UDC 620.193:675.046.14
DOI: 10.52957/27821900_2021_02_187

INVESTIGATION OF THE CORROSION PROPERTIES OF PIGMENTS BY THE METHOD OF INTEGRATED THERMAL ANALYSIS

O. P. Filippova, E. S. Sergeyev

Filippova O.P., Doctor of Technical Sciences, Professor; Sergeyev E.S., Magister
Institute of Chemistry and Chemical Technology, Yaroslavl State Technical University, Moskovsky ave., 88, Yaroslavl, Russia, 150023
E-mail: filippovaop@ystu.ru

Keywords:
corrosion, anticorrosive pigment, method of integrated thermal analysis, model mixtures, polarization curves.

The article considers the process of obtaining anticorrosive pigments from high-tonnage galvanic waste by high-temperature treatment of a suspension with different ratios of ferrite-forming components. The integrated thermal analysis was used to study the processes during the heating of the reaction mixture.

Machinery and apparatus made of metals and alloys are corroded when used in natural or technological environments. Corrosion comes from the Latin word «corrodere» - corrode. Metal corrosion is the spontaneous destruction of metals and alloys due to their interaction with the environment. This interaction is based on chemical and electrochemical reactions and sometimes on the mechanical effects of the environment. The ability of metals to resist environmental effects is called corrosion resistance or chemical resistance of a material. The metal being corroded is called the corroding metal and the medium in which the corrosive process takes place is called the corrosive medium. Corrosion changes the properties of metals and often results in a deterioration of their functional properties [1].

Corrosion is a both physical and chemical process. The general laws of thermodynamics and kinetics of heterogeneous systems determine it. There are internal and external corrosion factors. The internal characterize the influence of the nature of the metals (composition, structure, etc.) on the type and rate of corrosion. The external determine the effect of corrosive medium composition and corrosion conditions (temperature, pressure, etc.).

More attention is being paid to obtaining pigments from waste materials with the rising cost of manufacturing corrosion protection pigments from conventional raw materials and the problem of natural resources dwindling. In terms of the fact the raw materials are industrial waste, the choice of conditions for producing the ferritic pigment did not rule out the possible influence of impurity compounds on the reaction described below. To investigate the processes occurring when heating the reaction medium, the method of complex thermal analysis was used [2].

Calcium ferrite is formed by an exchange reaction between iron oxide and calcium oxide at 800–900 °C:

$$CaO + Fe_2O_3 \rightarrow CaFe_2O_4$$

It has been proposed to use large-tonnage galvanic waste - galvanic sludges namely (GS) - to produce corrosion-resistant pigments. Galvanic sludges formed after electro-coagulation and reagent treatment of the waste water of galvanic processes contain iron, calcium hydroxides and the hydroxides of other heavy metals which may influence on the anticorrosion properties of the pigment.

Almost all GS contain zinc and chrome hydroxides. Compounds of these elements are widely used in the manufacture of corrosion-resistant pigments. Chromates are effective corrosion inhibitors. This fact determines the value of the GS components as raw material for obtaining protective coatings of sufficiently high efficiency.

During GS processing the hydroxides are converted to oxides and react with each other at certain temperatures.

The presence and quantity of reaction products is determined by the composition of the GS. It can be assumed that $CaFe_2O_4$, $ZnFe_2O_4$, $CuFe_2O_4$ are calcium, zinc and copper ferrites obtained from the GS calcination and are active anti-corrosion pigments. Therefore, a corrosion protection effect is expected not only from the calcium ferrite formation but also from the zinc and copper ferrite formation [3].

An anti-corrosive pigment is produced from GS by mixing prewashed GS in a suspension with various ratios of ferrite-forming components and calcining it at 900 °C.

Suspension mixing operation in compare with dry mixing results gives more uniform distribution of fine particles, which ensures better conditions for heterogeneous ferritization reactions.

The protective effect of calcium ferrites based on GS is that in the presence of atmospheric humidity, the hydrolysis of the pigment creates a basic environment beneath the paint film, and passivation of the steel surface occurs in the presence of chromate ions [4].

By the tests, it was found that the corrosion rate of steel in the presence of GS pigment was reduced by 94. Calcium ferrite pure components reduces corrosion rate by 11. It is due to the double mechanism of calcium ferrite action on the basis of GS, which is related to the formation of an optimal number of hydroxyl ions.

