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## ELECTRODEPOSITING IRON

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This invention relates to the art of plating iron from aqueous solutions of salts thereof onto articles in such a manner as to form a commercially useful iron coating thereon, and more particularly to the art of plating iron from alkaline solutions. The invention also relates to alkaline plating baths and to alkaline compositions of matter suitable for preparing iron plating solutions and/or replenishing partially depleted iron plating baths. The invention also relates to the iron-plated articles and electro-formed articles prepared by said plating process.

Electrodeposition of metals from alkaline solutions offers numerous advantages not to be found in the use of acid baths. The acid fumes in a plating room employing acid baths have created both health hazards and corrosion hazards. Many articles are attacked when immersed in an acid plating bath. Many articles have had such shapes that there have been corrosion problems at the low current density areas of the articles plated from acid baths. Platings which appeared satisfactory initially have sometimes developed blisters and other imperfections attributable to the use of an acid bath. For these and other reasons, electrochemists have sought to develop suitable alkaline plating processes for each metal employed significantly in the electrodeposition industries. As a result there has been widespread practice of alkaline plating of metals such as gold, silver, copper, zinc, cadmium, tin and lead. Such alkaline plating baths have generally had more uniform plate distribution and throwing power than acid baths.

For many decades there has been a continuing demand for an alkaline plating process for iron. There have been proposals for using cyanide complexes of iron in order to plate iron at very slow rates at low current efficiencies and at very small current densities, but such proposals have not been of commercial interest. Hence, the ferrocyanide techniques have not been mentioned in recent descriptions of industrial plating of iron.

Recent improvements relating to the electrochemistry of iron under alkaline conditions have concerned, not the deposition of a commercially useful iron plating, but other purposes. Iron powder has been prepared electrolytically under alkaline conditions. It has been proposed that a thick, viscous paste of alkalis and ferric hydroxide be subjected to electrolysis between closely spaced electrodes, but this process did not gain wide acceptance, partly because thick pastes are more difficult to use than liquid electrolytes. Iron oxide cathodes cannot be readily reduced by electrolysis of simple alkaline solutions, but a process was proposed for accomplishing such a reduction using both alkali hydroxides and alkali sulfides in the electrolyte. Although industrial use of electroplating of iron from acid baths has been increasing and although there have been numerous refinements in that art, although there has been a continuing and increasing demand for an alkaline iron plating method, and although there have been divers inven-

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tions concerning the alkaline electrochemistry of iron, still no commercially operable process for the alkaline plating of iron was heretofore developed.

It is an object of the present invention provide a commercially useful iron plating electrodeposited from an alkaline solution, which plating is satisfactorily adherent to its base, and which has the other good characteristics of an industrially useful metallic plating. In stating that an object is to provide a commercially useful iron plating, there are included requirements such as: that the plating be generally free from pits, pinholes, blisters and related imperfections; that the plating be free from excessive stress or brittleness; that the plating have structural strength appropriate in electroformed articles; that the process provides uniform plate distribution and good throwing power; and that the process provides relatively high current efficiencies. Such objectives are attained by means of a novel plating bath, a novel composition employed in preparing said plating bath, by a novel method of electroplating with said bath, and/or by other techniques and ways described herein-after.

Further objects of the invention are: to eliminate the corrosion problems incident to acid plating of iron; to eliminate the corrosive fumes incident to the use of an acid bath; to form consistently smooth deposits of iron in an economical manner and with relatively high current efficiencies; to form mechanically strong iron articles such as lithograph plates by electrodeposition of iron upon removable forms; to produce bright iron plating; and to conduct the iron plating rapidly, conveniently, with high current efficiency, and especially with reasonably uniform plate distribution, that is, with good throwing power.

