How to Choose Cationics for Fabric Softeners

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ABSTRACT

The choice of a cationic fabric softener for rinse, wash and dryer cycle applications is based upon an understanding of the physical and performance differences of the softeners. These differences are primarily governed by composition of fatty alkyl groups rather than differences in chemical types. In general, the more saturated alkyl fatty groups make softeners more difficult to handle and disperse but are the best for softening fabric. Unsaturation improves handling, rewet, and ease of formulation.

INTRODUCTION

Fabric softening has been an important part of the home laundry routine for nearly 30 years. During the last 10 years, we have seen many changes in product design and methods used to soften fabrics. The original fabric softeners were aqueous dispersions of cationic chemicals and were designed for use in the final rinse cycle of washing machines as well as for handwash. Rinse cycle softeners are still the most popular and the most effective way of imparting softness to fabric. In the early 70s, the dryer cycle softeners were introduced. Convenience of use and static control, especially for synthetic fabrics, made these products attractive to the consumer. From the first introduction of fabric softeners into the marketplace, there has been a desire for a single product which could be added to the wash cycle that would both clean and soften clothes. Today, we are involved again in the formulation of these detergent-softener combinations.

The three methods used in the home laundry to impart softness and static control to fabrics are: rinse cycle addition, wash cycle addition, and dryer cycle addition.

How do we choose the right cationic to perform in each of these methods of application? The chemical composition of the cationics used for fabric softeners must be considered first. With this information, we can then consider handling characteristics, formulation parameters, performance properties, and price.

TABLE I

Approximate Composition of "R Group"

	C14	C16	C18 Stearyl	C18' Oleyl
Oleyl		5	20	75
Tallow	5	30	20	45
Hydrogenated tallow	5	30	65	
Stearyl		5	95	

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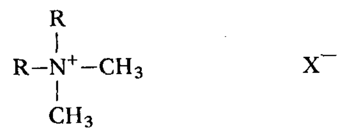
CHEMICAL TYPES OF CATIONICS FOR FABRIC SOFTENERS

There are three chemical types of cationics which are usually used for fabric softeners (1). They are all quaternary ammonium compounds, i.e., a nitrogen atom having four organic groups attached to it by covalent bonds. For each positive ion of the quaternized nitrogen, there is an associated anion, usually chloride or methyl sulfate (2). Type A is the dialkyl dimethyl quaternary ammonium compound with the general structure:

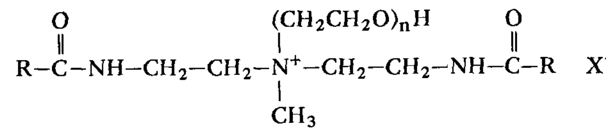
Type A



where X^- is either Cl^- or $CH_3SO_4^-$

Type B is the diamido alkoxylated quaternary ammonium compound with the general structure:

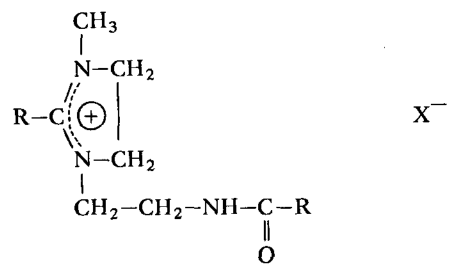
Type B



where X^- is usually $CH_3SO_4^-$

Type C is the amido imidazolinium compound with the general structure:

Type C



where X^- is usually $CH_3SO_4^-$

The fatty alkyl groups, R, are typically C_{14}-C_{18} derived from tallow, hydrogenated tallow, oleic, or stearic fatty acids. The approximate composition of the fatty alkyl groups is given in Table I. The unsaturated C_{18} contains one double bond in a *cis* isomer configuration. "Unsaturation" in a fat tends to lower the melting point and make it a liquid at room temperature (3). The saturated C_{18}

contains no double bonds, giving rigidity to the molecule, raising the melting point, and reducing fluidity.

