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Fabrication of Magnetic Ink Chromium Ferrite Using Iron Sand

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Abstract. In this research iron sand was used as raw material for fabrication of magnetic ink of chromium ferrite. The first step of research was synthesizing iron sand into pigment of chromium ferrite using powder metallurgy method. The second step was processing pigment into magnetic ink. The ink was produced by mixture pigment into binder solution of polyvinyl alcohol and heated. While stirring the mixture was added alcohol as a solvent and additives of polyethylene glycol, propylene glycol, and glycerine by certain composition. The variation of pigment mass was 6 g, 8 g, 10 g, 12 g, 14 g, and 14 g. The produced ink was characterized its properties, those were structure using XRD method, colour, density, viscosity, organoleptic, CCD microscope, and magnetic susceptibility. Using XRD was found that the pigment have a structure of $CrO.Fe_2O_3$ with size of 84.81nm. The colour of ink was dark green. The brightness of the ink decreases with increasing pigment mass. The coordinates values of a* and b* was fluctuated. The ink viscosity was around 7.64 cP until 19.59 cP, the density was around 0.954 gr/cm^3 until 1.007 gr/cm^3. By organoleptic study was found that the ink can be used on the whiteboard. From CCD microscope was known that distribution of ink more evenly white increasing of pigment mass. The value of magnetic susceptibility was around of 1.500175×10^{-5} m^3/kg until 1.504662×10^{-5} m^3/kg.

1. Introduction

Indonesia is a country rich in natural resources. One of the abundant and scattered natural resources in Indonesia is iron sand. Iron sand is sand in which iron (Fe) is very dominant. The iron content is generally oxidized to form iron oxides such as hematite (α-Fe_2O_3), magnetite (Fe_3O_4), and maghemite (γ-Fe_2O_3) [1]. So far, iron sand has only been mined and sold to consumers in its raw form so that its use has become less effective and less useful [2]; In fact, the magnetite in iron sand can be processed and used in various fields such as electronics, energy, ferrofluid, chemistry, catalysts, and medical diagnostics [3]. In recent years Fe_3O_4 has been widely used in various applications including high density information storage, magnetic resonance image formation (MRI), delivery systems for pharmaceuticals, cosmetics, dyes, inks and plays a role in various processes including adsorption. Fe3O4 is also applied as a coating to prevent further corrosion in steel making and has the potential to be used as an adsorbent for heavy metals [4].

One of the highlights of this iron sand study is how to make nanoparticles, analyze their crystal structure and their magnetic properties. Magnetic materials have many uses, including as a biosensor [5], localizer in hyperthermia therapy [6], corrosion protection for steelmaking and as an adsorbent for heavy metals.

Nano-sized magnetite as a ferimagnetic material has a wide opportunity in its application to meet the increasing demand for industrial raw materials in the electronics field [7].

The results of processing iron oxide into nanoparticles have wide applications, for example for paints, inks, rubber, plastics, cosmetics, and medical devices [8]. Modified magnetic nanoparticles [9,10] have recently been used to treat bone diseases (such as osteoporosis and infection), namely coating magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) with calcium phosphate. Iron oxide compounds that are commonly used as soft magnets, in nanoscale sizes, can be used for biomedical applications, including in drug supply and magnetic resonance imaging [11]. Iron oxide pigments are generally used as powder inks (toners) [12]. The result of the X-Ray Fluorescence (XRF) toner has a magnetite content of 95.01%. This magnetic mineral is the dominant mineral in toners with a composition of> 90% [13]. This high magnetic property supports this type of magnetic pigment to be used as magnetic ink.

The background above encourages researchers to develop green magnetic ink, namely by using ferrite chromium compounds. The provision of green pigments is based on Erlinawati's research [14]. The green color was chosen because the magnetic ink produced in this decade tends to be black. In addition, green is chosen to add color aesthetic value to magnetic ink when applied.

