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PREPARATION OF CHROMIC ACID AND SPARINGLY SOLUBLE CHROMATES

Richard Edgar Pearson and Walter Villa Gilbert, London, England; said Pearson assignor to said Gilbert

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This invention is for improvements in or relating to the preparation of chromic acid and sparingly soluble chromates and is concerned with the type of process in which a solution is submitted to electrolysis and the solution in the neighbourhood of the anode can be isolated from that in the neighbourhood of the cathode.

The objects of the invention are, inter alia, the production from crude materials of solutions of chromic acid and of sparingly soluble chromates free from hydrochloric, sulphuric and nitric acids and their salts and which shall in consequence, be suitable for use as anti-corrosion agents.

It is known that sparingly soluble chromates are useful as inhibitors of corrosion in metals. For this purpose it has been found necessary that these chromates shall be substantially free from certain impurities such as chlorides, sulphates and nitrates with which even the purest materials hitherto on the market have been found to be contaminated and which are themselves promotors of corrosion, whereas other impurities such as oxides of the respective metals are inert. The present invention provides a process which enables chromates to be made from crude materials and while the products are not necessarily chemically pure, they are free from those impurities which interfere with their anti-corrosive action.

It has been proposed hitherto to carry out the electrolysis of an alkali carbonate or hydroxide using a chromium alloy such as ferrochrome as an anode, whereby the alkali chromate is formed, and also to continue the electrolysis until there is a complete transformation of the neutral alkali chromate into bichromate. In the process of the present invention the electrolysis is carried on still further, and, according to whether the metal of the anode is a chromium alloy or another metal, there is formed in the electrolyte chromic acid and/or a salt of chromic acid.

It has also been proposed to prepare salts of heavy metals, including chromates, thereof, by employing the said heavy metals (for example, lead) in an electrolyte containing in addition to the required salt, such as a chromate, a dissolving constituent such as a chlorate. In the process of the present invention, the dissolving constituent is not employed and is highly undesirable as tending to introduce impurities which it is an object of this invention to avoid.

The present invention is for a process for preparing chromic acid and/or metallic chromates which comprises submitting to electrolysis an aqueous solution of a chromate (for example, sodium bichromate) without the addition of salts of other acids and continuing the electrolysis until there is present in the electrolyte an amount of chromic acid above that required to form the alkali bichromate or alternatively, a salt of chromic acid with the metal of the anode.

In one form the invention is directed to the preparation of chromic acid, in which case the metal selected as anode is chromium or a chromium alloy, or a chromium-containing material, and chromic acid is separated from the solution obtained. Where a chromium alloy is employed a suitable alloy is ferrochrome, and for the purpose of the invention the ferrochrome ordinarily sold for the purpose of steel making is suitable. The price of ferrochrome, however, depends largely upon the carbon content, but for the purpose of the invention the carbon content is immaterial, so that the low grade alloy containing 60–70% chromium and up to 10% carbon is suitable. Other chromium alloys or materials may be employed where the ultimate product required admits of the presence of the alloying metal or materials in the final product.

In carrying out the invention with a ferrochrome alloy, chromic acid is formed at the anode and caustic soda at the cathode. Where no porous diaphragm is employed the chromic acid content of the solution is continually increased, but the soda content remains stationary, and, as will be described hereinafter, may be eliminated by the employment of a porous partition.

In carrying out the process for the purpose of preparing a metallic chromate such as zinc chromate the anode selected is the metal the chromate of which it is desired to prepare.

In preparing the chromate, for example, it is sufficient to carry out the electrolysis of sodium bichromate using a zinc anode without any porous diaphragm. The zinc anode dissolves in the chromic acid as it is liberated, and is immediately precipitated as a chromate of zinc owing to diffusion in the electrolyte and neutralization by the soda liberated at the cathode. As the electrolysis proceeds, the chromate precipitated will become more and more basic which will be observed by a change of colour of the precipitate formed, while the solution is getting more alkaline owing to the liberation of sodium at the cathode and precipitation of the chromic acid liberated at the anode. It is thus possible by separating the precipitate at intervals during the electrolysis, to obtain a series of zinc chromates varying from the more acid to the more basic chromates.