Over the years, specific cationics have been found to perform particularly well in each of the methods for applying softener to fabrics. Three products are commonly used for rinse cycle softeners: type A based on hydrogenated tallow, type B based on tallow, and type C based on tallow. Dryer cycle softeners usually contain type A based on hydrogenated tallow and generally the methyl sulfate anion. The market for detergent-softener combinations is new compared to rinse and dryer cycle products so specific cationics have not evolved. The oleyl versions of all three types are the easiest to use for clear liquid detergent-softeners. The higher melting versions, i.e., stearic or hydrogenated tallow, find application in powdered detergent-softeners.

HANDLING AND FORMULATION PROPERTIES

Handling characteristics and formulation parameters are very closely related and are governed by the composition of the fatty alkyl groups. As an example of how the fatty alkyl groups affect the handling and formulation parameters, consider the family of oleyl, tallow, and hydrogenated tallow derivatives of the amido imidazolium compounds, type C. At 75% total solids in isopropyl alcohol, the oleyl version is a clear amber liquid at room temperature; the tallow version is an opaque liquid requiring heating to ca. 110 F (43 C) to clarify; and the hydrogenated tallow version is a nonpourable opaque paste. These observations also hold true for types A and B compounds.

Rinse cycle softeners are aqueous dispersons of the cationic chemicals and contain 5–7% total solids for a concentrated "blue" fabric softener and 3–4% for a regular "pink" fabric softener. The hydrogenated tallow versions of all three softener types require heat to melt and hot water to form stable dispersions. The tallow versions usually require some heat to clarify the softener and provide maximum dispersion stability; however, the temperatures needed range only from 90 to 120 F (32–48 C). The oleyl based softeners are liquid at room temperature, but the aqueous phase should be heated to 70–80 F (21–26 C) for optimum dispersion stability.

The viscosity of rinse cycle softeners also varies with fatty alkyl composition. The longer the alkyl chain and the higher the degree of saturation, the higher the viscosity of the aqueous disperson. Disperson viscosity can be controlled, though, by using inorganic salts, such as sodium chloride, sodium sulfate or sodium acetate. The tallow version of type B has become the most widely used softener of all other types of alkyl chain composition. This chemical is unique, forming stable aqueous dispersions at 3.0% total solids without the use of extra emulsifiers or stabilizers. All other softeners have a lower limit of 4.0% total solids.

Wash cycle softeners have been designed three different ways. One approach is a 9–15% total solids aqueous dispersion of a cationic softener added at the beginning of the wash cycle along with any powdered or liquid detergent. Another type is a powdered detergent to which the fabric softener is added. The third type is a liquid detergent preferably based on a nonionic surfactant blended with a suitable cationic.

The first type wash cycle softener has the same formulation parameters as rinse cycle softeners. The higher total solids content presents special problems with viscosity. The hydrogenated tallow based cationic softeners form gels or very viscous dispersions at 9–15% total solids. Stability problems are created by the high levels of salt required to reduce the viscosity adequately. Either the tallow or oleyl versions will formulate acceptable products.

The second type is powdered wash cycle softeners. These wash cycle softeners formulate easily by simply blending a powdered fabric softener with a suitable detergent base. The stearic version of type A can be obtained in powdered form.

The liquid detergent plus fabric softener is the third type and is gaining in popularity. These can be formulated at room temperature by using the oleyl version of type A, B or C. When formulated with a suitable nonionic surfactant, these oleyl based fabric softeners make clear detergent-softener products. Translucent to hazy products are produced when tallow and hydrogenated tallow based softeners are used.

The handling and formulation properties for dryer cycle softeners is radically different from the liquid rinse or wash cycle softeners. The main formulation parameter is melting point. In most products, the melting point of the hydrogenated tallow version of type A is modified by a nonionic commonly referred to as a "dispersing aid." The methyl sulfate anion is "safe" for dryer cycle use. The chloride anion was found to soften the linings in the dryer drum, eventually leading to corrosion. Dryer cycle softener systems are usually supplied at 92–100% total solids. The cationic portion can range from 20% to 90% of the composition. Handling properties depend upon the method of coating the nonwoven substrate and the available heating and alcohol recovery systems.

