Chemical Changes in Unsaturated Oils upon Aging and Subsequent Effects on Fabric Yellowing and Soil Removal

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Aging of unsaturated oily soils on polyester/cotton fabric was explored with oleic acid, triolein and squalene as model soils in terms of the relationship between changes in their chemical structure and fabric appearance. Among the three unsaturated oily soils studied, yellowing was observed only with squalene-soiled and aged fabric swatches after aging for 2 to 46 wk. The yellow material formed upon aging was not completely removed by laundering or organic solvent extraction. In extraction, the more polar solvents removed more yellow material from the fabric. Radiotracer analysis of labeled oily soils showed that all three soils volatilized from fabric upon aging with their characteristic volatility patterns. The amount volatilized increased with aging time and temperature. Removal of triolein and squalene increased remarkably after aging when applied as single soil. Higher aging temperature (40°C) increased soil removal more dramatically than a lower temperature (21°C). In a mixed soil system, removal of triolein by detergency increased up to 8 wk of aging; a decrease in removal was observed for a specimen aged from 8 to 26 wk at 21°C. Removal of oleic acid decreased gradually during aging in both single and mixed soil systems. Separation of aged products by thin-layer chromatography (TLC) revealed that unsaturated oily soils chemically changed into various polar oxidation products that were more easily removed by detergency. Infrared (IR) spectra of the aged oils substantiated the appearance of polar groups, such as O-H, C=O and C-O. Osmium tetroxide treatment proved disappearance of double bonds of unsaturated oils upon aging. The fabric yellowing observed for squalene-soiled fabric is related to the formation of yellow, polar, resinous material due to rapid oxidation, as evidenced by TLC, IR spectra, volatility pattern and rigidity of aged fabric. Oxidation products of squalene with conjugated C=O groups are proposed as the cause of fabric yellowing upon aging, and a possible mechanism for their formation is proposed.

KEY WORDS: Aging, detergency, laundering, oil, oleic acid, oxidation, squalene, textiles, triolein, volatilization, yellowing.

Soiling and the removal of soils from fabrics have been problems because dinginess and yellowness of fabric limit the usefulness of clothing despite frequent washing. Many different factors are involved in the gradual yellowing of white fabrics. Chemical changes in cellulose, particularly the formation of carbonyl and carboxyl groups by oxidation of the hydroxyl groups, cause yellowing (1,2). Storage of white fabrics and garments in polyethylene bags or packages also causes yellowing (3,4). The causative agent of this yellowing is the yellow oxidation product of 3,5-di-*tert*-butyl-*p*-quinone methide (BHT). Conditions necessary for such yellowing to occur are the presence of BHT, nitrogen dioxide, moisture and alkaline-finished fabrics (4). Rochas and Martin (5) related the yellowing of nylon fiber at elevated temperatures to the formation of pyrrole rings. Gradual yellowing of textiles in use has been related also to a buildup of natural inorganic soils, such as clay and iron oxide (6); the accumulation and oxidation of residual oil, mainly sebum (7–17); and the presence of nitrogenous soil (7,9,18).

The major source of oily soil on a textile is human sebum originating from the body of the wearer. Because approximately 50% of the fatty acids in sebum are unsaturated, sebum on the fabric is believed to undergo chemical changes that render it more difficult to remove and cause yellowing of the fabric (7,12). Walter (19) reported that the proportion of unsaturated compounds is smaller in aged sebum than in fresh. There have been reports about polar, yellow and brown polymeric compounds resulting from aging reactions of sebum (10,17). Oldenroth (11) recognized that the oxidation of squalene contributed to the yellowing of fabric. Rapid oxidation of squalene into a resinous, brown, polar material is well known (12). In laundering studies with cotton fabrics, Wagg *et al.* (16) found that yellow color was produced with artificial soils of squalene, cholesterol and linolenic acid. McLendon and Richardson (8) tested six components, including oleic acid, cholesterol, triolein, tristearin, stearic acid and cetyl alcohol, and they concluded that high relative humidity is an important factor in causing yellowing during storage of fabrics containing residual oily soil. Spangler *et al.* (18) used the yellowing of synthetic sebum, containing squalene, as a means of evaluating detergency.

The carbon–carbon double bonds of unsaturated fatty acids are easily attacked by oxygen in the air (20–23). The reaction of oxygen with an unsaturated lipid produces fatty acid hydroperoxide as the primary product of autoxidation by hydrogen abstraction from the allylic methylenes, in which electrons are delocalized through 3-carbon interactions (on carbon-8 and carbon-11 in case of oleate) (20). In free-radical autoxidation, initiation takes place in the presence of radicals, light or heat. The resulting free radicals (R*) react with oxygen to form peroxy radicals (ROO*), which react with more oleate (RH) to form a mixture of 8-, 9-, 10- and 11-hydroperoxide isomers. Oleate hydroperoxides react further with oxygen to form secondary oxidation products, such as epoxyhydroperoxides, ketohydroperoxides and dihydroperoxides (23). These secondary products, as well as the primary product monohydroperoxide, decompose into volatile breakdown products, including aldehydes, ketones, alcohols, hydrocarbons and acids of shorter carbon length. These breakdown products are produced by the mechanism of carbon–carbon cleavage on either side of the alkoxy radical intermediates produced from hydroperoxides (23,24). Hydroperoxides can also condense to form dimers and polymers by radical combination and radical addition (22,25,26). Predominant oxidation products on a relative time scale, defined by Frankel *et al.* (23), are presented in Figure 1.

