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RESEARCH ARTICLE

EFFECTS OF PROCESS PARAMETERS ON Fe_2O_3/α-AL_2O_3 LUSTER PIGMENTS PRODUCED BY PRECIPITATION METHOD

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Abstract

Common known examples of substrate-based pigments are mica/TiO_2 and mica/Fe_2O_3 luster pigments produced using wet chemical methods and gas-phase reaction techniques. Luster coatings, in particular those prepared using iron(III) oxide, come into prominence thanks to their characteristics of good hiding power and weather resistance, to name a few. Mica/Fluorphlogopite/Silica-based luster pigments have certain disadvantages due to following reasons: natural mica contains iron (Fe_2O_3) impurity which imparts a yellow color to the material, synthetic fluorphlogopite is quite expensive compared to natural mica and silica has a high production cost. In addition to these, fragility of mica bases due to their low mechanical strength adversely affects the luster effect. Reaction kinetics control is easier in wet chemical methods than in gas-phase reaction techniques since the coarse substrate particles can be kept suspended more easily by stirring. In this study, α-Al_2O_3/Fe_2O_3 luster pigments were produced using the wet chemical method/precipitation method by preferring plate-like alumina substrates in order to eliminate the afore-said problems. The pigments produced were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX) methods and color analysis was performed. As a result, it was determined that the increase in titration flow rate and stirring rate in the production process of Fe_2O_3/α-Al_2O_3 luster pigment using the wet chemical method had no effect on the crystal structure of the resulting coating. However, while the stirring rate does not have a significant effect on the quality of coating, the increase in titration flow rate adversely affects the quality of coating.

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Introduction:-

Luster pigments are a special group of pigments which reflect different colors based on the observation angle of the observer. They are frequently used in consumer markets, particularly in textile, cosmetics, automotive, construction and food industries. This pigment group is obtained with the production of different layers of metal oxide coatings (TiO_2, Fe_2O_3 etc.) on various substrates (mica, silica and α-Al_2O_3 etc.). Iron oxide-mica luster pigments are produced as a result of the calcination process, following the precipitation of iron (II) or iron (III) ions on the mica substrate in the aqueous solution. This pigment type, which has a good hiding power, is also water resistant. Fe_2O_3/mica pigments can also be produced by oxidizing the iron pentacarbonyl ($Fe(CO)_5$) compound and depositing it as Fe_2O_3 on the surface of the mica substrate using fluidized bed-chemical vapor deposition (CVD) method[1]. Another group of luster pigments containing iron oxide coating are silica-based Fe_2O_3 pigments which are produced by the precipitation of the hydrated iron oxide on transparent SiO_2 flakes[2]. Pfaff and Reynders stated in their literature review consisting of a compilation of the studies on luster pigments, that plate-like alumina substrates are more suitable for the production of luster pigments compared to mica, synthetic fluorphlogopite and SiO_2 etc. substrates. One of the main obstacles limiting the use of mica substrates is that the natural mica contains as little as 1-2% iron oxide (Fe_2O_3) which leads to the formation of yellow color. Furthermore, when mica-based Fe_2O_3 pigments are produced using the hydrothermal method in an alkaline environment, this leads to the formation of a matte black color which is an unfavorable condition in luster pigment applications. Modifications adapted to the production method in order to render the product appealing lead to delays and cost losses[3]. Another factor that restricts the use of mica substrates is the weak bond between the Fe_2O_3 coating and the mica base and the spalling of the coating from the surface due to external factors, particularly in plastic surface applications[4]. Although synthetic fluorphlogopite does not contain iron impurity, it is a quite expensive material compared to natural mica. On the other hand, SiO_2 has a high production cost. For all these reasons, alumina substrates stand out in material selection. The study conducted by Pfaff et al. revealed that the most important factor that can restrict the use of alumina substrates is the production method and it has been stated that the alumina substrates produced using molten salt synthesis method are quite suitable for the production of luster pigments thanks to advantages such as the ability to control thickness and produce alumina platelets in uniform thickness[3].

