United States Patent [19]

Crowther

[11] **3,766,028**

[45] **Oct. 16, 1973**

[54] **ELECTROWINNING OF CHROMIUM METAL**

[75] Inventor: **John Cooper Crowther**, Harrogate, England

[73] Assignee: **Albright & Wilson Limited**, Oldbury, England

[22] Filed: **Mar. 30, 1972**

[21] Appl. No.: **239,718**

[30] **Foreign Application Priority Data**

Apr. 2, 1971 Great Britain 8,522/71

[52] **U.S. Cl.** .... **204/105 R**, 423/551

[51] **Int. Cl.** **C22d 1/00**, C23b 5/06

[58] **Field of Search** .... 204/105 R, 551; 423/551

[56] **References Cited**

UNITED STATES PATENTS

2,849,354	8/1958	Carosella	204/105 R
2,803,594	8/1957	Westby	204/105 R
2,771,413	11/1956	Dean et al.	204/105 R
2,663,686	12/1953	Lloyd et al.	204/105 R

Primary Examiner—John H. Mack
Assistant Examiner—R. L. Andrews
Attorney—Herbert H. Goodman

[57] **ABSTRACT**

A method for the integrated production of chromium metal and a tanning composition which comprises acidifying an aqueous solution of sodium chromate with sufficient of an aqueous solution consisting essentially of sulphuric acid to form sodium dichromate, reducing the dichromate with sulphur dioxide to form an aqueous tanning solution of basic chromic sulphate and sodium sulphate, using a part of the tanning solution diluted to a concentration of from 40 to 180 g/l chromium as feed to a chromium electrowinning operation which comprises passing a current having a density of between 30 and 300 amps/sq. ft. through an electrolyte having a pH between 1.0 and 2.8 and a temperature between 27° and 80° C and thereby producing chromium metal, an acidic anolyte and a chromium lean catholyte, maintaining the anolyte and the catholyte in separate compartments, recycling the catholyte and combining it with the tanning solution, recycling the anolyte and adding it to the alkali metal chromate as part of the said aqueous solution consisting essentially of sulphuric acid to effect part of the acidification thereof, and recovering the chromium metal and part of the tanning solution as products, the proportion of chromium metal to chromium in the total products being less than 1:3.

4 Claims, No Drawings

ELECTROWINNING OF CHROMIUM METAL

It is known to make chromium metal by electrowinning in a diaphragm cell using a solution of chrome ammonium alum derived from ferrochrome as feed. It is also known to make basic chromium sulphate tanning salts by reducing sodium dichromate derived from chromite ore as the basic raw material via sodium chromate as an intermediate.

The present invention provides an integrated method for the manufacture of tanning salts and chromium metal which comprises acidifying an aqueous solution of alkali metal chromate to form the dichromate, reducing the dichromate to an aqueous tanning solution of chromic salt and alkali metal salt, taking a part of the tanning solution diluted to a concentration of from 40 to 180g/1 chromium as feed to a diaphragm cell adapted for the electrowinning of chromium, producing, in the cell, chromium metal, an acidic anolyte and a chromium lean cathloyte, recycling the catholyte and combining it with the tanning solution, recycling the anolyte and adding it to the alkali metal chromate to effect part of the acidification thereof and recovering the chromium metal and part of the tanning solution as products, the proportion of chromium metal to chromium in the total products being not greater than 1:3.

The invention has the advantage of providing an integrated manufacture of chromium metal and tanning salts from the same chromite raw material with full economical usage of the effluents from the chromium cell.

This invention relates to the electrowinning of chromium from metal solutions containing trivalent chromium salts. In particular it relates to a process for electrowinning of chromium metal which is part of an integrated chromium chemical operation.

It is well known to manufacture chromium metal by passing aqueous solutions of chromic sulphate and ammonium sulphate, (chrome ammonium alum) to an electrolytic cell divided into cathode and anode compartments by a permeable diaphragm. The anode is typically of lead and the chromium metal plates onto a stainless steep cathode. The spent anolyte and spent catholyte are withdrawn from the cell separately. The former is acidic due to the formation of sulphuric acid at the anode, while the latter is depleted in chromium compared with the feed. There is a description of a typical apparatus and process for electrowinning chromium in J. Electrochem. Soc. Vol. 97 P.227.

A problem in operating any commercial process for electrowinning chromium is the utilisation of the effluent anolyte and catholyte. Hitherto the solutions proposed to this problem have been adapted to production via chrome alum using ferrochrome as basic raw material. We have now discovered that chromium metal may be economically produced starting from alkali metal chromate (which is the primary product obtained from the extraction of chromite ore with alkali metal carbonate) as part of an integrated process for the manufacture of chromium sulphate based tanning compositions and chromium metal.

The manufacture of sodium chromate involves heating the chromite ore with sodium carbonate in a rotary kiln and lixivating the residue with water. The chromate may then be acidified, for example with sulphuric acid to form sodium dichromate and sodium sulphate. The sulphate may be crystallised out by evaporating the solution. Reduction of the dichromate, for example with sulphur dioxide provides a solution containing a mixture of 33 percent basic chromic sulphate and sodium sulphate.

