Investigation of Zn Corrosion in Chromium (VI) - SO₄²⁻ - PO₄³⁻ Acidic Solutions

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The aim of the investigation is to determine some of the regularities of PO_4^{3-} ion influence on a process of zinc corrosion with the formation of a solid phase on the surface. It was determined by analytical methods that PO_4^{3-} ions in pure chromic acid solution did not appreciably induce reactions of zinc oxidation – Cr (VI) reduction. However, PO_4^{3-} ions introduced into an acidic $Cr^{6+} - SO_4^{2-}$ solution had an influence on the kinetics of zinc corrosion and the formation of a solid phase. A dissolving speed of zinc did not depend upon PO_4^{3-} concentration. In the meanwhile, the distribution of corrosion products between a solution and solid phase differed considerably: the amount of oxidized zinc and Cr^{3+} formed in a solution was larger when the tested solution contained PO_4^{3-} ions. Most probably, it was related to the increase of the general concentration of hydrogen ions. These additional hydrogen ions appeared in the solution owing to proton donors – the particles containing PO_4^{3-} . They dissolved a solid phase on the surface of zinc, i.e. they dissolved film in the state of its formation. Consequently, the quantities of the oxidized zinc and Cr^{3+} in the solution increased.

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In water solutions, especially those containing acid, metallic Zn is not stable. In a number of stages Zn atom leaves the metallic lattice and passes into a solution in form of Zn^{2+} ion $(Zn - 2e \rightarrow Zn^{2+})$. The released electrons are bound in the cathodic stage, which supports the anodic process (Ox + 2e \rightarrow Red). Depending on the nature of the oxidizer Ox (molybdates¹, tungstates², permanganates³, vanadates³, bichromates⁴⁻⁵, H⁺, nitrates⁶) as well as on the cationic and anionic composition of a solution, Zn can corrode till the full passing into a solution (e.g. HCl, HNO₃ solutions) or remain practically passive for an unlimitedly long period of time (e.g. CrO₃ solutions). From practical viewpoint especially significant are the cases, when in the process of Zn corrosion the phase layers of insoluble compounds precipitate on its surface. These treatments convert the Zn metal surface to a superficial layer containing a complex mixture of compounds of dissolved Zn, reduced Ox and other components of solution. In metal finishing field such layers are known as oxide, molybdate, phosphate, vanadate, permanganate, and chromate conversion coatings. The latter are widely used in extra protection of zinc galvanic coatings. They improve the corrosion resistance of zinc coating and help the zinc coated steel articles keep their decorative appearance during lifetime. Chromating, as a matter of fact, is a specially provoked process of zinc corrosion in acidic Cr^{6+} solution with forming of solid phase on the surface of metal. During the contact of Zn with an acidic solution of Cr⁶⁺, the reactions of Zn oxidation and reduction of Cr^{6+} to Cr^{3+} take place, which in general could be outlined as follows⁶:

$$1,5nZn+H_{2-z}Cr_{n}O_{3n+1}^{z-}+(6n+z-nq)H^{+} \rightarrow \\ \rightarrow 1,5nZn^{2+}+nCr(OH)_{q}^{3-q}+(3n+1-nq)H_{2}O.$$
(1)

General reaction (1) is conditional in the sense, that the formed Zn^{2+} and Cr^{3+} ions in the vicinity of anodic and cathodic reactions can bind not only with OH⁻ ions, but also, depending on the composition of the chromating solution, with anions of chromic, sulphur, phosphoric acids, etc.

The process according to the scheme (1) goes on by consumption of H^+ ions, which results in alkalification of the surface layer of the solution. The Zn^{2+} and Cr^{3+} ions in the shape of slightly soluble compounds (hydroxides, hydroxychromates, chromichromates, etc.) precipitate on the zinc surface, forming a conversion chromate coating.

In the result of the above-mentioned process in pure chromic acid Zn surface is immediately covered with a very thin, imperceptible with the naked eye, but apparently, very dense primary chromate film, which restricts the reaction of Zn oxidation and Cr^{6+} reduction, and so restricts the forming of the thicker corrosion resistant conversion chromate coating, as well. That is why the chromating solution must include components, which permit to proceed the reactions of Zn oxidation and Cr^{6+} reduction to Cr^{3+} with the forming of conversion chromate coating. Usually different anions, introduced into a chromating solution in the form of acids or their salts, serve as activating components.

