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METHOD AND ELECTROLYTES FOR ELECTRO-DEPOSITING BLACK CHROMIUM**John B. Nelson, Jr., Indianapolis, Ind., assignor to Diamond Shamrock Corporation, a corporation of Delaware****No Drawing. Filed Nov. 18, 1966, Ser. No. 595,364****The portion of the term of the patent subsequent to Dec. 31, 1985, has been disclaimed****Int. Cl. C23b 5/06, 5/46****U.S. Cl. 204—51****8 Claims****ABSTRACT OF THE DISCLOSURE**

The present invention relates to a composition and method for obtaining black, chromium-containing deposits on electrically conductive substrates. These deposits may be obtained by subjecting the substrate to be plated to electrolysis in an aqueous solution containing chromic acid, a fluoride catalyst and an additive compound selected from the group consisting of trivalent chromium and mixtures of trivalent chromium with an inorganic nitrogen-containing compound, said aqueous solution being free of sulfate ions.

This invention relates to a composition and method for the electrodeposition of chromium-containing coatings on a conductive metal substrate as the cathode and more particularly relates to the electrodeposition of chromium coatings on such substrates in such physical and chemical form as to produce a black surface having a high degree of absorptivity for both heat and visible light.

Black chromium deposits find use in areas where their heat and light absorbing properties are important, one example of which is the military field where such items as firearms, communications equipment, personnel ornament, etc. are so coated. Such deposits are also valuable for decorative purposes such as on metal furniture, automobile parts, plumbing fixtures, etc., where their corrosion resistance coupled with their appearance make them superior to other black finishes such as paint.

While several processes and plating bath compositions have heretofore been disclosed in the art for producing black chromium electrodeposits, they have not received wide commercial acceptance for a variety of reasons. For example in one process, a grey-black deposit is obtained from a chromic acid bath having a low (less than 0.07%) sulfate content to which has been added a small amount of a carboxylic acid, preferably acetic acid. The chief disadvantages of this bath arise from the conditions for electrodepositing the black chromium whereby very high current densities, i.e., 10,000 to 20,000 amperes per square meter (935 to 1870 amperes per square foot), must be used at relatively low temperatures, i.e., about 20° C. Therefore, in addition to the excessive consumption of current, refrigerating means must be provided to maintain the proper temperature in this process.

It has also been disclosed that dark grey to black electrodeposits may be obtained from a chromic acid bath from which the sulfate has been removed and which contains large amounts of acetic acid. While this bath is said to operate at low current densities, its effective current density range is quite limited, i.e., 40 to 90 amperes per square foot, and this bath also has the further disadvantages that steam coils must be provided to maintain the desired temperatures for plating 90° to 115° F., and that an exhaust fan is required to remove the noxious acetic acid vapors.

In a more recent process, a black chromium deposit is obtained from an aqueous bath consisting of chromic acid and a fluoride catalyst. While the current density and tem-

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perature ranges recommended are satisfactory, reproduction of good results is still quite difficult to attain because of the criticality of the fluoride catalyst concentration and the necessity according to this teaching of eliminating all other catalytic ions from the bath. Thus, in addition to precluding the presence of sulfate in the bath, it is also necessary to use deionized or distilled water for bath make-up and pre-bath rinsing procedures in order that no foreign ions be introduced. Consequently this type of bath is difficult to control and not suitable for large scale commercial applications.

It is an object of the present invention to provide an improved bath composition and easily operable process whereby uniform, black, chromium-containing electrodeposits may be obtained.

It is another object of the present invention to provide an improved bath composition which is highly effective over a wide range of operating conditions for electrodepositing black, chromium-containing coatings.

These and other objects of this invention will become apparent from the specification and claims that follow.

It has now been found that uniform, black, chromium-containing coatings may be electro-deposited on an electrically conductive member by making said member the cathode in an aqueous solution consisting essentially of from at least 60 grams per liter up to saturation of chromic acid, a fluoride-containing catalyst in an amount sufficient to supply from about 0.03 to about 1 gram fluoride in solution per liter and an additive compound selected from the group consisting of from 1 to 25 grams of trivalent chromium per liter and mixtures of from 1 to 25 grams of trivalent chromium per liter with an inorganic nitrogen-containing compound in an amount sufficient to supply from 0.35 to 3.5 grams of (NO₂) radical per liter, said aqueous solution being substantially free of sulfate ions, and passing a direct current between said cathode and an anode immersed in said solution at a current density of from about 30 to 1500 amperes per square foot while maintaining the solution at a temperature of from about 65° to 140° F.

