June 10, 1952 G. SAGEN 2,600,171

REGENERATION OF CHROMIC ACID BATHS UTILIZED IN ELECTRODEPOSITION OF CHROMIUM

Filed Dec. 29, 1947

FIG. 1

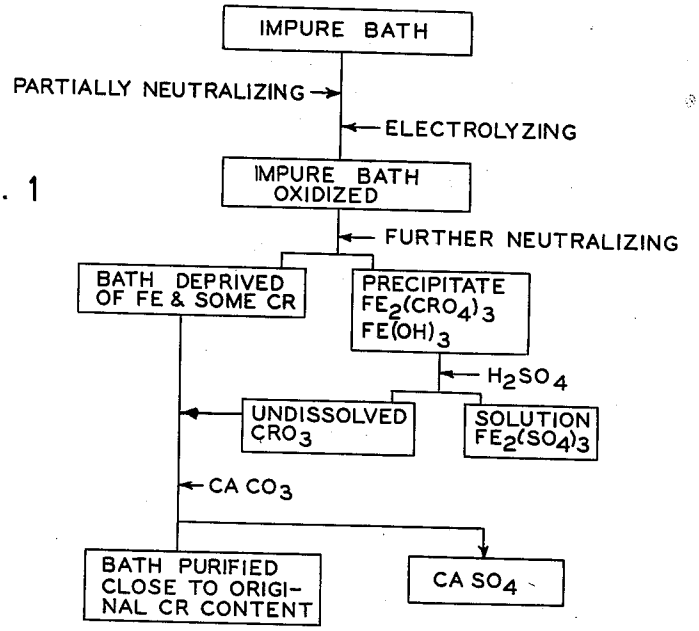
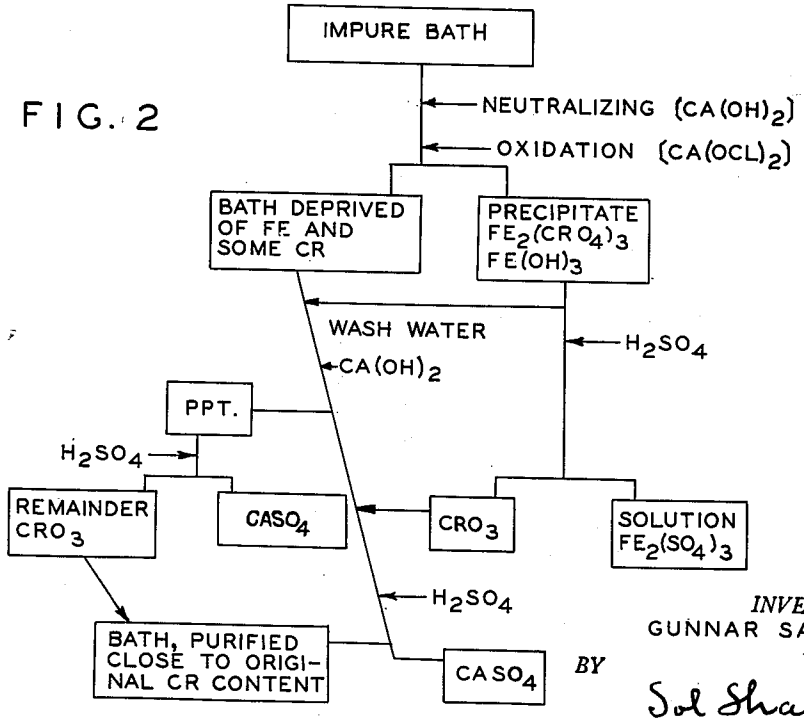


