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Characterization of Iron Pigments Recovered From Magnetite Ore Sourced From Enugu State in Nigeria

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Abstract
The aim of this research is to synthesize and characterize iron pigments locally sourced from enugu magnetite for coating applications. Iron pigment was extacted with appropriate techniques and filtered using permanent magnets. The filtered pigment was characterized using X-ray diffraction (XRD) and X-ray Fluorescence (XRF) to determine the compounds contained therein and their various characteristics. The filtered pigment was heated at temperatures of 800°C and 900°C for 5 hours in the furnace. It was allowed to cool before XRD and XRF characterization. Based on the x-ray diffraction analysis, a single phase Fe_3O_4 was formed after a 900 ° C heating process for 2 hours. The extracted pigments was utilized in paint production and yield a positive results which concludes that the extracted iron pigment can be successfully used for coating applications.
Keywords: *Iron pigment, Characterization, Coating*

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I. Introduction

The development of inorganic pigments has been one of the major commercial pursuits of man from time memorial. One of the reasons for their popularity is their high temperature stability. In general, inorganic pigments are capable of providing excellent resistance to heat, light, weathering, solvents and chemicals, and in those respects they can offer technical advantage over most organic pigments (Sandhya, 2012, Prim *et al.*, 2011). Inorganic pigments are high refractive index materials which are capable of giving high opacity while organic pigments are of low refractive index and consequently transparent (Christie, 2001). The ability either to provide opacity or to ensure transparency provides a further contrast between inorganic and organic pigments. The colored pigments have found a wide variety of applications in various fields such as paints, varnishes, plastics artists, colours, printing inks for paper and textiles, leather decoration, building materials (cement, renderings, concrete bricks and tiles), imitation leather, floor coverings, rubber, paper, cosmetics, ceramic glazes, and enamels (Buxbaum, 2003; Haw *et al.,* 2010; Montes-Hernandez *et al.,* 2006; Kijima *et al.,* 2011). In recent times, the use of pigments is increasing as which provides no alternatives to inorganic pigments for colouring (Jansen and Letschert, 2000; Saiful *et al.,* 2018). Paint films must not be too thick; therefore, pigments with good tinting strength and hiding power combined with optimum dispersing properties are needed. The coloring properties (e.g., colour, tinting strength or lightening power and hiding power) are important in determining application efficiency and hence economics (Wu *et al*., 2008; Gupta

and Gupta 2005). Paints consist of binder, a pigment which contributes obscurities in colour, hardness and bulk to the film, and a solvent or thinner which controls the consistency (Talbert, 2007, Verges *et al.,* 2007). Frolova *et al.,* (2013) worked on natural iron oxide pigments for the construction industry from waste (sludge) hydraulic and borehole mining. From their studies they developed high-quality pigments. They studied the influence of plasticizers, dispersants on the colloidal properties of the iron oxide pigments are the most effective surfactants and optimal dosages.

Over dependency on importation of raw material has degraded the usefulness of local materials within our vicinity which can serve similar purpose. The high cost of imported raw materials for the production of emulsion paint in the paint industry, which at the end of the production affect the market price, thereby causing economy constrain. There is the need therefore to lookout for those locally raw materials such as pigments and extenders which will give such desirable qualities and properties as those of imported raw materials. Research shows that local resources within us are under-utilized and has resulted into wastage. This study therefore, will highlight the potentials of locally sourced iron oxide pigments from Amorji deposits for its uses in paint industry and also to reduce the high cost of emulsion paint formulation and production by minimizing the importation of

raw materials such as titanium dioxide and thereby disclosing a local raw material from our natural domain which could also be used for the same purpose

The aim of this study is to extract and characterize iron pigment locally sourced from Enugu Magnetite ore, characterize the extracted pigments using X-ray fluorescence and X-ray diffractometer and utilize the extracted pigment in paint production.

II. Materials And Methods

2.1 Materials

The materials used are; alkyl resins, antifoam, ammonia, Biocide calcium carbonate, magnetite stone, powder thickener, titanium dioxide, kaolin clay and styrene acrylic.

2.2 Equipment

The equipment used in this research work include: Electric stirrer, morter and pestle, X-Ray Fluorescence Spectrophotometer (skyray EDX 3600B), X-Ray Diffractometer spectrophotometer (GBC EMMA 100), kiln milling machine and Weighing scale.

