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PROCESS FOR THE MANUFACTURE OF
CHROMATES AND DICHROMATES

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This invention relates to the manufacture of chromates and dichromates.

Chromates are in general manufactured by roasting chromium ores in the presence of alkali in a furnace at a high temperature.

Such a process is usually effected by heating the finest ground chromium ore in admixture with sodium carbonate and lime in a stream of air to about 1000° C. and converting the extracted monochromate with sulphuric acid into dichromate.

Another method consists in roasting the ore with a larger quantity of lime at 1200°–1300° C. in a cement furnace and treating the calcium chromate—lime mixture with sodium bisulphate.

The great disadvantage of the first mentioned process is that alkali losses by vaporization cannot be avoided. In addition however in the subsequent decomposition of the mono-chromate with sulphuric acid one equivalent of alkali is lost in the form of valueless sodium sulphate.

The process through calcium chromate is uneconomic insofar as for the decomposition of the chromate roast product rich in lime disproportionately large quantities of sodium disulphate are required. Now, however, sodium bisulphate, since the manufacture of nitric acid by the Caro process, has become a less and less common product which can no longer be obtained in sufficient quantity and at a cheap rate. On this account the very existence of this latter process appears to be endangered. In both processes the great disadvantage is the furnace working and the high costs which are necessary for the maintenance of the furnace plant. Both processes consume large quantities of lime which do not appear in the finished product. Accordingly there has been no lack of proposals to manufacture chromates from metallic chromium or from the iron chromium alloy manufactured technically on a large scale.

Thus it has become known that alkali chromate can be obtained by treating ferrochrome with fused caustic alkali. Other proposals relate to the electrolytic oxidation of ferrochrome in the presence of alkalies or alkali salts to monochromate or dichromate. The excessive current costs, however, render the process uneconomic.

Attempts have therefore been made to oxidize finely powdered chrome iron alloys rich in carbon in the presence of alkali carbonate and saltpetre as oxidizing agent to chromate. The reaction of this thermally very active mixture is started up by means of an ignition pellet whereupon the oxidation proceeds without external

supply of heat. Towards the end however it becomes necessary to pump air into the fused mass or to support the further advance of the oxidation by means of electrical energy.

According to another proposal ferrochrome in the presence of alkali carbonate is converted into chromate by heating above 1000° C.

All these processes starting from ferrochrome are however uneconomic on account of the fact that the oxidation by electrical means or in the presence of oxidizing substances such as saltpetre is too expensive. In the last named process on account of the not inconsiderable vapour tension of the sodium carbonate losses of alkali take place which can no longer be disregarded. In addition the above processes which start from ferrochrome with the exception of the electrolytic process have in common the great disadvantage that they only lead to the formation of monochromate and that herefore in the subsequent conversion into dichromate at the same time one alkali equivalent is lost as valueless sulphate.

In accordance with the present invention the oxidation of metallic chromium, its alloys or mixtures containing chromium is effected in a very simple and economic manner. The process of the invention is by subjecting these substances to wet alkaline opening up treatment with oxidizing agents in particular oxidizing gases under pressure, whereby according to the quantity of alkali introduced either monochromate or dichromate or a mixture of monochrome and dichromate can be obtained as required. Since in the oxidation to dichromate, monochromate is first formed, it is clear that instead of alkalies also monochromates can be employed all of which are referred to herein as alkaline agents. I may accordingly, for the purpose of positive definition, state that the term alkaline agent is used herein to designate a substance which behaves with relation to an acid as a base, and may include oxides, hydroxides, carbonates, and dicarbonates, of both alkali metals and alkaline earths as well as monochromates and other substances.

The oxidation of the suitably finely powdered starting materials, whether pure chromium metal or substances containing chromium, takes place with the greatest ease and in quantitative yield. It is sufficient to introduce these substances to be brought into reaction in stoichiometric proportions although it is certainly of advantage to apply a slight excess of alkali or chromium when it is desired quantitatively to employ either the introduced chromium or the alkali.

In working up for example to dichromate the

main interest is to employ the alkali and monochromate present exhaustively in order to obtain a dichromate solution free from monochromate. It is to be recommended therefore to employ chromium in slight excess. The residue containing some chromium in an alkaline oxidizing subsequent treatment gives up its chromium content with great ease and in a quantitative manner. The alkaline lyes containing chromium are again employed for a new opening up treatment.

It may be remarked that from the point of view of oxidizability chromium metal or its alloys or mixtures behave apparently as equivalents provided that they are applied in a suitably finely divided condition which is certainly also necessary in the case of chromium ore. As a matter of fact it is the cheapest iron chromium alloys i. e. the most rich in carbon, which are easiest pulverized. The carbon, advantageously the chemically combined carbon, is likewise taken up in the oxidizing process and appears in the form of carbon dioxide. It may therefore be recommended to remove the latter during the process or to bind it chemically in order not to increase the pressure in the apparatus unnecessarily.

As alkaline agents can be employed caustic alkalies, alkali carbonates, bicarbonates, monochromates and also alkaline earth and alkali metal oxides, hydroxides, carbonates, dicarbonates and monochromates or mixtures in which connection it may be remarked that the alkaline earths are less suited to the formation of dichromate. Suitably they are employed in aqueous solution or suspension.

The formation of monochromate in general takes place very easily and rapidly and at relatively low temperature whereas for the dichromate formation it is suitable to increase the temperature above 200° C. when oxidizing with air or oxygen under pressure and at about 250°–300° C. the reaction velocity is so rapid that the oxidation takes place in a few hours with quantitative dichromate formation.

