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Characterization of iron ore and scale for synthesizing vinyl paint

Mohammed Tayeb ABEDGHARS[a*], Mokhtar GHERS[b], Salah BOUHOUCHE[a] and Belgacem BEZZINA[a]

[a]*Research Center in Industrial Technologies CRTI: P.O. Box 64, Cheraga 16014 Algiers, Algeria*
[b]*Department of Physics, Badji Mokhtar University, Annaba, Algeria*

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ABSTRACT

Two materials are studied to synthesize a vinyl painting. Iron ore is an iron pigment with an oolithic structure containing phosphorus. The second material is a steel by-product. The raw materials proprieties were studied by chemical, particle size, thermal, XRD and spectrophotometric analysis. The iron contents of the pigment and scale are respectively 53.18% and 73.83%. The grindability of scale is better than that of the pigment. The particle volume distribution is 0.7 to 32 µm for scale and 0.6 to 40 µm for pigment. TGA and DTA tests show that the pigment loses weight with phase dissolution by consuming energy and the scale gains weight with the formation of a new phase when the temperature increases. The SEM of the scale showed a homogeneous structure of iron oxide grains ranging from 1 to 10 µm. XRD analysis shows that the iron in the pigment is in the form of (Fe_2O_3) and FeO (OH)) and very little (Fe_2SiO_4). The iron in the scale is in the form of (FeO, Fe_2O_3 and Fe_3O_4). Spectrophotometric tests show that the two materials have no absorption and their reflection is maximum (100%) in the visible range.

1. Introduction

The red pigments are iron ore deposits. Their operation in the field of paints is dictated by certain technical conditions.

– Scale counts among the fatal productions of secondary materials generated by the steel industry, we find this by-product in different mills. Chen and Yuen (2005) and Umadevi et al. (2013) showed that the scale is formed by oxidation at high temperature during the cooling of the products in continuous cast steel and during the reheating treatment and hot forming.

Pigments are chemical compounds presenting absorption only at certain wavelengths of the visible spectrum. It is this property which makes their color.

– The pigments are mostly in the form of fine dry particles and are almost soluble in all solvents. The first ones used the properties of these compounds, 30.000 years ago in prehistoric caves. Today, artists use pigments such as ocher, yellow and red clay or iron oxide.

There are different types of pigments:

– Nature: Plants, soil, animals, flowers, plants, trees

– Chemical: Obtained by mixing or fusion of various materials

The use of pigments has continued to increase and is widely used in the following applications: toner, paint, coating, ink, plastic, rubber, textile, cosmetic, food and pharmaceutical.

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* *Corresponding author: Mohammed Tayeb ABEDGHARS, abedghars@yahoo.fr*

Morvan (2002) showed that the analysis of the particle size of the pigments could influence the properties of final products such as: optical properties, color, shade, opacity, viscosity, shine, durability and sedimentation.

Hematite has a dark red color and a granulometric distribution which are sufficient properties to be used as a chromophore for encapsulation in pigment production and this is demonstrated by Della et al. (2007). Pigments production is still carried out according to the classical mechanical methods. The lands are extracted first manually from careers then cleaned, dried and finely ground. Their purity and fineness of their grinding determine the later possibilities of use as was described by Philip (2010) in Histoire Vivante des Couleurs.

Husband et al. (2006) wrote that pigments are generally powders. The fineness and particle shape can change the color of ground pigment considerably by acting on the proportion of light rays reflected from the surface of grains compared to those crossing.

Particle size effects on:

- *The optical properties*, the size of pigment particles can affect the final aspect of the coated surface, e.g., a painting can be glossy, matt or satiny, depending on particle size. This effect is related to phenomena of diffusion, reflection and refraction of light.

- *The final performance of the coating*, the ease of a pigment applying or paint is determined by the particle size distribution of the coloring elements. The particle size determines the coloring strength or color depth directly.

- *Rheological properties*, e.g., work done by Husband et al. (2006) and Brinke et al. (2007) on the influence of the shape of the pigment particles on the tensile properties in the plane of the kaolin-based coating layers, have shown that the intrinsic viscosity (μ) of particles having the same volume is directly related to their aspect ratio. The viscosity is increased by the presence of finer particles, which allows limiting the sedimentation and flocculation. These two phenomena can notably change the color intensity of a formulation in a meaningful way.

