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METHOD OF ELECTROPLATING CHROMIUM AND COMPOSITIONS THEREFOR

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20 Claims

ABSTRACT OF THE DISCLOSURE

A bright decorative plating process for electroplating chromium on a basis metal having an atomic number from 24 to 30, characterized by high coverage and throwing power, utilizes an aqueous chromic acid plating bath containing the anion of an aliphatic monocarboxylic or dicarboxylic acid having at least three, preferably 3 to 7, carbon atoms. The baths are of high CrO_3 to catalyst ratio, e.g. 125–550:1. They may be of the self-regulating type. The carboxylic acid anion may be added by introducing into the bath the acid itself, or a soluble salt of the acid, or the acid anhydride. The anion of succinic acid is a preferred dicarboxylic acid anion, and the anion of propionic acid is a preferred monocarboxylic acid anion. The concentration of the carboxylic acid anion is preferably from 25 to 100 grams per liter, but higher concentrations up to saturation may be used.

This application is a continuation-in-part of our application Ser. No. 402,619, filed Oct. 8, 1964, and now abandoned.

This invention relates to a novel process for electrodeposition of bright decorative chromium. More particularly, it relates to a chromium plating process characterized by highly satisfactory coverage of low current density areas.

As is well known to those skilled-in-the-art, chromium may be plated onto various basis metals. During chromium plating, it has been found that the coverage may not be completely satisfactory in low current density areas (typically below about 3–4 ASD) and these areas may frequently receive little or no plate at all. Prior attempts to remedy this defect have included the use of auxiliary anodes; while this step may give some improvement, the disadvantages thereof are numerous and well known. Typically the burden of properly positioning the required anodes is undesirable and the cost of maintaining them on plating racks is very high.

Other techniques which have been tried include the use of various additives in the baths, but these additives have either been unable to give the desired result or have concurrently contributed some additional defect to the plate or to the process. Such defects may include the production of a blotchy plate containing passivity spots, or result in an undesirably high degree of anode corrosion. Corrosion of lead anodes in chromium plating systems is undesirable in that a massive sludge is formed on the bottom of the tank; and the lead anodes are eaten away and must be replaced at regular intervals. Because of these problems, it is well recognized that prior art attempts to attain high coverage over the entire surface of the cathode and particularly in the areas of low current density have not been completely successful.

It is an object of this invention to provide a process for electrodepositing bright decorative chromium plate, characterized by its high coverage of low current density

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areas. Other objects will be apparent to those skilled-in-the-art on inspection of the following description.

In accordance with certain of its aspects, the process of this invention, characterized by high coverage and by high throwing power, for electrodepositing a bright decorative chromium plate onto a basis metal having an atomic number of 24–30 may comprise maintaining an aqueous hexavalent chromium plating bath containing chromic acid and sulfate (or sulfate plus silicofluoride) catalyst in ratio of 125–550:1, and at least about 25 grams per liter of an anion of an organic acid selected from the group consisting of aliphatic monocarboxylic acids and dicarboxylic acids having at least three carbon atoms, and electrodepositing a chromium plate from said bath onto said basis metal as cathode in said bath.

The chromium plating bath which may be employed in practice of this invention may be an aqueous solution containing 150 g./l.–500 g./l., typically 250 g./l.–400 g./l., say 250 g./l. of chromic acid CrO_3 and 0.4 g./l.–3.3 g./l., say 1.2 g./l. of sulfate ion $\text{SO}_4^{=}$, typically added as sodium sulfate. In practice of this invention, the ratio of $\text{CrO}_3:\text{SO}_4^{=}$ may preferably be maintained at 125–550:1, typically 200–300:1, say 250:1.

