

## Conversion Coatings for Zinc Substrates from Acidic Solutions of Cr(III) Compounds

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Influence of the components of acidic solution: Cr (III) nitrate – malonic acid – Co(II) salt and treatment conditions on zinc dissolution and formation of chromate films as well as on their decorative and protective properties have been studied using the analytical, XPS, structural and accelerated corrosion test methods. The organic acid is the main component, which has essential influence on zinc dissolution and formation of chromate films as well as their decorative and protective properties. The influence of organic acid is directly related with the state of  $\text{Cr}^{3+}$  ions in chromating solution. When  $\text{Cr}^{3+}$  ions are in the form of hexaaquaions, the organic acid increases the quantities of the zinc dissolved and the Cr(III) deposited on the zinc surface (especially at 60°C). It also predetermines formation of a thick, porous chromate film with big cracks at 60°C. Its decorative and protective properties are rather poor. When  $\text{Cr}^{3+}$  ions are in the form of a complex with organic acid, the quantities of the zinc dissolved and the Cr(III) deposited on the zinc surface significantly decrease and thinner chromate films with an even surface, good decorative appearance and high corrosion resistance are formed. Decorative blue-bright Cr(VI)-free films with a slight iridescent tint, obtained in solution, containing Cr(III) nitrate (0.2), malonic acid (0.3) and cobalt (II) nitrate (0.02)  $\text{mol} \cdot \text{dm}^{-3}$ , at pH 1.6 to 2.0 at room temperature over 30-60 s, possess corrosion resistance (192-240 h in salt spray chamber) similar to that of iridescent chromate films, obtained in acidic Cr(VI) solution.

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Zinc coatings widely used in corrosion protection of steel articles mostly are further chromated, i.e. treated in acidic solutions of Cr(VI) compounds. As a result of this treatment the zinc surface is coated with a conversion chromate (containing Cr(VI) and Cr(III)) film, which improves corrosion resistance of zinc coating and helps the exploited articles to keep their decorative appearance.

However, Cr(VI) compounds are very toxic, that is why it was started to chromate zinc coatings in acidic solutions of Cr(III) compounds, which are much less toxic, and beside that, it is much simpler to treat their wastewaters.

The main components of such acidic solutions are compounds of Cr(III) and the activating system  $H^+$  ions / oxidizer (mostly  $NO_3^-$  ions)<sup>1-8</sup>. When the zinc coating is immersed into solution, zinc oxidation (dissolution) and reduction of oxidizer ( $NO_3^-$  ions) take place<sup>9</sup>.

The technologies of obtaining blue-bright and iridescent conversion chromate films containing only Cr(III) on the zinc surface in acidic solutions of Cr(III) compounds have been developed in recent years. The films formed are thicker and possess a significantly higher corrosion resistance (up to 200-300 hours in a salt spray chamber). These technologies have found their application in anti-corrosion processing of automobile articles and can be used for effective corrosion protection of different zinc-plated articles.

In modern technological processes solutions with the following main components are used to obtain conversion chromate Cr(VI)-free films with a high corrosion resistance on the zinc surface<sup>10-13</sup>:

- Cr(III) salt;
- organic acid, capable to form a complex with  $Cr^{3+}$  ion, kinetically less inert than a  $Cr^{3+}$  hexaaquacomplex  $[Cr(H_2O)_6]^{3+}$ .

Conversion chromate films in these solutions are formed, undoubtedly, according to the scheme: zinc oxidation and reduction of  $NO_3^-$  ions – alkalization of the solution – deposition of  $Zn^{2+}$ ,  $Cr^{3+}$  and other metal ions present in the solution in the form of barely soluble hydroxide compounds on the zinc surface. The high corrosion resistance of the films formed (called by the authors<sup>10-13</sup> “chromites”) is predetermined, according to the authors, by properly chosen ligands and high solution temperature. The  $Cr^{3+}$  ions and the ligands form complexes, being kinetically less inert than a  $Cr^{3+}$  hexaaquacomplex.