In the patent developed by Armanini et al., a $FeCl_3$ solution was prepared and added to a mica suspension to produce a $Fe(OH)_3$ coating on mica platelets at a specific pH value and the resulting $Fe(OH)_3$ layer was transformed into a crystal hematite coating with the use of an additional heat treatment step[4]. In the study conducted by Stengl et al., various mica-metal oxide pigments were produced by coating mica substrates with oxide-hydroxide forms of different metals such as Ti, Cr, Fe, Al, Co, Ni, Zn and Cu. Homogeneous precipitation method was used for the production of pigments and the final colors of the pigments produced were obtained by heat treatment of the precipitates at 150-800°C[5]. In their study, Tohidifar et al., performed an optimization process using the response surface methodology (RSM) technique to control the factors that affect the production process considering the fact that the desired luster effect cannot be achieved if the coating layer obtained in the production of mica-hematite (α-Fe_2O_3/mica) pigments is not uniform. In this study, optimum values were determined for effective process parameters such as reaction temperature, synthesis time and urea concentration of mica-hematite pigments produced using hydrolysis method and the desired luster effect was achieved in the finished product[6]. Hosseini-Zori produced nano-encapsulated iron oxide in zirconium oxide-coated mica pigments using the homogeneous precipitation method[7].

As can be seen in the studies outlined above, there exists an extensive literature on the production of Fe_2O_3/mica luster pigments, whereas studies on the production of Fe_2O_3/α-Al_2O_3 pigments are rather limited. Similar to the suggestion of Armanini et al., Franz et al. stated that structures obtained by coating the plate-like mica substrates with oxides such as Al_2O_3 etc. could be used as plate-like substrate derivatives[8]. Using the fluidized bed method, a gas-phase reaction technique, Ostertag produced Fe_2O_3/aluminum pigments from the metal platelet-based iron oxide pigments, a different subgroup of luster pigments[9]. Meanwhile, Nitta et al. coated plate-like α-Al_2O_3 powders with TiO_2 and Fe_2O_3 using the wet chemical method[10]. Apart from this study, no publications on the production of Fe_2O_3/α-Al_2O_3 pigments by precipitation, especially by means of the wet chemical method have been found in the current literature. Also, there is no up-to-date publication available that establishes a cause and effect relation between process parameters and final coating properties. Current studies have focused on the development of nanocomposite Fe-(Al_2O_3) materials in different pigment groups, such as core-shell pigments. For example; in their studies on nanoparticle pigment production, Mehdikhani and Borhani added Fe-Cr-Ti in the α-Al_2O_3 matrix using the mechanochemical method for use in ceramic glazes[11]. In both wet chemical and gas-phase reaction methods, the desired coating thickness can be achieved by controlling the coating (reaction) time. In the wet chemical

methods, coarse substrate particles (5-30 μm) can be kept suspended by stirring during the process. Therefore, control of the coating time is much easier in the wet chemical methods than in the gas-phase precipitation methods. Considering this fact, in this study, Fe_2O_3/α-Al_2O_3 luster pigments were produced using the precipitation method, which is a wet chemical method, and the effects of process parameters such as stirring rate, number of washing steps and titration speed on phase composition and coating morphology were studied.

Material and Method:-

In this study, plate-like α-Al_2O_3 powders used as substrate material were produced by the molten salt synthesis method, similar to the procedure applied by Li-hui and Qing-Wei[12]. Technical properties of the platelets produced are given in Table 1.

Table 1:- Technical properties of platelets.

d10 (μm)	4.784
d50 (μm)	18.349
d90 (μm)	57.466
Average Thickness (μm)	2
Specific Surface Area (m^2/g)	1.7

A diluted suspension was obtained by dispersing the substrate platelets in pure water, with a solid content of 25% (w/v %). The obtained suspension was heated to 75°C using a magnetic stirrer with heater, thus the platelet surfaces were activated before the coating process and stirred in order to keep the platelets suspended during the titration process. A 20% iron nitrate ($Fe(NO_3)_3.9H_2O$, Acros, +99%) solution was prepared before the titration process. The iron nitrate solution prepared was taken into a titration burette to be added to the suspension containing the platelets to be coated with the apparatus shown in Figure 1. During the titration process, a 10% NaOH (Sigma-Aldrich, 98-100.5%) solution was used to keep the pH-value constant at 3. The flow diagram outlining the production and characterization steps is given in Figure 1.