While solutions containing chromic acid and a fluoride-containing catalyst have previously been used to obtain black, chromium-containing electrodeposits, it has now been found that the inclusion of small amounts of an additive compound selected from the group consisting of trivalent chromium and mixtures of trivalent chromium with an inorganic nitrogen-containing compound provides substantial advantages. With the use of said additives a uniform, black, chromium-containing electrodeposit is readily obtained over a wider range of current densities than would be possible without their use.

Any commercially available grade of chromic anhydride (CrO₃) may be used in the practice of this invention, but since commercial chromic anhydride generally contains significant quantities of sulfates which interfere with the formation of the desired black, chromium-containing deposits, it is necessary that the chromic acid solutions described herein be treated before use to remove these sulfates. This treatment may be easily effected by the addition to the solution of a source of barium ion such as barium carbonate or barium oxide. The addition of 5 to 20 grams per liter of barium carbonate will generally provide a sufficient excess to insure a sulfate-free plating solution. The amount of chromic anhydride used may be within the range of from at least 60 grams per liter up to saturation, preferably about 300 to 500 grams per liter. Particularly preferred at this time is a concentration of 450 grams per liter.

Any of the fluoride-containing chromium plating catalysts known to the art which supply fluoride in solutions of chromic acid may be used in the bath compositions of

this invention. Examples of these catalysts are hydrofluoric acid, fluoboric acid, fluosilicic acid and water soluble alkali metal, alkaline earth metal, heavy metal and ammonium salts thereof. Preferred fluoride-containing catalysts are those obtained by reacting a hexavalent chromium compound such as chromic acid, an organic reducing agent such as sucrose and a fluoride-silicon compound such as fluosilicic acid as described in U.S. Pat. No. 2,841,540. The amounts of fluoride-containing catalyst useful in this invention will vary according to the amount of fluoride which the catalyst can supply to the chromic acid solution, and the amount of fluoride in solution may be varied from about 0.03 to about 1 gram per liter, preferably from about 0.1 to 0.25 gram per liter.

The manner of providing the trivalent chromium in the solutions of this invention is not critical. Conveniently, this may be accomplished by the addition of a reducing agent, such as sucrose or hydrogen peroxide, to the solution prior to its use. If sucrose is to be used as the reducing agent, about 1 gram of sucrose is required for each 2.2 grams of trivalent chromium to be formed at a chromic acid concentration of about 450 grams per liter. As stated hereinabove, amounts in the range of from about 1 to about 25 grams of trivalent chromium per liter of solution are effective in the practice of this invention. Especially preferred at this time are amounts within the range of about 4 to about 10 grams per liter. In addition to the above described use of a reducing agent to obtain the desired trivalent chromium concentration it is also possible to obtain same by electrolysis of the solution in a special manner. This "pre-electrolysis" is carried out under the normal operating conditions of the bath but using a cathode to anode surface area ratio of greater than 1:1, e.g. 20:1. The amount of trivalent chromium present in the bath may be readily determined for purposes of addition and control by any of the known analytical techniques.

The inorganic nitrogen-containing compounds effective in the solutions of the present invention in combination with trivalent chromium are nitric acid and nitrous acid and the alkali metal, alkaline earth metal and ammonium salts thereof, nitric acid and sodium nitrate being preferred at present by reason of their ready availability and comparatively low price. These inorganic nitrogen-containing compounds are effective for the purposes of the present invention in combination with the above stated amounts of trivalent chromium and in amounts sufficient to supply the equivalent of about 0.35 to about 3.5 grams of (NO_2) radical per liter, preferably about 0.7 to 2 grams of (NO_2) radical per liter. While amounts in excess of 3.5 grams per liter (NO_2) may be used, they are without apparent additional beneficial effect. Thus, by way of example, if sodium nitrate is used in the practice of this invention amounts within the range of from about 0.52 to about 5.2 grams per liter, preferably 1 to 3 grams per liter will be effective; if sodium nitrate is used, amounts within the range of from about 0.65 to about 6.5 grams per liter, preferably 1.3 to 3.7 grams per liter, will be effective.

