Patented Aug. 20, 1935 2,012,061

UNITED STATES PATENT OFFICE

2,012,061

PROCESS FOR THE PREPARATION OF MONOCHROMATES AND DICHROMATES

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No Drawing. Application May 25, 1933, Serial No. 672,904. In France May 26, 1932

8 Claims. (Cl. 23—56)

The present invention relates to the manufacture of monochromates and dichromates.

In my prior Patent No. 1,955,326, dated April 17, 1934, I have described and claimed a process for manufacturing monochromates and dichromates with oxidizing ferro-chrome or a substance containing metallic chromium, as starting materials, in the presence of water and an alkaline agent by means of an oxidizing gas under pressure. I have already proposed to prepare monochromates by subjecting at temperatures above 100° C., chromium hydroxide, hydrated chromium oxide, chromium oxide or chrome ore or substances containing the same, to an oxidizing decomposition in the presence of alkaline- or alkaline earth hydroxides, carbonates or bicarbonates in an aqueous medium.

In my prior Patent No. 1,924,710 dated August 29, 1933 I have proposed to prepare dichromates by subjecting at temperatures above 100° C., chromium hydroxide, hydrated chromium oxide, chromium oxide or substances containing the same or chrome ore, to an oxidizing decomposition in the presence of alkaline- or alkaline earth hydroxides, carbonates or bicarbonates or monochromates in an aqueous medium, the quantity of alkaline agent employed being such that 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. According to the invention it is possible to employ instead of or together with these 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 monochromates, in general all compounds capable of yielding their alkaline principle under oxidizing conditions 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 oxidation process the substances added undergo a splitting up 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 my present invention the use of oxides, hydroxides of alkali or alkali earth metals taken alone. Nor do I claim the use of carbonates of alkali or alkali earth metals taken alone. Neither do I claim as a part of my present invention the use of monochromates per se as a substance capable of giving up free acting cations to the substance containing chromium oxide under the influence of the oxidizing reaction.

As compounds which in themselves are not bases, but in the presence of an oxidizing reaction are capable of giving up their alkaline principle to the chromium it is possible to employ the most varied salts of strong or weak inorganic or organic acids or also oxygen containing compounds of a salt like character for example alkaline- or alkaline earth sulphates, chlorides, phosphates, acetates, monochromates, silicates, aluminates, nitrates, chlorates, per-salts, manganates, permanganates and the like. It may be remarked that these latter compounds can act at the same time as oxidizing agents and when decomposed as alkaline agents. They can even be used only as oxidizing agents together with true alkaline agents or other agents capable of giving up their alkaline principle. As alkaline agents may be used alkaline- or alkaline earth hydroxides, carbonates or bicarbonates or monochromates.

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, while in the case of certain others it is to be recommended that they should be used in conjunction with substances acting as neutralizing agents as for example the oxides or carbonates of the alkaline earths. By way of example which is in no way limiting of the present process the following examples are given and it may be remarked that Example 1 illustrates the splitting up of sodium sulphate under the action of the oxidizing decomposition of trivalent chromium.

As a matter of fact, the salts just indicated above are 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, 7, and 8.

Examples

(1) 9.38 parts of hydrated chromium oxide (containing 81% of Cr_2O_3), 7.1 parts of anhydrous sodium sulphate and 200 parts of water are heated to 280–290° C. for 6½ hours in a stirring autoclave. Before commencing the heating of the apparatus it is filled with oxygen under 15 atmospheres.

By removing the contents of the apparatus it is found that a large part of the hydrated chromium oxide is converted into sodium bichromate together with free mineral acid.

The yield is 22.16%. The concentration of the sulphuric acid in the solution is about 0.5%. It may be remarked that the reaction does not progress beyond a decomposition corresponding to about 0.5% H_2SO_4. The yield can be considerably increased by a further dilution in order to avoid exceeding this limiting acidity.

(2) 9.38 parts of hydrated chromium oxide (containing 81% of Cr_2O_3), 7.1 parts of sodium sulphate, 5 parts of calcium carbonate and 200 parts of water are heated to 280–290° C. for about 10–15 hours in the presence of oxygen under 15 atmospheres in a stirring autoclave.

After cooling a bichromate liquor is withdrawn from the apparatus leaving a residue consisting for the most part of calcium sulphate.

The yield is 95–97% bichromate.

(3) 9.38 parts of hydrated chromium oxide (containing 81% of Cr_2O_3), 17.42 parts of crystallized trisodium phosphate (10 molecules of water) and 225 parts of water are heated to 280–290° C. for about 9 hours in the presence of oxygen under 15 atmospheres in a stirring autoclave.

Sodium bichromate and mono-sodium phosphate are formed according to the reaction;

$$Cr_2O_3+3O+Na_3PO_4+H_2O=Na_2Cr_2O_7+NaH_2PO_4.$$

The yield of bichromate is 93.3%.

If instead of trisodium phosphate an equivalent quantity of disodium phosphate is employed the oxidation likewise takes place with good yield.

