Patented Aug. 23, 1938 2,127,495

UNITED STATES PATENT OFFICE

2,127,495

MANUFACTURE OF NITROGEN BASE SALTS OF ACID ALKYL ESTERS

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No Drawing. Application June 20, 1936, Serial No. 86,339. In the Netherlands June 26, 1935

9 Claims. (Cl. 260—460)

This invention relates to the production of organic nitrogen base salts of acid alkyl esters of polybasic acids. It provides a particularly advantageous method for the manufacture of high molecular weight salts of this type in a very pure condition and with excellent wetting and dispersing powers. Another object of the invention is the preparation of novel nitrogen base soaps of this type from the organic nitrogen bases of acid sludges obtainable in the refining of petroleum products.

The process of the invention is broadly applicable to the manufacture of any organic nitrogen base salt of any acid alkyl ester of a polybasic acid regardless of the source or method of preparation of said bases and acid esters. Suitable organic nitrogen bases which may be used are, for example, the mono- or poly-aliphatic, aralkyl, carbocyclic and heterocyclic amines whether of primary, secondary or tertiary character as butyr-amine, isopropylamine, diethylamine, methyl ethyl amine, trimethylamine, the hexyl and/or cetyl amines, dimethyl aniline, diethyl benzylamine, cyclo-hexylamine, 2-amino pyridine, ethylene diamine, phenylene diamine, benzidine, etc.; amides as acetamide, the mixed amides of vegetable and animal oils, fats and waxes as those of cocoanut oil, sardine oil, castor oil, soya bean oil, etc., acetanilide, benzamide, urea and the like, and cyclic nitrogen bases as pyrrole, indole, pyridine, quinoline, piperidine, pyrazole, naphthoquinoline, the azines whether di-, tri-, ox- or thiazines, including those containing the cyanuric nucleus, the purines, the barbituric acid derivatives, the acridines, the acridones, the azoles whether simple, thio-, oxo- or triazoles, etc. The saturated or unsaturated homologues, analogues and substitution products (e. g. containing halogen, hydroxyl and/or other substituents, such for example as the alkylolamines whether mono- or poly-substituted, as mono-methanolamine, di-ethanolamine, triisopropanolamine, N-ethyl-mono-propanolamine, N-phenyl-N-ethanolamine, mono- or di-ethanolethylene diamine, etc.) of the above and like nitrogen base compounds as well as suitable quaternary ammonium bases. Instead of the free organic nitrogen bases, their salts may be used, such as the sulfates, phosphates, halides, borates, sulfonates, oxalates, chloracetates, etc., of the above. Particularly suitable are the relatively water-soluble nitrogen base salts, especially salts of quinoline and the like and those of nitrogen bases derived from mineral oils and their products, such as from petroleum sludge acid, etc.

Included among the wide variety of acid alkyl esters which are suitable for reaction, in accordance with the invention, with organic nitrogen bases such as the above, are, for example, methyl, ethyl, propyl, isopropyl, n-, secondary and/or tertiary butyl, the amyl, hexyl, and higher alkyl acid esters of dithionic, sulfuric, phosphoric, prophosphoric, boric and like polybasic acids. As with the above described organic nitrogen bases, the alkyl esters are most preferably used in the form of their salts, the alkali, alkaline earth, ammonium or other inorganic salts being suitable. In all cases the alkyl acid esters or their salts are used, although in the case of phosphoric and like acids more than one alkyl group may be present.

The alkyl acid esters may be prepared from the corresponding alcohols or olefines or other suitable starting material in any appropriate manner. Suitable methods for preparing acid alkyl esters from the corresponding olefines are described, for example, in United States Patents Nos. 1,744,164, 1,790,518 and 1,810,192. Similar processes applied to higher olefines are described in British Patents Nos. 343,872 and 360,602 which also give methods for converting the acid esters to salts. Other processes which use alcohols of various kinds and sources are described in British Patents Nos. 247,714, 308,824, and 318,610.

