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METHOD OF MAKING ALKALI METAL ACETATES

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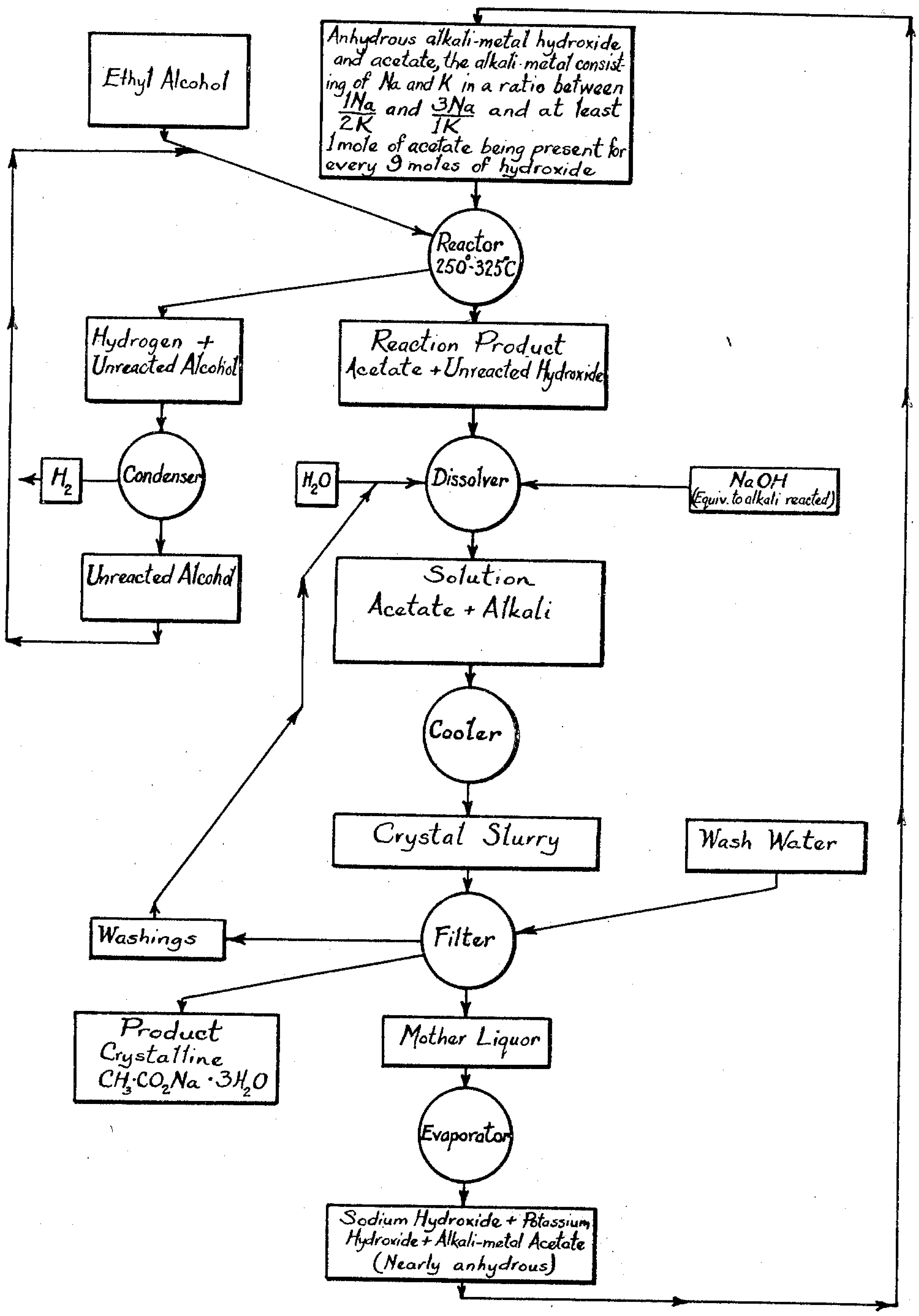

Fig. 1

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METHOD OF MAKING ALKALI METAL ACETATES

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The present invention concerns an improved method for making alkali metal acetates, particularly sodium acetate, through reacting ethyl alcohol with fused alkali metal hydroxides.