2. Methods
2.1. Pigment manufacture
The first step to produce green pigment is extraction of iron sand which has been done manually using laboratory magnet. This extraction process was repeated 5 times, the result was that iron sand magnetite obtained a purity of 99%. The extraction results are then ground using a ball-mill to get a powder size of below 1 micron. Pigments are made using the powder metallurgy method. A mixture of magnetite, iron sand, chromium, added with alcohol, and wet milled using a ball milling machine for 19 hours. After drying the material is calcined using a furnace at a temperature of 800°C for 3 hours. The result is a dark green powdered chromium ferrite pigment.

2.2. Ink making
The steps in making magnetic ink are as follows:
a. Making an adhesive solution from PVA dissolved with distilled water in a ratio 8: 100, 8gram for PVA and 100 ml for distilled water. This adhesive solution serves as a pigment binder as a carrier for the ink and other additives used.
b. Stir the mixture at 70˚C until the emulsion is formed homogeneously. Heating is done to speed up the homogenization process of the adhesive ocean.
c. Taking 50 ml of the adhesive solution then added to it the ferrite chromium pigment. The mass of the pigment added are 6 g, 8 g, 10 g, 12 g, 14 g, and 16 g for sample A and 4 g, 4.5 g, 5 g, 5.5 g, 6 g, and 6.5 g for sample B. The 20 ml of distilled water was also added because the adhesive solution was too thick.
d. Adding 30 ml of alcohol in the form of alcohol, 3 ml of polyethylene glycol 400, 3 ml of propylene glycol, and 2 ml of glycerin.

3. Results and Discussion
3.1. XRD characterization
The XRD characterization of chromium ferrite pigments was carried out using the PANanalytical - X'Pert3 instrument at the Physics Laboratory of the State University of Semarang. XRD characterization used a radiation source in the form of CuKα with a wavelength of 1.5406 angtroom generated using a current of 300 mA and a potential difference of 400 kV. The measuring angle ranges from 10o to 90o. The diffractogram pattern obtained is identical to the chromium ferrite pigment diffractogram which refers to the JCPDS database number 00-035-1112. There are ferrite chromium peaks at angles of 25.67˚, 33.5˚, 36.2˚, 41.4˚, 50.2˚, 54.8˚, and 65.1˚, where at 33.5 angles is the highest peak. Pigment crystal size is determined based on the highest peak data. Using the Scherrer formula, the pigment crystal size was 84.81 nm.

3.2. Color characterization

The resulting pigment is in the form of a powder that has gone through the refining, sieving, and heating process. Refining is done in order to obtain a small pigment size while sifting is to filter and obtain the same pigment size. The heating was carried out at a temperature of 800°C with a holding time of 3 hours. The pigment is green.

The ink sample that has been successfully made was applied to paper measuring 6×5 cm^2. The application of ink to the substrate uses the same method for each sample. From this application, it was known that the distribution of the ink particles on the paper substrate is getting tighter as the pigment used increases. This was known from the differences in sample A1 to sample A6 whose distribution is more evenly distributed. This causes the green color of the substrate to become darker because the ink covering it was evenly and thicker. In sample B, the difference in the distribution of ink particles from samples B1 to B6 was not very clear. This is due to the small increase in pigment mass which causes the pigment carrying the ink to not increase as well.

The color of the ink on the paper substrate was characterized using an AMT 500 colorimeter. The data resulting from the characterization were L * a * b * color coordinates. The L * coordinate shows the color brightness level, the a * coordinate shows the color gradation from the green to red dimensions, and the b * coordinate shows the color dimensions from blue to yellow [15]. The results of L * a * b * characterization can be seen in Table 1.

