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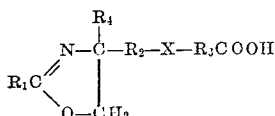
EXAMPLE I

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**FATTY OXAZOLINE SURFACTANTS AND A
 PROCESS FOR THEIR PREPARATION**
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 9 Claims. (Cl. 260—307)

The present application relates to novel surfactants, and it particularly relates to a high molecular weight fatty oxazoline surfactant having high effectiveness in a wide variety of acidities and alkalinities.

It is among the objects of the present invention to provide a highly effective detergent which will maintain a high fine bubble foam over long periods of time in textile processing, without deterioration or loss of effective foam properties and without decreasing the volume of the foam regardless of the change in pH, whether it become strongly acid or become strongly alkaline, regardless of the salts that may be present or the pH of the bath in which the foam is being produced, and which will have unusually high corrosive inhibiting properties and which may be widely utilized in metal processing such as electroplating, radiator liquids, and coolants for metal working processes.

The preferred oil and water soluble surface active compounds have the following general formula:



where R_1 represents a hydrocarbon group containing from 7 to 21 carbon atoms, R_2 , R_3 and R_4 are short chain hydrocarbon groups containing 1 to 6 carbon atoms, and X represents oxygen taking the form of an ether.

The alkali metal salts of these fatty complexes are water soluble and are versatile adjuncts in such diverse fields as cosmetic and shampoo preparations, industrial and household cleaners, detergent and scouring agents for processing textiles, emulsifiers and corrosion inhibitors.

These compounds are anionic in basic solution and cationic in acid solution; and in the range of pH 5.0 to 9.0, they exhibit both cationic and anionic properties, being truly amphoteric.

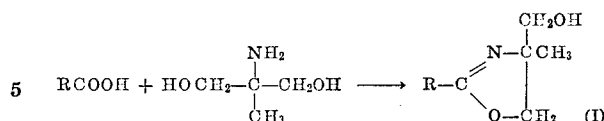
As fatty oxazoline nitrogen carboxylic acids, they are soluble in polar and non-polar solvents, and may be neutralized with amines to form oil soluble salts. Both the carboxylic acids and their amine salts are excellent film forming compounds, exhibiting outstanding corrosion inhibiting properties.

They are effective as petroleum additives, detergents, asphalt wetting and anti-stripping agents and biocidal agents.

To give the chemical equations which are involved in making the above compounds, coconut fatty acid, oleic fatty acid, tall oil fatty acid, stearic acid or sebacic acid are combined starting at 300° F. and increasing up to 450° F. with amino hydroxy compounds which contain at least one primary amino group and two or more hydroxy groups as set forth below:

2-amino-2-methyl-1,3-propanediol
 2-amino-2-ethyl-1,3-propanediol
 tris (hydroxymethyl)aminomethane

The reaction between the fatty acid and the amine compound is represented as follows.



in which R is an alkyl group having 8 to 22 carbon atoms and the amine is 2-amino-2-methyl-1,3-propanediol.

Then to one mol of these oxazoline compounds is added in dropwise fashion one mol of an acrylic compound, such as methyl acrylonitrile or methyl acrylate at a temperature of 100° to 150° F.

The acrylic compounds should desirably have one unsaturated double bond in the aliphatic chain and contain from one to four carbon atoms, and they have terminal —CN or —COOH groups.

They also have methyl, ethyl or propyl groups either as terminal groups or as side chains.

Desirably, a three-neck flask is utilized with a condenser connected to one neck, an agitator connected through the other neck and a funnel or thermometer is connected in the third neck.

The acrylic compound is dropped for about one hour, followed by heating for about one and one-half to three hours at 180° to 230° F. with the final processing and elevated temperature treatment taking place at 15 to 18 inches vacuum.

After this combination, with the acrylic compounds, has been completed, the reaction product is treated with equimolar proportions of caustic soda in 25% concentration and at temperature of about 200° F. for about one and one-half to three hours.

In these compounds, the R group is desirably derived from oleic acid, tall oil fatty acid or coconut fatty acid and less desirably from sebacic acid.

They are surprisingly effective as detergents, emulsifiers and corrosion inhibitors in very small concentrations. They may be used in shampoos, in soaps, in emulsion polymerization, as oven cleaners, as industrial cleaners, in electroplating, in cosmetics, for textile scouring, dyeing and lubrication, in sanitizers, in paints, and in leather treating.

The high molecular weight fatty oxazolines are formed by the reaction of carboxylic acids, esters, acid chlorides and acid anhydrides containing 8 to 32 carbon atoms in the molecule with alkylol amines as monoethanolamine, diethanolamine, 2-amino-2-methyl-1,3-propanediol and tris(hydroxymethyl)-aminomethane.

EXAMPLE II

The long chain oxazolines are manufactured from 1,2-hydroxyamine by acylation and cyclodehydration.

