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3,555,041

IMIDAZOLINE SURFACTANT HAVING AMPHOTERIC PROPERTIES

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1 Claim

ABSTRACT OF THE DISCLOSURE

1-aminoethyl-2-imidazoline and 1-hydroxyethyl-2-imidazoline derivatives which are useful as surfactants.

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

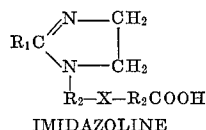
It is among the objects of the present invention to provide a high effective detergent which will maintain a high fine bubble foam over long periods of time in textile processing, without deterioration or loss of effective foam properties and without decreasing the volume of the foam regardless of the change in pH whether it be strongly acid or become strongly alkaline.

Another object is to provide novel procedure for making highly effective detergent materials of high foaming properties which will produce a very fine bubble stable foam in very small concentration and relatively great dilution regardless of the salts that may be present or the pH of the bath in which the foam is being produced.

Another object is to provide a novel high molecular weight fatty nitrogenous heterocyclic compound which in extremely small dilutions 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.

Still further objects and advantages will appear in the more detailed description set forth below, it being understood, however, that this more detailed description is given by way of illustration and explanation only and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

The preferred oil and water soluble surface active compounds are derived from the following ring compound:



where R_1 represents a hydrocarbon group containing from 7 to 21 carbon atoms, R_2 is a short chain hydrocarbon group containing 1 to 6 carbon atoms, and X represents either oxygen or nitrogen taking the form of ether or secondary or tertiary amine linkages.

The alkali metal salts of these imidazoline 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 imidazoline 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

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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.

The synthesis involves the reaction of long chain imidazoline compounds containing amino alkyl or hydroxy alkyl substituent groups with such adduct forming compounds as acrylonitrile, methyl acrylate and beta-propiolactone. In the case of the beta-lactones, the carboxylic acid is formed directly; the nitrile and acrylate adducts are saponified in basic media to form the alkali metal salt.

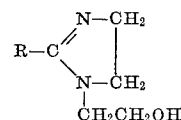
The preferred adduct compound is methyl acrylate and it is much more satisfactory.

In the preferred form of the invention, there are provided at least two to four $-\text{CH}_2-$ groups between the amine and the amide groups, and the amine should initially be a primary or secondary amine. Then the primary or secondary amine group is finally modified to form a heterocyclic tertiary amine.

The basic steps involve first reacting a fatty polyamine, such as an aminoethylethanolamine, in the amount of 1 to $1\frac{1}{2}$ mols with one mol of the fatty acid having 11 to 18 carbon atoms at a temperature of 250 to 450° F., desirably under vacuum which increases.

A preferred aliphatic polyamine is aminoethylethanolamine.

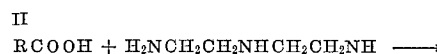
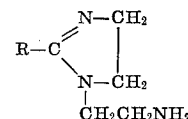
The typical first step equation is the following:



in which R is derived from a fatty acid having 8 to 22 carbon atoms, such as coconut, oleic, tall oil, stearic or sebacic fatty acid and the amine is aminoethylethanolamine.

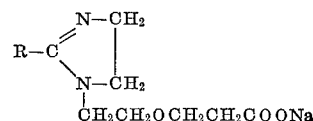
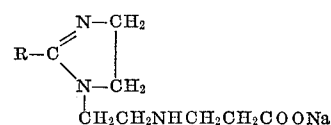
As an alternative procedure, it is possible to use an aliphatic polyamine such as diethylene triamine, tetraethylene pentamine or triethylene tetramine.

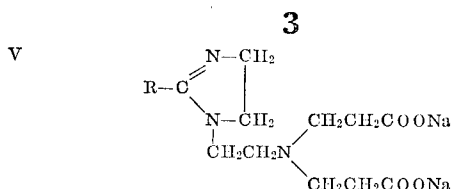
Desirably in this reaction, one mol of polyamine is combined with one or two mols of the fatty acid, first by heating under a low vacuum of 15 to 20 inches for about one and one-half to three hours at 350° F. and then continuing at 450° F., under a high vacuum of 25 to 29 inches for five to eight hours. The typical equation is:



in which R is a fatty acid as in Equation I and the amine used is diethylene triamine.

