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RECOVERY OF ORGANIC COMPOUNDS

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This invention relates to improvements in the recovery of organic compounds and, more particularly, the recovery of fatty acids from their salts.

In many industrial processes quantities of metal salts of the distillable fatty acids are made available and it is the object of the present invention to provide an efficient and cheap method of recovering the acids from these salts and, more particularly where the salts are alkali metal salts, to provide also for the recovery of the bases as well as the acids. The invention is of greatest importance as applied to the treatment of sodium and potassium acetate which are obtained in large quantities in such processes as the saponification of cellulose acetate textile materials and will be described more particularly in connection with the treatment of these salts.

According to the present invention alkali metal salts of distillable fatty acids are subjected to reaction with boric acid so as to liberate and distil from the reaction mixture the free fatty acid. The reaction between boric acid and sodium acetate, for example, yields acetic acid and a residue of sodium borate. It has been found possible to recover the base from the sodium borate by subjecting the sodium borate in aqueous or other solution to reaction with carbon dioxide. According to the conditions and particular borate employed in this recovery sodium bicarbonate or free boric acid is precipitated, the solution remaining being of different composition from that of the solution started with and thus effecting a separation of the acid and base. The present invention includes within its scope a process in which starting with an alkali metal salt the fatty acid is first liberated and distilled off and subsequently the base is recovered in the manner described.

The reaction between sodium acetate or other alkali metal salt of a distillable fatty acid and boric acid can be conducted in either the liquid or solid phase.

As regards a liquid phase process it has been found most effective to add the sodium acetate or other salt in powdered form to a strong or even saturated solution of boric acid, e. g. one containing 35–40 or more grams of boric acid per 100 grams of water, and to heat the mixture so as to distil off the free acid. It has been found in practice that under these conditions the boric acid is liable to distil in steam and thus pass over with the acetic acid and water. This can be minimised by employing an azeotroping agent to reduce the temperature at which the water and acetic acid distil from the reaction mixture. A petroleum fraction of medium boiling point, e. g. 85–95° C., has been found most effective for use in this connection and to enable the production from such a reaction mixture as that described of an aqueous solution of the fatty acid substantially free from boric acid.

The process can be carried out in the solid phase very simply by stirring together the finely powdered sodium acetate or other salt and boric acid and heating the mixture dry or with a little water to a temperature sufficiently high to effect distillation of the fatty acid, say to a temperature of between 100 and 150° C. With sodium acetate a temperature of 120 to 130° C. has been found to be adequate and to make possible the direct production of aqueous acetic acid of some 40% concentration or even higher.

It has been found desirable to use rather more boric acid than is theoretically required to react with sodium acetate or other salt employed, especially when employing a solid phase reaction, when it is found desirable to use between 3 and 5 times the quantity of boric acid theoretically required, while an even larger quantity can be used if desired. During the process the boric acid which does not react with the fatty acid salt is dehydrated with the production of meta-boric acid, the water thus liberated diluting the fatty acid produced in the process, although, on concentration, a solution of the residue yields crystals of a penta-borate of the composition $Na_2O.5B_2O_3.4H_2O$. The diluting effect of water thus liberated can be minimised by using as the starting materials the fatty acid salt in admixture with sufficient ortho-boric acid to react therewith, part or all of the excess boric acid being meta-boric acid. In this way a fatty acid of quite high concentration can be obtained. The use of meta-boric acid alone is, however, unsatisfactory for the purposes of the invention.

As previously indicated the reaction employed in the process of the invention yields a residue of sodium borate and, where the process is carried out in the solid phase, this product consists mainly of sodium meta-borate together with free meta-boric acid. The solution of sodium borate obtained with a liquid phase process or the solution obtained by dissolving the residue from the solid phase process can be subjected to reaction with carbon dioxide for the recovery of the base. This reaction can be carried out at normal atmospheric pressure, but higher pressures may be used, e. g. pressures of 40–50 lbs. per square inch, while considerably higher pressures, e. g. pres-

sures of 500–800 lbs. per square inch or more, can be used if desired.

With sodium meta-borate a satisfactory recovery of the base can be effected by precipitation of sodium bicarbonate. This result is best achieved by dissolving the meta-borate to form a strong aqueous solution, e. g. one part by weight of the meta-borate to 1½ to 3 parts of water, when carbon dioxide even at atmospheric pressure causes precipitation first of sodium tetraborate and later of a mixture of this salt and sodium bicarbonate; fractional precipitation is most satisfactory in this case. From solutions of the penta-borate $Na_2O.5B_2O_3.4H_2O$, suitably of 20–30% concentration, ortho-boric acid of 80–90% purity can be precipitated by means of carbon dioxide at room temperature or lower, e. g. 5 to 10° C., and at atmospheric pressure, leaving a solution enriched in base. On concentration, borax crystallises from this solution, leaving a mother-liquor containing both borax and penta-borate which can be again subjected to treatment with carbon dioxide to recover further boric acid. As borax can be used in many cases in place of a free base, this operation thus provides a sufficient recovery of both acid and base.

Instead of employing carbon dioxide to effect a direct replacement of the boric acid residue in the sodium borate to be treated an indirect method may be used. Thus, where free caustic alkali is required, it has been found best to react the sodium borate with lime, the calcium borate produced being separated from the caustic soda solution and reacted with ammonium carbonate to obtain calcium carbonate and ammonium borate by double decomposition. Ammonia can be distilled from the ammonium borate solution by boiling the latter during passage of a current of air through the solution, leaving the boric acid in solution.

