A Study on the Adsorption of Dialkyldimethyl Ammonium Chloride

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ABSTRACT

A study was made on the structure, adsorption behavior toward fabrics and dependence upon particle size of an aqueous dispersion of di(hydrogenated tallow)dimethyl ammonium chloride (purified Arquad 2HT), the most widely used softener base. From the results of analyses by X-ray diffraction, differential scanning calorimetry (DSC) and electron microscopy, it was found that the dispersed phase of Arquad 2HT dispersion consisted of hydrated particles having a similar structure to that of the multilayered liposomes (or vesicles) of phospholipids and that these particles were adsorbed onto fabrics by softening treatment. It was also found that finely dispersed particles showed better softening and antistatic performances in addition to a superior storage stability, due to their higher rate and uniformity of adsorption compared to roughly dispersed particles.

INTRODUCTION

So far, there have been only a few reports (1-4) on the structure of aqueous dispersion of distearyldimethyl ammonium chloride (DSDMAC), whereas a fair number of studies (5-12) have been made relating to factors influencing the amount of DSDMAC adsorbed.

This report describes experiments carried out to elucidate the structure and the adsorption behavior of an aqueous dispersion of purified Arquad 2HT (di[hydrogenated tallow] dimethyl ammonium chloride) (2HT), whose main constituent is DSDMAC. Moreover, the dependence of the adsorption behavior and the storage stability of this dispersion on the size of dispersed particles was also investigated through a comparative study of fine (micronized) and coarse (macronized) dispersion.

EXPERIMENTAL PROCEDURES

Materials

Arquad 2HT (Lion Akzo Co.), or di(hydrogenated tallow) dimethyl ammonium chloride, was purified by repeated crystallization from acetone and dried over P_2O_5 in vacuum. Its purity was confirmed by the modified reverse-titration method applying ISO 2271-1972. According to high performance liquid chromatography (HPLC) analysis (13), 63 wt% of the purified Arquad 2HT was DSDMAC, and the other ingredients were a series of ammonium salts of mono- and tristearyl, mono-, di- and tri-$C_{14,16}$ alkyl, and the unquaternized amines. The HPLC system consisted of a Model LC-3A chromatograph (Shimazu Seisakusho Co.), a Model RE-11 differential refractometer (Showa Denko Co.) and a Chromatopac C-E4A data processor (Shimazu Seisakusho Co.).

A micronized dispersion of 5 wt% 2HT was prepared using a high-speed agitator (Jet Agitor of Shimazaki Seisakusho Co.) with constant feeding of melted 2HT into water containing nonionic dispersant by 0.4 wt% at 50 C and cooled to room temperature, whereas a macronized dispersion was prepared using low-speed agitation.

The water used in all the experiments was deionized and distilled.

As standard materials for the adsorption experiments, cotton towel, acrylic jersey, polyester jersey and nylon tricot were used following a thorough pretreatment of detergent-washing and rinsing.

Structural Analysis of Dispersion

Melting point and amount of hydration water. The melting point of hydrated 2HT gel was measured using a differential scanning calorimeter (DSC) (Dainiseikosha Co. Model SSC 560). In addition, the water of hydration of 2HT was calculated from the melting peak area of frozen water, assuming that only water present in the bulk state was detectable at 0 C (3).

Samples were frozen beforehand with dry ice/ethanol.

Crystallography. Melted 2HT was thoroughly mixed with water by 5-100 wt% at ca. 100 C, and then cooled to room temperature for crystallographical analysis using an X-ray diffractometer with a small angle diffraction apparatus (Rigaku Denki Co., Model Geigerflex RAD II-A).

Electron microscopy. The structure of 2HT dispersion was observed with a transmission electron microscope (TEM) (Hitachi Model H-660) using the freeze-fracture replica technique, while the adsorption state on fabrics was observed with a scanning electron microscope (SEM) (Hitachi-Akashi Model MSM-4).

