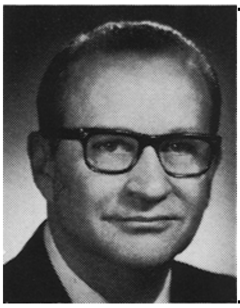

Cationic Surface Active Agents as Fabric Softeners

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ABSTRACT

Rinse cycle, wash cycle, and dryer type softeners are reviewed and their compositions discussed. Ashland's conclusions are: (a) Rinse cycle softeners give the best performance from a softening and anti-static point of view. They are, however, less convenient to use since they must be introduced into the final rinse. (b) Wash cycle softeners are convenient to use, but higher use levels are necessary to impart adequate softening and anti-static properties making their use more expensive. They also tend to decrease the cleaning properties of the detergent used. (c) Dryer type softeners are convenient to use, but they impart less softening because of nonuniform deposition of softener on the fabric. The anti-static properties, on the other hand, imparted by these softeners are very good.

INTRODUCTION

Fabric softeners were introduced to the consumer market in the U.S. in the early 1950s. The need for fabric softeners in the household was prompted by the trend away from washing clothes with soap to the use of detergents. Since hard water soap deposits were no longer being left on the fabric when detergents were used, the clothes, even though cleaner, took on a harsh uncomfortable feel that was highly undesirable to the user or wearer. Thus the need for a fabric softener in the household was established. The popularity of fabric softeners in the U.S. has grown to the point where they are considered necessities by most housewives and has created a market which consumes an estimated 68 to 72 million pounds of anhydrous cationic softener base per year. The use of fabric softeners in industrial and hospital laundries adds another 3 to 4 million pounds to this figure. The U.S. market continues to grow at the rate of 8 to 10% per year.

CHEMICAL TYPES OF FABRIC SOFTENER BASES

It can generally be said that all fatty quaternary ammoniums add substantivity to fabric, particularly to cotton. They, of course, impart different degrees of softening and anti-static functionality. It is not surprising, therefore, that three basic types of quaternary ammonium compounds have emerged as the most effective softeners and anti-stats. They are: difatty alkyldimethyl ammonium compounds, difatty amido alkoxylated ammonium compounds, and fatty alkyl fatty amido imidazolinium compounds.

Type A: Alkyl Dimethyl Ammonium Compounds

The first commercial softeners produced in the U.S. were based upon di (hydrogenated tallow) dimethyl ammonium chlorides. This material is still one of the most popular softener bases in the U.S. The di (hydrogenated tallow) dimethyl ammonium methyl sulfates are also used and are rapidly becoming of extreme importance. The preparation of these materials is shown in Equations 1-3. The preparation starts, of course, from the corresponding hydrogenated tallow fatty acids. Usually no attempt is made to isolate the amide.

$$RCOOH + NH_3 \xrightarrow{\Delta} \underset{\text{amide}}{RCONH_2} + H_2O$$

Equation 1

$$RCONH_2 \xrightarrow{\Delta} \underset{\text{nitrile}}{RC \equiv N} + H_2O$$

Equation 2

$$RC \equiv N + 4[H] \underset{\text{pressure}}{\overset{\text{cat.}}{\rightleftharpoons}} \underset{\text{primary amine}}{RCH_2NH_2}$$

Equation 3

$$2RNH_2 \overset{\Delta}{\rightleftharpoons} \underset{\text{secondary amine}}{R_2NH} + NH_3$$

Equation 4

$$R_2NH + 2CH_3Cl + NaOH \longrightarrow \underset{\text{quaternary}}{[R_2N(CH_3)_2]^+Cl^-} + NaCl + H_2O$$

Equation 5

The nitrile is reduced to the primary amine which may be isolated if desired. In softener quat preparation, the amine is converted directly to the secondary amine. If the chloride quat is desired, the secondary amine is exhaustively methylated in isopropanol, and the by-product NaCl is removed by filtering or centrifuging.