Into a two-liter three-neck flask equipped with moisture trap, condenser, stirrer and thermometer was charged 282 grams of oleic acid and 120 grams (1.1 mol) of 2-amino-2-methyl-1,3-propanediol.

The contents was heated with agitation to 150° C. and held at this temperature until one mol (18 milliliters) of water was obtained in the moisture trap. The temperature was then raised to 200° C. and maintained at this temperature, until another mol (18 milliliters) of water was obtained in the moisture trap at which time the cyclodehydration step was complete and the liquid oxazoline analyzed 92% 2-oleyl-4-methyl-4-hydroxymethyl oxazoline.

The moisture trap was removed and the flask rearranged

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for reflux, and cooled to 50° C. Five milliliters of a 25% sodium methylate solution were added as a catalyst for the addition reaction and then one mol of methyl acrylate was added slowly through a dropping funnel and the mixture stirred at 50°–70° C. for two hours.

Upon completion of the reaction, at which time analysis showed less than 1% residual methylacrylate, the 2-oleyl-4-methyl-4-methoxy methyl propionate oxazoline was a brown liquid, soluble in both polar and non-polar solvents.

200 grams of 20% sodium hydroxide was then added to the contents of the flask over a period of one hour with stirring and then the temperature raised to 95° C. for two hours when test samples showed the saponification to be complete. The resulting 2-oleyl or heptadecenyl-4-methyl-4-methoxy sodium propionate oxazoline solution was then diluted to 33% active matter.

EXAMPLE III.—SUBSTITUTED OXAZOLINES

In making 2-undecyl-4,4'-bis(methoxysodium propionate)-2-oxazoline, the equipment necessary to prepare this derivative is the same as described in the previous example.

Lauric acid and tris(hydroxymethyl) amino methane are reacted in equimolar quantities.

The temperature employed in carrying out the reaction for the amide formation is 150° C. to 180° C. after which the temperature is increased to 215° C. for the cyclodehydration process to form the oxazoline ring.

The oxazoline was cooled to 50° C. and 2 mols of methyl acrylate or acrylonitrile containing 0.1% NaOCH₃ was added over a period of one hour. The temperature was then slowly raised to 100° C. and held there until tests showed all the methyl acrylate or acrylonitrile had reacted to form the bis(methoxypropionitrile) or equivalent derivative.

Two mols of caustic soda (50% aqueous solution) were then added and the reaction product saponified to the carboxylic acid-sodium salt.

The methyl acrylate or acrylonitrile adducts of these long chain oxazoline nitrogen compounds are oil soluble surfactants. They are dispersible in water, lowering the surface tension of water to 30 dynes/centimeters at 0.1 concentration.

The compounds are completely soluble in alcohols, ketones, ethers, and aromatic and aliphatic hydrocarbons. They act as good corrosion inhibitors, filming compounds, dewatering agents and show selective fungicidal and biocidal activity, either by themselves or in the form of the acetate of hydrochloride salt.

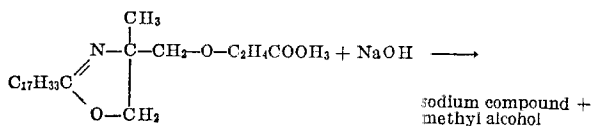
The water soluble alkali propionates of these long chain oxazoline nitrogen compounds have been found to be detergents in the wet processing of textiles and leather, excellent wetting and emulsifying agents, dyeing assistants, and finishing compounds.

As petroleum additives, they serve as corrosion inhibitors for aqueous salt and acid solutions, filming compounds on metals, dewatering agents, in the mining industry as flotation agents, frothing compounds and selective mineral wetting agents.

In the pharmaceutical industry, these compounds offer combined detergency with germicidal properties.

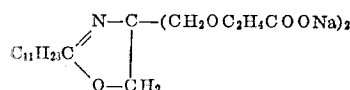
The alkanolic acids of these long chain oxazoline nitrogen compounds may be combined with amines to form both oil and water soluble emulsifiers with corrosion inhibiting properties.

EXAMPLE IV

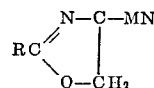


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EXAMPLE V



General Formula



Where a fatty acid group having 8 to 22 carbon atoms and where M or N or both are a



grouping and the remaining M or N is hydrogen or an alkyl having 1 to 6 carbon atoms.

In the process of producing the above identified surfactants, the following are the important steps:

- (a) Slow addition of the acrylate
 - (b) The use of methyl acrylate
 - (c) The temperature range from 140° to 212° F. or 60° C. to 100° C.
 - (d) The finishing operation at higher temperature
 - (e) The stripping of any excess
 - (f) The production of 98% yield.
- As additional examples:

EXAMPLE VII

An excellent scouring and softening agent for textiles was prepared by reacting methyl stearate with trishydroxymethyl amino methane at 150–200° C. to form the oxazoline derivative which was then reacted with two moles of ethyl acrylate (one mole for each available hydroxy group of the above oxazoline). The fatty dimethoxyethylpropionate oxazoline was saponified with two moles of NaOH dissolved in water to form a white paste containing 20% active matter.

