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ETHENOXY N-MONOETHANOLAMIDES OF TALL OIL

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This invention relates to a novel class of nonionic surface-active agents and to methods for the preparation thereof. More specifically, the invention is directed to the production of ethenoxy N-monoethanolamides of tall oil acid mixtures, these being new compositions of matter having good wetting and detergent properties.

As is well known, ordinary tall oil is a mixture consisting predominantly of abietic or rosin acid and higher fatty acids most of which are of about 16–18 carbon atoms together with about 5–10% of unsaponifiables. Mixtures of this type containing from about 30% to 60% by weight of abietic acid and about 40% to 60% of fatty acids represent the ordinary tall oil of commerce. So-called crude tall oils contain, in addition to the indicated quantities of abietic and fatty acids, about 5–7% of unsaponifiables, most of which are lignins and sterols. Refined tall oils are obtained from these crudes by any of several purification methods; in most cases the crude is extracted with a solvent or subjected to vacuum steam distillation or both. When distillation processes are employed the ratio of fatty acids to abietic acid can of course be altered by fractionation, and compositions containing as little as 20% of abietic acid and as much as 80% of higher fatty acids are commercially available. These mixtures constitute the starting materials for use in preparing the novel compositions of the present invention.

We have prepared monoethanolamides of acids from crude tall oil and refined tall oil, and have condensed these monoethanolamides with ethylene oxide. The resulting ethenoxy N-monoethanolamides have been evaluated as wetting agents and as detergents for cotton and woolen textiles. By this means we have found that ethenoxy N-monoethanolamides of the class described containing from about 4 to about 50 mols of combined ethylene oxide per mol of monoethanolamide possess good softening, wetting and detergent properties and can be used commercially as nonionic surface-active agents for these purposes.

The importance of this discovery will be apparent to those familiar with the wetting agents and detergents now on the market. Most of these are obtained either from fatty acid triglycerides, which are highly strategic materials in war time, or from coal tar or petroleum derivatives such as benzene or toluene which require high temperature sulfonation procedures in acid resistant equipment. The present invention, on the other hand, employs raw materials which are very cheap and abundant and require no specialized or acid-proof manufacturing equipment. On the contrary, crude tall oil is the cheapest and most abundant known source of organic acids, and it is most remarkable that high grade wetting agents and detergents can be prepared from such a crude and readily available material.

Although useful wetting agents and detergents are obtainable from ethenoxy N-monoethanolamides of tall oil acids when these compounds contain from 4 to about 50

ethenoxy groups per molecule, we find that improved detergency is obtained in those compounds containing from about 8 to about 25 mols of combined ethylene oxide. Thus, for example, the detergency of ethenoxy derivatives of crude tall oil and abietic acid ethanolamides on wool and on cotton percale at a concentration of 0.25% active detergent is given in the following table:

CRUDE TALL OIL ETHANOLAMIDE

Mols Combined Ethylene Oxide	Detergency On—	
	Cotton	Wool
4	−2	0
6		8.7
8	29.0	57.8
10	37.1	47.3
12	56.6	
16	57.0	14.3
20	50.8	6.5
30	30.2	

The detergency values given above represent the percent return to original reflectance of samples impregnated with a "standard soil" composed of carbon black, lard and hydrocarbon oil after three 20-minute soapings at 130° F. in accordance with the standard A. A. T. C. C. method. The results show that a high degree of detergency is possessed by those products containing from 8 to 30 mols of combined ethylene oxide per mol of ethanolamide, but the product containing only 4 mols of combined ethylene oxide had little or no detergency. The table also shows that maximum detergency on cotton is obtained when condensation products containing from 12 to about 20 mols of combined ethylene oxide are used.

The method of preparing our new compositions consists generally in the steps of first reacting the desired tall oil mixture with monoethanolamine in substantially equimolecular quantities at temperatures sufficiently high to produce the monoethanolamide, followed by condensation with ethylene oxide.

We find that the best method of producing the N-monoethanolamides of tall oil fatty acid-abietic acid mixtures consists in preparing a solvent-free mixture of the reagents containing an equimolecular quantity plus a small excess of monoethanolamine on the order of 3–10% and heating this mixture at its boiling point (140–200° C.) at atmospheric pressure while condensing and removing the water formed by the reaction. After the water evolution has ceased the heating is continued for an additional 1–2 hours, or until titration of a sample of the reaction shows a free acid content of less than 3%, calculated as abietic acid. A vacuum is then applied to the reaction mixture and the excess monoethanolamine is distilled from the product.