The final compounds are heterocyclic compounds of the general formulations as given below:





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

They also may 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 preferred methyl acrylate compound is added over a period of 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 methyl acrylate compound, 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.

The long chain imidazolines may be synthesized by the reaction of fatty acids with substituted 1,2-diamines or polyethylene-polyamines; the reaction of fatty acid chlorides with polyamines; fatty nitriles with polyamines or fatty amides with 1,2-diamines.

Imidazolines may also be synthesized by the reaction of di-basic acids such as sebacic acid or dimerized fatty acids with diethylene triamine or aminoethylethanolamine.

Bis-imidazolines may be synthesized from two mols of fatty acid and one mol of tetraethylene pentamine or pentaethylene hexamine.

EXAMPLE VI

Imidazoline derivative

Into a one liter three-necked flask equipped with stirrer, Stark-Dean Water Trap and thermometer was placed 210 grams of coconut fatty acids (1 mol) and 115.5 grams of aminoethylethanolamine (1.1 mol). The flask was heated to 100° C. and then 100 milliliter xylol added.

Heating was continued until at 140° C. the water of reaction and xylol formed an azeotrope and distilled into the trap where the water separated and the xylol returned to the reaction mass.

The temperature was held at 140–150° C. for two hours and then raised to 180° C. over a period of two hours. At this time 36 milliliters (2 mols) of water has collected in the trap, and the reaction to form 1-hydroxyethyl-2-undecyl imidazoline was complete. The xylol was stripped from the reaction mass under vacuum leaving a clear yellow liquid which analyzed 94% yield of imidazoline.

The flask containing the imidazoline was cooled to 60° C., Stark-Dean Water Trap removed and replaced with a reflux condenser and dropping funnel.

To the stirred liquid was added 94.6 grams (1.1 mols) of methyl acrylate slowly through the dropping funnel over a period of one hour and then the temperature gradually raised to 100° C. and held at this temperature for an additional two hours and at the end of this period, the excess methyl acrylate was stripped off under vacuum leaving a yield of 98% adduct formation.

The resulting 1-(ethoxy-methyl propionate), 2-undecyl-imidazoline was a clear yellow liquid with a mild fatty odor.

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40 grams (1 mol) NaOH was dissolved in 300 milliliters water and slowly added to the fatty imidazoline adduct at 175° C. over a period of one hour. The saponification of the methyl ester was almost simultaneous with the addition of the caustic solution.

After an additional hour of stirring at 95° C., the saponification was complete and 200 milliliters of hot water was added to make an active solution. The resulting product is a clear yellow liquid, soluble in water in all proportions, showing excellent wetting properties, high foaming stability and outstanding detergency. It is stable to high concentrations of salts, alkali and acids and shows true amphoteric properties.

EXAMPLE VII

Imidazoline derivatives

A three-neck one liter flask equipped with stirrer, thermometer and moisture trap was charged with one mol methyl oleate and one mol diethylene triamine.

A vacuum of 100 milliliters was applied to the system and the temperature raised to 150° C. and held for two hours at the end of which time one mol of methanol was observed in the receiver.

The temperature was then raised to 235° C. and held at this temperature until 18 milliliters of water was recovered in the receiver at which time the reaction was complete. The resulting product was a clear yellow liquid with a slight fatty amine odor. It analyzed 95% tertiary amine based on its structure 1-aminoethyl, 2-heptadecenyl, imidazoline.

The reaction mass was cooled to 70° C. and arranged for reflux. One mol of acrylonitrile was slowly added through a dropping funnel to the stirred imidazoline maintaining the temperature at 60° to 75° C. until the addition of acrylonitrile was completed.

The temperature was then raised to 100° C. and held at this temperature for two hours, and the small amount of reflux, noted at the initial stages of the addition reaction had disappeared and the formation of the propionitrile derivative was complete.

The heptadecenyl imidazoline ethylaminopropionitrile contained in the flask was saponified by the addition of one mol sodium hydroxide dissolved in 300 milliliters of water. The mixture was stirred at this temperature 95°–100° C. until all the ammonia was evolved and the sodium salt was formed. An additional 400 milliliters of hot water was added to the mixture to make a 40% active product.

