

Electrolytic and Chemical CONVERSION COATINGS

a Concise Survey of Their
Production, Properties and Testing

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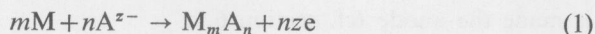
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1. INTRODUCTION

THE term 'conversion coating' applies to the coatings produced on metal surfaces by reaction of their external atomic layers with anions of a suitably selected medium:



where:

M = metal reacting with the medium

A = the medium anion.

Thus, the process of formation of the conversion coating is an artificially induced and controlled corrosion process yielding on the metal surface a layer firmly bonded to the basis metal, practically insoluble in water and the given medium, and having electrical insulating properties.

This shows that the conversion coating, unlike coatings applied, for example, by electrodeposition, is produced on the metal surface with the direct participation of the basis metal in the process.

In fact, however, the process of formation of conversion coatings is more complicated than is shown in Eq. (1) and as a result of the more-or-less intricate electrochemical, physicochemical and chemical processes which may proceed as accompanying or secondary reactions, the coatings obtained are never typical conversion coatings.

A characteristic example of the complicated process of conversion coating formation is the phosphating process which may proceed in two environments reacting differently with the metal but both forming a phosphate coating. In one solution containing alkali metal ions iron phosphate, i.e. a typical conversion coating, is formed on steel, whereas in the second solution containing heavy metal ions (Zn, Mn) a coating which consists of phosphates of these metals is formed. This points to secondary processes proceeding during phosphating.

To differentiate between both types of coatings the present authors have assumed the following terms:

Conversion coatings for coatings which indeed are formed according to Eq. (1),

Pseudoconversion coatings for coatings which are formed when secondary processes dominate.

The literature gives only the definitions of environments in which processes of formation of conversion coatings may proceed, distinguishing solutions which produce coatings and those in which coatings cannot form.

This classification is explained in more detail when discussing the phosphating processes.

The processes of formation of conversion coatings may be classified into chemical processes, where the coating is formed by simple immersion of metal in solution, and electrochemical (anodic) processes, where electric current is the main factor controlling the process and the metal treated is made the anode (cf. section 6.1).

Because of the complicated processes that take place during the formation of conversion coatings and the different compositions of such coatings, a detailed classification of the particular processes or coatings is quite difficult. The criterion adopted for this purpose by the present authors was the composition of the conversion coatings which also indicates the dominating process in their formation.

The methods of obtaining conversion coatings may be classified into the following three groups:

- (a) Methods involving simple immersion of the treated articles in the reactive solution.
- (b) Methods consisting in spraying the solution onto the metal surface.
- (c) Methods consisting in covering the treated metal with a concentrated reactive solution.

Conversion coatings have found extensive application. They are used mainly for purposes of corrosion protection. However, owing to the high porosity most of them require additional sealing treatment. This may be carried out by the application of special solutions (e.g., in the case of oxide coatings on aluminium), mineral oils, greases or paint. In the last case conversion coatings improve considerably the adhesion of paint coatings to the metal substrate and prevent the spreading of undercoat corrosion in the event of local coating damage.

The second extensive application of conversion coatings is in the cold working of metals (phosphating, oxalate coating). In this case the conversion coating plays the role of lubricant which decreases friction and enables application of higher loads. Phosphate coatings have found also application as anti-friction (anti-seizing) coatings.

Conversion coatings either have an attractive and decorative appearance or, owing to their absorption properties, may be coloured to various shades with both organic and inorganic dyes.

Conversion coatings can be produced on the surface of almost all metals having any commercial application in industry—for example aluminium, zinc, cadmium, iron, copper and its alloys, magnesium alloys, silver, etc.

Methods of production and properties of conversion coatings are discussed below with special emphasis on their application for anticorrosion protection. Other engineering applications are also considered but metal colouring processes, because of their typically decorative applications, are not discussed.

2. CHROMATING

1. GENERAL

a. Definition and General Description of the Process

In the last two decades a significant progress and extension of the range of application of metal chromating processes has been noted.

The term 'chromating' applies to the chemical or electrochemical treatment of metals and metallic coatings in solutions containing chromic acid, chromates or dichromates as the main constituents^(1,2). As a result of such a treatment a protective conversion coating is produced on the metal surface composed of tri- and hexavalent chromium compounds.

The metal corrosion inhibiting properties of chromates are well known. Small amounts of these substances added to circulating water systems passivate the metal surface and hence prevent corrosion.

The following possibilities of deposition of insoluble compounds on the metal surfaces are decisive for obtaining chromate coatings by the application of hexavalent chromium compounds⁽³⁾:

(a) Chromates, being strongly oxidizing agents in acidic solutions, may promote the formation of insoluble salts on the metal surface or increase the thickness of natural oxide films.

