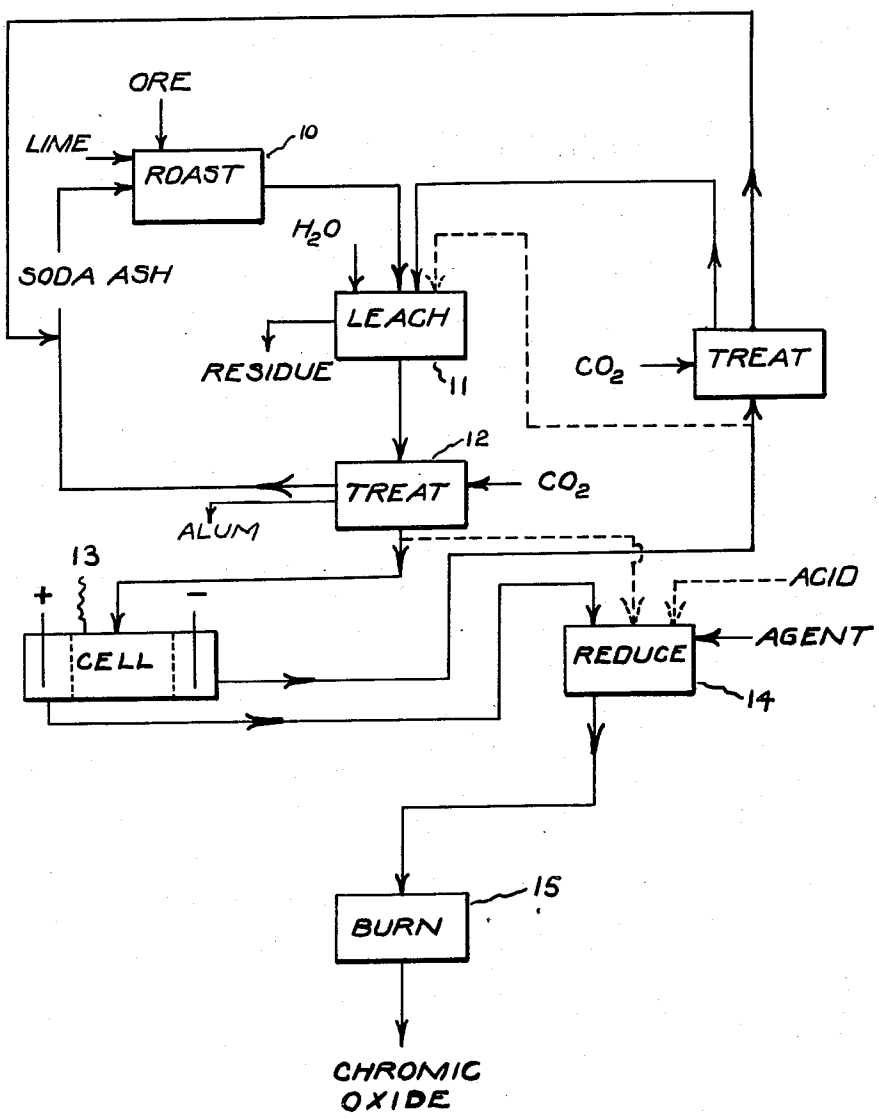
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PROCESS FOR PRODUCTION OF CHROMIC OXIDE

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PROCESS FOR PRODUCTION OF CHROMIC OXIDE

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1

This invention relates to a process for producing chromic oxide, Cr_2O_3, and is especially adapted to production of said compound when starting from the ore chromite, though the invention may also be used when starting at a point further along in the process flow sheet as will be seen as this specification proceeds.

In the past chromic oxide has been produced by a variety of methods most of which call for reduction of a hexavalent chromium compound to the tri-valent state. Many such processes introduce sulfur or compounds of sulfur into the product. One of the objects of the present invention is to eliminate the introduction of sulfur or sulfur compounds in the finished chromic oxide.

Other processes require the use of a large amount of reducing agent as it is necessary to reduce all the chromium to the tri-valent state. In the present invention I have aimed at a method of producing chromic oxide without the necessity of reducing all of the chromium from the hexavalent to the trivalent state by the use of reducing agents. Other objects and advantages of my process will be seen as the specification develops.

While the roasting of chromite ore is old in the art and I do not claim such a step as a part of my invention, I prefer to illustrate my process starting with the raw ore since my process allows recovery of soda ash which can be re-used in the roasting process, thus producing a saving. To illustrate further I now refer to the accompanying flow sheet in which 10 represents a roasting operation in which the ground chromite is roasted with soda ash and other ingredients in a manner well known to the art, 11 represents the leaching operation, also well known; from the leach I prefer to run to a treating tank 12, wherein the leach liquor is treated with CO_2 so as to adjust the pH to a point whereat alum, etc. is precipitated. This step is known to the art.