The final product was a clear yellow viscous liquid with good wetting and detergency properties as shown by wash tests on cotton, wool and synthetic fibers. It was stable in acids and alkalies, and an aqueous solution containing ½% of the above product was an excellent corrosion inhibitor for ferrous metals.

The methyl acrylate adducts of these long chain imidazoline compounds are oil soluble surfactants. They are dispersible in water, lowering the surface tension of water to 30 dynes/centimeters at 0.17 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.

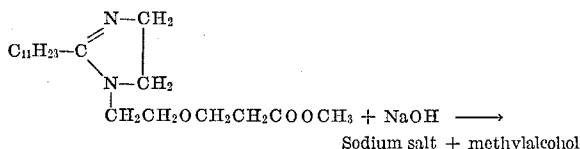
The water soluble alkali propionates of these long chain imidazoline compounds have been found to be detergents in the wet processing of textiles and leather, excellent wetting and emulsifying agents, dyeing assistants, and finishing compounds. As petroleum additives, they serve as corrosion inhibitors 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 imidazoline nitrogen compounds with amines to form both oil and water soluble emulsifiers with corrosion inhibiting properties.

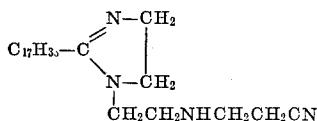
The above examples will produce compounds having the following probable formulae:

EXAMPLE VIII

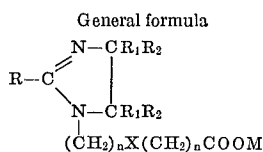


This compound is oil soluble.

EXAMPLE IX



This compound is oil soluble.



Where R is a saturated or unsaturated alkyl containing 8 to 22 carbon atoms, R₁ and R₂ are hydrogen or alkyl group having 1 to 5 carbon atoms, n is an integer having from 1 to 6, X is —O— or —NH— linkage and M is an alkali metal.

EXAMPLE X

On gram molecular weight of 1-hydroxyethyl, 2-nonyl-imidazoline is weighed into a four neck flask equipped with an agitator, reflux condenser, thermometer and dropping funnel. One gram molecular weight of methyl acrylate is added slowly over a period of one to two hours at 20–30° C., stirred for an additional two hours and then raised to 95° C. for one hour. At this point a sample showed 98% adduct formation. The product was cooled to 30° C. and 500 ml. of water containing 40 grams of sodium hydroxide was added and the mixture was stirred for 20 minutes while heating to 75° C. at which temperature a clear yellow foamy liquid resulted. This product had high salt stability, was soluble in 20% NaOH and 30% HCl. It is an outstanding wetting agent for use in textile, paper and leather processing.

EXAMPLE XI

One mol of lauric acid and one mol of N-beta hydroxy propyl propylene diamine are reacted as outlined in references to form the 1-beta hydroxypropyl, 2-undecyl, 4-methyl imidazoline. This product was then reacted with one mol of methyl acrylate as outlined in previous example. The resulting adduct compound was saponified at 80° C. with 500 ml. water containing 56 grams of potassium hydroxide. The finished amphoteric surfactant was a clear yellow liquid and showed excellent detergent properties in wool scouring.

EXAMPLE XII

One mol of 1-hydroxyethyl, 2-heptadecyl imidazoline was melted at 45° C. and one mol of ethyl acrylate added thereto slowly over a period of 1½ hours. The resulting 1-(ethoxy methyl propionate), 2-heptadecyl imidazoline was a white wax at room temperature. It was remelted and poured into one liter of boiling water to form the zwitterion. Upon cooling the resulting product was a soft white paste which had exceptional softening properties and anti-static properties on all types of fabrics.

It can also be used with other finishes such as waterproofing agents, resins and other finishes without interfering with the properties of the other textile finishing agents.

EXAMPLE XIII

One mol of 1-hydroxyethyl, 2-octyl-imidazoline was placed in a four neck flask and reacted with one mol of ethyl acrylate to form the 1-ethoxy ethylpropionate adduct. This compound was poured into one liter of boiling water with stirring; within 20 minutes the mixture turned completely clear and the zwitterion was found to be completely soluble in both acidic and caustic solutions exhibiting wetting and corrosion inhibiting properties in steel pickling with hydrochloric acid.

