Obtaining and painting properties of red iron oxide pigment from spent pickling solutions

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Abstract. A technique has been developed for producing iron oxide pigment based on galvanic waste. The effect of the norm, concentration and nature of the precipitant, temperature and time on the deposition of Fe(OH)₃ was studied. To determine the effect of the nature of the neutralizer on the phase composition of the pigments, an X-ray phase and thermogravimetric analysis was carried out. It was established that the main phase is Ca₂Fe₂O₅, and β-Ca₂SiO₄ is present as an impurity. The basic physicochemical properties of the obtained pigment were studied.

1. Introduction

Today, iron oxides are one of the most widespread powder materials that are used in various industries in the production of pigments and fillers, information carriers, catalysts, sorbents, etc. [1-7]. There are various methods of obtaining iron oxides [8-11], including from the waste of various industries [12,13], which is currently, when the whole world pays special attention to the problem of processing waste and secondary raw materials, is very important.

In the last ten years, environmentally friendly coating technologies have appeared. However, galvanic production is still relevant, in which it is impossible to refuse electrolysis and pickling. Each of these processes requires not only modern equipment for production and energy consumption, but also careful disposal of galvanic production wastes, since often these wastes are chemically quite aggressive and toxic.

The possibility of obtaining pigments from hydrochloric acid etching solutions containing iron chloride by the thermal method was previously shown [14]. However, the pigment obtained in this way, as a rule, has increased hardness and, in addition, very high particle aggregates are formed during high-temperature processing, which complicates the grinding process.

2. Results and discussion

We have investigated the possibility of obtaining a red iron oxide pigment from the spent solution formed during the etching of printed circuit boards by the sediment-calcining method. Marble dust, ammonia, soda ash were used as a neutralizer. For comparison, we studied the optimal deposition parameters of Fe (III) in model systems FeCl₃-CaCO₃-H₂O и FeCl₃-NH₄OH-H₂O.

An analysis of the data obtained showed that in model and real systems the best neutralizer is ammonia and that the norm of the neutralizer is the main factor affecting the completeness of Fe (III) deposition.

A study of the filterability of suspensions formed during the neutralization of spent pickling solution (SPS) by marble dust, soda, and ammonia showed that the filtration performance of iron (III) hydroxide by dry sediment is 4.83 times higher than in the second and 6.08 times higher than in the third. The filtration performance of the filtrate in the first case is 1.63 tons 2.34 times greater than in the second and third, respectively. The specific resistance of the sediment in the first case is 3,1·10¹⁵ м², and in the second and third case, respectively, 8,6·10¹⁵ and 12,9·10¹⁵ см², i.e. more than 2.8 and 4.1 times, and the filtration rate,
respectively, less than in the first case, 1.8 and 2.5 times. Such a big difference in the filtration rate between the suspensions obtained by neutralizing SPS with marble dust, soda and ammonia is explained by the presence of an undecomposed part of the marble dust in the first suspension and, accordingly, an increase in the concentration of the suspension, which leads to the formation of a precipitate with larger pores and lower resistivity.

The study of the physicochemical and painting properties of the pigments obtained from SPS showed that the synthesized pigments are not inferior to the K-2 brand pigment by the main characteristics (Table 1). The exception is the pigment of sample 1, which contains a certain amount of marble dust, however, there is evidence of using calcium carbonate as a filler to increase the protective properties of paint coatings and to obtain lighter weather-resistant coatings.

Table 1. Physico-chemical characteristics of iron oxide pigments obtained from etching solutions.

