

# ANTICORROSION PROPERTIES OF MANGANESE-CONTAINING COMPLEX OXIDES, OBTAINED BY THE CALCINATION METHOD

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## Introduction

The steady increase in the number of objects made of carbon steel, highly vulnerable to corrosion combined with the increased aggressive environmental impact caused by the development of industrial plants generating waste that has a damaging effect on various materials, make it obvious that this process should be counteracted. The most common way to protect steel objects from environmental corrosive effects is dyeing. The coatings applied to the surface of various substrates are usually multi-layered and the first pre-coating layer has the main protective load. Anti-corrosive effectiveness of primers is provided by including of inhibiting pigments in their structure.

Compounds containing chromium in the highest degree of oxidation have demonstrated the highest anticorrosive efficiency, among the pigments of this type that have been used until recently. The other side of chromium-containing pigments' high inhibitory ability is ecotoxicity, which is associated with their long-term circulation in the environment. In many industrialized countries, the use of pigments of this type is prohibited at the legislative level (EU Directive 2000/53 / EC allows transport vehicles to be covered with only by two grams of hexavalent chromium). However, despite active searches, it is necessary to state that a complete low-toxic alternative to chromate pigments has not yet been found.

Elemental base analysis for anticorrosive pigments capable of replacing chromates shows that manganese (d-element of the adjacent group of Mendeleev's Periodic System) is close in property to chromium. Like chromium, it can be in different degrees of oxidation and has the ability for complex formation. An important advantage of manganese-containing compounds compared to chromium-containing compounds is significantly lower toxicity. Another advantage of manganese is its high average content in the earth's crust, amounting to  $8,5 \cdot 10^{-2}$  % (mass.). This fact leads to the wide use of its compounds in various fields of science and technology.

One of the areas of search for the replacement of chromate pigments in anti-corrosion coatings is the use of complex metal oxides [1]. It should be admitted that, in spite of the above mentioned, there is unfairly small amount of works related to the use of manganese-containing compounds of this type for anti-corrosion purposes. Manganese compounds are used as pigments (manganese black, umber, manganese brown, manganese blue, manganese violet, manganese green) in paints production, but their main application area is the manufacture of paints and varnishes for decorative purposes [2].

## Experimental

### Syntheses of manganates

The thermoanalytic study of the synthesis was carried out on an OD-3425-1500 derivatograph, in the range of 20-1000 ° C with a heating rate of 15 deg / min.

The process of samples obtaining consisted of the following operations: load preparation, its calcination in a muffle furnace, washing with water, drying at 120 ° C and grinding in a planetary mill.

### Synthesis products' identification

The degree of manganese oxidation in the obtained pigments was determined by the method described in [4].

### X-ray photoelectron spectroscopy method

The samples were studied by X-ray photoelectron spectroscopy on an ES 2401 apparatus using MgK $\alpha$  radiation (1253,6 eV). Vacuum in the spectrometer chamber 10<sup>-6</sup> Pa. The relative error in determining the concentration of elements is  $\pm 3\%$  of the measured value. The results were processed using the CasaXPS licensed program.

### Physicochemical properties the resulting products as pigments.

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Determination of oil absorption according to ISO 787-5-80.

The density of pigments was determined by the pycnometric method according to GOST 21119.5-75.

The mass fraction of substances soluble in water was determined by the method of hot extraction according to ISO 787-3-79.

The reaction of the pigment aqueous extract was determined according to GOST 21119.4-75.

### Methods for testing pigments' anticorrosive properties

The pigments' inhibiting ability was evaluated by the values of the potential and the corrosion current of steel in an aqueous extract containing 3% sodium chloride.

The corrosion potential of steel was measured using a pH-340 potentiometer.

A three-electrode electrochemical cell was used to determine the corrosion current. It was prepared by gluing a hollow glass cylinder with 3 cm inner diameter onto the steel sample surface. The section of steel surface forming the bottom of the resulting glass was used as working electrode. 20 ml of electrolyte was poured in the resulting cell. The platinized platinum auxiliary electrode was lowered into the electrolyte solution. A silver chloride electrode that was placed in Luggin served as the reference electrode.

The electrochemical cell was connected to a PI-50-1 potentiostat with a PR-8 programmer. After the stationary potential had been established the cathode polarization of the steel sample was carried out for 15 min at minus 30 mV. Polarization curves (current versus potential) required for current calculation were recorded in the sphere of slight potential deflections from the stationary value (from minus 30 to 30 mV) using the small linear polarization method. This method guarantees minimal perturbations introduced into the metal dissolution process during electrochemical measurements. The corrosion current according to the results of polarization measurements was calculated using a computer program based on the Stern - Geary equation solving [5, 6].