Condensation of ethylene oxide with the monoethanolamides prepared as described above is preferably carried out in the presence of an alkaline catalyst at elevated temperatures on the order of 100–150° C. and, if desired, under the corresponding superatmospheric pressures. Although any suitable alkaline catalyst may be employed such as sodium alcoholate, sodium or potassium hydroxide, aliphatic amines of 2–4 carbon atoms such as mono- or diethylamine, propylamine or butylamine, or even in some cases an excess of monoethanolamine, we prefer to employ sodium hydroxide as the catalyst as it is both cheap and efficient. The ethenoxy derivatives of the N-ethanolamides of crude and refined tall oils are most conveniently prepared by adding about 5 mol percent of the catalyst, heating the monoethanolamide to about 120° C. in a reaction vessel provided with an agitator and surmounted by a condenser, and introducing the desired

quantity of ethylene oxide at a reaction temperature of 120–150° C. and at such a rate as to maintain a slow reflux. After the ethylene oxide introduction is completed the reaction mixture is preferably agitated for an additional ½ hour to ensure completion of the addition reaction.

The new condensation products of our invention vary in form from liquids of low water solubility to soft, waxy solids which give clear aqueous solutions. The compounds prepared from crude and purified tall oils and which contain from 8 mols or less to about 16 mols of combined ethylene oxide are heavy syrups which vary in color from dark brown to light amber, depending on whether crude or purified tall oil is used. Those products containing 16 to about 30 mols of combined ethylene oxide are dark brown pastes. The products containing from 30–50 mols and more of combined ethylene oxide are solids.

The invention will be described in greater detail by the following examples which show specific embodiments thereof. It should be understood, however, that these examples are given primarily for purposes of illustration and not by way of limitation, and that variations and substitutions of equivalents may be resorted to within the scope of the appended claims.

EXAMPLE 1

Preparation of N-ethanolamides

A number of commercially available tall oil compositions were assembled and their physical and chemical characteristics were obtained from the supplier. In addition to the distilled compositions sold commercially as "Farac" two pure artificial mixtures were prepared by mixing abietic acid with distilled tall oil fatty acids. These compositions, together with their analyses, are listed in the following table:

TABLE I.—TALL OIL COMPOSITIONS

Composition No.	Supplier's Designation	Equivalent Weight	Acid No.[1]	Percent Fatty Acids [1]	Percent Resin Acids	Iodine No.[1]	Percent Unsaponifiable	Appearance
1	Mixture I [2]	292		24	74			Light amber paste.
2	Arizona Crude I	342	168	43.8	48.5	175	6.9	Dark brown mixture.
3	Arizona Crude II	349	174	44.7	47.7	175	6.9	Do.
4	Arizona Crude III	337	168	47.9	44.4	172	7.0	Do.
5	Mixture II [2]	302		48.1	48.8			Light amber mixture.
6	Unitol	343	165	45–51	43–48	155–175	7.0	Do.
7	Ligro	345	160–170	45–50	42–48	190–210	6–9	Do.
8	Indusoil		180–185	57–62	33–36		5–7	Light brown mixture.
9	Farac I	296	189	68	30		Refined	Golden orange syrup.
10	Farac II	294	191	80	18–20		do	Do.

[1] Reported by supplier.
[2] Made by mixing tall oil abietic acid and distilled tall oil fatty acids.

The production of N-monoethanolamides from these crude and refined tall oil and other mixtures of abietic and fatty acids was not easy. When volatile solvents of the type of xylene and solvent naphtha were used the fatty acid ethanolamides were formed, but abietic acid ethanolamide formation was incomplete. This was due to the fact that as the internal temperature of the reaction mixture was increased the ethanolamine and water produced by the reaction were distilled.