A feature of the invention is the use of a plating bath complying with seven requirements, each of the seven requirements being absolutely necessary to the combination. The plating bath is aqueous and generally the molar concentration of water is greater than the concentration of any other component. An alkali such as sodium hydroxide must be present in a significant concentration in excess of 0.5 molar but less than 5 molar. An organic amine such as triethanolamine must be utilized in a significant concentration in excess of 0.5 molar but less than 5 molar. An organic sequestering agent such as the sodium salt of ethylenediaminetetraacetic acid cooperates with the organic amine in preventing the precipitation of the iron, the ratio of the molar concentration of the sequestering agent to the molar concentration of iron being from 0.5 to 1.5. During the plating operation, the iron must be present predominantly as ferric iron, and if a bath is prepared initially using ferrous salts, an opportunity should be given for converting most of the ferrous iron to ferric iron before extensive commercial plating therewith. Exposure to the air rapidly converts strongly alkaline ferrous solutions to predominantly ferric solutions. The concentration of the iron must be more than 0.02 molar and less than approximately 0.5 molar. Viscosity modifiers, wetting agents, surface tension modifiers, salts, and other additives for a plating bath may be present if desired. However, the alkalinity of the solution must be great enough to provide a pH greater than 11.

In even slightly alkaline solutions, ferric hydroxide is insoluble, as indicated by a solubility product of  $4 \times 10^{-38}$ . Ferric hydroxide differs greatly from aluminum hydroxide in that even in strongly alkaline solutions, only small amounts of ferric hydroxide dissolve. However, the commercial plating baths of the present invention employ a minimum of 0.02 molar concentrations of iron, desirably a concentration of approximately 0.3 molar iron and up to 0.5 molar iron. That is, the commercial plat-

ing baths of the present invention have an iron concentration within the range of from about 1 to 28 and preferably about 20 grams of iron per liter of plating bath. Thus the plating baths contain exceptionally large concentrations of iron in alkaline solutions.

In the development of the present invention, it was found that an aqueous solution of triethanolamine formed a blue-green precipitate with iron compounds if the pH was below 11, but did form a green solution above pH 11. Thus it was discovered that the combination of triethanolamine and sodium hydroxide dissolved greater amounts of iron than either a solution of sodium hydroxide or a solution of triethanolamine. The amount of iron thus dissolved in triethanolamine and sodium hydroxide mixtures was much greater when ferric salts were employed instead of ferrous salts. A solution containing 1 M triethanolamine and 2.5 M sodium hydroxide dissolved 20 grams per liter of iron as ferric chloride, but no satisfactory method of commercially electroplating with such a solution was found notwithstanding its exceptionally high concentration of iron.

The sodium salt of ethylenediaminetetraacetic acid (hereinafter sometimes referred to as EDTA acid) formed reddish brown precipitates with moderate concentrations of iron under alkaline conditions. In the development of the present invention, it was found that the combination of triethanolamine and the sodium salt of EDTA acid was very much more than additive, and that the combination made it possible to conduct satisfactory electroplating with the plating baths complying with the enumerated requirements. Even with the remarkable combination of sodium hydroxide, triethanolamine and the salt of EDTA acid, the significant amounts of iron could not be kept in solution at mildly alkaline conditions, the traces of suspended precipitate imparting a red color to the solution below pH 11. From a practical standpoint it was found best to maintain the alkalinity and triethanolamine concentration high enough to preserve the green color and to prevent the brownish or red coloration indicative of low alkalinity, using the solution as an inherent indicator of pH. The measurement of pH at high alkalinity is affected by such factors as salt concentration, temperature and other variables which result in less accuracy than in nearly neutral solutions. For any combination of ingredients there is a critical alkalinity which must be exceeded to achieve the necessary solubility of iron and/or satisfactory plating, which critical point is above pH 11 by some conventional measuring method, and which is also detectable by a transition having some similarity to the red to green transformation described.