FIG. 2



INVENTOR.
GUNNAR SAGEN

BY Sol Shapiro

ATTORNEY

Patented June 10, 1952

2,600,171

UNITED STATES PATENT OFFICE

2,600,171

REGENERATION OF CHROMIC ACID BATHS UTILIZED IN ELECTRODEPOSITION OF CHROMIUM

Gunnar Sagen, Copenhagen, Denmark

Application December 29, 1947, Serial No. 794,441
In Denmark October 24, 1942

Section 1, Public Law 690, August 8, 1946
Patent expires October 24, 1962

3 Claims. (Cl. 204—51)

1

This invention has for its object a method of purifying solutions of chromic acid for removing impurities restraining their use for the electrodeposition of chromium. Another object of the present invention is to provide a regenerated bath for the electrodeposition of chromium which bath suffers from none of the drawbacks inherent in used electrolytic baths for the electrodepositon of said metal and a third object of the invention is to provide a concentrate of chromic acid compounds in connection with the impurities normally contained in used baths for the electrodeposition of chromium, which concentrate is adapted to be used for the production of chromic acid anhydride thereof.

The impurities in electrolytic baths for the electrodeposition of chromium which particularly will be enriched during use are iron and compounds of trivalent chromium which when they occur in proportions exceeding certain limits dependent on the conditions of electrolysis make such baths unsuited or less suited for electrolytic deposition of chromium.

From the specification of the German Patents Nos. 608,806 and 619,883 it is known to deprive chromic acid solution of iron by neutralization, but it is not mentioned therein that the iron will substantially precipitate in the form of a chromium compound consisting substantially in basic ferric chromate and that the greater part of the trivalent chromium will precipitate under the same conditions. It is, however, a fact that the main part of the trivalent chromium will be precipitated as chromic chromate under these conditions.

When the iron is precipitated in this manner the contents of chromium in the chromic acid solution will thus be substantially reduced, the more as the precipitate is rather voluminous and therefore adsorbs a considerable amount of chromic acid which is particularly the case when a substantial proportion of trivalent chromium is present. This chromium is lost or it must be recovered by metallurgical methods.

These drawbacks are avoided according to the present invention by first precipitating the compounds of the impurities, f. inst. iron present in the chromic acid solution and soluble in acid by adding neutralizing agent. The hexavalent chromium is then recovered from the precipitate thus formed by converting it into chromic acid anhydride by subjecting it to a treatment with an acid in which chromic acid anhydride is only slightly soluble and removing the precipitate of chromic acid anhydride from the impurities soluble in the acid used for converting the chromium of the precipitate into chromic acid anhydride.

2

In connection with the present invention there is shown in the accompanying drawing in

Figure 1, a flow sheet illustrating one form of the invention, and in

Figure 2, a flow sheet representing another form of the present invention.

When treating the solution with neutralizing agents the iron is precipitated substantially as chromate and at the same time more or less of the chromium having a valency below 6 present in the chromic acid solution is precipitated as chromic chromate. In order to avoid the latter part of the precipitation if so desired, the chromic acid solution may be subjected before neutralization to an oxidizing process consisting in an electrolysis or a chemical oxidation, whereby all chromium of lower valency than 6 is oxidized to hexavalent chromium to such an extent that the precipitate formed when adding neutralizing agents will be substantially free from compounds of trivalent chromium.

If such an oxidation of the chromic acid solution has not been carried out prior to the precipitation of the acid soluble compounds there will be trivalent chromium in the precipitate formed if there are substantial amounts of trivalent chromium in the solution which is normally the case in used electrolytic baths. This chromium will not be converted to chromic acid anhydride when the precipitate is treated by an acid in which chromic acid anhydride is only slightly soluble, but on the contrary it will be dissolved as chromic salt in the acid and thereby it will be lost together with the iron salts dissolved in the acid.

To avoid this, the precipitate formed by the addition of neutralizing agents to the chromic acid solution may be subjected to oxidation prior to the conversion of its content of hexavalent chromium into chromic acid anhydride.

The separation of the precipitate of chromic acid anhydride from the impurities especially iron compounds soluble in the acids employed for the precipitation of this precipitate may be carried out by decantation or filtration or by a combination of both methods. Preferably the chromic acid anhydride precipitate, after filtration, is washed with the acid in question.

