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HYDROLYSIS OF ALKYL SULPHATE ESTERS

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This invention relates to the hydrolysis of the lower alkyl sulphate esters to form alcohol and/or ether.

It is known to be possible to separate mixtures of olefines obtained by various processes into substantially pure gases, or gaseous mixtures containing substantially one olefine. For example, substantially pure ethylene, or a gas mixture consisting of ethylene diluted only with saturated hydrocarbons may be readily obtained by known processes. It is common knowledge that such pure ethylene or ethylene mixture may be absorbed by and reacted with sulphuric acid, forming mixtures containing acid ethyl sulphate, diethyl sulphate and uncombined sulphuric acid, of varying composition, dependent on the conditions of absorption,—and that these mixtures may be treated with water and converted to alcohol, ether and free sulphuric acid.

Various processes have been devised for treating these mixed alkyl esters with water, specifying—hydrolysis with a large quantity of water, as for example 2–4 parts by weight of water per part of ester mixture; maintenance of low acid concentration to prevent the decomposition of alkyl radicals with consequent loss of yield and production of foul smelling decomposition products; preliminary separation of polymerizable materials produced in the absorption process by using a large amount of water for hydrolysis and commonly known settling apparatus. Although these specific requirements may be necessary when treating esters containing more than three carbon atoms they are marked by many disadvantages among which may be mentioned:—length of time required for hydrolysis of the mixed alkyl esters and separation of polymerized materials which subsequently tend to distill over with the alcohol or ether product; large size of apparatus and building space required to take care of the long cycle of operation and large volume of material to be handled per volume of final product produced; the quantity of fuel requirement to maintain these large volumes of material at the proper temperature for complete hydrolysis and distillation of products, and finally the quantity of fuel consumed in the concentration of the dilute acid.

The present invention affords improvements in the hydrolysis of alkyl sulphates, or mixtures of alkyl sulphates derived from olefines having less than four carbon atoms, tending to eliminate or ameliorate the disadvantages above named; and further to obtain advantageous use of polymerized materials produced in the alkyl esters during the absorption process and subsequent treatment. The term mixed esters may apply to such mixtures as dialkyl or acid alkyl esters of sulphuric acid, or mixtures of different alkyl group esters.

I have discovered that alkyl sulphates, mixtures of alkyl sulphates, or alkyl acid sulphate mixtures, derived from olefines or olefine mixtures, where the olefines are constituted as to contain no more than 3 carbon atoms per molecule may be satisfactorily converted to alcohols and ethers by a rapid hydrolysis method, taking place in two stages. I find that if the sulphate esters obtained from the olefine absorption processes are mixed with approximately an equal weight of water by such methods as will produce a state of very fine subdivision, or emulsion, and this mixture is heated to 70° C. or higher the dialkyl sulphates go into solution rapidly, and the hydrolysis may be represented by the reaction:—

$$R_2SO_4+H_2O=ROH+RHSO_4$$

where R is the alkyl radical containing less than 4 carbon atoms. Any polymerized material or unhydrolyzable isomeric matter produced in the olefine absorption process will remain in complete solution in this hydrolysis product. If the temperature is maintained at 70° C. with vigorous agitation this stage of the hydrolysis may be effected completely in a period of 45 minutes to 1 hour. If the temperature is maintained at 75° C. this period is reduced to 15–20 minutes. If the mass is at a boiling temperature this solution and hydrolysis of dialkyl sulphate is practically instantaneous. Under this last condition, however, vapors which are evolved may advantageously be condensed in a reflux condenser, since they will carry a certain amount of unhydrolyzed dialkyl ester. It has been found that under these conditions superficial water absorption by the condensed globules of dialkyl sulphate create hydrolysis conditions that produce decompositions to ether and hydrocarbons and other non-condensible bodies, and a loss of yield results. With temperatures lower than 70° C. the time required for complete solution or hydrolysis is increased rapidly in proportion to decreasing temperature.

I have found that, if the alkyl ester mixture is insufficiently agitated so that the separated dialkyl ester forms in globules, a much longer period of initial hydrolysis is required and a decreased yield results due to absorption of water by the dialkyl ester globules, and hydrolysis in

the globule, under conditions which produce excessive amounts of ether or hydrocarbons.