PERFORMANCE PROPERTIES

The performance properties of cationics for use as fabric softeners include softening, static control, rewet or water absorbency, and detergent compatibility for wash cycle products.

Softening

Without doubt, softening depends on alkyl chain length and, for best softening, two alkyl chains are preferred (4). Straight chain derivatives are better than branched chains and unsaturation in the fatty alkyl group reduces softening. Therefore, within a given type, the hydrogenated tallow version is a better softener than the tallow version and the oleyl version is slightly less effective.

As mentioned earlier, three cationic products have become very popular in the formulation of rinse cycle softeners. When these three products are evaluated for softening at a treatment level of 0.1% based upon the dry weight of the fabric bundle, the following order of softening is found: hydrogenated tallow type A > tallow type C > tallow type B. In controlled laboratory tests using clean fabric bundles, no detergent in the wash cycle and the softener added to rinse cycle, it was found that at least 0.135% type C tallow and 0.18% type B tallow are needed to match the softening efficiency of 0.1% type A hydrogenated tallow. The reasons include differences in rates of deposition, molecular weight and fabric substantivity. In home use, these differences in efficiency become less apparent due to the presence of soil and detergent carryover to the rinse cycle. All combinations of fatty alkyl group and chemical type are very effective fabric softeners.

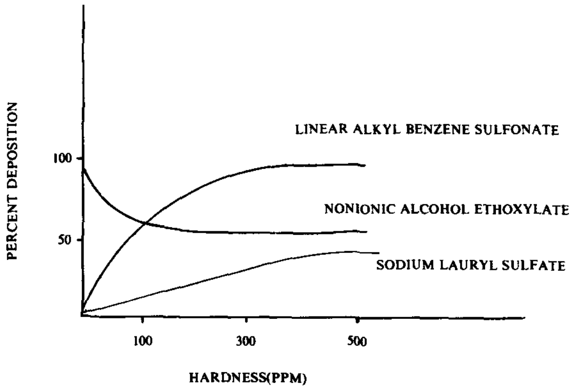


FIG. 1. Deposition of tallow imidazolinium quaternary in the presence of detergent surfactants and varying water hardness (8).

TABLE II

Inhibition of Softener Deposition by Detergent Components in Distilled Water (% cationic deposited)

Component or mixture	Type A hydrogenated tallow	Type C tallow
None	100%	100%
Nonionic surfactant	100%	100%
STP	100%	75%
Na_2CO_3	100%	62%
CMC	0%	62%
ABS	0%	0%
SXS	0%	0%
SLS	0%	0%
Nonionic/STP	88%	25%
Nonionic/Na_2CO_3	81%	25%

Each new method of applying softener onto fabric has lead to a redefinition of the term softness. When rinse cycle softeners were first introduced, the treatment levels were 0.075–0.15% (based on dry weight of fabric), resulting in exceptionally soft fabrics. This was especially true for cottons which had been washed in a heavy-duty synthetic detergent. For those who wanted a "fuller-bodied" softness, products emerged which had a treatment level of 0.05–0.07%.

The method of application of the softener and the degree of softening for dryer cycle products differs from that of rinse cycle softeners. Rinse cycle softeners are adsorbed onto fabric and the softener can be found evenly distributed throughout the fabric bundle. Dryer cycle softeners work by the physical transfer of softener from the coated dryer cycle sheet to the fabric load. As the temperature in the dryer increases, the softener becomes nearly melted and is easily transferred to the damp fabric when the two come in contact. The dryer cycle softeners, therefore, only coat the outer surfaces of fabric—and in a somewhat "hit and miss" pattern. The degree of softening for dryer cycle softeners is less than that of most rinse cycle softeners.