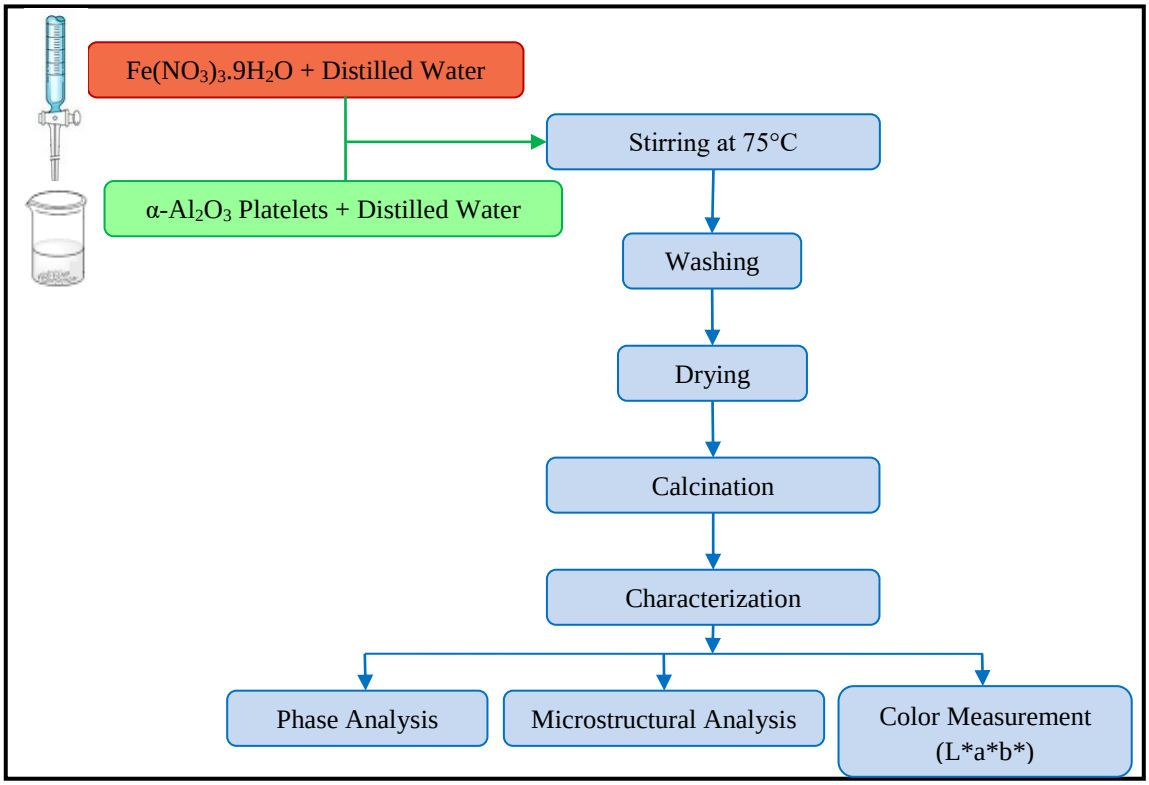

Figure 1:- Production flow chart of Fe_2O_3/α-Al_2O_3 luster pigments.

Since the by-products (such as $NaNO_3$) formed during precipitation can easily dissolve in water, they are removed by simple washing processes (redispersion/centrifugation, filtration etc.)[13–16]. In this study, 3 washing steps were performed to remove salts. Washing process basically consists of two steps. In the first step, luster pigment samples mixed with 175 ml of pure water, were stirred for 10 minutes in a magnetic stirrer which was heated to 75°C. Following the stirring step, the suspensions were centrifuged in a NF 1200 model Nüve benchtop centrifuge device for 10 minutes at 4500 rpm. In order to determine the boundary values of the process parameters, the trials shown in Table 2 were performed.

The precipitates obtained by centrifugation were dried in a drying-oven at 40°C. It was observed that the drying process carried out at 40°C did not cause any deformation on the coated platelets. In the drying processes carried out above 40°C, it was determined that the products developed a structural deterioration (a partial combustion reaction occurred); therefore, the optimum temperature for the drying process was set at 40°C. The coated platelets were heat treated at 900°C for 2 hours with a heating rate of 5°/min in a laboratory scale chest-type oven in order to obtain the final coating phase (hematite, α-Fe_2O_3), and thus the production process of luster pigments was completed.

Table 2:- Process parameter values of experiments.