(b) Products of reduction of chromic acid are usually insoluble, as for example chromium trioxide Cr_2O_3 .

(c) Metal chromates are often insoluble (for instance zinc chromate).

(d) Chromates may take part in a number of complex reactions, particularly in the presence of certain additives, giving deposits of mixed compounds including ions of the treated metal.

Most frequently chromate coatings are produced on zinc (zinc castings, electroplated and hot-dipped zinc coatings) and cadmium (generally electroplated coatings). Nevertheless, they are also used, especially recently, for the protection of other metals, e.g. magnesium, copper, aluminium, silver, tin, nickel, zirconium, beryllium and alloys of some of these metals. The most important processes of chromating various metals, the basic

constituents of the solutions, and the kind and composition of coatings are listed after Cole⁽⁴⁾ in Table 2.1.

The chromate coatings can be applied on products of the machine-building, electrical, electronic, telecommunications and automotive-industries. They also play an important role in some applications by enabling the substitution of certain metals in short supply. A typical example is the possibility of replacing cadmium coatings in many cases by chromated zinc coatings.

The most important purposes of applying metal chromating include:

(a) Raising the corrosion resistance of the metal or metallic protective coating; in the latter case this may concern prolongation of the time in which the first corrosion sites appear both on the coating metal and on the basis metal.

(b) Decreasing the surface liability to finger-marking.

(c) Increasing adhesion of paint or other organic coatings.

(d) Obtaining colour or decorative effects.

Metals subjected to chromating are listed in Table 2.2 according to the purpose of applying this treatment.

Depending on the mode of operation the practical methods of chromating may be classified into two groups, viz:

(a) Chemical methods consisting exclusively in immersing the articles in chromating solutions, and

(b) Electrochemical methods involving immersion of the articles in the solutions plus the application of an external source of current.

Irrespective of the above, two other types of chromating processes may be distinguished:

(a) Processes producing compact chromate coatings on a clean metal surface so that they constitute the actual coating, and

(b) Processes supporting or supplementing the protective action of other types of coatings, e.g. oxide or phosphate coatings. The latter types of coating are discussed in the respective chapters on oxidization and phosphating.

The chromating processes can be conducted manually, semi-automatically or fully-automatically.

They have gained popularity owing to the simplicity of operation, short time of treatment, availability and low price of chemicals, and, finally, the specific properties of the coatings produced.

According to Westchester⁽⁵⁾ the corrosion resistance of chromate coatings is higher than that of phosphate ones. The same conclusion has been reached by Mock⁽⁶⁾, who discusses the protective properties of chromate coatings and compares them with those of phosphate ones.

Table 2.1. Principal chromating processes (after Cole⁽⁴⁾)

Basis metal	Treatment	Solution composition	Coating composition
Aluminium and its alloys	(a) immersion in alkaline solution	alkaline chromate	oxide and hydroxide possibly with small amount of chromate
	(b) immersion in acid solution No. 1	acid chromate, fluoride, phosphate	phosphate possibly with small amount of chromate
	(c) immersion in acid solution No. 2	acid chromate, fluoride, nitrate	unknown, chromates probably the main constituent
	(d) immersion in acid solution No. 3	acid chromate, sulphate, phosphate	very thin, may possibly contain chromates
	(e) sealing of anodic films	chromates and dichromates in the pH range 5-7	sealing pores with hydroxide and chromates
Cadmium and zinc	immersion in acid solution	acid chromate, sulphate, sometimes other additives	thin, hydrated chromium chromate film
Copper	immersion in acid solution	acid chromate, sulphate	very thin films possibly containing chromates
Iron and steel	rinsing after phosphating	diluted chromate solution with or without phosphate	probably a certain amount of basic chromates deposited in the phosphate coating pores
Magnesium alloys	(a) immersion in strongly acid solution	acid chromate, nitrate	thin chromium chromate film
	(b) immersion in moderately acid solution	chromate, sulphate with addition of buffer, pH 4-5	thick chromium chromate film
	(c) immersion in slightly acid solution	chromate, sulphate, pH 6, at high temperature or anodically	thick chromium chromate film
Silver	(d) sealing of anodic films	neutral chromate	chromates in oxide coating
	(a) immersion	chromate and complexing salt	very thin films possibly containing chromates
Tin	(b) anodic treatment in alkaline solution	alkaline chromate	very thin films possibly containing chromates
	immersion	alkaline chromate	very thin films possibly containing chromates

