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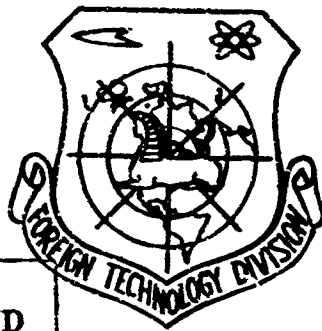
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By

D. Cermakova, J. Nemcova, and J. Dohnalova



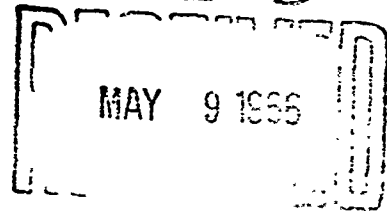
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CORROSION AND PROTECTION OF MATERIALS

ORGANIC CHROMES AS CORROSION INHIBITORS IN BASIC PAINTS

D. Cernakova, J. Nemcova, J. Dohnalova

When studying organic chromes as anticorrosive admixtures to basic paints and lacquers, best results were obtained with paint with 1.8% CrO_4 in the form chromium of 1-methylcyclohexanol-1, with which the protective effectiveness was increased by perhaps 10 times* against paint with 13.8% - in the form of zinc chromium. Organic chromium reduces the tendency of paint toward blistering.

Protection of the effect of paint increases pigments, which improve the properties of paint alone, because it prevents corrosion of the metal under the paint.

Protective action of inorganic chromium in paints is limited by their low solubility in this medium. Chromium is merely dissolved in paint but protects it therefore, in the vicinity of dispersed particles. Addition of chromium must therefore be very high, which subsequently has an unfavorable effect in the increase of blisters in the paint under the effect of water of diluted portions of inorganic chromium.

* Evaluated for CSN 03 8140

FTD-TT-65-1425/1+2+4

The assumption of greater success during application of organic chromium acid derivative as inhibition of corrosion admixtures in paints is the fulfillment of several basic presuppositions. Organic chromium must, first of all, be soluble in a nonpolar medium, i. e., in paint matter and in content of paint with water it must be sufficiently hydrolyzed and form so in the damp medium conditions, after which iron is passive.

Experimental Part.

Our experiments intended to verify the mentioned properties of organic chromium acid derivatives, were carried out with paint matters prepared with alkyd resin of pentaerythritic type (X 261) with pigmented ferrous oxide of 90% critically volumetric concentrations, event, without further pigmentation. In some cases organic chromium was added to commercial basic paint matters which were inconceivable of anticorrosive admixtures, event, to lacquer (S 1109, S 60, C 1005).

Organic derivatives of chromium acid, mainly esters of this acid with tertiary aliphatic and cycloaliphatic alcohols and salts with primary, secondary and tertiary amines and nitrogen heterocycles, were prepared altogether by the first reaction of alcohol or amine with chromium oxide.

Results and Discussion.

From various types of organic derivatives of chromium (esters and tertiary alcohols, added salts of chromium acids with aliphatic amines or heterocycle nitrogen) are in water and in benzene the most soluble esters of chromium acid with tertiary alcohols. Added chromium salts have a substantially

lower solubility in a nonpolar medium.

From the viewpoint of solubility in benzene and in water, the best of the mentioned substances is chromium 2-methylpropanol-2. But its great oxidation capacity and too rapid irreversibly occurring hydrolysis would not be a guarantee of sufficient supplies of chromium anion in the paint (1). Chromium 1-methylcyclohexanol is more convenient from ester for paints, and from additive salts, chromium of trimethylamine and tertiary butylamine.

The extraction of chromium tertiary methylcyclohexanol was determined by establishing the concentration of chromium anion, which passed from paint into aqueous phase. We have also investigated whether the solution obtains minimum effective quantities of this composition necessary for passivation, i. e., 0.006 g per 1 liter (2).

The rate of transition of organic chromium into aqueous phase follows at first to a definite value and then it is only constant. The rate is not relatively too great which is a guarantee, that it will not reach excessive losses of the effective inhibition corrosion compound, but it is sufficient to guarantee passivation of the basic material, which was repeated in the results of corrosion experiments. Liberation of an amount of chromium anion is sufficient also for the protection of copper, zinc, brass, aluminum and magnesium (3).

