REPORT A66-23

EFFECTS OF HEATING CHROMATE CONVERSION COATINGS

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DEPARTMENT OF THE ARMY
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Philadelphia, Pa. 19137

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ABSTRACT

Chemical chromate conversion coated zinc, cadmium, aluminum and magnesium were oven heated at temperatures from 50 to 200° C and subsequently tested for salt spray corrosion resistance.

Chromated zinc and aluminum were particularly adversely affected in corrosion resistance after exposure to air temperatures above 100° C. Exposure to elevated temperatures resulted in insolubilization of hexavalent chromium and cracking of the chromate coating.

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● THE FACT THAT THE PROTECTIVE PROPERTIES of chromate conversion coatings applied to various metals are adversely affected when heated at approximately 65°C or higher is generally recognized.[1-4] The open literature, however, lacks specific details relating the degree of damage occurring to chromate coatings to the heating over a range of temperatures. Recurring inquiries and needs for such information, associated with chromated metal parts which must encounter heat during fabrication of assemblies, or while in use in operating equipment, required that specific information be acquired concerning the extent of damage resulting from heating and the effect of such damage on the protective qualities of chromate coatings applied to various metals.

Investigations reported herein pertain to chromate conversion coatings on zinc, cadmium, aluminum, and magnesium.

Procedure

Preparation: Details for the preparation of chromated specimens of the four metals are given in Table I.

Heating: A group of eight chromated panels for each metal were heated for two hours in a forced-draft oven at each of the following temperatures: 50°, 75°, 100°, 150°, and 200°C. Half of these were used to determine the availability of hexavalent chromium from the conversion film by leaching with water. The remaining specimens were subjected to salt-fog to determine the corrosion resistance. Control specimens (chromated, unheated) and bare metal specimens were included in each of the tests.

Initially, chromated zinc specimens which had been heated at each of the temperatures and for periods of one-half, two, and eight hours were tested as described above. On the basis of the results obtained, which revealed that the specimens were affected to approximately the same degree, the two-hour heating period was established for this work.

Leaching: Leaching was accomplished by immersing each specimen, separately, for one hour, in two liters of boiling distilled water. The quantity of hexavalent chromium attracted in each case was determined colorimetrically by the diphenylcarbazide method.[5]

Corrosion resistance: A measure of the corrosion resistance was made by subjecting the specimens to five per cent neutral salt fog (ASTM Method B-117). The specimens were examined at intervals, and were rated for degree of corrosive attack according to the following arbitrary scale:

5—no attack	2—moderate
4 — trace	1—heavy
3—slight	0—very heavy

Surface condition: Photomicrographs (1000X) of the chromate conversion coating on each metal were taken after successive heatings of the specimen for two hours at each of the temperatures. The same area of the specimen was photographed each time.

Eight chromated zinc specimens were exposed for two hours in a steam chamber at 100°C. Four of the

TABLE I. Preparation of Specimens

Metal	*Cleaning*	*Chromating*	*Draining, rinsing, drying*	*Aging*
Cadmium or zinc electroplated on mild steel panels (10 cm × 15 cm)	None. used directly.	Immersed 20 seconds in solution of: Sodium dichromate ..... 200 g/l Sulfuric acid (s.g. 1.84) 6 ml/l 25°C, pH 0.8	Drained for 5	
Aluminum 2024-T3 panels (10 cm × 15 cm)	Degreased; caustic etched 30 seconds at 70°C; rinsed; desmutted in 50% by volume HNO_3, (s.g. 1.42); rinsed	Immersed 5 minutes in solution* of: Chromic anhydride ..... 5 g/l Potassium ferricyanide 1 " Barium nitrate 1.9 " Sodium fluosilicate ..... 1.35 " 25°C, pH 1.5	seconds: rinsed in flowing water at	Three days
Magnesium AZ 31 panels (10 cm × 15 cm)	Degreased; cleaned 15 minutes in a solution of commercial sodium orthosilicate (60 g/l) at 95°C: rinsed; deoxidized 1 minute in 20% CrO_3 at 95°C; rinsed; pickled 15 seconds in 8% HNO_3 (s.g. 1.42) + 2% H_2SO_4 (s.g. 1.84) by volume at 25°C: rinsed.	Immersed 1 minute in solution of: Sodium dichromate ..... 80 g/l Nitric Acid (s.g. 1.42) 188 ml/l 25°C	25°C for 50 seconds: drained and dried at ambient conditions.	at ambient conditions.