Experiment No	Stirring Rate (rpm)	Titration/Flow Rate (ml/min)	Number of Washing Steps for Pigments
Pigment-1 (P1)	250	0.05	3
Pigment-2 (P2)	250	0.25	3
Pigment-3 (P3)	250	0.5	3
Pigment-4 (P4)	250	1	3
Pigment-5 (P5)	400	0.05	3
Pigment-6 (P6)	400	0.25	3
Pigment-7 (P7)	400	0.5	3
Pigment-8 (P8)	400	1	3

The crystal phases formed in the luster pigments produced were identified with the Rigaku Rint 2000 model XRD (X-Ray Diffractometer) device with $CuK_{\alpha 1}$ radiation (λ=1.54056 Å) at a scan rate of 2°/min. The patterns obtained were compared with those in the JCPDS-ICDD index and phase analyzes of the luster pigments were completed. Microstructure studies and elemental analyzes of the luster pigments produced were performed in FEI Nova Nano 650 model scanning electron microscope (SEM) equipped with EDAX energy-dispersive X-ray spectrophotometer (EDX). All samples were coated with a thin layer of gold film to ensure the surface conductivity of the non-conductive ceramic material. In microstructure studies, images were taken with secondary electrons (SE). Color measurements of luster pigments were performed with Konica Minolta CM-2300d model portable spectrophotometer.

Results and Discussion:-

In Figure 2, XRD pattern and microstructure image of α-Al_2O_3 platelets produced by the molten salt method is given. Platelets with different thickness values that crystallize in the Corundum (α-Al_2O_3, JCPDS-ICDD: 10-0173) phase exhibit a hexagonal morphology.

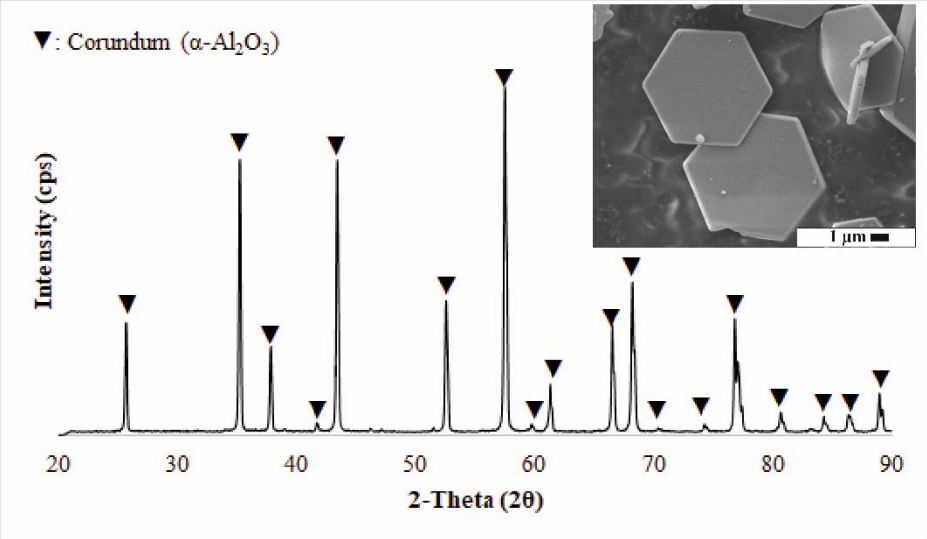

Figure 2:- XRD pattern and microstructure image of the platelets used as substrates.

When the $Fe(NO_3)_3$ solution prepared during the precipitation process is added to the suspension in which the substrates were dispersed, the reactions given in Equation 1 and Equation 2 occur.

$Fe(NO_3)_3.9H_2O \rightarrow Fe(NO_3)_3+9H_2O$ (Equation 1)

$Fe(NO_3)_3+3NaOH \rightarrow Fe(OH)_3+3NaNO_3$ (Equation 2)

XRD patterns of the calcined luster pigments are given in Figure 4 - Figure 7. The presence of hematite (α-Fe_2O_3, JCPDS-ICDD: 33-0664) and corundum (α-Al_2O_3, JCPDS-ICDD: 10-0173) phases were detected in all samples. In Equation 2, the iron (III) hydroxide ($Fe(OH)_3$) compound, which precipitates on the α-Al_2O_3 substrate surfaces, transforms into hematite (α-Fe_2O_3) phase after calcination. The inclination angle increasing towards right in XRD patterns of pigments is due to the fluorescence property of the Fe element. In earlier phase analysis studies conducted by different researchers on samples containing iron, it was stated that the high noise background observed in XRD patterns was caused by the fluorescence effect, and that this effect could be eliminated with applications such as the use of monochromators. However, it was underlined that these applications would bring along disadvantages such as loss of peak intensity and low penetration depth[17].