Sodium dichromate is reduced with sulphur dioxide according to the following equation

$$3SO_2 + Na_2Cr_2O_7 + H_2O \rightarrow Cr_2(OH)_2(SO_4)_2 + Na_2SO_4$$

(33 percent basic sulphate)

Basicity is expressed as follows

$Cr_2(SO_4)_3$	= NIL Basic
$Cr_2(OH)_2(SO_4)_2$	= 33% Basic
$Cr_2(OH)_4\,SO_4$	= 66% Basic
$Cr_2(OH)_6$	= 100% Basic

Thus the percentage basicity refers to the percentage replacement of the three (SO_4)s in nil basic chromic sulphate by (OH).

This equimolar mixture of chromic and sodium sulphates is suitably adjusted in production to give a liquor containing about 13 percent Cr_2O_3 and this liquor can be spray dried to give a solid product containing about 26 percent Cr_2O_3. The 13 percent Cr_2O_3 solution contains 8 – 10 percent by weight of chromium or 120 – 180g. per litre.

We have now discovered that part of the solution obtained from the reduction of dichromate as aforesaid may conveniently be diluted and used as the feed to an electrolytic cell for the electrowinning of chromium. We have further discovered that, provided the proportion of chromium produced is kept within certain limits, the partially spent catholyte may be recycled and combined with the original chromium salt solution to provide a product which is leaner in chromium than the original product but still entirely acceptable for tanning purposes. Finally we have discovered that the anolyte may be recycled and added to the alkali metal chromate to provide a part of the acid required to form the dichromate.

Our invention, therefore, provides a method for the integrated production of chromium metal and a tanning composition, which comprises acidifying an aqueous solution of alkali metal chromate to form the dichromate, reducing the dichromate to an aqueous tanning solution of chromic salt and alkali metal salt, taking a part of the tanning solution diluted to a concentration of from 40 to 180 g/l Cr. as feed to a diaphragm cell adapted for the electrowinning of chromium, producing, in the cell, chromium metal, an acidic anolyte and a chromium lead catholyte, recycling the catholyte and combining it with the tanning solution, recycling the anolyte and adding it to the alkali metal chromate to effect part of the acidification thereof, and recovering the chromium metal and part of the tanning solution as products, the proportion of chromium metal or chromium in the total products being not greater than 1:3, preferably 1:10 or less.

The alkali metal is preferably sodium. The chromate may be acidified with any acid whose relevant salts have the necessary tanning properties and are suitable for use in electrowinning, sulphuric acid being preferred. The dichromate is preferably reduced with sulphur dioxide, but other reductants are not excluded.

The cell may be any of those described for the electrowinning of chromium in the prior art or preferably a non-diaphragm cell. The cell is preferably operated so that the atomic proportion of sodium to chromium in the catholyte does not exceed 4:1 and is most preferably from 2:1 to 2.5:1.

To start the cell it is preferred to charge the anolyte compartment with sulphuric acid and the catholyte compartment with a solution containing about 45 g/l Cr and 40 g/l Na as sulphates, and having a pH of 1.5 – 2.5. The tanning solution is fed to the catholyte compartment at a concentration of from 40 to 180 g/litre chromium, preferably 90 gm/litre chromium. Since the original tanning solution sometimes has a concentration as high as 180 g/litre, as chromium, it may require dilution with water to produce the preferred concentrations. As electrolysis proceeds the excess sulphuric acid generated is bled from the anolyte compartment and recycled for use in the acidification of the chromate. The chromium content of the catholyte falls and is maintained at a concentration of between 20 and 60 g/litre chromium e.g., 45 gm/litre chromium and an alkali metal: Cr. ionic ratio of approximately 2:1 by continuous addition of feed solution and continuous withdrawal of catholyte to maintain constant catholyte volume. The sodium concentration in the catholyte stabilises at a level equal to that of the feed. Thus when operating at constant catholyte volume, for maximum proportion of Cr plated/Cr fed the Na concentration in the catholyte must be as high as possible consistent with obtaining a satisfactory metal product. The withdrawn catholyte is recombined with the original tanning solution, a major part of which is then withdrawn and may be evaporated to dryness to yield the tanning salt as a product. The recycle of catholyte may be carried out in various ways: for example it is possible to plate out half the chromium entering in the feed and to recycle all the remainder to a reservoir of tanning solution from which both the tanning product and the cell feed are withdrawn. A preferred method involves cooling at least a part of the purged catholyte to crystallise out sodium sulphate, filtering the liquor, which may have a Na:Cr mole ratio of 1:1, and using the filtered liquor instead of water as a diluent for the concentrated tanning solution in the preparation of the cell feed. The proportion of liquor used as diluent in this way can be adjusted according to concentration requirements, and the remainder of the purged catholyte can be returned to a reservoir of concentrated tanning solution.