Among the fatal productions of secondary materials generated by the steel industry, we find the scale of different mills. The scale is formed by oxidation at high temperature during the cooling of the products in continuous cast steel and during the heating treatment, and hot forming as illustrated by Umadevi et al. (2013).

Our objective in this preliminary study is to characterize the mixtures for synthesizing of pigment. In this part we will determine the microstructure of two components, the grindability and finally the particle size by laser granulometry. Differential Thermal Analysis (DTA), Thermal Variation of Enthalpy (DSC), X-Ray Diffraction Analysis and Visible Light Spectrophotometer are performed.

2. Materials and Methods

Chemical analysis of the material was carried out by X-Ray Fluorescence spectrometry (XFR). The grinding time depends on the initial state of raw materials. The Determination of the optimal grinding time is required for each component. Control of the grain size is carried out after each grinding session to the mesh 32 microns. The particle size distribution of the two samples is investigated using a laser micro-granulometer - Mastersizer 2000 / Malvern. It works with the sample preparer Hydro MU.

In the study of the contribution of grain size analysis by laser granulometry in the physical characterization of calcareous fillers, Michel and Courard (1986) showed that this laser scattering analysis is an indirect measurement technique commonly used to determine particle size distribution of powdered materials. The principle of the method is as follows.

The optical unit of the particle size analyzer records the diffusion (diffraction, reflection, refraction) of monochromatic radiation by a suspension of particles. Diffusion images are calculated from a diffusion model, according to theoretical particle size distributions. The calculated images and the measured image are adjusted by the least squares method

A device of type TA Instruments SDT.Q.600 is used for the study of the Differential Thermal Analysis (DTA) and the Thermal Variation of the Enthalpy (DSC) of the raw materials.

An amount of scale is gradually added to the natural pigment in the range of (5, 10, 15, 20, 25% and 35%) to optimize the synthetic mixture. According to the experimental procedures cited by Thirion (2016), heating is ensured at 50°C per minute until a temperature of 1100°C in an alumina crucible. The Scanning Electron Microscope (SEM) used in the framework of mineralogical quantization is a microscope type of Quanta 250 with an Analyzer Ametek. The crystallographic structure of our materials was studied using an X-Ray Diffractometer (XRD) – a Rigaku equipped with a copper anticathode tube. Optical transmission measurements at room temperature on our samples (absorption and reflection) were carried out by a UV-Visible-IR spectrophotometer, Brand Agilent type Carry 5000.

3. Results and Discussion

3.1. Chemical Analysis

Both materials consist mainly of iron oxide. Like all minerals, the pigment contains oxides from the dross. The analysis is given by table 1.

Hematite and magnetite in the ore are calculated from the contents of total iron and ferrous iron. By a simplified calculation method, the pigment contains 72.48% of hematite and 3.44% of magnetite.

$$\text{Total Hematite} = (Fe^{T}\text{-}Fe^{+2}) \times 1{,}43 \quad (1)$$

$$\text{Magnetite} = FeO \times \left(\frac{232}{72}\right) \quad (2)$$

$$\text{Hematite combined} = FeO + \left(\frac{232}{72}\right) - FeO \quad (3)$$

Hematite free = Total Hematite – Hematite combined

3.2. Grinding

The choice of particles sizes has consequences for dispersions stabilization modes.

Indeed, the particles of micrometric size are attracted by Van der Waals strength of high intensity and scale comparable to their sizes.

According to Cabane (2003), more generally, the particle shapes have a significant effect on the mechanical properties of aggregated dispersions.

The sampling process conditions and grinding are the same for the two materials, namely:

- Raw materials crushed to less than 160 microns
- Drying at 200°C
- Test taking equal to 10 g ± 0.3
- Screening time: 3 minutes (suction) through a mesh sieve of 32 microns.
- Depression (suction) of 1500 Pascal

We retain the initial results that the scale has a better yield of grindability than the pigment. Grinding of the iron pigment is carried out at 3, 5, 8, 12 and 15 minutes. The results are shown in figure 1. According to the first indications, the scale is not hard and it is easy to grind. For this reason, grinding of the scale LRB is carried out at 1, 2, 3, 4 and 5 minutes. The results are shown in figure 2. We conclude that the optimum time for the grinding of pigment and scale are respectively 5 and 01 minutes.

