MECHTA
International Journal of
Mechanical Engineering Technologies and Applications
V. 01 N. 2
ISSN 2722-3213 Article No. 5, pp. 69 - 76, 2020

Dewi Elok Rahmawati
Chemistry Department
Islamic State University Maulana Malik Ibrahim, Gajayana, 50
Malang, Jawa-Timur, INDONESIA
failedelokrahmawati@gmail.com

Lilik Miftahul Khoiroh
Chemistry Department
Islamic State University Maulana Malik Ibrahim, Gajayana, 50
Malang, Jawa-Timur, INDONESIA
lilikmfx@kim.uin-malang.ac.id

Rachmawati Ningsih
Chemistry Department
Islamic State University Maulana Malik Ibrahim, Gajayana, 50
Malang, Jawa-Timur, INDONESIA
rachmawati_ningsih@kim.uin-malang.ac.id

Febi Yusniyanti
Chemistry Department
Islamic State University Maulana Malik Ibrahim, Gajayana, 50
Malang, Jawa-Timur, INDONESIA
febi100292@gmail.com

Wariatus Solawati
Chemistry Department
Islamic State University Maulana Malik Ibrahim, Gajayana, 50
Malang, Jawa-Timur, INDONESIA
wariatus1999@gmail.com

Puspa Sari
Chemistry Department
Islamic State University Maulana Malik Ibrahim, Gajayana, 50
Malang, Jawa-Timur, INDONESIA
puspa9172994@gmail.com

Synthesis of Hematite Pigment (A-Fe_2O_3) from Iron Lathe Waste using Precipitation-Sonication Method as Anti-Swelling on Wood

Iron lathe waste powder has the potential as a raw material in the synthesis of hematite pigments. Hematite pigments have many advantages, one of which is anti-swelling properties that can maintain the dimensions of wood. Hematite pigment synthesis was carried out using the precipitation-sonication method. The precipitation stage uses an ammonium hydroxide solution as a precipitating agent. Stages of sonication using the PEG-6000 template were performed at different times were 30, 45, and 90 minutes then calcined at 750 ° C for 3 hours. The samples were characterized by X-ray diffraction (XRD), color reader, and scanning electron microscope-energy dispersive X-Ray (SEM-EDX). The result confirmed that a ferrihydrite phase obtained after the precipitation process and transform into hematite after the calcination process with the highest degree of crystallinity for 90-minute sonication. From a color reader, the brightness and redness degrees decrease with increasing time. Scanning electron microscope results illustrated that the morphology was not uniform with the particle size getting smaller with increasing sonication time. The EDX results show that hematite pigments still contain impurities such as carbon. The swelling test indicated that the highest stability in hematite-pigmented wood increased as increasing in the weight of pigment.

Keywords: *Lathe Waste, Pigment, Hematite, Sonochemistry, Nanoparticle*

1. INTRODUCTION

Iron lathe waste powder is one of the wastes produced by the iron lathe industry that discharged directly without processing so that it has the potential to pollute the environment. Iron lathe waste still contains 97.11% iron which can be used as a raw material for synthesis of iron oxide [1]. Iron oxides that have been found in nature are classified into 16 compounds, which have quite extensive industrial applications including nanocatalysts, adsorbents, gas sensors, biomedical, and especially pigments [2]. One of the most consumed iron oxide pigments is hematite pigment (α-Fe_2O_3) which has several advantages including corrosion resistance, a distinctive red color, chemically stable in an aqueous system, high strength in staining, non-toxic, high durability and good durability [3], and resistant to high temperatures [4].

Synthesis of hematite pigments can be done by various methods such as sonochemistry [5], hydrothermal, solvothermal, electrochemical, microwave-calcination, and precipitation-calcination routes [1][6][7]. Precipitation-calcination is a method with a simple, easy procedure [10][3], inexpensive, and gives abundant results with relatively low temperatures [8]. Hematite synthesis with this method produces hematite compounds with high crystallinity but still provides morphology and distribution of diverse and large particle sizes. In this research, synthesis uses the method of precipitation-sonication to obtain nanoparticle size. The sonication method is based on ultrasonic waves that are radiated to the sample. Delmifiana and Astuti [9] and Katsuki [10] showed that sonication duration can affect the crystallinity, color, and size of the compounds

Corresponding Author: lilikmfx@kim.uin-malang.ac.id Received on: June 2020 Accepted on: June 2020

produced. For this reason, the sonication stage in this study is carried out at varied sonication duration to determine the effect given to the sample.

