

REVIEW

Imidazoline and Its Derivatives : An Overview

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Abstract: Imidazoline derivatives, a class of novel cationic surfactants are presently gaining importance in global detergent market due to their wide range of applications. These are extensively used mainly as fabric softeners and antistatic agents. The present communication reviews the preparation, reaction scheme, reaction rates and properties of imidazoline derivatives. The analysis of imidazoline derivatives, its mode of action, their biodegradation and various applications have also been discussed.

Key words: imidazoline, imidazoline derivative, cationic surfactant, fabric softener, bio-degradation

1 INTRODUCTION

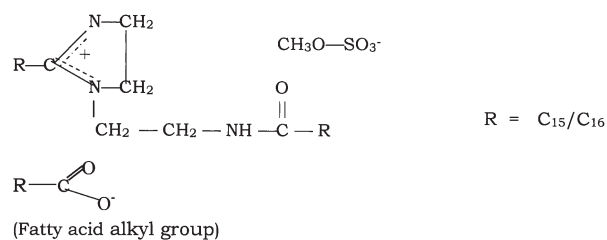
Cationic surfactants first found use as dye leveling agents¹⁾ in the textile industry in the 1930s. Their softening properties were discovered as a side benefit. Stapuf and Downy were first introduced fabric softeners as household product during 1950s which were aqueous dispersions containing 3-8 wt.% cationic softener active. Connell²⁾, Souplin and coworkers launched household product in Europe and Japan in the 1960s. Mannheimer³⁾ in 1950s synthesized imidazolinium surfactants. All of these systems, that were first introduced, in which 1-(2-hydroxyethyl) 2-Alkyl-2-imidazoline (H.E.A.I.) was allowed to react with sodium monochloroacetate. During 1970's and 1980's esterquats rinse added softeners started gaining importance.

Literally hundreds of molecules have been patented for their fabric softening properties. Several thousands patents have been filed in the last 30 years covering variation and combinations of new and old molecules as well as formations of softeners actives with different cosurfactants and functional additives⁴⁻⁸⁾. In practice, the molecules DHTDMAC, diamidoamine, imidazoline and esterquats are probably 99% of the cationic actives being used in rinse added fabric softeners around the world today as a result of their ability to meet regional performance requirement.

Cationic surfactants are compounds with a positively charged nitrogen atom and at least one hydrophobic, long chain substituent in the molecule. Important products are

quaternary ammonium compounds, imidazolinium derivatives or pyridinium compounds. Because of their fabric-softening and antistatic properties they are used as active materials in fabric-softening formulations.

Imidazolinium compounds are second to the quaternary ammonium compound in tonnage of cationic surfactants produced for fabric softeners. Imidazoline is isomeric with pyrazole. Imidazolinium compounds belong to the class of heterocyclic compounds containing five membered ring compound having two N atoms in the ring. The imidazole nucleus is also found in natural product, viz. Histidine (an α -amino acids), Purines and also as a Riboside. The reduced product of imidazole is known as imidazoline. Representatives of imidazolines are as follows :



The most widely used representative of this group is the tallow alkyl derivative. It is supplied as a liquid and is easily processed in fabric softeners. The imidazolinium derivative with a hydrogenated tallow chain gives better softening effect than the nonhydrogenated formulation to obtain a finished product. The oleyl derivative has recently gained

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importance because it has less hydrophobizing effect with relatively good softening performance. Thus textile treated with it keeps almost all their natural absorbency properties. In practice, imidazolinium compounds are frequently blended with distearyl dimethyl ammonium compounds to attain a higher degree of softening performance.

2 PREPARATION OF IMIDAZOLINE

Imidazolinium softeners are based on the reaction of triglycerides or fatty acids with DETA. Earl G.W. *et al.*⁽⁹⁾ prepared imidazoline by the reaction of triglycerides with DETA. However, rather than forming the tertiary amine via ethoxylation, the diamidoamine formed in the first step is subjected to elevated temperature and vacuum resulting in loss of molecule of water. The imidazoline is then alkylated with dimethyl sulfate (DMS) which can react at either of the ring nitrogen's (and does so in specific ratio) to give the imidazolinium quaternary ammonium methyl sulfates (IQAMS). Warner and co-workers⁽¹⁰⁾ also prepared imidazoline based on the reaction of fatty acid with DETA.

Hofmann first prepared the 2-alkyl 2-imidazoline the homologous series from the fatty acid and ethylene diamine. Characterization⁽¹¹⁻¹³⁾ of such compounds concluded that the 2-alkyl 2-imidazoline would not impart sufficient hydrophobicity. However, the fatty acid derivative of higher molecular weight polyamines, such as diethylene triamine (DETA) might be sufficiently hydrophobic. Acleyle⁽¹⁴⁾ reacted fatty acids with DETA to prepare the fatty imidazolines, which in crude form were quaternized to produce fabric softeners.

Krejcar *et al.*⁽¹⁵⁾ similarly prepared imidazolinium compounds at 270°C under vacuum of 5 mm Hg in 2 h when the reactants were mixed below 100°C.

Butler and coworkers⁽¹⁶⁾ observed amine salt formation which were dehydrated at 130°C to a diamide fatty acid complex and finally at 180°C. The liberated diamide, identified as $(C_{17}H_{35}CONHCH_2CH_2)_2NH$ continued heating at 240-260°C for 48 h yielded imidazoline.