The plating solutions disclosed herein for electrodepositing black, chromium-containing coatings are easier to control than prior art solutions in that it is not necessary to use deionized or distilled water in either the make-up of the solutions or in the rinsing steps prior to immersion of the article to be coated in the solution. The solutions may be used effectively in producing electrodeposits for long periods of time without detrimental effects due to decomposition products and employing only the precautions used in the operation of conventional chromium plating solutions to prevent the introduction of foreign ions.

Uniform, black, chromium-containing deposits are readily obtained over a current density range of about 30 to 1500 amperes per square foot. The temperature of the bath may be maintained within the range from

about 65° to 140° F., preferably from about 70° to 95° F., thereby eliminating the need for either heating or cooling means in most cases.

While the time required to electrodeposit the black, chromium-containing coatings will vary somewhat depending on the solution composition, temperature, and the thickness of coating desired, 1 to 5 minutes at a current density within the above mentioned range will generally give a uniform, black, chromium-containing deposit having good corrosion resistance.

Any of the insoluble anodes used with conventional chromium plating baths may be employed. Especially to be preferred are lead or lead alloy anodes. Corrosion and erosion of these lead or lead alloy anodes when used in the practice of this invention is on a level equivalent with that experienced in conventional chromium plating solutions. Tanks employed for containing the solutions of the present invention may be lined with any suitable corrosion-resistant material such as glass, ceramic material, polyvinyl chloride, lead and the like.

While the best results are obtained by subjecting the electrically conductive member to be plated by the process of this invention to a nickel strike treatment, i.e., cathodically plating nickel on said member for a short period at any conventional current density, quite satisfactory coatings may be obtained by plating directly onto copper, zinc, iron, steel, aluminum, stainless steel, conventional chromium deposits and other conductive bases.

As is the practice in conventional chromium plating, mist suppressants may be added to the solution before plating. Many of the commercially available products for this purpose (which are generally proprietary surfactant-containing compositions) are acceptable.

In order that the compositions and process of this invention may be more readily understood by those skilled in the art, the following specific examples are provided. Unless otherwise noted, the examples that follow are the results of evaluation of the compositions and process of this invention in a modified 267 milliliter Hull Cell using as the cathode brass panels, 2.5 by 4 inches, which have been given a thin, uniform nickel coating by electro-deposition from a commercial bright nickel plating bath. The standard 267 milliliter Hull Cell is a trapezoidal box of non-conductive material in the opposite ends of which are positioned anode and cathode plates as is more particularly described in U.S. Pat. No. 2,149,344. By the use of this device it is possible to easily determine the effective plating range of a plating composition under varying conditions. The current density at any point on the cathode is determined according to the formula

$$A = C (27.7 - 48.7 \log L)$$

wherein A is the current density at the selected point, C is the total current applied to the cell and L is the distance of the selected point from the high current density end of the plate. In the modified version used herein, holes are provided in the sides of the Hull Cell adjacent the anode and cathode whereby, upon immersion of the cell in a container of plating solution, improved electrolyte circulation and consequently improved temperature control is afforded as is more particularly described in an article by J. P. Branciaroli appearing on page 257, March 1959 issue of Plating, vol. 46, No. 3 (a publication of the American Electroplater's Society, Inc.).

EXAMPLE 1

An aqueous plating solution is made containing 450 grams per liter of CrO_3 , 1 gram per liter of fluoride-containing catalyst (the reaction product of a chromium compound, an organic reducing agent and fluosilicic acid as is more particularly described in U.S. Pat. No. 2,841,540 and containing 25% by weight chromium, 25% by weight fluoride and 16% by weight silicon) and about 8 grams of barium carbonate to precipitate the sulfate. A panel is electroplated for 3 minutes at 10 amperes applied cur-

rent and a bath temperature of 89° F. A black electrodeposit is obtained from the high current density end of the panel to a current density of about 200 amperes per square foot, a value corresponding to 37% coverage.

To the above bath is added, with agitation for dissolution, reaction and dispersion, 4 grams per liter of granular sucrose, an amount sufficient to give about 10.5 grams per liter Cr³⁺. A second panel is electroplated for 3 minutes at 10 amperes and a temperature of 94° F. The black deposit range is now found to extend to about 70 amperes per square foot or 62% coverage. Thus the addition of trivalent chromium is shown to greatly extend the effective plating range of the solution.