It is a particular feature of this invention that the novel results may be attained (a) in a standard, non-self regulating bath as described supra or (b) in a mixed catalyst bath or (c) in a self-regulating bath. A typical mixed catalyst bath which may be employed may contain 150–550 g./l., typically 250–440 g./l., say 250 g./l. of chromic acid CrO_3 and 0.05–2.0 g./l., say 0.6 g./l. of sulfate $\text{SO}_4^{=}$; and 0.05–2.0 g./l., say 0.6 g./l. of silicofluoride $\text{SiF}_6^{=}$ ion. It will be noted that the ratio as the term is used in this application refers to the ratio

$$\frac{\text{CrO}_3}{\text{SO}_4^{=} + \text{SiF}_6^{=}}$$

wherein each of the quantities is expressed in grams. Other fluorides, including complex fluorides, may be employed. When no other fluoride such as $\text{SiF}_6^{=}$ is present, the ratio may become $\text{CrO}_3/\text{SO}_4^{=}$. In practice, the ratio of CrO_3 to $\text{SO}_4^{=}$ plus $\text{SiF}_6^{=}$ may preferably be maintained at 125–550:1, typically 200–300:1, say 250:1. In the specification and claims, the ratio may, for convenience, be referred to as the ratio of chromic acid to sulfate; but it will be understood that the ratio as so designated may include as equivalent to sulfate, other inorganic ions including fluoride ions such as the silicofluoride ion, the fluoroborate ion, the fluotitanate ion, etc. Thus the designation “chromic acid to sulfate” includes chromic acid to sulfate plus other fluoride such as silicofluoride if and when the latter is present.

This invention may also be used in a self-regulating bath, e.g. of the sulfate type, which may contain 150–500 g./l., typically 250–400 g./l., say 250 g./l. of chromic acid; and 0.6–8.3 g./l., say 5 g./l. of strontium sulfate; plus a source of excess strontium ion, such as strontium hydroxide, strontium chromate, etc. in amounts to provide 0–12 g./l., say 4.5 g./l. of strontium ion, Sr^{++} .

The anions may commonly be provided in the bath from the corresponding acids. The acids which may be added, either as such or as their anhydrides or salts (typically the sodium salt), either individually or in a mixture, to chromium plating baths in practice of this invention include aliphatic monocarboxylic acids and aliphatic dicarboxylic acids having at least three carbon atoms.

Typical illustrative aliphatic dicarboxylic acids having at least three carbon atoms which may be employed may include: malonic acid, fumaric acid, succinic acid, glutaric acid, adipic acid, pimelic acid.

Typical illustrative aliphatic monocarboxylic acids which may be employed may include: propionic acid,

butyric acid, pentanoic acid, isobutyric acid, and cyclohexane monocarboxylic acid.

The preferred acids may include aliphatic dicarboxylic acids having 3-7 carbon atoms and most preferably succinic acid or adipic acid. A preferred mixture of acids which may be employed may include 25-75 parts of acetic acid and 25-75 parts of succinic acid, preferably 50 parts of each.

In practice of this invention, the acid may be added to the electroplating bath preferably in amounts of from at least about 25 g./l. up to saturation, preferably 25-100 g./l., and most preferably 25-50 g./l. The acids employed will be those having a solubility in the plating bath within this range.

A typical composition which may be premixed, and added to a water solution in which the concentration of $\text{SO}_4^{=}$ ion and components including, e.g., $\text{SiF}_6^{=}$, may be adjusted separately, may include the following (here as elsewhere, unless otherwise indicated, all parts are parts by weight). It will be apparent that these compositions, should preferably be formed, maintained, and stored in a manner to minimize contact with extraneous organic compositions and materials; and preferably they will be formed, stored, and maintained at temperature below 80° C. It will also be apparent that in compositions hereinafter designated as containing "organic acid," equivalent amounts of anhydride, salt, etc. may be employed, thus yielding appropriate amounts of the desired ion.

TABLE I

Component	Max.	Min.	Preferred A	Preferred B
CrO_3	500	150	250	400
Organic acid.....	100	25	30	40

A preferred composition may include:

TABLE II

Component	Max.	Min.	Preferred A	Preferred B
CrO_3	500	150	250	400
Succinic acid.....	100	25	30	40

The organic acid may be added as such, as the anhydride, or as the salt, typically as the sodium salt. In the preferred embodiment, the additive may be admixed with the other ingredients to be used to make up the bath. Typically such a composition may include:

TABLE III

Component	Max.	Min.	Preferred A	Preferred B
CrO_3	500	150	250	400
$\text{SO}_4^{=}$	3.3	0.4	1.0	1.9
Organic acid.....	100	25	30	40

*Typically supplied as, e.g. sodium sulfate.