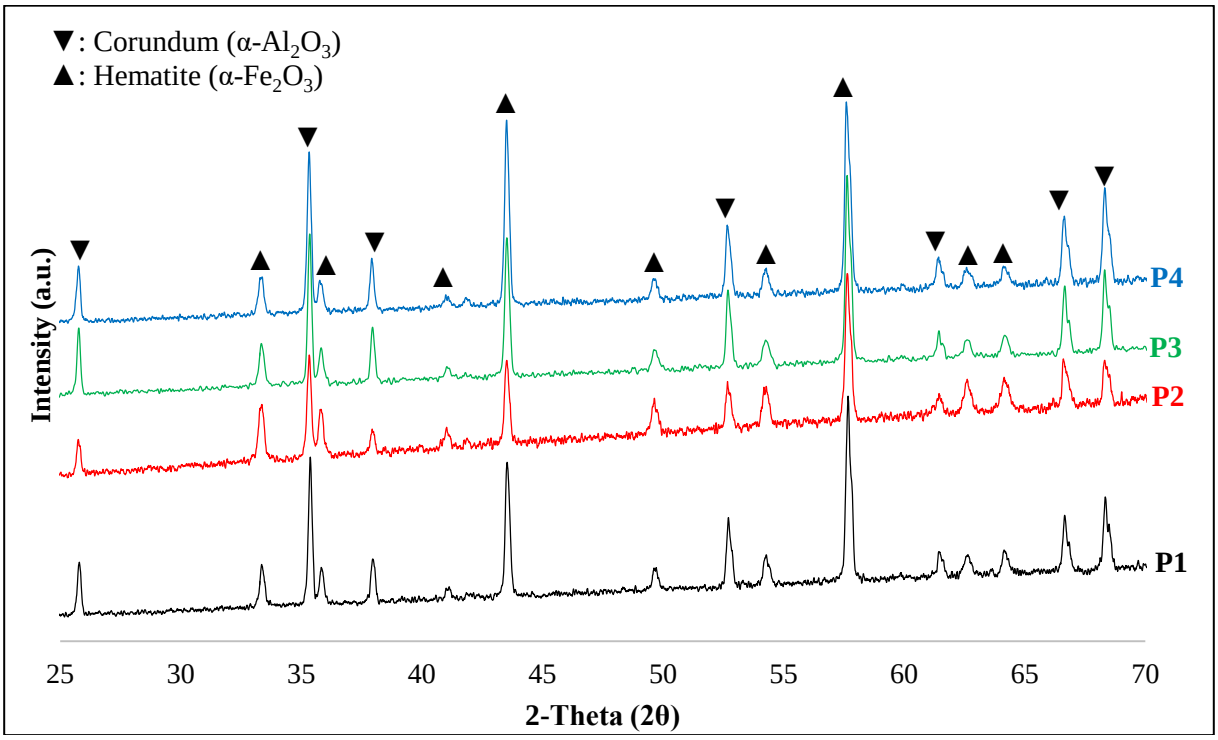

Figure 3. XRD patterns of the calcined luster pigments (P1-P4).

