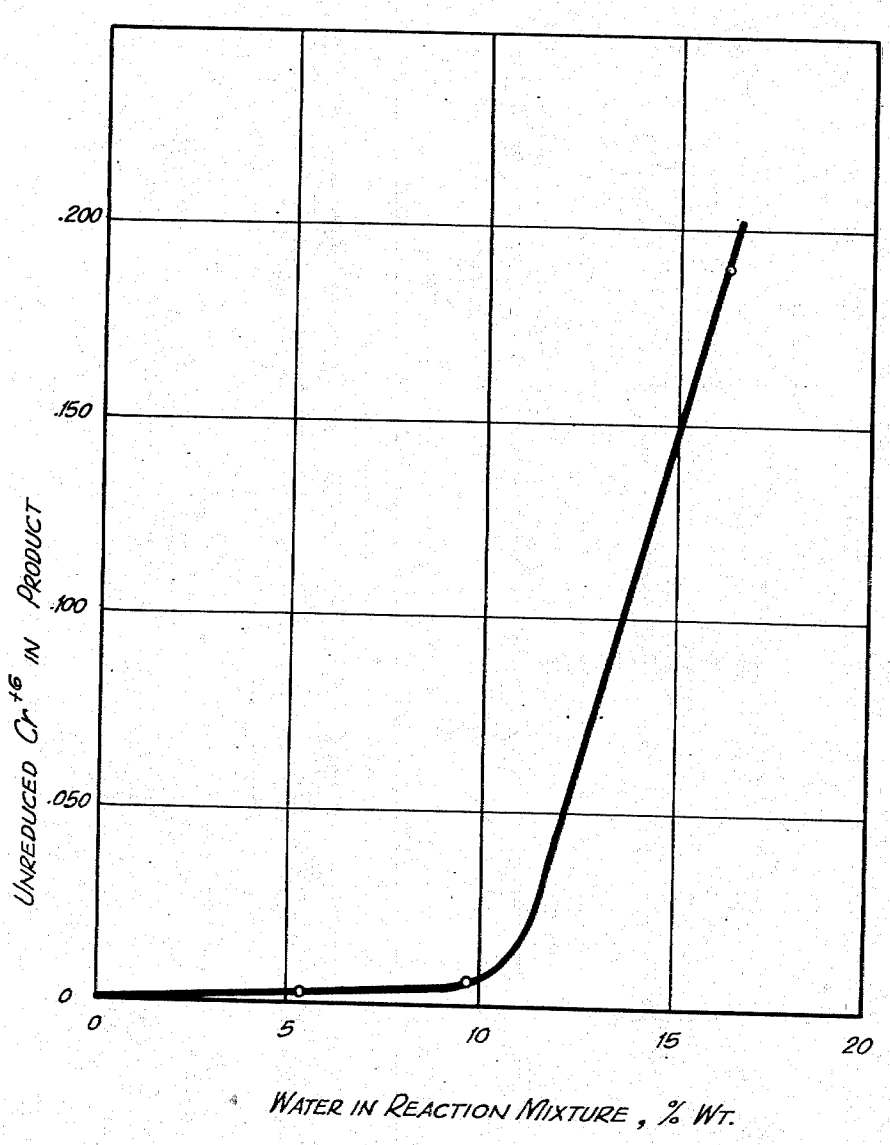
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PREPARATION OF CHROMIC SALTS

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INVENTOR.
WILLIAM A. STOVER
BY Raymond W. Barclay
ATTORNEY

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PREPARATION OF CHROMIC SALTS

William A. Stover, Pitman, N. J., assignor to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

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7 Claims. (Cl. 260—438)

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This application is a continuation-in-part of my copending application Serial No. 174,594, filed July 18, 1950, and issued as U. S. Patent No. 2,615,031 on October 21, 1952. There is described and claimed in the latter application a process for preparing a chromic salt of a low molecular weight fatty acid, such as chromic acetate, by reducing a hexavalent chromium compound with glycolic acid in the presence of a low molecular weight fatty acid.

The present invention relates specifically to an improvement in such process. More particularly, the instant invention is concerned with an improved procedure for the production of chromic acetate.