3.3. Particle Size

As noted above, the particle size affects the optical properties, the final performance of the coating and the rheological properties. The viscosity is increased by the presence of finer particles, which allows limiting the sedimentation and flocculation. These two phenomena can notably change the color intensity of a formulation significantly. According Bohic (2007), the particle size is generally between 0.1 and 50 microns. D_{50} is between 1 and 10 microns. Particle size analysis measured by a laser granulometer (Hydro 2000MU) gave us a volume distribution with particle size between 0.7 and 32 microns for scale and between 0.6 and 40 microns for the pigment. Thus, as can be seen, the average diameters (D_{50}) are 6.31 microns for the scale and 7.97 microns for the pigment milled respectively to 01 and 05 minutes. Their specific areas

Table1- Chemical analysis of iron pigment and calamine.

%	FeT	FeO	CaO	SiO_2	MgO	Al_2O_3	MnO	P_2O_5	ZnO	Fe_2O_3	Fe_3O_4
Pigment	53.18	1.07	0.76	4.23	0.36	2.13	0.64	1.63	0.75	72.48	3.44
Scale	73.83	56.9	0.42	0.14	0.37						

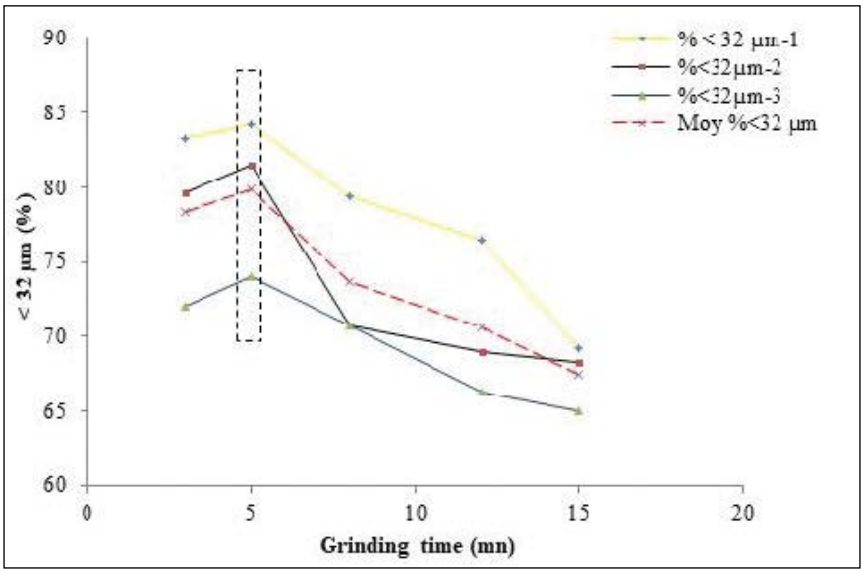

Figure 1- Grindability iron pigment.

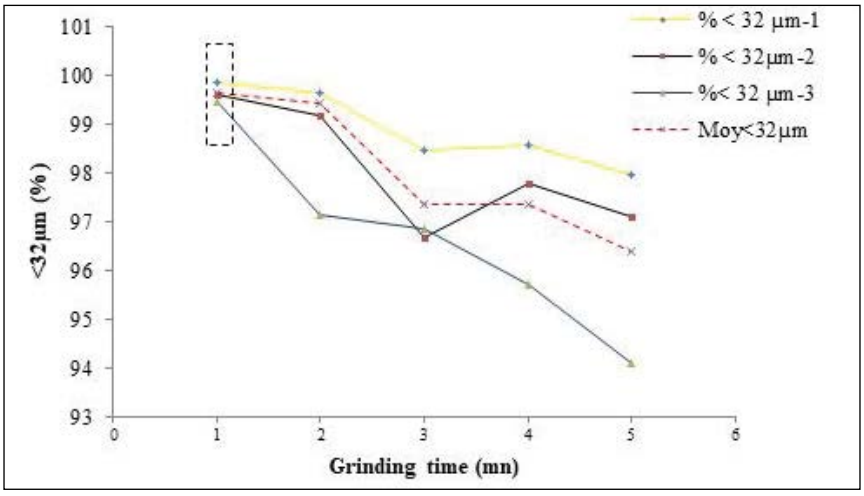

Figure 2- Grindability of the LRB scale.

are 1.6 and 1.5 m^2/g. The grinding is carried out with a laboratory disc mill and it is mostly sufficient for the development of paint with outstanding surface characteristics.