Heretofore metals have ordinarily been electrodeposited from a lower oxidation state, but according to the present invention, advantageous results are achieved by deposition of iron from a ferric-type bath. The iron kept in solution by the combination of EDTA salt, amine, and alkali is predominantly in the ferric condition. Although ferrous iron may exist near the cathode, or even in the body of the solution, still for most practical purposes the solution can be treated as if it were a ferric solution. An analysis of the solution using titanous chloride indicated that the quantity of ferrous iron present was less than could be detected by the analytical procedure. Even if the presence of ferrous iron was indicated by some other analysis, still the plating solution could be treated as if all iron was present as ferric iron, thus achieving very important advantages. For example, the plating solutions can be agitated by compressed air. None of the precautions required for preserving sensitive ferrous solutions need be observed, thus greatly simplifying commercial iron plating practice. In preparing the plating bath, ferric salts are desirably employed. If ferrous salts are added to an otherwise complete bath, they are not dissolved immediately, but only after oxidation thereof to the ferric iron. Strongly alkaline solutions of ferrous

compounds are readily oxidized to ferric compounds by exposure to air.

In order that those skilled in the art may better understand how the present invention may be practiced, the following examples are given by way of illustration and not by way of limitation.

#### EXAMPLE 1

A plating bath was prepared consisting of sodium hydroxide, triethanolamine, the sodium salt of ethylenediaminetetraacetic (EDTA) acid, a ferric salt, and water, as follows:

NaOH	-----g	100
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	-----g	231
((NaO <sub>2</sub> CCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub>	-----g	132
Fe <sup>+++</sup>	-----g	20
H <sub>2</sub> O, q. s.	-----l	1

A sheet of copper was made the cathode of a plating cell having sheet steel anodes, and a direct current was passed through said plating bath at a current density of 40 amperes per square foot. The temperature of the bath was 180° F. A bright coating resulted. The current efficiency was found to be 88%.

#### EXAMPLE 2

The effect of varying amounts of alkali was measured by determining the current efficiency at 158° F. and 40 amperes per square foot. In each case the bath contained: triethanolamine, the sodium salt of ethylenediaminetetraacetic acid, a ferric salt and water as follows:

(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	-----g	154
((NaO <sub>2</sub> CCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub>	-----g	132
Fe <sup>+++</sup>	-----g	20
H <sub>2</sub> O, q. s. to	-----l	1

The variable in the series of experiments was the concentration of alkali, as shown in the following table.

Table 1

NaOH, g./l.	Condition of Surface	Current Efficiency, percent		
		Run #1	Run #2	Average
25	Bright	12	14	13
30	do	12	13	13
45	Milky	19	24	22
60	Milky to frosty	27	-----	27
90	Matte	40	42	41
100	do	46	-----	46
120	Frosty to matte	44	46	45
150	do	47	45	46
180	do	44	46	45
210	do	42	-----	42

From such data it was concluded that the optimum concentration of alkali was approximately 2.5 molar. Separate tests demonstrated that a solution containing 10 molar sodium hydroxide did not dissolve significant amounts of the sodium salt of EDTA acid. Very low current efficiencies were observed in plating with 7.5 molar alkali. By such methods it was established that the alkali concentration should be from 0.5 to 5 molar.

#### EXAMPLE 3

The molar ratios of sequestering agent to amine and the molar ratios of sequestering agent to iron were investigated. In each test the following conditions and bath components were maintained.

NaOH	-----g	100
Fe <sup>+++</sup>	-----g	20
H <sub>2</sub> O, q. s.	-----l	1
T	-----°F	180
C. D.	-----amp/sq. ft	40

In the following table, A refers to the molar ratio of sequestering agent to amine, B refers to the molar ratio of sequestering agent to iron, C refers to the grams per

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liter of triethanolamine, D refers to the grams per liter of the sodium salt of EDTA acid, and E refers to current efficiency.

A	B	C	D	E
				Percent
0.48	1.390	154	198	68
0.16	0.462	154	66	75
0.32	0.925	154	132	72
0.63	0.925	77	132	71
0.21	0.925	231	132	66

By tests such as outlined above it was established that the molar ratio of the sequestering agent to iron must be within the range from 0.5 to 1.5, but that the ratio of sequestering agent to amine, which would rarely if ever exceed 1.0, was not critical if the amine concentration exceeded 0.5 molar but was less than 5 molar. The molar ratio of amine to iron would in any case exceed 1.0.

