Cationic Surfactants in Laundry Detergents and Laundry Aftertreatment Aids

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ABSTRACT

Cationic surfactants have a positively charged nitrogen atom and at least one hydrophobic, long-chain substituent in the molecule. Because of their fabric-softening and antistatic properties, they are used as active materials in fabric-softening agents. Suitable cationic surfactants are mostly quaternary ammonium salts, and to a lesser extent, imidazolinium salts with two long hydrophobic alkyl chains. Alkylated, partly ethoxylated polyamines, amine amides, ester amines and di-quaternary compounds also have recently been used or proposed. Fabric softeners generally are aqueous dispersions of distearyl dimethyl ammonium chloride or tallow alkylated imidazolinium derivatives in concentrations of 1-9%. Concentrated fabric softeners have recently been pushed into the market as double, triple or 10-fold concentrates. Fabric softeners used in the forms of aerosol sprays, pads or sheets, are not used in the washing machine but can be used in the laundry dryer. The combination of laundry detergent and fabric softener is a single product is impaired by anionic surfactants normally contained in laundry detergents because they react with the cationics to form neutral salts. With the so-called soft detergents, one attempts to circumvent these difficulties by means of special formulations, e.g., with nonionics or by using definite physical-chemical mechanisms. They represent a compromise with regard to detergency performance and softening effect.

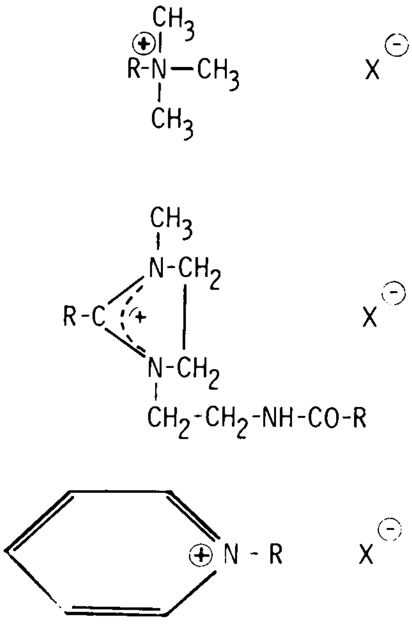
INTRODUCTION

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, as shown in Figure 1. The Ra substituents originate from fatty acids or fatty alcohols. They always consist of a mixture of various homologues, depending on the source of the fatty acids or fatty alcohols. They frequently originate from coconut oil or tallow and can be saturated or partly unsaturated. There can also be a benzyl group in place of one methyl group.

The properties of these compounds are very strongly influenced by the type of the substituent. Chain length, degree of saturation, branching or the presence and number of hydroxylic or ethoxy groups mainly determine the properties of the surfactant.

Cationic surfactants became technically important after Domagk (1) discovered their bacteriostatic properties, hence their use as germicides and fungicides in cosmetic and antiseptic preparations. Cationic surfactants, however, can also have textile-softening, antistatic and water-repelling properties, and also display foam-depressing and corrosion-inhibiting effects. Their growth after World War II can be attributed to these properties. They have been used, for instance, as fabric-softening agents, antistatics, flotation chemicals and as additives to asphalt concrete. Cationic surfactants are also used in the recovery of crude oil (2). The proportion of cationic surfactants with respect to the total production of surfactants is assessed at ca. 7-8%. This would mean, that 60,000-70,000 tons of cationics (as 100% active) were produced in Europe in 1981.

A comprehensive review of the chemistry (4) and a detailed review of the use of cationics based on US patient references (5) are available. The great importance of cationics to the detergent industry is exclusively due to fabric softening and antistatic properties. An abridged review of the use of cationic surfactants in laundry detergents and laundry aftertreatment aids is given here. All data presented refer solely to those types of cationic surfactants that are used in laundry detergents and laundry aftertreatment aids, if not otherwise indicated.



$R = C_8$ to C_{26} $X = Cl$ or $CH_3\text{-}O\text{-}SO_3$

FIG. 1. Representative compounds of various types of cationic surfactants.

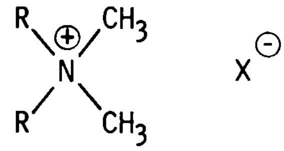
CATIONIC SURFACTANTS WITH TEXTILE-CONDITIONING PROPERTIES

Cationic surfactants having softening and antistatic properties are characterized by two long hydrophobic alkyl chains in the molecule (Fig. 2). Cationics of the quaternary ammonium and imidazolinium type are still the most important compounds used to improve the surface properties of textiles. At the same time, other types of compounds which have appeared in recent years are used only in minor amounts.

Quaternary ammonium and imidazolinium compounds used in laundry detergents and aftertreatment aids are poorly soluble in water. However, they can be converted readily into stable dispersions.

Why is Conditioning of Textiles Necessary as an Accompanying Treatment after Washing?

Special properties are imparted to textiles by finishing and



$R = C_{16}/C_{18}$ $X = Cl$ or $CH_3\text{-}O\text{-}SO_3$

FIG. 2. Distearyl dimethyl ammonium chloride.

conditioning processes in their production. Textiles worn or used in contact with the skin, e.g., underwear, terry toweling, hand towels and blankets, are finished with preparations to give them a pleasant, soft and fluffy feel. These properties are lost during washing (6): first, because the finishing is washed off, and secondly, because modern washing and drying treatments additionally tend to make the textiles feel harsh. By using cationic-based additives in domestic washing machines, these lost properties are reimparted to the textiles.

Mechanism of the Action of Cationic Surfactants

It is a prerequisite for the softening and antistatic effect of cationic surfactants that they are adsorbed on textile substrates (7-11). A high degree of substantivity between the negatively charged textile surfaces and the positively charged part of the cationic surfactant molecules in the aqueous phase exists (Fig. 3). Under the conditions of the rinse bath, for instance, wool or cotton adsorb more than 90% of the quaternary ammonium compounds from the aqueous phase.

The adsorption depends on numerous parameters such as the molecular structure of the cationic surfactants themselves (chain length and type of the alkyl substituent), textile substrate, time of action, temperature, pH value and the presence of other surfactants or builders. Particularly important is the pH value of the rinse bath: although the amounts 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 adsorbtion of the quaternary ammonium compounds. Under alkaline conditions, quaternary ammonium compounds show an uneven distribution on the textile surface (10). By washing with detergents of usual composition, the adsorbed quaternary ammonium compounds are almost completely desorbed (7, 9). Imidazolinium compounds behave similarly with regard to their adsorptive properties (9).

