Fabric Treatment with Cationic Softeners

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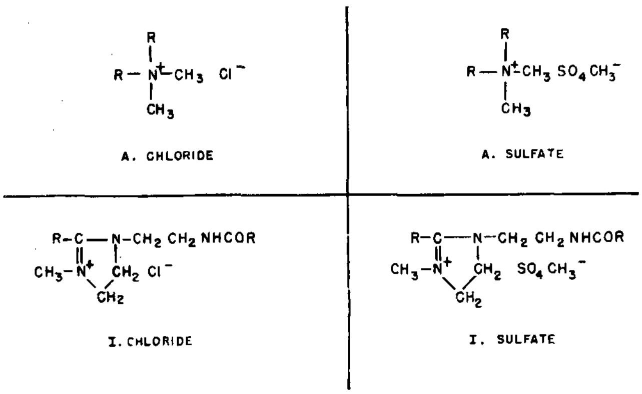
During the past two decades the treatment of fabrics with cationic softeners has gained widespread acceptance in the textile-finishing and textile-maintenance fields. The term cationic softener covers a wide range of chemical structures, as was pointed out in a recent review article by DuBrow and Linfield (1). The present investigation is restricted to four quaternary ammonium compounds derived from partially or completely hydrogenated tallow. These compounds are labeled A. chloride, A. sulfate, I. chloride, and I. sulfate for the sake of brevity. Their structural formulas follow:



R represents an alkyl radical of 16 to 18 carbon atoms in the fatty amine derivatives or 15 to 17 carbons in the imidazoline compounds.

These compounds possess a marked substantivity for cellulosic fibers, such as cotton or rayon, which means that their solutions will be depleted partially or completely by preferential adsorption. To obtain a better understanding of the mode of application of these softeners and to arrive at practical directions for their use it was necessary to follow quantitatively the course of the exhaustion of these softeners upon cotton fabric under varying conditions of concentration, temperature, and pH.

In investigating exhaustion rates, it was found that under certain conditions the exhaustion could occur extremely rapidly. It was reasonable to assume that the softener would be deposited on the fabric far more unevenly than if a slower exhaustion rate were maintained. To demonstrate visually that this assumption was a valid one, a staining technique was developed which indicated the amount of softener present on the fabric by the color intensity of the stain.

Besides bringing about the soft "handle" of treated fabric, the cationic softeners also imparted other physical properties to the treated fabric. Unlike the softness, some of these other properties could be measured fairly precisely. Of particular importance in the laundry application was the wettability of treated fabric. Obviously a decrease in absorbency would be undesirable. The absorptive capacity of treated fabrics was unaffected by the softener whereas the rate of absorption of water is a function of the amount of cationic softener.

Lastly another aspect of cationics was investigated in a quantitative manner. Antistatic properties could be readily measured with the aid of a friction device connected to an electrostatic voltmeter. Since the cellulosic fibers were of a sufficiently polar nature, the experimental work was confined to synthetic fibers or to modified cellulose, particularly acetate. As a rule the antistatic effect was a function of the amount of cationic material on the fabric. In addition, certain compounds have a specific antistatic effect on a specific fiber. It is premature to attempt to correlate the chemical structure of the fiber with that of the cationic.

Experimental Procedures

Rates of Exhaustion. New Indianhead swatches were pretreated to remove sizing by washing and rinsing through two cycles of a domestic washing machine, using a built anionic detergent. This was followed by a wash with a nonionic detergent of the ethoxylated alkylphenol type and two subsequent deep rinses in tap water. One hundred grams of fabric were then treated in a Terg-o-tometer with one liter of treatment solution at temperatures of 70 and 90°F. A pH of 5 was attained by adjustment with sodium silicofluoride, and a pH of 8 by adjustment with sodium carbonate. Aliquot portions of 25 ml. were withdrawn at one-minute intervals and titrated for cationic content with a standardized 2.0×10^{-4} N solution of sodium dodecylbenzenesulfonate to a methylene blue end-point, according to the method of Hartley and Runnicles (4) and Epton (2). Percentages of original quaternary compound remaining in each aliquot were calculated from the ratio of test titration to that of the original solution prior to treatment. The difference from 100% thus gave the percentage of exhaustion.

Figure 1 shows the course of exhaustion of compound I. sulfate to a fixed final concentration of 0.1% softener on the fabric at temperatures of 70 and 90°F. and pH values of 5 and 8. The effect of pH is quite pronounced; the rate is considerably slower at the lower pH. The effect of a temperature rise from 70 to 90°F. likewise has the effect of accelerating the exhaustion rate, particularly at a pH of 5.