A specific composition may include:

TABLE IV

Component	Max.	Min.	Preferred A	Preferred B
CrO_3	500	150	250	400
SrSO_4	10	4	5	8
SrCrO_4	5	0	4.5	0
Succinic Anhydride.....	100	25	30	40

A preferred sulfate self-regulating composition may typically include:

TABLE V

Component	Max.	Min.	Preferred
CrO_3	450	225	375
SrSO_4	10	4	8
SrCrO_4	5		
Succinic acid.....	100	25	40

A typical mixed catalyst composition may include:

TABLE VI

Component	Max.	Min.	Preferred A	Preferred B
CrO_3	500	150	250	400
$\text{SO}_4^{=}$	2.0	0.05	0.5	1.3
$\text{SiF}_6^{=}$	2.0	0.05	0.5	0.7
Organic acid.....	100	25	30	40

*Typically added as sodium sulfate.

**Typically added as sodium silicofluoride.

A preferred mixed catalyst composition may include:

TABLE VII

Component	Max.	Min.	Preferred A	Preferred B
CrO_3	500	150	250	400
Sodium Sulfate.....	3.0	0.075	0.75	1.9
Sodium Silicofluoride.....	2.7	0.065	0.65	0.9
Succinic acid.....	100	25	30	40

A typical self-regulating composition having both sulfate and siliconfluoride may include:

TABLE VIII

Component	Max.	Min.	Preferred A	Preferred B
CrO_3	500	150	250	400
$\text{SO}_4^{=}$	2.0	0.05	0.5	1.3
$\text{SiF}_6^{=}$	2.0	0.05	0.5	0.7
Sr^{++}	9	0.2	5.0	2.6
K^{+}	27	6.0	15	27
Organic acid.....	100	25	30	40

A preferred self-regulating composition may include:

TABLE IX

Component	Max.	Min.	Preferred A	Preferred B
CrO_3	500	150	200	325
SrSO_4	8	0.1	2.0	4.0
K_2SiF_6	6	0.75	2.0	3.5
SrCO_3	15	0	9	6
$\text{K}_2\text{Cr}_2\text{O}_7$	100	25	75	100
Succinic acid.....	100	25	30	40

The baths useful in practice of this invention may be formed by dissolving the above compositions in aqueous medium to form baths containing e.g. 150-550 g./l. of CrO_3 and corresponding quantities of the other components.

It is found that particularly outstanding results, in terms of handleability, packaging, ease of manufacture, as well as maximum coverage and brilliance of chromium deposit accompanied by a minimum of lead anode corrosion may be obtained when in the compositions of Tables I, III, IV, and VIII, the organic acid is an aliphatic dicarboxylic acid having at least three carbon atoms; and such compositions are most highly preferred, because of their peculiarly unexpected superiority.

The baths of this invention which may be employed to readily and conveniently electrodeposit chromium plate, are characterized by high coverage and by high throwing power. These baths may be used to deposit chromium on a basis metal having an atomic number of 24-30. Typical of such basis metals may be chromium (24), manganese (25), iron (26), cobalt (27), nickel (28), copper (29), and zinc (30). Mixture or alloys of these metals may be plated; typically brass, stainless steel, etc.

The preferred basis metal may be nickel, and preferably active nickel.

The preferred active nickel basis metal may be attained by electrodeposition of nickel onto a suitable substrate metal (such as iron).

Active nickel may be nickel which is highly receptive to the deposition thereon of a bright clear decorative plate and which has a surface which may be free of nickel compounds such as the oxide. Typically nickel may be active when freshly plated onto a cathode. If not already active, the nickel may be rendered active by cathodic or other reducing treatment prior to the deposition of chromium plate thereon. Preferably this may be effected by maintaining the nickel as cathode in an aqueous electrolyte solution, preferably containing an acid. The preferred acids for use in either electrolytic or non-electrolytic techniques may include the common mineral acids such as hydrochloric acid, sulfuric acid, etc. and more preferably aliphatic dicarboxylic acids having at least three carbon atoms or aliphatic monocarboxylic acids. The preferred acid may be succinic acid. When the aqueous electrolyte solution is other than acid, it may preferably be followed by an acid dip.