Wash cycle softeners also have a particular softening level. In order to obtain softening along with detergency in the wash cycle, two to three times more fabric softener is needed. The detergent, whether nonionic or anionic, interferes with the adsorption of the softener onto the fabric. The softening level for most wash cycle products is therefore slightly less than the softening of dryer cycle softeners.

The same correlation of softening ability and chemical composition holds for wash cycle as for rinse cycle softeners. Hydrogenated tallow versions are better than tallow, which are better than oleyl versions. However, factors such as formulation stability or clarity, rather than softening, usually influence of choice of cationic.

Static Control

Static control has become a very important attribute for fabric softeners. The increased use of synthetic fibers has made the consumer more aware of the advantage of using fiber softeners to eliminate static cling.

Like rinse cycle softening, the degree of static control is dependent upon the amount of softener adsorbed. Some static control is observed at use levels as low as 0.025% based on the dry weight of the fabric. In rinse cycle systems, a comparison of the three types of softeners generally used gives the following ranking of static control: type C, tallow > type A, hydrogenated tallow > type B, tallow (5).

Both dryer cycle softeners and wash cycle softeners, if formulated properly can control static better than rinse cycle softeners. By using a Simco Electrostatic Locator to measure the electrical discharge of fabrics as they come from a home dryer, we typically observe the following ranges of static reduction (6): rinse cycle softeners (treatment level is 0.1% based on dry weight of fabric) 60–80%; wash cycle softeners (liquid detergent-softeners containing nonionic surfactants and cationic softeners) 80–95%; and dryer cycle softeners, 98–100%.

These ranges show that dryer cycle softeners are the best for controlling static cling and that wash cycle softeners (liquid nonionic detergent with added softener) are better than rinse cycle systems.

Rewet

Rewet or water absorbency is important because too much fabric softener can waterproof cloth (5). A general rule for any method of application is the more softener on the fabric, the poorer the water absorbency will be. Also, as softness increases, absorbency decreases (5, 7). Small amounts of nonionic surfactant are sometimes added to rinse cycle formulations to improve rewet.

Again, we can consider the chemical composition of the cationics to determine the ones with the best rewet properties. The longer the fatty alkyl group and the more saturation in the group, the poorer the rewet properties. This means that the hydrogenated tallow versions of any of the three types results in poorer rewet properties than the tallow versions. Oleyl based products demonstrate the best water absorbency. For the three products commonly used for rinse cycle softening, type B tallow possesses the best rewet properties.

Detergent-Compatability

When cationic fabric softeners are added to anionic based detergents, the cleaning efficiency of the detergent and the efficiency of the fabric softener are diminished. This has been the major disadvantage of wash cycle products, especially the 9–15% aqueous dispersion types. The introduction of liquid detergents and particularly the increased use of nonionic detergents has created a new means of incorporating cationic fabric softener into a detergent system.

We have found that the choice of detergent rather than the type of cationic softener is important in formulating

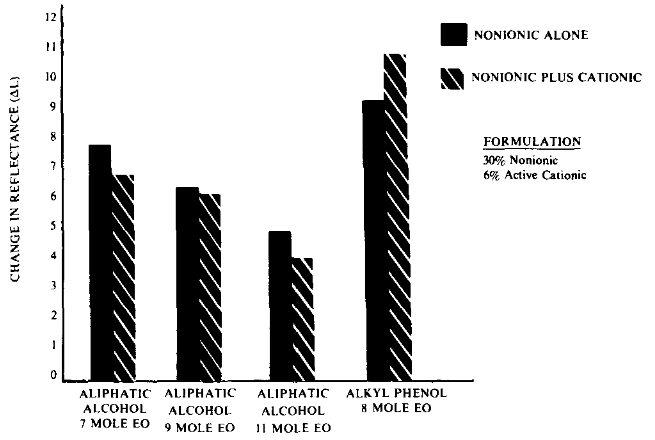


FIG. 2. Effect of imidazolinium quaternary on the detergency of nonionic surfactants (US Testing soiled cotton).