*U.S. Pat. 2,796,371

TABLE II
Salt Fog Corrosion Resistance of Chromated Metals
Corrosion Rating — (Av. four specimens)

Salt fog exposure, hours	*Unheated*		*Chromated metals, heated two hours*				
	Bare	*Chromated*	*50°C*	*75°C*	*100°C*	*150°C*	*200°C*
			Zinc				
24	0	5	4½	4	2	1	½
48	0	5	4½	4	2	1	0
96	0	5	3½	2½	1	0	0
192	0	4	2	1½	0	0	0
			Cadmium				
24	2	5	5	4	3	3	3
48	2	5	5	3	3	3	3
96	2	5	5	3	2½	2	2
192	2	4	3½	2½	2	2	2
			Aluminum				
24	0	5	5	3½	2	1	0
48	0	5	5	2	2	1	0
96	0	5	1½	2	1	0	0
168	0	4	4	2	1	0	0
240	0	4	2½	0	0	0	0
			Magnesium				
12	1	4	3	3½	4	3	3
24	1	2	2	2	3½	3	3
40	0	1½	2	1½	2½	3	3
96	0	1	1	1	1	1	1

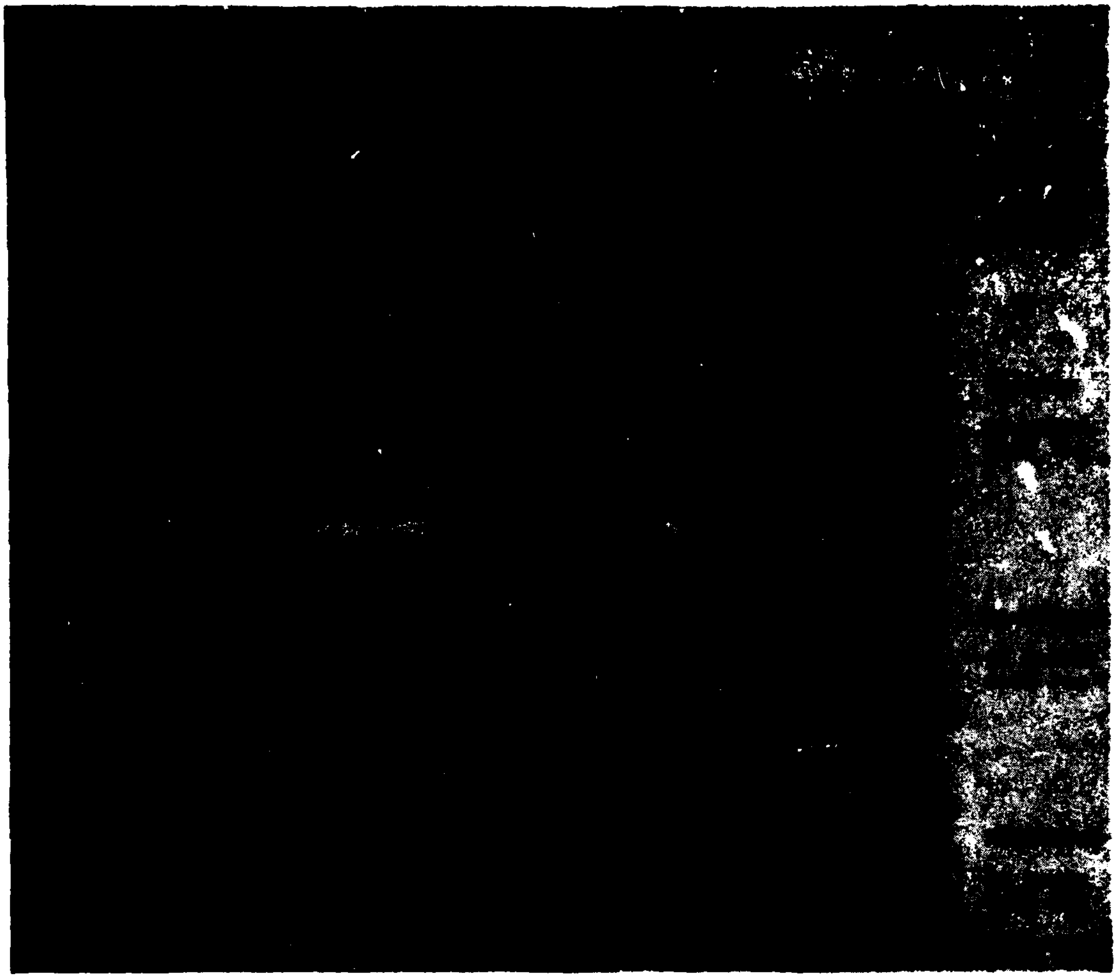

Fig. 1. Corrosion resistance of chromated metals heated at various temperatures.

specimens were then placed in salt-fog and four were leached, as described previously. Ratings for corrosion resistance and analyses for soluble chromates were accomplished as indicated above.