If the methyl sulfate is desired, the secondary amine must first be converted to the methyl tertiary amine since the secondary amines cannot be quaternized directly with dimethyl sulfate. The secondary amine is usually converted to the tertiary amine by reductive methylation as shown in Equations 6 and 7. The resulting amine is then quaternized with dimethyl sulfate.

$$R_2NH + H_2C = O + 2[H] \rightarrow \underset{\text{tertiary amine}}{R_2NCH_3} + H_2O$$

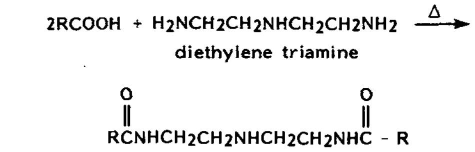
Equation 6

$$R_2NCH_3 + (CH_3)_2SO_4 \longrightarrow [R_2N(CH_3)_2]^+CH_3SO_4^-$$

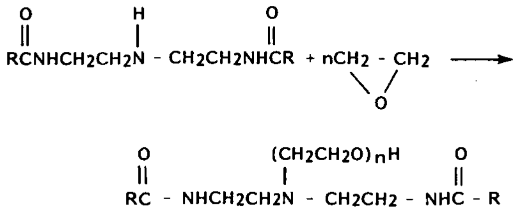
Equation 7

Type B: Amido Alkoxylated Ammonium Compounds

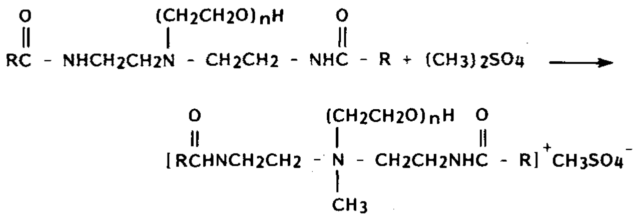
These compounds can be made from fatty acids or triglycerides. Examples of their preparation are shown in Equations 8-10. The nitrogen source is diethylene triamine. The most desirable quaternary from this type of amido/amine is the methyl sulfate derivative. Again the secondary amine cannot be quaternized satisfactorily from dimethyl sulfate. The amine, however, can be alkoxylated to a tertiary amine with either ethylene oxide or propylene oxide as shown in Equation 9. The resulting tertiary amine can be readily quaternized with dimethyl sulfate. Equation 10 shows this reaction.



Equation 8



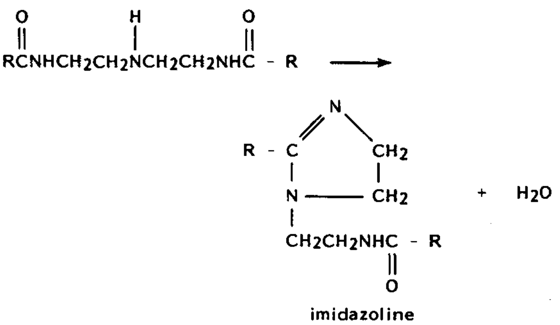
Equation 9



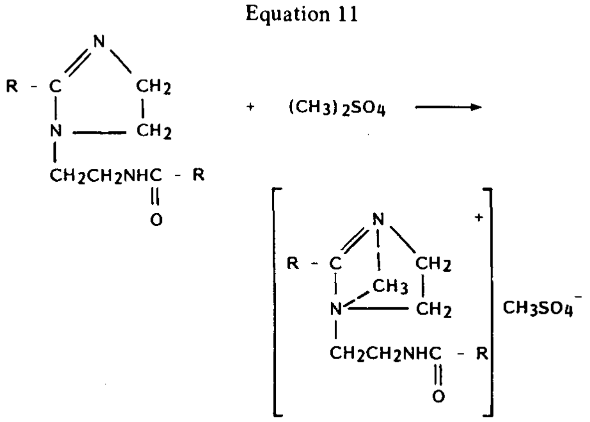
Equation 10

Type C: Amido Imidazolines

If the amido/amine shown in Equation 9 is merely heated to a higher temperature instead of being alkoxylated, ring closure to an imidazoline occurs as shown in Equation 11. Temperatures of 350 to 450 F are required. The resulting imidazoline can be readily quaternized with dimethyl sulfate as seen in Equation 12.