As the investigations and practice have shown, the sulphur acid anions are the most effective and practically necessary activating components of the chromating solution.

A number of works⁴⁻⁸ are devoted to investigation of chromating process, including the activating role of $SO_4^{2^-}$ ions. As it was shown in the detailed investigation⁶, the primary activating influence of the sulphates on the Zn corrosion process in acidic solutions of Cr^{6^+} is in the fact, that in such solutions (with pH value near to 1,0) their dominating form of existence is hydrosulphate ions (K₂=1,15 \cdot 10⁻²). When the hydrosulphate ions get into the alkalized by cathodic process by-electrode layer at zinc surface, they dissociate in it according to the scheme HSO $_4^- \leftrightarrow H^+ + SO_4^{2^-}$. Thereby they do not only work as buffering addition, restraining increase of pH, but at the same time turn into an energetic ligand, which forms stable readily soluble complexes of the Cr (III) - the products of chromate reduction. Either of them suppresses the classical passivating of zinc, as if keeping part of its surface active (i.e. not covered by Cr^{3^+} and Zn^{2^+} hydroxide compounds, which retards the cathodic and anodic processes). As a result the thick conversion chromate coating forms.

The patent publications of recent years⁹⁻¹² show, that one of the basic components of solutions for obtaining colour conversion chromate coating on Zn, especially on zinc alloys with alloying additions (Co, Ni, Fe), are the anions of phosphoric acid (PO_4^{3-}). In combination with the other activating anions of the solution they make definite influence on the Zn corrosion process and on the quality of conversion chromate coating. However, the literature data¹³ on the role of PO_4^{3-} ions in the process of Zn chromating is not numerous and obviously insufficient.

Therefore the further investigation of the activating effect of PO_4^{3-} ions on Zn oxidation, reduction of Cr^{6+} to Cr^{3+} and forming of solid phase on Zn surface is topical for perfection of metal passivating technologies.

Experimental procedure

The examined solutions were prepared by dissolving CrO_3 (source of Cr^{6+} ions), Na_2SO_4 (source of SO_4^{2-} ions) and H_3PO_4 (source of PO_4^{3-} ions) in the distilled water, acidity of the solution was corrected till 1,1 pH value by adding the 2,5 mole/L NaOH solution.

For investigation of the Zn chromating process the steel plates of 60-cm2 size of visible working surface were used. The steel plates were Zn plated in the cyanide electrolyte, containing, g/L: NaOH – 80, NaCN – 85, ZnO – 45, temperature of the electrolyte = $20\pm2^{\circ}$ C, density of cathode current $i_{k}=1,5$ A/dm². Thickness of Zn coating was not less than 7 μ m.

Every freshly Zn coated plate, after bright dipping in 0,25% HNO₃ solution and rinsing under cold running water, was dipped into a separate portion of the examined solution, exposed immobile for 60 s, taken out and rinsed in distilled water. The rinsing waters were quantitavely collected and added into the tested chromating solution, in which further were analyzed the quantities of oxidized zinc, i.e. the Zn^{2+} ions, and reduced Cr^{6+} ions, i.e. Cr^{3+} ions. Simultaneously the quantities of Zn^{2+} , Cr^{3+} and Cr^{6+} in the chromate film, obtained in the tested solution, were analyzed. For this purpose from one part of the plates the chromate film was dissolved according to method⁵ immediately after their preparation, and in the obtained solution quantity of Zn^{2+} was determined. From the other part of plates the film was dissolved according to method¹⁴ in 24 h after their preparation, and the quantities of Cr^{3+} and Cr^{6+} in the obtained solution were analyzed.

Zn in the analyzed solutions was determined by method of atomic absorption spectroscopy with spectrophotometer AAS-603 ("Perkin-Elmer", USA). Cr^{3+} in the analyzed solutions was determined by potentiometric titration¹⁵, Cr^{6+} - by classical iodometric titration with 0,005 mole/L Na₂S₂O₃ solution.

