

UNITED STATES PATENT OFFICE

2,012,062

PROCESS FOR THE PREPARATION OF
MONOCHROMATES AND DICHROMATES

Jules Emile Demant, Cuise-Lamotte, France, as-
signor to Bozel-Maletra, Société Industrielle de
Produits Chimiques, Paris, France, a corpora-
tion of France

No Drawing. Application May 25, 1933, Serial
No. 672,905. In France May 26, 1932

8 Claims. (Cl. 23—56)

This invention relates to the manufacture of chromates and dichromates.

I have already proposed in my Patent No. 1,955,326, dated April 17, 1934, a process for the manufacture of monochromates and dichromates consisting in subjecting at temperatures above 100° C., metallic chromium or substances containing the same or chromium alloys to an oxidizing reaction in the presence of alkaline—or alkaline earth hydroxides, carbonates, or bicarbonates or of monochromates in an aqueous medium, the quantity of the alkaline agent employed being such that for the case of the formation of dichromates it remains below that required for the formation of monochromates.

In accordance with the present invention it has been found that for the formation of monochromates or dichromates the presence of alkaline—or alkaline earth hydroxides, carbonates, or bicarbonates or of monochromates is not absolutely necessary. In accordance with the invention it is possible to employ instead of or together with alkaline—or alkaline earth agents and, in the case of the preparation of dichromates, instead of or together with alkaline—or alkaline earth agents or of monochromates, in general all compounds capable of giving up their alkaline principle under the oxidizing action in the course of the process.

By such "oxidizing conditions" it is to be understood, as disclosed by the examples given in this specification later on, that the reaction takes place with a current of oxygen or air under artificial pressure or with oxygen developed during the reaction through the initial introduction of an oxygen-yielding reagent like potassium chlorate.

The tendency of chromium to be converted into hexavalent chromium is so marked that in the course of the oxidizing process the added substances undergo a decomposition which causes them to give up their alkaline principle to the chromium; according to the quantity of the alkaline principle entering into reaction it is possible to obtain either monochromates or dichromates or mixtures of these two compounds.

In order to properly distinguish between an "alkaline agent" per se and a substance which in this case under proper oxidizing conditions will give up its "alkaline principle" to the chromium, it is well to remember that:

A solution of an acid contains hydrogen ions (cations) and non-metallic ions (anions); a solution of a base contains hydroxyl ions (anions) and metallic ions (cations); and a solution of a

salt contains non-metallic (anions) and metallic ions (cations).

In an acid the anions are the active elements which combine with the attacked metal, forming chlorides, sulphates, phosphates, nitrates, etc., freeing the hydrogen. In a base or "alkaline agent" it is the cation which is the active element, while in a salt solution the anions and cations bind and neutralize each other, as long as no decomposition takes place. Only when and after such decomposition is effected under special circumstances, free acting cations are liberated and a chemical reaction is realized. Thus a substance which normally cannot be classified as base, can become an alkaline agent.

While an alkaline agent contains its cation in a free state, the substances employed according to the present invention are those capable of liberating their cations generally under the oxidizing action of the reaction.

I do not claim as part of my invention the use of oxides, hydroxides of alkali or alkali earth metals per se. Nor do I claim the use of carbonates of alkali or alkali earth metals per se.

I do not claim as part of my present invention the use of monochromates, taken alone, as substances capable of giving up free acting cations to the chromium under the influence of the oxidizing reaction.

As compounds which in themselves are not base but in the presence of an oxidizing reaction are capable of giving up their alkaline principle, there can be employed the most varied salts of strong or weak inorganic or organic acids or also oxygen compounds of a salt like character, for example alkaline or alkaline earth sulphates, chlorides, phosphates, monochromates, acetates, silicates, aluminates, nitrates, chlorates, the persalts, manganates, permanganates or the like. It may be remarked that these latter compounds can act both as oxidizing agents and when decomposed as alkaline agents. They can even be utilized only as oxidizing agents together with true alkaline agents or other agents capable of giving up their alkaline principle. As alkaline agents are used alkaline or alkaline earth hydroxides, carbonates or bicarbonates or monochromates. As a matter of fact, the salts just above indicated are normally not bases but are capable of giving up their cations under the action of the oxidizing reaction. Said characteristic is clearly exemplified by the following Examples 1, 2, and 3.

If for example organic derivatives are employed, the organic principle is in general oxidized

to carbon dioxide which can conveniently be eliminated during the operation.

Certain compounds capable of giving up their alkaline principle can be used alone, whilst for certain others it is to be recommended to use them in combination with substances acting as neutralizing agents, as for example the oxides or carbonates of alkaline earths.

By way of example which is in no way limiting of the execution of the present process the following examples are given and it may be remarked that Example 5 illustrates the splitting up of potassium sulphate under the oxidizing decomposition action of trivalent chromium.

Examples

(1) 16 parts of finely pulverized ferrochrome containing 65% Cr and 9.5% C, 14.2 parts of anhydrous sodium sulphate, 10 parts of calcium carbonate, 200 parts of water are heated in an autoclave with good agitation at 280–290° C.; a current of oxygen or air is passed through under pressure.

The progress of the reaction is controlled by means of the content of carbonic acid which is determined in the gas leaving the apparatus.

