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(54) Improvement for processes for continuous coating of metal surfaces with chromium metal and chromium oxide.

(57) The processes for coating metal surfaces with chromium metal and chromium oxide (Cr-CrOx) are improved by introducing a pretreatment consisting in at least one anodic pulse of brief duration applied to the metallic body to be coated immersed in the same chroming solution immediately prior to Cr-CrOx deposition.

In this way it is possible to perform this type of coating also on surfaces consisting of aluminium or alloys thereof, which has hitherto been impossible. Moreover the improvement ensures uniform adherent coatings which provide a firm anchor for subsequent painting. Finally there is a marked upgrading in resistance to corrosion, especially that of the cosmetic type.

The present invention concerns an improvement to processes for continuous coating of metal surfaces with chromium metal and chromium oxide. More precisely it concerns anodic pretreatment which can extend the range of metal substrates on which these coatings can be applied. Hence it is possible to apply chromium metal/chromium oxide coatings also to bases consisting of aluminium and alloys thereof.

The call for ever-improved performance to effectively combat corrosion in the most diverse sectors such as those concerned with household electrical appliances and car bodies has necessitated the utilization of new precoated materials instead of simply-painted steel.

In particular, in this latter sector ever-wider use is made of precoated materials not only for parts most exposed to corrosion (structural elements and underframe) but also for external parts of the bodywork. Hence materials are required that are resistant to both perforating and cosmetic corrosion.

Within the framework of these problems, previous research has revealed the importance of the use of zinc which is electrochemically sacrificial vis-à-vis steel.

The employment of hot-dip galvanized and electrogalvanized materials has certainly improved the product that can be attained and has satisfied primary needs.

In an attempt to optimize the product obtainable, various alternatives have been proposed. A common tendency on some markets is to produce hot-dipped materials with thicknesses in excess of ten microns, thus emphasizing the importance and efficacy of the coating thickness rather than of the type of coating. Adequate cathodic protection of the steel against perforating corrosion is assured in this manner but problems arise regarding cosmetic corrosion, formability (break-up and peeling of the coating), weldability and paintability.

With the introduction of Zn alloys, an attempt has been made to diversity away from conventional galvanized or paint-protected sheet. For instance Zn-Ni alloys have been proposed, but they do not appear to be capable of ensuring adequate sacrificial protection for the steel when the coating is damaged.

Use has also been made of Zn-Fe coatings which provide good corrosion resistance thanks to their phosphatability.

However, in this case, while a higher iron content ensures better behaviour regarding paintability it also increases perforating corrosion problems bound up with the rapid appearance of red rust.

There are also numerous examples of multilayer coatings such as Zn/Zn-Ni or Zn-Cr/Zn-Ni or Zn-Fe/Fe-P. However, even these only assure given properties, for instance, thin coatings, perforating corrosion resistance, cosmetic corrosion resistance or adhesiveness, but they do not ensure all the desired properties at the same time.

Previous research performed by the Inventors concerned the electrodeposition of a film of chromium metal and chromium oxide on electrogalvanized steel. Following the good results already obtained and with a view to optimizing them, they have now turned their attention not only to the deposition of a film of Cr-CrOx on steels electrically or hot-dip coated with zinc and alloys thereof, but also to the sectors of the market requiring products resistant to high temperature (for instance car exhaust silencers), involving aluminium, alloys thereof and aluminized materials which hitherto could not be coated in this manner, using traditional production techniques.

An object of the present invention is to permit the formation of a protective film of chromium metal and chromium oxide also on aluminium and alloys thereof and on coatings of aluminium and alloys thereof by means of an innovative electrochemical process.

Other object of this invention are to ensure an increase in resistance to corrosion, especially the cosmetic type, and to attain surface characteristics such as to provide a good appearance after painting.

A further object of the invention is to eliminate the phosphating phase in the painting cycle, since the Cr-CrOx film replaces the functions of the phosphate layer, thus assuring cost and space savings in production, particularly in processes of the coil-coating type.

A final object of the invention is to favour spot-weldability while increasing electrode life. More precisely, by avoiding direct contact between the zinc-based coatings and the copper of the electrodes, the life of the latter has been increased by at least six times.

The improvement provided by this invention, in which a continuous metallic body is immersed in an electrolytic solution of known type, in movement and strongly acidic due to chromic acid, is characterized by the fact that said metallic body is subjected in said electrolytic solution to an anodic pretreatment consisting in the imposition of at least one pulse of current having a density between 5 and 50 A/dm² for a time between 0.5 and 3 seconds, and subsequently in the same solution to a treatment, known per se, consisting in electrolytic deposition of chromium metal and chromium oxide, said solution having a pH between 0 and 2, at a relative velocity with respect to said metallic body between 0.5 and 4 m/s and a treatment temperature between 40 and 80 °C.

