CHARACTERISTICS OF CALAMINE AND NATURAL PIGMENT FOR ANTI-RUST PAINTINGS

M. T. AbedGhars[1]; M. Ghers[2]; S. Bouhouche[1]; B. Bezzina[1]

1 . Research Center in Industrial Technologies CRTI: P.O. Box 64, Cheraga 16014 Algiers - Algeria.
2. Department of Physics, Badji Mokhtar University ,Annaba -Algeria

Mail : m.abedghars@crti.dz ou abedghars@yahoo.fr

Abstract.

This work has a double objective. On the one hand, the valorization of natural raw materials, in particular, the oolithic iron ores which do not find their use in iron and steel because of their high phosphorus content and on the other hand the recycling of steel by-products.. The ultimate goal is to synthesize an anti-corrosion paint.
In this first part, we will study the characterization of these two components by their chemical analysis, their grinding (fineness) and their thermal analysis (TGA, DSC).
Chemical analysis showed that the pigment contains 53.18% of total iron and gangue dominated by silica. Calamine in turn contains 73.83% of iron in the form of iron oxides (FeO, Fe_3O_4 and Fe_2O_3).
Iron pigment is composed mainly of hematite with a little of goethite.
Grinding tests showed that the scale is much more suitable for grinding than pigment. The granulometric analysis measured by a laser granulometer (Hydro 2000MU) gave us a volume distribution of the particles with a size between 0.7 and 32 microns for scale and between 0.6 and 40 microns for the pigment and Their specific areas are 1.6 and 1.5 m^2 / g..
Thermogravimetric analysis (TGA) and the thermal variation of flow (DSC) showed that the iron pigment loses weight with phase dissolution by consuming energy when the temperature increases. Scale gains weight by the formation of new phase with heat.
Exploration picture by scanning electron microscope of red iron pigment shows a grain aggregate formed rounded over at least iron oxide and gangue. The analysis by EDS shows a predominance of iron with a relatively large matrix containing the four predominant oxides in the case of iron ore deposits. Chemical elements forming these four oxides are silicon, calcium, aluminum and magnesium.
The observation scale milled for 5 min SEM showed a homogeneous structure composed of sizes of iron oxide grains and shapes ranging from 1 µm to 10 µm.

Keywords: Pigment iron, scale (calamine), iron oxides, grinding, , Simultaneous thermal analysis.

Introduction

The red pigments are iron ore deposits. Their operation in the field of paints is dictated by certain technical conditions.
Calamine counts among the fatal productions of secondary materials generated by the steel industry, we find this by-product in different mills. 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 [1]
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, and food, pharmaceutical.
Analysis of the particle size of the pigments can 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 [2]. Pigments production is still carried out according to 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 [3]. Pigments are generally powders. The fineness and particle shape can change considerably the color of ground pigment by acting on the proportion of light rays reflected from the surface of grains compared to those crossing. [3]

Particle size has an effect on:

the optical properties: The size of pigment particles can affect the final aspect of the coated surface. For example, 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 directly the coloring strength or color depth.

• 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 in a meaningful way [4].

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 [5].

1. Objectives

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), thermogravimetric (TGA) and the thermal variation of flow (DSC) were carried out.

2. Used Materials

Chemical analysis of the material was carried out by fluorescence spectrometry X rays. The grinding time depends on the initial state of raw materials. The Determination of the optimal grinding time is required for each component. To do this, a 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 by means of a laser micro- granulometer Mastersizer 2000 / Malvern. It works with the sample preparer Hydro MU.

A device of type TA Instruments SDT.Q.600 is used to study the thermal analysis of 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. Heating is ensured at 50 ° C per minute until a temperature of 1100 ° C in an alumina crucible.

The scanning electron microscope used in the framework of mineralogical quantization is a microscope type of Quanta 250 with an analyzer Ametek.

3. Results and discussion

3.1. Chemical analysis

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

	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						

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.

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

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

$$Hématite\ combined = FeO + \left(\frac{232}{72}\right) - FeO \qquad (3)$$

Hématite free= Total Hematite – Hématite combined

3.2. Grinding

The choice of particles sizes has consequences for dispersions stabilization modes.
Indeed, the particles of micrometric and micrometric size are attracted by Van der Waals strength of high intensity and scale comparable to their sizes.
More generally, the particle shapes have a significant effect on the mechanical properties of aggregated dispersions. [7]
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: 03 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, 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.