## EXAMPLE 4

A plating bath was prepared consisting of sodium hydroxide, triethanolamine, the sodium salt of ethylenediaminetetraacetic acid, a ferric salt and water as follows:

NaOH	g	120
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	g	193
((NaO <sub>2</sub> CCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub>	g	165
Fe <sup>+++</sup>	g	25
H <sub>2</sub> O, q. s.	l	1

Said solution was employed under conditions including:

T	° F	158
C. D.	amp/sq. ft.	40

The average current efficiency in duplicate runs was 44%. The same current efficiency was measured when the alkali concentration was increased to 150 grams per liter.

Such solutions were more viscous than those containing the optimum concentration of 20 grams per liter of ferric iron. It was established that 1 molar iron was beyond the upper workable limit, which was approximately 0.5 molar. Commercial plating would not be attempted below the lower limit of 0.02 molar ferric iron, or approximately 1 gram per liter.

On the basis of experiments such as outlined, the bath composition requirements using said components (i. e. sodium hydroxide, triethanolamine, the sodium salt of ethylenediaminetetraacetic acid, a ferric salt and water) were set as follows, expressed as molarities:

	Min.	Opt.	Max.
NaOH	0.5	2.5	5.0
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	0.5	1.0	5.0
((NaO <sub>2</sub> CCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub>	0.01	0.33	0.7
Fe <sup>+++</sup>	0.02	0.36	0.5
seq./Fe <sup>+++</sup> ratio	0.5	0.93	1.5
seq./RNH <sub>2</sub> ratio	(1)	(1)	(1)
pH	11	13	14.5

<sup>1</sup> Not critical.

Such concentrations are equivalently expressed in grams per liter as follows:

NaOH	20	100	200
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	75	149	745
((NaO <sub>2</sub> CCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub>	4	132	280
Fe <sup>+++</sup>	1	20	28

## EXAMPLE 5

A series of tests were made to determine the effect of temperature upon current efficiency. Each test was conducted for 10 minutes at 40 amperes per square foot, using a bath containing sodium hydroxide, triethanol-

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amine, the sodium salt of ethylenediaminetetraacetic acid, a ferric salt and water, as follows:

NaOH	g	100
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	g	154
((NaO <sub>2</sub> CCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub>	g	132
Fe <sup>+++</sup>	g	20
H <sub>2</sub> O, q. s.	l	1

The results are summarized in Table 2.

Table 2

Temp., ° F.	Condition of Surface	Current Efficiency, Percent		
		Run #1	Run #2	Average
93	Bright milky	9	8	8.5
127	Bright	11	12	11.5
142	Bright with milky haze	28	23	25.5
158	Matte	40	46	46
181	do	75	70	72.5
206	do	88	83	85.5

These data show that temperatures above 100° F. permit higher current efficiencies. A temperature of 180° F. was selected as the optimum.

## EXAMPLE 6

Although elevated temperatures are advantageous, commercially satisfactory plating can be performed at room temperature. A bath was prepared consisting of sodium hydroxide, triethanolamine, the sodium salt of ethylenediaminetetraacetic acid, a ferric salt and water, as follows:

NaOH	g	30
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	g	116
((NaO <sub>2</sub> CCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub>	g	99
Fe <sup>+++</sup>	g	10
H <sub>2</sub> O, q. s.	l	1

A bright plate was obtained at room temperature employing current densities up to 230 amperes per square foot of cathode.

## EXAMPLE 7

The bath of Example 4 was employed for ten minutes per test at 158° F. to determine the effect of current density upon current efficiency.

Table 3

Current Density, amp./sq. ft.	Current Efficiency, Percent		
	Run #1	Run #2	Average
5	35	39	37
10	70	70	70
20	78	75	76.5
40	75	70	72.5
100	55	47	51

The same solution was employed at 180° F. in a series of tests uniformly using 40 ampere-minutes of current with the following results.