3.4. Simultaneous Thermal Analysis

Simultaneous Thermal Analysis for scale shows an increase in weight (3.602%) between 400 and 1000°C, which is attributed to the oxidation reaction of iron oxides (new phase formation) according to the reaction.

$$3FeO + \frac{1}{2} O_2 = Fe_3O_4 \quad (4)$$

Between 850°C and 1150°C, the system remains stable, according to the reaction.

$$2Fe_3O_4 + \frac{1}{2} O_2 = 3Fe_2O_3 \quad (5)$$

This oxidation is accompanied by weight gain and heat generation (exothermic reaction) respectively of 3.602% and 1.128 W/g (Figure 3).

For iron pigment, this analysis shows a mass loss which is attributed to the evaporation of water formation of iron hydroxides (goethite FeOOH dissolution). This decrease is 11.05% between temperatures 289°C and 349°C. This dissolution is accompanied by absorption of heat (endothermic)

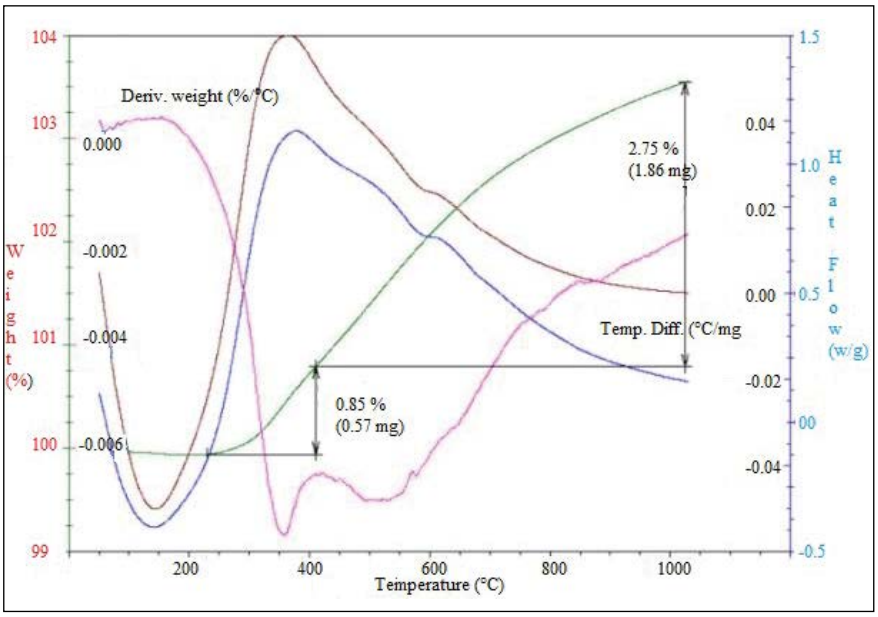

Figure 3- Simultaneous thermal analysis of the scale.

equal to 1.926 W/g as shown in figure 4. Kinetically, according Goss (1987), the transformation of αFeOOH (goethite) to αFe_2O_3 (hematite) during the heating higher than 255°C is evidenced by a loss of weight during the test. The dehydration mechanism involves the elimination of H_2O. Hematite begins to grow starting only from a weight loss of 3.97% when we have the synthetic goethite. The transformation of the product (dehydration) is done starting from the surface towards the inside of the grains by the formation of pores the release of water vapor.

In figure 4, we also noticed that there's a first small endothermic peak corresponding to the fact of a quantity of heat required to evaporate moisture from the pigment at a temperature lower than 200°C. Thermal analysis mixtures synthesized with the addition of (5, 10, 15, 20, 25 and 35%) of scale in the natural iron pigment showed a weight loss fall. This