Element composition on the surface and in depth of chromate film was determined by method of X-ray photo electronic spectroscopy. The element specters were recorded by spectrometer "ESCALAB MK II" (VG Scientific, UK). The composition of chromate films was determined in the analytical chamber in super high vacuum $-10^{-8}-10^{-9}$ Torr. For excitation of electrons magnesium anode (MgK_a – 1256,6 eV) was used by power 300 W and analyzer energy 20 eV. To determine the distribution of elements in depth of chromate film, the film was etched with Ar⁺ ions by ion gun, current 100 μ A/cm² (corresponding to etching speed ~10 nm/min.) and vacuum 7x10⁻⁵ Torr. The specters of elements Cr2p_{3/2}, Ols, Zn2p_{3/2}, S2p, P2p were recorded.

The composition of chromate film was carried out after exposition of the samples in laboratory atmosphere no less than 24 h.

General (analytical) concentration of H^+ ions (C_{H^+}) in the tested solutions was determined alkali metrically: the constant quantity (25 ml) of the solution was titrated by 0,5 mole/L NaOH solution; pH value during the titration was registered by universal pH-meter ÝB-74 (Russia) with glass electrode ÝNË-43-04.

Method of theoretical calculation and experimental determination of general (analytical) H^+ ions concentration in acidic Cr^{6+} solution is in more detail stated in¹⁶.

Results and Discussion

It should not be forgotten in the further discussion about the role of PO₄³⁻ and SO₄²⁻, that they obtain the above-named form only in the coating, but in the volume of acidic chromating solution the first practically attend only in the form of acid (K₁=7,1 \cdot 10⁻³) and dihydrophosphate ions (K₂ = 6,2 \cdot 10⁻²), not taking into account sulphates in form of complexes.

Influence of PO $_{4}^{3-}$ and SO $_{4}^{2-}$ ions on formation of conversion chromate coating in acidic Cr⁶⁺ solutions is shown in Table 1.

In the solutions of pure chromic acid and with additives of 0,025-0,200 mole/L of PO $_4^{3-}$ ions the visible with naked eye chromate film does not form (solutions 2.1–2.4). The products of Zn oxidation and Cr⁶⁺ reduction reactions, i.e. Zn²⁺ and Cr³⁺ ions were also not found in these solutions appreciable by used analytical methods.

| Table 1 | | | | | | | | |
|--|--------------------------------|-------------------|------------------|---|--|--|--|--|
| Influence of PO $_{4}^{3-}$ and SO $_{4}^{2-}$ ions on formation of conversion chromate coating in acidic Cr ⁶⁺ solutions by constant pH 1,1. Duration of chromating 60 s. | | | | | | | | |
| Solution No. | Components of solution, mole/L | | | | | | | |
| | Cr ⁶⁺ | PO $\frac{3-}{4}$ | SO $\frac{2}{4}$ | Appearance of conversion chromate coating | | | | |
| 1.1 | 0,2 | - | - | Film imperceptible with the naked eye. | | | | |
| 2.1 | 0,2 | 0,025 | - | The same. | | | | |
| 2.2 | 0,2 | 0,050 | - | The same. | | | | |
| 2.3 | 0,2 | 0,100 | - | The same. | | | | |
| 2.4 | 0,2 | 0,200 | - | The same. | | | | |
| 3.1 | 0,2 | - | 0,025 | Bright iridescent film. | | | | |
| 3.2 | 0,2 | - | 0,050 | The same. | | | | |
| 3.3 | 0,2 | - | 0,100 | The same. | | | | |
| 3.4 | 0,2 | - | 0,200 | Yellow film. | | | | |
| 4.1 | 0,2 | 0,025 | 0,100 | Green film. | | | | |
| 4.2 | 0,2 | 0,050 | 0,100 | Khaki film. | | | | |
| 4.3 | 0,2 | 0,100 | 0,100 | Greenish yellow film. | | | | |
| 4.4 | 0,2 | 0,200 | 0,100 | Film imperceptible with the naked eye. | | | | |

Thus it may be supposed that the phosphate ions themselves do not activate the zinc corrosion process in acidic solutions of Cr^{6+} .