Yue *et al.*⁽¹⁷⁾ prepared an imidazoline cationic surfactant from oleic acid, N-(2-hydroxyethyl) ethylene diamine. Inokoshi *et al.*⁽¹⁸⁾ synthesized imidazolinium compounds as softening agents, the title agents contain 4-40% mixture comprising imidazoline derivative ($R=C_{15-21}$ saturated or unsaturated hydrocarbonyl). 16-22 saturated or unsaturated fatty acid; inorganic acids or $C \leq 6$ organic acids at a specified molar ratio.

Rosario-Jansen *et al.*⁽¹⁹⁾ prepared fabric softening and antistatic compositions containing a quaternized disubstituted imidazoline ester fabric softening compound with a nonionic fabric softening compound.

Hasegawa and coworkers⁽²⁰⁾ manufactured solid fabric softeners with improved dispersibility in water. The soft-

eners comprise 40.0-99.99% of 95-10:5-90 (wt. ratio) mixture of imidazoline derivatives. Caswell *et al.*⁽²¹⁾ manufactured imidazoline derivative anionic surfactants ion-pair complexes as conditioning agents for fabrics and hair. Kato *et al.*⁽²²⁾ manufactured reusable nonwoven fabric softeners for worked garments in dryers.

Linfield and co-workers⁽²³⁾ prepared imidazoline for which diethylenetriamine (DETA), 51.5g. (0.50 mol) was added to stearic acid, 270.4 g. (0.95 mol) at 90°C, temperature quickly increased and gelling occurred as a result of amine soap formation. This was overcome by warming above 125°C. Heating at 150°C was continued for 6 h. At this stage formation of diamidoamine takes place. Heating was continued at 150°C for 2 h under 0.3 mm Hg. In this step, cyclization of diamidoamine takes place by removal of one water molecule and imidazoline was formed.

Quaternization of the imidazoline derivatives is given by Mannheimer⁽³⁾. In a 200 ml flask equipped with a reflux condenser and a dropping funnel, there were placed 30 g. (0.112 mol) of HEAI ($R = C_{11}H_{23}$) and 10 ml of isopropanol, and the reaction mixture was kept at 80°C with magnetic stirring. Diethyl sulfate (34.5 g. 0.224 mol) was dropped during 15 min to the solution which was stirred for 4 h at 80°C. Then 20 ml of water was added to the solution, which was stirred for one additional hour at 80°C. After cooling, the resulting solution was adjusted to pH 4-5 with 0.5 N KOH, and concentrated under reduced pressure. The residue was dissolved in isopropanol and filtered. The filtrate was concentrated to afford 49.9 g. of the quaternized product.

Cretu *et al.*⁽²⁴⁾ synthesized a quaternary salt of ammonium from substituted 2-imidazolines. Surfactants were manufactured by quaternization of imidazoline derivatives ($R^1 = C_{8-12}$ alkyl, $R^2 = H$ or Me) with dihaloalkanes at 1: (1.5-6.5) mol ratio, 1-5 h and 80-140°C optionally in an alcohol solvents. Thus 175 parts 1, 2 dichloro methane was added in 2 h to a 30% isopropyl alcohol solution of $R = C_{12}H_{23}$, $R=H$ at 70-80 and the reaction was heated an additional 10 h, to give a yellow quaternary salt that produce a softening and static effect.

2.1 Reaction scheme of preparation of imidazoline :

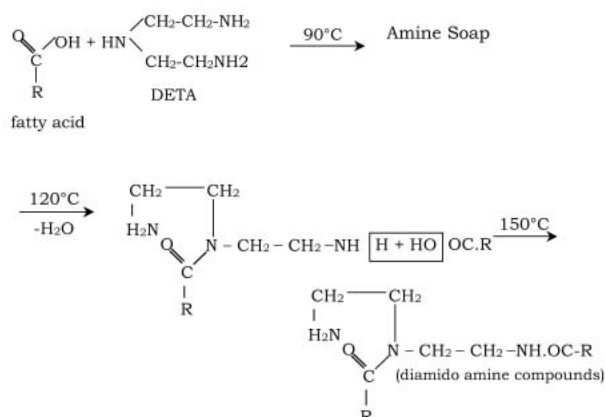
In **Scheme I** imidazoline was prepared by the reaction between fatty acid and diethylene triamine. The preparation of imidazoline takes places in the following three steps:

The reaction **Scheme II** was proposed by Earl GW *et al.*⁽⁹⁾ in which reaction takes place between triglyceride and diethylene triamine.

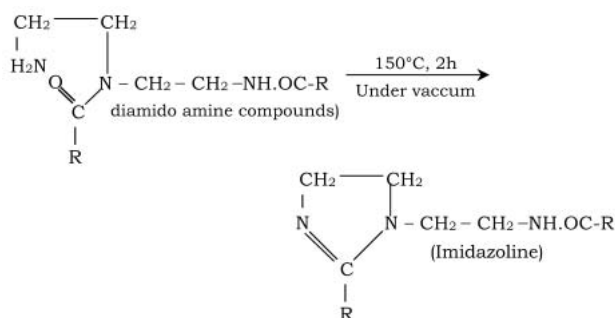
3 REACTION RATES

Linfield and coworkers⁽¹⁰⁾ studied the reaction rate of

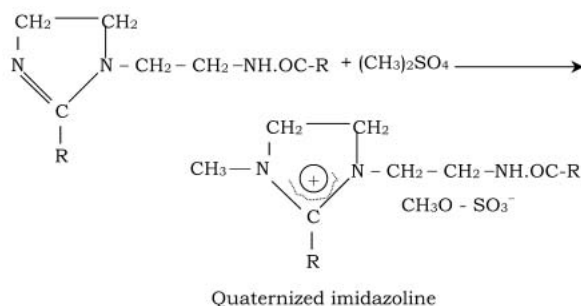
Step 1 Synthesis of diamidoamine compounds



