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PROCESS FOR THE TREATMENT OF ALKYLOLAMINE SOAPS AND RELATED PRODUCTS

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The invention appertains broadly to the recovery of alkylolamines from their soaps with fatty acids and more particularly is concerned with the recovery of alkylolamines from the extracts obtained in the refining of liquefied or normally liquid masses (containing fatty acids, naphthenic acids, etc.) with alkylolamine, said extracts being described in our Patent No. 1,885,859 issued November 1, 1932 as being derivable from animal oils, vegetable oils, fats, waxes, resins and the like.

As the refining of fatty oils and similar masses, as described above, with alkylolamine is carried out with an excess of alkylolamine over the stoichiometric requirements of the free fatty acid present in said oleaginous material, such excess serving as a solvent for the alkylolamine salts (soaps) of the fatty acids and other extracts (such as coloring matter, ketones and other components soluble in alkylolamine and desirable to remove by extraction therewith) and as a means of attaining the proper volume relationships between the glyceride and alkylolamine phases necessary for efficiently effecting their separation by centrifuging, settling or equivalent physical modes; the condition of the alkylolamine in the extract is as both free and combined alkylolamine.

The free alkylolamine can be removed from the extracts, in question, by distillation, although it is preferable to conduct the operation at reduced pressures, whereby an avoidance of superheating is obtained. Of course, this separation holds true only when the boiling temperature of the alkylolamine is below that of the fatty acid (which has been extracted in the combined form as a soap or salt). Superheating, or elevating the temperature of the extract to the boiling temperature of the alkylolamine at atmospheric pressure enhances certain chemical changes in the extract which it may be desirable to avoid. These are amidization of the fatty acid of any glycerides (which are soluble to a slight extent in the extract) and liberation of their glycerol, and modification or decomposition of other sensitive substances, such as ketones and aldehydes, which may be contained in the extract. It is preferable also to conduct this distillation for free alkylolamine recovery at reduced (subatmospheric) pressures in the presence of steam, as an aid to the removal of alkylolamine vapor from the distillation system, to facilitate its removal at lower temperatures, and to suppress amidization of the fatty acid of glycerides or amidization of the alkylolamine-combined fatty acid. Thus, by suitably reducing the pressure, it is possible to recover the free alkylolamine, for example, monoethanolamine, entirely from the extracts at temperatures as low as 60° C.

As the extract becomes concentrated with respect to combined alkylolamine, it assumes the

gelatinous consistency of alkylolamine soap, and this state interferes with the conductance of the distillation. By maintaining the vacuum and elevating the temperature in the still boiler above the melting temperature of the soap gel at the existing pressure, or by lowering the reduced pressure and raising the temperature, these soap gels again become fluid and the distillation may be carried on further with steam. A substantially complete recovery of the free alkylolamine may be obtained.

With the free alkylolamine are recovered also certain volatile components of the extract, such as, in the case of coconut oil, methyl ketones, and in the case of sardine oil, low boiling amines and odorous principles. These, on account of their high volatility are associated with the first material distilled over and may be separated as tops from the purer alkylolamine coming over later. In the case of the use of steam in the distillation, the distillation apparatus may be so designed as to provide for a fractional condensation of alkylolamine and water and a separation of the alkylolamine from the distillation vapors substantially as alkylolamine with a low water content.

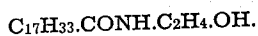
We have found that the combined alkylolamine may be recovered from its salts with the fatty acids by the steam hydrolysis of the same. While this combined alkylolamine may be recovered by chemical means, such as liberation from the salt by adding alkali and distilling, as in the case of free alkylolamine recovery, or by acidifying with a suitable acid as sulfuric acid to liberate the fatty acid, skimming off the liberated fatty acid, liberating the alkylolamine by interaction of the alkylolamine sulfate with a suitable base such as the alkaline earth oxides, hydroxides, carbonates, etc. to form an insoluble inorganic salt, as, for example, calcium sulfate and an aqueous solution of the freed alkylolamine which may then be concentrated; it is preferable to recover it by the physical means of steam distillation.

In conducting the distillation or hydrolysis with steam of alkylolamine soaps for the recovery of the combined alkylolamine, the charge is brought to a temperature necessary for liquefying the soap gel. The temperature selected is dependent upon the vacuum applied. For instance, working with combined ethanolamine at 100 mm. Hg. pressure, a suitable temperature is 140° C. while at pressures below 20 mm. Hg. recovery of ethanolamine is effective at 120° C.

