Patented June 16, 1936 2,044,244

UNITED STATES PATENT OFFICE

2,044,244

CHROMATE-ION REACTION

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No Drawing. Application January 17, 1933, Serial No. 652,197

11 Claims. (Cl. 23—57)

In reactions with chromate ions heretofore, it has been customary to operate on soluble alkali metal salts and in relatively high concentration. Such procedure has incurred undesirable by-products which have occasioned manufacturing complications and loss, in the effort at their elimination. In contrast, the present invention now makes possible an advantageous manufacturing operation, with avoidance of such difficulties, and allowing a wide range of control on the character of the product formed.

To the accomplishment of the foregoing and related ends, the invention, then, consists of the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however, of but a few of the various ways in which the principle of the invention may be employed.

In its general aspects, the invention contemplates reacting with chromic acid upon a sparingly soluble lead compound in the presence of water and an addition or control agent. Employing a lead compound such for instance as lead oxide, particularly litharge, or lead carbonate, basic lead carbonate, etc., this is made up in desired amount in suspension or slurry in water, and the addition or control agent is added. The function of this addition agent is to increase the solubility or reactibility of the lead compound. This agent is in small amount, and is preferably an acid, a lead salt or an alkali. A salt with a base other than lead may be used if it has the effect of increasing the solubility of the lead compound. The acid may be for instance acetic acid, nitric acid, hydrofluoric acid, fluo-boric acid, fluo-silicic acid, hydrochloric acid, perchloric acid, formic acid, etc. which react with the lead oxide or carbonate to form a soluble lead salt in small amount which is then reacted on by the chromic acid, with regeneration of the original (catalytic) acid ion and the cycle repeats. As apparent, the acid ion can be introduced as a salt, either of lead as above mentioned or other base, as a modification. If an alkali be used instead of acid, such alkalies as caustic soda, caustic potash and ammonium hydroxide, are applicable, or again such salts as sodium chloride, ammonium nitrate, aluminum acetate, aluminum nitrate, etc., that is, agents having a tendency to dissolve the lead compound. Considerable variation in results can be had by selection of the particular addition or control agent to be employed. The amount of such addition or control agent may be varied somewhat, but in general is desirably kept low, in practice usually not to exceed 5 per cent as referred to the theoretical amount which could react molecularly with the lead compound, and more usually from ½ to 3 per cent.

To the slurry or suspension of litharge or the like, the addition or control agent is added, and then with thorough agitation the chromic acid is introduced gradually. The amount of addition or control agent in such circumstances will not ordinarily run much over 0.1 per cent of the total amount of water in the finished reaction. By adding the chromic acid gradually, it reacts with the lead which is in solution, and the relative amount of lead so available for reaction at any given instant is controlled by the addition agent, the less of the addition agent employed the slower the making available of the lead for reaction with the chromic acid, and the higher the amount of control agent the more rapid the making available of the lead for action by the chromic acid. The chromic acid should not be run in faster than it is taken up by the lead salt in solution. The time of reaction may be quite widely varied, from a few minutes up to two or three hours. The smaller the amount of control agent, the slower is the permissible rate of addition of chromic acid. For most purposes 15 minutes to one hour is a desirable time for the reaction, and preferably about 30 minutes. The temperature may range from ordinary atmospheric temperature down to lower temperatures; on the other hand up to 60° C. or in some cases even 100° C., the character of the product varying somewhat correspondingly, the color of the product tending to run darker with the higher temperatures.

As an example: 69 parts of litharge are stirred into a slurry with 400 parts of water (by weight), and 1 part of acetic acid is added. While actively stirring, a solution of chromic acid (8 per cent in water) is gradually introduced, the chromic acid being supplied until substantially molecular reacting equivalents have been used and the lead compound is all converted. The precipitate which forms is lead chromate, and this may be washed and dried, and be employed for any of the customary usages of lead chromate.

Where the reaction is run for the purpose of producing a color-pigment, the shade thereof may be varied by the amount of the control agent and by the temperature to some extent; also by the rate of reaction. From the standpoint of ease of washing and economy, the smallest amount of control agents used the better. Larger amounts are more expensive and require more washing of

the end product. The darker shades may be made by adding less than molecular equivalents of chromic acid. As for example: 69 parts of litharge are stirred into a slurry with 400 parts of water, and 1 part of nitric acid is added. While actively stirring, 20 parts of chromic anhydride in 200 parts of water are gradually introduced. The precipitate which forms is a basic lead chromate of dark orange color. The lighter shades containing lead sulphate may be made in a similar manner by reacting a mixture of chromic and sulphuric acids on a sparingly soluble lead compound in the presence of an addition agent. In general, the invention is thus seen to provide a convenient and nicely controllable reaction where chromate ions are to be reacted with a lead base, or for the formation of chromates requiring particularity in grade and characteristics.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

I therefore particularly point out and distinctly claim as my invention:—

1. A process of reacting with chromate ions, which comprises subjecting a sparingly soluble lead compound from the group consisting of divalent oxides and carbonates, in suspension in water in the presence of a salt tending to dissolve the lead compound, to the action of chromic acid.

2. A process of reacting with chromate ions, which comprises subjecting to the action of chromic acid a sparingly soluble lead compound from the group consisting of divalent oxides and carbonates in suspension in water in the presence of a lead salt, which is more soluble than the said sparingly soluble lead compound.

3. A process of reacting with chromate ions, which comprises subjecting a sparingly soluble lead compound from the group consisting of divalent oxides and carbonates, in suspension in water in the presence of a small amount of acetic acid, to the action of chromic acid.

4. A process of reacting with chromate ions, which comprises subjecting a slurry of litharge in the presence of a small amount of acetic acid, to the action of chromic acid.

5. A process of reacting with chromate ions, which comprises subjecting a sparingly soluble lead compound from the group consisting of divalent oxides and carbonates, in suspension in water in the presence of a small amount of hydrofluoric acid, to the action of chromic acid.

6. A process of reacting with chromate ions, which comprises adding to a slurry of litharge a small amount of acetic acid, and stirring in chromic acid at a rate not faster than it is taken up by lead salt in solution.

7. A process of reacting with chromate ions, which comprises subjecting a sparingly soluble lead compound from the group consisting of divalent oxides and carbonates in suspension in water, in the presence of a small amount of an acid ion catalyst for increasing the reactability of the lead compound, to the action of chromic acid at a rate no faster than taken up by reaction.

8. A process of reacting with chromate ions, which comprises reacting between a sparingly soluble lead compound from the group consisting of divalent oxides and carbonates in suspension in water and chromic acid, and controlling the reaction by a small amount of a catalyst for increasing the reactability of the lead compound and by introducing one reaction component gradually at a rate no faster than taken up by reaction.

9. A process of reacting with chromate ions, which comprises subjecting a sparingly soluble oxygen-containing lead compound from the group consisting of divalent oxides and carbonates in suspension in water, in the presence of a small amount of a fluorine-containing acid catalyst, to the action of chromic acid.

10. A process of reacting with chromate ions, which comprises subjecting a sparingly soluble lead compound from the group consisting of divalent oxides and carbonates, in suspension in water in the presence of a small amount of hydrofluoric acid, to the action of chromic acid, and stirring in chromic acid at a rate not faster than it is taken up by reaction.

11. A process of reacting with chromate ions, which comprises subjecting a sparingly soluble lead compound from the group consisting of divalent oxides and carbonates, in suspension in water in the presence of a small amount of acetic acid, to the action of chromic acid, and stirring in chromic acid at a rate not faster than it is taken up by reaction.

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