Step 2 Synthesis of imidazoline



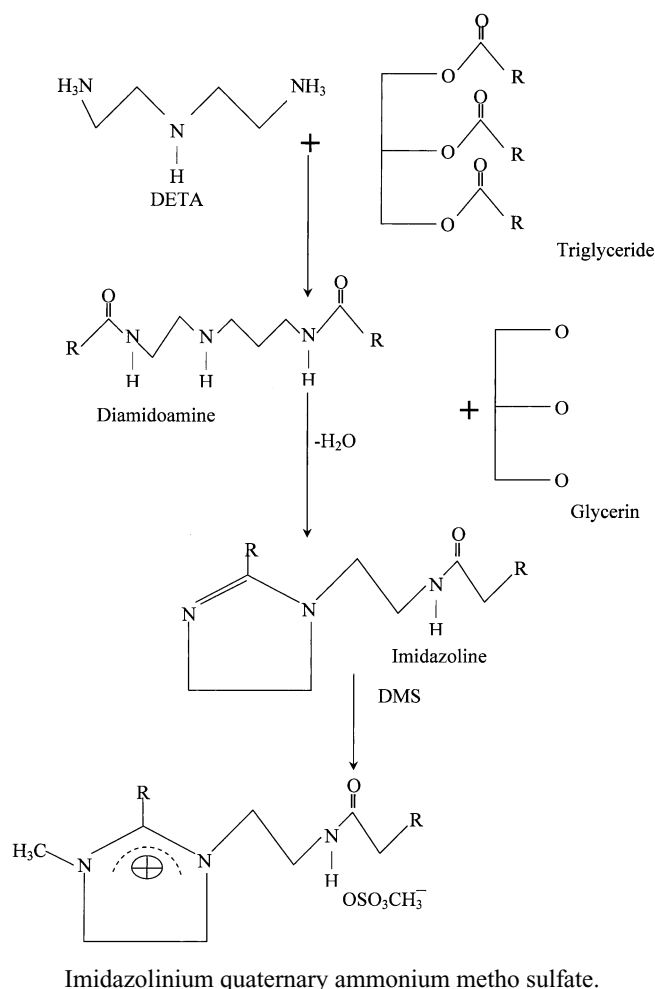
Step 3 Synthesis of quaternary imidazoline



Scheme I

fatty acid and DETA reaction. A series of fatty acid-DETA reactions were carried out at 120°C, 150°C, 175°C and 200°C and the distillates were collected for analysis. Result showed that excessive amounts of DETA codistilled with the water formed from the reaction at 175°C and 200°C. Only small amounts of DETA were found in the distillate from the 150°C reaction. It was concluded that 150°C was the optimum temperature for the reaction.

The reaction was conducted at 150°C under atmospheric pressure, using 2 mol tallow fatty acids and 1 mol DETA. Initially and at 2 h intervals, samples were withdrawn for analysis of free fatty acid, primary, secondary, and tertiary amine, and the results are shown in Fig. 1.



Scheme II

Within the first 2 h period, the amount of available fatty acid decreased to 1/3 of the original value. This indicated that DETA and fatty acid did not react in a 1:1 molar ratio. However, during the same period, the meq/g of secondary amine dropped to an insignificant amount, whereas only a 1/3 reduction was detected for primary amine. This indicated clearly that in a nonaqueous system the secondary amino group was more reactive than the primary one as has been reported in aqueous systems²⁴. After the reaction had proceeded for 6 h at 150°C, the free fatty acid content was less than 5% and the meq/g of primary amine reached a constant value roughly equivalent to one free amino group. Thus, the structure of the intermediate is $\text{RCON}(\text{CH}_2\text{CH}_2\text{NH}_2)\text{CH}_2\text{CH}_2\text{NHCOR}$.

Cyclization to the imidazoline was completed after heating 2 h at 150°C under 0.2 mm Hg pressure in a 92% yield. The amount of tertiary amine rapidly increased, approaching the theoretical value for the fatty imidazoline, while only traces of primary and secondary amines were found in the reaction product. The structure of the imidazoline is

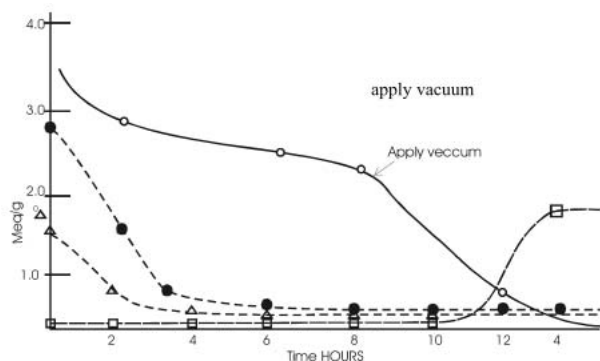
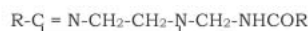
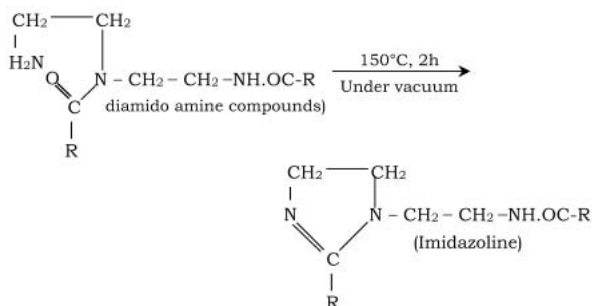
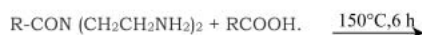
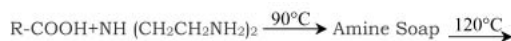


Fig. 1 Reaction Rate Study, 2 mol Tallow Fatty Acid Per mol of DETA. ● Tallow Fatty Acid, ○ Primary Amine, △ Secondary Amine, □ Tertiary Amine (Imidazoline).

presumably -



with only one of the two tertiary amine groups being titratable.