Table 2.2. Metals subjected to chromating according to purpose of treatment

Purpose of treatment	Advantages	Metal chromated							
		Ag	Al	Cd	Cu	Mg	Steel	Sn	Zn
To increase corrosion resistance	the non-porous chromate coating prolongs the time to corrosion appearance	+	+	+	+	+	+	+	+
To improve the decorative effect	possibility of obtaining coatings of different colours, or of additional colouring owing to the ability to absorb dyes	-	+	+	○	○	-	-	+
To increase the adhesion of paint coatings	structure of chromate coatings ensures better adhesion of paint coats, lower paint consumption and higher corrosion resistance	○	+	+	○	+	○	+	+

Legend: ○ — metals rarely subjected to chromating for the given application,
 + — metals often subjected to chromating for the given application,
 - — metals practically never subjected to chromating for the given application.

The factors decisive for the selection of a given type of chromate coating for commercial application are comprehensively discussed by Drysdale⁽⁷⁾.

A review of chromating processes and applications of chromate coatings in the USA is given by Meckelburg⁽⁸⁾.

Annual reviews of patent literature on chromating of various metals (mainly aluminium, magnesium, zinc and cadmium) covering the years 1969–1972 have been published by Möller^(9–12).

The corrosion resistance and other properties of chromate coatings depend first of all on the basis metal, its surface structure and method of surface preparation; the treatment solution, its chemical composition, temperature and pH; time of immersion; the course of the chromating process itself; and possibly the additional treatment of the chromate coatings obtained, e.g. applying oil or a paint coating. In the case of chromate coatings obtained by electrochemical methods, the current density plays an important role.

b. Development of Chromating Processes as Applied to Particular Metals

Initially the process of metal chromating was applied in 1924 to magnesium. The chromate coatings produced at that time, incidentally on a very small scale, and by the methods then used, were brown or olive in colour. Usually acidic sodium dichromate solutions with or without the addition of certain metal salts⁽¹³⁾ were used for the purpose.

In the period 1924–1936 a number of patents concerning the chromating of magnesium, zinc, cadmium, copper and its alloys were released. From the methods of treatment given in these patents, the one recommending a solution for obtaining bright coatings on cadmium found somewhat greater application⁽¹⁴⁾.

Undoubtedly, the most noteworthy is the process in which the bath containing dichromate and sulphuric acid is used. This process, patented in 1936, is well known as the 'Cronak' process. Chromate coatings obtained by this method on zinc and cadmium are slightly opalescent, yellow or brown^(15,16).

A further improvement in this sphere was the application of solutions containing chromic acid and sulphates followed by rinsing in dilute acid or alkali solutions to obtain a bright surface appearance^(17,18).

In the days of the second world war a process was developed enabling the formation of olive-green chromate coatings on zinc and cadmium.

These coatings showed higher corrosion resistance as compared with that of the slightly opalescent to brown coatings produced hitherto^(19,20). Apart from olive-green coatings it was also possible to obtain by this method black and other colours by suitable dyeing of the olive-green coatings⁽¹⁹⁾.

A further improvement was the application of electrolytic treatment of zinc in the chromating solution^(21,22).

Many of the older zinc and cadmium chromating processes recommending the use of dichromate and sulphuric acid solutions are with some modifications, still in current use.

The chromate-based solutions were also applied for the surface treatment of copper and its alloys but initially only as polishing baths, simultaneously increasing the corrosion resistance owing to the formation of a thin chromate film. At present, thicker coatings of better protective properties may be obtained in those cases where the appearance is not critical.

The chromate coatings on magnesium were applied mostly by the producers of this metal. During the past three decades very many processes of magnesium chromating have been suggested but, only few are still in commercial use. The process most frequently used today employs chromate baths.

In recent years treatment of aluminium in chromate-containing solutions has found extensive application.

Two of the earlier used and more interesting processes, consisting in the application of hexavalent chromium compounds, cannot be classified with full precision in the group of processes of treatment in chromate solutions. The first involves treatment of aluminium in alkaline solutions to obtain grey oxide coatings which are subsequently subjected to 'protective' treatment in potassium dichromate solutions⁽²³⁾. The second process employs solutions containing chromic and phosphoric acids as main components and gives light-green phosphate-chromate coatings⁽²⁴⁾.

The first typical aluminium chromating process was applied on a commercial scale in 1950⁽²⁵⁾. The high degree of anticorrosion protection of the resulting coatings and simple method of processing have contributed to the widespread use of this process.

The application of chromate coatings for anticorrosion purposes on a commercial scale was initiated during the second world war. Such coatings were particularly suitable for corrosion protection of military equipment transported by sea to hot and humid theatres of war. After the termination of hostilities many producers then included chromate coatings on articles in common use and, in this way, the methods of metal chromating were developed and propagated in industry.