The preferred conditions for producing the initial hydrolysis according to the present invention include: use of equal or substantially equal weights of water and alkyl ester mixture thoroughly mixed to a well defined suspension of dialkyl sulphate in water and a temperature of 70–75° C. for a period of 20 minutes to one hour. When solution of the dialkyl sulphate is complete no immiscibility is found in the liquid mass and all dialkyl sulphate is converted to alcohol and acid alkyl sulphate.

For the completion of the process of hydrolyzing esters or alkyl ester mixtures to alcohols or ethers, I have found that under conditions of increasing acidity and continuous removal of alkyl alcohol or ether, as carried out in the second stage of my process, the hydrolysis of or conversion of the acid alkyl sulphate to alcohol is rapid and complete; that there is substantially no loss of alkyl radical; that concentrations are sufficient to keep the polymerized and high boiling isomeric impurities of the original alkyl sulphate mixture in solution in the acid, thus producing an alcohol which may be purified and rectified by usual refining methods common to the alcohol industry; that the residual acid is recovered in suitable strength for further treatment, and that the reduction in volume of reacting material described, results in eliminating and ameliorating the disadvantages of already existing processes, reducing the initial capital expense necessary to put the process in operation and cost of operating the process sufficiently to constitute a decided improvement in the method.

This second stage of the process consists in transferring the clear solution of free alcohol, acid alkyl ester, and free sulphuric acid obtained as the product of the first stage of the reaction, described above, to a distilling apparatus of suitable construction to withstand the action of the acid, with or without rectifying columns or other fractionating device. Here it is heated to boiling and the vapors of ether and alcohol distilled from the boiler and condensed in the usual manner except that refrigeration is used at the first part of the distillation to condense completely low boiling materials including ethers produced. This distillation is carried out until the specific gravity of the distillate is .999 as determined by the Westphal balance or other recognized method of determining the specific gravity. At this point, in the case of ethyl sulphates, the liquid in the boiler will have a boiling point of approximately 162–168° C., and consists of sulphuric acid of 67–72% H_2SO_4 strength, containing the polymers and isomers more or less sulphonated and largely in solution.

I have found that the alkyl group value of the alcohol and ester recovered is 97–99% of the alkyl equivalent of the olefine or mixed olefines originally absorbed in the acid to produce the alkyl ester mixture. The unrecovered alkyl material is present as polymers or isomers, uncombined, or combined with the free acid liberated by the hydrolysis. The carbon equivalent of this difference is largely recoverable by certain processes, indicating that the amount of available valuable alkyl radicals broken down is substantially negligible, and the loss, if any, is more than balanced by savings in capital and operating costs obtained in this process, claiming substantially equal weight hydrolysis as the improvement in method.

Acid concentrations obtained in the process when hydrolyzing the ethyl acid sulphate, diethyl sulphate and free acid mixtures, obtained by the absorption of ethylene in sulphuric acid, with an equal weight of water are:

(*a*) After the first stage of hydrolysis 4–10% free H_2SO_4, 25–30% combined H_2SO_4 present as acid ethyl sulphate. (*b*) During the second stage of the process the combined H_2SO_4 is rapidly converted to free H_2SO_4, and by removing water and the hydrolyzed ethyl product from the boiler, the acid concentration reaches 67–72% at the end of the second stage of hydrolysis. The acid conditions result in the formation of definite amounts of ether, which is distilled over with the alcohol and subsequently separated from it by a subsequent rectification; or the separation may be made directly during the second stage of the hydrolysis by use of suitable fractionating apparatus, negligible amounts of ether being formed during the concentration. When equal weights of water and ester are used the amount of ether produced will be 2–4% of the total alkyl group equivalent. If it is desired to recover a greater amount of ether, the amount of water used in the hydrolysis may be cut down to produce acid concentrations sufficient to yield the amount of ether desired. This decrease in the amount of water may be carried to a point where three-fourths of the weight of water for a given weight of ester is used in the hydrolysis process. If water is used in smaller amounts than this, side reactions involving splitting up of the alkyl radical and conversion of acid alkyl esters to hydrocarbons occur, resulting in a lowering of the yield of recoverable alkyl equivalent originally absorbed from the olefines which react with the acid. When .75 part by weight of water per weight of alkyl ester mixture is employed, approximately 50% of the alkyl value is recoverable as alcohol, the balance as ether. By choice of definite mixtures for hydrolysis particularly between these two points any desired production of alcohol or ether may be obtained with excellent yields.