Particle size distribution. Particle size distribution of hydrated 2HT particles was measured by the visible light absorbance of diluted samples using Micron Photo Sizer (Seishin Co.) following centrifugal separation, when necessary.

The measurement is based upon the photoextinction and the sedimentation (Stokes' equation) principles.

The conditions under which measurements were carried out were as follows: wavelength of the visible light, 400-600 nm; concentration of samples, 0.4 wt% as 2HT.

Viscosity measurement. Sample viscosity was measured with a B-type viscometer (Tokyo Keiki Co.).

Performance

Softening treatment and softness evaluation. The standard conditions employed for adsorption experiment were as follows: 2HT concentration, 0.0033 wt%; liquor ratio, 30:1; temperature, 25 C, time, 3 min.

After an overnight equilibration at 25 C, 65 %RH, the softness of the treated materials was evaluated by trained panel testers using a subjective method whereby the panel testers rated the softness from 0 to 5, with a rating of 0 being the harshest (untreated control) and 5 being the softest. Fabrics treated with known softeners were also included as reference samples.

The amount of 2HT adsorbed onto a fabric was determined from titration of residual (unadsorbed) 2HT after a given time of treatment.

Antistatic performance. The antistatic performance of test fabrics of the abovementioned synthetic fibers was characterized by the half-period of voltage discharge.

The conditions under which measurements were carried out were as follows: equilibration of test fabric, 25 C, 65 %RH, 3 days; measuring apparatus, Static Honestometer (Shishido Shokai Co.); charged voltage, 7 kV (DC); electrode height, 2 cm.

RESULTS AND DISCUSSION

The Structure of Arquad 2HT Aqueous Dispersion

Since a fabric softener imparts softening and antistatic properties to fabrics by being adsorbed onto their surface, it is extremely important to determine the manner of adsorption of Arquad 2HT, which may possibly be influenced by the structure of the aqueous dispersion.

Since the saturated concentration of a monomolecular dispersion of DSDMAC is 4.6×10^{-6} (mol/L) (1), ca. 90% of the 2HT molecules are estimated to be dispersed as colloidal particles at a concentration for practical use (0.067 wt% as softener or 3.6×10^{-5} mol/L as DSDMAC contained in 2HT), as in the case of a household fabric softener, provided that 2HT is contained in the softener by 5 wt%.

Melting point of hydrated 2HT gel. Figure 1 shows the DSC heating curve for a 5 wt% 2HT dispersion. Since the hydrated 2HT melts at 34 C as shown in Figure 1, it is considered to exist as a hydrated solid at the usual temperature for softening treatment. Also, according to DSC data, the water of hydration of 2HT molecules has been calculated from the melting peak area of frozen water to be ca. 7 (mol H_2O/ mol 2HT).

Crystallography of 2HT dispersion. The hydrated 2HT gel was analyzed by X-ray diffraction. Figure 2 shows the X-ray diffraction patterns for various 2HT content. Each sample had a characteristic pattern which should render the following analysis reasonable.

First, pure 2HT gave a sharp peak at 34 Å as a long spacing and some peaks of shorter spacing at 17, 11.2, 8.4, 5.5 Å, etc. The ratio among these interplanar spacings becomes a fractional one in a regular order as 1/1: 1/2: 1/3: 1/4: 1/6. The periodicity of multilamellar liposome of DSDMAC gel was previously reported to be ca. 30 Å by Deguchi (3) and this seems to suggest that 2HT forms bimolecular layers of 34 Å in width, with the alkyl groups facing each other. Peaks of shorter spacings such as 4.7, 4.2, 3.9 and 3.7 Å signify the packing structure of hydrophobic hydrocarbon chain to be a triclinic system in terms of crystallography. Secondly, as 80 wt% 2HT has almost the same peaks as pure 2HT except a new strong one at 15 Å, the crystal system should remain triclinic. 2HT less than 70 wt% gave patterns showing weakened peaks of 34 and 15 Å, the remaining 4.1 Å and the disappearance of 4.7 Å and some others. The weakened 34 and 15 Å peaks are probably due to the dilution of 2HT, whereas both of the remaining 4.1 Å and the sudden disappearance of 4.7 Å and certain others signify that the crystal system probably shifts from triclinic one to hexagonal one.