Most of the above-mentioned patent and advertising – technical<sup>14-19</sup> literature concerns chromating zinc in acidic solutions of Cr(III) compounds. There is scarcely any data on kinetics of chromating process, that is why the more detailed research is necessary, which would permit to improve the technologies of obtaining Cr(VI)-free conversion chromate films.

The aim of this work was to study the regularities of zinc oxidation (dissolution) and deposition of barely soluble hydroxide Cr(III) and Zn(II) compounds on the zinc surface, i.e. formation of a chromate film, to determine how the rate of the process, morphology of the films and corrosion resistance depend on the composition of acidic solution of Cr(III) compounds, pH, temperature and treatment duration.

## Experimental procedure

The quantities of  $\text{Zn}^{2+}$  dissolved ions and  $\text{Cr(III)}$  deposited on zinc surface were determined by the analytical method, the appearance of chromate films – by visual inspection, the morphology – by microphotography, elemental and phase composition – by X-ray photoelectron spectroscopy (XPS), corrosion resistance – by the accelerated corrosion test method.

On the basis of patents<sup>10-13</sup> and advertising – technical<sup>14-19</sup> literature along with the results of preliminary experiments the composition of studied solution was the following:  $\text{Cr(NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.2), organic ligand – dicarboxylic (malonic) acid (0.3), and an additive –  $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.02)  $\text{mol} \cdot \text{dm}^{-3}$ . Acidity of solutions was adjusted with 1  $\text{mol} \cdot \text{dm}^{-3}$   $\text{NaOH}$  and 50%  $\text{HNO}_3$ .

To electrochemically deposit zinc coatings a weakly acidic bright zinc-plating electrolyte<sup>20</sup> was applied.

Concentrations of zinc and chromium in the analyzed solutions were determined with a direct current plasma emission spectrometer Beckman Spectraspan VI (BECKMAN, USA). For measuring Zn 202.548 nm (detection limit 6  $\mu\text{g} \cdot \text{dm}^{-3}$ , straight dynamic diapason 0.06-600  $\text{mg} \cdot \text{dm}^{-3}$ ) and Cr 284,984 nm (detection limit 7  $\mu\text{g} \cdot \text{dm}^{-3}$ , straight dynamic diapason 0.07-1000  $\text{mg} \cdot \text{dm}^{-3}$ ) optical lines were used.

The presented data is the mean of at least three tested solution portions.

Appearance of chromate films was evaluated visually by the naked eye in daylight.

Morphology of chromate films was investigated by a rastric electronic microscope – micro-analyzer JXA-50A (JEOL, Japan).

The XPS method was applied to determine the elemental and phase composition of the films. Spectra of elements were recorded with a spectrometer ESCALAB MK II (VG Scientific, Great Britain). The composition of chromate films was determined in an analyzing chamber at super high vacuum –  $10^{-8}$ - $10^{-9}$  Torr. The magnesium anode ( $\text{MgK}_\alpha$  – 1253.6 eV), was used to excite the electrons at a power of 300 W and an analyzer energy of 20 eV. The method of etching with ionized  $\text{Ar}^+$  ions was applied to determine the distribution of elements throughout the whole depth. The film was etched by an ionic gun AG-21. The energy of ionized  $\text{Ar}^+$  ions was about 4 keV. The ionic etching of the sample was carried out at a current of 100  $\mu\text{A}/\text{cm}^2$  which corresponds to an etching rate of  $\sim 10$  nm/min and vacuum of  $7 \cdot 10^{-5}$  Torr. The following spectra of elements were recorded:  $\text{Cr}2p_{3/2}$ ,  $\text{O}1s$ ,  $\text{Zn}2p_{3/2}$ ,  $\text{Co}2p_{3/2}$ .

Corrosion resistance of chromate films was evaluated in two ways:

- with a 5% solution of lead acetate according to ISO 3613-80 (“express” method)<sup>21</sup>;
- by the neutral salt spray test according to ISO 9227<sup>22</sup>.

The presented corrosion resistance data for chromate films is the mean of at least three samples.

## Results and Discussion

Dependences of both the quantities of dissolved zinc and  $\text{Cr(III)}$  deposited on the zinc surface on the temperature of chromium (III) nitrate solution and the duration of chromating are presented in Fig. 1.

