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PROCESS FOR THE MANUFACTURE OF DICHROMATES

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This invention relates to the manufacture of dichromates.

Dichromates, in particular sodium dichromate, are technically manufactured in such a manner that the alkali chromates obtained by the oxidizing opening up of chromium ore in the presence of alkalies or alkali carbonates are treated with sulphuric acid or also bisulphate, whereby one equivalent of alkali is taken from the neutral chromate and separated in the form of alkali sulphate. When sodium dichromate is manufactured in this manner this causes a quite considerable loss of alkali since sodium sulphate can no longer be passed back into the process. As it also always contains small quantities of chromate which render it discoloured the sulphate is mostly a troublesome valueless secondary product and is consigned as waste.

The method also proposed hitherto of effecting the conversion of the neutral chromate into dichromate with the aid of carbon dioxide for the purpose of separating half of the alkali in the form of sodium bicarbonate has hitherto failed on account of the difficulties of effecting this conversion in anything like a satisfactory yield. It needs very high carbon dioxide pressure in order to displace the equilibrium in the favor of bicarbonate formation and by this means the economy of this process is reduced considerably.

Another method is that through calcium chromate which is obtained by the oxidizing opening up of chrome ore with lime at very high temperature. In this case the excess of lime must be neutralized and the calcium chromate treated with sodium bisulphate. Accordingly very large quantities of bisulphate are necessary. Now however since the manufacture of nitric acid from ammonia the bisulphate is obtained less and less as a waste product so that the calcium chromate process is greatly endangered.

If for lack of bisulphate sulphuric acid were to be employed, then on account of the high acid costs the process would no longer be economic.

In accordance with the present invention these difficulties can be avoided. According to the process of the invention alkali chromate obtained in the known manner is treated in the aqueous phase together with an equivalent quantity of chromium hydroxide, hydrated chromium oxide, chromium oxide or also metallic chromium or alloys or mixtures containing chromium at temperatures above 100° C. under pressure with oxygen or gases containing oxygen.

It is however not at all necessary that the chromate should be present in the pure state but, and herein lies the great advantage of the invention, it suffices to employ a chrome ore frit obtained in the known manner whereby the cost of extraction can be saved.

Prior to the further working up of the chromate frit to dichromate the content of chromate and if desired also the content of free alkali may be determined and the addition of trivalent chromium containing oxygen correspondingly ascertained. Instead of trivalent chromium oxygen compounds also chromium metal or its alloys such as ferrochrome can be added.

The mixture is now heated in the aqueous phase with gases containing oxygen under pressure to a temperature above 100° C. suitably to 250–300° C. whereby the whole of the chromium added is converted into dichromate. The alkali in free state or combined under the form of monochromate is thereby entirely utilized and the cost of sulphuric acid or bisulphate is saved.

The trivalent chromium oxygen compound, in the form of chromium hydroxide, hydrated chromium oxide or chromium oxide can be produced by known processes and it is also in this case quite unnecessary that it should be isolated in the pure condition prior to the further working up. If it is obtained for example by reduction of a chromate frit then after reduction the mass is extracted with water in order to remove the alkali content and the residue is conveyed to the oxidation process. Even if it is possible directly to convert a reduced frit in the presence of an equivalent quantity of alkali by pressure oxidation into dichromate, yet it is much more economic to effect the oxidation in the presence of chromate or chromatic frit since thereby the cost of reduction is saved. As already mentioned instead of trivalent chromium oxygen compounds, chromium metal, alloys, or mixtures, thus for example ferrochrome can be subjected to the pressure oxidation in the aqueous phase in the presence of chromate or a chromate frit.

This process is rendered very simple and economic on account of the fact that the opening up of the chromium ore can also be effected without disadvantage with considerable alkali excess since the latter is again combined by the ferrochrome in the pressure oxidation.

It may further be remarked that the execution of the process is in no way dependent upon the absence of lime. It is therefore quite possible to employ the roasted product obtained according to the lime-soda process. Also in the reduction and the subsequent application of the reduction product a content of lime is not detrimental.

In such a case it is suitable to convert the lime in an appropriate manner into calcium carbonate and thus to avoid its alkaline action towards dichromate.

As an example the process can also be effected very advantageously by first carrying out the oxidizing opening up process to the half way stage, extracting the chromate from the roast by leaching and subjecting the residue to a further exhaustive oxidation. The roast finally obtained is reduced in the known manner, freed from alkali and together with the extracted chromate of the first operation subjected to the pressure oxidation. In this manner it is also possible to effect the exhaustive oxidation without loss of alkali by means of an excess of alkali which is recovered.