Equation 11



Equation 12

From these three classes of cationic softeners, five products appear to be the most frequently used in the U.S. according to Ashland's analysis of consumer products purchased in supermarkets across the U.S. These five are most commonly found in the brand name and the private label softeners. They are identified in Compounds I-V.

$[R_2N(CH_3)_2]^+Cl^-$

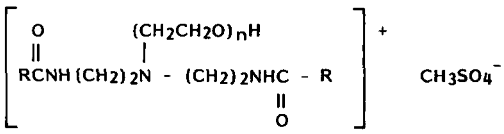
R = hydrogenated tallow alkyl

Compound I

$[R_2N(CH_3)_2]^+CH_3SO_4^-$

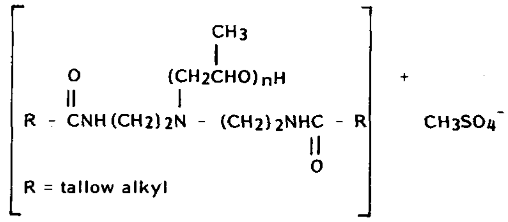
R = hydrogenated tallow alkyl

Compound II

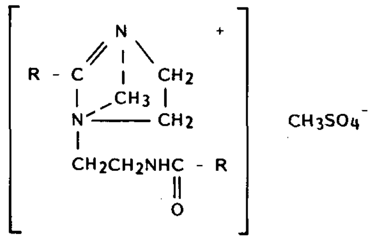


R = tallow alkyl

Compound III



Compound IV



Compound V

These products are commonly sold as 75% concentrates in isopropanol or isopropanol and water.

There are three types of consumer softeners that have gained great popularity in the U.S.: (a) softeners to be used in the final rinse, (b) softeners to be used in the wash cycle, and (c) softeners to be used in the dryer.

The first two types are generally liquid aqueous softener dispersions which are added to the rinse or wash water. Currently the dryer type softeners are products in which the softener has been impregnated onto sheets of a nonwoven fabric or polyurethane foam. Softeners for the rinse cycle were the first to be introduced, those for the wash cycle were next, and the most recent to come to the marketplace is the dryer type.

Three major performance properties are usually measured when a fabric softening quaternary is evaluated. They are softening, anti-static, and rewetting properties.

SOFTENING PROPERTIES

No good mechanical method has yet been devised for the quantitative measurement of softness. As a result, the Ashland laboratories use a panel "feel" test in their evaluations. Desized bath toweling is used for this test. The towels are put through the wash and rinse cycles of an automatic washer with the softener being added to the final rinse. Sufficient softener is used so that 0.1% by weight of actual quat is present based upon the weight of fabric. One set of towels will be washed without softener added as a control. Another set of towels is washed and softened with 0.1% of the Compound I type softener (dihydrogenated tallow dimethyl ammonium chloride) based upon fabric weight and is used as the second control. The Compound I type softener was chosen as a control because it has the best softening properties of any commercially available fabric softener base. It is surprising that the first quat softener introduced to the consumer market has remained the best from a softening standpoint for over 25 years.

A panel consisting of at least five people is then asked to rate the softness of the test towels. Usually three other softener compounds are being evaluated in a given test. The panel members are allowed individually to feel the sets of towels and rate their softness on a scale of 1 through 5 with 1 being the harshest and 5 being the softest. On the basis of this test, Ashland rates the softeners in the order shown in Table I.

TABLE I

Softening Performance

Softener	Rating
Compound I Type	5.0
Compound II Type	4.5
Compound V Type	4.0
Compound III Type	3.0
Compound IV Type	2.5

It should be remembered that all of the compounds compared here are effective softeners and that they are being rated in the order of panel softening preference and not in percentage of effectiveness.

ANTI-STATIC PROPERTIES

The measurement of the dissipation of static charge from fabric is difficult to say the least. Many factors influence this measurement including the amount of buildup of static charge, the relative humidity, and the time from maximum buildup and the time of measurement.

In the Ashland laboratories, we measure the static charge in volts on clothes coming immediately from the dryer using the Simco Static Locator (The Simco Co., Inc., Lansdale, PA). By using softener-treated and untreated clothes, a measure of reduction of static charge buildup can be obtained. The precision of the method is not as good as we would like, but with a large enough number of tests, an order of performance can be established for each compound type. By the Ashland test method we rate the reduction of static charge by the quat molecules in the following order of best performance. All of these softener molecules are apparently effective as far as the consumer is concerned. Anti-static performance ratings were: Compounds V>II>I >III>IV.