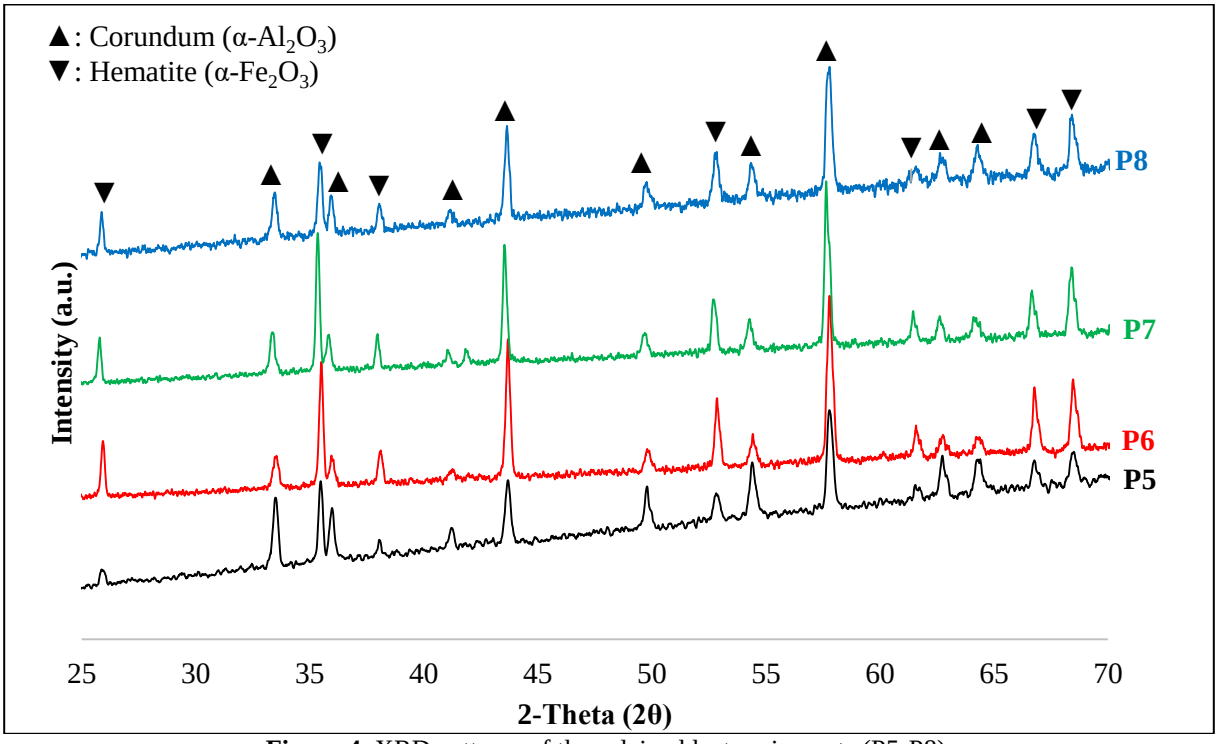

Figure 4. XRD patterns of the calcined luster pigments (P5-P8).

Microstructure images of selected pigments are given in Figure 7. In these images, the coatings formed on the platelet surfaces can be seen clearly and the discontinuous structure of the coating layer especially at high flow rates (P4 and P8) is noteworthy. In other words, titration flow rate increase makes the coating difficult to produce and/or

adversely affects the coating quality (P4 and P8 in Figure 7). As the increasing titration flow rate shortens the titration time, the suspension time of the platelets decreases and therefore the coating density and quality on the platelet surface decreases as well. On the other hand, there was no significant effect of stirring rate increase on coating quality/thickness and continuity (P1 and P5 in Figure 7). Moreover, upon the examination of microstructure images, it can be seen that if the titration rate is increased (e.g. P1 and P4), the boundary value necessary for the heterogeneous nucleation of iron(III) hydroxide on platelet surfaces is exceeded during the precipitation process and in certain areas homogeneous nucleated iron(III) hydroxide forms agglomerates on the alumina platelet. The results of the EDX (Figure 8) applied to the coated areas of the platelets given in Figure 7 confirm that the coating developed on the substrate surfaces is Fe_2O_3 which supports the XRD results. Since EDX results are similar to each other, only the result of the EDX analysis applied to the P5-coded luster pigment is given in Figure 8. The aluminum (Al), oxygen (O), iron (Fe) peaks seen in the EDX results are based on the coating phase and the substrate material, while the gold (Au) peak is based on the layer of gold film coated on the surface of the sample.