After the separation of the chromic acid anhydride precipitate this precipitate may be dissolved in water and the solution added to the chromic acid solution purified by the addition of

the neutralizing agent or the precipitate may be added thereto without previous solution. The chromic acid solution is thereby brought to substantially its original content of chromium, but has been deprived of certain impurities, particularly iron. If the solution has not been oxidized previous to the addition of neutralizing agents such oxidation may be carried out before or after the addition of the chromic acid anhydride recovered, whereby the content of trivalent chromium may be reduced to the desired value.

In order to avoid the introduction of undesired ions into the chromic acid solution there may be used a compound, f. inst. an oxide, a hydroxide or a carbonate of a base forming a slightly soluble compound with the acid used for liberating the chromic acid anhydride. If f. inst. sulphuric acid is used for liberating the chromic acid anhydride a calcium compound may be used as neutralizing agent.

By this it is attained that the acid present in the chromic acid anhydride precipitate when this precipitate is added to the chromic acid solution treated with the neutralizing agent will react with the excess of the acid neutralizing agent and with the amounts of the cation of the same present in the solution, so that a precipitate is formed which can be removed f. inst. by filtration. The remaining base residue or acid residue may then be removed afterwards or at the same time by further adding an acid capable of precipitating the base residue or a base capable of precipitating the acid residue. By using a calcium compound as neutralizing agent for precipitating the iron precipitate and sulphuric acid for precipitating the chromic acid anhydride and for dissolving the iron present in the precipitate, calcium sulphate will be precipitated when the chromic acid anhydride is brought into the filtrate from the iron precipitate, whereas remaining calcium ion or sulphate ion may be precipitated by addition of either sulphuric acid or chalk.

If desired a compound of another base residue may be used for neutralizing the last part of the acid after the main precipitate has been removed from the solution and for this purpose a base residue capable of precipitating the acid more completely may be used. When employing sulphuric acid for precipitating the chromic acid anhydride barium carbonate may be used for the last neutralization.

In order to explain the practical employment of the method the following examples are described.

Example 1

This example refers to the regeneration and purification of 5 liters of a chromic acid solution used for electrodeposition of chromium and containing 240 g. CrO_3, 30 g. Cr_2O_3, 30 g. Fe and 11 g. H_2SO_4 per liter.

By cautiously adding 100 g. $BaCO_3$ the contents of sulphuric acid is reduced from 11 to 1 g. per liter. The trivalent chromium is then electrolytically oxidized to chromic acid, a copper wire being used for a cathode, a lead plate being used for anode, at 3.3 volts and about 100 amp./m.^{2}. After the current has flowed for 2 hours the contents of trivalent chromium has decreased from 30 to 4 g. per liter.

Now 600 g. $CaCO_3$ are added in small portions to the solution. After the precipitate formed has settled 3 liters of the liquid are removed by decanting.

After agitation and standing, another 0.5 liter of the solution is decanted from the precipitate.

To the precipitate is added 1.4 kgs. concentrated sulphuric acid to precipitate the chromic acid. The iron which is now dissolved as ferric sulphate is removed by standing and decantation and subsequent washing with 1 kg. of 70 per cent sulphuric acid after which the mixture is left to stand and decanted and filtered. The chromic acid anhydride containing sulphuric acid is then added to the solution decanted from the first precipitate and after this 200 g. $CaCO_3$ are further added to precipitate the remaining sulphuric acid after which the precipitate is removed by filtration.

Figure 1 of the drawing shows a flow sheet illustrating the method set forth in Example 1, the various steps employed, and the results obtained which with the legends thereon shown is self-explanatory.

Example 2

This example relates to the regeneration and purification of 10 liters of a chromic acid solution used for electrodeposition of chromium and containing 197 g. CrO_3, 14 g. Cr_2O_3 and 34 g. Fe per liter.

For the precipitation 800 g. $Ca(OH)_2$ dispersed in about 1 liter water is employed. After standing 6 liters are removed by decanting.