The reaction product is filtered. The liquid contains pure sodium dichromate.

Yield 97%.

(2) 16 parts of finely pulverized ferrochrome containing 65% Cr and 9.5% C, 28.4 parts of anhydrous sodium sulphate, 20 parts of calcium carbonate, 200 parts of water are treated as indicated in Example 1.

After filtration of the reaction product a liquid is obtained containing sodium monochromate. Yield quantitative.

(3) 16 parts of finely pulverized ferrochrome containing 65% Cr and 9.5% C, 39.2 parts of potassium chlorate, 10 parts of calcium carbonate, 200 parts of water, are heated in an autoclave for some hours to 290–300° C. Towards the end of the reaction a little oxygen under pressure is passed through in order to facilitate the elimination of carbonic acid formed and to support the oxidation.

There are easily obtained yields of potassium dichromate exceeding 70%.

(4) 16 parts of finely pulverized ferrochrome containing 65% Cr and 9.5% C, 139 parts of trisodium phosphate 10 Aq, 200 parts of water, are heated in an autoclave with good agitation for some hours to 280–300° C. and a current of air or oxygen is passed through with the practically complete elimination of the carbonic acid produced from the ferrochrome. There is obtained after filtration a monochromatic liquor together with disodium phosphate which is separated by crystallization.

Yield about 80%.

(5) 17.3 parts of ferrochrome of 60% Cr, 35 parts of potassium sulphate, 200 parts of water are heated for some hours in a current of oxygen at 280–300° C. in an autoclave with good agitation.

The reaction product is filtered and there is obtained an acid liquid containing potassium dichromate. The splitting up of the potassium sulphate has produced alkali which is absorbed by the hexavalent chromium on one hand and the free sulphuric acid on the other hand.

The free acid present prevents the reaction from progressing beyond a content of free acid of about 0.5% H_2SO_4 .

The yield obtained is 16–20% for the above example.

By working in a more dilute medium in such a

manner as to remain below a content of free acid of 0.5% H_2SO_4 the yield can be considerably increased. In this case it is desirable to increase the content of potassium sulphate.

This method of working presents the inconvenience of producing acid dichromate liquors of low content and by reason of this fact it is to be recommended to neutralize the free acid formed during the reaction preferably by adding an alkaline earth oxide or carbonate as shown in Examples 1–3.

I claim:

1. Process for the manufacture of monochromates or dichromates consisting in subjecting a substance containing metallic chromium to oxidizing decomposition at temperatures above 100° C., under pressure and in an aqueous medium, in the presence of a compound being not normally classified as a base but other than a monochromate and capable of giving up free acting cations to the chromium under the influence of the oxidizing reaction.

2. Process for the manufacture of monochromates or dichromates consisting in subjecting a substance containing metallic chromium to oxidizing decomposition at temperatures above 100° C., under pressure and in an aqueous medium, in the presence of a compound being not normally classified as a base but other than a monochromate and capable of giving up free acting cations to the chromium under the influence of the oxidizing reaction, and in the presence of an alkaline agent.

3. Process for the manufacture of monochromates or dichromates consisting in subjecting a substance containing metallic chromium to oxidizing decomposition at temperatures above 100° C., under pressure and in an aqueous medium, in the presence of a compound being not normally classified as a base but other than a monochromate and capable of giving up free acting cations to the chromium under the influence of the oxidizing reaction, and acting at the same time as an oxidizing agent.

4. Process for the manufacture of monochromates or dichromates consisting in subjecting a substance containing metallic chromium to oxidizing decomposition at temperatures above 100° C., under pressure and in an aqueous medium, in the presence of a compound being not normally classified as a base but other than a monochromate and capable of giving up free acting cations to the chromium under the influence of the oxidizing reaction, and acting at the same time as an oxidizing agent and in the presence of an alkaline agent.

5. Process for the manufacture of monochromates or dichromates consisting in subjecting ferrochrome to oxidizing decomposition at temperatures above 100° C., under pressure and in an aqueous medium in the presence of a compound being not normally classified as a base but other than a monochromate and capable of giving up free acting cations to the chromium under the influence of the oxidizing reaction.

6. Process for the manufacture of monochromates or dichromates consisting in subjecting ferrochrome to oxidizing decomposition at temperatures above 100° C., under pressure and in an aqueous medium, in the presence of a compound being not normally classified as a base but other than a monochromate and capable of giving up free acting cations to the chromium under the influence of the oxidizing reaction, and in the presence of an alkaline agent.

7. Process for the manufacture of monochromates or dichromates consisting in subjecting ferrochrome to oxidizing decomposition at temperatures above 100° C., under pressure and in an aqueous medium, in the presence of a compound being not normally classified as a base but other than a monochromate and capable of giving up free acting cations to the chromium under the influence of the oxidizing reaction, and acting at the same time as an oxidizing agent.

chromates or dichromates consisting in subjecting ferrochrome to oxidizing decomposition at temperatures above 100° C., under pressure and in an aqueous medium, in the presence of a compound being not normally classified as a base but other than a monochromate and capable of giving up free acting cations to the chromium under the influence of the oxidizing reaction, and acting at the same time as an oxidizing agent and in the presence of an alkaline agent.

8. Process for the manufacture of mono-

JULES EMILE DEMANT.