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# Characterization of Black Pigment Based on Iron Oxide from Mill Scale by Simple Burning Method

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## Info Articles

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## Abstract

Pigment is material that we use in many application such as paint, ink, material protection, and much more. There are two groups of pigment, organics pigment (dyes) that are derived from animals or plants and inorganic pigment that are derived from mineral compound. Black pigment based on iron oxide is one of inorganic pigment groups. We got iron ion (ferrous Fe2+ and ferrite Fe3+) from mill scale that we know as steel industrial's waste. Mill scale was dried under sunlight then milled to get powder form. Mill scale powders calcined on 800°C temperature in furnace and kept 2 hours so we had more homogeny and dry material with dark red-purple color. Composition of mixture solution varied from 5%, 10%, 15% and 20% weight of powder. The next process, powders was added into mixture solution of sodium hydroxide (NaOH) and ammonia hydroxide ($NH_4OH$) so we got sludge material. Sludge burned in furnace at temperature 900°C and with 3 hours holding time so we got black material that we expect as black pigment. Black pigment samples were analyzed using XRD showed that black pigment form is hematite ($Fe_2O_3$) and the optimum color in CIELab color system are L=18.94, a=5.81, b=7.15. Commonly black pigment form is magnetite ($Fe_3O_4$), but we got it dominant in hematite form.



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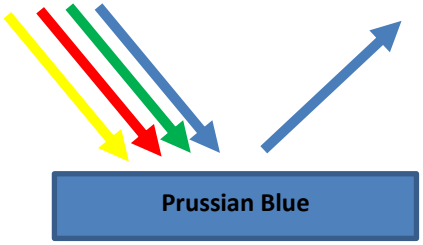
## INTRODUCTION

The word pigment means a substance consisting of small particles that is practically insoluble in the applied medium and is used on account of its coloring, protective, or magnetic properties.[1] There are two group of pigment, the first is organic pigment (usually we call it with "dyes") and second is inorganic pigment. The dyes pigment commonly are derived from plants and animal products like rose madder, bone black, etc. While for inorganic pigments are derived from mineral compound especially the oxide group like iron oxides, titanium dioxide, chromium oxide, etc. Inorganic pigments are currently used in many application, especially in those of paints, inks, plastics, rubbers, ceramics, enamels, and glasses. These pigments may impart coloristic properties, and protect the coating from the effects of visible including invisible like ultraviolet and infrared light.[2] According to import commodity from ministry of industry, Indonesia had imported pigments with the values about 443.331.000 US$ (2012), 418.599.900 US$ (2013), 386.674.800 US$ (2014), and 327.843.400 US$ (2015).[3] Black pigments are commonly create from mixture or pure oxides of metals, and the most important oxides in this class of dyes are: cobalt, iron, chromium, and nickel.[4] Black pigments are used in the ceramic industry approximately 25% of the total consumption, and there are two main crystalline structures: hematite and spinel.[5][6][7]

Steel mills and steel structure companies produced waste in hot rolling or cold rolling process is called mill scale and very attractive because industrial waste due to its richness in iron (about = 72 % Fe).[8] Commonly the component of mill scale are: 68% of Fe total, 10.14% of FeO, 85.7% of $Fe_2O_3$ and 1% of $SiO_2$.[9] Mill scale can be processed and used in many applications like iron fortification, chemicals, brazing, soft magnetic products, metallurgy, surface coating, welding, etc. [10]

Color is the most important properties of pigment in common application, because we know that pigment mainly use for coloring, painting art, religious rituals, etc. Color is physical phenomena that appear because the material reflect and absorb certain wavelength of light. We know the white light consists of several visible light that mixture into one. Color appear from the wavelength has reflected by the material. For example, the blue color material will absorb all wavelength of visible light except blue light that will be reflected see the illustration figure 1. White color appear because




all visible light reflect, on black color happen when nothing light reflect by material.