Table 1. L * a * b * coordinate test results

Sample	L*	a*	b*	C*	H°
A1	33.5	-0.5	3.1	3.14	-9.146
A2	30.3	0.2	1.9	1.91	5.994
A3	27.6	0.7	1.4	1.565	26.565
A4	29.9	0.2	2	2.01	5.71
A5	27.9	0	1.1	1.1	0
A6	27	-0.1	1.3	1.304	-4.403
B1	67	0.3	6.7	6.707	2.576
B2	59.1	-0.4	8.1	8.11	-2.805
B3	58.2	-1.3	8.9	8.994	-8.306
B4	59.1	-0.5	6.9	6.918	-4.004
B5	59.7	-0.8	8.8	8.836	-5.143
B6	56.6	-0.5	8.2	8.215	-3.491

Based on table 1, it is known that the L * coordinate of sample A tends to decrease with the increase in the amount of ferrite chromium pigment. Decreasing the L * coordinate value indicates that the ink is getting darker. The notation L * indicates the color from black to white with a coordinate range of 0–100 which affects the brightness of the ink. The decreasing L * coordinate value is due to the more pigment carrying the ink which causes the ink to stick to the substrate evenly and the more it covers the white substrate of the paper. The a * coordinate shows the color gradation from the green to red dimension with a coordinate range of -120 to +120. The coordinates -a * represent the green direction and + a* indicates the red direction. Based on the measurement results, the overall a * coordinate value is in the middle between green and red, which is in the range of 0. Although there are those that tend to be red in the data because it is positive, overall the resulting color is green but very dark. This is also proven by physical examination (vision).

Besides the L * and a * coordinate factor, the b * coordinate also affects the brightness of the ink color. The b * notation denotes the color dimension from blue to yellow with a coordinate range of -120 to +120. The coordinates -b * indicate the blue direction and + b indicates the yellow direction. The green color is a combination of yellow and blue. From the measurement results, the b * coordinate, the

b * coordinate values are all positive. This indicates that the resulting color is green which tends to lead to yellow. In the coordinate data a * sample B, almost all of them are negative only in sample B1 which is positive. This indicates that sample B1 tends towards red, while samples B2 to B6 tend towards green. And with the naked eye can be seen bright green. In the result of the b * coordinate data, all values are positive. And this also indicates that the ink color is green and tends to be yellow.

3.3. Convert coordinates L * a * b *

Based on the existing color theory, actually all colors are composed of three primary colors, namely red, green, and blue. An example is orange where orange is a secondary color composed of red and yellow. Therefore, the L * a * b * coordinate data from the test results are then converted into data in the form of Red (red), Green (green), and Blue (blue) values or commonly referred to as RGB to determine the value of RGB. RGB values range from 0 to 255.

The L * a * b * coordinate values are also converted into Hue (H), Saturation (S), Lightness (L), and Brightness (B) values. Data conversion is performed using the Colorizer application. And here is a Table 2 of the conversion results using the Colorizer application.

Table 2. The results of the conversion of L * a * b * data A coordinates using a colorizer

Sample	RGB			HSLB			
	R	G	B	H%	S%	L%	B%
A1	80.12	78.83	73.89	47.6	4.04	30.2	31.42
A2	72.98	71.12	68.4	35.6	3.24	27.72	28.62
A3	67.23	64.73	63.04	24.13	3.22	25.54	26.37
A4	72.12	70.19	67.33	35.81	3.43	27.34	28.28
A5	66.6	65.77	64.15	39.57	1.87	25.64	26.12
A6	66.58	65.8	63.85	43.02	2.09	25.57	26.11

Based on the data in Table 2, the RGB value has decreased from sample A1 to sample A6. However, the RGB value in sample A4 has increased. This can occur because the ink sample on the substrate is not evenly distributed, causing the ink layer to be thin, which causes the RGB value to rise. The decrease in value occurs with the addition of the pigment mass as the ink carrier. With the RGB composition decreasing, this indicates that the resulting green color is darker.