The reaction of DETA with tallow and methyl tallowate were similarly investigated and the results are shown in Fig 2 & 3. The amount of ester present, determined by spectroscopy and amine distribution by titration were also determined at regular intervals. Since infra-red IR determination of ester content is accurate only at 10%, higher percentages have been estimated, based on the consumption of secondary amine and are indicated by the dotted line on Fig. 3. Tallow reacted rapidly with DETA (Fig. 2), at a rate similar to that of the above reaction with fatty acid (Fig. 1). The content of secondary amine quickly dropped to a low level, the primary amine at plateau value, and the tertiary amine increased, showed 28% of imidazoline after 6 h

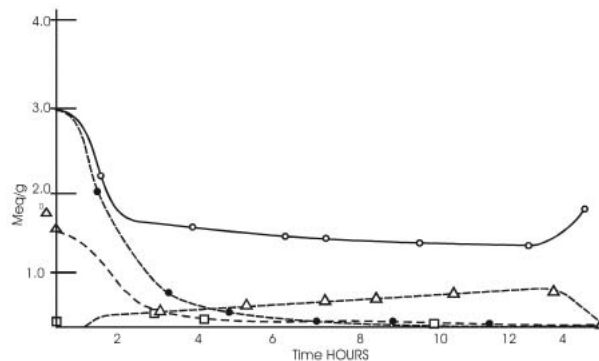


Fig. 2 Reaction Rate Study, Tallow, and Diethylenetriamine, ● Ester; ○ Primary Amine, △ Secondary Amine, □ Tertiary Amine (Imidazoline).

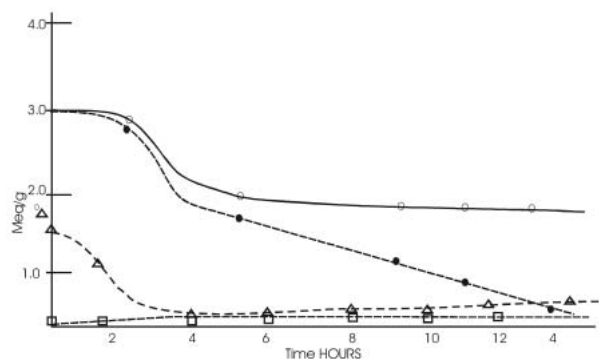


Fig. 3 Reaction Rate Study, 2 mol Methyl Tallowate Per mol Diethylenetriamine, ● Ester, ○ Primary Amine, □ Secondary Amine, △ Tertiary Amine (Imidazoline), -Estimated.

reaction time at atmosphere pressure. In this reaction period the glyceride ester content decreased to less than 6%.

The reaction of DETA with methyl tallowate (Fig. 3) proceeded more slowly and required 13 h to reach same end point. It is not known why the methyl ester is less reactive than triglycerides or fatty acid. Alkali caused amidation of methyl ester usually proceeds rapidly. Perhaps the water from the ring closure inhibit the reaction. Since 16% imidazoline was found in the reaction carried out under atmospheric conditions. The use of methyl ester eliminated on the basis of high energy and time requirements.

The DETA-tallow reaction also had a serious disadvantage. The problem of separation of ca. 10%, glycerine formed in the reaction product. Glycerine retention resulted in a product with undesirable hydrophilic properties, and glycerine removal proved difficult and very time consuming.

The diamides formed from each of the above reactions

were readily cyclized to the imidazoline by applying vacuum for 2 h at 150°C. In the reactions of DETA with the tallow, tallow fatty acid, or methyl tallowate in fatty material was used to minimize the formation of RCON (CH₂CH₂NH₂)₂. This low melting waxy material has wetting properties similar to those of the dialkanolamides, RCON (CH₂CH₂OH)₂ and, if present in large amounts, would counteract water repellency.

4 PROPERTIES OF IMIDAZOLINES

4.1 Solubility behaviour

The higher molecular weight components of the imidazoline were not very soluble in organic solvents at room temperature. Data showing the solubility behaviour of the palmitic acid and derivatives in various organic solvents are given in Table 1. The more polar imidazoline was more soluble. Imidazoline was most soluble in ethanol.

4.2 Imidazoline stability

Imidazolines are not stable chemical entities. 4. The tertiary amine content of saturated imidazolines decreased by 5-8% over an 18-month period, even when the product was stored in a closed glass container. Furthermore, the addition of 2% water to a reaction product containing 38% imidazoline, resulted decrease to 6% in 72 h with a further reduction to 4.5% after 6 days. Therefore, when used as intermediates, imidazolines should be reacted promptly and prolonged storage should be avoided.

4.3 Melting properties

The melting point data are shown in Table 2. The imidazolines melt at lower temperature and over a much wider temperature range (45-90°C) than the corresponding primary amides (98-112°C). The imidazoline of oleic acid was liquid at room temperature (cf. oleamide 75-76°C), whereas its elaidic counterpart melted at 46-47°C and elaidamide 93-94°C.