The weak peaks of the longest spacings such as 54 Å of 50 wt% or 135 Å of 20 wt% detected by small angle diffraction seem to suggest the formation of certain types of layers or spacings by dilution, whereas 39 Å of 70-80 wt% may be attributed to the broadening width of the bimolecular layers. The relationship of these spacings to 2HT content is shown in Figure 3 and will be discussed later along with the results of TEM observation.

Microscopy. In the case of a moderate dispersion of 5 wt% 2HT, many 10 μm or smaller spherical particles were observed with an optical microscope as shown in Figure 4. Moreover, with TEM, by applying the freeze-fracture replica technique, it became clear that all these particles formed the multilayered liposome (vesicle) structure shown in Figure 5. In each of these particles, the concentric circles should be bimolecular lamellar layers with the sandwitched parts being the entrapped water as shown in Figure 6. By a comparison of the TEM photographs of diluted 2HT (0.1 wt%) and 5 wt% 2HT, it was also found that the former still retained the same structure as the latter despite the widening distance between the lamellar layers.

Comparing this with the abovementioned Figure 3, the longest spacings detected by small angle diffraction may be

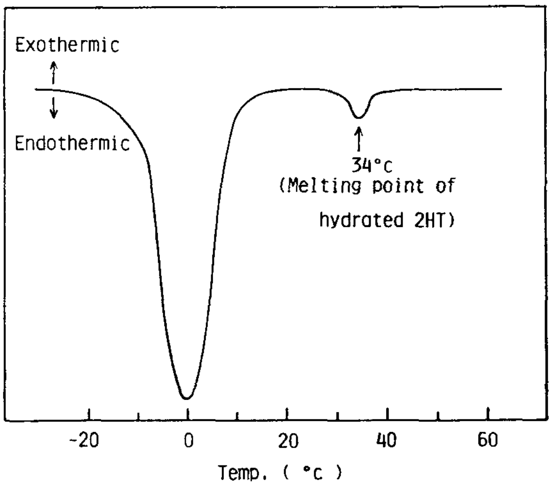


FIG. 1. DSC curve of Arquad 2HT dispersion.

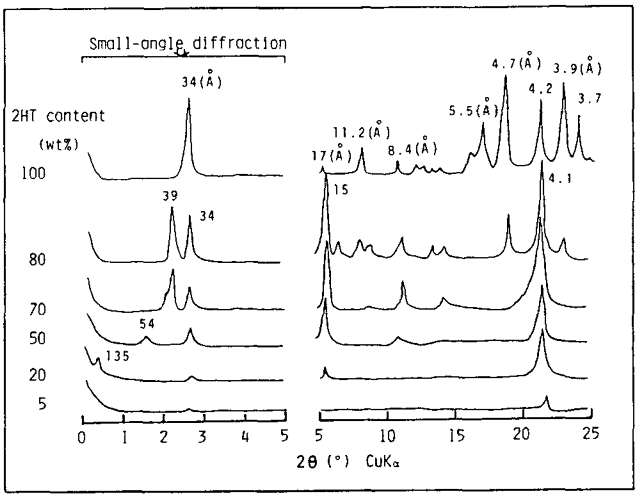


FIG. 2. X-ray diffraction patterns of hydrated Arquad 2HT.