Results and Discussion

Salt-fog exposure results with heated specimens, with bare specimens, and with chromated, unheated (control) specimens are given in Table II. Since the numerical rating of the four replicates within each group were generally within one rating unit, an average was taken for each group, to the nearest half unit.

Heating chromate conversion coatings on cadmium, zinc, and aluminum within the temperature range of 50° to 200°C reduced the effectiveness of the coating to provide corrosion resistance. From the salt-fog tests it was evident that heating the coatings at 50° resulted in a slight adverse change; however, heating the coating at higher temperatures, i.e., 75°, 100°, 150°, and 200°C, resulted in progessive damage. Heating at 150° or 200°C completely nullified the protective value of the chromate conversion coatings, as can be seen in Fig. 1 by comparing corrosion of the bare metal specimens with that of the chromated metals heated at the higher temperatures. Heated chromate coatings on magnesium were found to yield corrosion resistances which were rather unexpected. Specimens heated at 50° or 75°C were comparable to the controls, while specimens heated at 100°, 150°, or 200°C were more corrosion resistant than the controls after 24 and 40 hours in salt-fog. Thus, the heating of chromated magnesium at temperatures of 100° to 200°C was beneficial. With continued exposure, up to 96 hours, all specimens, including the controls, corroded to approximately the same degree.

The leaching tests revealed that, as the temperature of heating was increased, the water-soluble chromium compounds in the conversion coating diminished markedly. A plot of the leachable chromates is shown in Fig. 2. Specimens of chromated cadmium, zinc, or aluminum which had been heated at 100°C yielded less than three per cent of the soluble chromates found in the control (unheated) specimens. This low level of soluble chromates was not reached in the case of the magnesium specimens until they were heated at 200°C. Chromated magnesium specimens heated at 100°C re-

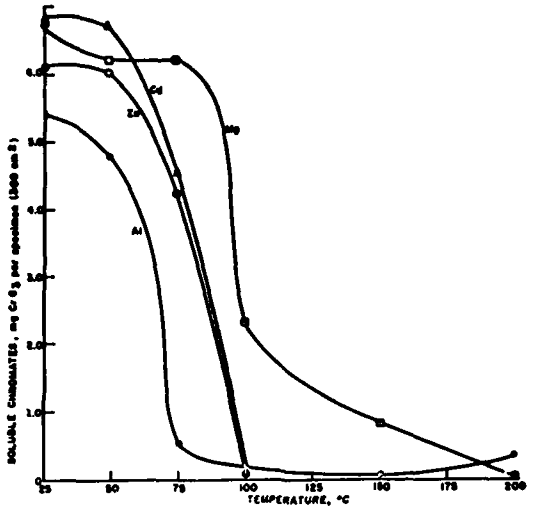

Fig. 2. Leachable chromates from conversion coatings on metals heated at various temperatures.

tained approximately 35 per cent of the original amount of soluble chromates.

Spencer[1] and Ostrander[2] have stated that the damaging of chromate conversion coatings is attributed to dehydration of the coating, and to insolubilization of the chromate compounds in the coating. The latter is supported by the results of the leaching performed on oven-heated specimens. It was reasoned that, if the heating were to be conducted in a "wet" atmosphere, dehydration of the coating and insolubilization of chromates in the coating might be prevented. This was borne out by results obtained with the chromated zinc specimens which had been heated in a steam chamber. The salt-fog and water leaching results were essentially identical to those of the unheated control specimens.

Photomicrographs of the chromated specimens, before and after heating for two hours at each of the temperatures, showed that heating produces a network of "cracks" in the coating. "Cracking" occurred in the coating on cadmium after heating at 50°C, and in coatings of the other metals after heating at 75°C. At the higher temperatures the "cracks" became enlarged. The crack pattern in the coating on each of the metals was similar, although the "crack"-bounded areas were smaller in the cases of magnesium and aluminum specimens. This condition is illustrated with the coating on zinc (Fig. 3). "Cracking" did not occur in the chromate film on zinc specimens which had been heated at 100°C in a steam chamber.