From the results of investigating strength and ductility of determined oxidation effect on pojidla (?) (foods) (see Figure 1), it is possible to judge that the addition of chromium does somewhat increase the network of pojidla (?) (increasing strength); but simply we do not deal here merely that the

film should become fragile (changes in ductibility are almost neglected).

The time dependence of the old food (pojidla) comprising the addition of organic, investigated with the aid of infrared spectroscopy is shown in Figure 2. Oxidation is not expressive.

Obtained curves of electrochemical potentials of steel samples of the investigated paints (Figures 4, 5, 6) have three main sections. The initial drop is the result of rapid water penetration and of oxygen of the macropores of the paint and light attachment of the base material. The level will soon begin liberating the chromium anion, and oxide layer will begin forming on the surface of the metal and on the potention curves is an evident increase.

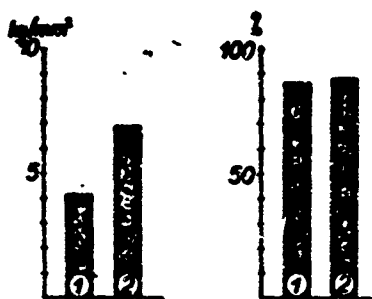


Figure 1. Change in Mechanical property of Paint from Pojidlo (?) X 261 with an Addition of Organic Chromium (1.76%). Measured on the "Schopper 3" device with a Scale Extent of up to 3 kg at a Shift in the Lower Jaw of 200/mm/min at $2 \pm 0.5^\circ\text{C}$.

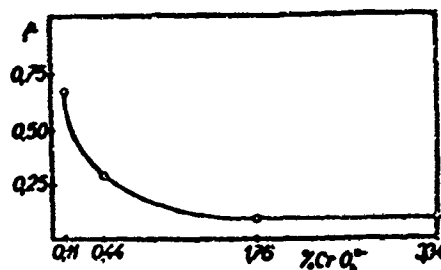


Figure 2. Oxidation of Alkyd Resin X 261 at an Addition of Organic Chromium. Investigated by Infrared Spectroscopy. 1-CO Group (1745 cm^{-1}); 2-CH Group (2925 cm^{-1}).

The increase in maximum and the time necessary to attain maximum is a measure of effectiveness of the inhibition component of the paint. The best was paint with 2% CrO₄ (addition of 0.44% CrO₄ is not sufficient, Table 2).

After 6 to 8 days it will penetrate the corrosion medium and the micropores and by intermolecular spaces into the paint and the corrosive effect will begin iterately to apply.

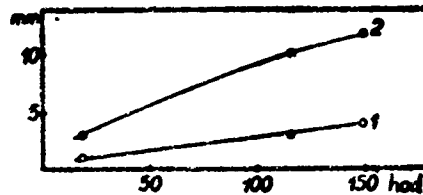
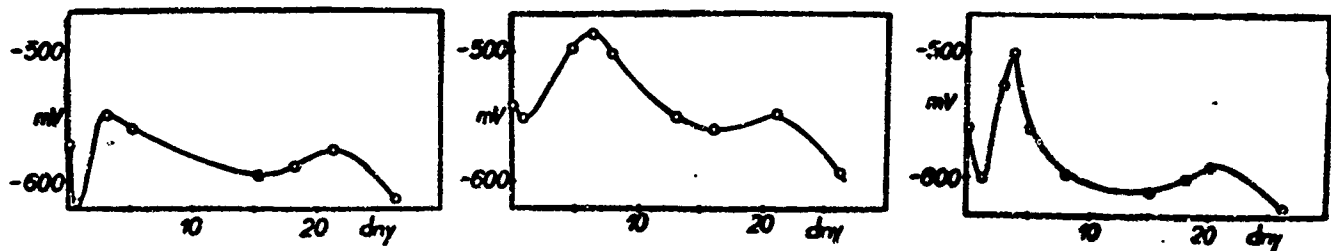


Figure 3. Effect of Concentration of Chromium Anion in Form of Organic Chromium on the Reduction of Corrosion Under Paint (according to CSN 03 8140).

on potential curves a decrease is visible. Under the effect of continuous swelling and beginning of blistering will improve the contact of the solution with inhibitor with basic material, which will appear in mild advancement of the curve after about 15 days, but it also moved the adhesion of the paing toward the basic material and corrosion begins taking place more intensively.

This method of evaluating the protective effectiveness of basic paints was found to be highly convenient. Changes on potential curves and the processes which promoted time conformance with these processes which were visually investigated.