With the acid, alcohol, and acid alkyl ester concentrations obtained after the first stage of hydrolysis, all polymers, isomers or side reaction products, that are non-hydrolyzable remain in solution. They are, for the most part, high boiling, and being completely miscible with the partially hydrolized liquor do not distill with the alcohol or ether, giving the alcohol and ether such quality that final purification may be made by simple fractionation methods. During the second stage of my process, I have found that these materials are sulphonated or otherwise converted to a greater or less degree to products with extremely low vapor pressures. These are decreasingly less soluble as the acid concentrations increase, but their vapor pressure is so low that but a very small amount is steamed over into the alcohol product during the latter part of the second stage of my process. The large proportion of this material remains in the residual acid, and its presence is of decided advantage in subsequent treatment of this acid for the production of commercial products. A process on which I have filed application for Letters Patent, pertains to the method of treating this acid by heating the same above its normal boiling point to produce desirable products, notably carbon, and demonstrates the advantage of conducting the hydrolysis by this specified process, in that a source of highly adsorptive carbon is provided by choosing hydrol-

ysis mixtures of preferably between three-fourths and one unit weight of water per weight of alkyl ester mixture, whereby polymers and isomers derived from the absorption of olefines in sulfuric acid are retained for the most part in the sulphuric acid recovered on hydrolysis of the alkyl sulphates. Furthermore carrying out my process in this specified manner results in a recovered acid of the proper strength, without any further concentration, and at a temperature requiring only a small input of fuel to carry out the pressure heating as claimed in the other process which I have invented and filed claim to, specified above.

I have further discovered that improvement in the process may be made by utilizing the net heats of reaction involved in the first stage of the process and heat of solution of free acid and acid alkyl ester contained in the mixture and produced in the usual hydrolysis. By using water at from 55–60° C., and hydrolysis mixtures of three-fourths to one part by weight of water per unit weight of mixed alkyl ester hydrolyzed, sufficient heat is liberated to raise the temperature of the mixed mass to 70–75° C., a temperature which I have shown to be desirable to effectually carry out the first stage of hydrolysis. With the other known processes using larger amounts of water extra heat must be applied to maintain the temperature of the larger mass at the desired point.

A specific embodiment of the application of the principles of my invention follows: One thousand pounds of water at 60° C. are charged in a closed tank or suitable container, equipped with a stirrer or suitable agitating device, and also connected to a reflux condenser. An equal amount of mixed ethyl sulphate, consisting of diethyl sulphate in preponderance, acid ethyl sulphate in substantial amounts and a small amount of free sulphuric acid, as obtained by the absorption of substantially pure ethylene, or pure ethylene diluted with saturated hydrocarbons or other inert gases, is added to the water, the mass being vigorously agitated during the addition and for 45–60 minutes after the addition is complete. The combined effect of heat of solution of the acid, reactions of hydrolysis of diethyl sulphate, and solution of acid ethyl sulphate is sufficient to raise the temperature of the mixture to 70–75° C. Under certain conditions heat may have to be applied or a longer or shorter time of agitation employed, the reaction being allowed to continue until a homogeneous solution containing no immiscible material is obtained. The hot clear solution is then transferred to the boiler of any suitably constructed distilling device commonly known or recognized in the arts, and boiled until all vapors of alcohol or ether are completely removed, these vapors being condensed in condensing equipment of the well known types, collecting the distillates in container of any desirable nature. This alcoholic-ether mixture is separated by fractionation and the alcohol rectified to the desired strength by usual methods, well known and long practiced in the alcohol industry. The end of the alcohol stripping is controlled by carrying out the boiling of the reaction mixture until the specific gravity of the distillate is .999 and the temperature of the boiling mixture is 162–168° C. The acid liquor may thereafter be subjected to a temperature equivalent to a few degrees above its normal boiling points whereby the organic impurities are carbonized and rendered separable as by filtration. This method of treatment is described in detail in my co-pending application, Serial Number 670,306, filed May 10, 1933. The acid filtrate is then concentrated to the desired strength and utilized again in the absorption of olefines.