In this treat step soda ash may be recovered, if desired, for return to the roast. I now take the treated alkaline liquor containing sodium chromate to an electrolytic cell represented by 13, preferably a diaphragm type cell though this type is not necessary, wherein, by the passage of a direct current there is formed an anolyte liquor high in dichromate or chromic acid, and a catholyte liquor high in sodium hydroxide and containing sodium chromate, this catholyte liquor can be retreated with CO_2 if desired to form soda ash containing sodium chromate, which mixture can be returned to the roast for re-use. The

2

anolyte liquor need not be free of sodium salts entirely, and I prefer to carry out the electrolysis until the anolyte consists of approximately 90% chromic acid and 10% sodium dichromate in a total concentration of approximately 200 grams of CrO_3 per liter. I now take this anolyte liquor to a reducing tank 14 where wood flour is added to the solution either cold or at elevated temperature. I have discovered that the wood flour is an excellent and cheap reducing agent for this liquor. I prefer to use Redwood flour though other wood flour also gives good results. My object in this step is to reduce only a part of the hexavalent chromium to the tri-valent state so that the tri-valent chromium formed will react with the hexavalent chromium in the liquor to form chromium dichromate, $Cr_2(Cr_2O_7)_3$, which compound becomes only slightly soluble at pH's above about 4.0 and therefore precipitates out as a dark brown compound. I therefore analyze my anolyte liquor and adjust the amount of wood flour to be added accordingly, after first running tests on any particular wood to determine its reducing power since this varies from wood to wood. It is seen that as the chromium dichromate is formed and as it is only slightly dissociated, the pH of the solution rises, finally reaching a value at which precipitation occurs, and it is a matter of chemical control as to the exact amount of wood flour needed for a given anolyte composition.

I prefer to add some excess wood flour over that theoretically needed to produce the chromium dichromate since I have found that the excess wood flour is a decided help if a filtering step is undertaken as follows:

I may now filter the chromium dichromate precipitate and then burn said precipitate in a furnace 15, which may be of any type, I have used a rotary tube furnace very successfully for such burning, and under the influence of the burning, with air available, the chromium dichromate breaks down to the desired product—green chromic oxide.

Instead of filtering as described above, I may add enough wood flour, which reacts very slowly with the anolyte liquor at pH's above about 4.5, to absorb most or all of the anolyte liquid remaining after the formation of the chromium dichromate precipitate, and burn the whole mass either directly or after drying to remove excess water. In this case the excess wood flour burns off during the furnacing operation and therefore does not contaminate the final product.

It will be seen that the reduction step de-

pends on the reaction between the wood flour and the dichromate, therefore the process could be operated by adding an inorganic nonreactive acid to the treat liquor so as to convert the chromate to dichromate and lower the pH to a low enough value to permit the reduction reaction to take place as illustrated alternatively by dash lines at **14**, then, after reduction, the pH could be raised by the use of neutralizing chemicals, or electrolysis, to precipitate the chromium dichromate. I have found sulfuric acid suitable for this purpose. Obviously other reducing agents could be substituted for the wood flour, such as sugar, etc., but I prefer wood flour due to its low cost and ease of burning to remove excess. My use of chromium dichromate is the soul of my invention since this compound may be formed with only a part of the total chromium in the reduced state, thus materially decreasing the amount of reducing agent needed and providing a great saving over the prior art.

One variation of my process might be to add an inorganic acid to the treat liquor to reduce the pH to about 1.0 and convert the chromate to dichromate, then reduce this acidified dichromate liquor completely with a reducing agent such as wood flour, in this case, if sulfuric acid were the acid used, a solution of chromic sulfate and sodium sulfate would be formed, this solution could then be added to some unreduced treat liquor containing sodium chromate and thus the chromium dichromate would be precipitated with the formation of sodium sulfate in solution which can be filtered away from the chromium dichromate, or can be left in the mass and leached out of the chromic oxide after burning.

The principal reaction that I rely on to make my process successful is the reaction forming chromium dichromate from tri-valent and hexavalent chromium compounds.

I am aware that due to the equilibrium between the dichromate and chromate ions, that there will be some variation in the actual compound formed, varying from chromium dichromate to chromium chromate, and it is to be understood that my references herein to chromium dichromate means whatever mixture of chromium dichromate and chromium chromate that happens to be formed, this of course, varies with the dichromate-chromate ion ratio.

It will be seen that I have provided a new and novel method of producing chromic oxide, and while I am aware that numerous changes might

be made in my flow sheet I have shown only my preferred form. Therefore, the above described methods should be construed as illustrative only and not as limiting the scope of the following claims.

I claim:

1. A method of producing chromic oxide which includes electrolyzing an aqueous solution of a chromate salt of an alkali metal so as to produce an anolyte solution consisting substantially of chromic acid, partially reducing said anolyte solution to form chromium dichromate thereby raising the pH of said solution to a value above about pH 4.5 to precipitate said chromium dichromate, separating said precipitate from said solution and thermally decomposing said chromium dichromate to produce chromic oxide.

2. A method of producing chromic oxide which includes electrolyzing an aqueous solution of sodium chromate so as to produce an anolyte solution consisting substantially of chromic acid, partially reducing said anolyte solution to form chromium dichromate thereby raising the pH of said solution to a value above pH 4.5 to precipitate said chromium dichromate, separating said precipitate from said solution and thermally decomposing said chromium dichromate to produce chromic oxide.

3. A method of producing chromic oxide which includes electrolyzing an aqueous solution of a chromate salt of an alkali metal so as to produce an anolyte solution consisting substantially of chromic acid, partially reducing said anolyte solution by the addition of wood flour to form chromium dichromate, and thermally decomposing said chromium dichromate in the presence of air to produce chromic oxide.

JOSEPH SCHULEIN.

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