A reaction procedure capable of producing a substantially complete amide formation, without the necessity of a large excess of monoethanolamine, was finally developed. The tall oil or other abietic acid-fatty acid mixture and an equimolecular quantity of ethanolamine plus a 5% excess were charged into a reaction vessel fitted with an agitator and a distilling tube equipped with a reflux condenser. The mixture, with continuous agitation, was heated at about 200° C. until no more water distilled. The heating was then continued at the same temperature for one additional hour. A sample was then withdrawn and titrated in aqueous alcohol with 0.1 N sodium hydroxide solution. When the reaction product contained less than 3% of acid, calculated as abietic acid, a vacuum was applied and the excess monoethanolamine was distilled from the product. All the N-ethanolamides listed in the following table were prepared by this procedure and contained less than 3% of free acid.

TABLE II.—N-ETHANOLAMIDES FROM TALL OILS

Tall Oil No. (From Table I)	Tall Oil		Monoethanolamine, Mols	Reaction Time, Hrs.	Percent Yield	Product No.	Appearance
	Grams	Mols					
1	277	0.95	1.05	7.0	99	2	Greenish amber glass.
2	1,026	3	3.15	4.0	98	3	Viscous syrup.
3	1,000	2.87	3.15	5.0	99	4	Do.
4	1,350	4.00	4.4	6.5	98	5	Do.
5	260	0.9	1.0	5.5	99	6	Brown paste.
6	675	1.97	2.10	5.0	97	7	Semi-solid.
7	1,035	3.0	3.15	4.0	98	8	Do.
8	909	3.0	3.3	7.0	97	9	Brown paste.
9	1,184	4.0	4.2	5.5	98	10	Tan wax.
10	1,030	3.5	3.68	4.5	98	11	Do.

These products were condensed with varying quantities of ethylene oxide to produce the corresponding ethenoxy N-ethanolamides, as will be described in subsequent examples.

EXAMPLE 2

Ethylene oxide condensation products of monoethanolamides of crude tall oils were prepared by the following procedure. The N-ethanolamide prepared as described in Example 1, and having the composition shown in Table II, was charged into a reaction flask together with 5 mol percent of 40% aqueous sodium hydroxide solution. The reaction flask was fitted with a stirrer, an ice-water cooled condenser and a gas inlet tube. The ethanolamide was heated to 120° C. and the desired amount of ethylene oxide was added at a reaction temperature of 120–140° C. at such a rate as would maintain a slow reflux, the reflux condenser being open to atmospheric pressure. The reaction was exothermic and very little external heat was required to maintain a temperature of 130–140° C. in the reaction vessel. When the desired ratio of ethylene oxide to tall oil N-monoethanolamide was approached the flow of ethylene oxide gas was interrupted and the reaction mixture was stirred for ½ hour at 120° C. and weighed. Sufficient ethylene oxide was then added slowly to produce the theoretical weight of product and the heating and stirring were continued until this final increment was combined.

By this procedure it was possible to combine as much

as 50 mols of ethylene oxide for each mol of tall oil N-ethanolamide. The quantities of the reagents used, the reaction times and the appearance of the products are listed in Table III. The products obtained are unusual in that those containing a relatively high molar ratio of combined ethylene oxide (20–50 mols and more) are solids whereas the products having a lower ratio of combined ethylene oxide are liquids or pastes. This is the reverse of the results obtained when monoethanolamides of relatively pure abietic acid are used.

TABLE III.—ETHENOXY N-ETHANOLAMIDES OF CRUDE TALL OILS

Product No.	Ethanolamide		Ethylene Oxide		Reaction Time, Hrs.	Appearance of Product
	No. (Table II)	Mols Used	Grams Used	Mol. Ratio (x:1)		
1	3	1.0	89	2.0	2.5	Dark green-brown liquid.
2	3	0.6	66	2.5	2.5	Do.
3	3	0.5	66	3.0	3.25	Do.
4	3	0.9	159	4.0	4.0	Do.
5	4	0.75	132	4.0	6.0	Do.
6	3	0.8	211	6.0	7.0	Do.
7	3	0.83	295	8.0	7.0	Do.
8	4	0.66	232	8.0	6.5	Do.
9	3	0.77	305	9.0	7.3	Do.
10	3	0.74	325	10	8.5	Do.
11	4	0.68	299	10	7.0	Do.
12	3	0.7	339	11	7.5	Dark green-brown syrup.
13	3	0.65	345	12	7.5	Do.
14	4	0.53	278	12	9.0	Do.
15	4	0.4	282	16	8.5	Dark green-brown paste.
16	3	0.55	386	16	10.0	Do.
17	2	0.55	388	16	9.0	Do.
18	7	0.58	408	16	9.5	Do.
19	6	0.65	458	16	10.0	Do.
20	3	0.48	422	20	9.0	Dark green-brown solid.
21	4	0.2	176	20	9.5	Do.
22	2	0.6	528	20	13.5	Do.
23	7	0.35	308	20	9.5	Do.
24	6	0.3	264	20	10.0	Do.
25	2	0.28	295	24	10.5	Do.
26	3	0.20	264	30	9.5	Dark brown solid.
27	3	0.23	503	50	15.0	Light brown solid.