The hue (color identity) of the color has decreased. This indicates the smaller the percentage of green ink color. The color intensity (saturation) of the sample has decreased. The decrease in color intensity occurs due to the addition of the pigment mass in the ink, which causes the color of the ink to become dimmer. Lightness (brightness) has decreased due to the increase in the mass of the pigment as well as the intensity of the color. The lower the lightness value, the more blurry the resulting color will appear. For brightness (sharpness) also decreases with increasing pigment mass in the ink. The lower the brightness of a color, the less bright and sharp it looks.

Table 3. Results of conversion of L * a * b * B data coordinates using a colorizer

Sample	RGB			HSLB			
	R	G	B	H	S%	L%	B%
B1	168.82	162.4	151.08	38.29	9.33	62.72	66.2
B2	147.56	141.92	128.1	42.59	8.3	54.05	57.87
B3	144.16	140.03	124.39	47.46	8.19	52.66	56.53
B4	146.55	142.04	130.19	43.48	7.01	54.26	57.47
B5	148.91	143.66	128.4	44.63	8.81	54.37	58.4
B6	140.92	135.49	121.57	43.18	7.82	51.47	55.26

The results of the L * a * b * coordinate data conversion of sample B in Table 3 show that the RGB value decreases as the mass of the pigment used increases. However, in samples B4 and B5, the RGB value has increased. Just like with sample A4, the RGB values of samples B4 and B5 have increased because the ink on the substrate is less evenly thick so that there are parts of the sample that have a thin layer so that the color looks brighter and causes the RGB value to rise. The RGB value in sample B is higher than sample A. This is because the carrier pigments in the sample are less and the ink layer on the substrate is thinner so that the resulting color is brighter. Hue (color identity), saturation (intensity), lightness (brightness), and brightness (sharpness) color samples have increased and decreased.

3.4. Ink Viscosity and Density
The viscosity value of the ink samples was characterized using an Ostwald viscometer, namely by knowing the time required for the ink to pass through two points as a constant distance parameter. The time obtained is multiplied by the density of the ink sample and compared with the density and flow time of the fluid. The fluid here is water which has a viscosity of about 0.0089 g / cm.s. The results of the viscosity characterization of the ink for samples A can be seen in Figures 1.

In Figure 1 it can be observed that the smallest viscosity value in sample A is in the number 9.69 cP while the highest viscosity value was at 19.59 cP. This means that the increasing mass of the pigment used in the ink, the viscosity value produced by the ink will increase. The increased viscosity value is due to the large particles in the pigment so that the ink type resistance is greater because the pigment particles inhibit the flow rate of the carrier and binder (binder). The addition of additives in the manufacture of ink also affects the viscosity value, although very slightly. This is because there are additives that have high viscosity such as propylene glycol, PEG 400, and glycerin and there are also additives with low viscosity values such as alcohol and distilled water. The results of measuring the viscosity value in sample B have similar properties to sample A. The viscosity value of sample B is smaller than that of sample A. This is because in sample B, the carrier pigment in the ink is less. And the addition of pigment is also not too much, so the distance to increase the viscosity is not too much.
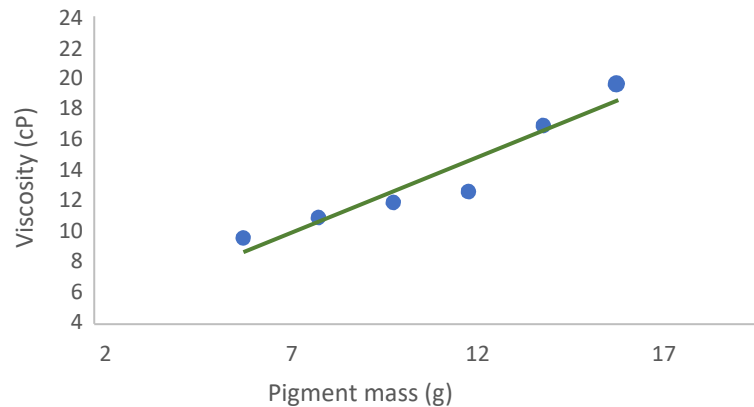
Figure 1. Effect of pigment mass on viscosity of sample A