Quaternary Ammonium Compounds

Quaternary ammonium compounds are at present the largest volume of cationic surfactants used for conditioning of textiles by means of laundry detergents and aftertreatment aids. The quaternary ammonium compound with two long alkyl substituents derived from hydrogenated tallow, distearyl dimethyl ammonium chloride (DSDMAC), is the most important cationic surfactant. Its long-chain alkyl substituents are mainly a mixture of the C_{16} and C_{18} homologues.

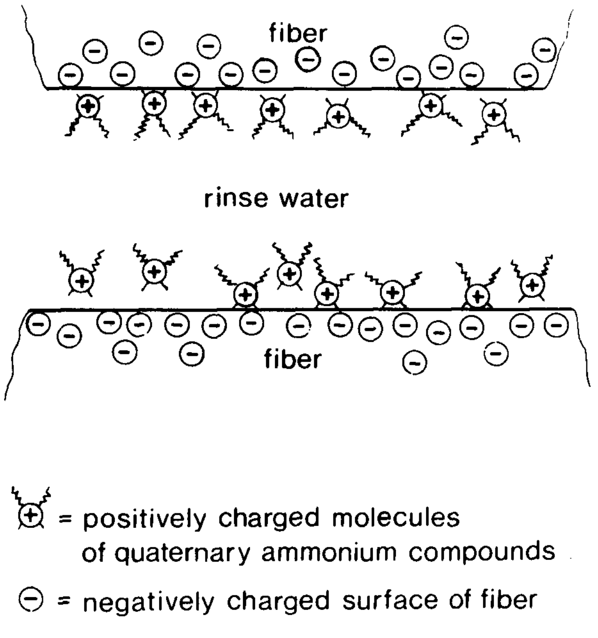
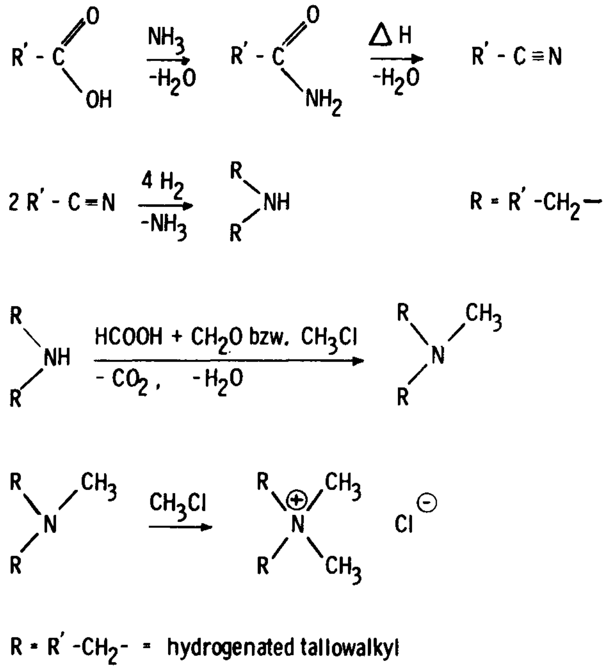


FIG. 3. Substantivity of cationic compounds.

In Europe, the anion of this type of compound is almost always chloride. In the USA, methyl sulfates are also found to an appreciable extent in addition to chlorides.

DSDMAC is produced by two main processes. The first starts with fatty acids (Fig. 4) which are then converted to nitriles. These are hydrogenated to form the secondary amines that is subsequently converted either with formaldehyde and formic acid or with methyl chloride to the tertiary amines which, in a subsequent step, reacts with methyl chloride to form the quaternary ammonium compound (12). The second method uses fatty alcohol as the starting material (Fig. 5) from which the secondary amine is produced (13). This amine is methylated with methyl chloride. An additional mole of methyl chloride is used to form the quaternary ammonium compound. To



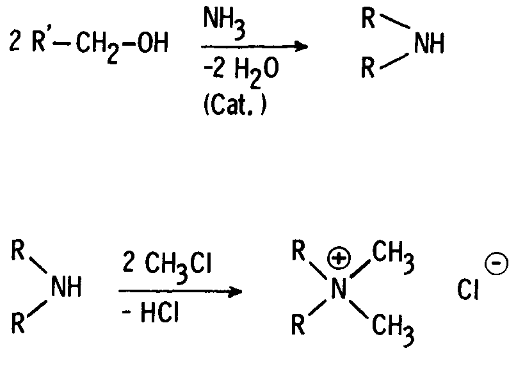


FIG. 5. Production of distearyl dimethyl ammonium chloride from fatty alcohol.

obtain methyl sulfate as the anion, the last step is a methylation with dimethyl sulfate instead of methyl chloride.

The properties of quaternary ammonium compounds are determined largely by the structure of the substituent, particularly by its chain length, degree of saturation and number of oxygen atoms. Alterations of the saturated tallow-alkyl chain affect the softening performance and pourability of formulations. Hydroxy groups in the substituents of quaternary ammonium compounds and/or unsaturated fatty alkyl chains enhance the solubility, thereby improving the finished properties. Ditallow-alkylhydroxypropyl methyl ammonium chloride is a liquid in contrast to distearyl dimethyl ammonium chloride. Finishing of the product is also facilitated by using coco alkyl substituents that have a shorter carbon chain. Ether groups (14), e.g., in *bis*(fatty alkyl diethoxy)dimethyl ammonium chloride (Fig. 6) have the same influence. Polyethoxylated ammonium salts show an interdependence between the number of the ethoxy groups and the softening performance. The more ethoxy groups there are, the lower the softening effect is.

Advantageous properties with regard to color and odor are shown by conversion products of 1-chloro-2-hydroxy-3-alkoxypropane with secondary amines (15), e.g., *bis* (2-hydroxy-3-tallow-alkoxypropyl)dimethyl ammonium chloride (Fig. 7). Furthermore, dialkyl fatty ester dimethyl ammonium compounds (16), e.g., *bis*(tallow-alkylcarboxymethyl)dimethyl ammonium chloride (Fig. 8) have been proposed. The advantage of these esterammonium salts is explained by the fact that they form aqueous dispersions during their production. These dispersions do not contain inflammable alcohol and can be immediately used after adequate dilution.

Other kinds of diesters are the conversion products of dihydroxypropyl trimethylamine with fatty acids, e.g., 1,2-*bis*(tallow-alkylcarboxy)propyltrimethyl ammonium chloride (Fig. 9). Such diesterammonium salts show a greater textile-softening effect than the corresponding monoesterammonium salts (17).