From the above description it is seen that there is concerned in the case of the present invention a method of manufacture of unexpected elasticity, since it is possible, according to the conditions, to proceed by the most advantageous method.

The present process is distinguished economically by the fact that losses of alkali and high costs for acid are avoided, whereby naturally a considerable reduction of the manufacturing costs is effected.

It is immaterial to the execution of the process in what manner the chromate is manufactured, and whether excess of caustic alkali, alkali carbonate or alkali carbonate in the presence of alkaline earths is employed.

It is likewise immaterial in what manner and with what agent the reduction of the other part of the chromate is effected. It is essential that the ratio: trivalent chromium or metallic chromium alkali in free state or under form of alkali monochromate, is correctly adjusted, it being also optional to employ instead of the trivalent chromium metallic chromium or its alloys or mixtures.

According to the present invention it is therefore possible to solve the problem of the conversion of neutral chromate into acid chromate, so that one equivalent of alkali instead of being separated in a costly process as a valueless product, is combined with a further equivalent of chromium in a useful manner.

The following examples illustrate the invention, the parts being by weight:—

Example 1

(*a*) 300 parts of chrome ore 50 percent Cr_2O_3 content, 320 parts of fused caustic soda, and 100–200 parts of iron oxide or roast residue are intimately mixed and subjected to an oxidizing roasting for about 6–8 hours at 450–500° C. A 90–95 percent opening up is effected.

(*b*) 3 parts of the roast material obtained are heated in an autoclave with about 8–10 parts of water for about 12 hours to 300° C. and the pressure maintained by the supply of hydrogen at about 100 kg.

When the reduction is complete, the material containing chromium oxide hydrate is separated by filtration and washing from the caustic lye which, after suitable concentration, is again brought back into the process.

(*c*) The reduction product is now heated with one part of the chromate frit obtained according to (*a*) with about 15 parts of water in an autoclave for 4–6 hours to 280°–300° C. and the pressure adjusted by forcing in oxygen or air to about 100 kg. When the oxidation is complete, the sodium dichromate is separated from the residue by filtration and worked up in the known manner. The dichromate obtained is pure and free from alumina.

Example 2

300 parts of chrome ore 50 percent Cr_2O_3 content, 220 parts of sodium carbonate, 120 parts of slaked lime, and 150 parts of iron oxide are intimately mixed in a finely pulverized condition and subjected to an oxidizing roasting at 900–950° C. whereby an opening up of over 95 percent is obtained.

The resulting frit is, together with 175 parts of ferrochrome 60 percent Cr content, 10.5 percent C content, and 1.000 parts of water heated in an autoclave for about 6–8 hours to 280–300° C. and the pressure adjusted with oxygen to about 100 kg.

When the oxidation is complete, the dichromate solution is separated from the residue by filtration and worked up in the known manner.

In the present case the carbon dioxide obtained by oxidation of the carbon content is bound by the lime present.

The pressure oxidation can also take place with equal success by forcing in air. In this case the carbon dioxide is continuously removed with the air rich in nitrogen which is drawn off, and it is to be recommended at the end of the operation to convert the lime into carbonate by forcing in carbon dioxide and to decompose calcium chromate formed.

Example 3

300 parts of chrome ore 50 percent Cr_2O_3, 220 parts of sodium carbonate, and 200–300 parts of slaked lime are subjected to an oxidizing opening up operation at 900–950° C. One half of the roast material is exhaustively extracted with water and the chromate lye adjusted to about 10–15 percent Cr content.

The other half is treated at 400–600° C. in the furnace in a reducing atmosphere; thereby the alkali chromate is reduced to chromite. If there is in the reducing gases at the same time sufficient carbon dioxide, then all the alkali and also the lime are converted into carbonate. The reduced material, after cooling, is extracted with water, filtered, and in the presence of the chromate lye obtained above, heated in an autoclave for 6–8 hours to 280–300° C. and the pressure adjusted with oxygen or air to about 100 kgs.

When the oxidation is complete, the sodium dichromate is separated by filtration from the residue and worked up in the known manner. The alkali obtained in leaching the reduced material passes back into the opening up operation.

If the reduction is effected exclusively with hydrogen, then free caustic soda is obtained.

In this case it is to be recommended to treat the material before or after oxidation, with carbon dioxide for the purpose of converting the caustic lime into carbonate.