2.3 Methods

2.3.1 Sample collection

The stone samples used in this study were collected from Amorji Nike, Enugu East local Government Area in Enugu State. The samples were collected at different locations and stored in sack bags. The samples were taken to project development institute (PRODA) for processing.

2.3.2 Sample Preparation

The sand lump stone of mass 240 grams was crushed into pieces and were loaded into ball milling machine and was milled for three days. The milled samples were sieved through the 120mm sieve and then soaked in 100 litres of water. The sieved solution was allowed to settle for 24 hours and successive decanting was done. The semi-dry cast was left to dry in air thereafter it was finally oven dried to cake. The dried cake was subsequently ground by pestle and mortar to fine powder which was then sieved through the 120mm sieve.

2.4 Chemical Analysis

2.4.1 X-ray Diffractometer

The Powder X-ray diffraction technique was also used for characterizing the samples using a model of PANalytical X-ray Diffractometer to determine its contents using Cu Kα (1.54056 Å) radiation. X-ray analysis was conducted on portions of the sieved, mortar-ground samples. The diffraction patterns were recorded in the range of 5° to 80° having scanning speed of 2°/minute Glancing angles ranging from 0 – 100 degrees were used. The angle of diffraction, theta (θ), the d-spacing, d, and the wavelength, λ were all measured. θ was then used to calculate for 2θ.

2.4.2 X-ray fluorescence

The samples were subjected to X-ray Fluorescence analysis using Philips PW2400 XRF Spectrometer and calibration software prepared from standard reference materials to determine the percentage composition of the compounds presents.

2.5 Formulation of paints

The processed iron pigment was used in the formulation of paint using three different binders as shown in Tables 1, 2, 3 respectively.

Table 1. Formulation of paints with extracted fayalite ore and PVA

Code	PVA (%)	Fayalite ore(%)	$CaCO_3$ (%)	Additives (%)
A1	40	0.5	58	1.5
B1	45	1	52	2.0
C1	50	1.5	47	1.5
D1	55	2	42	1.0
E1	60	2.5	32	5.5
F1	40	2.5	56.5	1.0
G1	45	2	47	6.0
H1	50	1.5	47	1.5
I1	55	1	43	1.0
J1	60	0.5	37.7	2.0

Table 2 Mix proportions of paints with extracted fayalite ore and Styrene Acrylic

Sample code	Styrene Acrylic (%)	Fayalite ore(%)	$CaCO_3$ (%)	Additives (%)
A2	40	0.5	58	1.5
B2	45	1	52	2.0
C2	50	1.5	47	1.5
D2	55	2	42	1.0
E2	60	2.5	32	5.5
F2	40	2.5	56.5	1.0

G2	45	2	47	6.0
H2	50	1.5	47	1.5
I2	55	1	43	1.0
J1	60	0.5	37.7	2.0

Table 3. Mix proportions of paints with fayalite ore and Epoxy Resin

Sample Code	Epoxy Resin (%)	Fayalite ore(%)	$CaCO_3$ (%)	Additives (%)
A3	40	0.5	58	1.5
B3	45	1	52	2.0
C3	50	1.5	47	1.5
D3	55	2	42	1.0
E3	60	2.5	32	5.5
F3	40	2.5	56.5	1.0
G3	45	2	47	6.0
H3	50	1.5	47	1.5
I3	55	1	43	1.0
J3	60	0.5	37.7	2.0

2.6 Characterization of the formulated paint mixture

The mixtures are evaluated under the following parameters: colour homogeneity or variability, viscosity, abrasion resistance and durability test.

The depth of the blue colour was visually compared using 2% phthalo blue paint weight bases and rating was given accordingly.

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2.6.1 Colour homogeneity

The depth of the colour was visually compared using 2% phthalo blue paint weight bases and rating was given accordingly.

2.6.2 Viscosity

The kinematic viscosity was evaluated through the flow time in a Ford viscosity cup, based on ASTM D-1200 (ASTM International, 2010). The apparatus has cylinder volume of 105,7 cm^3 and a n°5 orifice (5.8 mm) was used. The test was performed at 20°C and results are the average of four measurements.

2.6.3 Abrasion resistance

Paint was applied to card and allowed to dry for two days. The painted panel was kept unfolded at 30^oC with an average weight of 10 kg for 4 hours. The panel was opened to check the degree of stickiness and non-stickiness.