Other cationics particularly recommended for the production of homogenous concentrated fabric softener dispersions are *bis*(2-alkylamidoethyl)dimethyl ammonium salts (18), e.g., *bis*(tallow-amidoethyl)dimethyl ammonium chloride (Fig. 10). Ethoxy groups may be incorporated between the amide and ethylene groups. Good finishing properties are said to be shown by quaternary ammonium compounds which simultaneously have an ester and an amide group as substituents at the nitrogen atom (19). Of both long substituents, one is an alkyl chain directly linked to the nitrogen atom and the other is a fatty acid substituent connected via an ester group to ethyl or propyl. A representative of this class would be tallow-alkyl(tallow-alkylcarboxyethyl)-acetamidoethyl ammonium chloride (Fig. 11).

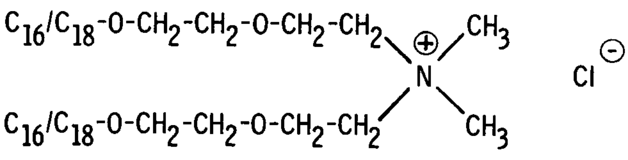


FIG. 6. *bis*(Tallow-alkyldiethoxy)dimethyl ammonium chloride.

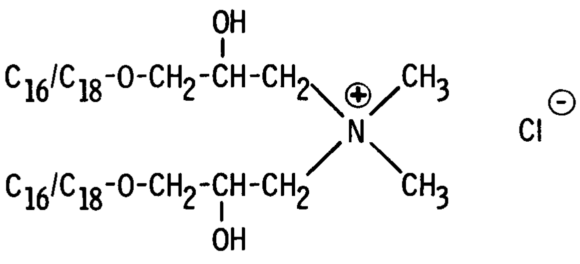


FIG. 7. *bis*(2-Hydroxy-3-tallow-alkoxypropyl)dimethyl ammonium chloride.

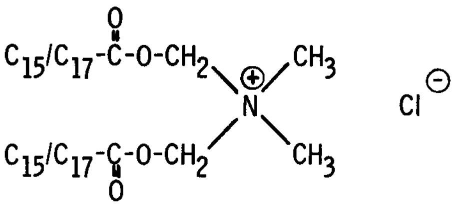


FIG. 8. *bis*(Tallow-alkylcarboxymethyl)dimethyl ammonium chloride.

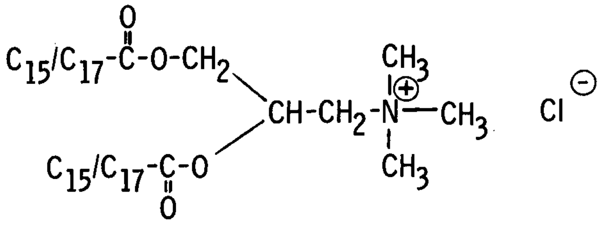


FIG. 9. 1,2 *Bis* (Tallow-alkylcarboxy) propyltrimethyl ammonium chloride.

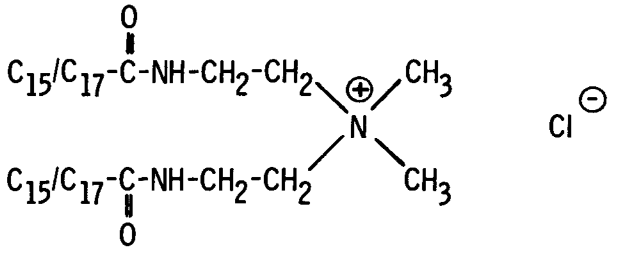


FIG. 10. *bis*(Tallow-amidoethyl)dimethyl ammonium chloride.

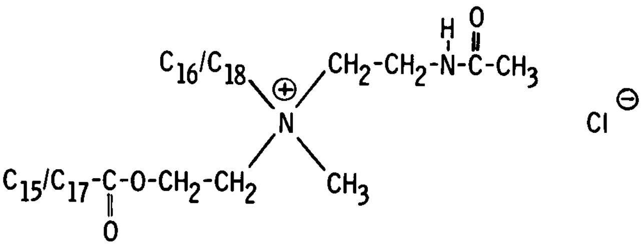


FIG. 11. Tallow-alkyl-(tallow-alkylcarboxyethyl) acetamidoethyl ammonium chloride.

Imidazolinium Compounds

Imidazolinium compounds are second to the quaternary ammonium compounds in tonnage of cationic surfactants produced for fabric softeners. Representatives are imidazolines substituted in the 1-, 2- and 3-position (Fig. 12) with a fatty acid amidoethyl chain at the first carbon atom, a long-chain alkyl substituent at the second C atom, and a methyl group at the third (20). In contrast to the quaternary ammonium compounds, imidazolinium compounds exclusively have methyl sulfate as anion.

The most widely used representative of this group is the tallow-alkyl derivative. It is supplied as a liquid and is easily processed (e.g., in the cold) to fabric softeners. The imidazolinium derivative with a hydrogenated tallow chain gives a better softening effect than the nonhydrogenated tallow derivative (20, 21) but requires a more complex formulation to obtain a finished product. The oleyl derivative has recently gained importance because it has less hydrophobizing effect with relatively good softening performance. Thus, textiles treated with it keep almost all their natural absorbency properties. In addition, the oleyl derivative has excellent properties with respect to incorporation in finished, highly concentrated fabric softeners (22). In practice, imidazolinium compounds are frequently blended with distearyl dimethyl ammonium compounds to attain a higher degree of softening performance.

The production of the imidazolinium compounds (Fig. 13) starts from fatty acid and diethylenetriamine. They are condensed under ring closure, and the imidazoline formed is then converted with dimethyl sulfate to the imidazolinium salt (12, 20, 23, 24). By condensation of triethylenetetraamine with fatty acids and subsequent ring closure with additional acid, 1,3-*bis*(fatty acid amidoethyl)-2-alkyl-imidazolinium salts are obtained (Fig. 14). These *bis*-amidoethyl substituted imidazolinium derivatives are particularly suitable for crystallization (25).