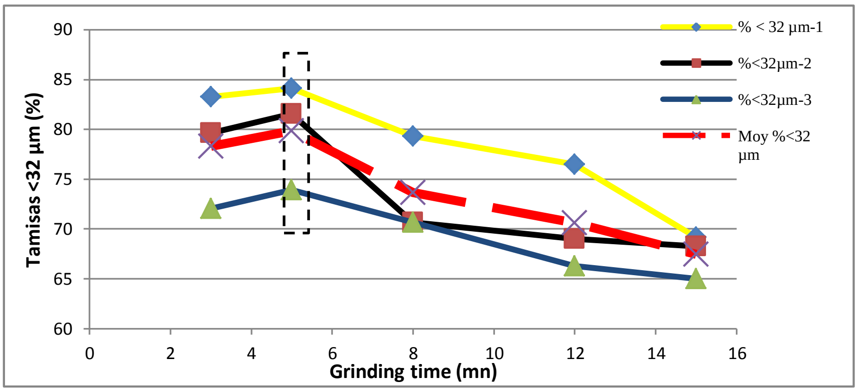

Figure 1. Grindability iron pigment

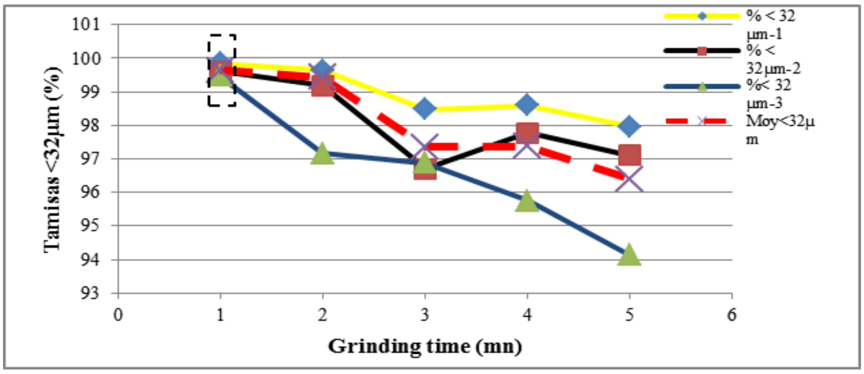

Figure 2. Grindability of the LRB scale.

3.3. Particle size

As noted above, the particle size has an effect on 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 [4,8]. The particle size is generally between 0.1 and 50 microns. D_{50} is between 1 and 10 microns [9].

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 (Figure 3).

Thus, as can be seen, the average diameters (D50) are 6.31 microns for the scale and 7.97 microns for the pigment milled respectively to 01 and 05 minutes. Their specific areas are 1.6 and 1.5 m^2/g.

The grinding is carried out with a laboratory disc mill, it is largely sufficient for the development of paint with very good surface characteristics.

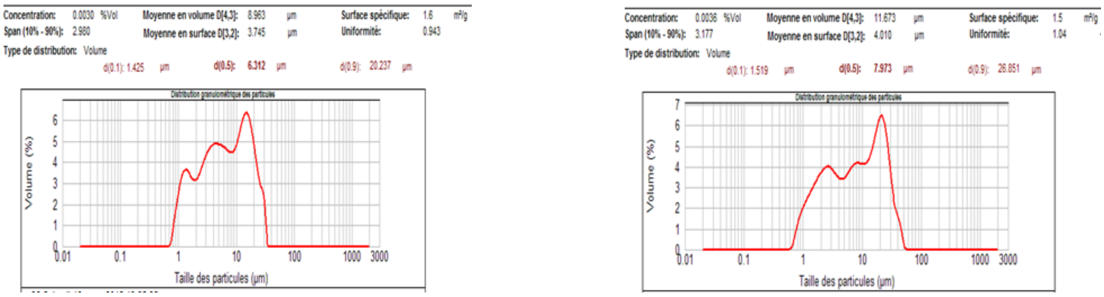

Figure 3. Particle size curves of the scale and the pigment given by the Hydro 2000.MU

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.

$$3FeO + \frac{1}{2}O2 = Fe3O4 \qquad (4)$$

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

$$2Fe3O4 + \frac{1}{2}O2 = 3Fe2O3 \qquad (5)$$

This oxidation is accompanied by weight gain and heat generation (exothermic reaction) respectively of 3.602% and 1.128 W/g, it is shown by Figure 4.

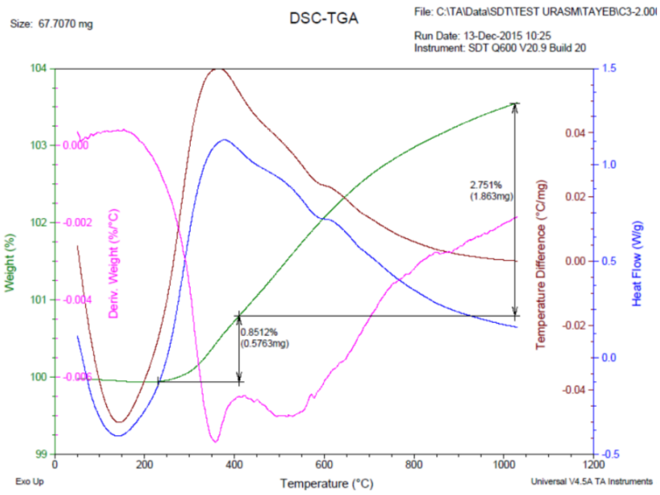

Figure 4. Simultaneous thermal analysis of the scale

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) equal to 1.926 W/g as shown in Figure 5. 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 ATG test [10]. 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.