Thus, the presence of heavy cations in GS not only does not impair the properties of the pigment based on, but also contributes to a significant improvement of its anticorrosion properties.

To research the processes occurring when heating the reaction mixture, the method of integrated thermal analysis was used. Experiments were carried out with a derivatograph OD-3425-1500.

Registration parameters: sample weight 250 mg, heating in the range 20–1100 °C at a heating rate of 15 °C/min. The preparation of the initial charge consisted of mixing the pure ingredients in a mortar and removing the water by drying at 100–110 °C.

The reaction goes in the ferritization process:

$$CaO + Fe_2O_3 \rightarrow CaFe_2O_4$$

The results of the thermal analysis shown in Fig. 1 suggest that three endothermic and one exothermic process are occurring when heating the charge. The first shows vague endothermic effect observed in the temperature range 100–200 °C refers to removal of adsorbed

water; the second one is observed at 450 °C and lead to dehydration of calcium hydroxide; the third one is observed at 676 °C dwells with dissociation of calcium carbonate contained in the calcium-containing waste material. A blurred exothermic effect, starting at 800 °C and continuing up to 1050 °C, corresponds to the formation of ferrite.

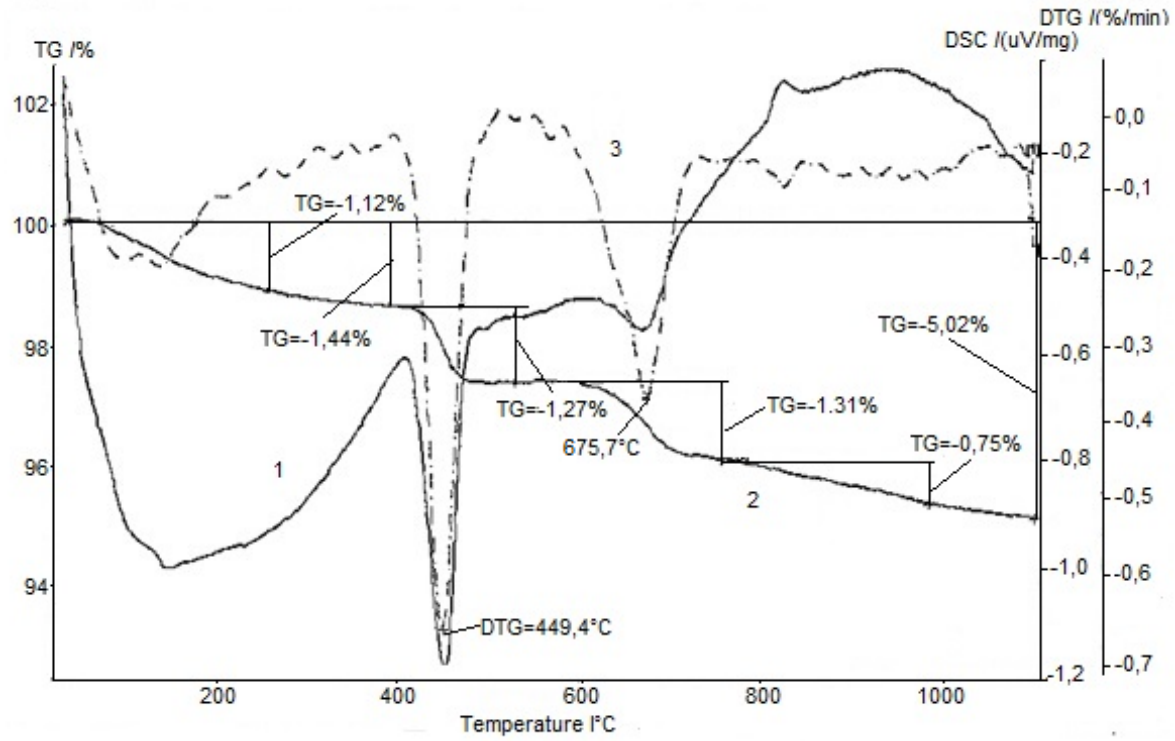

Fig. 1 Results of integrated thermal analysis of the charge:
1 - Differential thermal analysis curve; 2 - Thermal imaging curve; 3 - Differential thermal imaging curve

The results of the thermal analysis were taken into account in the subsequent search for optimum conditions of pigment synthesis [5].