Hematite pigments can be applied to furniture made from wood as an anti-swelling. Hematite pigmented wood shows better properties than wood without pigments, e.g. smooth wood surface, slow weathering and higher resistant to water and UV radiation [11].

2. MATERIALS AND METHODS

2.1 Materials

Iron waste powder from the iron lathe industry in Malang, distilled water, HNO_3 65% , NaOH pa, NH_4OH pa, shellac, woodblocks, and methanol pa.

2.2 Precursors Preparation

The precursor was prepared by dissolving lathe waste in HNO_3 7M. The mixtures were left for 24 hours at room temperature and then heated to solid. To indicate the ferric precursor, NaOH solution was used. When precursor was ready, a reddish brown precipitate would be formed.

2.3 Hematite Synthesis

In the next step, the precursors were prepared in dilute nitric acid. Then, ammonium hydroxide (NH4OH) 25% was added to the solution as the precipitating agent until pH achieved 6. After that, the mixutre was being heated at 70 °C for 1 hour and stirred at 750 rpm, then cooled for 24 hours at room temperature and decanted. The precipitate obtained was added with PEG-6000 which has been melted (1:2), continued with sonication at high temperatures for 30, 60, and 90 minutes and dried. Then the solid was calcined at 750° C for 3 hours.

2.4 Application of pigments in wood

Synthesized hematite pigment was dissolved in a mixture solution of shellac and methanol. The amount of hematite pigment used was 10, 20, and 30 mg. The pigment solution was applied to the wood and was analyzed swelling ratio at intervals of 2, 4, 6, and 8 days.

2.5 Characterization of Hematite Pigment

The precursor was analyzed using XRF PANalytical Mini-Pal 4. The crystal structure of the synthesis results was characterized using XRD X'pert PRO PANalytical. Crystal size was obtained through calculations from XRD data using the debye Scherer equation. Pigment colors were analyzed by using a CR10 color reader. The morphology and composition of the sample were analyzed using SEM-EDX JSM-6510, and the strength of the pigment was known through changes in the volume of wood (swelling), which were then analyzed by using swelling ratio and anti-swelling efficiency (ASE). The morphology surface of the wood using the Nikon SMZ-1500 binocular optical microscope.

3. RESULTS

3.1 X-Ray Fluorescence (XRF)

Table 1 shows the highest elemental content of ferric nitrate precursors is iron. Besides iron, there are other elements but excessively small. The high iron content in lathe waste has the potential as a precursor in the synthesis of hematite pigments

Table 1. XRF result of iron lathe

Content	Fe	Si	P	Ca	Cr	Mn	Cu	Br	La	Eu	Os
%	96,58	0,49	0,21	0,12	0,24	0,54	0,22	0,51	0,06	0,76	3,25

3.2 X-Ray Diffraction (XRD)

X-Ray diffraction was used to characterize the structure, crystal size, and intensity. This characterization was carried out on samples before and after calcination. Figure 1 shows the XRD pattern after calcination according to hematite standards. The size of the crystals is obtained through a diffraction pattern using the Debye Scherrer equation shown in Table 2.