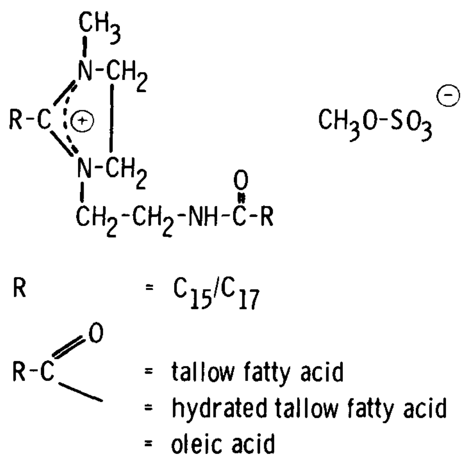


FIG. 12. 1-(Fatty acid amidoethyl)-2-(fatty alkyl)-3-methyl-imidazolinium methyl sulfate.

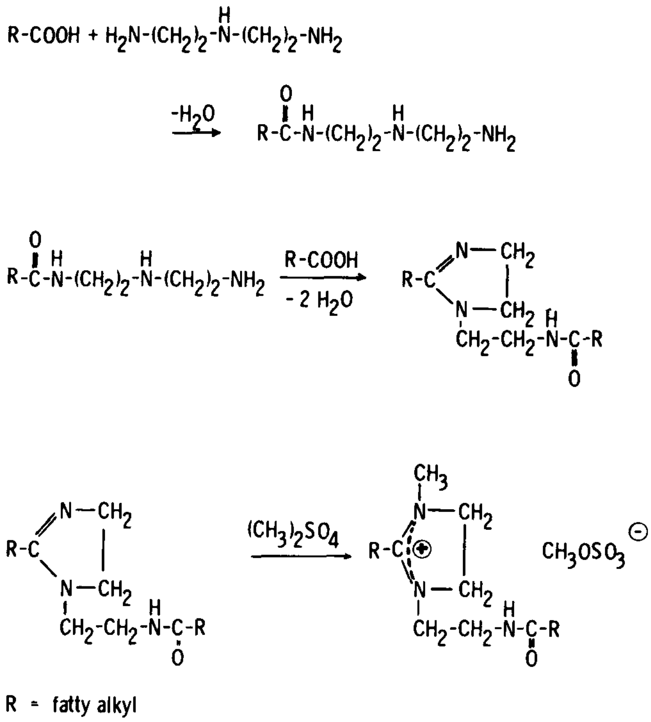


FIG. 13. Production of imidazolinium compounds.

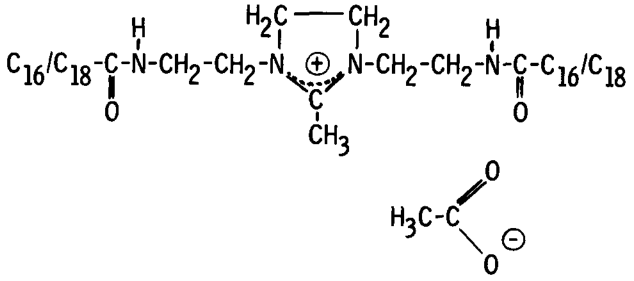


FIG. 14. 1,3-*bis*(Tallow-amidoethyl)-2-methyl-imidazolinium acetate.

Miscellaneous Cationic Surfactants for Conditioninig Textiles

Numerous cationics cannot be derived directly from the tetraalkylammonium ion or imidazolinium ion. Quite a number of compounds belong to these cationic surfactants to which softening and antistatic effects on textiles are attributed. They are also recommended or incorporated in fabric softeners or laundry detergents. They are cationic or partly cationic conversion products of di-, tri- or polyamines or of nitrogen-containing heterocyclic compounds with fatty alcohols or fatty acids. They play only a minor part and are frequently recommended only as aids to the finishing of formulations based on quaternary ammonium or imidazolinium compounds.

β-Hydroxyethyl ethylenediamine derivatives. Conversion products of β-hydroxyethyl ethylenediamine with fatty acids are indeed not cationic surfactants in a narrow sense. They should be mentioned, however, because representatives of this type of compound have already been used as softening agents.

In the reaction of fatty acids or fatty esters with β-hydroxyethyl ethylenediamine, a mixture of esters, amides or ester amides is formed (Fig. 15) depending on whether

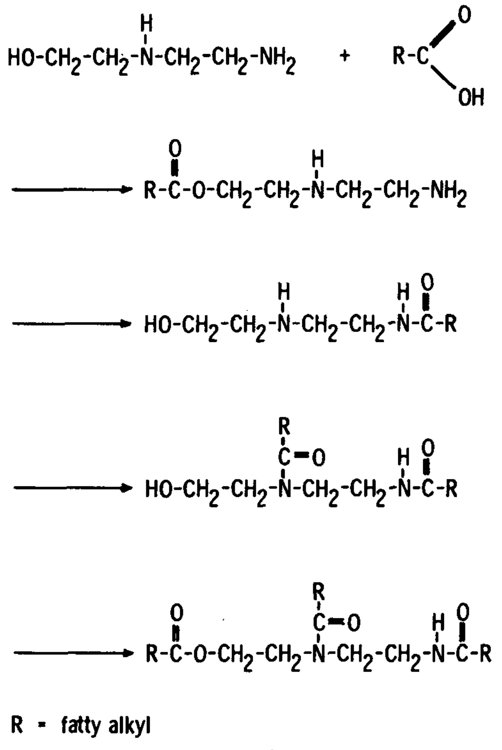


FIG. 15. Conversion products of fatty acids and β-hydroxyethyl ethylenediamine.

condensation with the fatty acid occurs at the oxygen atom or at one or both nitrogen atoms (26).

The partly protonated reaction product formed, the degree of protonization of which depends on the extent of the excess of fatty acids used, is suitable for the production of fabric softeners (27) or for incorporation in laundry detergents (26).

Di-quaternary compounds. Di-quaternary ammonium compounds, e.g., N-tallow-alkyl-trihydroxyethylpropylenediammonium dichloride (Fig. 16) or diamines substituted with alkoxyesters of fatty acids (Fig. 17) have been described as preferred aids to the production of finished, highly concentrated fabric softeners (28, 29). Diammonium salts render textiles less water-adsorbing in comparison with the corresponding monoammonium compounds (30). *bis*-Imidazolinium compounds (Fig. 18) have been described for the production of fabric softeners with improved physical properties (31).

Polyammonium compounds. Polyammonium compounds (Fig. 19) are used as agents substantive to textiles. They have been used in combination with classic fabric-softening quaternary ammonium or imidazolinium compounds to transfer to nonionic fabric-softening compounds (sorbitol or glycerol esters) substantivity to textiles (32). They are also claimed for the production of highly concentrated fabric softeners (28). They are said to impart improved pourability and dispersing properties.