The process of my invention essentially comprises reacting an alkyl acid ester or a mixture of such esters, or the corresponding alkyl acid ester salt or salts, preferably in the absence of neutral alkyl esters with one or more organic nitrogen bases or salts thereof. The reaction is carried out at normal or slightly elevated temperatures, which should in general not exceed about 100° C., since otherwise decomposition of the reaction components or of the nitrogen base salts formed in the reaction is liable to occur. In most cases temperatures below about 50° C. are applied.

For the purpose of making my invention more clear it will be described with more particular reference to the reaction of acid alkyl esters produced by absorption of olefines in strong polybasic mineral acids, but it will be understood that this implies no limitation since, as explained above, alkyl acid esters from other sources may also be used.

In the absorption of olefines in strong polybasic acids neutral alkyl esters and, usually, also polymers may be formed besides acid alkyl esters. In order to efficiently utilize all the absorbed fine content the neutral alkyl esters should be converted to acid alkyl compounds. Such a con-

version is best effected at an elevated temperature. However, this heating of an olefine absorption product neutralized with an organic nitrogen base, results in decomposition of the organic nitrogen base salts produced by the neutralization. I have found that organic nitrogen base salts of acid alkyl esters may be obtained in high yield, whether calculated on the basis of alkyl ester present or on the nitrogen base used, and in an exceptional state of purity by reacting the base with alkyl acid esters freed from neutral alkyl esters, preferably by conversion of the latter into acid alkyl compounds.

Several different procedures are available for the separation and/or conversion of the neutral alkyl ester content. One may operate in the presence or absence of free acid. Where it is preferred first to remove any free acid present either extraction, preferably using the process of my co-pending application Serial No. 27,048 filed June 17, 1935, or neutralization may be used. The resulting liquor may be treated with an inorganic alkaline agent under such conditions of concentration and temperature that either the acid ester content only is selectively converted to the salt or salts after which the neutral alkyl ester may be separately treated or the conditions may be made more severe by operating at higher temperatures with larger amounts of alkali to susbtantially convert both the acid and neutral alkyl esters to salts. Alternatively, the liquor, preferably rendered free of free acid, may be first separated into two phases, one of which contains the greater part of the alkyl acid ester content while the other phase contains a greater part of the neutral ester content. Besides aqueous dilution, organic solvents for the neutral alkyl esters such as suitable hydrocarbons and the like may be used to effect the separation. By using aqueous alkali for dilution the stratification may be carried out in such a manner that the alkyl acid ester content is simultaneously converted into the salt while it is being separated.

The neutral alkyl esters so separated from the olefine absorption product may be converted into alkyl acid ester salts either by treatment with an alkaline agent at an elevated temperature or by addition of acid to produce alkyl acid esters which may be used directly or which may then be converted to said salts by the use of the same alkaline agent. The same treatment used for separation of the neutral alkyl esters may be applied for the removal of polymers, if present, since these give an impure final product. While several different methods of operation, involving the use of either alkyl acid esters or alkyl acid ester salts, are thus available, I generally prefer, because of its simplicity, the conversion of neutral alkyl esters to alkyl acid ester salts without separation of the two types of esters.

Also, I prefer to use salts of organic nitrogen bases as reactants and most preferably salts of the same polybasic acid used in the preparation of the alkyl ester or esters involved. In this manner the reaction may be particularly advantageously carried out as a metathesis between an organic nitrogen base salt and an alkali or alkaline earth metal salt of the acid alkyl ester or esters. For this modification of my invention the salts of organic nitrogen bases required for the double conversion can be very suitably caused to react with the potassium or sodium alkyl esters already formed in the absorption liquor, since the conversion of neutral alkyl esters into acid alkyl compounds and the separation of the polymers in general may be suitably effected by heating with a basic agent such as sodium or potassium or ammonium or calcium or magnesium or like hydroxides, bicarbonates, acetates and other suitable basic compounds. Moreover, when using this method of procedure there is a reduced loss of organic nitrogen base since the excess free polybasic acid remaining after olefine absorption is first rendered innocuous as above described so that expensive organic bases need not be used for this purpose. It has further been found that this metathesis procedure, in an acid medium, results in the stratification of the reacted solution into two phases, one of which contains an aqueous solution of the organic nitrogen base salt of the alkyl acid esters. The salt may be extracted from this solution by means of a suitable organic solvent and recovered in a very pure condition.