EXAMPLE XIV

The reaction of castor fatty acids with hydroxyethyl ethylenediamine to form the 1-hydroxyethyl fatty imidazoline was carried out as in the Wilson U.S. Pat. 2,267,965. One mol of this imidazoline was reacted with one mol of methyl acrylate by slow addition over a period of two hours. Analysis showed that the methyl acrylate had reacted completely and the beta alkoxy propionate was then saponified with caustic soda to form a liquid surfactant which showed outstanding rewetting properties, anti-static properties and plasticizing properties as an additive to either the beater in pulp production or in the finishing of paper.

The invention as set forth above is particularly applicable to 1-alkoxy propionates of long chain 2-alkyl imidazolines. These compounds were found to be amphoteric in nature and form zwitterions with the free carboxylic acid group. They are outstanding surfactants having excellent detergent, wetting and emulsifying properties throughout the entire pH range and also in strong acids and alkalies. These compounds are synthesized by reacting high molecular weight imidazolines (200–600 range) containing hydroxyalkyl group or groups in the 1 position of the imidazoline ring, with acrylic esters such as methyl, ethyl or isopropyl acrylates to form 2-long chain alkyl, 1-alkoxypropionic imidazolines.

Although acrylic monomers are difficult to use as chemical intermediates since they prefer to polymerize rather than react with active hydrogen atoms such as the hydrogen in the hydroxyl groups of alcohols and although the acrylic monomers will transesterify with hydroxyl groups to form new acrylic esters, it was found that hydroxyalkyl groups attached to long chain heterocyclic amines such as imidazolines, oxazolines, piperazines did not transesterify with the acrylic ester, nor did these heterocyclic nitrogen compounds cause their monomeric acrylates to polymerize immediately. Thus it was found that with heterocyclic long chain nitrogen compounds containing a hydroxy alkyl group in the heterocyclic ring, the hydrogen of the hydroxyl group would react almost quantitatively with the acrylic ester to form beta substituted propionates (alkoxypropionates).

The imidazolines used to make these new compounds may be synthesized by numerous methods as described in U.S. Pats. 2,267,965; 2,355,837; 2,268,273; 2,267,965; 2,355,837; British Pat. 512,846 and also such fatty imidazolines as prepared in U.S. Pats. No. 2,017,356; 2,987,521 and 2,987,515. The fatty imidazolines are preferably prepared from hydroxy alkyl 1,2 diamines by acylation with fatty acids (C₆ to C₂₂) followed by cyclodehydration to form the desired hydroxy alkyl imidazoline.

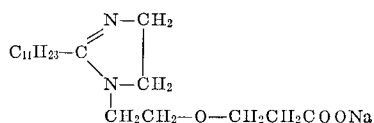
The acrylate monomers suitable for reaction with the hydrogen of the hydroxyl radical may be methyl acrylate, ethyl acrylate, isopropyl acrylate and/or acrylonitrile. The acrylate esters are preferred for the inner carboxylic zwitterion can be formed by simply adding the long chain imidazoline alkoxypropionate to boiling water and stirring until the mixture is clear.

The reaction of an acrylic monomer with the hydroxy group of a 1-substituted fatty imidazoline to form alkoxy-

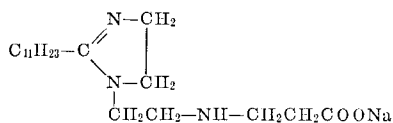
propionates gives almost theoretical yields under specific conditions. It was found that no catalyst was needed as described in the literature. The investigations showed that the basicity of the tertiary nitrogen atoms or atom in the heterocyclic ring structure was ideal to self catalyze the acrylic monomer adduct reaction to produce beta alkoxy propionates. Yields of 90% to 98% adduct formation can be achieved by slowly adding the monomer acrylate to the liquid imidazoline at room temperature, stirring for one hour, gradually increasing temperature to 90–100° C. and stripping any excess or untreated acrylic monomer off under vacuum, if necessary. This yield was entirely unexpected for adduct formation with high molecular weight organic compounds is very sluggish and alkoxy propionate yields are extremely poor (20–40%) as noted in U.S. Pat. No. 2,504,151 wherein one mol of furfuryl alcohol per mol of methyl acrylate using metallic sodium catalyst resulted in a 30% adduct yield.