What I claim is:

1. Process for the manufacture of dichromates by treating an alkali metal chromate in the aqueous solution together with an equivalent quantity of substances selected from the group consisting of hydrated chromium oxide, chromium oxide, metallic chromium, chromium alloys, and mixtures containing chromium, at temperature above 100° C. under pressure, with gases containing oxygen.

2. Process for the manufacture of dichromates which consists of treating aqueous extract of a

frit obtained by an alkaline oxidizing operation of a material containing chromium, together with an equivalent quantity of a substance containing a trivalent chromium oxygen compound in the aqueous solution, at a temperature above 100° C. under pressure, with a gas containing oxygen.

3. Process for the manufacture of dichromates which consists of treating aqueous extract of a frit obtained by an alkaline oxidizing operation of a material containing chromium, together with an equivalent quantity of a substance containing metallic chromium in the aqueous solution, at a temperature above 100° C. under pressure, with a gas containing oxygen.

4. Process for the manufacture of dichromates which consists of treating a frit obtained by an alkaline oxidizing operation of a material containing chromium, together with an equivalent quantity of a trivalent chromium oxygen compound in the aqueous solution above 100° C. under pressure, with a gas containing oxygen.

5. Process for the manufacture of dichromates which consists of treating a frit obtained by an alkaline oxidizing operation of a material containing chromium, together with an equivalent quantity of a substance containing metallic chromium in the aqueous solution above 100° C. under pressure, with a gas containing oxygen.

6. Process for the manufacture of dichromates which consists of reducing a chromate frit obtained by an alkaline oxidizing operation of a material containing chromium, removing the basic compounds formed and oxidizing the product obtained, in the aqueous solution above 100° C. under pressure with a gas containing oxygen in the presence of an equivalent quantity of a basic compound.

7. Process for the manufacture of dichromates which consists of reducing a chromate frit obtained by an alkaline oxidizing operation of a material containing chromium, removing the basic compounds formed and oxidizing the product obtained, in the aqueous solution above 100° C. under pressure with a gas containing oxygen in the presence of an equivalent quantity of an alkali metal monochromate.

8. Process for the manufacture of dichromates which consists of reducing a chromate frit obtained by an alkaline oxidizing operation of a material containing chromium, removing the basic compounds formed and oxidizing the product obtained in the aqueous solution above 100° C. under pressure with a gas containing oxygen in the presence of an equivalent quantity of a chromate frit obtained by an alkaline oxidizing operation of a material containing chromium.

9. Process for the manufacture of dichromates which consists of preparing a chromate frit by an alkaline oxidizing operation of a substance containing chromium in the presence of a basic alkaline earth metal compound used as a diluent, neutralizing said basic alkaline earth metal compound and then treating the said chromate frit together with an equivalent quantity of a trivalent chromium oxygen compound in the aqueous solution at a temperature above 100° C., under pressure, with a gas containing oxygen.

10. Process for the manufacture of dichromates which consists of preparing a chromate frit by an alkaline oxidizing operation of a substance containing chromium in the presence of a basic alkaline earth metal compound used as a diluent, treating the said chromate frit together with an equivalent quantity of a trivalent chromium oxygen compound in the aqueous solution at a temperature above 100° C., under pressure, with a gas containing oxygen and simultaneously neutralizing said basic alkaline earth metal compound.

11. Process for the manufacture of dichromates which consists of preparing a chromate frit by an alkaline oxidizing operation of a substance containing chromium in the presence of a basic alkaline earth metal compound used as a diluent, neutralizing said basic alkaline earth metal compound and then treating the said chromate frit together with an equivalent quantity of a substance containing metallic chromium, in the aqueous solution at a temperature above 100° C., under pressure, with a gas containing oxygen.

12. Process for the manufacture of dichromates which consists of preparing a chromate frit by an alkaline oxidizing operation of a substance containing chromium in the presence of a basic alkaline earth metal compound used as a diluent, treating the said chromate frit together with an equivalent quantity of a substance containing metallic chromium, in the aqueous solution at a temperature above 100° C., under pressure, with a gas containing oxygen and simultaneously neutralizing said basic alkaline earth metal compound.

13. Process for the manufacture of dichromates as claimed in claim 1 in which in place of an alkali metal chromate, an alkaline earth metal chromate is used.

14. Process for the manufacture of dichromates as claimed in claim 7 in which in place of an alkali metal chromate, an alkaline earth metal chromate is used.

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