Taking into account the input components are industrial waste, should be considered the possible influence of impurities on the quality of the resulting pigment [6].

Based on the chemical analysis of the galvanic sludge model mixtures of pure components were prepared. We used these models to study the influence of heavy metals on the corrosion-resistant properties of pigments [7].

Thus, we synthesized the following model pigments. Ratio of pure components:

1. Fe_2O_3 :CaO = 1 : 1
2. Fe_2O_3 :CaO : Cr_2O_3 = 1 : 1 : 0,01
3. Fe_2O_3 :CaO : ZnO = 1 : 1 : 0,15
4. Fe_2O_3 :CaO : Cr_2O_3 : ZnO = 1 : 1 : 0,01 : 0,15

We calcified the charge at temperature of 900 °C for an hour.

The samples react between individual oxide in these conditions. Since the main components of the charge are iron and calcium hydroxides, the first reaction will be calcium ferrite one [7]. Since GS is a mixture of hydroxides, there are other reactions that produce zinc ferrite and zinc and calcium chromates, which are currently used as anticorrosion pigments.

$$CaO + Fe_2O_3 \rightarrow CaFe_2O_4$$
$$CaO + Cr_2O_3 \rightarrow CaCr_2O_4$$

$$CaCr_2O_4 + CaO + 1{,}5O_2 \rightarrow 2CaCrO_4$$
$$ZnO + Fe_2O_3 \rightarrow ZnFe_2O_4$$
$$ZnO + Cr_2O_3 + 1{,}5O_2 \rightarrow ZnCrO_4$$

Fig. 2-5 show polarization curves of model pigments No. 1–4.