REWETTING PROPERTIES

Rewetting properties are important because they give an indication of the absorbency characteristics of fabric after treatment with a softener. If too much fabric softener is used, it is possible to waterproof the cloth.

In the Ashland laboratories, a standard wicking test is used to evaluate rewetting characteristics in which a strip of softener-treated fabric is dipped into water containing a dye, and the height to which the water will climb the strip is measured. A control using untreated fabric is used for comparison. The higher the water climbs the test strip, the better the rewet property. By this test, the softener Compounds III and IV were better than V which was better than I and II. The best softener is the poorest rewetter. It is interesting to note that while competent laboratories invariably note these rewet differences, housewives in numerous consumer panel tests known to the author do not note rewetting as being a problem with any of these softeners.

Other important considerations in the selection of a fabric softener base are, of course, ease of handling and cost.

EASE OF HANDLING PROPERTIES

The methyl sulfate quats at the 75% concentration all tend to be liquids at or slightly above room temperature. They are easily dispersed in water to prepare 4.0 to 6.0% aqueous dispersions. The water temperature for best dispersion is usually 38 to 60 C with one exception. The Compound IV type gives the most stable dispersions at room temperature.

The Compound I type is a solid at room temperature. It melts at 40 to 50 C. It is best dispersed, after melting, in water preheated to 55 to 60 C. Good agitation is required to give stable aqueous dispersions. This means that heating facilities are necessary if the raw material is contained in drums or stored in bulk.

COST CONSIDERATIONS

Cost considerations, of course, are important when formulating a finished fabric softener but do not need detailed attention in a report of this kind. Briefly, the relative costs of the 75% softener concentrates are shown in descending order: Compound I>II>V>III and IV.

The mechanism whereby a fabric softener functions is not completely understood. Drs. Leonard Hughes and Marvin Deviney and their associates of the Ashland Chemical Company's Research Department have been studying this problem for the past three years. Although the problem is by no means resolved, their investigations have been revealing, and some of their observations follow.

Hughes and Deviney confined their studies to softeners of the Compound I type (dihydrogenated tallow dimethyl ammonium chloride) and Compound V type (the imidazoline methyl sulfate) and using desized cotton as the fabric to be softened. The softener molecules were radioactively tagged in the cation or anion as needed so that their behavior could be readily followed. In summary, the following important observations have been made as a result of this work (1-3).

RINSE CYCLE SOFTENING

When the softener is used in the rinse cycle, the composition of the detergent used to wash the clothes plays an important role, particularly in inorganic builders used. Traces of these builders are carried on the fabric into the rinse cycle. Polyphosphate residues on the fabric seem to promote or enhance the deposition of the softener. Carbonate or silicate residues on the cloth repress the softener deposition by at least 25 to 30% and require more softener to give the same results as residues high in polyphosphates.

Calcium and magnesium ions promote the deposition of fabric softeners in the presence of an anionic surfactant.

The particle size of dispersions of at least the dihydrogenated tallow dimethyl ammonium chlorides (Compound I type) apparently is not important for softener adsorption.

The imidazoline methyl sulfate (Compound V type) was studied in the rinse cycle. It was shown that none of the methyl sulfate anion was deposited on the fabrics. This tends to suggest that only the cation of the softener is deposited on the fabric and that some sort of ion exchange mechanism at the surface of the fabric is involved with softener deposition.

WASH CYCLE SOFTENER

The study of the functionality of softeners in the wash cycle in the presence of an anionic-based detergent is, of course, much more involved. Considerably more work is necessary in this area, but some observations developed to date are of interest.

Hughes et al. used systems containing only softener, sodium lauryl sulfate as a typical anionic surfactant, and mixtures of softener and Na lauryl sulfate.