Figure 2 shows a comparison of exhaustion rates of the four test compounds at pH 5 and 70°F. Here the imidazoline species exhausts more slowly than

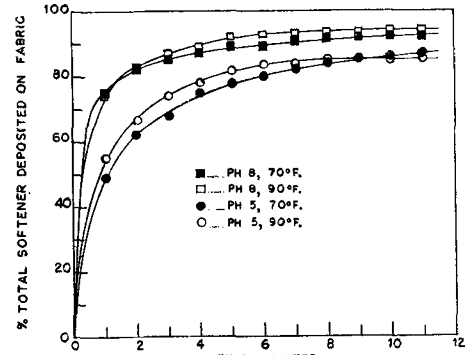


FIG. 1. Variation of exhaustion rate with pH and temperature.

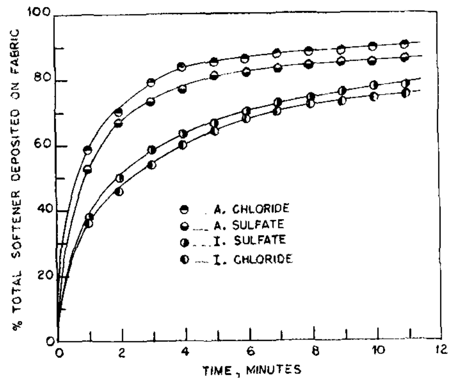


FIG. 2. Comparative exhaustion rates of four test softeners.

the other type. The chloride is faster in one case and the sulfate in the other. The effect of the anion however seems to be relatively minor. It should be noted that the curves for I. sulfate at pH 5 and 70°F. in Figures 1 and 2 show discrepancies since they represent two different test series carried out at different times. Figure 3 shows the effect of initial concentration upon exhaustion rate. The A. chloride at an initial concentration of 0.1% exhausts relatively faster than one of 0.2%, both being at 70°F. and at a pH of 5.

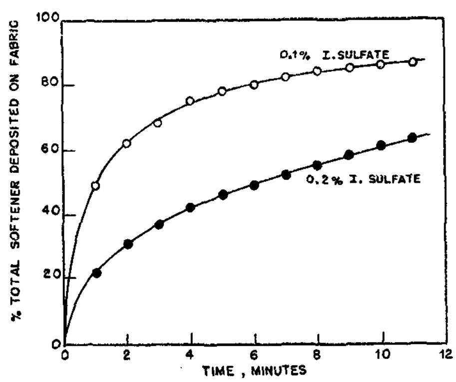


FIG. 3. Variation of exhaustion rate with concentration.

The practical significance of these results is that the softeners should be applied at a pH of about 5 and at a temperature of about 70°F. and that doubling the amount of softener under these conditions of temperature and pH will not result in a much higher add-on than can be achieved with the recommended amount of 0.1% on the weight of the fabric.

Evenness of Exhaustion. In order to compare the evenness of distribution the treated swatches were rinsed in cold tap water and then agitated in a bath of an 0.02% bromphenol blue solution, the pH of which was adjusted to 8, for a period of three minutes, rinsed in cold tap water, and ironed dry. A swatch treated with softener at a pH of 5 and 70°F. shows an even distribution of the softener whereas a swatch having been softened at a pH of 8 shows obvious unevenness of application.

Absorbency Studies. The method used was the one adopted by the Diaper Service Institute of America (5). The rate of absorption is measured in terms of the time required for a folded fabric packet approximately 5 in. square to submerge in distilled water at a temperature of 25°C. Absorptive capacity is determined by weighing the fabric after 30 seconds of immersion, having allowed the unfolded fabric to drain until the steady stream falling from the lowest point breaks into discrete drops. It is expressed in terms of ratio of weight of water held to weight of dry fabric.

Fabrics were cotton gauze and birdseye of the type commonly used in the manufacture of diapers, also terry cloth toweling. The fabrics were carefully desized and scoured before test. Five replicates of each type of fabric were impregnated by exhaustion at concentration levels of 0.10, 0.25, 0.50, and 1.00% fabric softener basis fabric weight. A Naxonette washing machine was used for the impregnation. A liquor to fabric ratio of 40:1 at a temperature of 70°F. was used. The fabrics first were scoured with sodium silicofluoride for two minutes. The fabric softener was then introduced at the desired level, and impregnation followed for 10 min. The fabrics were dried, and rate of absorption and absorptive capacity were determined. Data are summarized in Tables I and II.