It was found that, when the chromated zinc or cadmium specimens which had been heated at 200°C were rechromated without removal of the heat-affected

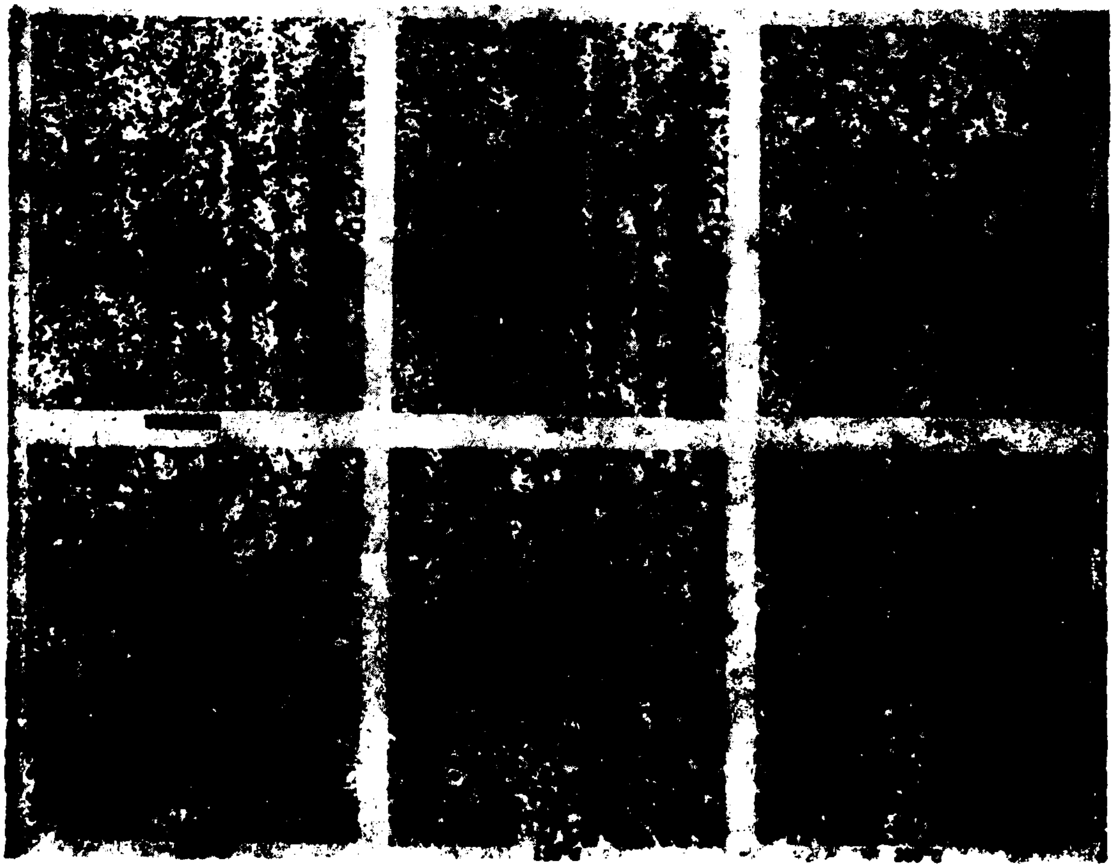

Fig. 3. Photomicrographs of chromated zinc surface heated at various temperatures.