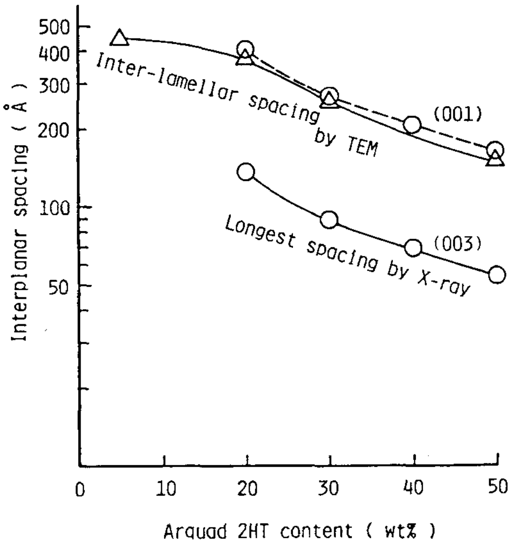


FIG. 3. Relationship between 2HT content and interplanar spacing.

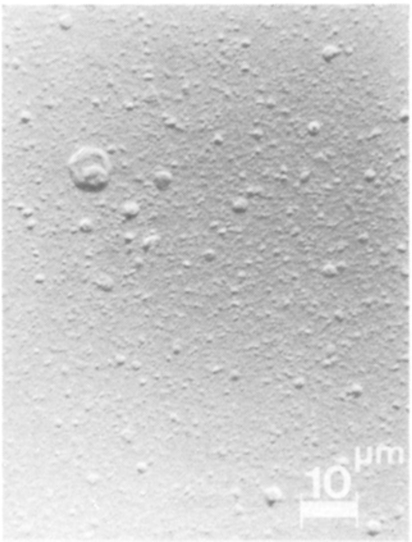


FIG. 4. Optical micrograph of a moderate dispersion.

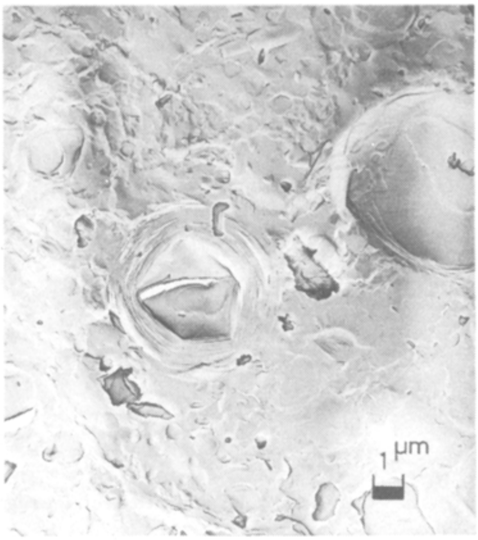
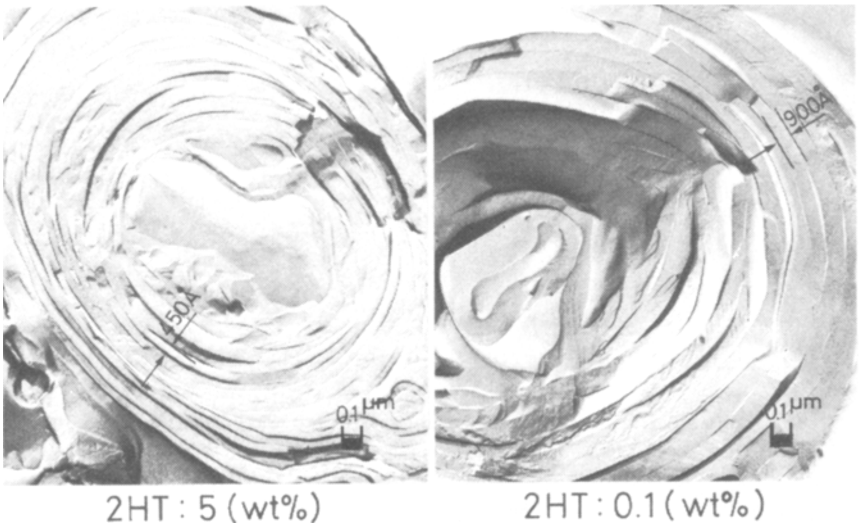


FIG. 5. Transmission electron micrograph (TEM) of a moderate dispersion.