**Figure 1**.. Blue Color

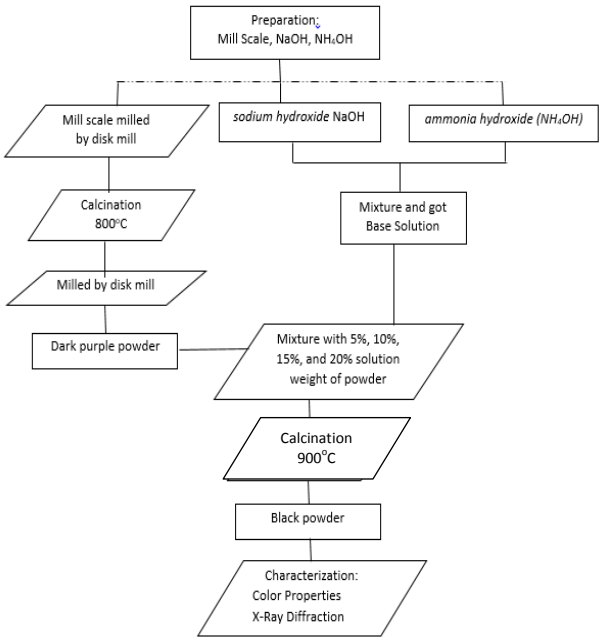
Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for production of various industrially useful materials and practice in 65 countries. There three group of combustion method, conventional SHS of nano-scale materials with process are in solid state (condensed phase combustion). Solution-combustion synthesis (SCS) of Nano sized powders initial reaction medium is aqueous solution. Synthesis of nanoparticles in flame, gas-phase combustion. [11]

## METHODS

The research begin with prepared materials and laboratory equipment. The materials are mill scale from PT Krakatau Steel, sodium hydroxide (NaOH) and ammonia hydroxide ($NH_4OH$). Black pigment synthesis with simple burning method (combustion). See flowchart of the research in Figure 2.

Mill scale got from industrial waste dried under sunlight and calcined 800°C holding time 2 hours to remove impurity inside it. Mill scale that has been calcined then milled by disk mill

to get dark purple powder (MS) for 5 minutes. Base solution made by mixture of sodium hydroxide (NaOH) and ammonia hydroxide ($NH_4OH$). The ratio of sodium hydroxide (NaOH) and ammonia hydroxide ($NH_4OH$) is 1:1. We are prefer use base solution than acid on synthesis black pigment to avoid result acidic pigment. Acidic pigment can impact corrosion on several material when the pigment will be applied. MS powder added with base solution 5%, 10%, 15% and 20% so we got dark brown sludge. Sludge burned in furnace with




temperature 900ºC holding time 3 hours until the sludge had dried and we got agglomerate. Agglomerate mashed with mortar to get black powder.

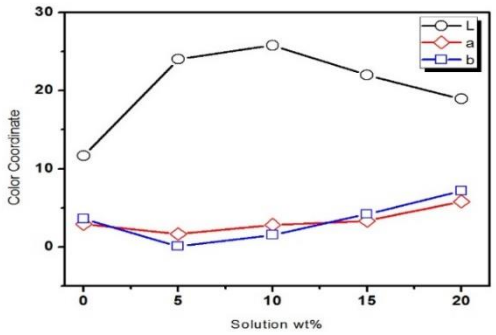
The sample characterize on color properties (CIELab Color System) use Colorimeter and crystal structure use X-Ray Diffraction. XRD characterization also confirmed the matter has been formed.

**Figure 1**. Flowchart of research

## RESULTS AND DISCUSSION

### 1. Color Properties

The main function of pigment is giving color to material besides other function such as heat resistance, corrosion resistance, rust resistant and much more. The color properties of black pigment characterized by CIELab Color System using Colorimeter/Chromameter BYK-Gardner GmbH 82538 Geretsried. CIELab Color System has three axis that build a coordinates which represent a color, there L-axis for lightness; a-axis for green (minus value) to red (positive value) and b-axis for blue (minus value) to yellow (positive value). We know that color is physical phenomena depend on material abilities to absorb and reflect light




waves. In the theory black color absorb all wavelengths of light and none reflected, that was be expected to occur on a black pigment. So black pigment should absorb all the light and the CIELab Color System showed zero point to all color axis (L=0; a*=0; b*=0), but that is an ideal state and upstream.

