated paint. Hence, the Aningene clay should be used in production of emulsion paint and Nwangene clay should be used in the production of harsh paints.

Keywords:

Emulsion Paint, Calcium Trioxocarbonate(IV), Aningene Clay, Nwangene Clay, XRF, SEM

1. Introduction

The coating industry plays an important role in the growth of the economy and as such, there is need for sustainability in the industry. Over the years, there has been ongoing research to find alternative raw materials to primitive ones used in paint production.

Paints are any liquid, liquefiable, or mastic composition that after application to a substance in a thin layer, converts to a solid film. It is most commonly used to protect or provide texture to objects and surfaces [1]. Paint can be made or purchased in many colors and in many different types, such as water-color, synthetic, etc. Paint is typically stored, sold, and applied as a liquid, but most types dry into a solid. It can also be used to describe liquid material before application and coating after it has been applied and dried. The purpose of paint is to protect the surface of metals and wood from attack by rain, dust and gases in the air, it can also be applied to impart beauty and protection. Paint is a term used to describe a number of substances that consist of a pigment dispersed in a liquid or paste called vehicle such as oil or water. It provides an economic protection, preservation, and decoration, aesthetic and adds functionality to structures [1]. Today paints are used for coloring and protecting many surfaces, including houses, cars, road markings and underground storage vessels. Paint is essentially composed of a binder, pigment and solvent. However, paint constituents depend on the purpose which the paint will serve [2]. The commonly used paint is the emulsion paint which its constituents include the solvent which is usually water, the pigment impacts color to mixture, titanium (ii) oxide is most popular pigment used in production, one of the reason is because it protects the paint film by way of reflecting ultra-violet radiation from the sun that would cause degradation of the film. The extender-pigment acts to reduce cost of pigment and increase durability of the mixture and then the additives like preservatives, defoamer which is added to improve other properties of the paint [3].

In recent years, the extender-pigment has been noted to have a crucial effect on the rheological properties of paint and also in the general economics of paint production in the sense that it reduces the cost of pigment used for production. Research shows that a number of compounds have been used as extender-pigment in the production of emulsion paint of which they have shown different effects on the properties of the paint. Some of these compounds include: barium sulfate in its natural crystalline form of barite, magnesium silicate having trade names as talc and asbestine, ordinary silicon (ii) oxide is also used but the most commonly used extender-pigment is calcium carbonate [4]. Clay has also shown interesting effects when it is used as an extender-pigment in paint production.

Clays have been used indispensably as extenders in architectural and industrial paints, and other industries such as in agriculture, in construction as a building material, in oil industry as drilling mud to protect the cutting bit while drilling, filtering and deodorizing agents in the refining of petroleum, in clarifying water and wine, in purifying sewage as an adsorbent, in textile and sugar industries to remove color and other impurities, and in the paper, plastics, and rubber industries as fillers, its sustainable and benign to the environment [5]. Thus, this research is aimed at harnessing the effects of some local clays in Nigeria for emulsion paint paint production.

2. Materials and Methods

2.1. Sample Collection and Preparation

The clay was sourced from two locations; Aningene clay was obtained from Umudike, Asaba, Delta State and Nwangene clay was obtained from Ogwuada Owerre-Ezukala, Anambra State, Nigeria. The samples obtained were washed, allowed to sediment and then dried. The dried clay samples was ground and sieved to get fine particles of mesh size 50µm.

2.1.1. Preparation of Extender for Paint Production

The two sieved clay samples were divided into two parts respectively. One part of each of the two clay samples were calcined at 750℃ and its surface morphology was determined with the aid of scanning electron microscope (cc Tenex, Made in China). Also, the elemental composition was determined via X-Ray fluorescence (cc Tenex, Made in China). The samples were used to formulate emulsion paint, the control had calcium trioxocarbonate(iv) incorporated into it, sample A had Aningene clay both the normal and calcined samples incorporated into it and sample B had Nwangene clay both the normal and calcined sample were incorporated into it.

2.1.2. Formulae for the Production of the Emulsion Paints

The formulation of the emulsion paints with calcium trioxocarbonate(iv), Aningene clay as sample A and Nwangene clay as sample B is as shown in Table1. The Table shows the list of materials used in the production, their function and the weight percentage in the formulation. The sample A and B are for the normal and calcined.