Good finishing properties, simultaneously with good softening performance, are shown by ethoxylated polyammonium compounds which are formed by conversion of long-chain epoxides with polyamines (33). Particularly *bis*(β-hydroxytetradecyl)triethoxydipropylenetriamine (Fig. 20) has optimal properties with regard to formulation of special fabric-softening agents (34). Because fabric softeners are adjusted to slightly acidic pH values, the triamine molecule has a cationic character.

Alkylpryidinium and pyrimidinium compounds. A group of cationic surfactants which is unimportant for practical fabric-softening formulations comprises the alkylpyridinium (28, 32) and tetrahydropyrimidinium compounds (35) (Fig. 21).

Cationic polymers. In this case, cationic guar gum has been described (36) as an additive to blends of cationic and nonionic softeners. It enhances their softening performance.

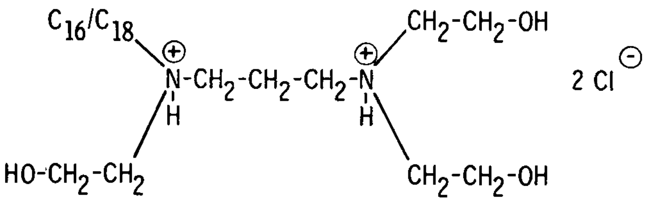


FIG. 16. N-Tallow-alkyl-N,N′,N′-*tris*(2-hydroxyethyl)-1,3-propanediammonium dichloride.

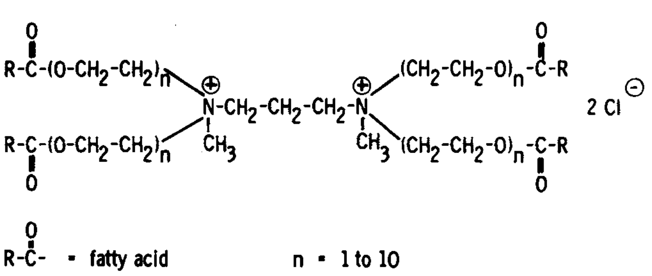


FIG. 17. Propylenediammonium chloride with fatty acid ethoxyester substitutes.

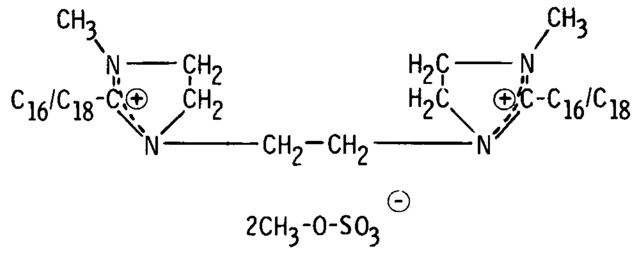


FIG. 18. 1,1-Ethylene-*bis*(2-tallow-alkyl-3-methyl-imidazolinium)-methyl sulfate.

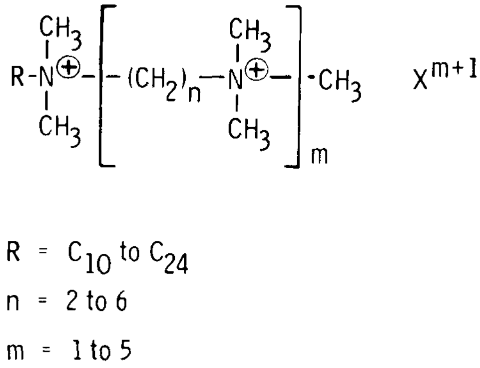


FIG. 19. Polyammonium salts.

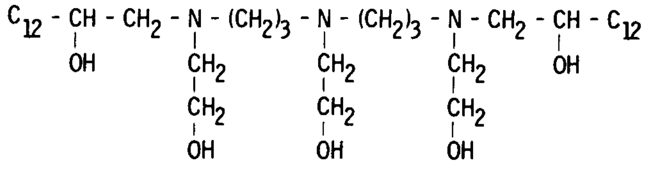


FIG. 20. *bis*(β-Hydroxytetradecyl)dipropylenetriamine-3 EO.

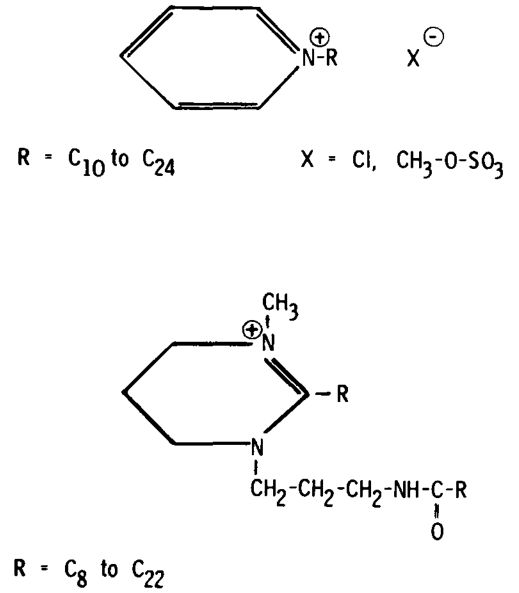


FIG. 21. Alkylpyridinium salts, alkyltetrahydropyrimidinium salts.

FABRIC SOFTENERS

In West Germany, ca. 400,000 tons of fabric softeners are sold yearly for domestic use and cationic surfactants are the main ingredients.

In the USA, fabric softeners were introduced into the market in the early 1950s (37); in Europe they were launched about 10 years later. Changes in laundering methods in Europe during the 1960s brought about striking differences in the condition of the laundry after washing. So far, laundry had been washed by hand or in tubs and drying of the laundry had taken place mostly outdoors where it was tossed about by the wind. With the introduction of washing machines, the laundry was dried in indoor drying rooms without movement of the laundry at all. This caused the laundry to get a particularly harsh feel from the strong mechanical action of machine washing that brings disorder to the pile of the fibers at the fabric surface, which is subsequently fixed by static drying (6).

The aspect of fabric softening has not been as important in the USA as in Europe, due to the use of relatively large agitator-type washing machines with shorter washing times, and also because of the more extensive use of laundry dryers and the much higher proportion of synthetic fibers. Instead, antistatic conditioning has been emphasized more in the USA than in Europe.