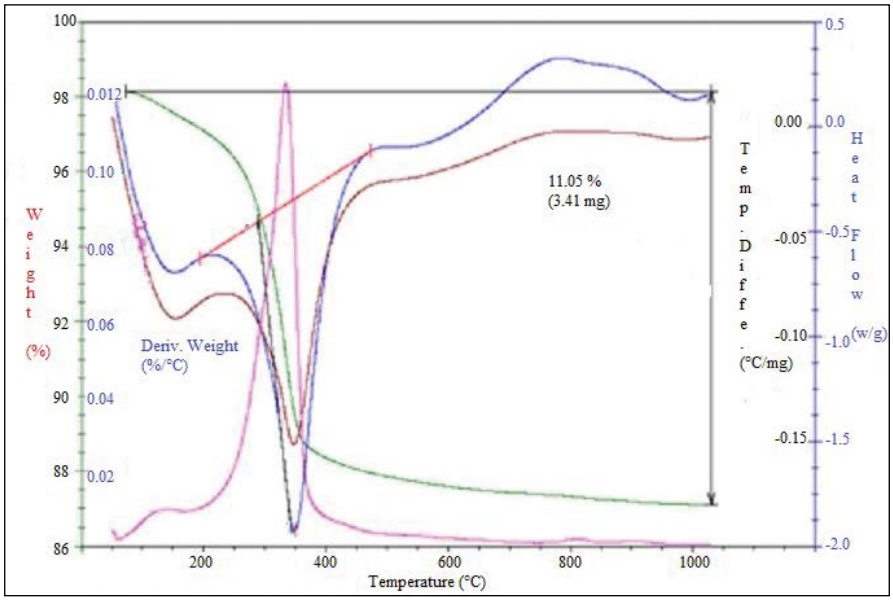

Figure 4- Simultaneous thermal analysis of iron pigment.

phenomenon can be explained by the decrease in the amount of iron pigment in favor of the scale. Loss of weight is proportional to the rate of addition of mill scale, when the injection rate of scale increases, the weight loss decreases. The heat flux takes an increasing polynomial pace, the energy expended for the dissolution of iron hydroxides (goethite dissociation) in the iron pigment is offset by the energy released by the scale (oxidation reactions).

3.5. Scanning Electron Microscope (SEM)

The observation scale milled during 5 min on the SEM showed a homogeneous structure composed of iron oxide grains with sizes and forms ranging from 1 and 10 micrometers (Figure 5a). Chemical analysis on all ranging in observation in the range given by EDS shows the dominant existence of iron with very little of manganese and some traces of silicon and aluminum. Iron is the main component of the steel from which the scale was formed (oxidized iron), manganese is in the chemical composition of the steel. Traces of Si and Al can originate either from the chemical composition of the iron-carbon alloy (steel) or from the powder of the continuous casting.

Exploration picture by scanning electron microscope of red iron pigment shows a grain aggregate rounded formed at least of iron oxide and gangue (Figure 5b). The analysis by EDS shows a predominance of iron with a rather important gangue containing the four predominant oxides in the case of iron ore deposits. Chemical elements forming these four oxides are silicon, calcium, aluminum and magnesium.

3.6. X-ray Diffraction Analysis (XRD)

The X-ray diffractogram (Figure 6) shows that the crystalline phases are mixtures of phases of wustite, magnetite and hematite for calamine. Wustite ($Fe_{0.94}O$) is of cubic structure, magnetite (Fe_3O_4) is orthorhombic and hematite (Fe_2O_3) is of trigonal structure. As for the pigment, the X-Ray Diffractogram (Figure 7) shows that the crystalline phases are also mixtures of 6 phases. These phases are goethite, hematite, fayalite, silica, phosphorus pentoxide, and hausmannite.

3.7. Spectrophotometer Analysis

The analysis of the absorption of light by the materials showed weak and constant absorption in the ultraviolet and visible light domains (Figure 8). In the visible domain (380 to 780 nm), we observe an almost zero absorbance. A coloring substance is most often defined by its ability to absorb light radiation in the visible spectrum of light. The analysis of the reflectance of these materials in the visible range has shown excellent reflectance, note that the curve is on average 120% (Figure 9). We can deduce that the constituents of these materials themselves become sources of radiation that can be added to the total reflected radiation. The incident radiation is totally reflected.