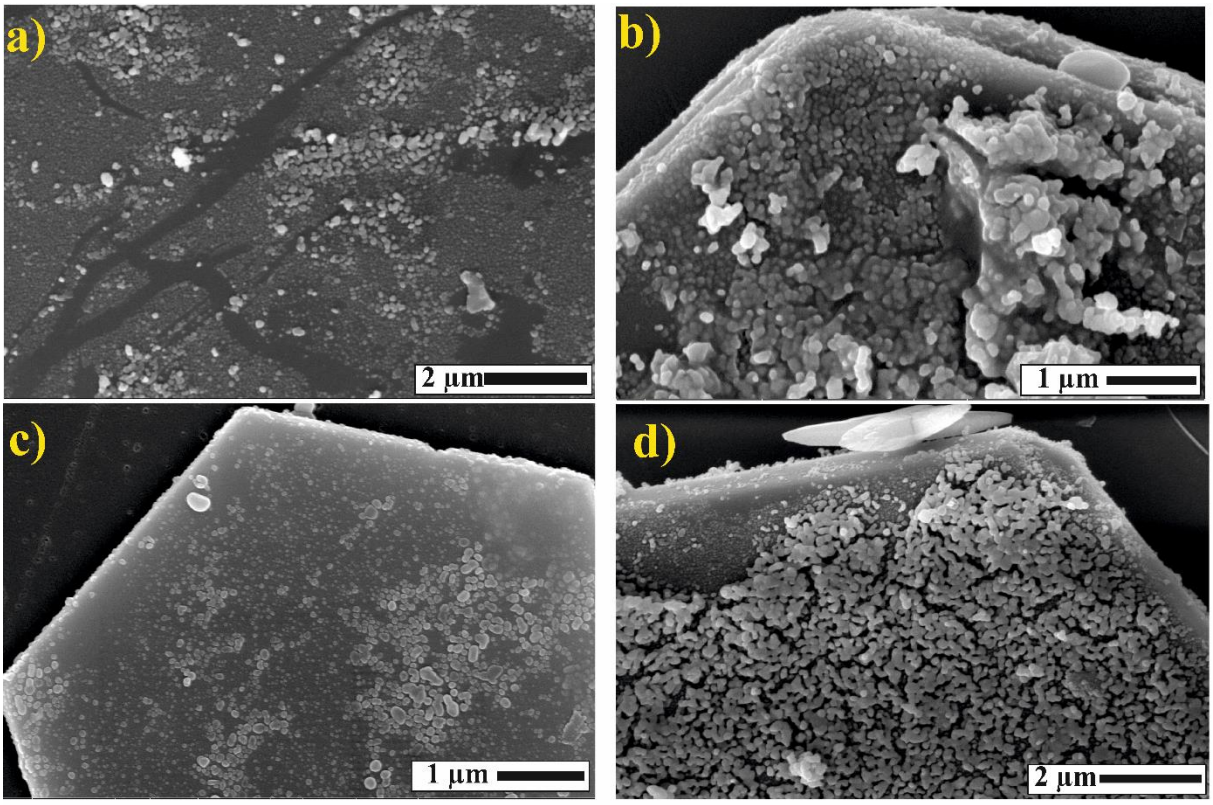

Figure 7:- Microstructure images of pigments; a) P1, b) P4, c) P5 and d) P8.

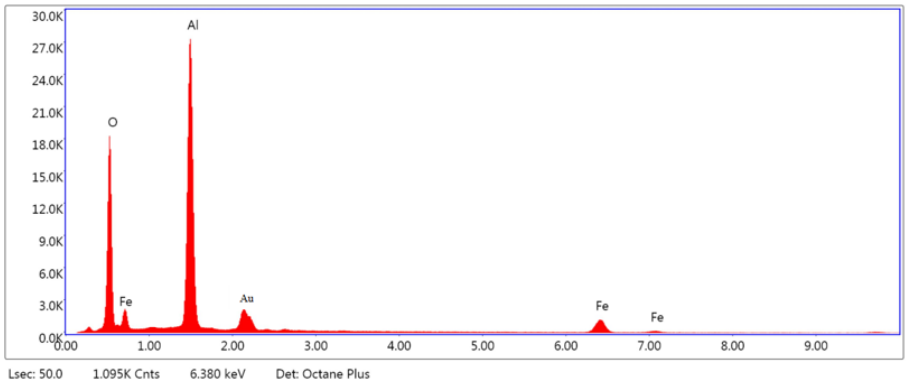

Figure 8:- The result of the EDX analysis applied to the coated area of the platelet in Figure 7c.

The high magnified microstructure image of P5-coded pigment produced at low titration flow rate is given in Figure 9. When this microstructure image is examined, the hematite grains coated on the alumina platelet can be seen clearly.