Rinse-Cycle Fabric Softeners

This type of fabric softener is added to the laundry during the last rinse cycle, i.e., at a time when soil and detergent residues have been almost completely removed. This is important because cationic ingredients of fabric softeners would be rendered ineffective by formation of neutral salts with the anionic surfactants from the laundry detergent. Soil would also have a negative effect because it would be competitive with the textile in terms of adsorption of cationic surfactants.

Conventional fabric softeners contain from 1 to 9% quaternary ammonium or imidazolinium compounds and, additionally, finishing aids, preservatives, sometimes optical brighteners and other additives, dispersed in water. They countereffect the disorder of the pile of the fiber at the textile surface as well as electrostatically charging the textiles. They impart fluffiness and antistatic properties to the fabrics. Thus, they give a more pleasant sensation to textiles worn close to the skin and give the impression of a longer lasting freshness. They effect more rapid drying because water is more readily released from the laundry. They also facilitate ironing (37).

The more rapid drying is a consequence of the larger extent of dewatering made possible by softened textiles. This hydrophobic effect of laundry treated with cationic surfactants is positive in this sense, yet is simultaneously a drawback in that the physically important absorbency of the textiles is reduced. Concentration and type of cationic surfactant determine the relevance of the reduced absorbency to the usability of the textiles.

The present economic importance of cationic surfactants is determined by their use in laundry fabric softeners (2). About 75% of all cationics are used for their production (Table I). Distearyl dimethyl ammonium chloride, almost exclusively used for the production of fabric softeners, is supplied as a paste containing 75% active material in isopropanol and water. It is melted at 60 C and added to 60 C warm water with stirring and addition of emulsifiers if necessary. 1-Tallow-amidoethyl-2-tallow-alkyl-3-methylimidazolinium methyl sulfate, principally used as the imidazolinium compound for fabric softeners, is supplied as a partly finished product containing 75% active material as well. It is an opaque liquid that can be dispersed in water at ambient temperature.

TABLE I

Fields of Application of Cationic Surfactants (2)

Application	Percentage
Fabric softeners	76.6
Intermediates	12.7
Textile industry	6.8
Road construction	2.2
Mining	1.1
Cosmetics	0.6

Conventional fabric softeners are sold in relatively large bottles, mostly 4-L plastic bottles in Germany.

Fabric-softener concentrates can be used in much smaller amounts than conventional fabric softeners. They offer several advantages (34): handling is facilitated, less shelf space is occupied, there is less transportation of water, less packaging material used, and production/packaging costs are less.

Based on an average content of 5% active material in conventional fabric softeners, the softener concentrates found on the European market today can be characterized (34) as:

- double concentrates with ca. 10% active material,
- triple concentrates with ca. 15% active material,
- 10-fold concentrates with ca. 50% active material.

Between double and triple concentrates on the one hand and the 10-fold concentrates on the other, there are substantial differences in appearance and application. Double and triple concentrates are, like conventional fabric softeners, aqueous dispersions of active material, whereas 10-fold concentrates represent solutions of fabric-softening agents with only a small proportion of water.

Furthermore, certain differences exist between the situations in the USA and in Europe with regard to the terminology. Whereas in the USA, fabric softeners usually contain from 3 to 4% active material, fabric softeners containing from 7 to 8% active matter are already characterized as "concentrates" (38). Because distearyl dimethyl ammonium chloride and tallow-alkyl imidazolinium compounds used for the production of low concentrated conventional fabric softeners cannot be readily incorporated in higher concentrations in storage stable formulations, concentrates make high demands on the active material with respect to finishing of the product, and require a well balanced system of selected emulsifiers. Ethoxylated polyamines such as stearylpropylenediamine-3 EO and fatty esters from mono- or polyvalent alcohols such as glycerol monostearate (39), ethoxylated fatty amides (40), aliphatic or aromatic polyoxethosylenes (41), water-soluble monoalkylammonium or imidazolinium salts and hydrocarbons (42), amine amides (43) and fatty alkyl diamines (44) are recommended. In addition to the classic ammonium and imidazolinium compounds, other cationic surfactants with softening and antistatic properties, such as polyammonium-*bis*-imidazolinium-, alkylpyridinium compounds and cationic polymers, have also been increasingly described in literature on fabric-softener concentrates.

Wash-Cycle Fabric Softeners

Wash-cycle fabric softeners should not be confused with detergents with incorporated fabric softeners. Wash-cycle fabric softeners are equally formulated as rinse-cycle fabric softeners. They differ from the latter in that they contain more active material. They are not applied in the last rinse bath but in the wash bath (45). Wash-cycle fabric softeners became known only in the US market. In a certain sense they represent an expediency resulting from the fact that many US washing machines do not have an automatic dispenser for fabric softeners so that the consumer is forced to observe the course of the washing program in order to add the fabric softener at the right moment. This troublesome procedure is circumvented when the consumer adds the fabric softener directly to the wash bath at the beginning of the washing process before addition of the laundry detergent. That is why these fabric softeners are also called "first-in" softeners (46). Wash-cycle fabric softeners are expedient because the effectiveness of the cationic active material is greatly limited by the anionic surfactants of the laundry detergent.

Solid Fabric Softeners

Fabric softeners, either the conventional or concentrated type, are usually supplied and used as liquids. Solid fabric softeners as spray-dried powder, ground product, granules or flakes are totally unimportant. Commercial products consist of DSDMAC which is converted into the solid state by spray-drying or thin film evaporization. They can also be fatty acid amidoethyl substituted imidazolinium compounds (25) obtained by condensation of fatty acids and polyamines.

Other compositions are also offered, such as, e.g., amines and quaternary ammonium salts combined with sheet silicates as carriers (47) or products that are obtained by melting dialkyldimethyl- and monoalkyltrimethylammonium salts (48). Furthermore, the ability of quaternary ammonium compounds to form inclusion compounds with urea is used for production of solid fabric softeners (49). Quaternary ammonium compounds in which one of the long alkyl chains is an ester of an unsaturated carbonic acid, are also described as particularly suitable (50) for such combinations with solid "diluents"as urea or sodium sulfate.

Solid fabric softeners are not only unimportant because of the domestic washing machines that are matched to liquid fabric softeners only, but also because of their slow dispersability in water. It frequently takes several hours for a sufficient dispersion to be attained. For this reason, solid fabric softeners are not used in domestic application but only for institutional washing where parent solutions are made from them overnight. Because neutralization of wash bath alkali and elimination of residual active chlorine in the rinse bath is frequently done in washing shops, such as solid fabric softeners additionally contain acidifying and dechlorinating agents (51).