EXAMPLE 3

Following the reaction method described in Example 2, N-ethanolamides of refined tall oils were reacted with from 4 mols to 50 mols of ethylene oxide. The quantities of reagents, the reaction times, and the appearance of the products are shown in the following table.

TABLE IV.—ETHENOXY N-ETHANOLAMIDES OF REFINED TALL OILS

Product No.	Ethanolamide		Ethylene Oxide		Reaction Time, Hrs.	Appearance of Product
	No. (Table II)	Mols Used	Grams Used	Mol. Ratio (x:1)		
31	1	0.6	212	8.0	6.5	Light amber syrup.
32	9	0.9	317	8.0	7.5	Dark brown syrup.
33	9	0.7	370	12	9.0	Dark brown paste.
34	5	0.55	291	12	5.0	Light amber syrup.
35	1	0.35	245	16	8.5	Do.
36	10	0.3	211	16	5.5	Dark brown paste.
37	9	0.6	423	16	10.0	Do.
38	8	0.55	387	16	10.0	Do.
39	10	0.5	440	20	12.0	Do.
40	9	0.5	440	20	12.0	Do.
41	8	0.25	202	20	12.0	Do.
42	9	0.35	462	30	11.5	Light brown solid.
43	9	0.25	550	50	14.0	Do.

This is a division of our copending application Serial No. 177,776 filed August 4, 1950, now abandoned.

What we claim is:

1. Ethenoxy N-monoethanolamides of tall oil acid mixtures containing about 80% to 20% by weight of fatty acids of 16–18 carbon atoms and about 20% to 75% by weight of abietic acid, said N-monoethanolamide derivatives containing about 4 to 50 ethenoxy groups per molecule.

2. Ethenoxy N-monoethanolamides of tall oil acid mixtures according to claim 1 and containing from about 8 to 25 ethenoxy groups per molecule.

3. Ethenoxy N-monoethanolamides of crude tall oil acids containing about 30% to 60% by weight of abietic acid, about 40% to 60% of fatty acids of 16–18 carbon atoms and about 5–10% of unsaponifiables, said N-monoethanolamide derivatives containing from about 4 to 25 ethenoxy groups per molecule.

4. A method of producing ethenoxy N-monoethanolamides of tall oil acid mixtures which comprises preparing a mixture of tall oil acids containing about 80% to 20% by weight of fatty acids of 16–18 carbon atoms and about 20% to 75% by weight of abietic acid and an equimolecular quantity plus a 3–10% excess of monoethanolamine, heating said mixture at about 200° C. while condensing and removing water, continuing the heating until the reaction product contains less than 3% of acid calculated as abietic acid, applying a vacuum and distilling excess monoethanolamine from the product, adding an alkaline condensation catalyst and introducing ethylene oxide while maintaining an internal temperature of about 100°–150° C., and continuing the ethylene oxide introduction until from 4 to about 50 mols per mol of tall oil acid N-monoethanolamide has reacted.

5. A method of producing ethenoxy N-monoethanolamides of tall oil acid mixtures which comprises preparing a solvent-free mixture of tall oil acids containing about 30% to 60% by weight of abietic acid and about 40% to 60% fatty acids of 16–18 carbon atoms and an equimolecular quantity plus a 3–10% excess of monoethanolamine, heating said mixture at its boiling point at atmospheric pressure while condensing and removing water, continuing the heating at approximately the same temperature after water evolution has ceased until the reaction product contains less than 3% of acid calculated as abietic acid, applying a vacuum and distilling excess monoethanolamine from the product, adding an alkaline condensation catalyst and introducing ethylene oxide while maintaining an internal temperature of 100–150° C., and continuing the ethylene oxide introduction until from 8 to about 50 mols per mol of tall oil acid N-monoethanolamide has reacted.

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