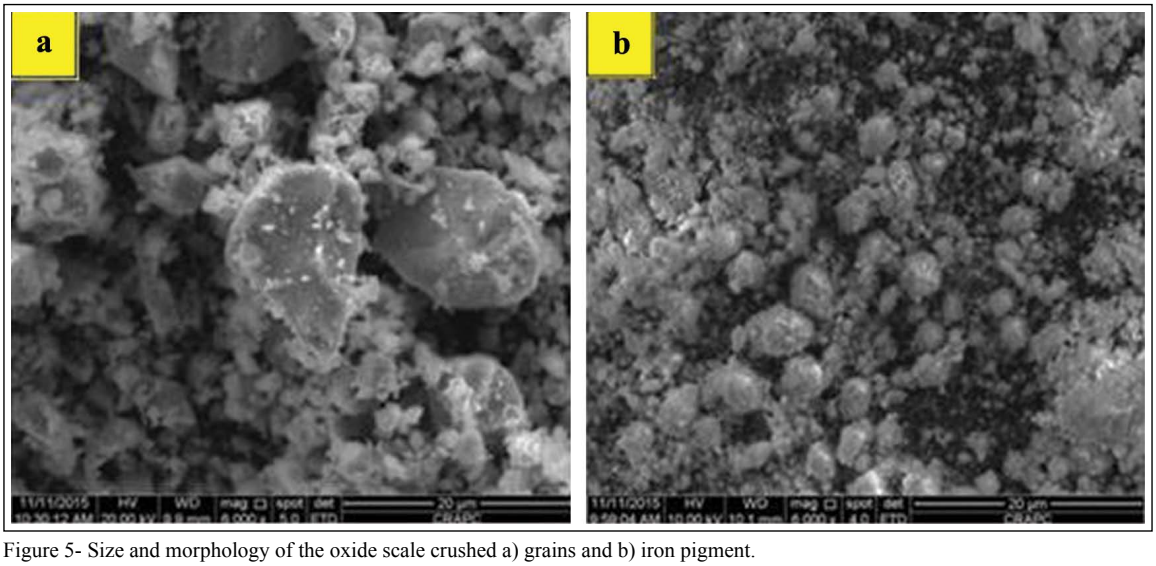

Figure 5- Size and morphology of the oxide scale crushed a) grains and b) iron pigment.

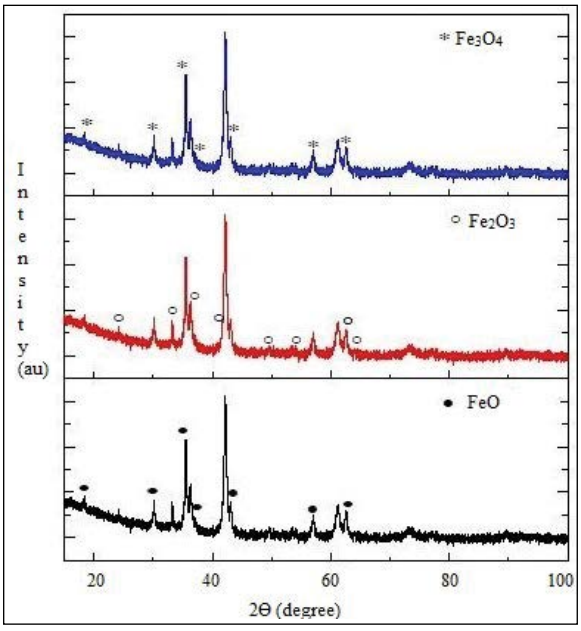

Figure 6- Calamine diffractometer (FeO-Cubic, Fe_2O_3-Orthorhombic and Fe_3O_4-trigonal).

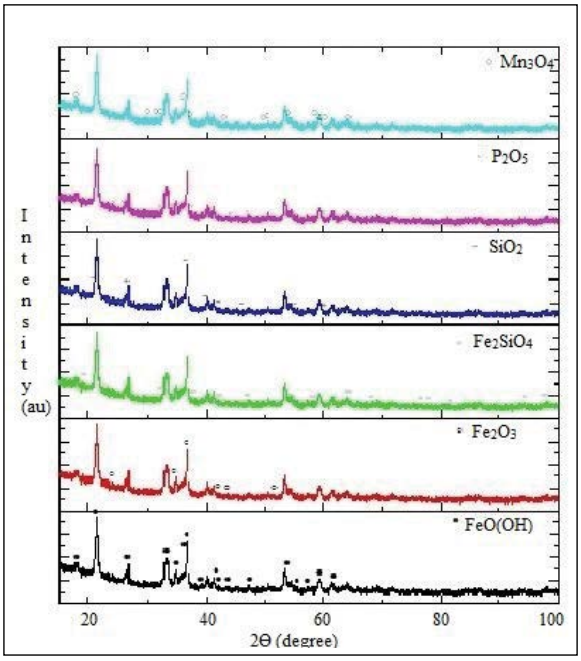

Figure 7- Iron pigment diffractometer (FeOOH, Fe_2O_3, Fe_2SiO_4, Mn_3O_4, SiO_2, P_2O_5).