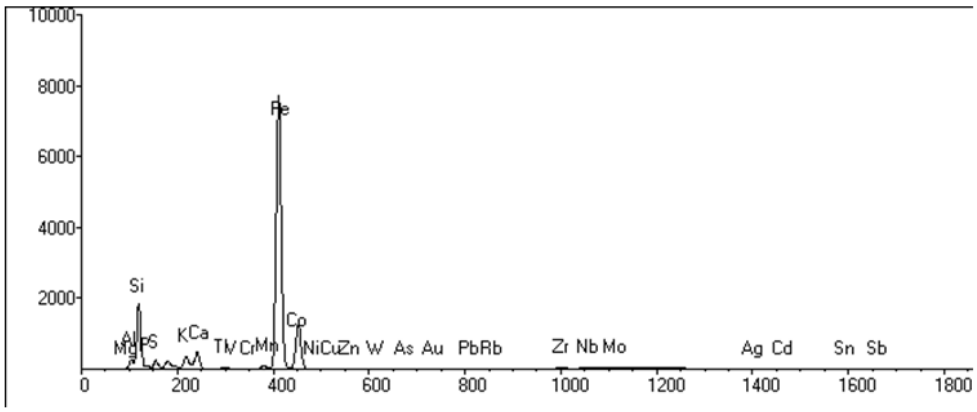
2.6.4 Durability test

It is one of the most important characteristic of coating. The resistance to separation of coating from the substrate is defined as adhesion.

III. Results And Discussion

XRD analysis of newly synthesized locally sourced iron pigments was employed to evaluate the size of ore and its crystalline nature. The XRD diffraction pattern peak of iron oxide magnetite obtained was compared with the standard [JCDPS file No.33-0664] and it shows that metal oxides are in pure α-Fe_3O_4 form. The diffraction peaks are quite identical to characteristic peaks of α- Fe_3O_4 crystals. The XRD diffraction pattern peaks of Fe_3O_4 become narrower with prolonging reaction time and narrow peaks suggested that α- Fe_3O_4 samples are highly crystalline and is testified that iron pigments crystals could be synthesized through mild extraction techniques. The XRD patterns of the samples show well-defined peaks, which clearly indicates that the samples are crystalline and the diffraction patterns of the different samples showed the same characteristic peaks belonging to standard α- Fe_3O_4 phase AS compared to Sadykov (2012) whose diffraction peak corresponding to (012) (104) (110) (113) (024) (116) and (214) respectively. The lattice parameters of the synthesized powder were determined using the least square fits. Both the diffraction peaks and lattice parameters of the samples were found to be in a good agreement with those reported for hematite in the literature (JCPDS Card no. 89-0529). Moreover, it was found that the ratio between the integrated intensities of (104) to (110) peaks ($I$104/$I$110) is greater than the unity which corresponds well to the standard XRD pattern of

hematite. It was observed that the gradual increase in the concentration of the binders led to an increasing relative intensity of the peaks indicating the improvement of crystallinity. The microstrain was estimated by analyzing the X-ray diffraction lines using Williamson and Hall method. This suggests that it has a smaller grain size and higher microstrain content. These results were found to be similar to those reported in the literature highlighting that large-sized crystals acquires small-lattice strain while small-sized crystals acquires high-lattice strain. The X-ray diffractograms showed also that the diffraction peaks became stronger and sharper as the concentration of pigments increased. This indicated improving of crystallinity and increasing of the particle size. The average crystal size was estimated by analyzing X-ray diffraction lines.



Nb	**0.0000**	**0.0000**
Mo	**0.0016**	**0.2052**
Cd	**0.0000**	**0.0000**
Sn	**0.0011**	**0.1885**
Sb	**0.0016**	**0.1886**

3.1 Effect of Changing Calcination Temperature

XRD patterns shows a series of different iron pigment samples produced at various temperatures ranging from 200 to 700˚C. The XRD patterns showed that the crystalline phase started to appear on calcination of the sample at 400˚C. When the temperature was not high enough to break down the surfactant, below 300˚C, the observed X-ray diffraction peaks were found to be slightly smooth and undefined. On the other hand, when the calcination temperature was raised between 380^{o}C to 400˚C, the surfactant breaks down and the XRD peaks appeared as broadened peaks. The presence of these broad peaks indicated the nano-size crystallite size of the formed product at this temperature. By raising calcination temperature, the peaks corresponding to α- Fe_3O_4 phase became predominant. When the temperature reached 500 ◦C, the XRD pattern of the sample agreed well with the standard α- Fe_3O_4 perfectly, indicating the end of phase transformation. Further calcination of the pigments improved the crystallinity of the products but did not cause any changes in phase composition.