In addition to the use of boric acid in the manner described, the present invention includes also the use of equivalent solid inorganic acids or hydrated acidic oxides, chief among such compounds being hydrated alumina and the hydrated silica known as silicic acid. Such compounds, in view of their insoluble nature, are best employed as a gel with which the sodium acetate or other fatty acid salt is thoroughly mixed, and the product obtained heated at temperatures of the order indicated to effect distillation of the free fatty acid. The residue obtained in such a process, consisting of the alkali metal silicate or aluminate, can be dissolved in water and treated with carbon dioxide to precipitate a free acid or acidic oxide, after which the solution may be sufficiently concentrated for the recovery of alkali metal carbonate or bicarbonate therefrom.

Although the invention has been described with particular reference to the treatment of alkali metal acetates, it may be applied also to the treatment of salts of other distillable fatty acids, e. g. propionic acid, including fatty acids in which one or more hydrogen atoms are replaced by other atoms or groups. Moreover, salts of metals other than alkali metals may be treated, for instance of the alkaline earth metals, e. g. calcium, and of magnesium. With such salts it is generally best to use boric acid as the reagent employed for liberating the free acid. Furthermore, the solutions employed for a liquid phase reaction for the liberation of the free fatty acid and likewise for the recovery of the inorganic acid used in the process, need not be aqueous or wholly aqueous, for instance aqueous alcoholic solutions may be employed if desired.

The following example illustrates the invention:

Example

Sodium acetate is mixed with about four times its weight of ortho-boric acid, the two substances being used in dry form and being thoroughly mixed. The mixture is heated with stirring until acetic acid begins to distil. Practically the whole of the combined acetic acid is recovered as a distillate containing about 20% of acetic acid, while if the distillate be condensed in fractions, some fractions of well over 40% concentration are obtainable.

The residue after acetic acid has been distilled is dissolved in water to form a 25% solution of sodium pentaborate, $Na_2O.5B_2O_3.4H_2O$. A slight excess of lime is then stirred in, the reaction being conducted at a temperature of about 5° C. Calcium borate is formed and can be filtered from the aqueous caustic soda solution remaining. The calcium borate is then stirred with ammonium carbonate solution of 4 to 6% concentration for one hour at 20° C. The calcium carbonate residue is filtered off and the filtrate refluxed with a slow current of air for three hours by which time almost the whole of the ammonia is recovered and can be utilised for regenerating ammonium carbonate by reaction with carbon dioxide and water. More than 95% of the boric acid is recovered from the remaining solution.

Having described my invention, what I desire to secure by Letters Patent is:

1. Process for the recovery of a distillable fatty acid from a salt thereof, which comprises subjecting the salt to reaction with a normally solid inorganic acid selected from the group consisting of boric acid, hydrated alumina and silicic acid so as to distill off from the reaction mixture the free fatty acid.

2. Process for the recovery of a lower aliphatic acid from an alkali metal salt thereof, which comprises subjecting the salt to reaction with a normally solid inorganic acid selected from the group consisting of boric acid, hydrated alumina and silicic acid so as to distill off from the reaction mixture the lower aliphatic acid.

3. Process for the recovery of acetic acid from an alkali metal acetate, which comprises subjecting the acetate to reaction with a normally solid inorganic acid selected from the group consisting of boric acid, hydrated alumina and silicic acid so as to distill off from the reaction mixture the free acetic acid.

4. Process for the recovery of acetic acid from sodium acetate, which comprises subjecting the sodium acetate to reaction with boric acid so as to liberate and distill from the reaction mixture free acetic acid.

5. Process for the recovery of acetic acid from sodium acetate, which comprises heating a mixture of solid boric acid and solid sodium acetate so as to liberate and distill from the mixture free acetic acid.

6. Process for the recovery of acetic acid from sodium acetate, which comprises heating a dry mixture of sodium acetate with 3 to 5 times the quantity of ortho-boric acid theoretically required to liberate the combined acetic acid and distilling off the acetic acid as it is formed.

7. Process for the recovery of a lower aliphatic

acid from an alkali metal salt thereof which comprises subjecting the salt to reaction with a normally solid inorganic acid selected from the group consisting of boric acid, hydrated alumina or silicic acid so as to distill off from the reaction mixture the free aliphatic acid and thereafter recovering the base from the inorganic acid salt formed by treatment of a solution thereof with carbon dioxide.

8. Process for the recovery of acetic acid from an alkali metal salt thereof, which comprises subjecting the salt to reaction with boric acid so as to liberate and distill from the reaction mixture free acetic acid and thereafter recovering the base from the borate formed by treatment of a solution thereof with carbon dioxide.

9. Process for the recovery of acetic acid from sodium acetate, which comprises subjecting the sodium acetate to reaction with ortho-boric acid so as to liberate and distill from the reaction mixture free acetic acid, dissolving sodium borate formed to produce a 20 to 30% aqueous solution of sodium pentaborate, passing carbon dioxide under atmospheric pressure and at a temperature of 5 to 10° C. into said solution so as to cause precipitation of ortho-boric acid, separating said ortho-boric acid and concentrating the remaining solution until borax crystallizes therefrom and thereafter removing said borax and again subjecting the liquor to reaction with carbon dioxide.

10. Modification of the process claimed in claim 8, wherein the sodium borate initially produced is subjected to reaction with lime to form the free base in solution and calcium borate and the calcium borate is subjected to reaction with ammonium carbonate to form calcium carbonate and free boric acid is recovered from the ammonium borate simultaneously produced.

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