EXAMPLE 2

An aqueous plating solution is made containing 450 grams of CrO₃ per liter, 0.125 gram of the fluoride catalyst described in Example 1 per liter, 4 grams of sucrose per liter and an excess of BaCO₃ over that required to precipitate the sulfate present. A panel is plated in the solution for 3 minutes at an applied current of 10 amperes and a temperature of 110° F. A black deposit is obtained from the high current density edge of the panel to an area corresponding to a current density of about 90 amperes per square foot. This example shows that even at relatively high temperatures and low fluoride catalyst concentrations the plating solutions of this invention are effective for obtaining the desired black deposit.

EXAMPLE 3

To show the use of the compositions of the present invention containing the additive compounds in varying proportions, Hull Cell panels as defined hereinabove are electroplated at an applied current of 10 amperes. The actual compositions of the baths, the conditions used and the results obtained are shown in Table I. Each of the solutions indicated is treated with an amount of BaCO₃ in excess of that required to precipitate the sulfate present.

	(1)	(2)	(3)		(4)	(5)
CrO ₃ g./l.	F g./l.	HNO ₃ g./l.	Cr ³⁺ g./l.	Temp., ° F.	Current Density, A.S.F.	Coverage, percent
450	1	-----	2.5	95	350	20
450	1	-----	2.5	97	125	53
450	1	-----	2.5	100	30	82
450	1	1	4.7	104	40	78
450	1	1	10.5	95	35	80
450	1	1	22	97	60	71
450	1	2	10.5	84	40	78
450	1	3	10.5	100	50	75
450	1	5	10.5	110	100	59

- (1) Catalyst as in Example 1.
- (2) Specific gravity 1.42.
- (3) Formed by adding sucrose to the bath.
- (4) Figures in this column indicate that an acceptable black deposit is obtained from the high current density edge of the panel to an area corresponding to the stated current density.
- (5) This column reports the percent of the total surface area of the panel that is covered by the black deposit.

A distinct improvement is shown using the combination of additives of this invention as opposed to a solution containing only chromic acid and fluoride. Additionally it is shown that the compositions are effective over a wide range of additive concentrations.

EXAMPLE 4

A solution is made consisting of 450 grams per liter CrO₃, 1 milliliter per liter HBF₄ (48% aqueous solution), 2 grams per liter sucrose (4.7 grams per liter Cr³⁺) and an amount of BaCO₃ in excess of that required to remove the sulfate by precipitation. A panel is made the cathode therein for 3 minutes at an applied current of 10 amperes and a temperature of 72° F. A black, chromium-

containing electrodeposit is obtained from the high current density edge of the panel to an area corresponding to a current density of about 60 amperes per square foot. This shows that with a different fluoride catalyst and a lower temperature than in previous examples, black deposits are still obtained over a wide current density range.

EXAMPLE 5

An aqueous solution is made consisting of 300 grams per liter CrO₃, 1 gram per liter of the fluoride catalyst as described in Example 1, 2 grams per liter sucrose (2.7 grams per liter Cr³⁺) and about 7 grams per liter BaCO₃. A panel is plated for 3 minutes at 10 amperes and a temperature of 75° F. Although there is evidence of some burning at the extreme high current density edge of the panel, even at this low CrO₃ concentration a black deposit is obtained to an area corresponding to about 275 amperes per square foot.

EXAMPLE 6

To the solution of Example 5 are added 300 grams per liter of CrO₃ and 4 grams of sucrose to give a total of 600 grams per liter CrO₃ and 14.5 grams per liter trivalent chromium. A panel is now electroplated for 3 minutes at 10 amperes applied current and a temperature of 110° F. Upon inspection of the plated panel it is found that there is no evidence of burning in the high current density area and that the plating range is extended to about 150 amperes per square foot. This shows the effectiveness of high CrO₃ and trivalent chromium concentrations in the practice of this invention.

EXAMPLE 7

To an aqueous solution containing 450 grams per liter CrO₃ and 1 gram per liter of the fluoride catalyst of Example 1 and which has been treated with an excess of BaCO₃ to remove the sulfate is added 8 milliliters per liter of a 30% aqueous solution of H₂O₂. This is an amount sufficient to form about 1.2 grams per liter of trivalent chromium. A panel, plated for 3 minutes at 10 amperes and 80° F. in this solution, shows a black, chromium-containing deposit from the high current density edge of the panel to about 150 amperes per square foot with evidence of only a slight burning at the extreme high current density edge of said panel. This shows the use of agents other than sucrose to obtain the desired trivalent chromium concentration.