It has been discovered, in accordance with the process described herein, that the efficiency of reduction of hexavalent chromium to trivalent chromium using a reducing agent of glycolic acid in the presence of a low molecular weight fatty acid is greatly improved when the reaction is carried out in the substantial absence of water. The absence of appreciable water in the aforesaid reaction results in the direct production of the chromic salt of the low molecular weight fatty acid present, giving rise to a product of improved quality.

Unreduced Cr^{+6} in the product is decreased to a negligible amount. While the description which follows hereinafter is directed particularly to the preparation of chromic acetate by reaction of glycolic acid, a dichromate, and acetic acid as the fatty acid, the instant method may likewise be employed with advantage in the production of the chromic salts of other low molecular weight fatty acids, the upper limit of molecular weight being defined by a mono-basic fatty acid having not over 6 carbon atoms.

The chromium reactant employed in the instant process is a water-soluble compound containing chromium of valence 6. Representative compounds include chromium trioxide, the water-soluble metal chromates and the water-soluble metal dichromates. The latter group of compounds and, in particular, the alkali metal dichromates are preferred for use in the present process. Particular preference is accorded sodium dichromate and potassium dichromate.

The procedure of the present process comprises contacting a chromium compound of the above type with a low molecular weight fatty acid in the substantial absence of water, i. e. under conditions such that the initial reaction mixture contains less than about 10 per cent by weight of water, heating this mixture to a temperature of at least 120° F. and thereafter slowly adding glycolic acid. After the addition of glycolic acid, the resulting mixture is digested at an elevated temperature until evolution of carbon dioxide has ceased. Preferably the temperature to which the initial mixture of chromium compound and fatty acid is heated should lie

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within the range of 120–230° F. although with the use of pressure, higher temperatures may be employed. Glycolic acid is preferably added to the hot initial mixture slowly and gradually over a period generally not exceeding about 8 hours. Thereafter, the mixture is maintained at a temperature of about 180 to about 230° F. until evolution of carbon dioxide ceases.

Having described in a general way the nature of this invention, the following specific examples will serve to illustrate the process described above:

Example 1

298 grams of sodium dichromate and 360 grams of glacial acetic acid were mixed and heated at atmospheric pressure in an autoclave equipped with an efficient reflux condenser and a mixer. After heating to a temperature of 120° F., 153 grams of glycolic acid in the form of a 71.6% by weight aqueous solution were slowly added over a period of approximately 1 hour, during which time the temperature was allowed to rise to the reflux temperature of 225–230° F. The amount of water in the reaction mixture was 5.3 per cent by weight. Following the addition of glycolic acid, the temperature was maintained at 225–230° F. for 1 hour, at which time evolution of carbon dioxide from the reaction mixture had ceased. Upon completion of the reaction, the mixture analyzed as follows:

Free Acid in Product		Unreduced Cr^{+6} in Product, Percent Wt.
Mols HA_c/Mol Cr	Percent of Total HA_c	
0.23	7.7	0.001

The calculated acetate/Cr^{+3} mol ratio of the above solution was 3 to 1. The extremely small amount of Cr^{+6} in the resulting product indicates that substantially complete reduction of sodium dichromate to chromic acetate was accomplished.

The following examples were carried out by the procedure of Example 1, that is, by adding glycolic acid to a boiling solution of sodium dichromate and acetic acid. Reflux was continued as in Example 1 until evolution of carbon dioxide ceased. In these examples, however, the water content of the reactants was altered by the use of aqueous solutions of acetic acid in place of the glacial acid used in Example 1

Example	Conc. of Acid, Percent Wt. Ha_c	Water in Reaction Mixture, Percent Wt.	Free Acid in Product		Unreduced Cr^{+6} in Product, Percent Wt.
			Mols HA_c/Mol Cr	Percent of Total HA_c	
2	90	9.8	0.35	11.7	0.004
3	75	16.4	0.46	15.3	0.190

From the above table, it will be seen that both the quality of the product as indicated by the free acid and the efficiency of reduction as indicated by the presence of unreduced Cr^{+6} in the product are impaired by the presence of an appreciable amount of water. From the results of the above data presented graphically in the attached drawing wherein the per cent weight of unreduced Cr^{+6} in the product is plotted against the per cent weight of water in the reaction mixture, it will be noted that the amount of unreduced Cr^{+6} is practically nil when the amount of water in the reaction mixture is less than about 10 per cent. It is further to be noted that when the amount of water in the reaction mixture rises above about 10 per cent by weight, the quantity of unreduced Cr^{+6} in the product greatly increases. It is accordingly preferred in accordance with the instant process to effect the reduction of dichromate with glycolic acid in the presence of a low molecular weight fatty acid and in the presence of not more than about 10 per cent by weight of water.