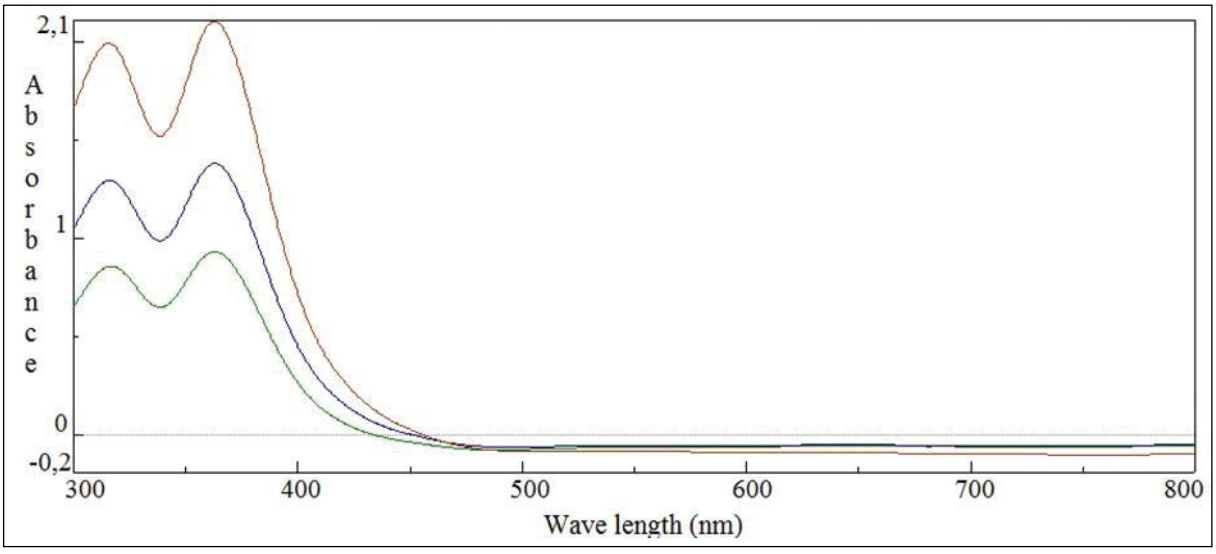

Figure 8- Absorbance of materials.

4. Conclusion

Chemical analysis shows that raw materials contain iron in the form of oxide. The scale has a uniform structure of magnetite. The pigment contains, in addition iron, a siliceous gangue. Calamine, in turn, consists of 98% iron oxides.

Preliminary grinding tests showed that the milling time of the iron pigment is more important than the scale.

The analysis of the particle sizes is carried out by the laser granulometer. It shows a density distribution of particles with a size between 0.7 and 32 µm for