EXAMPLE 8

A series of experiments is conducted to show the effect of temperature on the compositions of the present invention. In all instances the panels are electroplated at an applied current of 10 amperes and the solutions have been treated with an excess of BaCO₃ to precipitate the sulfate. The source of the fluoride, nitrate and trivalent chromium are as in Example 3.

CrO ₃ g./l.	F g./l.	HNO ₃ ml./l.	Cr ³⁺ g./l.	Temp., ° F.	Current ¹ Density, A.S.F.	Coverage, ¹ Percent
450	1	1	10.5	81	30	82
450	1	3	10.5	125	50	75
450	1	3	10.5	140	80	65

¹ As in Example 1.

It can be readily seen that while a slight loss in coverage occurs with an increase in temperature, the results obtained are still considered to be excellent.

EXAMPLE 9

A plating solution is made up containing 600 grams of CrO₃ per liter, 1 gram of the fluoride catalyst of Example

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1 per liter, 5 grams of Cr^{+3} per liter and 2.9 grams of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ per liter with an excess of BaCO_3 being added to precipitate the sulfate. A panel is plated for 3 minutes at an applied current of 10 amperes and a temperature of 90° F. A uniform, glossy black deposit is obtained from the high current density edge of the panel to an area on the panel corresponding to 50 amperes per square foot, i.e. 75% coverage of the panel.

This shows the operability of the compositions of the instant invention at higher CrO_3 concentration and using an inorganic nitrogen-containing compound different from the previous examples.

EXAMPLE 10

To illustrate the use of another inorganic nitrogen-containing compound, 1.5 grams of NaNO_3 per liter is added to a solution containing 450 grams of CrO_3 per liter, 1 gram of the fluoride-containing compound of Example 1 per liter and 4.7 grams of Cr^{+3} per liter which has been treated with 10 grams of BaCO_3 per liter. A panel is plated therein for 3 minutes at 10 amperes and a temperature of 98° F. The resultant black deposit extends from the high current density edge of the panel to an area corresponding to 60 amperes per square foot.

EXAMPLE 11

A further example of the use of various inorganic nitrogen-containing compounds in the compositions of this invention is afforded by the substitution of 1 gram of NaO_2 per liter for the NaNO_3 of the previous example. A panel electroplated in this solution at 78° F. for 3 minutes and 10 amperes applied current displays a uniform black deposit to a current density of 60 amperes per square foot.

EXAMPLE 12

A panel is electroplated for 3 minutes at 25 amperes applied current and 100° F. in a solution containing 450 grams of CrO_3 per liter, 1 gram of fluoride catalyst (as in Example 1) per liter, 3 ml. of HNO_3 (specific gravity 1.42) per liter, 10.5 grams of Cr^{+3} per liter and a sufficient excess of BaCO_3 to insure removal of the sulfate.

Owing to the high applied current it is possible to estimate that the effective plating range of the solution, as evidenced by the extent of the deposit, extends from 50 to a value in excess of 1300 amperes per square foot.

EXAMPLE 13

To illustrate the use of a fluoride-containing compound other than that of Example 1, 0.5 milliliter per liter of HF (49%) is added to a solution containing 450 grams of CrO_3 per liter, 2 ml. of HNO_3 (specific gravity 1.42) per liter, 4.7 grams of Cr^{+3} per liter and an excess of BaCO_3 to precipitate the sulfate. A panel is electrolyzed therein for 3 minutes at 80° F. and at 10 amperes applied current. A black deposit is obtained from the high current density edge of the panel to an area corresponding to 90 amperes per square foot.

EXAMPLE 14

As a further illustration of a useful fluoride compound, 1 ml. of HBF_4 (48%) is substituted for the HF of Example 13. A panel plated in this solution under the same conditions but at 72° F. has a uniform black deposit extending to an area corresponding to 120 amperes per square foot.