It is understood that my process is not limited by this example to this specified mixture or type of apparatus. It may be applied to pure alkyl sulphates containing less than 4 atoms of carbons per molecule, or mixed alkyl sulphates derived from the absorption or reactance of olefines, or mixtures of olefines in a suitable acid medium, such olefines containing not over 3 atoms of carbon per molecule of olefine of highest molecular weight in the mixture. Any type of apparatus for mixing may be used that will produce the necessary mixing and dispersion of the dialkyl sulphate that appears as a second, non-miscible liquid phase when the ester mixture is first introduced with the water. The method is not limited to the using of separate apparatus for each of the two stages specified, but both stages may be carried out in a single piece of apparatus, consisting of a boiler equipped with stirring or other agitating mechanism, and connected with suitable condensing equipment and receivers to condense and collect the distillates obtained in the second stage of the process as specified. The ester-water mixture is not necessarily made in apparatus as described but may be produced by running streams of water and ester into a centrifugal pump or other known types of turbo-mixers or agitators. Although a batch process is given as an example, the process may be applied to continuous methods where suitably constructed apparatus can carry out the first and second stages of the process continuously. Furthermore, fractionation of products to any desired degree may be obtained in the second stage of my process.

What I claim is:

1. The method of hydrolyzing alkyl esters of sulphuric acid consisting of substantial amounts of the dialkyl ester and monoalkyl ester and a relatively smaller amount of free sulphuric acid wherein the alkyl group contains less than four carbon atoms, which comprises intimately mixing the alkyl ester with not substantially more than an equal part by weight of water until an homogeneous solution is obtained and subsequently distilling the solution to recover the hydrolyzed alkyl products.

2. The method of hydrolyzing alkyl esters of sulphuric acid consisting of substantial amounts of the dialkyl ester and monoalkyl ester and a relatively smaller amount of free sulphuric acid wherein the alkyl group contains less than four carbon atoms, which comprises intimately mixing the alkyl ester with not substantially more than an equal part by weight of water until a homogeneous solution is obtained and subsequently distilling the solution to recover the hydrolyzed alkyl products, said method being further characterized in that the temperature of the mixture of water and the alkyl sulphate is maintained at approximately 70°–80° C. during the mixing operation.

3. The method of hydrolyzing alkyl esters of sulphuric acid consisting of substantial amounts of the dialkyl ester and monoalkyl ester and a relatively smaller amount of free sulphuric acid wherein the alkyl group contains less than four carbon atoms, which comprises intimately mixing the alkyl ester with not substantially more than an equal part by weight of water until a

homogeneous solution is obtained and subsequently distilling the solution to recover the hydrolyzed alkyl products, said method being further characterized in that the distillation is continued until the specific gravity of the distillate is substantially equivalent to that of water.

4. The method of hydrolyzing alkyl esters of sulphuric acid consisting of substantial amounts of the dialkyl ester and monoalkyl ester and a relatively smaller amount of free sulphuric acid wherein the alkyl group contains less than four carbon atoms, which comprises intimately mixing the alkyl ester with not substantially more than an equal part by weight of water until a homogeneous solution is obtained and subsequently distilling the solution to recover the hydrolyzed alkyl products, said method being further characterized in that the distillation is continued until the concentration of the acid mixture is approximately at 67–72% H_2SO_4.