| The name of indicators                  | Pigment sample | Red iron oxide pigment |
|----------------------------------------|----------------|------------------------|
|                                        | 1   | 2   | 3   |              |                  |
| FeO₃ content % of mass                 | 51,5| 88,3| 91,0| 89,0         |                  |
| The content of water-soluble salts, %  | 1,15| 0,66| 0,35| 1,00         |                  |
| The moisture content, % of the mass    | 0,70| 0,40| 0,20| 1,00         |                  |
| pH of the aqueous extract              | 6,80| 6,90| 6,90| 6,00         |                  |
| suspension pH                          | 7,30| 7,00| 6,90| 7,00         |                  |
| Spreading in terms of dry pigment, g/m²| 13,50| 8,00| 6,80| 8,00         |                  |
| Oil absorption in grams of oil per 100 g of pigment | 30,2| 36,9| 29,0| 40,0         |                  |
| Density, kg/m³                         | 3160| 4800| 4950| 4900         |                  |
| Specific surface, m²/g                 | 0,4 | 12,6| 27,5| -            |                  |
| Bulk weight, kg/m³                     | 1147| 914 | 1217| 1500         |                  |
| Bulk volume, l/kg                      | 0,87| 1,09| 0,82| -            |                  |
| Volume after manual shaking, l/kg      | 0,78| 0,87| 0,73| -            |                  |
| Mass loss on ignition, % mass          | 26,16| 3,16| 2,58| -            |                  |

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X-ray phase (Figure 1) and thermogravimetric (TG) analysis was performed. From the analysis of the diffraction patterns it follows that samples 2 (Figure 1b) and 3 (Figure 1c) are almost identical in composition and content: the main phase is α Fe₂O₃ hematite. Sample 1 is more complex (Figure 1a). The main phases of these samples are α-Fe₂O₃ hematite and CaCO₃ - calcite, in addition to the above phases, the maxima related to α-SiO₂ - quartz and CaCO₃·Cu(OH)₂ are noted in the diffractogram of sample 1.

To establish the effect of the nature of the neutralizer on the phase composition of the pigments, an Differential thermal analysis (DTA) shows (Figure 2) that the general appearance of the DTA curve and the TG gravimetric curve for samples 2 (Figure 2b) and 3 (Figure 2c) are quite close, and the derivatogram of pigment 1 differs from samples 2 and 3. As can be seen from the TG curve, mass loss is observed throughout the studied temperature range (40-450°C). For samples 1, 2 and 3, it is 26%, respectively; 5% and 4.4%. Mass loss is associated with the removal of hygroscopic moisture, as well as with the decomposition of compounds present as impurities. Significant weight loss in the range of 530-800°C (sample 1, Figure 2a) is mainly due to the decomposition of CaCO₃.
In addition, it is known that structural water entering Fe(OH)$_3$ is completely removed only at 940°C, i.e. when calcined at 550-600°C, part may remain as an impurity in the pigment. Dehydration is a multi-stage process that occurs in several stages with the formation of iron compounds of different hydration. The products of iron dehydration are X-ray amorphous, which explains the absence of lines in X-ray diffraction patterns. A number of thermal effects in the temperature range 200–400°C, apparently, can be caused by the melting of ammonium chloride impurities and the decomposition of copper and iron carbonates. Sample 1, in addition to α-Fe$_2$O$_3$, contains a rather significant amount of CaCO$_3$. When considering the thermogram of this sample, one should take into account the possibility of a solid-phase reaction between Fe$_2$O$_3$ and CaCO$_3$.

The authors found [15] that in the Fe$_2$O$_3$–CaO system, calcium ferrites CaFe$_2$O$_4$ and Ca$_2$Fe$_2$O$_5$ exist in the temperature range 1000°C and that the formation of ferrite occurs at a temperature above 600°C by the reaction:

\[ \text{CaCO}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{CaFe}_2\text{O}_4 + \text{CO}_2 \]

Taking into account these data, one can explain the complex form of endothermic effects at 612°C. One should also take into account the possibility of polymorphic transformation of α-quartz α-tridyllite at 870°C and the possibility of a reaction between SiO$_2$ and CaO with the formation of silicates. Indeed, an X-ray phase analysis of sample 1, carried out after heating to 1000°C, established that the main phase is Ca$_2$Fe$_2$O$_5$, a β-Ca$_2$SiO$_4$ is present as an impurity.

3. Conclusion

Thus, the results of laboratory studies and pilot tests have shown the possibility of obtaining red iron oxide pigment from spent pickling solutions, which in its performance is not inferior to pigment produced by industry.
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