It has been found when the high ratio baths of this invention are used to plate chromium onto bright nickel basis metal that it is advantageous to activate the bright nickel by applying to the cathode to be plated in the bath, a low voltage applied thereto at a time less than about five seconds after immersion and preferably to apply the voltage prior to immersion of the cathode. The low voltage may be sufficient to produce a cathode current density up to about 0.25–0.5 times the plating current density. Then the current density may be raised to its full operating value. This technique makes a bright nickel surface more receptive to the deposit of bright chromium from the baths of this invention.

The bath may be preferably at temperature of 30° C.–60° C., say 35° C.–50° C. Preferred cathode current density may be 0.3–40 amperes per square decimeter (ASD), preferably 0.5–20 ASD. Plating may be carried out with air or mechanical agitation for any time to obtain a desired thickness, but for decorative plate it is usually 1–10 minutes; and typically about five minutes may suffice.

During plating in accordance with the process of this invention, there is unexpectedly and surprisingly no appreciable loss of the organic acid by decomposition over extended periods of time. For example, in extended tests, adipic acid and succinic acid were found still to function satisfactorily after plating had been carried out for 110 ampere hours per liter and even longer.

At the conclusion of the plating time, the cathode will be found to be covered to a remarkable degree with clear, bright, decorative chromium plate. It is a particular feature of this invention that the plate is unexpectedly characterized by its high coverage without the need for conforming anodes. For example, a wire wheel for an automobile may be plated by the process of this invention (with no conforming anode) to unexpectedly yield a bright, uniform plate on both high and low current density areas. This has not heretofore been possible.

The plate produced by the novel process of this invention may be found to be highly satisfactory with respect to its unusually bright, decorative appearance and its resistance to corrosion.

In the following series of illustrative examples, chromium was electrodeposited onto a 100 mm. nickel-plated brass panel in a standard Hull Cell at 49° C. for five minutes and three amperes. A standard stock bath containing 300 g./l. chromic acid and 1.3 g./l. of sulfate (added as sulfuric acid) was employed. The organic acid was added in the amount (in g./l.) indicated. At the end of the test, the Hull Cell panel was inspected and the distance across the panel bearing a plate of clear bright chromium was measured in millimeters.

TABLE X

Example	Acid Added	G./l.	Coverage, mm.
1.	None	—	57
2.	Propionic acid	25	73
3.	do.	25	77
4.	do.	40	74
5.	do.	50	75
6.	do.	60	75
7.	do.	75	75
8.	do.	88	75
9.	do.	100	75
10.	do.	150	75
11.	do.	200	74
12.	do.	300	75
13.	n-Butyric acid	25	74
14.	do.	35	73
15.	do.	100	72
16.	iso-Butyric acid	25	72
17.	do.	(²)	71
18.	Pentanoic acid	25	68
19.	do.	(²)	67

¹ Extended test.

² Saturation.

From Example 1 of Table X, it may be observed that with no organic acid added, the panel was covered for a distance of 57 mm.; and this may be considered a control example for all the examples which follow. As the propionic acid concentration increased to 25 g./l. and higher, the coverage increased to as high as 77 mm. A difference of 2–3 mm. or more may be considered significant. Example 3 was carried out in a bath which had been functioning for 46 ampere hours per liter, thus indicating that the system including propionic acid was stable over an extended period. Thus it will be apparent from these examples, that practice of this invention permits attainment of a high degree of coverage.

Table XI sets forth the results attained with various polycarboxylic acids.