Table 1. *Formulation of Emulsion Paint with Calcium Carbonate and Clay Samples A and B.*

Components	Function	Control	Sample A	Sample B
Water	Solvent	40	40	40
Calgon PT	Anti re-depository	1	1	1
	agent/surfactant			
Poly(vinylacrylate)	Binder	7.5	7.5	7.5
Genapol	Emulsifier	1.5	1.5	1.5
Anti-fungi agent	Fungal growth	2	2	2
	Retardant			
Biocide	Preservative	2	2	2
Natrosol	cellulosic thickener	2	2	2
Ammonia	pH adjuster	1.5	1.5	1.5
Titanium dioxide	Pigment	7.5	-	-
Smooth marble dust	For coarseness	-	2.5	-
Clay A	Extender	-	40	-
Clay B	Extender	-	-	42.5
Calcium carbonate	Extender	35	-	-
	Total	100%	100%	100%

2.1.3. Procedure for Production of Emulsion Paint.

The production method described is for the production of the control, which is obtained by dividing the % by weight of each component by 20 [6]. The difference with this production method and that of the sample A&B is only the addition of Aningene clay (2.0g) and smooth marble dust(0.125g) for sample A and Nwangene clay(2.125g) for sample B. The materials used were properly weighed out in gram, with the aid of crucibles. Water was added to the bowl, calgonPT (0.05g) was dissolved and stirred for 2-5minutes. Poly vinylacrylate was added and stirring continued, calcium trioxocarbonate(iv) (1.75g) was also added followed by addition of titanium dioxide(0.375g) and the stirring continued for another 10minutes. The natrosol(0.1g) was dissolved in 50mL of water with another container for few minutes before being added, this was followed by addition of genapol (0.075g),biocide(0.1g),anti-fungal agent(0.1g) and ammonia(0.075mL) respectively to the mixture. The mixture was stirred thoroughly for another 10minutes to obtain a homogenous emulsion. The sample paints produced were kept for analysis and testing.

2.2. Quality Control Test

Quality control tests were carried out on the emulsion paint produced with calcium trioxocarbonate(iv) (CCEP), Aningene clay (ACEP) and Nwangene clay (NCEP). The tests and calculations were carried out using standard testing methods [7]. The tests carried out were specific gravity, viscosity, pH values, opacity and homogeneity test. The spreading rate was obtained from values generated from the opacity test.

2.2.1. Test for Homogeneity

The three paint samples were put in three different test tubes and put in a 6 test tube centrifuge; the other three test tubes were filled with water in other to balance out the sample test tubes. The centrifuge was closed and set to 4000 rotations per minute for 10minutes and then switched on. Observations were noted afterwards.

2.2.2. pH Test

The pH meter was switched on and then the electrode was dipped in a beaker containing a buffer solution of pH 7.0 in other to standardize it. The samples were each dissolved in 10ml of distilled water independently and then the pH of each of the samples was taken. The electrode was finally standardized cleaned, kept and switched off.

2.2.3. Viscosity

The viscometer was switched on, with the spindle fixed and auto-zeroed. Then each of the samples was put in a container and then the spindle is dipped in it. The viscometer was then switched on and the reading was taken, this was done independently for each of the samples at the temperature of 30 ℃ and the spindle speed was taken to be 0.1 rotation per minute.

2.2.4. Specific Gravity

The weight per litre cup was first weighed empty on a digital weighing scale. The value obtained was ‘tared’. The paint sample was poured into the cup and any excess paint cleaned off from the hole in the lid. The cup with the paint was weighed to obtain the wt per litre value of the paint. This was done independently for each of the samples.

2.2.5. Opacity Test

The paint samples were each applied on a surface area until the area was covered; this was done independently for each of the sample. The ratio of the area of painted surface to the volume of paint applied was taken for each of the samples.

2.2.6. Spreading Rate

The spreading rate of each of the sample was obtained from the values obtained from opacity and specific gravity tests.

3. Results and Discussion

The results of the tests and analyses carried out on the sample are discussed as follows.