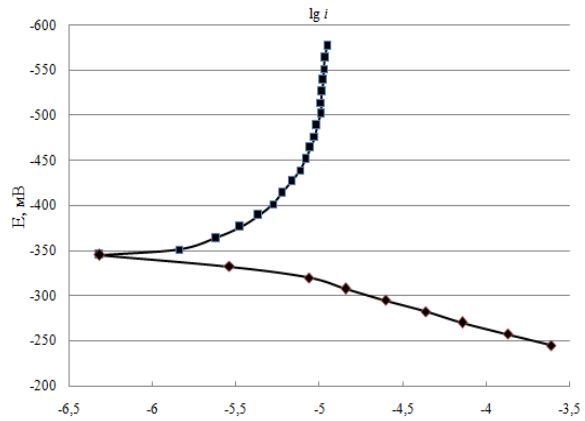

Fig. 2. Polarization curves of model pigment № 1

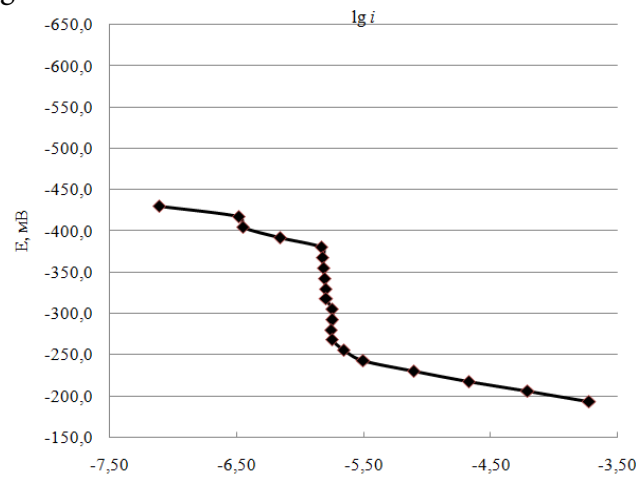

Fig. 3. Polarization curves of model pigment № 2

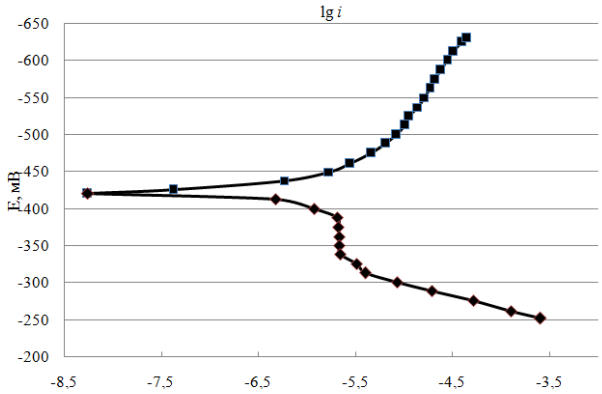

Fig. 4. Polarization curves of model pigment № 3

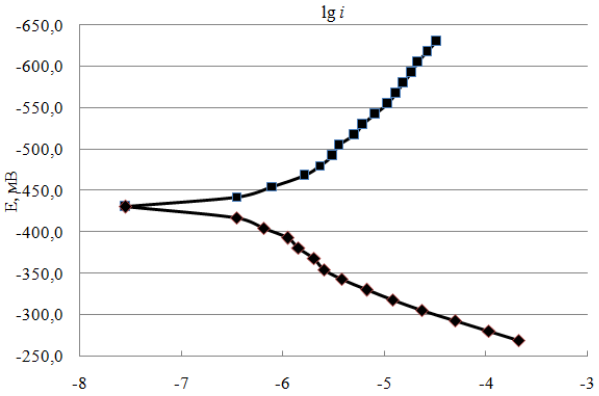

Fig. 5. Polarization curves for model pigment № 4

Corrosion current densities were determined graphically for quantitative analysis. The reduction in corrosion rate compared to background sodium chloride solution (3%) and the pigment efficiency were calculated [7].

The anticorrosion values for the model mixtures are shown in Table 1.

Table 1. The anticorrosion values for the model mixtures

Pigment formula	Corrosion current density, μA/cm²	Reduction ratio Corrosion rate	Efficiency, %
№1	7.31	15.35	93.48
№2	1.56	71.92	98.61
№3	3.16	35.51	97.18
№4	1.51	74.30	98.65

The prepared model mixtures have an anticorrosion activity. The presence of chrome and zinc compounds in the charge enhances the anticorrosive properties of the resulting pigment. Thus, GS can be used as a raw material for anticorrosion pigments preparation [8].

References

1. **Bahvalov G.T., Turkovskaya A.V.** Corrosion and metal protection. M.: Metallurgizdat, 2001. 400 p. (in Russian).
2. **Avdeev Ya.G., Kuznecov Yu.I.** High temperature corrosion of steels in acid solutions. Part 3. Inhibitory protection of steel by nytrogen-containing heterocyclic organic compounds and inorganic oxidants. Review. *Korroziya: materialy, zaschita.* 2021. N 2. P. 1-23. DOI: 10.31044 /1813 -7016-2021-0-2-1-23 (in Russian).
3. **Goncharova O.A., Luchkin A.Yu., Andreev N.N.** Volatile mix corrosion inhibitors of ferrous metals and universal preparations. *Korroziya: materialy, zaschita.* 2021. N 2. P. 33-40. DOI: 10.31044 /1813-7016-2021-0-2-33-40 (in Russian).
4. **Ziber M., Loautner S., Fasbender F.** Test method and device for evaluation of effective volatile corrosion inhibitors. *Korroziya: materialy, zaschita.* 2021. N 2. P. 41-48. DOI: 10.31044/1813-7016-2021-0-2-41-48 (in Russian).
5. **Bahterev V.V.** A comprehensive thermal analysis of the samples of brucite. *Ural'skij geofizicheskij vestnik*. 2018. N 1(31). P. 15-23. DOI: 10.25698/UGV.2018.1.2.15 (in Russian).
6. **Kozlova L.S., Sibileva S.B., Chesnokov D.V., Kutyrev A.E.** Corrosion inhibitors (review). *Aviacionnye materialy i tekhnologii*. 2015. N 2 (35). P. 67-65. DOI: 10/18577/2071 -9140-2015-0-2-67-75 (in Russian).
7. **Babak N.A., Maslennikova L.L., Saharova A.S., Surkov V.N.** Development of chemical classification signs of mineral waste for recycling. *Bashkirskij himicheskij zhurnal.* 2020. T. 27. N 3. P. 116-122. DOI: 10.17122/bcj-2020 -3-116 -122 (in Russian).
8. **Aubakirova I.U.** Use of sludge from water treatment plants in the production of building materials. *Voda i ekologiya: problemy i resheniya.* 2020. N 4(84). P. 32-37. DOI: 10.23968 /2305 -3488. 2020.25.4. 32-37 (in Russian).

Received 12.03.2021
Accepted 23.04.2021