TUMBLER AIDS

Tumbler aids are used like liquid fabric softeners and to impart a scent to washable textiles. They are, as can be deduced from the name, not added to the laundry in the washing machine during the wash or rinse cycle but to the laundry dryer before drying (46, 52).

There are several forms of application (34):

- as aerosol foam that is sprayed on a cloth or a laundry item added to the moist laundry in the dryer,
- as aerosol with which the internal side of the empty drying drum is sprayed before loading it with laundry,
- as a pad filled with active matter: the pad is fastened by sticking to one of the paddles in the drying drum,
- as sheets made from polyurethane foam or nonwoven material impregnated with active matter, to act as carrier.

Only carrier sheets made from polyurethane foam or particularly from cellulose or polyester nonwovens have been successful on the market. The carrier sheets are impregnated with distearyl dimethyl ammonium salt as the softening-effective component. In the USA, methyl sulfates are preferred because the corresponding chlorides are said to lead to corrosion of laundry dryers.

Exactly like wash-cycle fabric softeners, tumbler aids represent a solution of the problem caused by the fact that US washing machines fail to have dispensers for rinse-cycle liquid fabric softeners. They are, however, not a compromise, in contrast to wash-cycle fabric softeners, as they show good fabric-softening and antistatic effects. This fact and the extensive use of laundry dryers in American households explain the great success of tumbler aids in the USA. In Europe, tumbler aids are known only regionally at present.

LAUNDRY DETERGENTS WITH INCORPORATED FABRIC SOFTENERS– SOFT DETERGENTS

The separate use of laundry detergent and fabric softener can be an inconvenient procedure, especially when the washing machine does not have an automatic dispenser into which the fabric softener can be added at the beginning of the washing process. Because this situation is widely encountered in the USA, attempts to facilitate the addition of fabric softeners have been very intensive there. Wash-cycle fabric softeners and tumbler aids, as mentioned before, are only two of the results of these attempts. It is evident that the combination of cleaning action and fabric-softening effect in one product is the most elegant of all possible solutions to the problem. Even when there are separate dispensers for laundry detergent and fabric softener in the washing machine, this combination would be a real improvement.

The realization of this idea encountered technical difficulties due to the well known tendency of the formation of neutral salts with anionic surfactants. Many attempts have been made to circumvent these difficulties, in that anionic surfactants in the detergents were substituted by nonionic surfactants; or cationic surfactants in the presence of anionic surfactants were put in a state in whch interactions between both antagonistic substances are avoided so that their individual actions are not mutually reduced. Results obtained in this way, so far, represent a considerable improvement. However, it should not be suggested that the objective is reached when laundry detergents display a washing and softening performance equal to those of brand detergents with separately applied fabric softener.

As shown in Table II, the fabric-softening effects that are obtained with the so-called soft detergents are always much lower than those obtained with a separately applied fabric softener. The net detergency performance is, depending on type of textile and soil, also lower.

In spite of the fact that soft detergents have had regional market success, it cannot yet be said whether or not the statement "cationic surfactants" will not reach importance in formulations with overall good detergency performance in the future" (53) has been disproved in Europe. However, one fact is sure: current soft detergents are a compromise solution. The consumer has to decide whether the advantage of easier handling conpensates for the disadvantage of reduced performance.

Soft Detergents on an Anionic-Free Basis

The most obvious means of eliminating the anionic/cationic antagonism is to remove the anionics from the formulation and to formulate a detergent based on nonionic surfactants only. This is attained with combinations of ethoxylated fatty alcohols and/or nonylphenol ethoxylates with an average of 7–9 moles of ethylene oxide and cationic fabric-softening agents of the quaternary ammonium or imidazolinium type (54, 55) (Table III). Sodium aluminosilicates are used as builders for these formulations, e.g., zeolite A, and are recommended in addition to conventional poly-

TABLE II

Comparison of Detergency and Softening Performance of a Commercial Heavy-Duty Detergent with Incorporated Fabric Softener and a Heavy-Duty Detergent with Separate Fabric Softener.

Conditions: Automatic tumbler type washing machine Program: main wash cycle only 60 C Water hardness: 285 ppm (as $CaCO_3$) Wash load: 3.5 kg of naturally stained domestic laundry		Heavy-duty detergent with incorporated fabric softener	Heavy-duty detergent with separate fabric softener
Detergency performance (% reflectance[a])	Cotton Wool fat/ particulate soil[b] 7:1	62.2	66.0
	P/P Cotton Sebum/ particulate soil[b] 3:1	55.2	70.0
	Polyester/cotton Sebum/ particulate soil[b] 3:1	61.9	63.0
Softening performance Feel[c] (grading)	Terry cloth	2.6	4.8
	Beaverteen	3.8	5.9
	Polyester/cotton	3.5	4.8

[a] Zeiss-Elrepho RFC 3, filter 460 nm, without UV.

[b] Particulate soil: 86% kaolin; 8% carbon black; 4% iron oxide, black; 2% iron oxide, yellow.

[c] Subjective test, average values.

TABLE III

Composition of a Powder Soft Detergent Based on Nonionic Surfactants (54)

Material	Percentage
C_{16}/C_{18} Fatty alcohol-10 EO	3-6
C_{12}/C_{14} Fatty alcohol-4 EO	3-6
Coco fatty acid monoethanolamide	2-4
Sodium triphosphate	20-40
Sodium sulfate	30-45
Sodium silicate	3-7
Water	Balance

phosphates and phosphonic acids (56). Cationic-containing laundry detergents based on nonionic surfactants have been on the market for several years. Due to the very high content of nonionic surfactants, such formulations are frequently liquid (57, 58) (Table IV). Because of the unbalanced surfactant portion, these laundry detergents are recommended as specialties, preferably as special detergents for woollens.

TABLE IV

Composition of a Liquid Soft Detergent Based on Nonionic Surfactant

Material	Percentage
C_{14}/C_{15} Oxoalcohol-7 EO	5-18
C_{10}/C_{12} Fatty alcohol-6 EO	5-18
Ditallow-dimethyl ammonium chloride	3-7
Ethanol	2-6
1,2-Propylene glycol	2-6
Ethylene glycol stearate	0.1-0.5
Formaldehyde	0.005-0.05
Water, dyestuff, fragrance	Balance

Soft Detergents Based on Anionic Surfactants

Three methods are principally used to impart fabric-softening properties to laundry detergents based on anionic surfactants:

- addition of cationic surfactants with fabric-softening properties to conventional laundry detergent formulations,
- delayed release of cationic surfactants with fabric-softening properties in conventional laundry detergent formulations, and
- use of substitutes of cationic surfactants with fabric-softening properties.