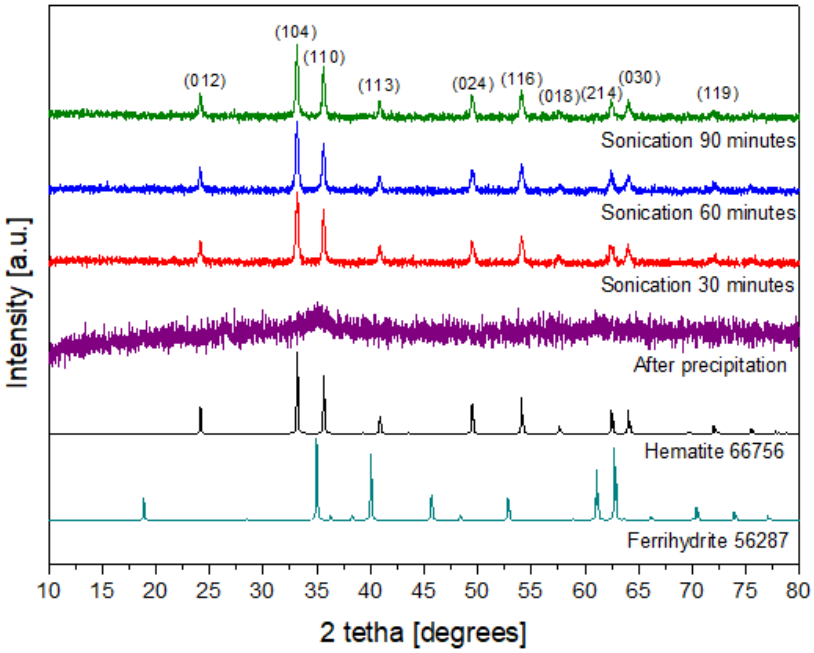

Figure 1: X-ray diffraction pattern of ferrihydrite and hematite compounds

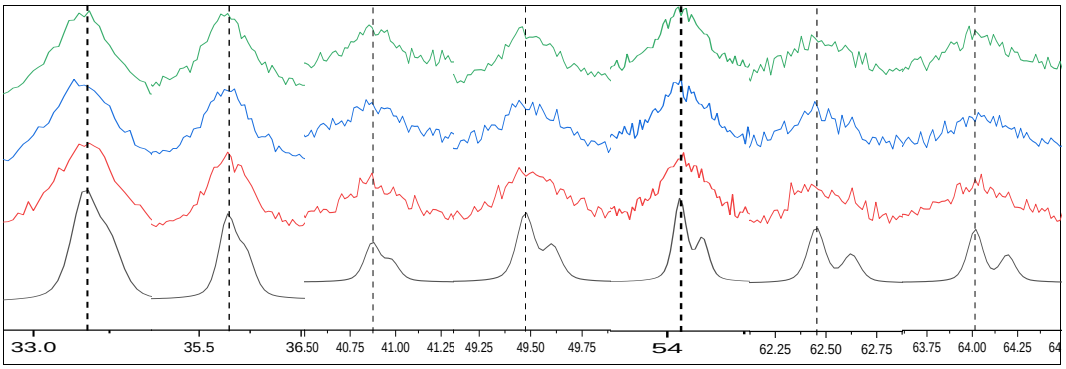

Figure 2: Magnification of X-ray diffraction patterns of hematite compounds (α-Fe_2O_3) with sonication time variations.

Table 2. The crystallite size of the sample compounds

Sample	2 tetha khas (°)	h (cts)	Crystal Size (nm)
Ferrihydrite	35,26	122.84	90,3538
Hematite 30 minutes sonication	33.2095	1628.65	61.3007
Hematite 60 minutes sonication	33.1294	1617.84	81.6765
Hematite 90 minutes sonication	33.1806	1683,38	61.2943

3.3 Color Reader

The color reader is used to determine the color level of the sample synthesized in Figure 3. The test results are obtained with several parameters namely the value L * (bright) describes the brightness, a * (-: green, +: red), b * (-: blue, +: yellow), C * (chroma) describes color pattern, and H (Color) describes purity. The results of the whole sample test show the color value of the sample with a standard range.

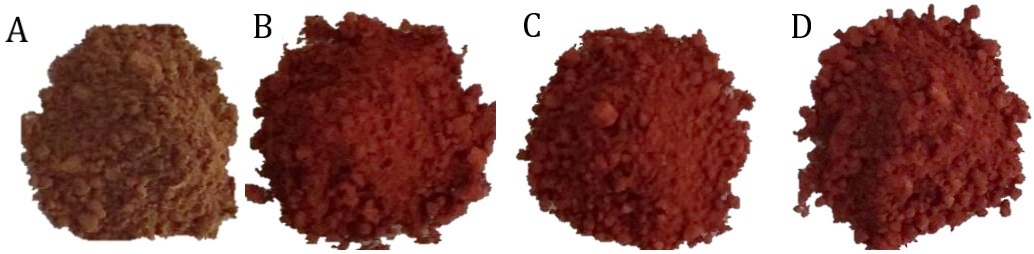

Figure 3: Results image A) sample after precipitation B) hematite 30 minutes sonication C) hematite 60 minutes sonication D) hematite 90 minutes sonication

Table 3. Results of sample color analysis

Sample	L	a*	b*	C*	H°
Ferrihydrite standards	23-56			10-39	44-63
After precipitation	45.1	6.2	12.5	13.953	63.618
Hematite standards	25-45			9-42	21-57
After calcination 30 minutes sonication	41.8	13.6	13.7	19.304	45.21
After calcination 60 minutes sonication	41.5	13.3	14	19.31	46.469
After calcination 90 minutes sonication	40.9	12.9	13.6	18.745	46.513

3.4 SEM-EDX

Scanning electron microscope characterization was used to determine the particle morphology shown in Figure 4. Particle size was analyzed using the ImageJ program. EDX analysis is used to determine the content of the synthesis results shown in Table 4.