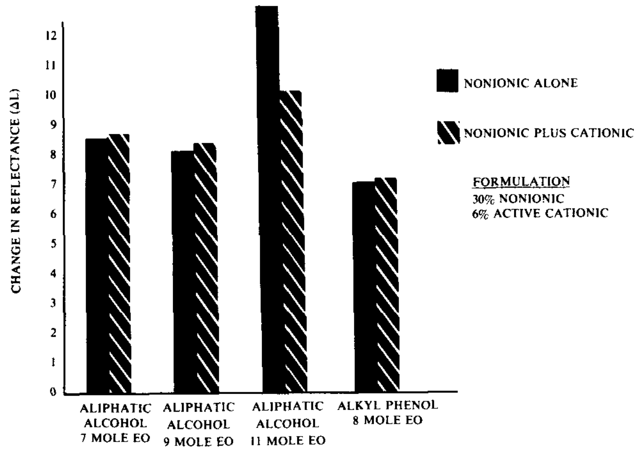


FIG. 3. Effect of imidazolinium cationic on the detergency of nonionic surfactants (scientific services dust-sebum soiled cotton).

detergent/softener systems. In a system in which nonionic surfactant and softener are mixed, but no hard water ions are present, we see that the deposition of cationic softener onto cotton fabric is nearly 100%. In a similar study with anionic surfactant, the deposition drops to 0% (Fig. 1). Increasing water hardness improves the deposition of a fabric softener in the presence of anionic surfactants, but deposition decreases to ca. 50% in the presence of nonionic surfactants (8). The effect of different builder components on the deposition of two types of cationic fabric softener is shown in Table II. Type C cationics are influenced more by builder salts (sodium tripolyphosphate [STP], sodium carbonate, carboxymethyl cellulose [CMC]) and combinations of these builders than type A cationics.

When anionic surfactants and cationic fabric softeners are combined a 1:1 molar complex is formed. The reaction is rapid and irreversible, and typically the complex is water insoluble. The use of nonionic detergents eliminates the chemical interaction of surfactant and softener. The addition of cationic softeners to nonionic detergents does not cause the reduction in detergency which is observed when softeners are added to anionic surfactants. In fact, the addition of cationic softener to nonionic surfactants does not significantly affect detergency.

The choice of nonionic surfactant has more impact on detergency than the addition of cationic. On US Testing soiled fabrics, an alkyl phenol ethoxylate containing 8 moles of ethylene oxide demonstrates better detergency than aliphatic alcohols with 7, 9 and 11 moles of ethylene oxide (Fig. 2). On dust-sebum soil, the aliphatic alcohol ethoxylates are better than the alkyl phenol ethoxylate (Fig. 3). There is no significant increase or decrease in detergency when cationic fabric softener is formulated with these nonionic surfactants.

PRICE

Cost considerations, of course, are important when formulating a finished fabric softener. A few guidelines can aid in selecting the right product at the right price. Within a given type of softener, the oleyl versions are usually more expensive than the hydrogenated tallow versions, and the tallow based products are third. This is due to added processing, such as hydrogenation, or the use of higher priced raw materials, such as oleic fatty acids. Type A cationics are usually more expensive than type B, and type C is the least expensive for a specific fatty alkyl group.

In many cases, the contribution of the cationic softener to the final product cost is more important than the price of the cationic. The contribution of softener price to a liquid finished product cost in dollars per gallon is calculated as follows:

$$\frac{\text{softener cost (\$/\#)} \times \text{\% softener in product} \times 8.3}{\text{concentration of the softener (\%)}}$$
$$= \text{cost of product due to softener}$$

Knowledge of the chemical composition of the cationics used as fabric softeners as well as an understanding of the influence of fatty alkyl composition on handling characteristics, formulation parameters, performance properties, and even price are necessary for the formulator to choose the best cationic for a fabric softener.

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