## Results and Discussion

Analysis of the composition of the above-mentioned manganese-containing synthetic pigments obtained by industrially thermal method showed that, for example, the composition of "manganese blue" ( $Ba_3(MnO_4)_2 \cdot nBaSO_4 \cdot mBaO$ , where  $n=10 \div 16$ ,  $m=1 \div 3$ ) includes barium / manganese composite oxide [7]. Testing has shown that this decorative pigment, intended for artistic paints production and plastics coloring, has the ability to suppress steel corrosion [8,9]. Therefore, planning the synthetic part of the work we proceeded from analogy. Manganese (IV) oxide, barium nitrate and barium sulfate were chosen as starting components for synthesis. In the load of this composition, manganese oxide is a reducing agent, barium nitrate is an oxidizing agent, and barium sulfate, apparently, performs stabilizing function.

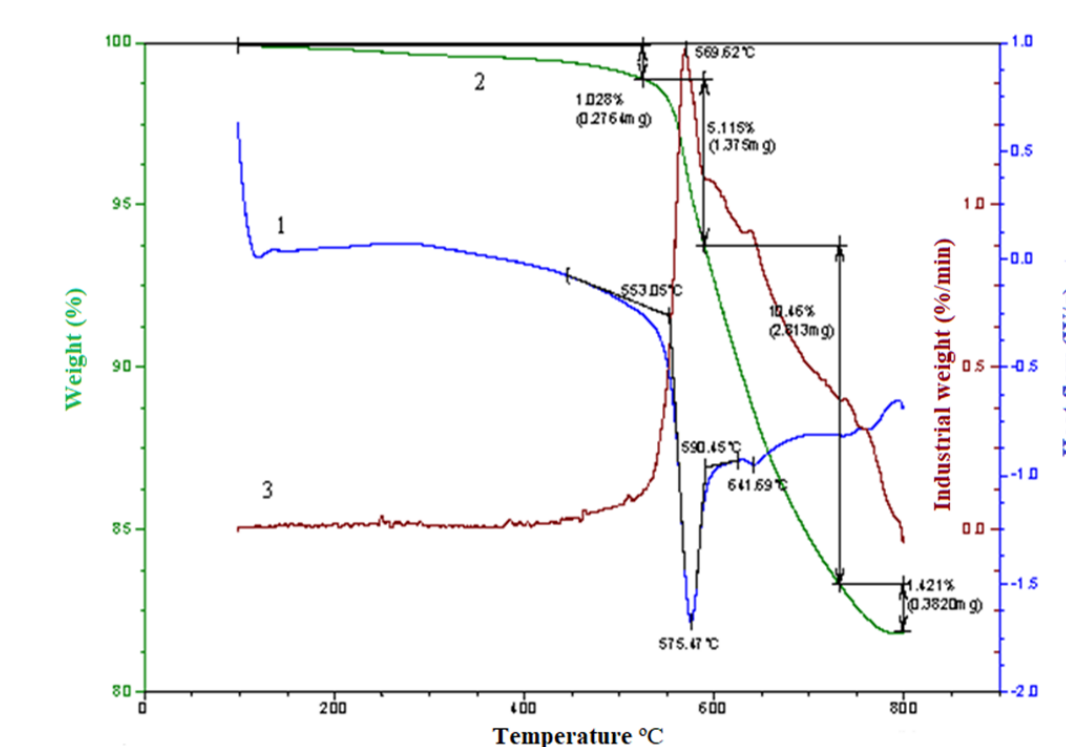


Figure 1 - The results of the charge thermal analysis. 1 - differential thermal analysis (DTA) curve, 2 - thermogravimetry curve (TG), 3 - differential thermogravimetry curve (DTG).