The following detailed examples illustrate suitable methods of executing the process of the invention. The first of these examples shows a preferred method of operation as applied to the production of novel salts of organic nitrogen bases from petroleum.

Example I

A cracked benzine fraction, boiling point 280–300° C., bromine number 53.3, obtained by cracking paraffin wax in the vapor phase, was sulfated for 1½ hours at 25–30° C. with a 1 molar quantity of 96% H_2SO_4 calculated on the bromine number. The reaction mixture was poured onto ice, the excess of acid separated as bottom layer and the upper layer heated to about 100° with an excess of NaOH solution, until the alkalinity no longer decreased, which was the case after 4 hours. The dialkyl sulfates present were thereby converted into sodium alkyl sulfates and alcohols. 0.7 part by volume of water was then added to the reaction mixture which was heated at 95–100° C. for 20 hours. The polymers present were thereby separated off. An aqueous solution of sodium alkyl sulfate, contaminated with a few per cent. of sodium sulfate, was obtained. To this solution there was subsequently added an equimolecular quantity of a sulfuric acid salt of a nitrogen base mixture, prepared from acid tar originating from the sulfuric acid treatment of cracked benzine. Care was taken that the pH of the liquid obtained was 3. The liquid was stirred for 1½ hours at room temperature. After having been left to stand for some time an aqueous upper layer containing the nitrogen base salt was separated off. From this layer the salt could be extracted with carbon disulfide or benzene, after which it could be obtained in a pure condition after evaporation of the extracting agent.

Instead of the cracked benzine fraction used above other fractions of wider or narrower boiling range obtainable by either liquid or vapor phase cracking of paraffin wax, petrolatum or other suitable hydrocarbons which yield substantially straight chain olefines of at least 10 carbon atoms per molecule may be used and very similar products obtained. For example, cracked fractions in which the olefines have substantially 10 to 16 carbon atoms, 12 to 20 carbon atoms, 14 to 18 carbon atoms or 15 to 20 carbon atoms can be used.

Nitrogen base mixtures suitable for the production of products such as those obtainable by the procedure of the above example may be prepared from petroleum or petroleum products or other suitable nitrogen-bearing hydrocarbon oils by the

methods described in United States Patents Nos. 911,553, 1,965,828 or 2,035,583 or other suitable procedures. Instead of the nitrogen base salts the free bases may be used and it will be understood that by the expression "organic nitrogen base compound" both the free base and the salts are included. Similarly in place of the alkyl acid ester salts the free acid esters may be substituted.

The products obtained by using nitrogen bases and/or salts thereof from petroleum sources are complex mixtures of organic nitrogen base salts of acid alkyl esters of polybasic acids which have excellent wetting and emulsifying powers. They are quite stable in the presence of dissolved calcium and magnesium compounds which makes them useful in textile treating and dyeing and the like.

Example II

A cracked benzine fraction, boiling point 220–300° C., bromine number 55, obtained by cracking paraffin wax in the vapor phase, and containing substantially olefines with 13 to 18 carbon atoms, was sulfated for 1 hour at 0–5° C. with a 2 molar quantity of 90% H_2SO_4 calculated on the bromine number. The reaction mixture was diluted with water, the excess of acid separated as bottom layer and the upper layer diluted with an equal volume of 35% ethyl alcohol, whereby the dialkyl sulfates and polymers were partly separated as an upper layer and subsequently completely removed by extraction with benzine. The aqueous solution of alkyl acid sulfates obtained in this manner was then neutralized with an equivalent amount of triethanolamine and the reaction mixture subsequently evaporated for the recovery of the triethanolamine salt of the alkyl acid sulfates.