Current Density, amp./sq. ft.	Current Efficiency, Percent
5	34
10	70
20	76
100	51

By methods such as those outlined, it was determined that the current density should be kept within the range of from 3 to 300 amperes per square foot. It was also noted that higher current densities were desirable when the temperature and/or the concentration of iron was relatively high. The use of abnormally high current densities with relatively low concentrations of iron and/or

low temperatures might contribute to the formation of porous, non-adherent or otherwise objectionable plates. The limitation of keeping the current density within the range of from 3 to 300 amperes per square foot is sufficient to aid a skilled electroplater to achieve the desired result.

## EXAMPLE 8

A plating bath might be prepared consisting of potassium hydroxide, piperidine, the sodium salt of EDTA acid, water and ferric chloride, as follows:

KOH	-----g--	114
HN(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NH	-----g--	220
((NaO <sub>2</sub> CCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub>	-----g--	132
FeCl <sub>3</sub>	-----g--	60
H <sub>2</sub> O, q. s. to	-----l--	1

Such a plating bath might be used for an electroplating operation at 100° F. using a current density of 40 amperes per square foot.

## EXAMPLE 9

A plating bath might be prepared using:

KOH	-----g--	114
(H <sub>5</sub> CCHOHCH <sub>2</sub> ) <sub>3</sub> N	-----g--	300
((NaO <sub>2</sub> CCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub>	-----g--	132
Fe(NO <sub>3</sub> ) <sub>2</sub>	-----g--	80
H <sub>2</sub> O, q. s. to	-----l--	1

Such a plating bath, consisting of potassium hydroxide, triisopropanolamine, the sodium salt of EDTA acid, water, and ferric nitrate, might be utilized for electroplating iron onto a base metal such as copper, using a current density of approximately 300 amperes per square foot and a temperature of 180° F.

## EXAMPLE 10

A plating bath might be prepared consisting of lithium hydroxide, triethanolamine, dimethyl formamide, water and ferric nitrate, as follows:

LiOH	-----g--	48
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	-----g--	500
(H <sub>3</sub> C) <sub>2</sub> NHCO	-----g--	35
Fe(NO <sub>3</sub> ) <sub>3</sub>	-----g--	80
H <sub>2</sub> O, q. s. to	-----l--	1

Such a bath might be used at room temperature for electroplating iron onto a copper base at a current density of 10 amperes per square foot.

## EXAMPLE 11

A plating bath might be prepared containing:

NaOH	-----g--	50
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	-----g--	300
NaO <sub>2</sub> C(CHOH) <sub>4</sub> CH <sub>2</sub> OH	-----g--	22
Fe(NO <sub>3</sub> ) <sub>3</sub>	-----g--	20
H <sub>2</sub> O, q. s. to	-----l--	1

Such a plating bath, containing sodium hydroxide, triethanolamine, sodium gluconate, water and ferric nitrate, might be used at room temperature for electroplating iron onto a graphite-coated wax mold at a current density of 20 amperes per square foot.

## EXAMPLE 12

The plating bath of Example 5 was used for the galvanic plating of iron onto aluminum. The aluminum sheet was well cleaned and then immersed for 10 seconds in said plating solution. After rinsing with water, the iron coating was sufficiently adherent to be suitable as a base for a subsequently applied electroplating of nickel.

## EXAMPLE 13

Controlled experiments were run to determine the desirability of stirring the plating bath. It was found that such agitation of the plating bath, although not ab-

solutely necessary for commercially useful platings, was generally desirable.

## EXAMPLE 14

Controlled experiments were run to determine the magnitude of loss of weight of iron anodes during the electrolysis when the bath did and did not contain significant amounts of chloride ion. It was found that the rate of anode dissolution was much more rapid when the halide ion was present.

## EXAMPLE 15

After any of the plating baths has become partially depleted in its iron content, the bath may be regenerated by the addition of those components necessary to bring the composition within the required concentration ranges. Ordinarily it is feasible to regenerate the partially depleted bath by the addition of an iron compound such as ferric chloride. Some decomposition of the EDTA acid does occur, and it is usually desirable to regenerate the partially depleted bath by means of a mixture consisting of one mole of sodium salt of EDTA acid and from 2 to 10 moles of a water soluble iron salt such as ferric chloride. The triethanolamine also decomposes, especially at elevated temperature electrolysis, but no amine to iron molar ratios for bath regeneration were established. Because excess amine is conventionally employed initially, no replenishment of the amine is ordinarily necessary.