(4) 9.38 parts of hydrated chromium oxide (containing 81% of Cr_2O_3), 11.73 parts of sodium silicate (containing 34.1% of sodium hydroxide) and 225 parts of water are heated to 280–290° C. for about 9 hours under 15 atmospheres of oxygen in a stirring autoclave.

The product obtained is a solution of bichromate with a residue of silicic acid. The yield is 95.3% of sodium bichromate.

(5) 9.38 parts of hydrated chromium oxide (containing 81% of Cr_2O_3), 10.11 parts of potassium nitrate, 5 parts of calcium carbonate and 225 parts of water are heated to 280–290° C. for about 10–15 hours under 15 atmospheres of oxygen in a stirring autoclave.

The product obtained is potassium bichromate together with calcium nitrate. The yield of hexavalent chromium is 90%.

(6) 9.38 parts of hydrated chromium oxide (containing 81% of Cr_2O_3), 12.25 parts of potassium chlorate, 5 parts of calcium carbonate and 200 parts of water are heated at 280–290° C. for about 10–15 hours and without the presence of oxygen in a stirring autoclave. The reaction is as follows:

$$Cr_2O_3+2KClO_3+CaCO_3=K_2Cr_2O_7+CaCl_2+3O+CO_2$$

After cooling there is found in the apparatus free oxygen under pressure. The yield of bichromate is about 88–90%.

If double the quantity of hydrated chromium oxide and an equivalent quantity of alkali are employed the oxygen formed will serve for the conversion of this additional quantity of hydrated chromium oxide according to the reaction

$$2Cr_2O_3+2KOH+2KClO_3+CaCO_3=2K_2Cr_2O_7+CaCl_2+CO_2+H_2O$$

(7) 9.38 parts of hydrated-chromium oxide containing 81% Cr_2O_3. 14.2 parts of anhydrous sodium sulphate, 10 parts of calcium carbonate, 200 parts of water are heated in an autoclave with good agitation for some hours to 150–300° C. in a current of oxygen or air under pressure greater than that of the vapour tension.

When the reaction is complete the residue of calcium sulphate is filtered and the monochromate is separated by known means. The yield is practically quantitative. Instead of calcium carbonate it is likewise possible to employ caustic lime.

(8) 7.6 parts of chromium oxide 90–95% Cr_2O_3, 14.5 parts of anhydrous sodium sulphate, 10 parts of calcium carbonate, 200 parts of water are heated for about 15 hours with good agitation in an autoclave to 300–350° C. A current of oxygen or air under pressure is caused to pass through. The progress of the reaction can be followed by the content of carbonic acid of the gas escaping from the apparatus.

At the end of the reaction residual calcium sulphate is filtered and the monochromate obtained in an excellent yield is separated by any known means.

(9) 9.38 parts of hydrated chromium oxide, 81% Cr_2O_3, 70 parts of trisodium phoshate 10 Aq., 225 parts of water are heated in an atmosphere of oxygen or in a current of air under pressure for 10–15 hours at 150–300° C.

The product of the reaction is composed of a liquor containing sodium monochromate and disodium phosphate; yield 90–95%.

(10) 9.5 parts of hydrated chromium oxide of 80% Cr_2O_3, 24.5 parts of potassium chlorate, 4.19 parts of magnesium oxide of 96.3% MgO, 200 parts of water are heated for 10–15 hours at 290–300° C. At the end of the reaction free oxygen under pressure is present in the apparatus.

The product of the reaction is filtered from a small quantity of magnesia and chromium substance which are not attacked.

The potassium chromate obtained is separated by crystallization.

Oxidation yield 80–90%.

I claim:

1. Process for the manufacture of monochromates or dichromates consisting in subjecting a substance containing chromium oxide to oxidizing decomposition at temperatures above 100° C. under pressure and in an aqueous medium, in the presence of a substance being not normally classified as 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 chromium oxide to oxidizing decomposition at temperatures above 100° C. under pressure and in an aqueous medium, in the presence of a substance being not normally classified as 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 chromium oxide to oxidizing decomposition at temperatures above 100° C. under pressure and in an aqueous medium, in the presence of a substance being not normally classified as 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 oxidizing agent.

4. Process for the manufacture of monochromates or dichromates consisting in subjecting a substance containing chromium oxide to oxidizing decomposition at temperatures above 100° C. under pressure and in an aqueous medium, in the presence of a substance being not normally classified as 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 oxidizing agent, and in the presence of an alkaline agent.

5. Process for the manufacture of monochromates or dichromates consisting in subjecting chrome ore to oxidizing decomposition at temperatures above 100° C. under pressure and in an aqueous medium, in the presence of a substance being not normally classified as 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 and dichromates consisting in subjecting chrome ore to oxidizing decomposition at temperatures above 100° C. under pressure and in an aqueous medium, in the presence of a substance being not normally classified as 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 chrome ore to oxidizing decomposition at temperatures above 100° C. under pressure and in an aqueous medium, in the presence of a substance being not normally classified as 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 oxidizing agent.

8. Process for the manufacture of monochromates or dichromates consisting in subjecting chrome ore to oxidizing decomposition at temperatures above 100° C. under pressure and in an aqueous medium, in the presence of a substance being not normally classified as 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 oxidizing agent, and in the presence of an alkaline agent.

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