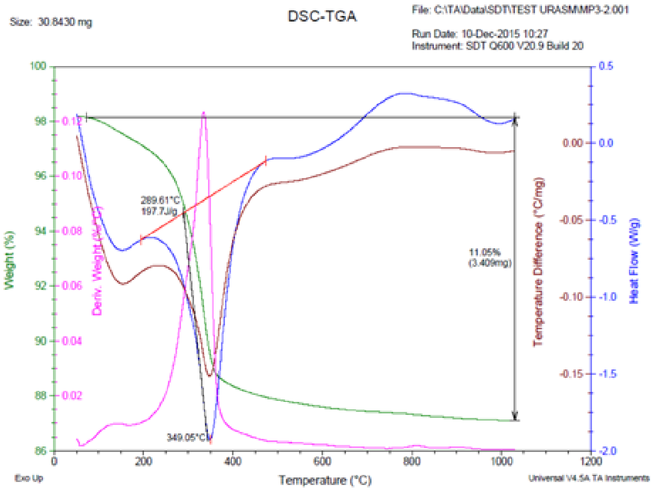

Figure 5. Simultaneous Thermal Analysis iron pigment

In this figure, we also notice 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 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 (Figure 6). This can be explained by the decrease in the amount of pigment in favor of the scale. This reduction in weight follows a linear trend of equation:

$$y = 14.799\,x - 11.905 \qquad (6)$$

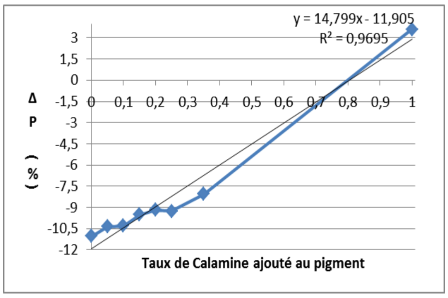

Figure 6. Mass loss during the thermogravimetric analysis of the mixture acco

With a correlation coefficient equal to 0.969. 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 (figure 7), 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). This rate follows an equation polynomial trend of the second degree.

$$y = 3.7395\ x^2 - 0.7323\ x - 1.8668 \qquad (7)$$

With a correlation coefficient equal to 0.977.

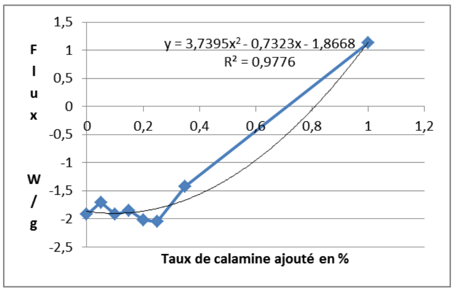

Figure 7. Variation of the heat flow in the differential thermal analysis

3.5. Scanning electron microscope

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 8A).

Chemical analysis on all ranging in observation in 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 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 8B). 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.

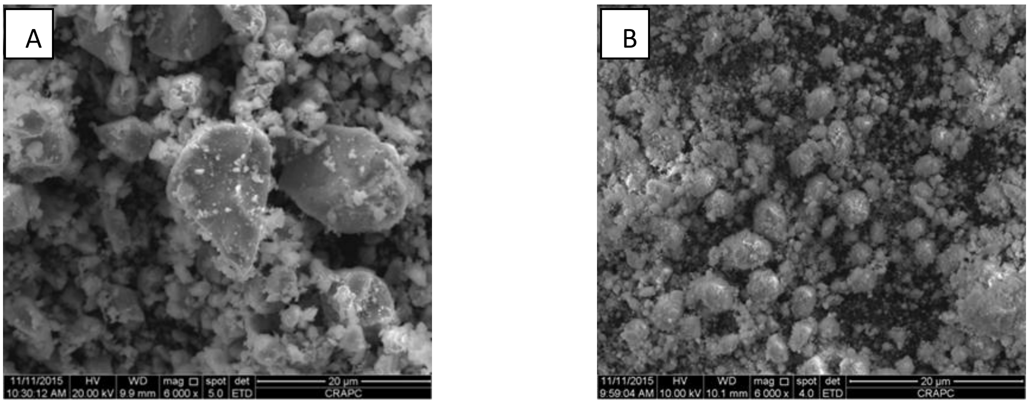

Figure 8. Size and morphology of the oxide scale crushed grains (A) and iron pigment (B). (X

4. Conclusion

Chemical analysis shows that the raw materials contain a lot of iron in the form of oxide. Microscopic observation in reflected light shows that the iron oxides in the pigment are in oolithique form surrounded by gangue. The scale has a structure mainly uniform of magnetite beach. 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. Indeed, the time required for grinding 10 g of the pigment to the mesh lower than 32 microns is 5 times larger 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 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 m2/g.

The magnetization Tests showed that the scale is ferrimagnetic and iron pigment is antiferromagnetic. The mill scale has a higher magnetic susceptibility of the fact that it contains magnetite. Iron pigment is composed mainly of hematite with very little goethite is classified as antiferromagnetic.

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).

For iron pigment, this analysis shows a mass loss which is attributed to the evaporation of water formation of iron hydroxides (goethite FeOOH dissolution).

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Exploration picture by scanning electron microscope of red iron pigment shows a grain aggregate rounded formed at least iron oxide and gangue.

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