As is seen from the  $C_{Zn^{2+}}$  values (Fig. 1 a), the highest rate of zinc dissolution is at the beginning of chromating process. The rate of zinc dissolution in acidic solution of chromium (III) nitrate at 60°C is significantly higher, than that at 20°C. The quantity of dissolved zinc with increase in chromating time increases proportionally to the dissolution rate in solutions at different temperatures: the quantities of zinc dissolved in 60 s are ~6 (20°C) and ~18 (60°C)  $mg \cdot dm^{-2}$ .

As is seen from the  $C_{Cr(III)}$  values (Fig. 1 b), the rate of deposition of barely soluble compounds of Cr(III) on the zinc surface is also the highest at the beginning of chromating process. The quantity of deposited Cr(III) with increase in chromating time increases proportionally to the rate of deposition at different temperatures: the quantities of Cr(III) deposited over 60 s are ~0.49 (20°C) and ~0.7 (60°C)  $mg \cdot dm^{-2}$ .

The dependences obtained allow to assert, that the barely soluble hydroxide compounds of Cr(III) and Zn(II), deposited at the beginning of chromating process, cover the zinc surface with a porous or/and electron conductive film, through which the zinc dissolution (oxidation) and deposition of Cr(III) and Zn(II) compounds on the zinc surface continues, though with a lower rate.

Influence of separate compounds of acidic chromating solution on the quantities of zinc dissolved and Cr(III) deposited on the zinc surface is shown in Fig. 2.

The data in Fig. 2 suggest, that addition of malonic acid to the acidic solution of chromium (III) nitrate significantly increases the quantity of dissolved zinc, the quantity of Cr(III) in the film increases less at a temperature of 60°C; and it almost does not influence their quantities at 20°C (compare solutions 1 and 2). This influence of organic dicarboxylic acid may be related with the acidifying of solution, which is especially significant at a higher (60°C) temperature. Addition of Co(II) salt has effect only when organic acid is present in the solution: it increases the quantities of dissolved zinc, and to a lesser degree the quantities of Cr(III) in the film at a temperature of 20°C, and almost has no influence at 60°C.

The above-presented dependences are characteristic of chromating solutions, in which  $Cr^{3+}$  are in the form of a hexaaquacomplex  $[Cr(H_2O)_6]^{3+}$ .

When  $Cr^{3+}$  in the chromating solution is in the form of a complex with malonic acid<sup>23</sup>, the quantities of dissolved zinc and Cr(III) in the film significantly decrease, comparing with those in  $[Cr(H_2O)_6]^{3+}$  solutions with analogous additives.

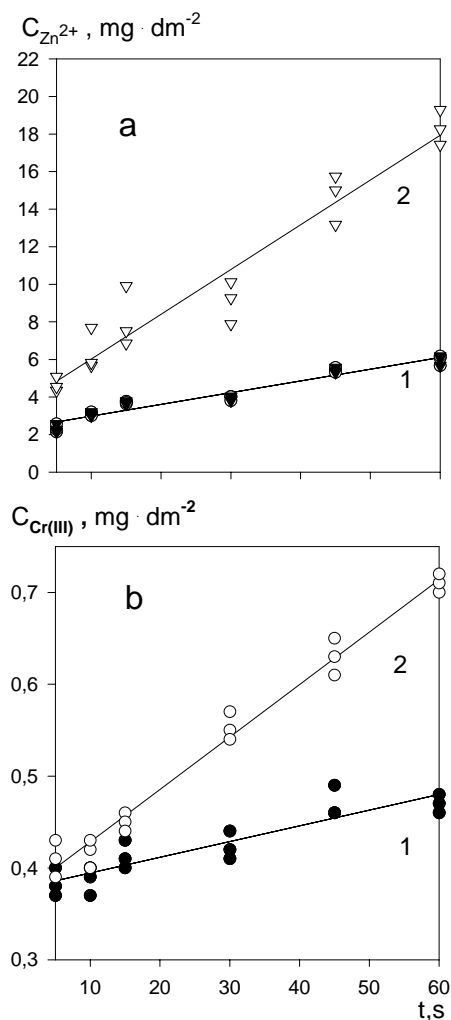


Figure 1. The quantities of dissolved  $Zn^{2+}$  (a) and Cr(III) in the film (b) versus the duration of chromating and temperature in solution of chromium (III) nitrate: 1 - 20°C, 2 - 60°C.  $C_{Cr^{3+}}$  in solution - 0.2 mol · dm<sup>-3</sup>, pH - 2.