It is, however, desirable to inhibit a free circulation of the electrolyte sufficiently to maintain the solution in the immediate neighbourhood of the anode in an acid state otherwise a precipitate of zinc chromate which forms in the immediate neighbourhood of the anode may build up and form a thick coating on the surface of the anode and interfere with the passage of the current. For this purpose, however, it is not necessary to inhibit circulation of the electrolyte to the extent to which a porous earthenware diaphragm will limit it. A loosely woven fabric will form a very suitable diaphragm and for this purpose we have found that woven asbestos cloth is suitable. The cathode is also liable to become coated, but this may be prevented by providing a suitably high current density at the cathode.

In the preparation of chromic acid the employment of a porous partition or diaphragm is desirable at some stage in the electrolysis in order to remove the soda originally present in the form of sodium bichromate.

Accordingly, the invention further comprises a process for preparing chromic acid and/or metallic chromates as hereinbefore described wherein the solution in the neighbourhood of the anode is separated from that in the neighbourhood of the cathode during electrolysis by one or more porous partitions (for example porous earthenware or woven asbestos) placed between the electrodes, and the product produced at the anode is separated before a substantial diffusion of the cathode liquor in the anode liquor has occurred.

In the preparation of chromic acid by the process of the invention a convenient way of working is to carry on the electrolysis of sodium bichromate using a ferrochrome anode without a diaphragm until a sufficient concentration of chromic acid has been obtained in the solution. The solution can then be transferred to a cell divided into two compartments by a sheet of woven asbestos, and the electrolysis continued. Chromic acid will then concentrate in the anode liquor and soda in the cathode liquor. Some of the iron obtained from the ferrochrome separates out in the first stage of the electrolysis (when working without a diaphragm) and the remainder of the iron is carried by the electrolysis into the cathode liquor where it collects as a mud consisting of ferric chromate and hydroxide. If a pure chromium anode or inert anode, such as lead, is used for this part of the electrolysis a practically pure solution of chromic acid can be obtained in the anode compartment.

The invention also comprises, therefore, a process for preparing chromic acid which includes a combination of the following steps:—

(*a*) Submitting to electrolysis an aqueous solution of a chromate (for example sodium bichromate) using ferrochrome as anode.

(*b*) Submitting the chromic acid—containing liquor obtained from (*a*) to further electrolysis in a cell provided with one or more porous partitions (for example woven asbestos) between the anode and the cathode using pure chromium or an inert conductor, such as carbon or lead, as anode.

(*c*) Separating the anode liquor before substantial diffusion therein of the solution in the neighbourhood of the cathode, with or without the further step of crystallizing chromic acid from the anode liquor.

In the preparation of zinc and other metallic chromates using a soluble anode it is desirable from the outset, in order to obtain a more uniform product, to separate the cell into anode and cathode compartments by a porous diaphragm. In this way an anode liquor is obtained which contains a solution of the zinc or other metal chromate in chromic acid. By pouring the anode liquor into a solution of sufficient alkali concentration, according as to whether a more acid or more basic chromate is required, the chromate is obtained as a precipitate, which may be easily filtered from the alkaline sodium chromate. The necessary alkali for precipitating the chromate may be obtained from the cathode liquor.

Another way of effecting precipitation of the metal chromate is to transfer the cathode to the anode compartment and the anode to the cathode compartment and continue electrolysis. In this way the cathode liquor, which now contains the anode, is re-converted first into bichromate and then into a chromic acid solution of the metal of the anode, while the anode liquor, which now contains the cathode, is first neutralized and then made alkaline, which effects the precipitation of the metal in solution therein.

In a modification, a plate of zinc, or other metal the chromate of which is desired, may be used as an anode and a similar plate as a cathode, both being disposed vertically in a solution of sodium dichromate and in proximity to, but not touching, one another. When the chromate settles on the face of the anode its removal can be effected by reversing the current and this reversal can be maintained and repeated as required, either plate functioning as the anode accordingly as the current is directed.