The rate of the hydrolysis with steam of alkylolamine salts of fatty acids is dependent upon raising the temperature of the material being hydrolyzed to a sufficient degree above the boiling temperature of free alkylolamine at the pressure within the system and providing good contact with an amount of steam preferably in excess of the absolute requirements for the hydrolysis. This procedure is to be adopted for the

relatively low-boiling alkylolamines such as monoethanolamine, monopropanolamine, monoisobutanolamine, and the like and fatty acids which are the usual run of acids to be found in most natural fatty oleaginous compositions, that is, such fatty acids having boiling temperatures approaching or exceeding 200° C. at 15 mm. Hg. pressure. Where the boiling temperature of the fatty acid is below that of the alkylolamine used, it will be seen that the fatty acid will distill over first or together with the alkylolamine.

In the case of distillation with an insufficient amount of steam, we have found that an alteration of alkylolamine soap takes place which corresponds to the amidization of a fatty acid by the dehydration of its ammonium salt. In the case of ethanolamine oleate, oleic acid amidol is formed, which has the formula.



The formation of acid amidols from alkylolamine salts of fatty acids during the course of a steam distillation with limited amounts of steam for the recovery of combined alkylolamine is evidenced by a rapid drop in the rate of alkylolamine recovery, low alkylolamine recoveries and by a residuum which is not clear but opaque and which, on cooling and standing, deposits white crystals easily distinguishable from normal free fatty acid crystals which might separate out from mixed fatty acids. The fatty acid amidols have a low solubility in organic solvents as gasoline, petroleum benzine, etc. and may be washed free of fatty acid and alkylolamine soap therewith. They are readily soluble in alcohol and fairly soluble in ether from which they may be recrystallized. The acid amidol from oleic acid and ethanolamine has a melting point of 91°–92° C. and is a white, fluffy micro-crystalline mass. This acid amidol as well as those of other fatty acids, particularly of unsaturated fatty acids, such as those in sardine oil, have characteristics which make them of value as emulsifying agents and paper sizes.

The amidization of alkylolamine salts of fatty acids may be suppressed by providing intimate contact of excess steam with material to be hydrolyzed. As there are certain difficulties in the way of providing for such perfect contact, which are: lack of means of suitable distribution of steam within the mass so as to prevent local superheating in the absence of sufficient water vapor, difficulty in controlling the excessive foaming which results when such intimate contact is provided, excessive dilution of the alkylolamine in the distillates with water, and excessive steam consumption,—another means of suppressing amidization was found.

We have discovered that the addition of alkali, such as the oxides, hydroxides, carbonates, etc. of sodium, potassium and the like, or alkali salts of fatty acids such as the sodium or potassium salts of oleic, palmitic, stearic acids, etc. in comparatively small amounts, very much less than the stoichiometrical requirements, acted strongly to suppress amide formation and consequently enhanced the alkylolamine recoveries from the steam hydrolysis of alkylolamine—fatty acid mixtures at reduced pressures, elevated temperatures and limited amounts of steam. Those alkalis are selected which will react with the fatty acid to form its soap and yet be sufficiently dispersed therein to effect suppression of amidization.

The following tables show the effect of variables on the recoveries of ethanolamine from ethanol-

amine-fatty acid mixtures (from neutral soaps to excess of fatty acid) by steam hydrolysis.

TABLE I

Effect of concentration of ethanolamine and temperature on the decomposition of ethanolamine-sardine oil fatty acids at 100 mm. Hg. and with a fixed steam rate, as determined by the ratio of water: ethanolamine in the distillates

Composition of charge mol ethanolamine per mol fatty acid	Temperature of decomposition	Weight ratio H ₂ O: ethanolamine
.20 .40 .60	120° C.	653.0 118.0 28.5
.20 .40 .60 1.00	130	109.0 31.2 9.0 2.4
.23 .40 .60 1.00	140	59.1 14.3 5.2 2.3
.23 .40 .69	150	36.3 11.1 2.8
.20 .40 .60	160	19.5 4.4 2.9

TABLE II

Effect of varying steam rate, composition of charge and KOH on the total recovery of ethanolamine from ethanolamine combined with fatty acid by steam distillation at 140° and 100 mm. Hg.

Composition of charge mols per mol	Steam rate gm./min./ kilo of charge	Ethanolamine recovery % of charge
1 Oleic acid.....	.57	46.7
1 Ethanolamine.....		
1 Oleic acid.....	1.20	53.3
1 Ethanolamine.....		
1 Stearic acid.....	1.00	46.6
1 Ethanolamine.....		
1 Oleic acid.....	1.20	39.2
.8 Ethanolamine.....		
1 Oleic acid.....	1.20	57.2
.8 Ethanolamine.....		
.06 KOH.....		