With similar concentrations of SO $_{4}^{2-}$ ions (0,025-0,200 mole/L) without PO $_{4}^{3-}$ ions in solutions, on the surface of zinc is formed a bright iridescent (solutions 3.1-3.3) or yellow (solution No. 3.4) chromate film. This is the result of zinc corrosion with forming of solid phase, activated, as mentioned above, by SO $_{4}^{2-}$ ions.

0,025-0,100 mole/L of PO₄³⁻ ions added into acidic sulphate-containing Cr⁶⁺ solution results in the change of colour of the formed conversion chromate coating (solutions 4.1-4.3), and addition of 0,200 mole/L – to the absence of chromate film seen with naked eye (solution 4.4). Thus, PO₄³⁻ ions combined with SO₄²⁻ ions in acidic Cr⁶⁺ solution influence the forming of solid phase on the corroding Zn surface.

Kinetics of Zn corrosion in acidic Cr^{6^+} solutions with additives of SO $_4^{2^-}$ and PO $_4^{3^-}$ ions in more detail and more exactly is revealed in the material balance of the products of Zn oxidation and Cr^{6^+} reduction reactions. It includes sum quantities of the oxidized Zn ($C_{Zn}^{2^+}$ (sum)) and reduced Cr^{6^+} ($C_{Cr}^{3^+}$ (sum)), their quantity in the solution ($C_{Zn}^{2^+}$ (s), $C_{Cr}^{3^+}$ (s)) and in the film ($C_{Zn}^{2^+}$ (f), $C_{Cr}^{3^+}$ (f)) and also the quantity of Cr^{6^+} in the film ($C_{Cr}^{6^+}$ (f)).



Material balance of Zn corrosion products in acidic Cr^{6+} - SO $\frac{2}{4}$ solutions with pH value 1,1 is presented in Fig. 1 and Table 2.

Fig. 1. Quantities of oxidised Zn (a) and formed $Cr^{3+}(b)$ in the film (1), solution (2), and general (3) in dependence on sulphate ions concentration in chromating solution: $Cr^{6+}-0.2 \text{ mole/L}, \text{ pH 1.1, } t=60s. 4 - quantity of Cr^{6+} in$ the film.

Fig. 2. Quantities of oxidized Zn (a) and formed $Cr^{3+}(b)$ in the film (1), solution (2) and general (3) in dependence on phosphate ions concentration in chromating solution: Cr^{6+} -0.2, sulphate - 0.1 mole/L, pH 1.1, t=60 s. 4 - quantity of Cr^{6+} in the film.

0.20

As it is seen from Fig. 1, with increasing of SO $_{4}^{2-}$ ions concentration in solution total quantity of oxidized Zn slightly increases (curve 3(a)), and quantity of formed Cr³⁺ practically remains constant (curve 3(b)).

Accordingly increases quantity of Zn^{2+} ions in the solution (curve 2(a)), as well as in the film (curve 1(a)), while quantity of Cr^{3+} ions increases in the solution (curve 2(b)), but decreases in the film (curve 1(b)).

Main part of Zn^{2+} ions is in the solutions, while more than a half of the formed Cr^{3+} ions are found in the chromate film (Table 2, solutions 3.1-3.3, and columns 2 and 3). It could be explained by difference of solubility products of hydroxide Zn^{2+} and Cr^{3+} compounds. Only by comparatively high concentration of SO_4^{2-} ions in solution (0,2 mole/L, solution 3.4) the main part of Cr^{3+} ions is in the solution as a result of forming of their soluble sulphate complexes; accordingly their quantity on Zn surface decreases in the form of slightly soluble hydroxide compounds.

Ratio of formation rates of slightly soluble hydroxide Cr^{3+} and Zn^{2+} compounds and their soluble complex compounds with SO $_{4}^{2-}$ ions stipulates the correlation of mass fractions of Cr^{3+} and Zn^{2+} compounds in chromate film.