TABLE XI

Example	Acid Added	G./l.	Coverage, mm.	Extended Test
20.	Malonic acid	25	70	—
21.	do.	35	70	—
22.	do.	50	69	—
23.	Succinic acid	25	67	71
24.	do.	50	71	80
25.	do.	75	78	74
26.	do.	100	77	73
27.	do.	(¹)	77	—
28.	Glutaric acid	25	71	—
29.	do.	50	75	72
30.	Adipic acid	25	65	—
31.	do.	50	78	73
32.	do.	75	77	—
33.	do.	(¹)	76	—
34.	Succinic anhydride	25	65	—
35.	do.	50	72	—
36.	do.	75	73	—
37.	Pimelic acid	25	61	—
38.	do.	40	75	—
39.	Fumaric acid	50	66	—
40.	do.	75	65	—

¹ Saturation.

From Table XI, it will be apparent that improved coverage may be attained by using polycarboxylic acids in the process of this invention. From Examples 23–26, 29 and 31, it will be further apparent that, after extended continuing test of 110 ampere hours per liter, the coverages attained are as good as at the beginning of the test; and in fact, some acids give improved results at the end of the extended test, e.g. Example 24.

Table XII sets forth the results attained in Hull Cell tests using the conditions set forth in the table. In all cases, plating was carried out for five minutes.

TABLE XII

Ex.	CrO ₃ , g./l.	CrO ₃ /SO ₄ ratio	Temp., ° C.	Current, Amps	Additive	G./l.	Cover age, mm.
41	150	200	43	3	Adipic acid	25	68
42	500	150	43	3	Succinic acid	100	70
43	500	200	43	3	do.	100	72
44	500	300	43	3	do.	100	72
45	250	100	43	3	None	None	*54
46	250	200	43	3	Succinic acid	50	71
47	250	300	43	3	do.	50	72
48	250	400	43	3	do.	50	74
49	250	400	43	3	do.	50	60
50	250	600	43	3	do.	50	57
51	400	200	43	3	Adipic acid	75	71
52	400	300	43	3	do.	75	75
53	250	300	32	1	do.	50	60
54	250	300	32	1	None	None	*42
55	250	300	38	1.5	Succinic acid	50	69
56	250	300	38	1.5	None	None	*55
57	250	200	57	7	Succinic acid	50	76
58	250	200	57	7	None	None	*72
59	250	300	57	7	Succinic acid	50	71
60	250	300	57	7	None	None	*68
61	400	200	32	1	Adipic acid	75	55
62	400	200	32	1	None	None	*41
63	400	400	32	1	Adipic acid	75	58
64	400	200	38	1.5	do.	75	59
65	400	200	38	1.5	None	None	*52
66	400	400	38	1.5	Adipic acid	75	58
67	400	200	57	7	do.	75	75
68	400	200	57	7	None	None	*70
69	375	125	49	3	Succinic anhydride	25	64
					Mixture of—		
					Succinic acid	75	
					and		
					Adipic acid	75	
70	500	230	49	3	Mixture of—		71
					Succinic acid	20	
					and		
					Acetic acid	20	
71	375	200	43	3			76

* Control for tests at that temperature and current.

From Table XII, it will be apparent that superior results may be attained when using the novel process of this invention. In particular a comparison of the control examples with the experimental examples shows that the novel process gives outstanding results in terms of coverage.

In the following series of examples, chromium was electrodeposited onto Hull Cell panels at 43° C. for five minutes and three amperes from a series of mixed catalyst baths containing chromic acid, sulfate (added as sodium sulfate), and SiF₆⁻ (added as sodium silicofluoride) as follows:

TABLES XIII

Bath:	CrO ₃ , g./l.	SO ₄ ⁻ , g./l.	SiF ₆ ⁻ , g./l.	CrO ₃ /SO ₄ ⁻ / SiF ₆ ⁻ Ratio
A	400	1.28	0.64	208
B	400	0.667	0.667	300
C	400	0.89	0.24	352
D	400	0.64	0.32	416

The results of the Hull Cell tests were as follows:

TABLE XIV

Example	Bath	Acid	G./l.	Coverage, mm.
72	A	None	None	54
73	A	Succinic acid	50	68
74	B	do.	50	76
75	C	do.	50	74
76	D	do.	50	70