TABLE III

Effect of KOH concentration on ethanolamine recovery by steam distillation at 120° and 14–35 mm. Hg. pressure

Composition of charge mols per mol	Steam rate gm./min./ kilo of charge	Ethanolamine recovery % of charge
1 Oleic acid.....	4.2	51.9
.815 Ethanolamine.....		
1 Oleic acid.....	8.0	66.8
.815 Ethanolamine.....		
.022 KOH.....	7.1	74.2
1 Oleic acid.....		
.815 Ethanolamine.....	7.2	79.9
.044 KOH.....		
1 Oleic acid.....	7.2	79.9
.815 Ethanolamine.....		
.110 KOH.....		

It has been shown that amounts of alkali less than 0.2 mol per mol of fatty acids are very effective in the recovery of free alkylolamine. Larger amounts may be used to accomplish the

same result. However, excesses are to be avoided as they necessitate other steps such as an acid treatment to recover the fatty acid (from the residues after alkylolamine removal).

5 The free fatty acid, remaining after alkylolamine removal, may be recovered from the distillation residues by steam distillation at an elevated temperature and at reduced pressures.

10 The data given in Tables I, II and III are designed to indicate, respectively, the minimum water requirements for the hydrolysis of alkylolamine soaps, the effect of small increases of water (over these minimum requirements) on alkylolamine recovery and the effect of alkali concentration on alkylolamine recovery. It has been found that alkylolamine recovery is dependent, under conditions where the hydrolysis of the soaps become possible, upon the suppression of amidization of the fatty acid. The data in Tables II and III demonstrate the effect of small increases of steam and small amount of alkali in suppressing amidization and effecting, therefore, increased ethanolamine recovery. With large amounts of steam, a substantially complete recovery of ethanolamine may be obtained. For example, in a distillation of neutral ethanolamine soap of cottonseed fatty acids with steam at approximately 60 gm. per min. per kilo of charge, with a starting temperature of 55° C. and an end temperature of 160°, at a pressure equal to the vapor pressure of water at 15° C., and continuation of the distillation until fatty acids congeal in the condenser, a 97.2% recovery of the ethanolamine was obtained.

35 It should be noted that the examples given represent the extremes between minimum steam requirements for the hydrolysis and a large excess of steam, using laboratory equipment. As is well-known, distillations of this type may be effected with much greater efficiencies in commercial equipment, for many devices operating to obtain improved contact between material and steam then may be used which could not be adapted to small laboratory equipment. Therefore the example of a 97.2% recovery of ethanolamine with steam alone should not be taken as specifying the use of excessive amounts of steam such as 60 gm. per min. per kilo of charge, but that a substantially complete recovery of ethanolamine may be obtained with the use of amounts of steam between say 5 to 60 gm. per kilo of charge in well designed commercial vacuum-steam distillation equipment. The amount of steam necessary to effect a substantially quantitative recovery of alkylolamine is first, the minimum amount necessary to effect hydrolysis, plus the amount necessary to prevent or suppress amidization (which may be offset by addition of alkali) plus an amount of steam which may be considered as a constant for the distillation equipment. The latter is dependent upon arrangements in the apparatus which tend toward intimate contact between ample volumes of steam and material being decomposed. Such devices are lacking in laboratory equipment and make the consumption of excessive amounts of steam necessary.

70 The alkylolamine soaps may be considered as pure compounds resulting from the interaction of an individual alkylolamine with an individual fatty acid or may comprise mixtures which can be obtained by the interaction of several alkylolamines with an individual fatty acid, by the interaction of an individual alkylolamine with several fatty acids, or by the interaction of several alkylolamines with several fatty acids.

The alkylolamines may be considered as ammonia substitution compounds in which one or more of the hydrogen atoms of the ammonia or partially substituted ammonia molecule are replaced by a corresponding number of hydroxylated alkyl groups which may or may not be further substituted. The term "alkylolamine" is intended to embrace the primary, secondary and tertiary alkylolamines of which monoethanolamine, methyl monoethanolamine, and dimethyl monoethanolamine may be considered as the first members as the corresponding methanol compounds do not exist. The homologous propanolamines, butanolamines, pentanolamines may be also recovered from their soaps.

15 The fatty acid component of the soap may be a saturated carboxylic acid as palmitic acid, stearic acid, etc. or may comprise an unsaturated carboxylic acid as oleic acid, elaidic acid, etc. Further, acids as hydnocarpic, chaulmoogric acid, etc. may be regarded as cyclic substituted fatty acids and are contemplated when reference is had to a "fatty acid". Polycarboxylic acid components may comprise the higher malonic homologues such as adipic, pimelic, suberic, azelaic, sebacic.