It has long been known that aliphatic alcohols containing more than six carbon atoms could be oxidized by caustic alkali to form alkali metal salts of the corresponding aliphatic acids in good yield. It has also been known that the lower aliphatic alcohols (e. g. those containing from 2 to 6 carbon atoms) could likewise be oxidized with caustic alkali (sodium or potassium hydroxide) to form alkali metal salts of the corresponding aliphatic acids, but during the course of such treatment, as previously carried out, considerable quantities of the alcohols were decomposed into methane, olefines, and polymerized into tarry masses, so that the desired product was always obtained in comparatively low yield and as an impure compound. For instance, we have found that when ethyl alcohol is reacted with a fused mixture of sodium and potassium hydroxides at about the temperature 280° C., more than 30 per cent of the alcohol which is reacted, is generally decomposed to form ethylene which passes from the reaction mixture in the effluent gases. Due to such difficulties, it has not been commercially practicable to prepare alkali metal acetates by means of such method.

We have now found that ethyl alcohol may be reacted with fused caustic alkali containing an alkali metal acetate and that under correct operating conditions with regard to temperature, etc. the desired alkali metal acetate may be formed in excellent yield and the formation of undesirable by-products, such as methane, olefines, polymerized masses, etc., may substantially be prevented.

To the accomplishment of the foregoing and related ends, the present invention, then, consists of the method hereinafter fully described and particularly pointed out in the claims, the annexed drawing and the following description setting forth in detail one mode of carrying out the invention, such disclosed mode illustrating, however, but one of the various ways in which the principle of our invention may be used.

Referring to the drawing, the flow sheet represents the sequence of steps and movement of materials in a continuous cyclic process employing a fused mixture containing alkali metal hydroxides as oxidizing agents and alkali metal acetate as a dehydration inhibitor. The alkali metal content of the fused mixture consists of sodium and potassium in respective amounts between the ratios of about

$$\frac{1Na}{2K} \text{ and about } \frac{3Na}{1K}$$

and said fused reaction mixture at all times contains at least 1 mole of alkali metal acetate to every 9 moles of alkali metal hydroxide. The fused mixture is stirred vigorously, maintained at a temperature between about 250° and about 325° C., and ethyl alcohol is gradually contacted therewith. The passage of alcohol into contact with the fused mass is continued, preferably, until about 90 to about 95 per cent of the caustic alkali, initially present in the fused mixture, is reacted, a mixture of sodium and potassium acetates being formed. During reaction, a gaseous mixture containing hydrogen, and which may contain unreacted alcohol, is evolved from the fused mass. The gases are passed through an efficient condenser wherein unreacted alcohol, if present, is separated as a liquid. Any alcohol condensed in such manner is returned to the system, and the hydrogen is collected. Under optimum operating conditions substantially all of the alcohol contacted with the fused reaction mixture may be reacted in a single pass, but ordinarily a fraction thereof requires recycling in order to effect complete reaction.

After the reaction is completed, the reaction mixture is dissolved in aqueous sodium hydroxide (preferably, but not necessarily, containing that quantity of sodium hydroxide required to replace the alkali metal hydroxide reacted) and sodium acetate, $CH_3—CO_2Na.3H_2O$, is crystallized from the resulting solution. The crystallization operation may be carried out in any of the usual ways, e. g. through cooling, evaporating, seeding, or otherwise treating the aqueous solution. Sodium acetate, being less soluble in the solution at ordinary temperature than is potassium acetate, may be separated readily in such manner. The crystals may be washed to remove adhering liquor and be obtained in substantially pure form, and the washings may be employed to dissolve subsequent batches of reacted materials.

The mother liquor, remaining after the above described crystallization step, is evaporated to dryness and the residual acetate and hydroxide is returned to the process.

Through operating with a mixed alkali in the manner described above, sodium acetate in pure form is the compound actually prepared from ethyl alcohol while potassium hydroxide and all unreacted materials are recycled continuously, and undesirable side reactions, such as the formation of methane, ethylene and polymerized masses, are substantially prevented.

It is desired to point out that sodium or potassium acetate, employed in the initial fused reaction mixture, serves to inhibit the occurrence of undesirable side reactions, such as those mentioned above. We have found that the presence of at least 1 mole of acetate in the initial fused mixture, for every 9 moles of alkali metal hydroxide present, has a marked effect in inhibiting decomposition and polymerization of the reactants. In practice we prefer to employ, as an initial fused mass, a mixture containing about equimolecular quantities of sodium and potassium hydroxides and containing alkali metal acetate in amount representing 40 per cent or more of the total number of moles of alkali metal hydroxide and acetate present in said mass.