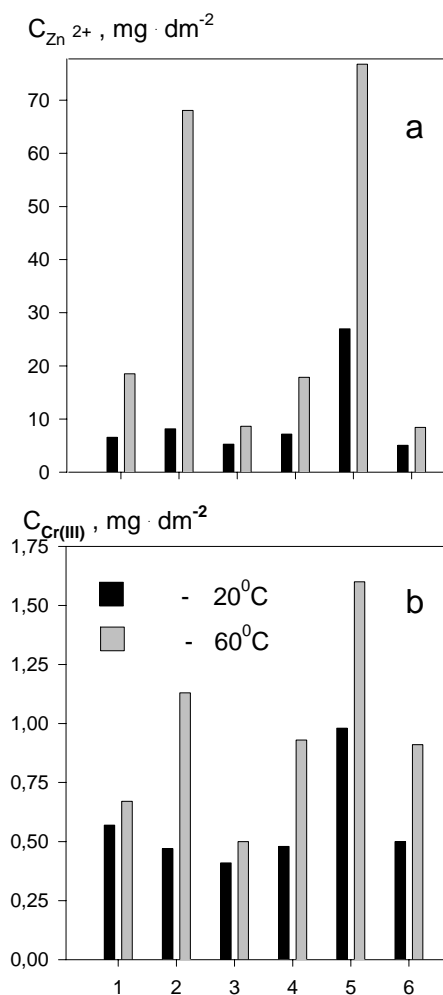


Figure 2. The quantities of dissolved  $Zn^{2+}$  (a) and Cr(III) in the film (b) versus the composition and temperature of chromating solution. The composition of solution: 1 - chromium (III) nitrate, 2 - chromium (III) nitrate + malonic acid, 3 - chromium (III) nitrate + malonic acid (complex), 4 - chromium (III) nitrate + Co(II) salt, 5 - chromium (III) nitrate + malonic acid + Co(II) salt, 6 - chromium (III) nitrate + malonic acid (complex) + Co(II) salt.  $C_{Cr^{3+}}$  in solution - 0.2,  $C_{malonic\ acid}$  - 0.3,  $C_{Co^{2+}}$  - 0.02 mol · dm<sup>-3</sup>. pH - 2, t - 45 s.

The elemental composition of the films, obtained in acidic solutions of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{Cr}^{3+}$  – complex of organic acid, at the surface and at different depths is shown in Table 1.

The data presented in Table 1 suggest, that the main elements, composing the film, are oxygen, zinc and chromium; the quantity of cobalt is one order lower.

Table 1. Dependence of elemental composition of chromate films on the form of  $\text{Cr}^{3+}$  ions in solution and on chromating conditions. The components of chromating solution: chromium (III) nitrate – 0.2, malonic acid – 0.3, Co(II) salt – 0.02 mol·dm<sup>-3</sup>, pH – 2.

Sample No.	The form of $\text{Cr}^{3+}$ ions in chromating solution, chromating conditions	Determined elements	Quantity of element in film, at. %							
			Etching time, min. / etched layer, nm							
			0/0	0,1/1	1/10	3/30	5/50	7/70	10/100	15/150
1.	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , T – 20°C, t – 45 s	Zn	12.1	31.9	24.9	25.1	24.5	29.5	32.0	100
		Cr	5.2	9.2	13.6	14.1	14.2	13.1	13.0	0
		O	82.6	58.6	61.1	60.4	61.0	57.0	54.7	0
		Co	0	0.3	0.3	0.5	0.4	0.4	0.3	0
2.	$\text{Cr}^{3+}$ - organic acid complex, T – 20°C, t – 45 s	Zn	7.5	24.0	19.9	43.3	96.0			
		Cr	4.2	10.0	14.7	7.5	0.7			
		O	88.3	65.3	64.8	48.9	3.2			
		Co	0	0.7	0.6	0.3	0			
3.	$\text{Cr}^{3+}$ - organic acid complex, T – 60°C, t – 45 s	Zn	7.1	21.0	18.7	37.7	97.3			
		Cr	7.1	12.9	16.7	9.4	0.3			
		O	85.0	64.8	63.7	52.6	2.4			
		Co	0.8	1.3	1.0	0.3	0			