In the following series of examples, chromium was electrodeposited onto Hull Cell panels at 43° C. for five minutes and three amperes from a series of self-regulating baths containing chromic acid, and sulfate (added as strontium sulfate) as follows:

TABLE XV

Bath:	CrO ₃ , g./l.	SO ₄ , g./l.
E	425	1.9
F	340	2.0

The results of the Hull Cell Tests were as follows:

TABLE XVI

Example	Bath	Acid	G./l.	Coverage, mm.
77	E	None	0	54
78	E	Succinic acid	75	75
79	F	Adipic acid	*75	70

*10 minute Hull Cell Test.

Example 80

In this example, 10 liters of a self-regulating bath was prepared from 375 g./l. CrO₃, 8 g./l. strontium sulfate, and 40 g./l. succinic anhydride. The bath was maintained at 35° C. with agitation to give an SO₄ content of 1.8 g./l. A nickel-plated brass strip, bent in the form of a Z-shape, was chromium plated at five amperes for one minute. The deposit on the cathode was bright and clear even in the deepest recesses to an extent not attainable by use of prior art techniques.

In the next series of examples, baths were prepared containing 250 g./l. CrO₃, and to separate aliquots there was added 40 g./l. succinic acid or 40 g./l. of adipic acid. Sulfate was added as strontium sulfate. Excess strontium ion was added as strontium carbonate in the amount shown in Table XVII. The baths were used to plate panels in a standard Hull Cell Test with three amperes at 32° C. for five minutes with agitation.

TABLE XVII

Example	SrCO ₃ , g./l.	SO ₄ , g./l.	Adipic	Succinic
81	1.68	1.35	84	
82	1.68	1.35		82
83	2.52	1.20	36	
84	2.52	1.20		83
85	3.36	1.05	87	
86	3.36	1.05		84
87	4.20	0.92	86	
88	4.20	0.92		84

From this table, it will be apparent that the addition of adipic acid or succinic acid in accordance with this invention gives superior coverage.

It is also a feature of the baths of this invention, that the organic carboxylic acids herein disclosed are characterized by the introduction into the bath of no un-

desirable components such as chloride, iodide, sulfate, etc., and by their substantially decreased degree of attack of lead anodes. This latter may be observed for example by immersing lead in two baths containing 300 g./l. CrO_3 , and 1.3 g./l. SO_4 , together with the indicated additive, for 72 hours at 49° C.

TABLE XVIII

Example	Additive	G./l.	Loss of Weight, g.
89.....	Succinic acid.....	75	0.1426
90.....	Trichloroacetic acid.....	25	0.67

Thus it will be seen that the loss in weight of the lead is much lower (only 21% as much) when the baths of this invention are used than when a bath is used containing trichloroacetic acid in amount of only one-third as great.

It had been believed that the organic compounds used in practice of this invention would be quickly oxidized in the presence of chromic acid, a well known oxidizing agent and thus be substantially inoperable. It is however a particular feature of the baths of this invention containing organic acids such as succinic acid, that they are unexpectedly highly stable over extended periods of operation.

In order to demonstrate the stability of the baths of this invention under severe operating conditions, a bath was prepared containing 300 g./l. CrO_3 , 1.3 g./l. SO_4 , and 75 g./l. of succinic acid. The bath was heated to 93° C. and electrolyzed at a high current density of 60 ASD (94 amperes per liter of solution). Electrolysis was continued over four hours at 93° C. using a lead anode and a steel cathode. At the conclusion of the test, the voltage drop across the bath was noted and found to be unchanged. This indicates that no trivalent or reduced chromium is present and thus that no succinic acid had been oxidized. As is well known to those skilled-in-the-art, acids such as citric acid, tartaric acid, oxalic acid, etc. (which are not within the scope of this invention), would oxidize substantially immediately on contact with chromium plating baths.