5. The process of producing ethyl alcohol and ether by hydrolyzing with water, the ethyl esters of sulphuric acid obtained by the reaction of concentrated sulphuric acid and ethylene and consisting of substantial amounts of the dialkyl ester and monoalkyl ester and relatively smaller amounts of free sulphuric acid characterized in that the ester mixture is mixed with water in the ratio of one part by weight of ester to .75–1.0 part of water under conditions to effect preliminary hydrolysis as evidenced by the complete dissolution of the dialkyl ester in the aqueous mixture and subsequently recovering the alcohol and ether product while completing the hydrolysis by distilling the mixture.

6. In the method of hydrolyzing alkyl sulphate esters, the alkyl group of which contains less than four carbon atoms, the said esters consisting of substantial amounts of the dialkyl ester and monoalkyl ester and a relatively smaller amount of free sulphuric acid; the steps of adding a sufficient quantity of water under intimately agitated conditions to hydrolyze the mixture to produce a homogeneous mixture but in insufficient quantity to effect separation from solution of organic by-products and subsequently distilling the mixture to recover the hydrolyzed alkyl products.

7. The method as defined in claim 6 and further characterized in that the initial hydrolysis with water is effected at 70°–80° C.

8. A process which comprises subjecting a mixture of substantial amounts of monoalkyl and dialkyl esters of sulphuric acid, the alkyl groups of said esters containing less than four carbon atoms, to hydrolysis with water until the alkyl sulphates are brought into solution and approximately ten per cent of free sulphuric acid is present, then subjecting the mixture to final hydrolysis while increasing the concentration of the acid mixture by distillation from approximately ten per cent free sulphuric acid to approximately seventy per cent free sulphuric acid.

9. The method of hydrolyzing alkyl sulphates wherein the alkyl group contains less than four carbon atoms said alkyl sulphates consisting of substantial amounts of the dialkyl sulphate and alkyl acid sulphate and relatively smaller amounts of free sulphuric acid by reacting .75 to 1.0 part by weight of water with each part of the sulphate to be hydrolyzed under vigorously agitated conditions while maintaining a temperature of 70°–80° C. until a homogeneous solution is obtained and subsequently completing the hydrolysis and recovering the hydrolyzed alkyl product by distilling the mixture.

10. The method as defined in claim 9 and further characterized in that the alkyl sulphates consist of a mixture of the dialkyl sulphates and alkyl acid sulphates.

11. The method as defined in claim 9 and further characterized in that the alkyl sulphates consist of a mixture of diethyl sulphate and ethyl acid sulphate.

12. The method as defined in claim 9 and further characterized in that the preliminary hydrolysis is effected while agitating vigorously the reaction mixture.

13. The method of hydrolyzing ethyl esters of sulphuric acid to produce ethyl alcohol obtained by the reaction of concentrated sulphuric acid and ethylene, said reacted mixture consisting of substantial amounts of diethyl sulphate and monoethyl sulphate and relatively smaller amounts of free sulphuric acid characterized in that equal parts by weight of the ester and water are agitated vigorously at 70–75° C. until a homogeneous mixture is obtained after which the alcohol product is distilled while the hydrolysis is being completed until the sulphuric acid attains a concentration of approximately 67–72% H_2SO_4.

14. The method as defined in claim 13 and further characterized in that the sulphuric acid obtained is heated above its normal boiling temperature at atmospheric pressure whereby an absorptive carbon is produced which is capable of separating impurities from the mixture, separating the carbon and subsequently further concentrating the acid thereby rendering it suitable for use again in the absorption of an olefine having less than four carbon atoms to produce an alkyl sulphate mixture.

15. The method of hydrolyzing ethyl esters of sulphuric acid present in a mixture of diethyl sulphate, ethyl acid sulphate and sulphuric acid, the diethyl sulphate being in preponderance, the ethyl acid sulphate in substantial amounts and the free sulphuric acid in lesser amounts, said method being characterized in that there is added to the mixture .75–1.0 part by weight of water for each part of the mixture to be hydrolyzed while agitating vigorously and maintaining a temperature of 70°–80° C. until a homogeneous solution is obtained, and subsequently completing the hydrolysis and recovering the hydrolyzed product simultaneously by distilling the mixture.

16. The method as defined in claim 15 and further characterized in that the distillation is effected until the concentration of the acid is approximately 67%–72% H_2SO_4.

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