3.2 Assessment of Samples as Pigments.

Evaluation of some samples as pigments was carried out according to the ASTM standard methods (2008) for evaluation of pigments. It was found that the specific gravity values of the samples were in the range between 4.89 and 5.36 which are slightly similar to the values () reported by Fouda *et al.*, (2012). These values are considered moderate values of specific gravity and make the prepared α- Fe_3O_4 particles suitable for application as pigments since high specific gravity values lead to settling of pigments in preparation of paint formulations. The calculated oil absorption values of the samples were found to be low. This leads to a reduction in the paint costs due to the small amount of oil needed to convert the prepared pigments to their corresponding paints.

3.3 Tinting Strength and Abrasion Resistance

The prepared samples showed high degrees of tinting. It was found also that the tinting strength of the synthesized pigments, which is defined as the ability of a pigment to influence the color of a dispersion containing other pigments, was improved as the particle size decreased.

The paint film formed using 0.1M of the iron salt showed the highest tinting power followed by those prepared using 0.2M and 0.4M of the iron salt, respectively. This is assigned to that the scattering efficiency of the film increased as the particle size decreased. The samples showed also a high level of hiding power. Therefore they

are capable of producing finished films whose opacity using a low concentration of the pigment is equivalent to that normally observed using higher concentration when using a coarser material which is in accordance to literature reported by Chaira *et al.,* (2019). Similarly, the hiding power was enhanced as the particle size decreased. This is related to the increased probability that light entering the applied film will be reflected away from the substrate, hence effectively hiding it from view.

The prepared pigments are all distinct for their excellent bleed resistance against various solvents such as water, ethanol, and tetrahydrofuran. Moreover, they revealed excellent resistance toward light and heat. This can be ascribed to the ability of these pigments, due to their small- and narrow-size distribution, to be well packed within the coating film surface. This property resulted in the formation of uniform surface finish. The surface uniformity in combination with the high scattering power associated with small particle size resulted in a high degree of gloss that is a desirable outcome for many applications. The small particle size also improved the weathering characteristics of coatings since large particles or agglomerates can be more easily dislodged from the coating, resulting in that the film surface rapidly loses its gloss. Overall, the good physical and chemical properties of the prepared samples showed that these compounds can be used satisfactorily as suitable pigments for coating applications.

3.4 XRF Characterization of the Composite Bodies

The results show that the samples contain 45.26% of titanium oxide by mass followed by 35.19% of Ferric oxide by mass and 2.45% silica. The amount of Alumina is minute (0.5%). All other minerals present are in such negligible proportion that their presence would not constitute threats to the efficiency of the formulated pigments as refractory materials as shown below:

Table 4: Elemental and oxide composition of Composite Body using X-ray Fluorescence

Element	Element in oxide form	% composition
Ti	TiO_2	45.26
Fe	Fe_2O_3	35.19
Al	Al_2O_3	7.65
Na	Na_2O	0.054
K	K_2O	0.049
Ca	CaO	0.068
Si	SiO_2	2.45

IV. Conclusion

Magnetite (Fe_3O_4) pigments were successfully formulated and synthesized using varying concentrations of iron sulfate. The prepared samples demonstrated good pigments properties showing that these compounds can be used satisfactorily for coating applications. The Fe_3O_4 sample synthesized using 0.1M of the ferric salt showed the best pigment properties. This can be ascribed to its higher scattering, reflection efficiency, and well-packing at them film surface which is related to its small particle size; it displayed the highest tinting and hiding powers followed by the samples prepared using 0.2 and 0.4M of the salt, respectively.

COMPETING INTERESTS DISCLAIMER:
Authors have declared that no competing interests exist. The raw materials used for this research are predominantly raw materials in our environment. There is absolutely no conflict of interest as this research is aimed for the advancement of knowledge. Also, the research was funded by personal efforts of the authors.

DATA AVAILABILITY STATEMENT
All materials and data are available

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