3.1. Compositional Analysis

The X-ray fluorescence (XRF) determinations on the calcined Aningene and Nwangene (750˚C) local clays are presented in Table 2.

Table 2. *X – Ray Flourescence Result Of Calcined Aningene Clay (Cac) And Nwangene Clay (CNC).*

S/N	CHEMICAL COMPOSTION	CACWt%	CNCWt%
1.	Al_20_3	23.92	27.50
2.	CaO	0.91	0.16
3.	Cr_2O_3	0.03	0.01
4.	Fe_2O_3	6.08	1.76
5.	K_2O	2.91	1.70
6.	MgO	2.61	0.21
7.	Na_2O	-	0.30
8.	P_2O_5	-	0.06
9.	Rb_2O	-	0.01
10.	SiO_2	43.05	66.20
11.	SO_3	-	0.11
12.	TiO_2	0.14	0.71
13.	ZrO_2	-	0.02

The result indicates the presence of silica (SiO_2) and aluminum oxide (Al_2O_3) in high proportions while the other constituents are present in smaller proportions as shown in Table 2. The calcined Aningene clay was found to contain 43.04% of SiO_2, 23.92% of Al_2O_3,6.08% of Fe_2O_3; this explains its reddish-brown appearance, and less than 5% of other constituents. While calcined Nwangene clay contained 66.20% of SiO_2, 27.50% of Al_2O_3, and less than 5% of the other constituents. The high proportion of silica and aluminium oxide in the clays is indicative of the kaolinite nature of the clays and the basis for the type of clay to be used for the production of clay paint. The oxide contents (SiO_2 and Al_2O_3) of these clays were consistent with other Nigerian clays. Some of these clays include; Obowo clay 67.08%, 21.6% and Ihitte-Uboma clay 56.4%, 29.3% [8]. Ibere clay 52.06%, 27.87% and Oboro clay 60.21%, 19.05% [9]. Mayo-Belwa clay 59.8%, 7.08% [10]. Omankwo Afikpo clay 87.13%, 6.70%; Okposi clay 53.04%, 19.70% [11]. The presence of the unreacted oxides in the clays is an indicative that paint formulated with the clays will function as anti-corrosive paints since the unreactive oxides will slow down the diffusion of corrosive species thereby delaying the phenomenon of corrosion in painted surface [12].

3.2. Morphological Analysis

The morphology of Aningene clay and Nwangene clay obtained by scanning electron microscope (SEM) are as shown in Figures 2 and 3 respectively. The particle size of the extender affects the properties of paint, thus the particle size range of the extender is usually specified for paints and other surface coatings. An extender particle size not exceeding 75µm is usually required for emulsion paint formulation (CAP, Plc, 2010). The extender particle size of these clays used was 50µm.

Figure 2. *SEM micrograph of calcined Aningene clay.*

Figure 3. *SEM micrograph of calcined Nwangene clay.*

3.3. Test for Homogeneity

The five emulsion paint samples showed no degree of separation after been subjected to a high spin speed. This suggests that the binder had good interaction with the extender and the other constituents and that the paint samples had high degree of compactness. Hence, settling is less likely to occur in the paint samples.

3.4. Viscosity

The effect of the extenders on the viscosity of the five emulsion paint samples varied and showed some interesting characteristics. The viscosity values are shown in Table 2. The viscosity of emulsion paint is an important paint property as it affects the consistency, flow and application properties of the paint. From the results the ACEP and NCEP had both higher viscosities than CCEP, this was different from the paint formulated with calcined clay. CACEP had lower viscosity than CCEP while CNCEP had higher viscosity, this means that calcinations had an effect on the structure of the clay. The explanation to this is that a lot of bonds were broken on calcination in the Aningene clay which affect the structure and invariably changed the rheological effect it had on the paint. The Nwangene clay had its bond strengthened on calcination this improved the rheological effect it had on the paint. It is deduced that the viscosities of the paint conformed to that of the NIS standard of viscosity ≥6 poise [13].