4.4 Surface properties

Hydrophobicity of the imidazoline were determined by contact angle measurements and percolation times and are recorded in Table 2. In general, contact angles increased as a function of molecular weight. Unsaturation in the fatty acid chain caused a drastic reduction in contact angle and the angle of the cis-derivative was much lower than that for the trans compound.

4.5 Spectral properties

In the IR region, the imidazolines displayed characteristic nil absorption at 3.03 μ is with a shoulder at 3.15 μ amide band and a shoulder at 6.03 μ on the 6.12 μ amide band. Absorption for the diamide derivatives was observed at 3.03 μ and 6.12 μ . In the ultraviolet (UV) region, the imidazolines displayed a broad C = N band at 250-220 nm (Peak at 230nm) with a shoulder, CONH, at 202 nm²⁵. The imidazoline content of an imidazoline diamide mixture can be determined by measuring in cm. the U.V. absorbance at 230 nm of an absolute 0.01% ethanolic solution. The imidazoline absorbance at 230 nm could be used to detect dilutions as low as 1 ppm.

5 ANALYSIS OF IMIDAZOLINES

The various analytical methods used for these chemicals serves several objectives, including routine quality control, identification and characterization, determination in mixtures and formulations. In general, the objective of the analysis will determine value method will be used. Routine quality control procedures will most often use wet methods or some simple instrumental techniques.

5.1 Analysis of fatty amines and their salts -

5.1.1 Wet methods

The commercial fatty amines include long chain primary, secondary and tertiary amines, diamines, amidoamines and imidazolines. The amine salts most often encountered are the hydrochlorides, the acetates and fatty acid salts such as the oleates.

Wet chemical tests are most often used to control the manufacture of these products. Since the free amines are basic they are readily titrated with standard acids either colorimetrically or potentiometrically. The AOCS and ASTM have developed methods and have done collaborative studies on a number of these tests²⁶⁻²⁸.

Table 3 shows the approved AOCS and ASTM wet tests for fatty nitrogen compounds. The most fundamental single analytical method is the amine value which is analogous to the acid value. The amine value is defined as the number of mg of KOH equivalent to the basicity in 1g sample. With one simple titration, one can obtain amine value, apparent molecular weight or neutralization equivalent (NE) and percentage of amine if the molecular weight (MW) is known. Table 4 shows how this data can be calculated from one titration.

Table 1

Solvent	Acetone	CCl ₄	Ethanol	Isopropanol	Toluene
Imidazoline	49°C	35-40°C	25°C	30°C	35°C

Table 2

R	MP °C	Contact angle	Percolation test
C ₈ H ₁₇	45-46	62	i ^c
C ₉ H ₁₉	48-49	59	i
Δ ¹⁰ C ₁₀ H ₁₉	40-41	37	i
C ₁₁ H ₂₃	67-68	95	1 hr
C ₁₃ H ₂₇	70-71	89	1.5 hr
C ₁₅ H ₃₁	78-79	97	7 days
C ₁₇ H ₃₅	84-85	103	>7 days
Δ ⁹ -C ₁₇ H ₃₃ -Cis	Liquid	0	5 min
Δ ⁹ -C ₁₇ H ₃₃ -Trans	46-47	55	5 min
C ₁₉ H ₃₉	88-89	104	>7 Days
C ₂₁ H ₄₃	92-93	103	>7 Days
Tallow derivatives Tallow	35-45	23	i
Tallow fatty acid ^a	40-50	54	i
Tallow fatty acid ^b	45-55	97	i
Hyd. tallow FA	65-75	78	>7 Days
Methyl tallowate	45-55	40	30 min

^aT-22 fatty acid C₁₈ cis = 36%; C₁₈ trans = 7%^bT-11 fatty acid C₁₈ cis = 6%; C₁₈ trans = 24%i^c-instantaneous**Table 3** Approved Wet Chemical Test Methods for Fatty Nitrogen Compounds.

Method	Designation	
	AOCS	ASTM
Total amine value of fatty amines : Potentiometric method Indicator method	T _f 1a T _f 1b	D 2073 D 2074
Primary, secondary and tertiary amine values of fatty amines : Potentiometric method Indicator method	T _f 2a-64 T _f 2b-64	D 2073 D 2074
Percentage, primary, secondary and tertiary amines in fatty amines.	T _f 30-64	D 2083
Iodine value of fatty amines modified wizes method.	T _g 2a	D 2075
Iodine value of fatty quaternary ammonium chlorides modified wizes method.	T _g 3a	D 2078
Average molecular weight of fatty quaternary chloride.	T _v 1a	D 2080

Table 4 Data Calculated From a Single Titration of an Amine.

$$\begin{aligned}\text{Amine value} &= \frac{V \times N \times 56.1}{\text{Wt. (g.)}} \\ \text{meq/g} &= \frac{N \times V}{\text{Wt. (g.)}} \\ \text{NE or apparent MW} &= \frac{\text{Wt. (g.)} \times 1000}{N \cdot V} \\ \% \text{ Amine} &= \frac{V \times N \times M \cdot W}{\text{Wt. (g.)} \times 10}\end{aligned}$$

Primary, secondary and tertiary amines can also be determined by a series of differential titration. This is usually accomplished by forming derivatives with the primary and secondary amines that do not titrate under normal conditions. Primary amines can form very weak Schiff's bases with aldehyde, leaving the secondary and tertiary amines that can be readily titrated.

Tertiary amines can be titrated after removal of the primary and secondary amines by acetylation or reaction with phenylisothiocyanate.

The acid part of amine salts can be titrated using standard base such as KOH. If the acid is relatively weak acid, such as acetic acid, the amine portion can also be titrated with strong acids such as hydrochloric or perchloric acid.