1. In distilled water at a concentration of 5.09×10^{-4} moles/liter under wash cycle conditions of 55 C for 20 min, no Na lauryl sulfate adsorption was observed.
2. Systems containing only a quaternary ammonium of the Compound I type and sodium lauryl sulfate were studied for deposition onto cotton. When the system contains an excess of quat, all of the anionic is converted to the quat/anionic complex, and both the quat and the quat/anionic complex are deposited. The quat/anionic complex is apparently suspended in solution by the quat, and particles of the quat/anionic complex surrounded by quat and positively charged are deposited onto the fabric.
3. When the system contains an excess of anionic surfactant, all of the quat is converted to the quat/anionic complex, and this complex, surrounded by anionic surfactant, is what is deposited onto the fabric. Smaller amounts of this complex are deposited onto the fabric than when the quat is present in excess.

These observations are consistent with the results observed in practical tests and with observations of changes in consumer softener concentrations or their use directions.

As examples, in the case of rinse cycle softeners, when low or no phosphate detergents were introduced into the American market, it was found that for adequate softening to be observed by the panel test, higher concentrations of softener were necessary. Simultaneously, it was noted that producers of consumer softeners either increased the softener concentration of their product or increased the use directions for their product.

If softeners are introduced into the wash cycle, particularly when anionic detergent-based cleaning agents are used, all of Ashland's tests show a decline in detergency. This cleaning decline is usually 25 to 30%, but a decrease as high as 50% with some systems has been observed.

If softener concentrations similar to those used in the rinse cycle are added to the wash cycle, little if any softening is observed. When higher concentrations of softener, three or four times the amount used in the rinse cycle, are added to the wash cycle softening *does* occur. But, if the bromphenol blue test is used to determine the uniformity of softener deposition, this test indicates that *no* softener has been deposited since no blue color develops on the fabric.

The bromphenol blue test is a simple procedure in which softener-treated fabric is immersed in a 0.01% solution of bromphenol blue, removed, rinsed with water, and dried. Wherever free quaternary softener is on the fabric surface, a complex forms with the dye giving a blue color. By this test, fabric softened in the rinse shows a uniform blue color over its entire surface. The observations that no blue coloration develops on the fabric when the softener has been introduced in the wash cycle but that softening does occur if enough softener is used are explained by the radio tracer studies. Any softener put into the wash cycle is immediately converted to the quat/anionic complex. Particles of this complex are suspended and are surrounded by the anionic surfactant. It is this quat/anionic suspension which is deposited onto the fabric. Since no free quat is on the surface no blue color develops when the bromphenol blue test is run. This phenomenon also accounts for the decline in detergency when softener is introduced into the wash cycle. Obviously as the quat/anionic complex forms part of the active anionic surfactant is being removed from solution and hence cleaning is reduced.

In all cases the wash cycle softeners, properly used, impart adequate anti-static properties.

DRYER TYPE SOFTENERS

The growth of dryer type softeners is rapidly increasing in the U.S. The mechanism whereby the softener is deposited onto the fabric by dryer type softeners is obviously quite different than that of the rinse cycle or wash cycle softeners.

Ashland's analysis of commercial dryer softener sheets shows that there are generally 2.5 to 3.0 grams of extractable material per sheet, most of which is cationic softener. Most commonly the Compound II softener is found. The remaining components seem to vary from product to product, but all tend to be nonionic in nature. This amount of softener approximates the amount that would be added to the rinse cycle if a liquid product were used as directed.

Ashland's evaluation of this type of softener shows that all impart effective anti-static properties to the treated fabric. The softening imparted to the cloth is less than that given by a rinse cycle softener. This is not surprising since extraction of a once used softener sheet shows that only about 50 to 70% of the softener is removed. If the bromphenol blue test is used on dryer-softened cloth, it is noted that the deposition of softener is nonuniform over the cloth surface with white areas randomly appearing. This also helps to account for the lower softening ratings given to dryer-softened fabric by the softening panel.

The anti-static properties imparted to the cloth by dryer softeners are excellent. Reductions of static charge of 90% or higher are not uncommon.

If softener sheets are used more than once, poor softening is obtained, but good anti-static performance is maintained through up to three uses. This observation is consistent with previous work which indicates far less cationic is necessary on the fabric to impart anti-static properties than is required for softening.

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