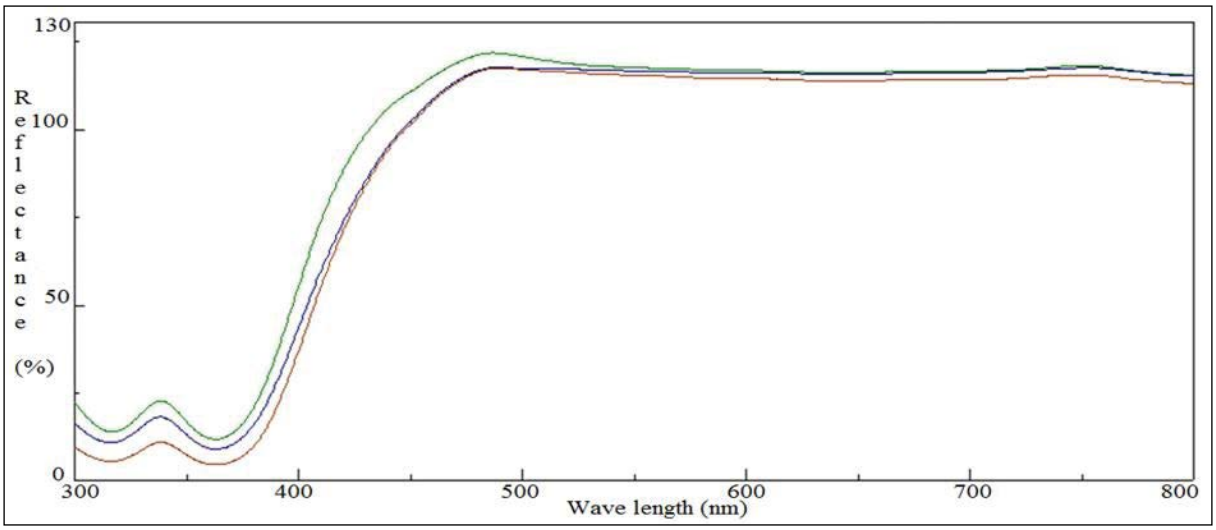

Figure 9- Reflectance of materials.

scale and between 0.6 and 40 µm for the pigment. Means that the average diameters D_{50} are 6.31 µm for the scale and 7.97 µm for the pigment milled respectively at 01 and 05 minutes. Their specific area is 1.6 and 1.5 m^2/g.

Simultaneous Thermal Analysis for calamine shows an increase in weight (3.602%) between 400 and 1000°C, which is attributed to the oxidation reaction of iron oxides (new phases formation).

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The analysis of the absorption of light by the materials showed weak and constant absorption in the ultraviolet and visible light domains.

The analysis of the reflectance of these materials in the visible range has shown excellent reflectance, note that the curve is on average.

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References

Bohic, M. 2007. Caractérisation de la surface de pigments traités par des polyesters acrylique, thèse de doctorat, école des mines de Paris.

Brinke, A. J. W., A., Bailey, L., B., Henk, Lekkerkerker, H. N. W., Maitland. G. C. 2007. Rheology modification in mixed shape colloidal dispersions. Part I: Pure components. Soft Matter 3, 1145–1162.

Cabane, B. 2003. Formulation des dispersions, Dossier techniques de l'ingénieur, J2 185, p.13.

Chen, R.Y., Yuen, W.Y.D. 2005. Examination of Oxide Scales of Hot Rolled Steel Products, ISIJ International 45(1), 52–59.

Della, V.P., Junkes, J.A., Montedo, O.R.K., Oliveira, A.P.N., Rambo, C.R., Hotza, D. 2007. Synthesis of hematite from steel scrap to produce ceramic pigments. Am Ceram Soc Bull 86 (5), 9101-9107.

Goss, C.J. 1987. The kinetics and reaction mechanism of the goethite to hematite transformation, Mineral Mag 51, 437-451

Husband, J.C. Preston, J.S. Gate, L.F. Storer, A. Creaton, P. 2006. The influence of pigment particle shape on the in-plane tensile strength properties of kaolin-based coating layers. TAPPI J 5(12), 3-8.

Michel, F., Courard, L. 1986. Apport de la granulométrie laser dans la caractérisation physique des fillers calcaires, Septième édition des Journées scientifiques du Regroupement francophone pour la recherche et la formation sur le béton, Toulouse, France 40-49.

Morvan, M. 2002. Fabrice, Elaboration, Caractérisation et développement de nouveaux grades de pigments aluminium, Thèse de doctorat en physico-chimie de la matière condensée, Université de Bordeaux I - France, Ecole doctorale des Sciences Chimiques, p-47, janvier.

Philip, B. 2010. Histoire vivante des couleurs, 5000 ans de peinture racontée par les pigments. Paris, Hazan.

Thirion, V.M. 2016. Spectrométrie de fluorescence X. Circulation et provenance des matériaux dans les sociétés anciennes, Collection Sciences Archéologiques, 9782813001634.

Umadevi, T., Brahmacharyulu, A., Karthik, P., Mahapatra, P.C., Prabhu, M., Ranjan, M. 2013. Recycling of steel plant mill scale via iron ore sintering plant. Journal Ironmaking and Steelmaking, Processes, Products and Applications 39(3), 222-227.