The preferred surfactants are:

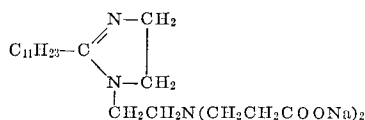
EXAMPLE XV



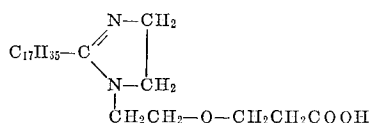
EXAMPLE XVI



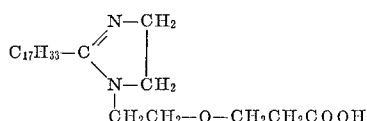
EXAMPLE XVII



EXAMPLE XVIII



EXAMPLE XIX



Instead of making the imidazoline, it may be purchased as inintermediate and reacted with methyl acrylate to give the desired surfactant.

Imidazoline derivatives of propionic, and derivatives containing oleic, stearyl or lauric fatty acid are generally preferred.

These compounds are surface active agents (surfactants) and by definition must therefore be detergents, emulsifiers and wetting agents. The hydrophobic part of the molecule (the fatty or oil soluble) is based on long chain (fatty) imidazoline tertiary amines which must contain short chain hydroxy alkyl groups attached to the imidazoline tertiary amine ring structure.

The reaction of the acrylo compounds is with the hydroxy group of this side chain to form alkoxy propionates.

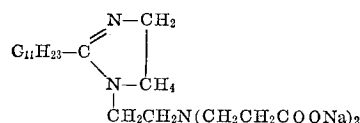
Up to my invention all surfactants involving tertiary amines have always attached some group to the tertiary nitrogen of the imidazoline ring structure and then perhaps to a side chain hydroxyl group.

What is new is that hydroxy groups in such high molecular weight aliphatic (long chain) imidazoline tertiary amines would be reactive with acrylo compounds and that the acrylo compound would be selectively catalyzed by the tertiary amine nitrogen of the ring to react with the hydroxyl group of the side chain.

That the adduct formation would take place to 90–98% yield was not predictable since it is known to chemists versed in the art that acrylo compounds prefer to polymerize or transesterify or transamidify (if there is any primary or secondary amine atoms present). Also that the resulting compounds when turned into their zwitterion or alkali salts have surface active properties and are excellent detergents etc., since these compounds belong to the amino-acid classification one would expect them to be like aspartic acid, hydrolyzed glue or hydrolyzed casein. However, the amphoteric surfactants of the present invention are not like aspartic acid, hydrolyzed glue or hydrolyzed casein. These amino-acids are not soluble in both alkalies and acids. Common subject matter of Example VI of the present application and Example XI of application Ser. No. 50,649, filed Nov. 7, 1961, and of Examples I and II of U.S. application Ser. No. 331,391 relates to the production of the compound 1-sodium ethoxypropionate-2-undecyl imidazoline or the corresponding free acid. The only difference is the method of preparation in that in the later examples water is used as a diluent in the amount of 361 grams. The water serves to cause hydrolysis to the free acid. Basically the process set forth is to combine coconut fatty acids or lauric acid and aminoethyl ethanolamine in substantially equimolar proportions with the addition of methylacrylate or ethylacrylate or acrylo-nitrile or beta-lactone to the reaction mixture with or without the addition of heat to cause the reaction. This is particularly shown in Example VI above which corresponds to Example XI of the parent application Ser. No. 532,861.

Having now particularly described and ascertained the nature of the invention, and in what manner the same is to be performed, what is claimed is:

1. The surfactant having the formula:



References Cited

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Riddle: Monomeric Acrylic Esters, pp. 146–8, New York, Reinhold, 1954.

NATALIE TROUSOF, Primary Examiner

U.S. Cl. X.R.

8—94.1; 117—139.5, 152; 252—8.57, 8.8, 117, 351, 392; 260—268, 307, 999