The results of the density measurement in sample A obtained prices ranging from 0.976 gr / cm3 to 1,007; while for sample B the price ranged between 0.954 and 0.967. The ink density value increases with the addition of the pigment mass in the ink solution. This is because pigment is a dense material, which affects the density of the ink. The more solid material is added, the greater the ink density value. This also results in an increased viscosity value. From the results obtained, the ink density values of both sample A and sample B are close to the density of the market whiteboard marker ink, namely 1.00 g / ml. According to the Indonesian national standard number 06-1567-1999, the required density of ink is at least 1 g / ml.

3.5. Magnetic Characterization
Susceptibility is a basic measure for determining the magnetic properties of a material. The tool used is the Bartington MS2B susceptibility meter belonging to the State University of Malang. The measurement method used is the Dual Frequency measurement method with a low frequency (Low Frequency) of 0.47 kHz and a high frequency (High Frequency) of 4.7 kHz. The test represents pigment susceptibility and ink susceptibility. The value of magnetic susceptibility indicates the number of magnetic particles and the magnetic properties of a material. The particle size affects the magnetic flushing value. Pigment composition elements also have an effect on the susceptibility value because each element has its own value of susceptibility. The magnetic susceptibility values of ferrite chromium pigments and inks are shown in Table 4.

Table 4. The susceptibility value of pigment and ferrite chromium ink.

Sample	High Frequency $(10^{-6}m^3/kg)$	Low Frequency $(10^{-6}m^3/kg)$	Deviation (%)	Class
Pigment	15.00175	15.04662	0.298214	Ferrimagnetic
Ink A	0.07496	0.090313	17	Weak Ferrimagnetic

Table 4 shows that the susceptibility value of the chromium ferrite pigment at heating temperature 800˚C which is 15.00175×10^{-6} m^3/kg at high frequency and 15.04662×10^{-6} m^3/kg at low frequency. And the ink magnetic susceptibility value is 0.07496×10^{-6} m^3/kg at high frequency and 0.090313×10^{-6} m^3/kg

low frequency. From these data shows that the value of pigment susceptibility after processing into ink is lower than before processing. The value of magnetic susceptibility is influenced by several factors, including the crystal structure and impurity content as well as the heating temperature used. The strength and weakness of the susceptibility value can be influenced by the crystal formed from a material. Increasing the temperature causes the magnetic properties of the material to decrease. This is because the increasing heating temperature causes the vibrations of the atoms in the crystal to get tighter and the orientation of the magnetic dipole of the material is getting more random, so that the magnetization of the material decreases, and causes its magnetic susceptibility to also decrease. The deviation value is the range of differences in high and low frequency susceptibility values. The deviation value for the original pigment is 0.298214%. However, the deviation value of the pigment after it was used to make the ink bigger was 17%. This is because the pigment has mixed with non-magnetic chemicals so that it can reduce the susceptibility value of the pigment. The more additives used in the ink-making process, the smaller the magnetic susceptibility value, which causes the loss of the pigment's magnetic properties.

4. Conclusion

Based on the results of the research that has been done, the following conclusions are obtained: Chromium ferrite magnetic ink has been successfully prepared by mixing pigments with adhesives (binders) and additives in the form of alcohol, polyethylene glycol, propylene glycol, and glycerin.Characterization of physical properties of chromium ferrite ink obtained is as follows, the crystal size of the ferrite chromium pigment in the XRD test was 84.81 nm. The results of testing the color of the substrate sample using a colorimeter obtained data on the L * coordinate value which is getting smaller the better, the coordinate value a * goes up and down, and the coordinate value b * is getting bigger, both sample A and sample B along with the addition of the pigment. Chromium ferrite pigment is ferrimagnetic and chromium ferrite ink is weakly ferromagnetic.

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