It is desired to point out, also, that by employing, as components of the initial reaction mass, a mixture of sodium and potassium compounds (acetates and hydroxides) rather than similar compounds of a single alkali metal, a reaction mixture which will remain fluid at relatively low temperatures is obtained. This is highly advantageous, as the reaction proceeds more smoothly if the mixture is substantially homogeneous during the reaction period. It is desired to emphasize the fact that stirring aids in maintaining a homogeneous mixture, hence in attaining smooth reaction. In the absence of stirring undesirable side reactions, such as olefine, methane, and carbonate formation may occur.

The following examples describe in detail but two of the various ways in which the principle of the invention may be employed. It is to be understood, however, that said examples are purely illustrative and are not to be construed as a limitation on the invention.

Example 1

Into a closed iron reactor, provided with a thermometer, mechanical stirrer, an inlet for alcohol arranged so that the alcohol is introduced into direct contact with the reaction mass, an outlet for effluent gases, was placed a mixture consisting of 33.4 grams (1.67 moles) of sodium hydroxide, 187 grams (3.33 moles) of potassium hydroxide, and 410 grams (5 moles) of commercial (98 per cent pure) sodium acetate. The reactor was heated in a bath of fused caustic alkali to such a temperature that the above described alkaline mixture became fused. Said mixture was maintained at a temperature between 285° and 295° C. during the course of the reaction. The reaction mixture was stirred and 572.5 grams of absolute ethyl alcohol was passed gradually into contact with the fused mass during a period of 5 hours. The effluent gases were passed first through an efficient condensing apparatus wherein the unreacted alcohol was separated as a liquid, and the residual gases were analyzed for their ethylene content, 0.12 moles of said compound being found. The ethylene formed corresponds to 5.5 grams (0.12 mole) of alcohol decomposed. There was condensed 337 grams of unreacted alcohol, showing that 235 grams (5.1 moles) of alcohol had been reacted. The fused mass was cooled to room temperature, dissolved in water, and aliquot portions of the resultant solution analyzed quantitatively to determine the respective quantities of alkali metal hydroxide, carbonate, and acetate in the reacted mixture. Said mixture was found to contain 0.248 moles of alkali metal hydroxide, 0.085 moles of alkali metal carbonate, and 9.525 moles of alkali metal acetate. There was, then, 4.525 moles of acetate formed during the reaction, hence the yield thereof was substantially 89 per cent of theoretical, based on the quantity of alcohol reacted. About 98 per cent of the caustic alkali and sodium acetate employed was accounted for in the reaction products so that about 95 per cent of the alkali metal hydroxide in the initial mixture reacted to form acetate. The quantity of ethylene formed represented less than 2.5 per cent of the quantity of alcohol reacted.

Example 2

Using apparatus similar to that described in Example 1, absolute ethyl alcohol was passed through a fused and stirred mixture, which initially consisted of 63.5 pounds (0.775 pound moles) of sodium acetate, 10.3 pounds (0.258 pound moles) of sodium hydroxide, and 29.0 pounds (0.517 pound moles) of potassium hydroxide, until 79 pounds (1.72 pound moles) of alcohol had reacted. The reaction mixture was maintained at a temperature between 285° and 295° C. during passage of the alcohol thereinto. The reacted mixture was then cooled to room temperature and dissolved in a dilute sodium hydroxide solution consisting of 19.1 pounds (0.478 pound moles) of sodium hydroxide and 164 pounds of water. The resultant solution was then cooled to about 30° C., whereupon sodium acetate, $CH_3-CO_2Na.3H_2O$, crystallized. The crystalline product was centrifuged from the mixture, washed with a relatively small quantity of water to remove traces of adhering mother liquor, and the washings were saved to be employed in diluting the reaction mixture from a successive batch of material. There was obtained 100 pounds (0.736 pound moles) of substantially pure, crystalline sodium acetate, $CH_3-CO_2Na.3H_2O$.