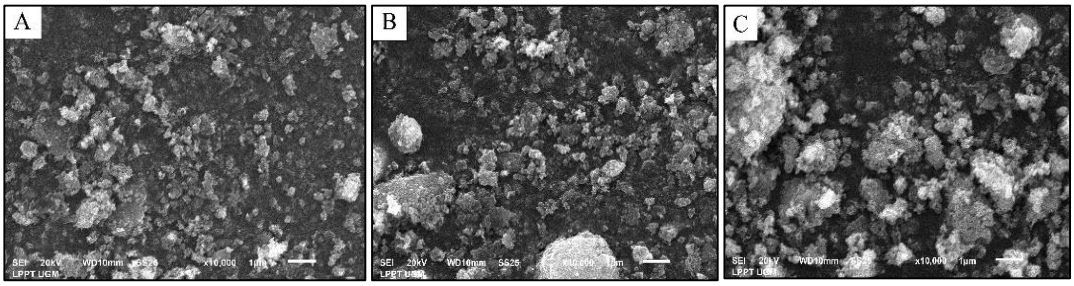

Figure 4: SEM results of 5000x magnification of sonication hematite samples A) 30 minutes B) 60 minutes C) 90 minutes

Table 4. Results of analysis of particle size

Sample sonication time variations	30 minutes	60 minutes	90 minutes
Particle Size (nm)	72.398	72.58	71.872

Table 5. The EDX result of Hematite components at sonication 90 minutes

Elements	Iron(Fe)	Carbon(C)	Oxygen(O)
Degree(%)	50,23	13,82	35,95

3.5 Swelling Test

The test is done by coating the surface of the wood with synthesized pigments with a sonication time of 90 minutes. Wooden surfaces before and after the test are shown through an optical microscope. Figure 5 shows the surface of the wood has evenly red color as the amount of pigment used increases.

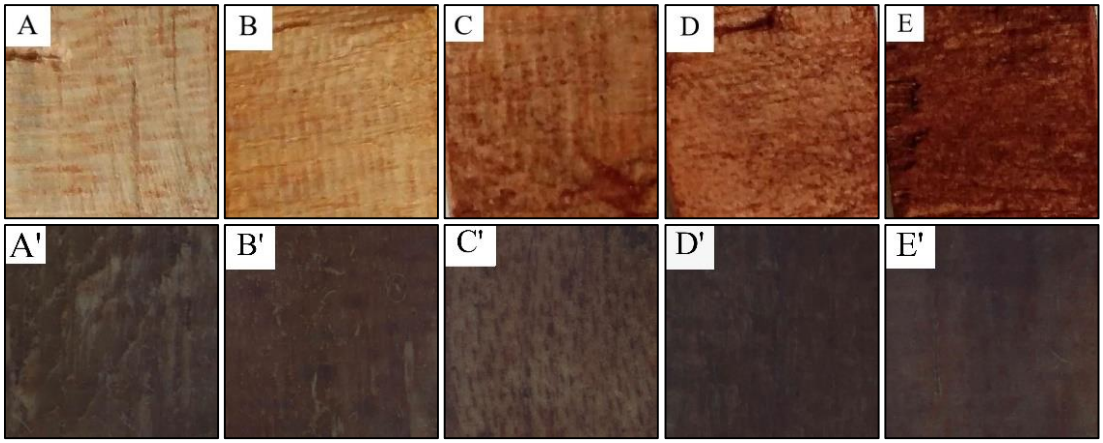

Figure 5: Display of wood surface before immersion A) Control B) shellac C) 10 mg pigment D) 20 mg pigment E) 30 mg pigment and after immersion.

Figure 6a shows the wood swelling power during the immersion process, the longer the immersion time, the higher the swelling power of the wood. Figure 6b shows the anti-swelling efficiency of wood, the more hematite pigments used, the higher the wood's stability.