2HT : 5 (wt%)   2HT : 0.1 (wt%)

FIG. 6. Liposome structure of Arquad 2HT dispersion.

attributed to the interlamellar spacings, because three times (001) the longest spacing (003) at each 2HT content coincides approximately with the distance between the lamellar layers observed in Figure 6. Therefore, it may be concluded tht hydrated 2HT forms the spherical liposome structure of multilayered bimolecular lamellars even in a diluted dispersion having a concentration approximately in the range of practical use of softeners.

Adsorption State of Arquad 2HT onto Fabrics

Figure 7 shows a comparison of SEM photographs of nontreated nylon tricot and that treated with a 0.0033 wt% 2HT dispersion, the approximate concentration for practical use. 2HT is adsorbed not as mono-or bilayers (6,11), but as multilayered particles onto the surface of fabrics. Thus, since it is apparently more advantageous to micronize particles with regard to the uniformity and rate of adsorption onto fabrics, the effect of particle size was investigated through a comparative study of micronized and macronized dispersions in the following.

Comparison of the Adsorption of Micronized and Macronized 2HT Dispersions

Appearance and structure of dispersion. The micronized dispersion is more transparent than the macronized one, mostly because of the wide difference in particle size as observed with an optical microscope (Fig. 8). Moreover, it was found by TEM observation (Fig. 9) that the micronized particles form a tight network structure in sharp contrast to a macronized dispersion in which particles are generally independent from each other.

Melting point and amount of hydration water. Since DSC curves of the micronized and the macronized dispersions are the same, both the melting point (34 C) of hydrated 2HT molecules and the amount of hydration water (ca. 7 mol H_2O/mol 2HT) are constant, despite micronization.

Manner of adsorption onto fabrics. SEM observation (Fig. 10) of the treated fabrics indicated that both the micronized and the macronized 2HT were adsorbed onto fabrics as particles; the former was adsorbed much more uniformly

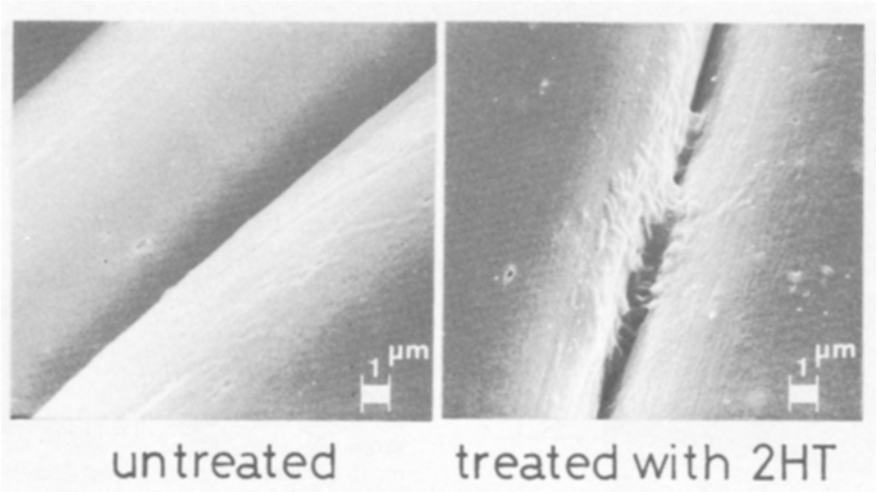


FIG. 7. Scanning electron micrographs (SEM) of untreated and 2HT-treated nylon tricot.