According to the last mentioned preferred embodiment, the ratio of chromium metal to chromium in the total products may be as high as 1:3. However, if the process is operated without recovery of sodium sulphate, then the ratio should not exceed 1:7 and is preferably 1:10 or less.

As in prior art electrowinning the pH of the electrolyte may conveniently be between 1.0 and 2.8, the temperature may be between 27° and 80° C and the current density between 30 and 300 amps/sq.ft.

The invention will be illustrated by the following example(s):

EXAMPLE 1

A solution of sodium chromate which had been treated to remove aluminium, vanadium and similar deleterious elements was acidified to pH 3–4 with sulphuric acid to form a solution of the dichromate and sodium sulphate. After separation of the sodium sulphate the dichromate was reduced by sulphur dioxide to give a tanning solution, whose concentration was adjusted by dilution with water to give 150g/l chromium in solution.

Part of the tanning solution was then diluted to 90g/l chromium and 40g/l Na and fed to an electrowinning cell, to maintain the catholyte concentration at 45g/l chromium and 40g/l Na. Addition of acid or alkali for pH control between 1.5 – 2.5 were made as required.

Cell purge liquor, containing 45g/l chromium and 40g/l Na was removed at the same rate, to maintain constant catholyte volume and recycled and combined with the tanning solution. The amount of weak recycle liquor was controlled so as not to exceed one-tenth the output of tanning solution both expressed as chromium. The chromium plated as metal was equal in quantity to that removed as purge, (i.e., 50 percent of feed was plated). The resulting tanning solution thus had a sodium/chromium ratio of 10/9, which was acceptable for tannage, and could be spray dried to give an acceptable solid tanning salt.

The anolyte from the cell, containing some hexavalent chromium in 30 percent H_2SO_4 solution, was withdrawn as required and replaced by water. The withdrawn anolyte was recycled to the production of dichromate from chromate step, replacing part of the sulphuric acid normally used.

EXAMPLE II

The process was operated as in Ex. 1, but the purged catholyte was not all recycled to the reservoir of tanning solution. Sodium sulphate was removed from part of the purge liquor by cooling to render the resulting liquor equimolar in Na and Cr, i.e., 45g/l Cr 20g/l Na. The filtered liquor was then used for dilution of strong feed liquor from the reservoir, containing 180g/l Cr (80g/l Na) at a ratio of 2 parts of recycle to 1 part of strong liquor. This gave a suitable feed liquor containing 90g/l Cr and 40g/l Na, which was used as feed to an electrowinning cell, containing 45g/l Cr and 40g/l Na in the catholyte.

The remainder of the cell purge liquor, untreated to remove sodium, was recycled to the reservoir as before. In this case, the return of chromium in the purge liquor enabled a smaller quantity of strong feed liquor (180g/l Cr) to be used than an Ex. 1, and also resulted in a smaller volume of return liquor to the reservoir. By operation in this fashion, about 75 percent of the chromium present in the strong liquor could be plated out as chromium, rather than the 50 percent quoted in Ex. 1. It is also possible to treat all the purge liquor to remove sodium sulphate, and recycle to the reservoir the part which is surplus to requirements for preparing the cell feed.

I claim:

1. A method for the integrated production of chromium metal and a tanning composition which comprises acidifying an aqueous solution of sodium chromate by adding sufficient of an aqueous solution consisting essentially of sulphuric acid to form sodium dichromate, reducing said sodium dichromate with sulphur dioxide to form an aqueous tanning solution of bacic chromic sulphate and sodium sulphate, diluting a portion of said tanning solution to a concentration of from 40 to 180 g/l chromium to form a chromium electrowinning feed solution, feeding said feed solution to the catholyte of a compartmented cell having a catholyte and an anolyte, maintaining said catholyte at a pH between 1.0 and 2.8 and at a temperature between 27° and 80° C, and electro-depositing chromium metal on a cathode from said catholyte by passing a current hav-

ing a current density of between 30 and 300 amps/sq. ft. through said catholyte, and thereby producing said chromium metal, an acidic anolyte and chromium lean catholyte, maintaining the anolyte and the catholyte in separate compartments, recycling the catholyte and combining it with the tanning solution, recycling the anolyte and adding it to the alakli metal chromate as part of the said aqueous solution consisting essentially of sulphuric acid to effect part of the acidification thereof, and recovering the chromium metal and a portion of the tanning solution as products, the ratio of chromium metal to chromium in the total of the chromium metal plus the chromium in the tanning solution product being less than 1:3.

2. A method according to claim **1** wherein the atomic proportion of sodium to chromium in the catholyte is maintained between 2:1 and 2.5:1.

3. A method according to claim **1** wherein the chromium content of the catholyte is maintained between 20 and 60g/l chromium.

4. A method according to claim **1** which comprises cooling the recycled catholyte to crystallise out sodium sulphate filtering the liquor to provide a sodium to chromium mole ratio of about 1:1 and using the filtered liquor as diluent for the concentrated tanning solution in preparation of the feed to the electrowinning operation.

* * * * *