Although the outstandingly high coverage herein noted may be attained by the several acids set forth, it may be found that monocarboxylic aliphatic acids having at least three carbon atoms are unexpectedly superior in that they permit operation at desirably high ratio (of e.g. CrO_3 to SO_4) with high coverage and minimum attack on anodes. For example, such acids typified by propionic acid, may give maximum coverage, with a lead anode corrosion which is unexpectedly and significantly less than about 72% of that attained when acetic acid is used. Furthermore, loss of acid such as propionic acid from plating baths may be found to be considerably less than evaporation than loss of acetic acid from these baths. These two factors, inter alia, dictate that, if aliphatic monocarboxylic acids are to be employed, the acids having more than two carbon atoms may permit attainment of unexpectedly superior advantages.

It is a particularly outstanding feature of the preferred embodiment of this invention using the dicarboxylic acids such as succinic acid and adipic acid that the coverage with chromium plate is extremely high—and interior portions of the cathodes are uniformly covered by a bright, decorative plate. Furthermore, the color, brilliance, and clarity of the plate on the open or exposed areas is far superior to that attained by use of the best prior art baths. The process is further characterized by freedom from anode attack and by substantially lower tendency toward undesirable development of "chromate-film" on low current density areas which would decrease the appearance and attractiveness of decorative plate.

Although this invention has been illustrated by reference to specific examples, numerous changes and modifications thereof which clearly fall within the scope of the invention will be apparent to those skilled in the art.

We claim:

1. The process characterized by high coverage and by high throwing power for electrodepositing a bright decorative chromium plate onto a basis metal having an atomic number of 24–30 which comprises maintaining an aqueous hexavalent chromium plating bath containing chromic acid and sulfate in ratio of 125–550:1 and at least about 25 grams per liter of an anion of an organic acid selected from the group consisting of aliphatic monocarboxylic and dicarboxylic acids having at least three carbon atoms and electrodepositing a bright decorative chromium plate from said bath onto said basis metal as cathode in said bath.

2. The process as claimed in claim 1 for electrodepositing a bright decorative chromium plate onto a basis metal wherein said acid is an aliphatic dicarboxylic acid having at least three carbon atoms.

3. The process as claimed in claim 1 for electrodepositing a bright decorative chromium plate onto a basis metal wherein said acid is succinic acid.

4. The process as claimed in claim 1 for electrodepositing a bright decorative chromium plate onto a basis metal wherein said acid is adipic acid.

5. The process as claimed in claim 1 for electrodepositing a bright decorative chromium plate onto a basis metal wherein said acid is propionic acid.

6. The process as claimed in claim 1 for electrodepositing a bright decorative chromium plate onto a basis metal wherein said organic acid is present in said bath in amount from 25 to 100 grams per liter.

7. The process characterized by high coverage and by high throwing power for electrodepositing a bright decorative chromium plate onto a basis metal having an atomic number of 24–30 which comprises maintaining an aqueous chromium plating bath containing 150–500 g./l. chromic acid and 0.4–3.3 g./l. sulfate ion, and a ratio of chromic acid to sulfate of 125–550:1, and at least about 25 grams per liter of an anion of an organic acid selected from the group consisting of aliphatic monocarboxylic and dicarboxylic acids having at least three carbon atoms and electrodepositing a bright decorative chromium plate from said bath onto said basis metal as cathode in said bath.

8. The process as claimed in claim 7 for electrodepositing a bright decorative chromium plate onto a basis metal wherein said organic acid is succinic acid.

9. The process as claimed in claim 7 for electrodepositing a bright decorative chromium plate onto a basic metal wherein said organic acid is present in amount from 25 to 100 g./l.

10. The process characterized by high coverage and high throwing power for electrodepositing a bright decorative chromium plate onto a basis metal having an atomic number of 24–30 which comprises maintaining an aqueous mixed-catalyst chromium plating bath containing the following components in the amounts indicated in grams per liter:

Component	Maximum	Minimum
Chromic acid.....	500	150
Sulfate ion.....	2.0	0.05
Silicofluoride ion.....	2.0	0.05
Organic acid.....	100	25

the ratio of chromic acid to sulfate plus silicofluoride being 125–550:1 and the organic acid being selected from the group consisting of aliphatic monocarboxylic and dicarboxylic acids having at least three carbon atoms and electrodepositing a bright decorative chromium plate from said bath onto said basis metal as cathode in said bath.