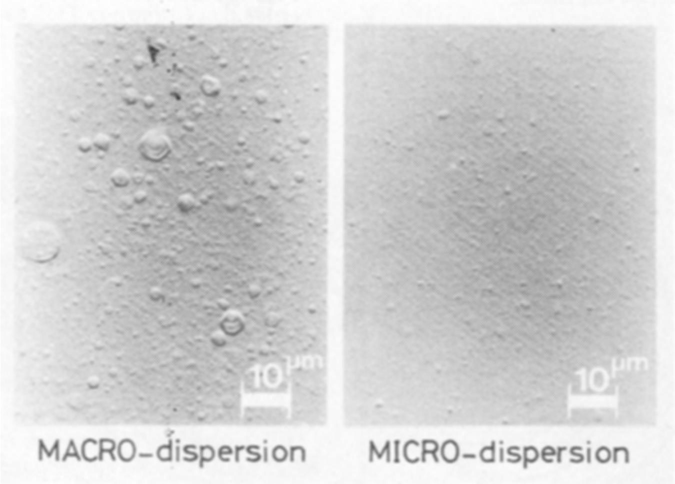


FIG. 8. Optical micrographs of the macro- and microdispersions.

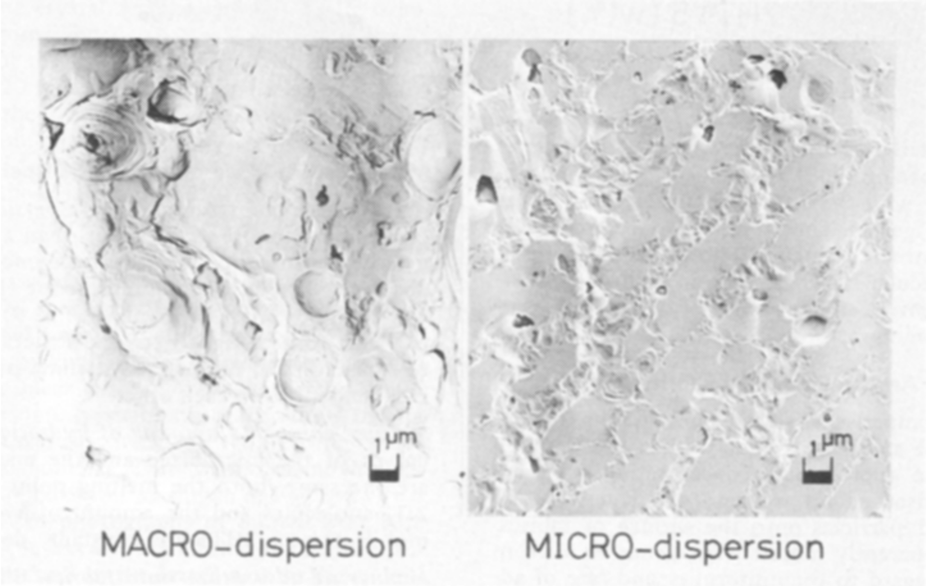


FIG. 9. TEM micrographs of the macro- and microdispersions.

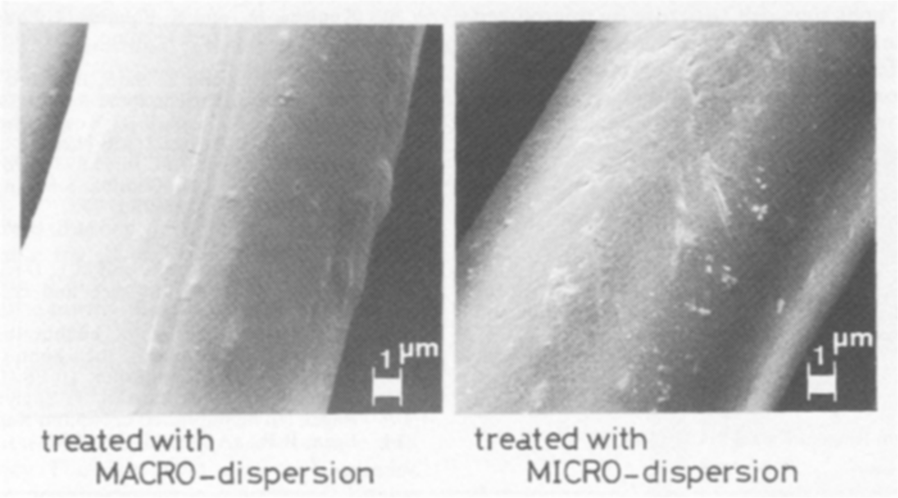


FIG. 10. Manner of adsorption onto nylon tricot (SEM).

than the latter.