The quantity of oxygen at the surface of film is the highest, undoubtedly, because of adsorbed oxygen and water. However, after film etching only for 0.1 min, the oxygen quantity decreases by 20-25%. At depth of the film, its quantity remains approximately constant, and, approaching the zinc surface, sharply decreases.

The quantities of Zn and Cr on the surface of film are the least, because the adsorbed water and oxygen reduce their relative atomic percentage (at. %) in the film. However, after etching only for 0.1 min, their quantities increase and at depth they change in a comparatively narrow range. Approaching the zinc surface, the quantity of Cr decreases, but that of Zn increases. The quantity of Co in the film changes in a very narrow range – 0.3-1.3 at. %.

The data presented in Table 1 suggest, that the time taken to etch the film by  $\text{Ar}^+$  ions almost to the surface of zinc, and at the same time its thickness, is significantly higher than that of the film, obtained in solution of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  – organic acid (Table 1, sample 1; 10 min., ~100 nm), when compared with the films, obtained in solution of  $\text{Cr}^{3+}$  – complex of organic acid (Table 1, samples 2, 3; 3 min., ~30 nm). Since the quantities of separate elements (at.%) in the films are similar, it is reasonable to think, that their absolute quantities in the former case are much higher than those in the latter. This is in agreement with the mentioned-above results of analytical research, which determine that the quantity of Cr(III) in the films, obtained in

solutions of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  – malonic acid is considerably higher, when compared to the films, obtained in solutions of a  $\text{Cr}^{3+}$  – complex of malonic acid.

The quantitative dependences of dissolved zinc and chromium (in some cases zinc and cobalt) in the film and the thickness of the film in solutions of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  – malonic acid and  $\text{Cr}^{3+}$  – complex of malonic acid are predetermined, in our opinion, by the kinetics of deposition of barely soluble Cr(III) hydroxide compounds on the zinc surface. According to<sup>24</sup>, when zinc dissolves and the acidity of solution at its surface decreases, Cr(III) hydroxide compounds begin to deposit at ~3 pH from a  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  complex and at ~4.5 pH from a  $[\text{Cr}^{3+}$  – organic ligand] complex. In the former case barely soluble compounds of Cr(III) deposit simultaneously with barely soluble compounds of Zn(II) and Co(II) on the zinc surface near the sites of active zinc dissolution, forming a thick, very porous film, through which zinc easily dissolves. In the latter case because of higher pH at the surface layer a greater quantity of barely soluble compounds of Cr(III) precipitates at the initial moment. They block a larger area of zinc surface, forming a compact less porous film, which more effectively stops further dissolution of zinc, which leads to the increase in the quantities of Cr(III), Zn(II) and Co(II) in the film and its thickness.

The data obtained have shown, that an essential component of the acidic solutions of Cr(III) compounds is organic dicarboxylic acid. However, it is not the presence of this component in acidic solution of chromium (III) nitrate that predetermines formation of a thinner and a more compact chromate film with a good decorative appearance and high corrosion resistance, but it is a complex of  $\text{Cr}^{3+}$  – organic acid formed under certain conditions.

The data of rastric electronic microscopy have shown, that morphology of chromate films is strongly dependent on the composition of chromating solution and its temperature. In the solution of chromium (III) nitrate at a temperature of 20°C the film with a rough and rather developed surface is formed. In the solution of chromium (III) nitrate with addition of malonic acid at a temperature of 20°C a chromate film with a more even surface is formed. The films of a very similar morphology are also obtained in solution of chromium (III) nitrate with addition of Co(II) salt. When solution of chromium (III) nitrate contains both malonic acid and Co(II) salt, at a temperature of 20°C an even film is formed, at 60°C – a much rougher film, but without any cracks. The above-described morphology is characteristic of the films, obtained in solutions, where  $\text{Cr}^{3+}$  is in the form of hexaaquaions.