TABLE I
Rates of Absorption of Treated Fabric
(expressed in seconds)

Fabric	Softener	Concentration of softener on fabric				
		0.0%	0.1%	0.25%	0.5%	1.0%
Gauze	A. chloride	1.6	13.0	156	424	540
Gauze	A. sulfate		1.8	16	22	1040
Gauze	I. chloride		3.2	48	31	199
Gauze	I. sulfate		2.4	12	14	269
Birdseye	A. chloride	2.5	20.0	89	201	261
Birdseye	A. sulfate		9.7	56	32	1146
Birdseye	I. chloride		11.0	40	50	60
Birdseye	I. sulfate		9.8	26	20	364
Terry cloth	A. chloride	5.7	12.0	32	104	870
Terry cloth	A. sulfate		17.0	46	691	1458
Terry cloth	I. chloride		12.0	12	21	68
Terry cloth	I. sulfate		14.0	16	26	63

TABLE II
Absorptive Capacity of Treated Fabric
(expressed as weight ratio water/fabric)

Fabric	Softener	Concentration of softener on fabric				
		0.0%	0.1%	0.25%	0.5%	1.0%
Gauze	A. chloride	5.1	5.0	5.2	5.4	5.1
Gauze	A. sulfate		5.0	5.1	5.2	5.3
Gauze	I. chloride		5.3	5.4	5.3	5.4
Gauze	I. sulfate		5.4	5.2	5.1	5.2
Birdseye	A. chloride	4.0	4.0	3.9	4.1	4.2
Birdseye	A. sulfate		4.1	4.1	4.2	3.9
Birdseye	I. chloride		4.3	4.3	4.3	4.2
Birdseye	I. sulfate		4.2	4.2	4.1	4.0
Terry cloth	A. chloride	4.1	4.5	4.3	4.4	4.4
Terry cloth	A. sulfate		4.5	4.4	4.3	4.4
Terry cloth	I. chloride		4.3	4.1	4.3	4.0
Terry cloth	I. sulfate		....	....	....	....

A second phase of this study was to determine the effect of increasing concentration of fabric softener on the absorption rate to reveal the nature of this sorption phenomenon. Cotton birdseye fabric was impregnated at 0.1% concentration intervals from 0.1 to 1.0%, using softener I. sulfate. The treatment liquor was analyzed before and after impregnation for concentration of softener, using a modified cetyl pyridinium bromide method (2, 4). The rate of water absorption and percentage of softener on fabric were then determined, and the results were plotted as shown in Figure 4.

The data in Tables I and II and Figure 4 indicate that the absorption rate or sinking time is roughly a

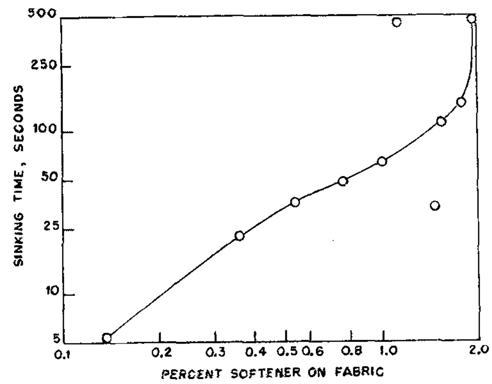


FIG. 4. Rate of water absorption as a function of percentage of softener on fabric.

logarithmic function of the concentration of softener on the fabric. Fortunately the water absorption rate is not impaired for all practical purposes at concentrations of up to 0.25%, which is the upper limit of practical application in the textile maintenance field. Surprisingly the absorptive capacity (Table II) is not at all affected by the presence of even large amounts of softener on the fabric.

Antistatic Effects. The tests were carried out on Nylon, Dacron, Orlon, and acetate. Before test the fabrics were desized where necessary and thoroughly rinsed to remove any trace of detergents. The test fabrics were cut to 12 x 4½ in. and treated with softeners A. chloride, I. chloride, and I. sulfate by immersion for 10 min. in an aqueous solution containing 0.1% of cationic softener by weight. The excess solution was removed by passing the fabric through a wringer, and the wet fabric was weighed and dried. From the difference between the wet and dry weights the percentage of add-on of softener to the fabric was calculated. Since substantivity of cationics to synthetic fibers is very low, it was ignored. The same procedure was repeated, using 0.25 and 0.5% solutions. After drying, the fabrics were conditioned in a constant temperature-constant humidity room held at 75 to 78°F. and 22 to 28% relatively humidity for a period of 24 hrs. prior to testing.