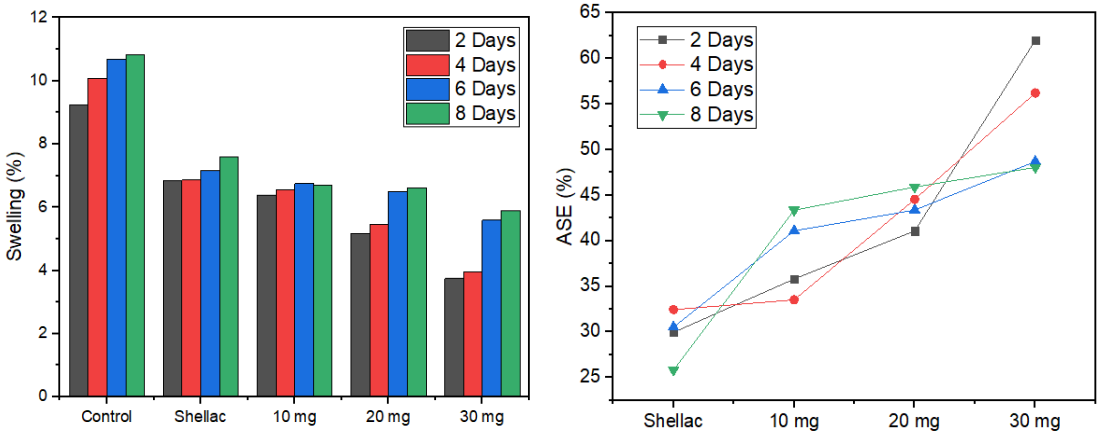

Figure 6: A) Swelling ratio of wood and B) Antiswelling efficiency (ASE) of wood

4. DISCUSSIONS

4.1 XRF

The test results showed the highest content of the precursor is iron. The precursor is a ferric ion (Fe^{3+}), which is known through qualitative testing. A positive reaction is characterized by the formation of red deposits when adding NaOH solution with the following reaction 1:

$$Fe^{3+}_{(aq)} + 3OH^{-}_{(aq)} \rightarrow Fe(OH)_{3(s)}\downarrow \quad (1)$$

The formation of iron ions greatly affects the results of the synthesis obtained. Ferric precursors will produce a single phase in contrast to mixed precursors (ferric and ferrous) will provide a heterogeneous phase [14][3].

4.2 Analysis of XRD characterization results

The diffraction pattern in the sample after precipitation agreed with the reference diffraction pattern of ferrihydrite standard (ICSD 56287) through the reaction 1.

$$Fe(NO_3)_3.\ nH_2O_{(s)} + NH_4OH_{(l)} \rightarrow Fe(OH)_{3(s)}\downarrow + 3NH_4NO_{3(aq)} + nH_2O_{(l)}$$

$$10Fe^{3+} + 30OH^{-} \rightarrow 5Fe_2O_3.9H_2O + 6H_2O \quad (2)$$

Figure 1 shows that a diffraction pattern of ferrihydrite phase was obtained is a broad peak with low intensity and high noise. The results indicate the sample is less pure and has a large size of the crystal. Furthermore, in a sample after sonication-calcination at high temperature undergoing phase change to be hematite by way of reaction 3. Samples after sonication-calcination using variations time of sonication are 30, 60, 90 minutes have diffraction pattern by the standard (ICSD Hematite 66756) and the results produce high intensity with low noise. This indicates that the sonication stage can increase the intensity and reduce the noise of compounds produced. The higher the intensity of diffraction is the higher the crystallinity level of the compound.

$$5Fe_2O_3.9H_2O \xrightarrow{\Delta} 5\text{-}\alpha Fe_2O_{3(s)} + 9H_2O_{(g)} \quad (3)$$

Table 1 shows the size of the crystal produced by the calculation of the **Debye-Scherrer** equation at some plane. Based on table 2, the crystal size of the sample after precipitation is greater than the sample after sonication-calcination. Crystal size decrease due to the effect of ultrasonic. The irradiation of ultrasonic waves from sonication causes particles to move in collision with others. The result, hematite compound has a rhombohedral structure with a lattice R-3c and unit cell parameters that change from the standard (a = b = 5.0342 Å and c = 13.746 Å). The 30 minute hematite sample sonication has cell parameters with values a = b = 6.641081 and c = 13.056124. The 60 minute hematite sample sonication has cell parameters with values a = b = 5.034200 and c = 13.746000. The 90 minute hematite sample sonication has cell parameters with values a = b = 6.626180 and c = 13.100387.