**Figure 2.** CIELab System value for black pigment depend on wt% solution; 0% solution is commercial black pigment

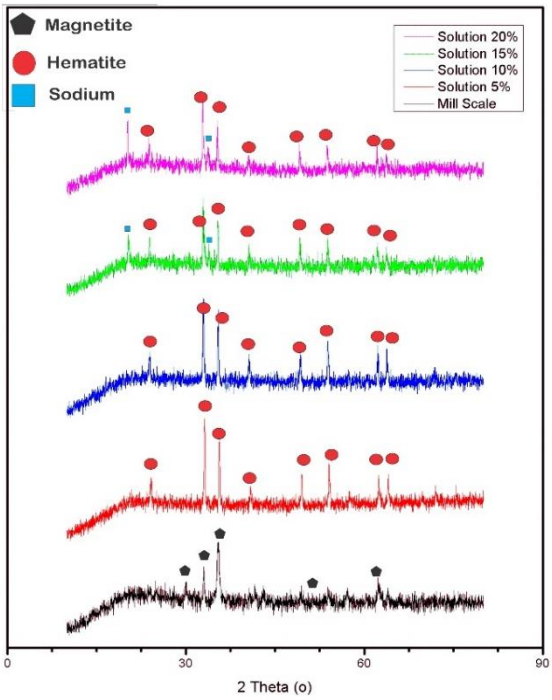
Commercial black pigment that had produced with color coordinates for L-axis did not approach to zero point. The pigment has L=11.65 for lightness value (see figure 3), however it mainly use in Indonesia painting industries. According to graphic on the figure 1 there are decrement of lightness value when solution decrease. For a-axis and b-axis there were no significant differences between commercial black pigment and black pigment has been synthesized (see Figure 3).

### 2. XRD Characterization for Black Pigment

XRD patterns of the samples prepared by simple burning are shown in Fig 2. We can see that the mill scale has change from magnetite (the dominant material in mill scale) to hematite. It is indicated by disappearing of peak

approximately 30° in 2 theta degrees (see Fig 3 on Mill Scale XRD pattern). In many journal peak in 30° of 2 theta is the peak of magnetite. [12] When the 30° peak has been decreased or disappear was indicated that magnetite was decreased or disappear and changed to another form of iron oxide like hematite.

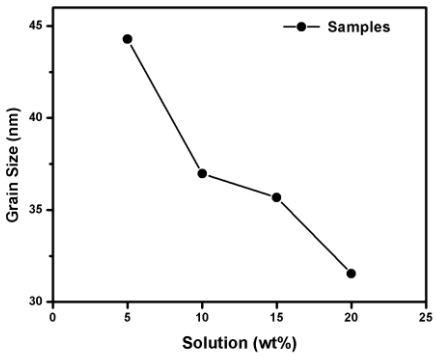
In addition of base solution 15% and 20%, one can see in XRD pattern appeared a peak about 33° of 2 theta degrees, it is indicated sodium element. In similar research that had topic synthesis magnetite ($Fe_3O_4$) by co-precipitation method with sodium hydroxide (NaOH) solution, then was found a peak in XRD pattern about 32,8° of 2 theta. [13] In the COD (Crystallography Open Database) database the black pigment has hexagonal crystal structure and identical to entry no. 96-900-0140. For the initial material (Mill scale) has cubic crystal structure and identical to entry no. 96-900-6200. These changes in crystal structure is predicted to affect the color




properties of black pigment.

**Figure 3**. XRD pattern depend on wt% solution.

We can predict the grain size of black pigment use Scherrer method. When base solution added on MS powder would impact the pH of MS powder on increasing of pH and




finally impact on decreasing of grain size see Figure 5. when the pH value is closer to normal the grain size will be smaller, the higher value of pH will be gotten bigger on grain size.[14]

**Figure 4.** The effect wt% solution to grain size

## CONCLUSION

Black pigment can be synthesized by simple burning method (combustion) from mill scale. The result of colorimeter, color properties of sample have 7.29 point difference for L-axis, in a-axis and b-axis there were no significant difference. Black pigment in the hematite form contained sodium impurity that we can see in XRD pattern on sample with 15% and 20% base solution. The next research will be improved with give variation on parameters of research such as the ratio of NaOH and $NH_4OH$, temperature calcination of combustion process, holding time, and pH value of sludge.

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