The mother liquor remaining after the above described crystallization contained 0.775 pound equivalents of acetate, 0.775 pound equivalents of combined sodium, 0.517 pound equivalents of combined potassium, 0.517 pound equivalents of hydroxide, and 124.5 pounds of water. By adding to said mother liquor, 10.3 pounds (0.258 pound moles) of sodium hydroxide and evaporating the mixture to dryness, there is obtained a residue having substantially the same composition as the fused alkaline mixture initially employed in the process. Said residue is suitable for re-employment as an oxidizing agent for additional quantities of ethyl alcohol, by repeating the procedure described above.

The principle of our invention may be employed in ways other than those previously described. In the examples, for instance, absolute ethyl alcohol was employed as a reactant and the reaction temperatures maintained were between 285° and 295° C. While, for reasons set forth below, we prefer to employ substantially anhydrous ethyl alcohol in our process and to maintain the reaction temperature within the limits stated, alcohol having a concentration of about 92 per cent or higher may be employed successfully as a reactant and the reaction temperature may be varied between the approximate limits of 250° and 325° C. and the reaction still proceed smoothly. When anhydrous alcohol is employed and the fused reaction mixture also is substantially anhydrous, the reaction temperature should not exceed 300° C. as oxidation of the acetate product occurs in appreciable quantity above that point. If the alcohol or reaction mixture contains an appreciable quantity of water the reaction tends to become sluggish, but the reaction temperature may be increased to about 325° C. without decomposition occurring. Apparently water tends simultaneously to inhibit the formation of undesirable by-products and to slow down the desired reaction itself. It is apparent, therefore, that the presence of a relatively small quantity of water in the reaction mixture may be highly desirable at times, but that the presence of any considerable quantity of water in said mixture is to be avoided.

In the examples, we have described the operation of our process when the reaction mixture is maintained under atmospheric pressure. It may be at times advantageous, however, to maintain the reaction mixture under a moderate pressure, e. g. between 1 and 4 atmospheres, when the alcohol employed as a reactant contains an appreciable quantity (1 to 8 per cent) of water or when the fused mass itself contains a relatively small quantity (1 to 15 per cent) of water.

The present invention in brief comprises reacting ethyl alcohol with a fused mixture initially containing alkali metal hydroxide and acetate, said mixture being maintained at a temperature between about 250° and about 325° C. during the reaction, whereby ethyl alcohol is oxidized to form alkali metal acetate and undesirable side reactions are inhibited. By suitable procedure, as hereinbefore described, sodium acetate may be recovered in substantially pure form from the reaction mixture and potassium compounds, residual alkali metal acetate and hydroxide, and other unreacted reagents may be recycled through the process.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. The method of making an alkali metal acetate which comprises reacting ethyl alcohol with a fused mixture of sodium and potassium hydroxides at a temperature between about 250° and about 300° C.

2. The method of making an alkali metal acetate which comprises reacting ethyl alcohol with a fused mixture, which initially contains sodium hydroxide, potassium hydroxide, and alkali metal acetate, at a temperature between about 250° and about 325° C.

3. The method of making an alkali metal acetate which comprises reacting ethyl alcohol with a fused mixture, which initially contains sodium hydroxide, potassium hydroxide, and sodium acetate, at a temperature between about 250° and about 300° C. while actively stirring the mixture.

4. The method of making sodium acetate which comprises reacting ethyl alcohol with a fused mixture which initially contains alkali metal acetates and hydroxides wherein the alkali metal portion consists of sodium and potassium in a ratio between about 1 sodium/2 potassium and about 3 sodium/1 potassium and wherein at least 1 mole of acetate is present for every 9 moles of hydroxide in the initial fused mixture, the latter being maintained at a temperature between about 250° and about 300° C. during the course of the reaction.

5. The method of making sodium acetate which comprises reacting substantially anhydrous ethyl alcohol with a fused mixture which initially contains alkali metal acetates and hydroxides wherein the alkali metal portion consists of sodium and potassium in a ratio between about 1 sodium/2 potassium and about 3 sodium/1 potassium and wherein acetate is present in amount representing from 40–60 per cent of the total number of moles of alkali metal acetate and hydroxide in the fused mixture, the latter being stirred and maintained at a temperature between about 285° and about 295° C. during the course of the reaction.