4.3 Color Reader

The results of the synthesis are yellowish-brown solids after precipitation and become red after calcination. The difference in sonication duration doesn't provide a significant color change. Table 3 displays the results of the color reader characterization of the sample in Figure 3. All samples have color that accordance with the standard range.

Sonication time variation produces brightness values (L *) which decreases with increasing sonication time. The difference in sample color brightness is due to the quantum confinement effect. Small particles undergo an electron change from continuous to discrete as a result of increased bandgap energy which causes colors to become more transparent [12]. The smaller the particles produced, the lower the brightness of the sample [13]. The effect also affects the redness of the sample, the greater the effect, the lower the redness of the sample.

4.4 SEM-EDX

A result of SEM characterization, the resulting size distribution is not uniform with diverse morphology of particle. Increased sonication time causes the agglomeration of particles to increase that is caused by the energy irradiated from sonication in the sample. High energy causes unstable particles and to stabilize the complex to form aggregates. Table 3 displays the particle sizes produced through the ImageJ program. The results show that the longer the sonication time, the smaller the particle size produced. This is due to the ultrasonic waves irradiated on the sample which causes the particles to collide with each other thereby reducing the size of the particles.

The EDX test results showed the synthesized hematite compound still contained impurities in the form of carbon. Carbon is derived from iron lathe waste that has a higher melting point (3652 °C) than the synthesis temperature used so that it cannot be removed during the synthesis process.

4.5 Application of pigments in wood

The results of the control wood (A') and wood (B') surface after swelling test have undergone peeling, but the surface of wood (C', D', and E') shows that the surface smooth. Figure 6.1 shows that control wood experiences the highest volume increase compared to wood pigmented with hematite. Wood coated with hematite pigment experiences a lower volume increase than control wood and wood coated with shellac (resin). The higher amount of pigment causes a volume of wood to decreased. This indicates that the hematite pigment has anti-swelling properties in wood.

Base on the analysis result (Figure 6), the highest swelling levels in wood without pigment and the high stability of wood has a high percent of anti-swelling efficiency (ASE) with hematite pigment amount 30 mg. The high percentage of anti-swelling produced has a high hiding power of the pigment in maintaining the dimensions of wood. The decrease swelling of wood is caused by the hiding properties of the pigment which is able to close the pores of wood and formation cross-links. The formation of cross-links occurs due to interactions between OH cellulose groups with Fe in hematite pigments which cause wood structure becomes

rigid thereby reducing the active group that is able to bind free OH in the air [14].

5. CONCLUSIONS

Hematite pigments were synthesized from iron lathe waste using the precipitation-sonication method were obtained a rhombohedral structure. The highest crystallinity was found in samples with sonication for 90 minutes. The morphology obtained varied with the smallest particle size in the sample with 90 minutes sonication (71.782 nm). Increased sonication time gives a higher level of agglomeration. The results of the synthesis still contain carbon impurities. The best anti-swelling properties were found in hematite wood as much as 30 mg.

6. ACKNOWLEDGMENTS

Thank you to Mrs. Lilik Miftahul Khoiroh, M.Si., as the supervisor of this paper and the parties concerned so that we can complete this paper.

7. REFERENCES

[1] KHOIROH, L. M., MARDIANA, D., SABARUDIN, A., *et al*., "Synthesis of Hematite Pigments (α-Fe_2O_3) by Thermal Transformations of FeOOH", *Journal Pure Application of Chemistry*, v. 2, n. 1, pp. 27–34, Apr. 2013.

[2] RAHMAN, T. P., SUKARTO, A., ROCHMAN, N. T., *et al*., "Sintesis Pigmen Besi Oksida Berbahan Baku Limbah Industri Baja (Mill Scale)", *Fisika Lembaga Ilmu Pengetahuan Indonesia*, v. 3, pp. 86–89, 2013.

[3] TADIĆ, M., ĈITAKOVIC, N., PANJAN, M., *et al., "*Synthesis, morphology, microstructure and magnetic properties of hematite submicron particles", *Journal of Alloys and Compounds*, v. 509, pp. 7639-7644, 2011.