Addition of cationic surfactants to conventional laundry detergent formulations. The simple addition of quaternary ammonium compounds to laundry detergents of conventional formulation, sometimes in quite high concentrations, (59), is an attempt to solve the problem equivalent to that of wash-cycle softeners. Instead of separate addition of the quaternary ammonium compound to the wash bath, it is incorporated directly in the laundry detergent. Fabric-softening effects can be expected to a very modest extent, as is the case with wash-cycle softeners. In the USA, antistatic effects are attributed to these formulations due to the formation of neutral salts, rather than fabric-softening performance. Ethoxylated N-fatty alkyl ethylenediamines (60) and condensation products from hydrogenated tallow and hydroxyethylethylenediamine (61) have been described as particularly compatible in formulations based on anionic surfactants.

Laundry detergents with delayed release of cationic surfactants. Developments comprising encapsulation of quaternary ammonium compounds by water-resistant substances or by material melting at higher temperatures, aim to release the cationic surfactants towards the end of the wash cycle, i.e., at a time at which the anionic surfactants have already removed the soil from the laundry, or not until during the rinse cycle or drying cycle. Suitable dispersion inhibitors are paraffin wax, alcohols, aliphatic carboxylic acids or their esters ethylene oxide condensates (62, 63), castor oil (64) and hydrogenated fatty acid triglycerides (65). Another method, described as a delayed release method, is to encase textile-softening quaternary ammonium compounds in a container that is insoluble in the detergent solution (66) or to add these compounds as solid granules to the laundry detergent (46, 48).

Soft detergents with substitutes of quaternary ammonium compounds compatible with anionic surfactants. Proposals to combine anionic surfactants with noncationic fabric softeners in soft detergent formulations represent the reverse of the principle of a combination of cationic fabric softeners with nonionic surfactants. As noncationic fabric softeners, sheet silicates of the montmorillonite, hectorite or saponite type have been proposed recently (67-69). Sheet silicates, however, are only an insufficient substitute of cationic fabric softeners. As a consequence, sheet silicates are enriched by addition of quaternary ammonium compounds that preferably act as an antistatic in addition to fabric-softening sheet silicates (70, 71).

A completely new principle in the application mechanism of cationic surfactants that aims to circumvent the mutual obstruction of anionic and cationic surfactants, is incorporated in the proposal of adding tertiary amines with two long alkyl chains to the detergent solution (72). Here, the charge reversal which certain tertiary fatty amines undergo when the pH value changes from the alkaline to the neutral range, is used. These tertiary fatty amines have a negative charge at a pH value of 9-10 in the detergent solution and therefore do not react with anionic surfactants. Because of their insolubility in water, they are retained by the textiles when the wash cycle changes to the rinse cycle. When the rinse water is added, the pH value changes to the neutral range. The tertiary amines are protonated and hence become cationic and are then adsorbed onto the fibers. The tertiary amines that exist during the wash cycle can be considered in this sense as crypto-quaternary ammonium compounds. This mechanism is now used in formulation of soft detergents with combinations of sheet silicates and pH-regulated crypto-quaternary ammonium compounds in the form of tertiary amines (73) (Table V). An improvement of the softening effect by this mechanism is attained by blending tertiary amines with two long (tallow) chains and tertiary amines with two shorter (coco) chains (74).

TABLE V

Composition of a Soft Detergent with Crypto-Quaternary Amonium Compound (73)

Material	Percentage
Alkylbenzene sulfonate	0-15
Tallow-alkyl sulfate	0-5
Soap	0-45
Sodium triphosphate	5-44
EDTA	0-0.2
Sodium perborate	7-25
Carboxymethylcellulose	0-0.8
Enzyme	0-0.5
Optical brightener	0-0.3
Dyestuff	0-0.3
Foam depressant	0-0.2
Sheet silicate (montmorillonite)	3-30
Ditallow-methylamine	2-20
Water, inorganic salts (sulfate, silicate, etc.)	Balance

Cationic Surfactants with Other Detergent-Relevant Properties

Whereas typical textile-conditioning actions, such as softening and antistatic properties, are performed by cationic surfactants with two long alkyl chains, cationic surfactants with only one long alkyl chain, e.g., cetyltrimethylammonium salts, improve the detergency performance when they are combined with nonionics (75-77). In this sense, proposals for formulations of soft detergents containing combinations of sheet silicates and amines or ammonium compounds with C_{10}/C_{14} alkyl chain (78) or of sheet silicates, water-insoluble tertiary amines with two long tallow-alkyl chains, and water-soluble C_{10}/C_{14} monoalkylamines or ammonium compounds (79), have to be considered as an attempt to enhance the performance of laundry detergents that contain fabric softeners by incorporation of monofatty alkyl amines.

A further application in detergents that diverges from the traditional purpose of cationic surfactants is use as foam inhibitor, for which fatty alkyl amines are still recommended (80). The detergency boosting effect of monofatty alkyl trimethylammonium bromide, for instance, is claimed for laundry boosters in the form of water-insoluble substrates that are impregnated with it and that are added to the laundry (81).

ECOLOGY OF CATIONIC SURFACTANTS

Much work has been done with respect to elucidation of behavior, especially of quaternary ammonium compounds, in the environment. Cationics can be considered ecologically innocuous as long as the amount of cationic surfactants released into sewage waters at present is not substantially increased.

Their ecological inocuousness is based on the fact that they are eliminated from sewage water in various ways. First, they are neutralized by anionic surfactants that exist in sewage water in concentrations that are several times higher (82). Secondly, they are – independent of their biological degradation – concentrated as colloids at the bottom of surface waters by their intensive interaction with mineral surfaces (83). There they are irreversibly retained to a substantial extent (84). Thirdly, they are eliminated in sewage water treatment plants because they are adsorbed by the activated sludge. They are also indications of real biological degradation (82, 85, 86). It appears to be certain that quaternary ammonium compounds used in fabric softeners do not represent a danger for sewage waters.

Although knowledge on the ecological behavior of imidazolinium compounds is not as comprehensive, there are at least indications that they are eliminated by activated sludge, and that the ecological data is of the magnitude of that of quaternary ammonium compounds of the distearyl dimethyl ammonium chloride type (87).

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