Ratio $C_{Cr}^{3+}(f) : C_{Zn}^{2+}(f)$ decreases by increasing of concentration of SO $_{4}^{2-}$ ions in solution (Table 2, column 4). This shows that quantity of slightly soluble Cr^{3+} and SO $_{4}^{2-}$ hydroxy complex compounds by increasing of SO $_{4}^{2-}$ ion concentration in chromate film decreases. This could be explained by acceleration of forming process of soluble Cr^{3+} and SO $_{4}^{2-}$ complex compounds by increasing of SO $_{4}^{2-}$ ion concentration in acidic Cr^{6+} solution, especially with $C_{SO}^{2-}_{4} = 0,2$ mole/L (solution 3.4).

Ratio $C_{Cr}^{3+}(f) : C_{Cr}^{6+}(f)$ practically does not depend on concentration of SO $_{4}^{2-}$ (0,025-0,2 mole/L) in solution and is near to 2 (Table 2, column 5). This indicates, that the major part of chromium in films, obtained on Zn surface in those solutions, is in the form of hydroxo compound of chromichromate type $Cr_2O_3 \cdot CrO_3 \cdot H_2O^4$.

As it was shown above, PO_4^{3-} ions do not activate the process of Zn corrosion in solution of pure chromic acid (i.e. they do not form soluble complex compounds with Cr^{3+} and Zn^{2+} ions), however, in combination with SO $_4^{2-}$ ions they influence the formation of solid phase.

Material balance of Zn corrosion products in acidic Cr^{6+} solutions with constant concentration of SO $_{4}^{2-}$ ions (0,100 mole/L) and changing concentration of PO $_{4}^{3-}$ ions (0-0,200 mole/L) by constant pH value 1,1 is presented in Fig. 2 and Table 2.

As it is seen from Fig. 2, with increase of PO_4^{3-} ions concentration in solution, slightly increase general quantities of oxidized Zn (curve 3(a)) and formed Cr^{3+} (curve 3(b)). In general they are near to the obtained in solution with analogous concentration of SO $_4^{2-}$ ions, but without PO_4^{3-} ions (solution 3.3). Meanwhile, the dissolved part of oxidized Zn (curve 2(a)) and formed Cr^{3+} (curve 2(b)) occurs to be higher than the entered into film (curves 1(a) and 1 (b) accordingly) and grows by increase of PO_4^{3-} ions concentration in solution (Table 2, solutions 4.1-4.4, columns 2 and 3). Quantity of Cr^{3+} in film slightly exceeds the quantity of oxidized Zn, still relation C_{Cr}^{3+} (f) : C_{Zn}^{2+} (f) remains practically constant (Table 2, column 4) by changing concentration of PO_4^{3-} ions in solution within 0-0,200mole/L.

It was shown by mean of electrochemical Zn corrosion modeling in chromate solutions⁶, that velocity of the process by scheme (1), conditioned by limiting current density of reduction Cr^{6+} to Cr^{3+} , is stipulated by limited hydrogen ions diffusion current onto zinc electrode surface, which is partly blocked by chromate coating. On the basis of ideas about mobile chemical equilibrium in Cr^{6+} solutions it was determined, that the

observed in them limited diffusion current of hydrogen ions is proportional to difference of volume and surface concentrations of proton donors.

Therefore, the obtained results, i.e. some increase of general oxidized Zn and formed Cr^{3+} quantities, as well as noticeable increase of their part in solution to compare with film, allow to assume, that the reason might be the increase of general (analytical) H⁺ ions concentration (C_H⁺) in surface layer of the solution as a result of additional presence in it of phosphoric acid and its acidic anions.

Water solution of CrO₃ has a complex system of oxoanions¹⁶. Beside the well-known HCrO₄⁻, CrO₄²⁻ and Cr₂O₇²⁻ there exist polychromate forms, e.g., Cr₃O₁₀²⁻ and Cr₄O₁₃²⁻.

When introducing mineral acids (HCl, H_2SO_4 , H_3PO_4) or their salts into CrO_3 water solution, the particles of corresponding substituted chromates form, for example, $CrO_3C\Gamma$, $CrSO_7^{2-}$, $HCrPO_7^{2-}$ and $H_2CrPO_7^{-17}$.