A 1% solution of the above paste imparted a soft hand to nylon, Acrilan, a trademark for an acrylic fiber, cellulose acetate and other synthetic fibers. The chemical structure can be described as 2-heptadecyl-4,4'-bis (methoxy sodium propionate)-2-oxazoline.

EXAMPLE VIII

One mole of dimer acids (mol. wt. 560) was reacted with two moles of aminoethyl propanediol at 150–200° C. under 20 inches of vacuum.

The di-oxazoline formed was a yellow oil, soluble in alcohols, ketones and hydrocarbons. It was cooled to 60° C. and two moles of methyl acrylate were slowly added, the mixture was then raised to 90° C. and held at this temperature for three hours. The infrared spectrum of the resulting adduct showed a steep ether peak and almost the complete absence of the original hydroxy groups.

The sodium salt was obtained by pouring this product into two liters of water containing two moles of NaOH and stirred for one hour at 85° C. until the pH dropped to 9.0 and the final product was soluble in water.

The amine salts of this compound may be prepared by substituting low molecular weight alkyl amines, alkylol amines and ether amines (di-butyl amine, tri-propylamine, monoethanolamine and morpholine) in place of the NaOH in the saponification step.

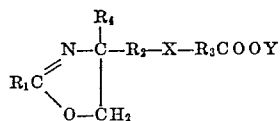
The amine salts of this derivative are soluble in alcohols, ethers, ketones, hydrocarbons such as kerosene and aromatic solvents such as toluene. They are excellent emulsifiers and exhibit outstanding filming properties as corrosion inhibitors.

Having now particularly described and ascertained the

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nature of the invention, and in what manner the same is to be performed, what is claimed is:

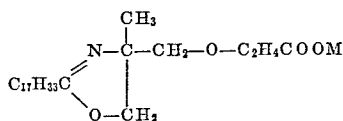
1. A fatty oxazoline surfactant having the formula



in which R_1 is selected from the group consisting of alkyl and alkenyl having 11 to 18 carbon atoms and R_2 , R_3 and R_4 are alkyl groups having 1 to 6 carbon atoms and X is a linkage consisting of an oxygen atom and Y is selected from the group consisting of hydrogen, alkali metal and a group of amines consisting of di-butyl amine, tripropylamine, monoethanolamine and morpholine.

2. The surfactant of claim 1, R_1 being a fatty acid radical selected from a group consisting of coconut fatty acid, oleic acid, tall oil fatty acid, stearic acid and sebacic acid.

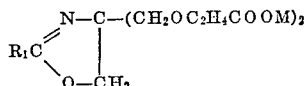
3. The surfactant of claim 1, consisting of



where M is selected from the group consisting of hydrogen and alkali metal and a low molecular weight amine selected from the group consisting of di-butyl amine, tripropylamine, monoethanolamine and morpholine.

4. The sodium salt of 4-carboxyethyloxymethyl-4-methyl-2-oleyl-2-oxazoline.

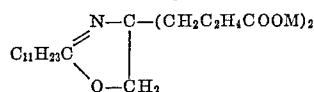
5. A surfactant consisting of



in which R_1 is selected from a group consisting of alkyl and alkenyl having 11 to 18 carbon atoms, and M is selected from the group consisting of hydrogen, alkali metal and a low molecular weight amine selected from the group consisting of di-butyl amine, tripropylamine, monoethanolamine and morpholine.

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6. The surfactant consisting of



where M is selected from the group consisting of hydrogen and alkali metal and a low molecular weight amine selected from the group consisting of di-butyl amine, tripropylamine, monoethanolamine and morpholine.

7. The disodium salt of 4,4-bis(carboxyethyloxymethyl)-2-undecyl-2-oxazoline.

8. The disodium salt of 4,4-bis(carboxyethyloxymethyl)-2-heptadecyl-2-oxazoline.

9. The process of making a surfactant in which a fatty acid having 7 to 21 carbon atoms is reacted with an amino compound selected from the group consisting of 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, tris(hydroxymethyl) aminomethane and 2-amino-1-butanol and in which 1 mol of said amino compound is combined with 1 to 2 mols of the fatty acid, first by heating under a low vacuum of 15 to 20 inches for about 1½ to 3 hours at 350° F. and then continuing at 450° F. under a high vacuum of 25 to 29 inches for 5 to 8 hours, and then adding drop by drop to the reaction mixture 1 mol of an acrylic compound selected from the group consisting of methyl acrylate, ethyl acrylate and acrylonitrile at a temperature of 100 to 150° F., said dropwise addition continuing for about 1 hour, then following by heating for about 1½ to 3 hours at 180° to 230° F. and increasing the vacuum to 15 to 18 inches and then treating the reaction mixture with caustic alkali.

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ALEX MAZEL, *Examiner*.

R. J. GALLAGHER, *Assistant Examiner*.