The composition of said electrolytic bath for implementation of the present invention is preferably selected in the range CrO₃ from 20 to 80 g/l, 40% HBF₄ from 0 to 5 ml/l, NaF from 0 to 2 g/l, 98% H₂SO₄ from 0 to 1 g/l.

For the purpose of exemplification, without limiting the objects and scope of the invention itself, the following

examples of the invention are given of production technique, products obtained and relative corrosion behaviour.

Examinations have been made on unpainted products and on products painted according to the car cycle up to cataphoresis, to evaluate corrosion resistance.

5 Operating conditions for some of the numerous tests performed are indicated in Table 1 where a deposition of 1g/m² of total chromium is considered.

For the unpainted samples the test technique involved exposure in the salt-spray cabinet (5%NaCl) as per ASTM B117, evaluating the time necessary for the appearance of red rust on the surface.

10 As regards the corrosion behaviour of samples in the unpainted state, the specimens with the Cr-CrOx coating obtained adopting anodic pretreatment all gave the same type of indications, resistance being at least equal to that -already good - provided by hot-dip coatings with a thickness in excess of that of a normal electrogalvanized coating.

The painted samples with one edge sheared and with a cross scribed to reveal the metal coating were exposed to forty alternate wet-dry cycles involving:

- 15 - 15 minutes immersion in 5NaCl solution
- 75 minutes drying at room temperature
- 22.5 hours in the static humidity cabinet at 40 °C and 98% relative humidity.

Subsequently the corrosion resistance of the same painted specimens was evaluated by:

- 20 - the standard strip test (using 3M N° 250 tape) to ascertain the surface area affected by paint peeling
- determination of the peeled area by QTM (Quantitative Television Microscope) analysis.

Table 2 sets forth the results obtained for paint peeling, expressed in mm², for samples of:

- Alu = aluminium alloy (94.9% Al, 5.1% Si)
- Lav = alloys consisting of 32.5% Al, 0.28% Si, 0.56% Mg, remainder Zn.

The meaning of the letters used in the Table is as follows:

- 25 - A = Cr-CrOx coatings with anodic pretreatment;
- B = Cr-CrOx coatings without anodic pretreatment;
- C = phosphated.

It is evident from the Table that in all cases the effect of the anodic pre-pulse on Cr-CrOx coatings (A) is to improve corrosion resistance.

30 Additionally, the Table reveals that when an attempt is made to obtain Cr-CrOx coatings on aluminium and alloys thereof using known techniques, in the worst cases the deposits are non-adherent and easily removed during cleaning, while even in the best cases the corrosion resistance of the specimens is decidedly worse than that of similar specimens which have been subjected to a preliminary anodic pulse, so they are certainly not capable of meeting market demands.

35 Encouraging results have also been obtained on substrates other than aluminium and alloys thereof.

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	PROCESS CHARACTERISTICS						BATH COMPOSITION				
	Pre-pulse (A/dm ²)	Dura- tion (sec)	Cathod. pulse (A/dm ²)	Dura- tion (sec)	Rel. vel. (m/sec)	T (°C)	CrO ₃ (g/l)	HBF ₄ 40% (ml/l)	NaF (g/l)	H ₂ SO ₄ (g/l)	pH
1	30	1	200	1.7	2.8	55	40	0.5	1	0.4	0.5
2	10	3	200	1.7	1.5	70	30	0.35	0.7	0.3	0.6
3	20	1.5	200	1.7	2.0	60	35	0.4	0.8	0.35	0.5
4	50	0.6	200	1.7	4	80	60	0.7	1.5	0.6	0.4
5	50	0.6	200	1.7	2.8	55	40	0.5	1	0.4	0.5
6	80	0.4	200	1.7	5	60	40	0.5	1	0.4	0.5
7	30	1	200	1.7	2.5	30	40	0.5	1	0.4	0.5
8	30	1	200	1.7	5	90	40	0.6	1	0.4	0.6

TABLE 1

	AREA OF PEELED PAINT (mm ²)					
	ALU			LAV		
	A	B	C	A	B	C
1	311	1350	504	232	595	261
2	388	1520	504	240	633	261
3	371	1499	504	230	572	261
4	294	1375	504	181	590	261
5	298	1340	504	191	608	261
6	550	1549	504	421	710	261
7	738	1455	504	608	688	261
8	668	1611	504	622	721	261

TABLE 2

Claims

1. Improvement of processes for the continuous coating of metal surfaces with chromium metal and chromium oxide in which a continuous metallic body is immersed in an electrolytic solution of known type, in movement and strongly acidic due to chromic acid, characterized by the fact that said metallic body in said electrolytic solution is subjected to an anodic pretreatment consisting in the imposition of at least one pulse of current whose density is between 5 and 50 A/dm² for a time between 0.5 and 3 seconds, and subsequently in the same solution to a treatment, in itself known, involving the electrolytic deposition of chromium metal and chromium oxide, said solution having a pH between 0 and 2, a relative velocity with respect to said metallic body of between 0.5 and 4 m/s and a treatment temperature of between 40 and 80 °C.