As in the process described in my copending application Serial No. 174,594, now U. S. 2,615,031, it is preferred in the present method to have an acetate/Cr^{+3} ratio of at least about 2.5. With the use of such a ratio, reduction of dichromate with glycolic acid in the presence of acetic acid under reflux and in the substantial absence of water provided better than 99% reduction and produced a more stable chromic acetate than was produced when the reaction was effected in the presence of an appreciable amount of water of greater than about 10 per cent by weight.

Different ratios of glycolic acid to dichromate may be used to accomplish reduction of the dichromate but it has been found that the most efficient reduction is obtained when about 1.4 moles of glycolic acid are reacted with 1 mole of dichromate in the presence of acetic acid.

An added advantage achieved by carrying out the reaction described herein in the substantial absence of water is that the minimum temperature which may be employed is appreciably lower than that wherein the reaction is carried out in an excessive amount of water. The use of a lower operating temperature, as will be apparent, is a distinct advantage from a commercial standpoint.

From the examples set forth herein, it will be noted that glycolic acid in the presence of a fatty acid, such as acetic acid, and in the presence of not more than about 10 per cent by weight of water provides an effective reducing medium for conversion of a chromium compound in which chromium has a valence of 6 to the fatty acid chromic salt. When such reaction is carried out in the substantial absence of water, the efficiency of reaction and the quality of the resulting product are distinctly improved as compared with the corresponding reduction carried out in the presence of an excessive amount of water.

It is to be understood that the above description is merely illustrative of preferred embodiments of the invention, of which many variations may be made within the scope of the following claims by those skilled in the art without departing from the spirit thereof.

I claim:

1. A process for preparing the chromic salt of a low molecular weight fatty acid, which comprises reducing Cr^{+6} to Cr^{+3}, in a reaction mixture containing not more than about 10 per cent by weight of water, with glycolic acid in the presence of a monobasic fatty acid having not more than 6 carbon atoms.

2. A process for preparing chromic acetate, which comprises reduction of Cr^{+6} to Cr^{+3} with glycolic acid in the presence of acetic acid and not more than about 10 percent by weight of water.

3. A process for preparing a chromic salt of a low molecular weight fatty acid, which comprises reducing a dichromate, in a reaction mixture containing not more than about 10 per cent by weight of water, with glycolic acid in the presence of a monobasic fatty acid having not more than 6 carbon atoms.

4. A process for preparing chromic acetate, which comprises reducing a dichromate, with glycolic acid in the presence of acetic acid, and not more than about 10 per cent by weight of water.

5. A process for preparing a chromic salt of a low molecular weight fatty acid, which comprises contacting, in a reaction mixture containing not more than about 10 per cent by weight of water, a metal dichromate and a monobasic fatty acid having not more than 6 carbon atoms, heating the resulting mixture to a temperature of at least 120° F., adding glycolic acid to the heated reaction mixture and, after completing the addition of glycolic acid, digesting the mixture at an elevated temperature until evolution of carbon dioxide therefrom has ceased.

6. A process for preparing chromic acetate, which comprises contacting, in a reaction mixture containing not more than about 10 per cent by weight of water, a metal dichromate and acetic acid, heating the resulting mixture to a temperature of at least 120° F., adding glycolic acid to the heated mixture and, after completing the addition of glycolic acid, digesting the mixture at an elevated temperature until evolution of carbon dioxide therefrom has ceased.

7. A process for preparing chromic acetate, which comprises contacting, in a reaction mixture containing not more than about 10 per cent by weight of water, an alkali metal dichromate and glacial acetic acid, heating the resulting mixture to a temperature of at least 120° F., gradually adding to the heated mixture about 1.4 moles of glycolic acid for each mole of alkali metal chromate contained therein and thereafter digesting the mixture at reflux temperature until evolution of carbon dioxide therefrom ceases.

WILLIAM A. STOVER.

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