## EXAMPLE 16

Any of the plating baths may advantageously employ sodium naphthyl sulfonate or other modifying agent suitable for alkaline plating baths.

## EXAMPLE 17

A plating bath similar to that of Example 5 was prepared making use of relatively large amounts of sodium carbonate, to which additional amounts of sodium hydroxide were added to raise and maintain the pH above 12. The absorption of carbon dioxide from the air increases the difficulty of preserving the alkalinity at the required level. The use of relatively large ratios of sodium carbonate to sodium hydroxide in formulating the bath helps in providing a bath having a longer period of usefulness under intermittent operating conditions.

## EXAMPLE 18

A series of experiments were conducted to show that the electroplating process of the present invention was operable when the voltage between the electrodes was varied from 1 volt to 6 volts. Under usual operating conditions, satisfactory control of the current density will result in a potential in excess of 3 volts.

Any conventional type of electroplating cell may be utilized. Cells, generally called Hull cells and Haring cells, were utilized in certain of the examples described.

The examples heretofore given are merely for purposes of illustration and are not intended to restrict the invention, which is defined in the appended claims.

The invention claimed is:

1. The process of electroplating iron onto an article which includes the step of preparing a bath containing water, from 0.5 to 5 molar alkali hydroxide, from 0.5 to 5 molar organic amine, from 0.02 to 0.5 molar ferric compound, and a salt of ethylenediaminetetraacetic acid in a molar ratio relative to the iron of from 0.5 to 1.5, the solution having a pH greater than 11, making the article to be coated a cathode in an electroplating cell, and passing an electric current through the cell at a current density of from 3 to 300 amperes per square foot of cathode surface.

2. The process of claim 1 in which the bath is maintained at an elevated temperature.

3. The process of electroplating iron upon an article which includes the steps of preparing a plating bath

consisting essentially of 100 grams per liter of sodium hydroxide, 154 grams per liter of triethanolamine, 132 grams per liter of the sodium salt of ethylenediaminetetraacetic acid, 20 grams per liter of iron in the ferric state, water, said aqueous solution having a pH greater than 11, causing said article to be a cathode immersed in said plating bath, causing an electric current to flow in said solution between an iron anode and said cathode at a current density of from 3 to 300 amperes per square foot of cathode surface, whereby an adherent, non-porous film of iron is plated onto said article.

4. The process of electroplating iron upon a cathode by the passage of an electric current through a solution containing concentrations of approximately 0.36 molar iron, 0.33 molar salt of ethylenediaminetetraacetic acid, and 3.5 molar base comprising at least 0.5 molar organic amine and at least 0.5 molar inorganic base and affording a pH greater than 11.

5. A plating solution adapted for the deposition of iron upon an article, said solution consisting essentially of water, the ferric salt of ethylenediaminetetraacetic acid in a concentration of from 0.02 to 0.4 molar, and a mix-

ture of an organic amine and an inorganic base each in a concentration greater than 0.5 molar and affording the solution a pH in excess of 11.

6. A concentrate for alkaline plating of iron, consisting essentially of a mixture of approximately seven moles of an alkali hydroxide, three moles of an alkanolamine, from 0.8 to 1.2 moles of a salt of ethylenediaminetetraacetic acid, and an iron compound providing one atomic weight of iron.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

1,729,607 Bezenberger ----- Oct. 1, 1929

##### FOREIGN PATENTS

731,102 Germany ----- Feb. 3, 1943

##### OTHER REFERENCES

Senderoff, Metal Finishing, vol. 48 (Sept. 1950), pp. 71-78.

Watts et al., Transactions American Electrochemical Society, vol. 25 (1914), pp. 529-536.