Table 3. *Viscosity of the five samples of emulsion paint.*

Paint sample	CCEP	ACEP	NCEP	CACEP	CNCEP
Viscosity(poise)	3696	17460	8250	2250	11460

3.5. pH Test

The results of the pH, specific gravity, opacity and spread rate values of the paint are presented in Table 4.

Table 4. *Paint properties of the formulated emulsion paint.*

Paint properties	**CCEP**	**ACEP**	**CACEP**	**NCEP**	**CNCEP**
pH value	9.06	8.45	8.48	7.23	7.16
Specific gravity	1.522	1.462	1.4595	1.209	1.356
Opacity	68.57	15.22	14.50	6.580	8.498
Spread rate	6.849	1.5234	1.455	0.66	0.85

The pH test of the clay formulated paint had lower values than that of the calcium trioxocarbonate(iv) formulated paint. This higher pH of CCEP can be attributed to the buffering capacity of $CaCO_3$ which is basic. Also, NCEP and CNCEP had lower pH value than that of ACEP and CACEP. The difference in their mineral content justifies the differences noticed in this pH values. In general the pH of the clay formulated paint conforms to pH range stipulated by NIS which is from 7.0-9.0.

3.6. Specific gravity

The values of the specific gravity of the formulated paints as presented in Table 4, showed that the specific gravities of the clay formulated paints are lower than that of the calcium trioxocarbonate (iv) formulated paint. The specific gravities of the calcined clay formulated paints showed higher values than that of their uncalcined counterparts. The low specific gravity obtained in this study is an indication that the Aningene clay and the Nwangene clay can be used in high proportions without having any adverse effect in the bulk density of the formulated paint. This is in agreement with the work of some other researchers [5].

3.7. Opacity Test

The results of opacity values of the formulated paints are also presented in Table 4. The opacity of the paint, which is also known as the hiding or obliterating power, is largely dependent on the nature and amount of pigment in the paint. The opacity of clay formulated paint was way lower than that of the calcium trioxocarbonate(iv) formulated paint, the values of the Nwangene clay formulated paint are also low when compared to those of the Aningene Clay formulated paint. The lower the refractive index of an extender the lower the specific gravity. The refractive indices of extenders have great influence on the scattering power of paints. Generally, extenders do not enhance the true opacity or color of the coating film. The low refractive indices of some extenders are responsible for the poor opacity exhibited in solvent paints [14]. The implication of this is that; a higher volume of clay formulated paints, especially NCEP and CNCEP will be required to cover a surface.

3.8. Spread Rate

The result of spread rate of the clay formulated paint is presented in Table 4.The spread rate is also known as coverage is that property of paint that refers to extent that paint can cover with respect to the volume. Spread rate/coverage is a function of volume solids. From Table 4, it can be noted that the calcium carbonate formulated paint has a larger spread than the clay formulated paints. The chart has it that the CCEP has the highest spread rate and the CNCEP has the lowest spread rate. The implication is that the CCEP is a better paint than the ACEP and the CACEP which are better than NCEP and the CNCEP when the spread rate criterion is in consideration.

4. Conclusion

The Nigerian clays investigated in this study; the Aningene clay and Nwangene clay and calcium carbonate have been successful incorporated into emulsion paint and compared through the Quality control test. The calcined Aningene clay formulated paint showed better paint properties than the uncalcined clay formulated paint while that of the calcined Nwangene clay formulated paint was also better than that of uncalcined formulated paint. The pH of the clay formulated paints was all within the standard range the same can be said for the calcium carbonate formulated paint. The Aningene clay formulated gave better paint properties than the Nwangene clay formulated paint.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Author Contributions

Conceptualization: P.U.C.O.; Methodology: R.W.U.U.; Software: R.W.U.U.; Validation: R.U. A.; I.M. I.; Formal analysis: P.U.C.O.; Investigation: R.W.U.U.; P.U.C.O.; Resources: R.W.U.U.; P.U.C.O.; Data Collation: R. W. Uche Uzoechi; P.U.C.O.; Writing – original draft preparation: R.W.U.U.; Writing – review and editing: P.U.C.O.; Visualization: R.U.A; I.M. I.; Supervision: P.U.C.O.; Project administration: P.U.C.O.; Funding acquisition: R.W.U.U.

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