[4] VUJTEK, M., ZBORIL, R., KUBINEK, R., *et al*., "Ultrafine Particles of Iron (III) Oxides by View of AFM–Novel Route for Study of Polymorphism in Nano-World", *Science, Technology and Education of Microscopy*, v. 1, pp. 1–8, 2003.

[5] KHALIL, M., YU, J., LIU, N., LEE, R. L., "Hydrothermal synthesis, characterization , and growth mechanism of hematite nanoparticles", *Journal Nanoparticle Res.*,n. 16, pp. 2362, March. 2014.

[6] LEGODI, M. A., WAAL, D. D, "The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste", *Dyes and Pigments*, v. 74, pp. 161-168, 2007.

[7] SEPTITYANA, K. D., ROCHMAN, N. T., PRASTYO, T., *et al., "*Sintesis dan karakterisasi pigmen hematit (α- Fe_2O_3) dari bijih besi alam melalui metode presipitasi", *Youngster Physics Journal*, v. 1, n. 4, pp. 95–100, Jul. 2013.

[8] ABDULKADIR, I., ALIYU, A. B., "Some wet routes for synthesis of hematite nanostructures", *African Journal of Pure and Applied Chemistry*, v. 7, n. 3, pp. 114-121, March. 2013.

[9] DELMIFIANA, B., ASTUTI., "Pengaruh Sonikasi Terhadap Struktur dan Morfologi Nanopartikel Magnetik yang Disintesi dengan Metode Kopresipitasi*", Jurnal Fisika FMIPA Universitas Andalas*, v. 2, n. 3, pp. 2011–2014, Jul. 2013.

[10] KATSUKI, H., "Role of α- Fe_2O_3 Morphology on the Color of Red Pigment for Porcelain", *Communication of the American Ceramic Socety*, v. 86, n. 1, pp. 183–185, Jan. 2003.

[11] ZHANG, Z., DU, H., WANG, W., WANG, Q., "Property changes of wood-fiber/HDPE composites colored by iron oxide pigments after accelerated UV weathering", *Journal of Forestry Research*, v. 21, n. 1, pp. 59–62, 2010.

[12] SHEVELL, S.K., *The Science of Color*, ELSEVIER: Departements of Psychology and Ophthalmology & Visual Science University of Chicago, 2003.

[13] CORNELL, R. M., AND SCHWERTMANN, U. *The iron oxides: structure, properties, reactions, occurrences, and uses*, 2 ed., Weinheim, Wiley-VCH, 2003.

[14] SOBIRIN, M., FITRIAWAN, M., ZANNAH, R., *et al., "*Sintesis dan Karakterisasi Pigmen Nano Hematit dari Limbah Baja (mill scale) dengan Metode laux", In: *Seminar Nasional Mahasiswa Fisika*, v. 2, pp. 2–5, Dec. 2015.

APPENDIX

Swelling test result

Day	Type	S*welling* average volume (cm^3)			*Anti-swelling Efficiency* (ASE) %	*% Swelling*
		Before	After	difference		
2	Control	0.47774	0.521865	0.044125		9.236169
	Shellac	0.452249	0.483147	0.030899	29.97402	6.832278
	10 mg	0.44420	0.472525	0.028325	35.80718	6.376632
	20 mg	0.501748	0.527748	0.026	41.07632	5.181884
	30 mg	0.447986	0.464754	0.0169769	61.99706	3.743146
4	Control	0.470586	0.518028	0.047442		10.08152
	Shellac	0.467234	0.49928	0.032046	32.45252	6.858669
	10 mg	0.480764	0.5123	0.0315365	33.52646	6.55967
	20 mg	0.482119	0.50843	0.026311	44.54039	5.457421
	30 mg	0.526726	0.5475	0.020775	56.21091	3.944085
6	Control	0.473768	0.524322	0.050554		10.67054
	Shellac	0.489824	0.52494	0.035116	30.53787	7.169024
	10 mg	0.441412	0.477138	0.029782062	41.08818	6.746999
	20 mg	0.43995	0.468573	0.028623	43.38091	6.505967
	30 mg	0.464001	0.489938	0.025937	48.69334	5.589939
8	Control	0.497116	0.550949	0.053833		10.829
	Shellac	0.526113	0.56604	0.039926	25.83232	7.588959
	10 mg	0.455346	0.485833	0.03048675	43.36765	6.69529
	20 mg	0.439638	0.468761	0.029124	45.90003	6.624431
	30 mg	0.473924	0.501887	0.027963	48.05578	5.90031