200 g. fresh chlorinated lime are added with agitation to the liquid remaining containing the precipitate. After standing for some time the precipitate is removed by filtration and washed with 1.5 liters of water. To the solution thus obtained there is added 1.5 kg. $Ca(OH)_2$ dispersed in the said washing water. After standing for a few days the precipitate is removed by filtration and washed with water. In order to liberate the chromic acid 2 kgs. sulphuric acid are added. After agitation for a few hours the chromic acid is filtered from the calcium sulphate and added to the solution decanted from the first precipitate.

The precipitate of compounds of iron and chromium remaining after the oxidation is treated as described in Example 1. Thus 2.5 kgs. concentrated sulphuric acid are added and the chromic acid anhydride precipitate is removed by filtration and washed on the filter with 1 kg. 70 per cent sulphuric acid after which the precipitate is added to the solution decanted from the first precipitate. 45 cm.^{3} 50 per cent sulphuric acid are added to precipitate the excess of calcium in the solution after which the precipitate is removed by filtration.

Figure 2 of the drawing shows a flow sheet illustrating the method set forth in Example 2, the various steps employed, and the results obtained which with the legends thereon shown is self-explanatory.

I claim:

1. Method of producing chromic acid solutions substantially free from trivalent chromium and iron from chromic acid baths utilized in the electro-deposition of chromium comprising the treatment of the bath by electrolysis to effect oxidation of trivalent chromium to hexavalent, adding a neutralizing agent selected from the group consisting of alkaline earth carbonates and alkaline earth hydroxides in a quantity sufficient for precipitating the iron of the solution partially in the form of ferric chromate, converting the contents of hexavalent chromium of the precipitate thereby formed into chromic acid

anhydride by a treatment with concentrated sulphuric acid, separating the chromic acid anhydride thereby formed from the solution simultaneously formed and adding the chromic acid anhydride to the original solution neutralized with the alkaline earth compounds.

2. Method of regenerating chromic acid solutions utilized in the electro-deposition of chromium comprising adding a neutralizing agent selected from the group consisting of alkaline earth carbonates and alkaline earth hydroxides in a quantity sufficient for precipitating the contents of trivalent chromium and iron from the solution, treating the precipitate thereby obtained by an oxidizing agent to oxidize any trivalent chromium present to hexavalent chromium, converting the insoluble chromates contained in the precipitate into chromic acid anhydride by a treatment with concentrated sulphuric acid, separating the chromic acid anhydride thereby precipitated from the solution and adding the chromic acid anhydride to the original solution neutralized with the alkaline earth compounds.

3. Method of regenerating chromic acid solutions utilized in the electro-deposition of chromium comprising adding a neutralizing agent selected from the group consisting of alkaline earth carbonates and alkaline earth hydroxides to the solution in a quantity sufficient for precipitating the contents of trivalent chromium and iron from the solution, treating the precipitate thereby obtained with a solution of chlorinated lime to oxidize any trivalent chromium present to hexavalent chromium, separating the precipitate from the solution and treating the precipitate with concentrated sulphuric acid to form solid chromic acid anhydride and a solution of the impurities of the original bath, separating the chromic acid anhydride from the solution and adding the chromic acid anhydride to the original solution neutralized with the alkaline earth compounds.

GUNNAR SAGEN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
630,612	Le Blanc	Aug. 8, 1899
1,851,603	Thomas	Mar. 29, 1932
1,878,918	Udy	Sept. 20, 1932
1,926,758	Udy	Sept. 12, 1933

FOREIGN PATENTS

Number	Country	Date
608,806	Germany	Feb. 1, 1935
619,883	Germany	Oct. 9, 1935

OTHER REFERENCES

Schneidewind et al., Transactions of American Electrochemical Society, vol. 53 (1928), pp. 499–507.

Hoover et al., Industrial and Engineering Chemistry, vol. 33 (1941) pp. 131–134.