The apparatus used for testing, which was developed by Fine (3), was placed in the constant temperature-humidity room. A schematic diagram of the device is given in Figure 5. The 12- x 4½-in. treated swatches were cut into strips measuring 12 x 1½ in., thus giving three replicates. The test piece was clamped to the reciprocating arm, the other end to a 100-g. weight and suspended over the bar assembly. The reciprocating arm drives the fabric 100 cycles per minute through a distance of 4 in. The electrostatic voltage reading was recorded every 15 seconds for a three-minute period, or until a charge of 2,000 electrostatic volts was built up, after which the reciprocating action was stopped and the charge was allowed to leak off. The discharge was recorded every 15 seconds for a three-minute period, or until a zero voltage reading had been attained, whichever occurred first. Untreated fabrics were used as control samples.

Data are represented as straight-line graphs, as shown in Figures 6 to 9. Deviations from straight-line relationships were very slight, so that the graphs are quite accurate.

The left sections of the graphs on Figures 6 to 9 show the time in seconds required for the electric

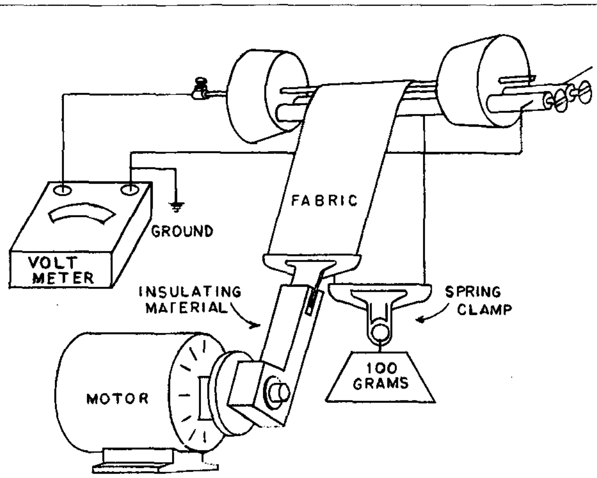


FIG. 5. Static generating apparatus.

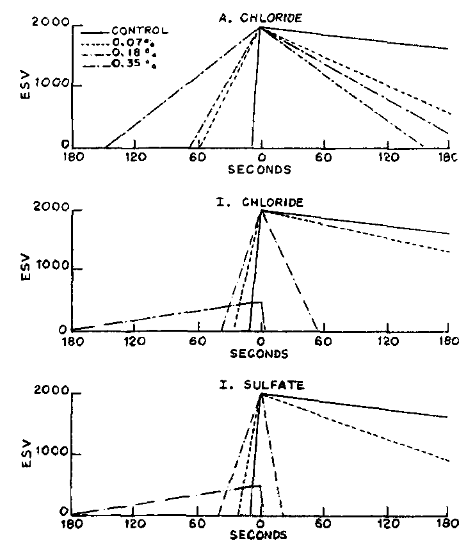


FIG. 6. Antistatic effects of softeners on Orlon.

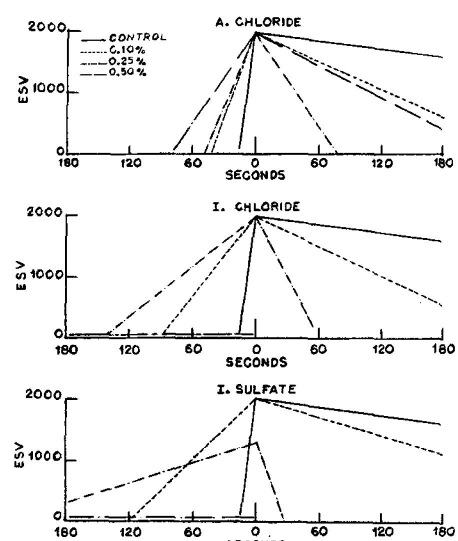


FIG. 7. Antistatic effect of softeners on acetate.

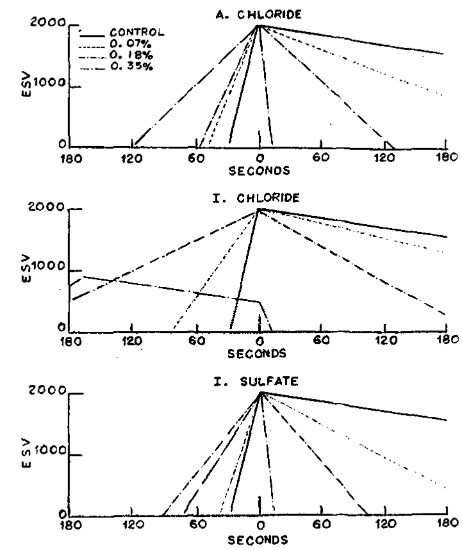


FIG. 8. Antistatic effect of softeners on Nylon.