EXAMPLE 15

In order to evaluate the ability of the compositions of this invention to produce a black, chromium-containing deposit on a variety of substrates other than the nickel-plated brass of the previous examples, a solution containing 450 grams of CrO_3 per liter, 1 gram of the fluoride catalyst of Example 1 per liter, 1 ml. of HNO_3 (specific

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gravity 1.42) per liter, 10.5 grams of Cr^{+3} per liter and an excess of BaCO_3 is prepared. A number of panels 4 by 2.5 inches in size and composed of various metals are prepared for electroplating. Panel A is a brass panel having a conventional chromium-plated surface. Panel B is made of brass and Panel C is stainless steel. Each of the panels is made the cathode in the above solution and electroplated at a current density of 1 ampere per square inch and a temperature of 85° F. for 3 minutes. The resultant deposit on each of the panels, while not as uniform as that obtainable on a nickel substrate, is quite acceptable for most purposes.

What is claimed is:

1. A composition of matter for use in the electrodeposition of black, chromium-containing deposits which is an aqueous solution consisting essentially of from about 60 grams per liter to saturation of chromic anhydride, a fluoride-containing catalyst in an amount sufficient to supply from about 0.03 to about 1 gram of fluoride in solution per liter, and from 1 to 25 grams of trivalent chrome per liter, said trivalent chrome being formed by the addition to the solution of sucrose as a reducing agent, said aqueous solution being substantially completely free of sulfate ions.

2. A composition as claimed in claim 1 wherein the fluoride-containing catalyst is selected from the group consisting of hydrofluoric acid, fluoboric acid, fluosilicic acid and water-soluble alkali metal, alkali earth metal and ammonium salts of hydrofluoric, fluoboric and fluosilicic acid.

3. A process for the electrodeposition of black chromium-containing deposits which comprises making the electrically conductive member to be plated the cathode in an aqueous solution consisting essentially of from about 60 grams per liter to saturation of chromic anhydride, a fluoride-containing catalyst in an amount sufficient to supply from about 0.03 to about 1 gram of fluoride in solution per liter and from 1 to 25 grams of trivalent chromium per liter, said trivalent chromium being formed by the addition to the solution of sucrose as a reducing agent, said aqueous solution being substantially completely free of sulfate ions, and passing direct current between said cathode and an anode immersed in said solution at a current density of from about 30 to about 1500 amperes per square foot while maintaining said aqueous solution at a temperature of from about 65° F. to about 140° F.

4. A process as claimed in claim 3 wherein said fluoride-containing catalyst is selected from the group consisting of hydrofluoric acid, fluoboric acid, fluosilicic acid and water soluble alkali metal, alkali earth metal and ammonium salts of hydrofluoric, fluoboric and fluosilicic acid.

5. A composition of matter for use in the electrodeposition of black, chromium-containing deposits which is an aqueous solution consisting essentially of from about 60 grams per liter to saturation of chromic anhydride, a fluoride-containing catalyst in an amount sufficient to supply from about 0.03 to about 1 gram of fluoride in solution per liter, from 1 to 25 grams of trivalent chromium per liter and an inorganic nitrogen-containing compound in an amount sufficient to supply from 0.35 to 3.5 grams of (NO_2) radical per liter, said aqueous solution being substantially completely free of sulfate ions.

6. A composition as claimed in claim 5 wherein the nitrogen-containing compound is selected from the group consisting of nitric and nitrous acid and the water-soluble alkali metal, alkali earth metal and ammonium salts thereof.

7. A process for the electrodeposition of black chromium-containing deposits which comprises making the electrically conductive member to be plated the cathode in an aqueous solution consisting essentially of from about 60 grams per liter to saturation of chromic anhy-

dride, a fluoride-containing catalyst in an amount sufficient to supply from about 0.03 to about 1 gram of fluoride in solution per liter, from 1 to 25 grams of trivalent chromium per liter and an inorganic nitrogen-containing compound in an amount sufficient to supply from 0.35 to 3.5 grams of (NO₂) radical per liter, said aqueous solution being substantially completely free of sulfate ions, and passing direct current between said cathode and an anode immersed in said solution at a current density of from about 30 to 1500 amperes per sq. ft. while maintaining said aqueous solution at a temperature of from about 65° F. to about 140° F.

8. A process as claimed in claim 7 wherein the nitrogen-containing compound is selected from the group consisting of nitric and nitrous acid and the water-soluble alkali metal, alkali earth metal and ammonium salts thereof.

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