5.1.2 Trace amine methods

Small quantities of amine salts in water can be determined colorimetrically using dye partition systems. The amine salts will form colored complexes with anionic dyes such as bromophenol blue, that can be extracted into chloroform or other water immiscible solvents. Such methods are valuable, not only for low concentration of amine salts, but they are also useful in differentiating amine salts from quats. Both amine salts and quats will give colored extracts at acidic pH. However, only quats will give positive colors at higher or basic pH levels.

A buffered indicator system have been found very useful for the dye partition analysis of small amounts of fatty amine as shown in **Table 5**. Other similar systems use methyl orange, methyl yellow, metal complexes and many other color forming system^{29,30}.

A modification of a method for small amounts of secondary amine can be applied for determining primary amine. This system for primary amines uses salicylaldehyde. A sample containing 3-18 mg of fatty amine hydrochloride is dissolved in isopropyl alcohol and reacted with salicylaldehyde and NaOH at 60°C for 30 min. The sample is made acidic and the color read at 405 nm. The advantage of this system is that solvent partitioning is not required. Small amounts of the fatty primary amines can

Table 5 Buffered Indicator for Amines.

- > 700 ml of 0.1M aqueous citric acid.
- > 300 ml of 0.2M aqueous disodium phosphate.
- > 50 ml of 0.2% bromophenol blue in methanol.
- > 50 ml of 0.2% bromocresol green in methanol.

be determined in water.

5.1.3 Instrumental methods for amine salts

The two instrumental techniques that are most useful for fatty amine analysis are gas chromatography (GC) and nuclear magnetic resonance (NMR). The gas chromatographic analysis of underivatized amines can be accomplished with base treated columns that use piezon greases, carbowax 20 M as liquid phases³¹⁻³³. Derivatization of the amines using trifluoroacetic anhydride, acetic anhydride or silylation makes it possible to use neutral columns such as DEGS to obtain separation of saturated and unsaturated and geometrical and positional isomers^{34,35}.

Proton NMR has been used to analyze mixtures of primary, secondary and tertiary amines in tri-fluoroacetic acid³⁶. More recently, carbon-13 NMR has been used to analyze fatty amines and their derivatives. With ¹³C-NMR, mixtures of primary, secondary and tertiary amines can be identified and quantified. **Table 6** shows the ppm shifts observed in the amine salts ¹³C-NMR spectra.

6 MODE OF THE ACTION OF IMIDAZOLINE

It is prerequisite for the softening and antistatic effect of cationic surfactants (imidazoline), that they are absorbed on the textile substrates³⁷⁻⁴¹. A high degree of substantivity between the negatively charged textile surfaces and the positively charged part of the cationic surfactants (imidazoline) molecules in the aqueous phase exists (**Fig. 4**) under the condition of rinse bath, for instance, wool or cotton absorb more than 90% of the quaternary ammonium derivative of imidazoline compounds from the aqueous phase.

7 PARAMETERS OF ADSORPTION OF CATIONIC SURFACTANTS

The adsorption depends on numerous parameters such as:

- 7.1 Molecular structure of cationic surfactants themselves [chain length and type of the alkyl surfactants].
- 7.2 Textile substrate
- 7.3 Time of action
- 7.4 Temperature

Table 6 A Comparison of Amines and Amine Salts Chemical Shifts.

Type of Amine	Type of Carbon	Amine Chemical Shift (ppm)	Salt Chemical Shift (ppm)
R - CH ₂ - NH ₂	- CH ₂ -	42.4	40.2
(R - CH ₂) ₂ - NH	- CH ₂ -	50.3	47.8
(R - CH ₂) ₂ - N	- CH ₂ -	54.6	52.8
R - CH ₂ - N (CH ₃) ₂	- CH ₂ -	60.2	58.0
	CH ₃ -	45.6	42.9
(R - CH ₂) ₂ N CH ₃	- CH ₂ -	58.2	55.9
	CH ₃ -	42.5	40.0

7.5 pH value

7.6 Presence of the surfactants or builders.

7.7 Particularly important is the pH value of the rinse bath. Although the amount adsorbed increase in the pH range of 2-9; it is more advantageous to perform the treatment in the neutral or slightly acidic pH range to warrant an even adsorption of the quaternary ammonium compounds show an uneven distribution on the textile surface⁴³⁾ by washing with detergent of usual composition, the adsorbed ammonium compounds are almost completely desorbed⁴²⁻⁴⁴⁾. Imidazolinium compounds behave similarly with regard to their adsorptive properties.

8 BIODEGRADATION

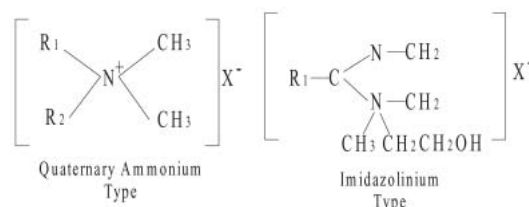
Surfactants of imidazoline often have a rather germicidal action. Care must be taken that their toxic threshold are not exceeded in studies of their biodegradation. But with suitable precautions many of them turn out to be unquestionably biodegradable.

Cationic and anionic surfactant can neutralize each other in many of their properties, including toxicity thus addition of anionic may promote biodegradation of a cationic. Fujiwara *et. al.*⁴³⁾ prepared biodegradable fabric softeners.