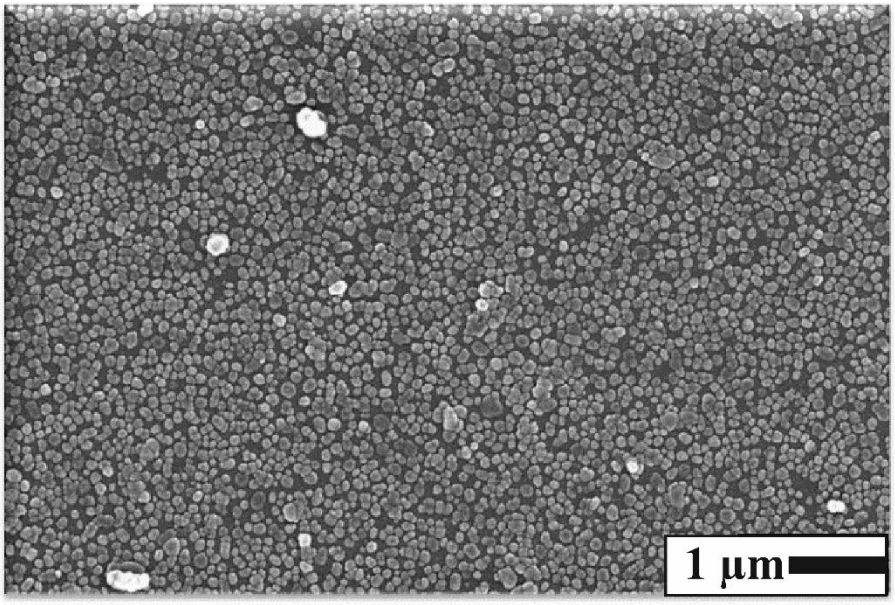

Figure 9:- Microstructure image of P5-coded pigment.

Depending on the light's angle of incidence, the thickness of the coating and the diffraction index of the coating, the coating on the pigment creates a phase difference between two light waves reflected from the coating and the substrate for a specific wavelength, and the related wavelength is absorbed when the appropriate phase difference is achieved[3,18]. The phase difference affecting the interference is related to the coating thickness and the diffraction index of the coating from a stationary observer angle. Therefore, control of both parameters is extremely important in order to achieve the desired luster effect. For mica substrates coated with hematite with a high diffraction index value of 2.9 on the Hunter scale, a 75 nm-thick coating corresponds to bronze and an 85-nm-thick coating corresponds to red from a stationary observer angle[19]. The results of L*a*b* analysis applied to the pigments obtained in this study are given in Table 2. The lightness coordinate is defined as (L*) and has a value ranging from 0-100 where 100 represents white while 0 represents black. A positive increase in the red/green coordinate (a*) indicates that the red color intensifies, and a negative increase indicates that the green color increases. The yellow/blue contrast indicated by b* refers to yellow in negative values and blue in positive values. Based on this information, by taking into consideration that iron oxide is a pigment that gives red color (and its derivatives: copper, bronze etc.), a correlation can be assumed to exist between the changing a* value and the coating thickness and/or density. In the study, a* value increased particularly in the samples where the flow rate decreased gradually (P4-P1, P8-P5). When reviewed with the microstructure analysis results, this evaluation supports the finding that denser/more continuous coatings can be obtained at low flow rates. A linear relation could not be established between the stirring rate and a* values.

Table 3:- Color analysis results.

No	L*	a*	b*
P1	38.42	29.35	26.05
P2	35.35	28.27	19.79
P3	40.30	27.89	25.30
P4	40.78	23.65	25.14
P5	31.79	28.55	14.91
P6	35.10	24.79	19.61
P7	37.26	24.31	20.58
P8	45.85	21.14	29.22

Conclusion:-

In this study which aims to analyze the effects of process parameters on Fe_2O_3/α-Al_2O_3 luster pigment properties, α-Al_2O_3 platelets produced by the molten salt method were coated with hematite (α-Fe_2O_3) using the precipitation method and in this way copper-bronze Fe_2O_3/α-Al_2O_3 luster pigments were produced. After the precipitation process, it was understood that the samples should have been washed at least three times in order to remove residual salts from the structure. It was determined that in the production process of pigments, increase in the titration flow rate and the stirring rate had no effect on the crystal structure of the resulting coating. However, while the stirring rate does not have a significant effect on the quality of coating, the increase in titration flow rate adversely affects the quality of coating. Therefore, in Fe_2O_3/α-Al_2O_3 luster pigment production by the wet chemical method, low titration flow rates should be used. More precise data may be provided about the coating thickness with the cross sectional images obtained by deforming the platelets using the techniques such as SEM-FIB in a controlled way and with an experiment apparatus modified to operate more precisely (in terms of the titration flow rate). In addition, a more detailed interpretation of the luster pigment quality can be introduced following a color analysis process to be performed with a gonio spectrometer device.

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