Assume CrO_3 water solution contains SO_4^{2-} and PO_4^{3-} ions. There establishes a complex equilibrium system of oxoanions, polychromates and substituted chromates¹⁷ in it. As it is known, general (analytical) acidity of the solution (C_H^+) together with so called free H^+ ions, to be more precise – the hydroxonium ions, includes also all other coexisting proton donors, the "acid" hydrogenous atoms of which neutralize before they reach the final point of alkali metric titration. This acidity in our system can be expressed by the following sum:

$$[H^{+}]+[HCrO_{4}^{-}]+2[Cr_{2}O_{7}^{2-}]+4[Cr_{3}O_{10}^{2-}]+$$

$$+2[CrSO_{7}^{2-}]+3[HCrPO_{7}^{2-}]+4[H_{2}CrPO_{7}^{2-}]+$$

$$+[HSO_{4}^{-}]+[HPO_{4}^{2-}]+2[H_{2}PO_{4}^{-}]+3[H_{3}PO_{4}] =$$

$$C_{H}^{+}$$
(2)

The readers should not be confused, that the terms of the sum (2) from the third to the fifth do not contain any visible hydrogen atoms, capable of taking part in neutralization of alkaline solution of titration. They are not present only so far as, according to the existing tradition, the solvating molecules of water are not included into the formula of hydrated ion. As a matter of fact, acidity of dichromate anion is incontestable: in order to transfer it into chromate, alkali is needed. The external water-anion balance of transition (after reduction of alike terms) is expressed by brutto equation:

$$Cr_2O_7^{2-} + 2OH^2 = 2CrO_4^{2-} + H_2O_2$$
 (3)

irrespective of whether the process is carried out in water solution, or by means of melting of solid phases⁸.

Even in this absolutely simplified balance form the equation (3) unanimously shows that during alkali metric titration the alkali expenditure for converting dichromate into chromate will inevitably enter the general acidity of the solution. However it is possible to bring all ionic equilibrium up to the canonic acid-alkalimetry view. It is enough to introduce into the dichromate ion formula even not all (as if following Brensted), but at least one of its solvating water molecules (without adding them, it would not be able even to solve). Then the approximate chain of equilibrium is easily seen. In equation (3) $Cr_2O_7^{2-}$ should be replaced by the chain of equilibriums, to recognize the typical Brensted's acid in a dichromate ion, and the classical acid-base titration – in the equation:

$$\{Cr_2O_7 \cdot H_2O\}^{2-} = H_2Cr_2O_8^{2-} = 2HCrO_4^{-} = 2CrO_4^{2-} + 2H^+\}$$
(4)

Applicability of the above-mentioned to the rest two, as well as to the other similar anions is obvious.

Taking into consideration the above-mentioned note, it can be stated, that in the examined chromate solutions with the same pH 1,1 general (analytical) H⁺ ions concentration in Cr^{6+} - SO_4^{2-} solutions must be less than in Cr^{6+} - PO_4^{3-} and Cr^{6+} - SO_4^{2-} - PO_4^{3-} solutions, concentration of SO_4^{2-} and PO_4^{3-} ions being equal.

| Table 2 Ratio quantities of Zn ²⁺ , Cr ³⁺ and Cr ⁶⁺ in the solution and in chromate film in dependence on composition of chromating solution. | | | | | | | | |
|--|----------------------------------|-------------------------------------|----------------------------------|-----------------------------------|--|--|--|--|
| Qui dina Nu * | Ratio | | | | | | | |
| Solution No.* | $C_{Zn}^{2+}(s): C_{Zn}^{2+}(f)$ | $C_{Cr}^{3+}(s)$: $C_{Cr}^{3+}(f)$ | $C_{Cr}^{3+}(f): C_{Zn}^{2+}(f)$ | $C_{Cr}^{3+}(f) : C_{Cr}^{6+}(f)$ | | | | |
| 1 | 2 | 3 | 4 | 5 | | | | |
| 3.1 | 6,16 | 0,81 | 2,08 | 1,83 | | | | |
| 3.2 | 3,75 | 0,65 | 1,40 | 2,35 | | | | |
| 3.3 | 3,29 | 0,82 | 1,04 | 2,32 | | | | |
| 3.4 | 3,70 | 2,35 | 0,54 | 2,31 | | | | |
| 4.1 | 4,45 | 1,31 | 1,02 | 7,00 | | | | |
| 4.2 | 3,63 | 1,30 | 1,33 | 10,86 | | | | |
| 4.3 | 6,70 | 2,49 | 1,13 | 13,25 | | | | |
| 4.4 | 16,79 | 5,16 | 1,63 | 10,33 | | | | |
| * For composition of solution see Table 1. | | | | | | | | |

The results of alkali metric titration of solutions are presented in Fig. 3 and Fig.4.