In the preparation of alkaline earth metal chromates, the alkaline earth oxides or carbonates may be insufficiently soluble in chromic acid to enable solutions of these chromates in chromic acid to be precipitated at the cathode during the production of chromic acid at the anode. Thus in the preparation of these chromates, it has been found preferable to surround the anode in a sodium dichromate electrolytic cell with the oxide or carbonate of the alkaline earth metal by suspending the latter in the anode liquor separated from the cathode liquor by a porous diaphragm. When the anode liquor has become sufficiently acid with chromic acid, the alkaline earth oxide or carbonate will have become converted into the chromate and may be filtered off. The free chromic acid washed out of the alkaline earth chromate may be used again in preparing the anode liquor for a further batch by mixing it with sodium dichromate. The anode in this case may be either of lead or chromium or if the presence of iron in the final chromate is permissible, it may be of ferro-chrome.

Lead chromate may be prepared in the same way as the alkaline earth chromates by suspending lead oxide or carbonate in the anode liquor.

In all these processes the alkaline sodium chromate obtained from the cathode liquor may be readily reconverted into sodium dichromate by electrolysis, using low grade (high carbon) ferro-chromium, as anode without any diaphragm. The iron will be mostly precipitated as hydrated oxide and chromate, and may be filtered off. It is not necessary for this purpose for the ferro-chromium anode to be in the form of a rod or plate, which would be expensive and difficult to produce, but the ordinary commercial product sold for metallurgical purposes in lumps or granular form may be assembled on a horizontal lead plate forming the anode at the bot-

tom of an electrolytic bath containing the sodium chromate.

The same apparatus and anode will be found suitable for the preparation of chromic acid. When a sufficient concentration of chromic acid has been obtained it may be separated from the dissolved iron and sodium bichromate by crystallization. It is preferable, however, to transfer the solution after filtering off ferric chromate to another vessel provided with a partition of woven asbestos and using a lead or pure chromium anode and a sheet iron cathode, and continue the electrolysis until the bulk of the iron has been assembled in the cathode liquor. This also removes the sodium from the anode liquor, which remains as a practically pure solution of chromic acid.

Chromium chromate may be prepared by the process according to the invention by submitting chromic acid to cathodic reduction in an acid electrolyte, but in order that the chromate shall be free from undesirable impurities neither hydrochloric, sulphuric, nor nitric acid should be used as the acid electrolyte. A convenient way of preparing chromium chromate according to the invention is to carry out the electrolysis of chromic acid in a cell provided with a porous partition using chromium electrodes. The solution in the cathode compartment is preferably a concentrated solution of chromic acid to allow for the transference of CrO_3 ions to the anode compartment. If the presence of iron in the chromium chromate is permissible ferrochrome may be used for both electrodes.

The following examples illustrate the principles on which the present invention is based.

Example I

Two porous pots standing in an open glass trough were filled with 50 per cent. sodium bichromate, and the glass trough was filled with the same solution up to a level of about 1 cm. below the tops of the porous pots. A rod of chromium metal was placed in one porous pot and a rod of stainless steel in the other, and the chromium was connected with the positive pole of a battery of accumulators and the stainless steel was connected to the negative pole. A current of about 5 amps. was passed through the electrolytic cell thus formed until the solution in the cathode pot had changed colour to the characteristic yellow of sodium chromate. The electrodes were then lifted out and the solutions immediately withdrawn from the porous pots. The solution in the anode pot was found to consist substantially of chromic acid containing a small proportion of sodium bichromate and that in the cathode pot was found to consist of sodium chromate containing a slight amount of silicious impurity from the porous pots.

Example II

The experiment described in Example I was repeated except that instead of a chromium rod as anode a zinc rod was used. The zinc rod was partly dissolved in the chromic acid produced at the anode, the reduction in weight being substantially equivalent to the amount of zinc in the chromic acid.

Example III

The solution obtained from the anode pot of Example II was filled into a porous pot into which a cathode of stainless steel was inserted. A fresh amount of 50 per cent. sodium bichromate solution was filled into another porous pot into which a zinc anode was inserted. Electrolysis was then carried out as in Example II and in this case as the colour of the solution in the cathode pot gradually changed to the characteristic light yellow of sodium chromate, there was also produced a precipitate of zinc chromate in the cathode pot, while in the anode pot a further quantity of zinc dissolved in chromic acid was produced.