Adsorption rate. From the results of an experiment based upon an idea that micronization would facilitate particle diffusion from a bulk dispersion and the adsorption onto the surface of fabrics, it was found that the adsorption of micronized particles was quicker than those macronized Fig. 11).

Therefore, in contradiction to previous reports (12,14), the particle size in a DSDMAC aqueous dispersion should be regarded as one of the determining factors of adsorption, as well as softener base concentration, temperature, pH, water hardness, liquor ratio, type of fabric and mechanical force of treatment.

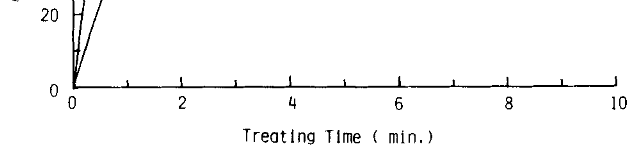


FIG. 11. Adsorption rate onto cotton towel.

Performance and Storage Stability

Performance. Table I shows the performance of a micronized dispersion along with particle size distribution, compared to a macronized dispersion. The former has superior softening and antistatic performance compared to the latter.

Storage stability. It is very important for softeners not to undergo any phase separation or viscosity change under any conditions even after long-term storage. As evident from Figure 12, the micronized dispersion shows not only better storage stability but less viscosity change than the macronized dispersion. This superior storage stability of the micronized dispersion is due possibly to the quicker formation of

TABLE I

Particle Size Distribution and Performance

Item	Sample	Macro-dispersion	Micro-dispersion
Particle size distribution (%)	under 1 μm	10	90
	1 - 5 μm	50	10
	5 - 10 μm	30	0
	over 10 μm	10	0
Softness rate (cotton towel)	Treatment time 1 min	3	4
	Treatment time 3 min	4.5	5
Half-period of charged voltage (sec)	Acrylic jersey	40	30
	Polyester jersey	180	140

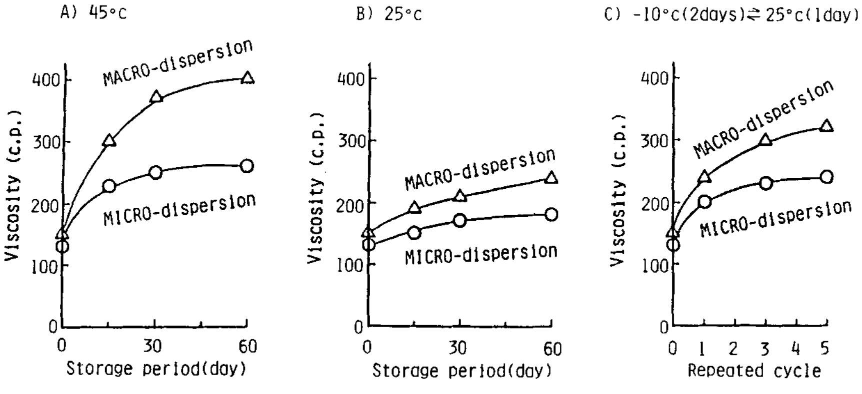


FIG. 12. Viscosity change under various storage condition.

the abovementioned tight network structure by micronized particles to overcome the separation force of buoyancy resulting from the difference in specific gravity between the dispersed and the continuous phases. The macronized dispersion tends to show phase separation as well as viscous instability due to insufficient formation of network structure.