11. The process as claimed in claim 10 wherein said bath contains 250 g./l. chromic acid, 0.5 g./l. sulfate ion, 0.5 g./l. silicofluoride ion and 30 g./l. of succinic acid.

12. The process characterized by high coverage by high throwing power for electrodepositing a bright decorative chromium plate onto a basis metal having an atomic number of 24–30 which comprises maintaining an aqueous

self-regulating chromium plating bath containing the following components in the designated grams per liter:

Component	Maximum	Minimum
Chromic acid.....	500	150
Sulfate ion.....	2.0	0.05
Silicofluoride ion.....	2.0	0.05
Strontium ion.....	9	0.2
Organic acid.....	100	25

the ratio of chromic acid to sulfate plus silicofluoride being 125-550:1 and the organic acid being selected from the group consisting of aliphatic monocarboxylic and dicarboxylic acids having at least three carbon atoms and electrodepositing a bright decorative chromium plate from said bath onto said basis metal as cathode in said bath.

13. The process as claimed in claim 12 wherein said bath contains 250 g./l. of chromic acid, 0.5 g./l. of sulfate ion, 0.5 g./l. of silicofluoride ion, 5.0 g./l. of strontium ion and 30 g./l. of succinic acid.

14. A composition for addition to aqueous medium to form baths for the electrodeposition of bright decorative chromium plate onto a basis metal having an atomic number of 24-30 consisting essentially of the following components in the designated parts by weight:

Component	Maximum	Minimum
Chromic acid.....	500	150
Sulfate ion.....	3.3	0.4
Organic acid.....	100	25

the ratio of chromic acid to sulfate being 125-550:1 and the organic acid being selected from the group consisting of aliphatic monocarboxylic and dicarboxylic acids having at least three carbon atoms.

15. A composition as claimed in claim 14 wherein said components are present in the following parts by weight:

Component:	Parts
Chromic acid	250
Sulfate ion	1.0
Succinic acid	30

16. A composition for addition to aqueous medium to form baths for the electrodeposition of bright decorative chromium plate onto a basis metal having an atomic number of 24-30 consisting essentially of the following components in the designated parts by weight:

Component	Maximum	Minimum
Chromic acid.....	500	150
Sulfate ion.....	2.0	0.05
Silicofluoride ion.....	2.0	0.05
Organic acid.....	100	25

the ratio of chromic acid to sulfate plus silicofluoride being 125-550:1 and the organic acid being selected from the group consisting of aliphatic monocarboxylic and dicarboxylic acids having at least three carbon atoms.

17. A composition as claimed in claim 16 wherein said components are present in the following parts by weight:

Component:	Parts
Chromic acid	250
Sulfate ion	0.5
Silicofluoride ion	0.5
Succinic acid	30

18. A composition for addition to aqueous medium to form baths for the electrodeposition of bright decorative chromium plate onto a basis metal having an atomic number of 24-30 consisting essentially of the following components in the designated parts by weight:

Component	Maximum	Minimum
Chromic acid.....	500	150
Sulfate ion.....	2.0	0.05
Silicofluoride ion.....	2.0	0.05
Strontium ion.....	9	0.2
Potassium ion.....	27	6.0
Organic acid.....	100	25

the ratio of chromic acid to sulfate plus silicofluoride being 125-550:1 and the organic acid being selected from the group consisting of aliphatic monocarboxylic and dicarboxylic acids having at least three carbon atoms.

19. A composition as claimed in claim 18 wherein said components are present in the following parts by weight:

Component:	Parts
Chromic acid	250
Sulfate ion	0.5
Silicofluoride ion	0.5
Strontium ion	5.0
Potassium ion	15
Succinic acid	30

20. A composition as claimed in claim 18 wherein said components are present in the following parts by weight:

Component:	Parts
Chromic acid	400
Sulfate ion	1.3
Silicofluoride ion	0.7
Strontium ion	2.6
Potassium ion	27
Succinic acid	40

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