Example IV

A 50 per cent. solution of chromic acid was prepared and filled into porous pots in the same way as the sodium bichromate of Example I. In this case both anode and cathode were made of chromium, and a current of five amps. was passed through the electrolytic cell thus formed until a precipitate was formed in the cathode compartment. On examining this precipitate it was found to consist of chromium chromate produced by electrolytic reduction of chromic acid at the cathode while in the anode pot a more concentrated solution of chromic acid was produced.

Example V

A solution of lime in chromic acid was produced by dissolving calcium hydroxide in chromic acid and filled into a porous pot. Another porous pot was filled with fifty per cent. sodium bichromate, and the two pots were stood in a bath of fifty per cent. sodium bichromate in the same way as in Example I. A chromium anode was inserted into the pot containing the sodium bichromate and a stainless steel cathode into the pot containing the solution of lime in chromic acid. A current was passed until the colour of the solution in the cathode pot changed from deep red to the characteristic colour of sodium chromate when there was found to be a precipitate in suspension which consisted of calcium chromate, the anode pot containing chromic acid.

The chromates produced by precipitation at the cathode as above described are in a very finely divided form and the precipitate dries to a very fine soft powder which is particularly suitable for incorporating with a vehicle for use in anti-corrosion preparations.

What we claim is:—

1. A process for preparing compounds of chromium which comprises in combination the following steps in the order named:—

(*a*) Submitting to electrolysis an aqueous solution of an alkali bichromate without the addition of salts of other acids, using a chromium containing anode,

(*b*) Submitting the chromic acid liquor from (*a*) to further electrolysis in a cell provided with a porous partition between the anode and the cathode, using pure chromium as the anode, and

(*c*) Separating the anode liquor before substantial diffusion therein of the solution in the neighborhood of the cathode.

2. A process for preparing compounds of chromium which comprises in combination the following steps in the order named:—

(*a*) Submitting to electrolysis an aqueous solution of an alkali bichromate without the addition of salts of other acids, using a ferrochrome anode,

(*b*) Submitting the chromic acid liquor from (*a*) to further electrolysis in a cell provided with a porous partition between the anode and the cathode, using pure chromium as anode and,

(*c*) Separating the anode liquor before substantial diffusion therein of the solution in the neighborhood of the cathode.

3. A process for preparing compounds of chromium which comprises in combination the following steps in the order named:—

(a) Submitting to electrolysis an aqueous solution of an alkali bichromate without the addition of salts of other acids, using a ferrochrome anode,

(b) Submitting the chromic acid liquor from (a) to further electrolysis in a cell provided with a porous partition between the anode and the cathode, using an inert conductor as anode, and

(c) Separating the anode liquor before substantial diffusion therein of the solution in the neighborhood of the cathode.

4. A process for preparing compounds of chromium which comprises in combination the following steps in the order named:—

(a) Submitting to electrolysis an aqueous solution of an alkali bichromate without the addition of salts of other acids, using a ferrochrome anode,

(b) Submitting the chromic acid liquor from (a) to further electrolysis in a cell provided with a porous partition between the anode and the cathode, using pure chromium as anode,

(c) Separating the anode liquor before substantial diffusion therein of the solution in the neighborhood of the cathode, and

(d) Crystallizing chromic acid from the anode liquor.

5. A process for preparing zinc chromate by electrolysis of an alkali chromate solution without the addition of salts of other acids and utilizing zinc as the anode whereby a precipitate of the metal chromate is formed in the electrolyte, characterized by the separation of the precipitate from time to time during progressive concentration of acid by electrolysis, whereby chromates of different chromic acid concentration are isolated.

6. A process for preparing metallic chromate by electrolysis of an alkali bichromate solution without the addition of salts of other acids, characterized by selecting as anode a metal which dissolves under anodic action and separating the solution in the neighborhood of the anode from that in the neighborhood of the cathode by a porous partition, the cathode and anode being of the same metal, and precipitating the chromate in the anode solution simultaneously with the production of fresh anode liquor by transferring the cathode to the anode compartment and the anode to the cathode compartment and continuing the electrolysis.

RICHARD EDGAR PEARSON.
WALTER VILLA GILBERT.