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Heavy-Duty Liquid Detergent

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ABSTRACT

A highly concentrated liquid detergent was developed. For the consumer, the quality and costs of this detergent correspond to the light-duty washing powders. The new detergent can be used in washing machines as well as for hand-washing. For the consumer, the liquid product is ready for immediate use, gives no solubility problems in the washing bath and saves both time and energy by excluding prewashing of textiles. Having a high concentration of surfactants and containing an enzyme, the liquid detergent is activated for stain removal. It is recommended especially for such stains as collar soil, blood, grass and many kinds of food stains. For the best result, the instruction advises the application of "Flytande Tvättmedel" directly on visible stains in a prespotting fashion.

A heavy-duty laundry detergent is a powdered or liquid product which is capable of removing heavy soil deposits from textiles during the washing process.

The first washing powders based on soap appeared at the end of the 19th century. The real built washing powders containing silicate and carbonate were not developed until the beginning of the 20th century. Many Europeans remember the first washing powder with a bleaching effect – Persil. Synthetic washing powders were not readily available until the 1950s.

Early liquid household detergents were principally potassium soaps of fatty acids or alcoholic solutions of soaps. The liquid detergents were mainly limited to personal use (shampoo, shaving cream, etc.) and medical use.

In the early 1960s, Nordtend produced a liquid light-duty detergent which was suitable primarily for hand-washing. The detergent consisted of triethanolamine salt of alkylaryl sulfonic acid, a small amount of ethoxylated nonylphenols, and potassium pyrophosphate. The active content was ca. 48% and pH of a 1% washing solution was neutral. Unfortunately, the time was not right for this innovation.

By the beginning of the 1970s the liquid detergents had already captured about a 4% share of the market in the USA, while Europe had to wait until the 1980s for the launching of the liquid detergents Liz and Vizir.

To answer the question whether the problems in the detergent fields in the United States and Europe really are different, it seems appropriate first to point out the factors influencing the washing process. The differences affect the detergent formulation.

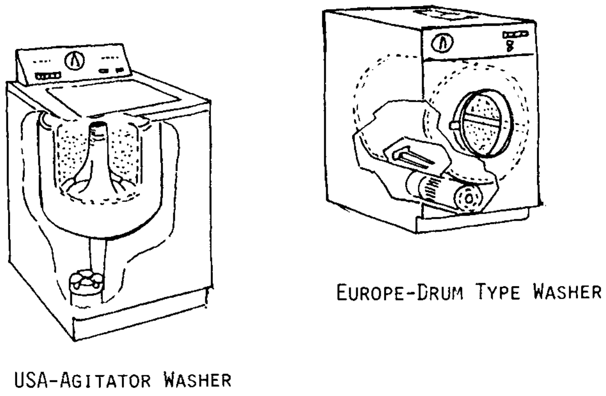

FIG. 1. Comparison of European and US automatic home washers.

There are differences in the washing medium, water. In the USA, only ca. 40% of the homes are affected by hard water. In Europe this number rises to ca. 80%, but in Sweden it falls to ca. 20%. The greatest differences between the United States and Europe are to be found in the construction of the washing machines. The top-loading agitator type of home washer is predominant in the United States. In Europe, on the other hand, the front-loading, horizontal drum type of washer is the most popular (Fig. 1). European automatic washers are fitted with electric heating elements and the washing process starts with cold water. American machines usually do not have a heating system, however – the washing starts with hot water. Consequently, these factors result in higher washing temperatures in European machines than in American machines. In Europe, more natural fibers, such as cotton, are used.

Currently, ordinary washing powders are still dominating the Swedish market and the total volume is estimated to be ca. 42,000 ton/year. The market shares for the major companies are as follows: Unilever (Sunlight), ca. 50%; Nordtend, ca. 20%; Colgate, ca. 8%; and Procter & Gamble, ca. 6%.