In fact, at the same initial pH the general (analytical) concentration of acid (C_{H^+}) in Cr^{6+} - SO $_4^{2-}$ solutions increases (approximately) from 0,3 to 0,44, i.e. by 0,14 mole/L along with increase of SO₄²⁻ ions concentration from 0 to 0,200 mole/L (Fig. 3(a)), and in Cr^{6+} - PO_4^{3-} solutions at the same increase of PO_4^{3-} ions concentration – from 0,3 to 0,7, i.e. by 0,4 mole/L (Fig. 3(b)).

It is obvious, that the phosphate ions, being the most weak proton donors, contribute relatively much more to the general (analytical) acidity of chromic acid solution than the sulphate-ions in equivalent quantities. Accordingly, in the solutions with constant SO₄²⁻ ions concentration (0,100 mole/L) by the increase of PO₄³⁻ ions concentration from 0 to 0,2 mole/L C_H⁺ increases (approximately) from 0,38 to 0,72 mole/L, i.e. by 0,34 mole/L (Fig. 4).

These additional sources of H⁺ ions in the diffusion layer of the solution, acting at shift of chemical equilibrium, must facilitate the cathodic process $Cr^{6+} \rightarrow Cr^{3+}$ and enlarge general quantities of forming Cr^{3+} and Zn^{2+} ions. Meanwhile, PO_4^{3-} ions can form slightly soluble compounds with Zn^{2+} and Cr^{3+} ions, which precipitating on zinc can lessen its surface activity. Calculation of ions distribution in chromate solution in dependence from its acidity, carried out by method¹⁷, has shown that in analogous solutions by changing their free acidity the beginning of $Zn_3(PO_4)_2$ precipitation is observed at pH=4,25.

In the result of contrary acting of these two factors general quantities of formed Cr^{3+} and Zn^{2-} ions with increase of PO₄³⁻ ions concentration in chromate solution increase insignificantly, and the additional H⁺ ions mainly restrict the precipitation of slightly soluble hydroxide compounds of Cr^{3+} and Zn^{2+} onto Zn surface. Finally, quantities of Cr^{3+} and Zn^{2+} in chromate film decrease, and in solution – increase. The first as well as the later^{4,18,19} investigations of conversion chromate coating show, the iridescent

chromate films, obtained on Zn surface in Cr⁶⁺ - SO₄²⁻ solutions, are formed basically by hydroxide compounds of Cr and Zn; minor quantities of SO $_{4}^{2-}$ ions are also included in the composition of the film.



Fig. 3. Dependence of general (analytical) H^+ ions concentration on concentration of sulphate ions (a) and phosphate ions (b) in the solution of 0.2 mole/L CrO₃, pH 1.1.

The element composition data, received by method of X-ray photo-electronic spectroscopy on the surface and in different depth (5, 35, 65, 100, 150, 200 nm) of chromate film, obtained in solution, containing, mole/L: Cr^{6+} -0,2, SO_4^{2-} -0,1, PO_4^{3-} -0,05 presented in Fig. 5.

It was determined; that the main film-forming elements are chrome (curve 2) and oxygen (curve 1), there is much less of zinc in the film (curve 3) and phosphorus (curve 4), less of all – sulphur (curve 5).

The concentration of chrome on surface of film is less than in depth. This is understood, as on surface of such films there are always present adsorbed oxygen and water, which decrease the relative atomic percentage of Cr. However, after removing the layer of the film by just 5 nm (etching duration by Ar^+ ions – 0,5 min.), Cr quantity in the film increases approximately twice and further in depth remains practically constant. Only after removing 150 nm of the layer, coming closer to zinc surface, Cr quantity in the film begins to decrease. Quantity of oxygen, contrary to chromium, is maximal on the surface of film (for the above-mentioned reasons), and by depth of 5 nm it decreases by 10 atomic %.