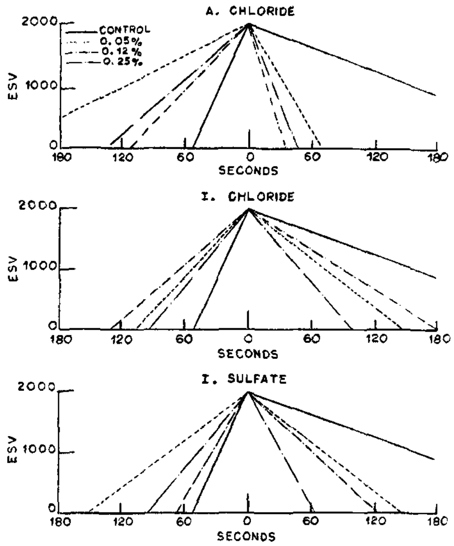


FIG. 9. Antistatic effect of softeners on Dacron.

charge to build up to a maximum of 2,000 volts, or the highest voltage attained in three minutes, whichever occurred first. The right-hand sections of the graphs illustrate the time rate of discharge. The control samples (solid lines) showed the fastest rate of build-up and the slowest rate of leak-off. Treatment of the test fabrics with the three softeners revealed two facts. As the concentration is increased, the rate of electrostatic leak-off is increased and the time required for the build-up is also increased. It should be noted that the percentages of softener on the fabrics are not the same for all four fabrics. For Dacron the wet pickup amounted to 50%, Nylon and Orlon 70%, and acetate 100%.

Figure 6 reveals that the I. chloride and sulfate are more efficient on Orlon than A. chloride. The I. sulfate in turn is a slightly better antistatic agent for Orlon than I. chloride. Figure 7 shows that the same relationship holds true also for acetate. For Nylon the I. chloride is the least effective whereas A. chloride and I. sulfate are about on a par; the I. sulfate has a slight edge over the A. compound. On Dacron (Figure 9) A. chloride is far more effective in bringing about the leak-off than either of the I. compounds. It is interesting to note however that the I. sulfate again has an edge over the corresponding chloride. It would appear that a quaternary methosulfate may be a more effective antistatic agent than the corresponding quaternary chloride having the same structure of the cation. It is obvious that the antistatic properties of a cationic agent depend not only on the chemical structure of the cation but also on the nature of the anion. Furthermore the antistatic effect is somewhat specific for individual synthetic fabrics.

Summary

The quaternary ammonium chlorides and methosulfates of a fatty amine derivative and a corresponding imidazoline derivative possess marked substantivity for cellulosic fabrics. The substantivity was determined quantitatively, and the rates of exhaustion were established. The exhaustion rate is increased with an increase of pH from 5 to 8 as well as with an increase of temperature from 70 to 90°F. Evenness of application appears to be related to slow rates of exhaustion. Evenness can be demonstrated visually by a bromphenol blue staining technique.

The amount of softener add-on has an effect upon the rate of water absorption of treated fabric; the relationship appears to be a logarithmic function. At low percentages of add-on, such as are used in the laundry industry, this is not objectionable.

The antistatic properties of three of the cationic agents on several synthetic nonpolar fabrics were studied by a dynamic friction procedure. The rates of charge build-up and leak-off depend upon the concentration of softener on the fabric. In general, the quaternary ammonium sulfates appear to be somewhat more effective than the corresponding chlorides. Furthermore the antistatic properties vary with the chemical structure of the cation and are somewhat specific for individual fabrics.

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Report of the Spectroscopy Committee, 1957-58

THE SPECTROSCOPY COMMITTEE met twice during the year ending with the 49th annual meeting of the Society in Memphis. The first session was held October 1, 1957, during the 31st fall meeting of the Society at the Netherland Hilton hotel, in Cincinnati, O. In the absence of the chairman, N. D. Fulton presided. The meeting was attended by five members or their duly authorized alternates: J. R. Chipault, Ralph Kelly (representing R. D. Mair), William Link, Hans Wolff, and Mr. Fulton. The following nonmembers attended: Erik von Sydow, University of Upsala, Sweden; William Ferran, Best Foods Inc.;