6. In a method of making sodium acetate the step which consists in reacting ethyl alcohol with a fused mixture, which initially contains sodium hydroxide, potassium hydroxide and sodium acetate, at a temperature between about 250° and about 300° C.

7. In a method of making sodium acetate the steps which consist in reacting ethyl alcohol with a fused mixture which initially contains alkali metal acetates and hydroxides, the alkali metal portion of said fused mixture consisting of sodium and potassium in a ratio between about 1 sodium/2 potassium and about 3 sodium/1 potassium and at least 1 mole of acetate being present for every 9 moles of hydroxide in the initial fused mixture, maintaining the reaction mixture at a temperature between about 250° and about 300° C. during the course of the reaction, condensing unreacted ethyl alcohol from gases which are evolved from the fused mass during the course of the reaction and returning the condensed alcohol to the reaction.

8. The cyclic method of making sodium acetate which comprises contacting ethyl alcohol of concentration greater than 92 per cent of said compound with a fused mixture which initially contains alkali metal acetates and hydroxides, the alkali metal portion of said fused mixture consisting of sodium and potassium in a ratio between about 1 sodium/2 potassium and about 3 sodium/1 potassium and at least 1 mole of acetate being present for every 9 moles of hydroxide in the fused mixture, stirring the latter and maintaining the same at a temperature between about 250° and about 325° C. during the course of the reaction, dissolving the reacted mixture in water, crystallizing and separating sodium acetate as $CH_3-CO_2Na.3H_2O$ from the resultant solution, evaporating the mother liquor to dryness and returning the residue to the process.

9. The cyclic method of making sodium acetate which comprises contacting ethyl alcohol of concentration greater than 92 per cent of the said compound with a fused mixture which initially contains alkali metal acetates and hydroxides, the alkali metal portion of said fused mixture consisting of sodium and potassium in a ratio between about 1 sodium/2 potassium and about 3 sodium/1 potassium and at least 1 mole of acetate being present for every 9 moles of hydroxide in the fused mixture, stirring the latter and maintaining the same at a temperature between about 250° and about 325° C. during the course of the reaction, condensing unreacted ethyl alcohol from gases which are evolved from the fused mass during the course of the reaction, returning the condensed alcohol to the reaction,

dissolving the reacted mixture in water, crystallizing and separating sodium acetate as

$$CH_3-CO_2Na.3H_2O$$

from the resultant solution, evaporating the mother liquor to dryness and returning the residue to the process.

10. In a cyclic method of making sodium acetate the steps which consist in gradually or periodically contacting substantially anhydrous ethyl alcohol with a fused mixture which initially contains alkali metal acetates and hydroxides, the alkali metal portion of said fused mixture consisting of sodium and potassium in a ratio between about 1 sodium/2 potassium and about 3 sodium/1 potassium and at least 1 mole of acetate being present for every 9 moles of hydroxide in the fused mixture, stirring the latter and maintaining the same at a temperature between about 285° and about 295° C. during the course of the reaction, condensing unreacted ethyl alcohol from gases which pass from the reaction mixture during the course of the reaction, returning the condensed alcohol to the reaction, dissolving the reacted mass in aqueous sodium hydroxide, crystallizing and separating sodium acetate from the resultant solution, evaporating the mother liquor which remains after such crystallization to dryness, and returning the residue to the process.

11. The method of inhibiting the formation of ethylene during the oxidation of ethyl alcohol to an alkali metal acetate by means of a fused mixture of sodium and potassium hydroxides, which comprises incorporating an alkali metal acetate with said alkali metal hydroxide mixture prior to employing the same as an agent for the oxidation of the ethyl alcohol.

12. The method of inhibiting the formation of ethylene during the oxidation of ethyl alcohol to acetate by means of a fused mixture of sodium and potassium hydroxides which comprises incorporating an alkali metal acetate with said alkali metal hydroxide mixture in amount representing at least 1 mole of acetate to every 9 moles of alkali in the initial fused mixture.

13. The method of inhibiting the formation of ethylene during the oxidation of ethyl alcohol to acetate by means of fused caustic alkali, which comprises incorporating an alkali metal acetate with the initial caustic alkali in amount representing at least 1 mole of acetate for every 9 moles of hydroxide, the alkali metal portion of said mixture of compounds consisting of sodium and potassium in a ratio between about 1 sodium/2 potassium and about 3 sodium/1 potassium.

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