Figures 4 - 6. Time Dependence of Electrochemical Potential (Fig. 4, Paint with 1.76%, Fig. 5 with 3.34% chromium Anion, in both Cases in the Form of Organic Chromium; Fig. 6 with 13.8% of Chromium Anion in the Form of Zinc Chromate.

Table 1.

Electrode Potentials of Steel with Paint Containing Corrosion Inhibition Admixtures (against saturation of calomel electrode) in 2% Solution of Sodium Chloride at 20°. Thickness of Paint - 70 Microns

Korozně inhibiční přísada 1)	Obsah CrO_4^{2-} % 2)	Potenciál i maximum (mV) 3)	Šířka maxime 4)
1-metylcyklohexanol-1 chroman 5)	3,34	-485	53
1-metylcyklohexanol-1 chroman	1,76	-550	57
zinkchromát 6)	13,80	-500	14

1) corrosion inhibition admixture; 2) content, CrO_4^{2-} % ; 3) potential i, maximum (mv); 4) width of maximum (mm.)

Table 2

Results of Corrosion Experiment in a Pure Condensation Chamber for CSN 038140 Experimentation Time 32 Days

Korozně inhibiční přísada 6)	Koncentrace CrO_4^{2-} (%) 7)	Korózní úbytek (mikrony) 8)
1-metylcyklohexanol-1 chroman 1)	3,34	0,09
1-metylcyklohexanol-1 chroman 2)	1,76	0,08
1-metylcyklohexanol-1 chroman 3)	0,44	0,29
1-metylcyklohexanol-1 chroman 4)	0,11	0,67
zinkchromát 5)	13,80	1,37

1-4) 1-methylcyclohexanol-1; 5) zinc chromate; 6) corrosion inhibition admixture; 7) concentration CrO_4^{2-} (%); 8) corrosion diminution (microns)

Table 3.

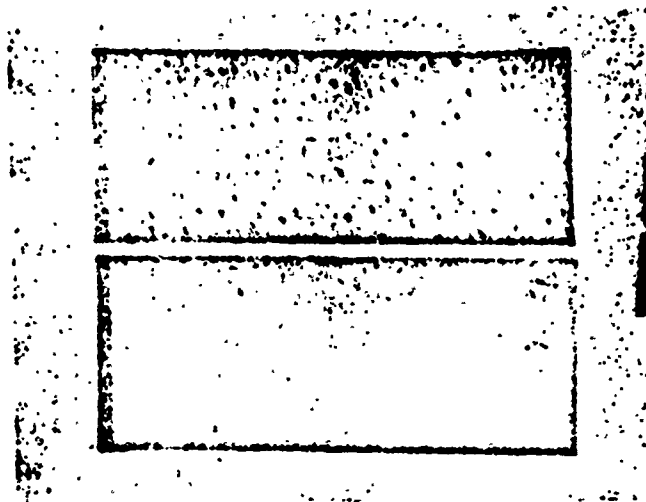
Increase in Protective Effectiveness of Lacquer S
1109. Values According to CSN 038140

Chromen 1)	Obsah CrO ₂ ³ 2)	Korozní abrytek 3)
1-metylcyklohexanol-1 chroman	0,7	0,80
1-methylcyklohexanol-1 chroman 4)	0,34	1,72
trimethylamin chroman 5)	0,35	1,59
"		2,33

1) chromium; 2) content CrO₂³, %; 3) corrosion drop μ ;
4) 1-methylcyclohexanol-1 Chromium; 5) trimethylamine
chromium.

From the results of corrosion investigations (Figure 3, Table 2) it is evident that chromium anion applied in the form of organic chromium appears more clearly than in the form of zinc chromate.

Practical experiments have also checked the possibility of using organic chromium to lacquers, which in this way become anticorrosive without losing transparency (Table 3). Advantages of organic chromiums lie also in the reduction of the tendency of the paint toward blistering, which at zinc chromate promotes a high content of water soluble share (Figure 7).



**GRAPHIC NOT
REPRODUCIBLE**

Figure 7. Degree of Blistering of Paint when Testing in a Condensation Chamber (at the top, basic zinc chromate paint, at the bottom, with organic chromium).

Literature

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2. L. Cerveny; R. Bartonicek: Chem. Reports 50, 188 (1956).
3. L. Cervany; R. Bartonicek: Chem. Industry 8, 622-628 (1958).