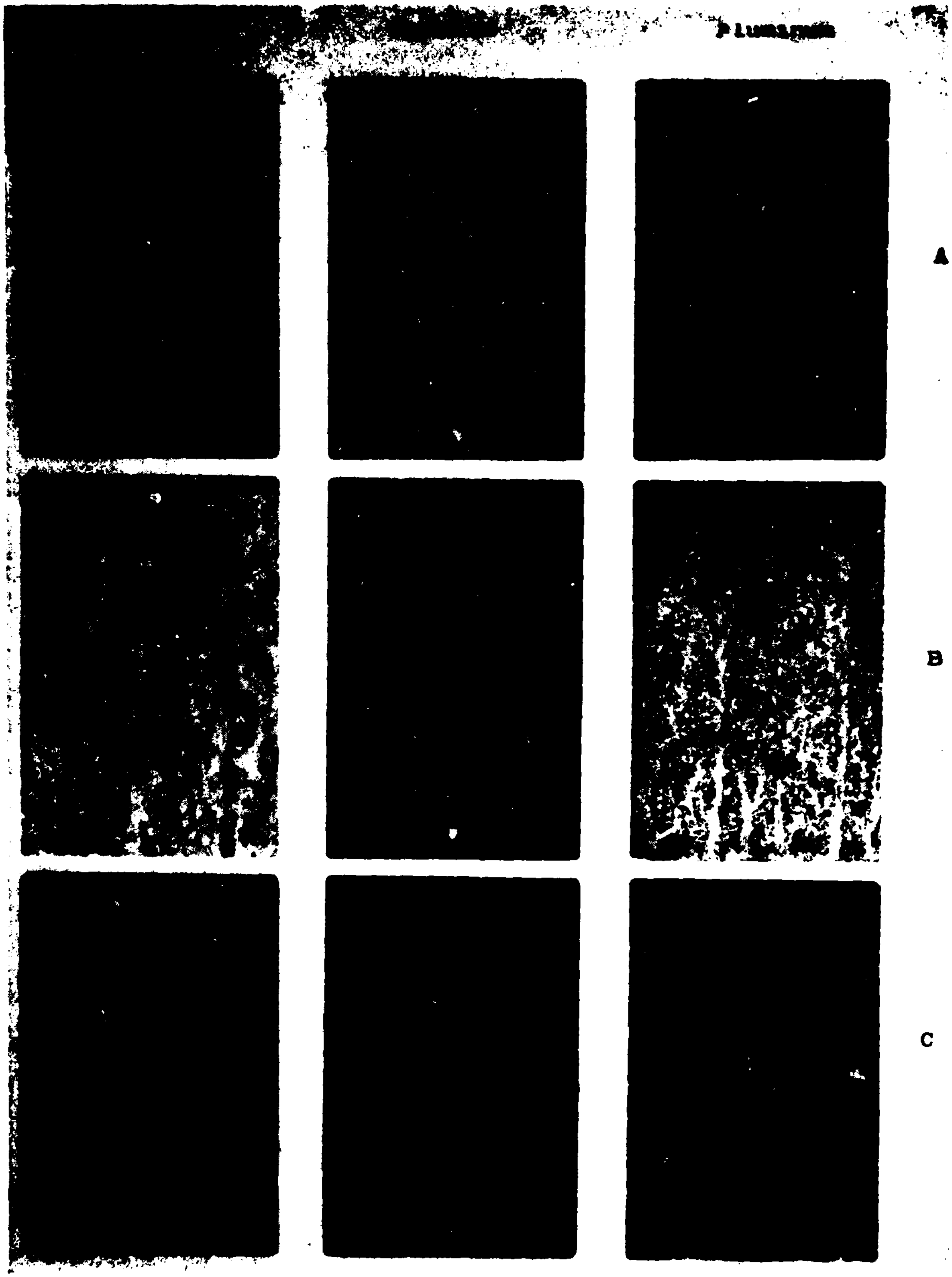

Fig. 4. Chromated specimens after 96 hours salt fog exposure. A. chromated; B. chromated, heated two hours at 200°C; C. chromated; heated two hours at 200°C, rechromated.

coating, the corrosion resistance was virtually entirely restored. Chromated aluminum specimens which had been heated at 200°C and rechromated were restored to a lesser degree (Fig. 4). Rechromating of heated magnesium specimens was not accomplished since the chromate coating on magnesium had not been damaged.

Conclusions

The corrosion resistance usually imparted to aluminum, cadmium, and zinc by the chromate conversion coatings is adversely affected by heat. Heating at 50°C produces a slight change and, at 75°C, a marked change; heating at temperatures from 100° to 200°C results in more pronounced change. The chromate coating on magnesium is not damaged by heating; in fact, heating from 100° to 200°C improves the protective value of the coating.

Heating above 50°C insolubilizes the chromates in chromate conversion coatings. At higher temperatures the insolubilization is more complete. Heating in steam, at 100°C, does not insolubilize the chromates.

Heating of chromate coatings on the various metals at 75°C or higher results in a network of "cracks" in the coatings. Heating in steam at 100°C does not produce "cracking" of the coating on zinc.

The protective value can be restored to heat-damaged chromate conversion coatings on cadmium and zinc by rechromating without prior removal of the heat-damaged coatings.

References

1. Spencer, L. F., Metal Finishing, **58**, 58 (1960).
2. Ostrander, C. W., Materials and Design Engineering, **52**, 116 (1961).
3. Pocock, W. E., Metal Finishing Guidebook, p. 486 (1964).
4. Cole, H. G., Selected Gov't. Research Reports, London, **2**, 53 (1949).
5. Sandell, E. B., Colorimetric Determination of Metals, Interscience Publishers, New York, p. 392 (1959).

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Zinc						
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Heat Resistance						

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