As oxidizing agents are advantageously employed oxygen, and oxygen containing or oxidizing gases.

For the execution of the process it is sufficient to heat the aqueous alkaline chromium suspension to a suitable temperature and pressure and to force in the oxidizing gas before or during the working process. The higher the temperature is maintained the more rapidly the oxidation takes place. The partial pressure of the oxidizing agent prevailing appears to play a smaller part in the oxidation than the temperature factor. It is suitable to lead off the carbon dioxide formed or to bind it chemically for example by the addition of lime (in working in a still atmosphere) in order to remove the partial pressure of the carbon dioxide.

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

Example 1

82.5 parts of ferrochrome of 63% Cr and 2–4% C, in the well powdered condition in order to facilitate the opening up, are mixed with 210–220 parts of caustic soda lye 40% and heated in a stirring autoclave for some hours at 150°–250° C. in the presence of oxygen or air. After cooling the chromates lye is filtered from the insoluble part, chiefly iron oxide, and worked up in the known manner to chromate or dichromate.

Example 2

80 kg. of ferrochrome of 68.2% Cr, 8–10% C are well pulverized and heated in the presence of 100 kg. of caustic soda lye 40% and 900 kg. of water in a stirring autoclave for about 6 hours to 250°–300° C. and oxygen or air passed through. After cooling the dichromate lye is separated from residue by filtration and worked up in the known manner.

The yield calculated on alkali is practically quantitative. The residues which contain some chromium pass back into the process.

Example 3

54.5 parts of chromium powder 95–96% Cr content are heated with 210–220 parts of caustic soda lye 40% and about 200 parts of water in a stirring autoclave with oxygen or air for 4–6 hours under pressure to 150°–250° C. After cooling the chromate lye is filtered from the residue of graphite or other impurities and worked up in the customary manner. The yield is practically quantitative.

Example 4

7.170 kg. of ferrochrome of 72.5% Cr and 6.8% C. are well pulverized and heated with 100 litres of normal caustic soda lye in a stirring autoclave for 4–6 hours at 200°–280° C. under pressure with oxygen or air. After cooling the dilute dichromate lye is separated from the residue and worked up.

Instead of caustic lye a solution of monochromate in equivalent quantity can be employed. The yield amounts to about 95%.

Example 5

152.5 parts of ferrochrome of 68.2% Cr and 8.10% C, well pulverized, are heated with 125 parts of calcium oxide (95–98%) or better with an equivalent quantity of slaked lime and about 400 parts of water for about 5–6 hours in the presence of oxygen to 150–250° C. After cooling, together with some chromate in solution, the majority of the chromate is found in the residue together with iron oxide and some graphite.

The conditions set out in the above examples can naturally vary within wide limits, according to the nature of the raw material to be worked up. It is essential that the opening up takes place in the aqueous phase and that the temperature and pressure are selected so that the reaction velocity is one which is practically applicable.

Although a high alkali concentration speeds up the reaction, the oxidation also takes place in very dilute solutions in a very satisfactory manner, as is seen from Example 4.

The carbon dioxide formed in the oxidation can be removed in a suitable manner. This operation is to be recommended in particular in working with alkali carbonates.

If oxidation is effected by means of a stream of air, the carbon dioxide is automatically removed.

Obviously other suitable oxidizing agents which act in the presence of alkalies can be employed for the oxidation in the aqueous phase, as, for example, hydrogen peroxide, ozonized oxygen or air, halogens and the like, ferricyanides and the like, although oxygen or air are more economic.

What I claim is:

1. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing a substance containing chromium in the presence of water and an alkaline agent by means of an oxidizing gas under pressure. 80
2. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing ferro-chromium in the presence of water and an alkaline agent by means of an oxidizing gas under pressure. 85
3. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing ferro-chromium in the presence of water and a carbonate of an alkali metal by means of an oxidizing gas under pressure. 90
4. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing ferro-chromium in the presence of water and a hydroxide of an alkali metal by means of an oxidizing gas under pressure. 95
5. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing ferro-chromium in the presence of water and a monochromate of an alkali metal by means of an oxidizing gas under pressure. 100
6. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing a substance containing chromium in the presence of water and an alkaline agent by means of oxygen under pressure. 105
7. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing ferro-chromium in the presence of water and an alkaline agent by means of oxygen under pressure. 110
8. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing a substance containing chromium in the presence of water and an alkaline agent by means of an oxidizing gas under pressure and removing the carbon dioxide produced. 115
9. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing a substance containing chromium in the presence of water and an alkaline agent by means of oxygen under pressure and removing the carbon dioxide produced. 120
10. Process for the manufacture of mono-chromates and dichromates which comprises oxidizing ferro-chromium in the presence of water and an alkaline agent by means of an oxidizing gas under pressure and removing the carbon dioxide produced. 125
11. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing a substance containing chromium in the presence of water and an alkaline agent by means of an oxidizing gas under pressure and binding chemically the carbon dioxide produced. 130
12. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing a substance containing chromium in the presence of water and an alkaline agent by means of oxidizing gas under pressure and binding chemically the carbon dioxide produced. 135
13. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing ferro-chromium in the presence of water and an alkaline agent by means of oxygen under pressure and binding chemically the carbon dioxide produced. 140
14. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing ferro-chromium in the presence of water and an alkaline agent by means of oxygen under pressure and binding chemically the carbon dioxide produced. 145
15. Process for the manufacture of mono-chromates and dichromates, which comprises oxidizing ferro-chromium in the presence of water and an alkaline agent by means of oxygen under pressure and removing the carbon dioxide produced. 150

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