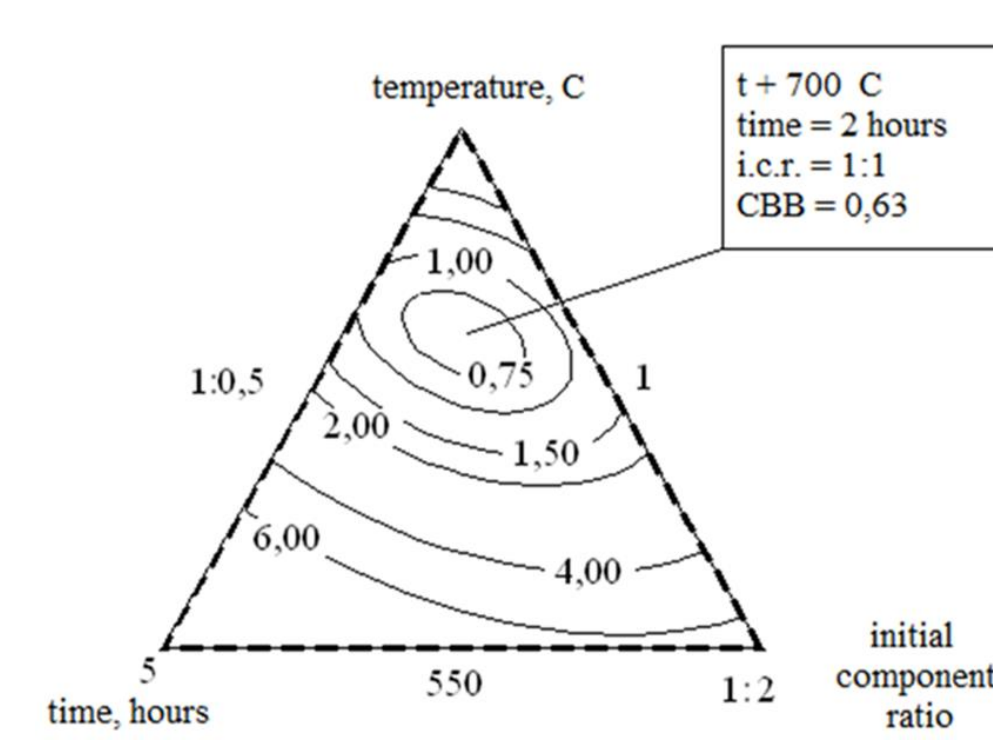


Figure 2 - Contour diagram: the conditions' influence on the synthesis of SME on SVLP in the resulting products.

As can be seen from the thermal study results presented in Fig. 1, DTA and DTG curves of the initial components' mixture are characterized by the presence of several effects, accompanied by a loss of mass. When the temperature rises to 100-110°C, the removal of mainly weakly bound adsorbed and interlayer water is recorded.

Starting with a temperature of 550°C, a reaction, leading to the formation of barium manganate sulfate (BMS) takes place. It is accompanied by significant weight loss due to decomposition of the charge nitrate component.

As a result of preliminary experiments, it was found that the anticorrosive and physicochemical characteristics of the product obtained depend on the synthesis' temperature and time conditions and the initial components' ratio.

With this in mind, a three-factor experiment was carried out in order to optimize the characteristics of the obtained product. The relationships between the components and the synthesis conditions were calculated using the Minitab 14.0 program, developed by DuPont specialists.

Temperature, time of the charge heat treatment and the charge composition were chosen as the parameters to be optimized. The response function was the corrosion current of steel in contact with aqueous extract of the synthesized product containing 3% sodium chloride and the content of water soluble substances (CWSS), which is an important characteristic of anti-corrosion pigments. It is known that the optimal values of CWSS are in the area less than 1% [10].

On the basis of the results obtained, approximation was carried out with the construction of contour diagrams. For example, figure 2 shows a diagram that allowed to determine the synthesis conditions for the product with minimum CWSS of 0.63%: time 2 h, temperature 7000 C, the ratio between the starting components:  $MnO_2 : BaSO_4 : Ba(NO_3)_2 - 2:1:1$ . We can take certain formal oxidation state of manganese that was +5 as confirmation of the correctness of the above gross formula of the product.

Additional assessment of different composition mixture physicochemical characteristics, calcined under different temperature and time conditions allowed to conclude the influence of these parameters on the color and stability of the obtained products. The conclusion about the instability of the latter was made in case of water extracts' coloring. Stable products were obtained only at the optimum temperature of 700°C, their color changed as the temperature increased from blue (650-700°C) through blue-green (700°C) to bright green (750°C and above). Probably stabilization is facilitated by the inclusion of sulfate component into the mixture.

In order to identify the sulfate component effect on the pigment's anti-corrosive properties, the composition of the charge was changed and barium sulfate was eliminated. As a result of the synthesis, a product was obtained with the formal oxidation state of manganese +4: barium manganite (MB)  $BaMnO_3$ , characterized by SWSS 0.4%.

### General physicochemical properties of synthesized manganites as anticorrosive pigments

Table 1 presents the main characteristics of calcium and barium manganites, that allow to make a conclusion about the possibility of their use as anti-corrosive pigments.

Table 1

Properties of the synthesized manganese-containing pigments		
Pigment designation	MB	MSB
Colour	brown	green
pH, aqueous extract	7,5	9,0
Oil absorption g/100g	21	10
Density kg/m <sup>3</sup>	5,46	4,33
Steel corrosion potential mV	125	121
Corrosion current density, I <sub>mcA</sub> / cm <sup>2</sup>	1,7	0,9

\*Steel corrosion current density, in contact with 3 % NaCl solution 16,5 mcA/cm<sup>2</sup>

The data presented in table 1, allow to conclude that both synthesized products have good prospects to be used as anti-corrosion pigments. Comparison of their properties makes it possible, in addition to stating their color difference, to conclude that they have a higher corrosion suppressive ability, which, apparently, is the consequence of its aqueous extract alkaline reaction.

In order to reduce the cost and, as a result, increase the competitiveness of the synthesized pigments, we investigated the possibility of replacing chemically pure manganese oxide (IV) with ore containing this oxide (pyrolusite) as the charge component.

## Conclusion

The complex oxides of manganese in the oxidation state +4 and +5 were synthesized using the method of calcination. Their physicochemical properties allow to use them as anti-corrosion pigments. The calcination product containing Mn (V) and BaSO<sub>4</sub>, possibly as a stabilizer, has higher anti-corrosion properties, probably due to the alkaline reaction of the aqueous extract. The proven possibility of using natural pyrolusite as a raw material containing manganese can contribute to the significant reduction in the cost and, consequently, increased competitiveness of the synthesized pigments.