Example III

The same cracked benzine fraction as used in Example II was sulfated in a similar manner as described in said example. The reaction mixture was diluted with water, the excess of acid separated as bottom layer and the upper layer heated with an excess of $Ca(OH)_2$-paste to about 100° C., until the alkalinity did not decrease any longer, which was the case after 4 hours. An equal volume of ethyl alcohol was subsequently added to the reaction mixture, which was then filtered while hot. The resulting dilute impure alcoholic solution of calcium alkyl sulfate was thereupon extracted with benzine in order to remove the polymers, and by evaporation in vacuo freed of the benzine and the greater part of the alcohol. To the resulting product there was added an equivalent amount of triethanolamine sulfate and the mixture was heated for ½ hour to about 80° C. The calcium sulfate formed by double conversion was then readily removed by filtration, whilst the solution of triethanolamine alkyl sulfate was subsequently evaporated, whereby the dry salt was obtained in a pure condition.

While I have in the foregoing described in some detail the preferred embodiment of my invention and some variants thereof, it will be understood that this is only for the purpose of making the invention more clear and that the invention is not to be regarded as limited to the details of operation described, nor is it dependent upon the soundness or accuracy of the theories advanced as to the advantageous results attained. On the other hand, the invention is to be regarded as limited only by the terms of the accompanying claims, in which it is my intention to claim all novelty inherent therein as broadly as is possible in view of the prior art.

I claim as my invention:

1. A process of producing an organic nitrogen base salt of an acid alkyl ester of a polybasic mineral acid, which comprises reacting an organic nitrogen base compound of the class consisting of free organic nitrogen bases and organic nitrogen base salts with an inorganic salt of an acid alkyl ester of a polybasic mineral acid.

2. A process of producing an organic nitrogen base salt of an acid alkyl ester of a polybasic mineral acid, which comprises reacting an organic nitrogen base salt with an inorganic salt of an acid alkyl ester of a polybasic mineral acid.

3. A process of producing an organic nitrogen base salt of an acid alkyl ester of a strong polybasic inorganic acid which comprises reacting an organic nitrogen base salt of a strong inorganic acid with a metal salt of an acid alkyl ester of a polybasic inorganic acid.

4. A process of producing an organic nitrogen base salt of an acid alkyl ester of a polybasic mineral acid, which comprises reacting an absorption product of an olefine in said acid with a basic metal compound at a temperature and for a time at which substantial conversion of the neutral alkyl ester content to the corresponding salt of the acid alkyl ester is effected and reacting said salt with an organic nitrogen base salt.

5. A process of producing an organic nitrogen base salt of an alkyl acid sulfate, which comprises reacting an organic nitrogen base sulfate with a metal salt of an alkyl acid sulfate in the substantial absence of dialkyl sulfates.

6. A process of producing an organic nitrogen base salt of an acid alkyl ester of a polybasic mineral acid which comprises reacting an absorption product of an olefine in said polybasic mineral acid with sufficient alkali metal base for conversion of neutral alkyl esters present to alkali metal salts thereof and reacting the resulting product with a heterocyclic nitrogen base compound.

7. A process of producing an organic nitrogen base salt of an acid alkyl ester of a polybasic mineral acid which comprises reacting an organic nitrogen base derived from nitrogen-bearing hydrocarbon oils with a metal salt of an acid alkyl ester.

8. A mixture of organic nitrogen base salts of acid alkyl sulfates resulting from the reaction of the mixed nitrogen bases of petroleum oil and at least one acid alkyl sulfate.

9. A mixture of organic nitrogen base salts of acid alkyl sulfates resulting from the reaction of the mixed nitrogen bases of petroleum oil and at least one substantially normal chain acid alkyl sulfate of at least 10 carbon atoms per molecule.

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