The anion of cationic surfactants are usually halogens, but also may be methylsulfate or dimethyl phosphate. At present fabric softener preparations are nearly exclusively limited to ditallow dimethyl ammonium chloride, and more particularly mainly distearyl dimethyl ammonium chloride (DSDMAC) and dialkyl imidazolinium salts (DAIC). Consumption of DAIC has increased partly due to a better, processibility.

The structural formulas of both compound types are represented in structure. Cationic surfactants of the DSDMAC type are relatively stable chemically and do not change under washing conditions. In contrast with this,

imidazolinium salts in



aqueous solution are susceptible to hydrolysis. After a short time as pH values exceeding 8, a hydrolytic degradation of the imidazoline ring occurs, forming amide structures⁴³⁾ (Fig. 5).

A particularly important property of cationics used in softeners with regard to their environmental behavior is determined by the electrically neutral salt formation, preferably with anionics: excess volumes of the latter are clearly found in wash liquor and in the effluent. Stoichiometric 6:1 ratios are common. The electrically neutral salts of linear alkylbenzene sulfonates and of DSDMAC and DAIC, that are most used in softeners, are largely insoluble in water and precipitate as, 2:1 up to 1:2 complexes at rather high concentrations. Their formation can be established, among other things, by pursuing the conductivity ratios.

Cationic surfactants concentrate on surfaces by chemisorption, and their electrochemical nature causes them to adsorb at negatively loaded binding sites. Extent and time-dependence of cationic surfactant fixation in living and sterilized activated sludge is represented in Fig. 6. It can be seen that the DAIC is bound by activated sludge to a considerable extent within 30 min, and has already reached an approximate equilibrium state. As there is no significant difference in the sorption capacity of both sludges, it must be assumed that, in the first place, a purely physicochemical process becomes active in the elimination of the cationic surfactant. This is fully confirmed by a series of more

recent examinations^{44,45}.

Two essential circumstances must be observed in rating effective toxicity in effluents and surface waters of cationic surfactants used in fabric softeners.

The electrically neutral salt formation of the anionic surfactants present in excess; with DSDMAC and DAIC, it leads to considerable decrease of toxicity. Electrically neutral salts from DSDMAC and LAS, for example, are on average one-sixth as toxic as DSDMAC. One may assume that this process begins in the washing machine, where both surfactant groups meet in the prewash. This process of mutual detoxification of anionic and cationic surfactants is probably based on a precipitation of electrically neutral salts and less on a change in electrochemical behaviour, such as extensive loss of surface activity.

9 APPLICATION OF IMIDAZOLINE DERIVATIVES

Imidazoline derivatives are extensively used in surfactant in small proportion for improving detergent quality for the various application purposes.

9.1 Softening Fabric softeners may be defined as “products which impart to clothing and fabrics a feel or handle which is soft and pleasing during wear or use. Fabric softeners have become a significant and valued dimension of fabric care, and are likely to remain so. The softeners are used on all kinds of fabrics including cotton, polyester-cotton, nylon etc.

Textile worn or used in contact with the skin, e.g. underwear, terry toweling, hand towels and blankets are finished with preparation to give them a pleasant, soft fluffy feel. These properties are lost during washing⁴⁷, first because finishing is washed off and secondly, because modern washing and drying treatments additionally tend to make the textile feels harsh. By using cationic based additive in domestic washing machines, these lost properties are reimported to the textiles.

Softeners may facilitate ironing, accelerate the rate of drying of wet cloths in machine dryers, and have a germicidal effect.

The following three types of fabric softeners are commonly used :

9.1.1 Rinse-cycle fabric softenes

9.1.2 Wash-cycle fabric softeners

9.1.3 Dryer-added fabric softeners

9.1.1 Rinse-cycle fabric softeners

This type of fabric softeners is added to the laundry during last rinse cycle, i.e. at a time when surfactant and soil detergent residues have been almost completely removed. Conventional fabric softeners contain from 1-9% imidazolinum compounds.

9.1.2 Wash-cycle fabric softener

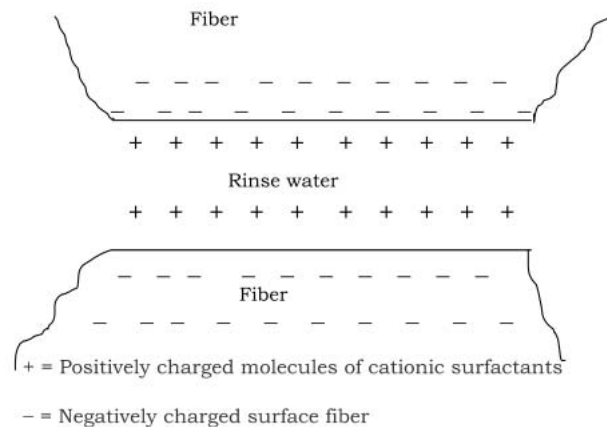


Fig. 4 Substantivity of Cationic (Imidazoline) Compounds.

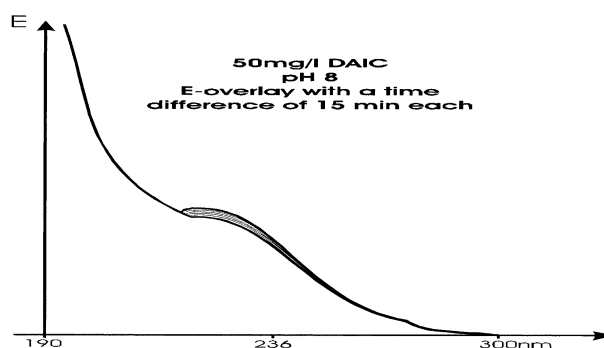


Fig. 5 Hydrolytic Degradation of DAIC at pH 8.