Zn quantity is minimal on the surface of film and noticeably increases in depth of it, while S and P concentrations are the highest on the surface and decrease in depth of film, however the decrease character is different. Quantity of sulphur is concentrated in 5 nm of the film and further its quantity is practically constant. Phosphorus concentration decreases in depth evenly and exceeds the concentration of sulphur for several times.

The discussed data of element composition of the film not only confirms the above-mentioned predominance of hydroxide compounds of Cr and Zn in iridescent conversion chromate coatings, but also gives additional information about the process of chromate film forming.

The fact, that sulphur is mainly concentrated on the surface of film, and it is considerably less of it in

depth, reinforces our conclusions about the activating influence of SO $_4^{2-}$ ions on the chromating process by forming soluble complexes with Cr^{3+} and SO $_4^{2-}$ ions and increasing the active surface of Zn. As the forming of complexes is going mainly on the border of solid phase and solution, the maximum quantity of S is on the surface of the film. Only little quantities of slightly soluble hydroxy-sulphate Cr^{3+} compounds are trapped by the film and remain in its depth.



Fig. 4. Dependence of general (analytical) H^+ ions concentration on concentration of phosphate ions in the solution: Cr^{6+} -0.2, sulphate -0.1 mole/L, pH=1.1.

The fact, that phosphorus is much more evenly distributed in the whole volume of the film (there is several times more of it than sulphur), and it is commeasurable with chromium and zinc by concentration in the film, shows, that PO_4^{3-} ions enter the chromate film like a component part, most probably, in the form of slightly soluble zinc phosphates. This confirms as well our suggestion about the possible shielding of zinc surface by its slightly soluble phosphates. The activating influence of phosphate ion on the process generally is based on their function of proton donors in surface layer of the solution, i.e. on forming and precipitation of slightly soluble hydroxide compounds of Cr^{3+} and Zn^{2+} on the surface of Zn.



Fig. 5. Dependence of distribution of elements: O -1, Cr -2, Zn -3, P -4, S -5 in chromate film, obtained in solution: Cr^{6+} -0.2, sulphate -0.1, phosphate -0.05 mole/L, pH 1.1, t=60s, -on duration of eatching by Ar^+ ions.

Conclusions

1. SO $_{4}^{2-}$ ions (0,025-0,200 mole/L) in 0,2 mole/L chromic acid solution (pH 1,1) stimulate zinc corrosion with forming conversion chromate film on zinc surface.

2. The activating influence of SO $_{4}^{2-}$ ions of the zinc chromating process comes out in its partial depassivation of zinc surface by partial bounding of Cr³⁺ and Zn²⁺ ions into soluble complexes. These cationic complexes, getting out into solution and, before that, moving towards the outward surface in the forming layer of solid products, during the appreciable period of time support the possibility of counter-penetration of chromate as

well as hydroxonium ions, necessary for continuing of cathodic and anodic reactions of purposive corrosion process of forming conversion coating, to the metal, i.e. they do not allow the process to be interrupted in the stage of primary passivation by molecular layer of Zn and Cr oxides.

3. PO_4^{3-} ions (0,025-0,200 mole/L) in chromic acid solution (0,2 mole/L, pH 1,1) themselves, appreciably, do not stimulate zinc corrosion and forming of conversion chromate coating. However, in combination with anions of sulphuric acid by insignificantly increasing general quantities of formed Zn^{2+} and Cr^{3+} , they essentially change the Zn^{2+} and Cr^{3+} distribution between the chromate film and solution by increasing the part of solubles.

4. The activating influence of ions of phosphoric acid on kinetics of zinc chromating process is stipulated by increase of general (analytical) H^+ ions concentration of the chromating solution, i.e. reduction of precipitation speed of slightly soluble hydroxide compounds of Cr^{3+} and Zn^{2+} on zinc surface, resulting in increase of H^+ ions concentration in surface layer of chromating solution.

5. PO_4^{3-} ions, contrary to SO_4^{2-} ions are one of basic components of conversion chromate film, most probably, in the form of slightly soluble zinc phosphates.

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