In the solutions, where  $\text{Cr}^{3+}$  is in the form of a complex with malonic acid, even films without any cracks are formed.

The data of rastric electronic microscopy have shown, that even and not cracked chromate films of good quality are obtained in solutions, where  $\text{Cr}^{3+}$  is in the form of a complex with organic acid and dissolution of zinc is not so intensive. Such films also demonstrate the highest corrosion resistance, i.e. clear correlation is observed between the state of the film surface and corrosion resistance determined by the “express” method.



### Data on corrosion resistance of chromate films obtained by the neutral salt spray test.

Dependence of corrosion resistance on the acidity of solution and duration of chromating is presented in Table 2. The data on corrosion resistance tests of iridescent chromate films, obtained in solution on the basis of Cr(VI) compounds<sup>20</sup>, are presented for reference. The tests were carried out simultaneously.

Table 2. Dependence of corrosion resistance of chromate films in neutral salt spray chamber on the composition of chromating solution and chromating conditions. Temperature of solution - 20°C.

Composition of chromating solution	Chromating conditions		Time till white products of zinc corrosion appear, h
	PH of solution	Duration of chromating, s	
1. On the basis of Cr(III) compounds: <ul style="list-style-type: none"><li>chromium (III) nitrate (0.2) – malonic acid (0.3) mol · dm<sup>-3</sup> (complex),</li><li>cobalt (II) nitrate – 0.02 mol · dm<sup>-3</sup></li></ul>	1.6	30	192
	1.6	30	192
	1.6	30	120
	1.6	60	240
	1.6	60	240
	1.6	60	240
	2.0	30	192
	2.0	30	168
	2.0	30	192
	2.0	60	216
	2.0	60	216
	2.0	60	216
2. On the basis of Cr(VI) compounds	1.8	30	240
	1.8	30	240
	1.8	30	240

As seen from the data, presented in Table 2, the time period till the first white zinc corrosion products appear on the surface of chromated samples varies from 120 to 240 h. The corrosion resistance of chromate films, obtained over 30 s, is 168-192, over 60 s – 216-240 h, i.e. increases with increase in chromating time at pH 1.6 and pH 2.0. This is predetermined by film thickness. On the whole, the corrosion resistance of chromate films, obtained on the zinc surface in studied Cr(III) acidic solution, is near to that of iridescent films, obtained in Cr(VI) solution (240 h) and is much higher than that of the films, obtained in Cr(III) acidic solutions of old generation (12-24 h).

The highest corrosion resistance is characteristic of the chromate films, obtained during 30 s in solution with pH 1.6 (240 h).

### Conclusions

In a studied solution of chromium (III) nitrate – malonic acid – Co(II) salt the organic dicarboxylic acid is the component, which has an essential influence on zinc dissolution and formation of chromate films as well as on their decorative and protective properties.



The influence of organic acid is directly related with the kind of  $\text{Cr}^{3+}$  complex in chromating solution.

When  $\text{Cr}^{3+}$  ions are in the form of hexaaquaions, the organic acid increases the quantities of the zinc dissolved and the Cr(III) deposited on the zinc surface (especially at 60°C). They also predetermine formation of a thick, porous chromate film with big cracks (at 60°C). Its decorative and protective properties are rather poor.

When  $\text{Cr}^{3+}$  ions are in the form of a complex with organic acid, the quantities of the zinc dissolved and the Cr(III) deposited on the zinc surface significantly decrease and thinner chromate films of even surface, good decorative appearance and high corrosion resistance are formed.

Decorative blue-bright Cr(VI)-free films with a slight iridescent tint, obtained in solution, containing chromium (III) nitrate (0.2), malonic acid (0.3) and cobalt (II) nitrate (0.02)  $\text{mol} \cdot \text{dm}^{-3}$ , at pH 1.6 to 2.0 at room temperature over 30-60 s, possess corrosion resistance (192-240 h in salt spray chamber) similar to that of iridescent chromate films, obtained in acidic Cr(VI) solution.

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