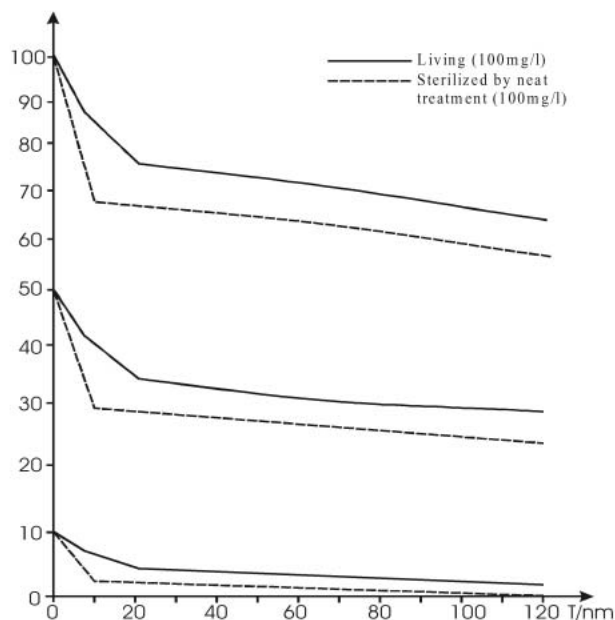


Fig. 6 Adsorption of DAIC to Activated Sludge.

Wash cycle fabric softeners should not be confused with detergent with incorporated fabric softeners. Wash-cycle fabric softeners are equally formulated as rinse-cycle fabric softeners. They differ from the later in that they contain more active material. They are not applied in the last rinse bath but in the wash bath.

9.1.3 Dryer-added fabric softeners

Dryer-added softeners products are added during the drying process. They are formed by spreading the melt products component on the suitable paper or fabric matrix and allowing them to freeze. As dryer-added softeners products are comparatively recent innovation versus liquid rinse-added products.

Yamamura *et al.*⁴⁸⁾ manufactured a fabric softeners for imparting improved softness and hygroscopicity to garments. Azoz⁴⁹⁾ prepared fabric softening composition to inhibit damage to cotton fibers. The title compound contains a fabric-softening imidazoline, which inhibit fabrication of cotton fibers of garments during washing and wearing and increase the life of garments. Rieck⁵⁰⁾ manufactured laundry product containing a softener. Laundry detergents are prepared which contain 1-10% quaternary ammonium compound. The ammonium compound absorbed the silicate, impart softness to fabric during laundering and compatible with anionic surfactants.

9.2 Dispersibility

Dispersions of a finely divided solid in a liquid resemble emulsions in many respects. Thus, there appear to be at least two distinct and important factors which contributes to the formation and persistence to dispersions, namely, the electrical charge and the adsorbed protective film. It appears probable that both these factors enter into the stability of imidazolinium derivatives and are mainly used in surfactants in small proportion to increase dispersion action.

Vodak⁵¹⁾ prepared imidazolinium compounds as stabilizer for aqueous dispersion of aminoamide fabric softeners. The title compound containing 15-90% aqueous dispersion of acetate or methosulfate salts of fatty acid amide with polyamines. Kolomiets *et al.*⁵²⁾ gave a method of preparing foaming or dispersing agent for synthetic detergents.

9.3 Resiliency

Cationic surfactants impart resiliency to the fabric. For this purpose generally 3-30% solution of quaternary ammonium salts of imidazoline are used.

Yamamura *et al.*⁵³⁾ prepared softeners for imparting improved resilience and bulk to fabrics. Hayase *et al.*⁵⁴⁾ manufactured the amine derivatives and liquid softeners containing them for imparting improved softness and resilience to fabric. A laundered cotton towel was treated with compound containing 15% mix. and hydrochloric salt for 1 min. at 25°C to give a soft towel with resilience rating

(+ 2 best, - 2 worst).

9.4 Hair and fabric conditioning

Cationic surfactants are also useful as fabric and hair conditioning agents. They act in such a way that it reduces inter fiber friction so as they feel silky and soft.

Oshima⁵⁵⁾ prepared shampoo compositions containing imidazolinium type amphoteric surfactants. The compounds have pearly gloss, good storage stability, and conditioning effect. Drach *et al.*⁵⁶⁾ prepared imidazolinium compound that are useful for softening and conditioning fibers, hair and skin, and as surfactants and debonders for cellulose pulp.

9.5 Antistaticness

The rapid growth of the synthetic fiber industry has greatly emphasized the importance of antistatic finishes. Cotton and viscose rayon under normal humidity condition do not generate static electricity to any troublesome extent. Acetate rayon and wood generate static electricity more readily and necessitate precautionary measure in the mill where they are fabricated.

Lambert⁵⁷⁾ manufactured hydroxy ethyl imidazoline derivatives, a antistatic agents in laundry detergents. Rasario-Jansen *et al.*⁵⁸⁾ prepared fabric softening and antistatic compositions containing a quaternized disubstituted imidazoline ester fabric softening compounds with a non-ionic fabric softening compound. The title compounds have good storage stability, viscosity, softening and antistatic properties⁵⁹⁾.

9.6 Rewettability

Rewet or water absorbency is important because too much fabric softeners can water proof cloth⁶⁰⁾. A general rule for any method of application is the more softeners on the fabric, the water absorbency decreases. Small amounts of nonionic surfactants are sometimes added to rinse cycle formulation to improve rewet.

The longer fatty alkyl group and the more saturation in the group, the poorer the rewet properties.

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