20 While we have in the foregoing described in some detail the preferred embodiment of our 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 which we have advanced as to the reasons for 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 our intention to claim all novelty inherent therein as broadly as is possible in view of the prior art.

We claim as our invention:

1. The process for the recovery of free alkylolamine from its compound with a fatty carboxylic acid which comprises liquefying said compound by the application of heat and distilling to separate the alkylolamine from the fatty carboxylic acid.
2. The process for the recovery of free alkylolamine from its compound with a fatty carboxylic acid which comprises subjecting said compound to a steam-distillation whereby the alkylolamine is recovered from the fatty carboxylic acid.
3. The process for the recovery of free alkylolamine from its compound with a fatty carboxylic acid which comprises subjecting said compound to a steam distillation under subatmospheric pressure whereby the alkylolamine is recovered.
4. The process for the recovery of free alkylolamine from its compound with a fatty carboxylic acid which comprises subjecting said compound to a distillation under subatmospheric pressure with an amount of steam at least sufficient to prevent the substantial dehydration of the compound whereby the alkylolamine is recovered.
5. The process for the recovery of free alkylolamine from its compound with a fatty carboxylic acid which comprises subjecting said compound to a distillation under subatmospheric pressure with an amount of steam in excess of the stoichiometric amount required to hydrolyze all of the compound present in the distillation unit at any one time whereby the alkylolamine is recovered.
6. The process for the recovery of free alkylolamine from its compound with a fatty carboxylic

acid which comprises subjecting it to a steam distillation at a subatmospheric pressure in the presence of a compound of an alkali-forming metal.

7. The process for the recovery of free alkylol-
amine from an alkylolamine extract obtained from
oils, fats and waxes of the ester type which com-
prises subjecting the alkylolamine extract to a
steam distillation at subatmospheric pressure in
the presence of a compound of an alkali-forming
metal.

8. The process for the recovery of free alkylol-
amine from an alkylolamine extract obtained
from oils, fats and waxes of the ester type which
extract contains alkylolamine in the free and
combined state which comprises distilling off sub-
stantially all of the free alkylolamine and then
subjecting the residue to a steam distillation at a
subatmospheric pressure whereby the combined
alkylolamine is set free and recovered.

9. The process for the recovery of free mono-
ethanolamine from its compound with a fatty
carboxylic acid which comprises subjecting said
ethanolamine compound to steam distillation at
subatmospheric pressure.

10. The process for the recovery of free mono-
ethanolamine from its compound with a fatty
carboxylic acid which comprises subjecting said
ethanolamine compound to a steam distillation at
subatmospheric pressure in the presence of a
compound of an alkali-forming metal.

11. The process for the recovery of free mono-
alkylolamine from a monoalkylolamine extract
obtained from oils, fats, and waxes of the ester
type which comprises subjecting said monoal-
kylolamine extract to a steam distillation at sub-
atmospheric pressure in the presence of a com-
pound of an alkali-forming metal.

12. The process for the recovery of free mono-
alkylolamine from a monoalkylolamine extract

obtained from oils, fats and waxes of the ester
type which comprises subjecting said monoalkyl-
olamine extract to a steam distillation in the pres-
ence of a compound of an alkali-forming metal.

13. The process for the recovery of free mono-
alkylolamine from a monoalkylolamine extract
obtained from oils, fats and waxes of the ester
type which comprises subjecting said mono-
alkylolamine extract to a steam distillation at
subatmospheric pressure in the presence of an
alkali-metal compound.

14. The recovery of free alkylolamine from an
alkylolamine compound of a fatty carboxylic acid
which comprises subjecting said compound to a
steam distillation operation in the presence of a
compound of an alkali-forming metal.

15. The recovery of free alkylolamine from an
alkylolamine compound of a fatty carboxylic acid
which comprises subjecting said compound to a
steam distillation operation at subatmospheric
pressure in the presence of a compound of an
alkali-forming metal.

16. The recovery of free alkylolamine from an
alkylolamine compound of a fatty carboxylic acid
which comprises subjecting said compound to a
steam distillation operation in the presence of a
basic alkali metal compound.

17. The recovery of free alkylolamine from an
alkylolamine compound of a fatty carboxylic acid
which comprises subjecting said compound to a
steam distillation operation in the presence of an
alkali metal salt of a carboxylic acid.

18. The recovery of free alkylolamine from an
alkylolamine compound of a fatty carboxylic acid
which comprises subjecting said compound to a
steam distillation operation in the presence of an
alkali metal salt of a fatty acid.

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