The problems connected with the oxidation of unsaturated oily soils include: (i) Volatile breakdown products possibly act as a source of undesirable odors on garments; (ii) removal of oily soil will be more difficult if larger molecules or polymers form as a consequence of oxidation reactions; (iii) hydroperoxides and some of their bifunctional breakdown products, *e.g.*, malonaldehydes, cause polymerization of

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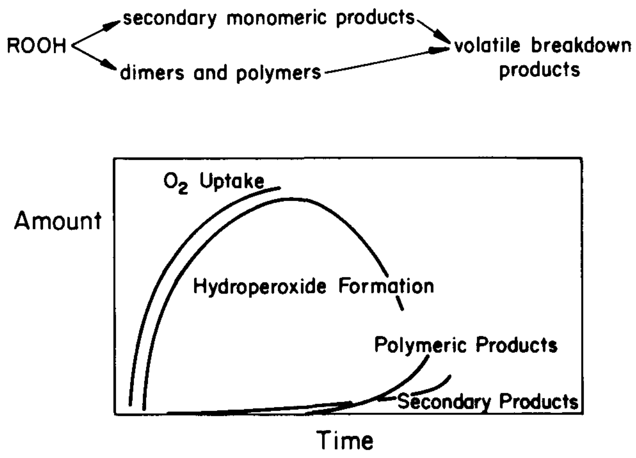


FIG. 1. Predominant oxidation products from the autoxidation of lipids on a relative time scale (23).

protein soils in a mixed soil system and may interact chemically with fibers. [Researchers have shown that these compounds interact with proteins, amino acids and enzymes often leading to the formation of colored, insoluble complexes (27)]; and (iv) chemical structural change of unsaturated oily soils affect the fabric's appearance.

When Powe (12) compared the typical composition of fresh adult sebum extracted from T-shirts after 24 h of wear and the residual oily soil after several years of normal use, the main differences in the composition of the aged oil were the lesser amounts of free fatty acid and squalene, the existence of dark-colored oxidation products comprising one-third of the residual oil and the presence of lime soaps. A comparison of fatty acid components between fresh and aged oily soils shows a smaller amount of unsaturated acids in aged soils relative to fresh soil (12).

Although analysis of aged oily soils by Powe (12,28) indicated that unsaturated oily soils undergo oxidation upon aging, there has been no detailed report about chemical composition of oxidation products on an aged fabric and the effect of chemical structure changes of oily soils on their removal from a fabric, except the indication of difficulty in the removal of oily soils from aged fabric (29–32). However, these researchers used a reflectance method or visual evaluation by using a trace of oil-soluble dye to measure soil removal, and they did not analyze the aging products.

In this study, with a quantitative method for measurement of mass to evaluate soil removal, effects of aging on volatility and soil removal of oily soils were studied with model oily soils of oleic acid, triolein and squalene that are the typical components of sebum and are also most likely to undergo chemical structural changes by oxidation. Effects of aging of oily soils on fabric yellowing and detergency were studied in single and mixed oil systems, and the results are explained by the analysis of chemical changes in these unsaturated oils.

EXPERIMENTAL PROCEDURES

Materials. A 50 polyester/50 cotton sheeting with durable-press finish was purchased from Testfabrics Inc. (Middlesex, NJ) Tide® powder, a commercial laundry detergent produced by The Procter & Gamble Company (Cincinnati, OH), was purchased in New York State in the fall of 1989. The major components of this built, powdered detergent were anionic surfactants and enzymes as cleaning agents, aluminosilicates and sodium carbonate as water softeners. The amounts of detergent needed during the experimental period were weighed at one time just after opening the package and stored in individual polyethylene bags to prevent the incorrect weighing of detergent due to moisture pickup.

Oleic acid, triolein and squalene were chosen as model oily soils and purchased at 99% purity from Sigma Chemical Company (St. Louis, MO). Radioactive [^{14}C(U)]-oleic acid, [9,10-^{3}H(N)]-triolein and [4,8,12,13,17,21,-^{3}H]-squalene were obtained from New England Nuclear Products (DuPont, Boston, MA).

Silica gel 60 F$_{254}$® TLC plates (25 cm × 25 cm) were obtained from EM Science Company (Elmsford, NY). Osmium tetroxide, E.M. grade, was obtained from Electron Microscopy Sciences (Fort Washington, PA). All solvents used were from Fisher Scientific (Fairlawn, NJ) and were ACS-grade (met American Chemical Society qualifications). All water used experimentally was distilled, deionized and then redistilled in glass.

Fabric cleaning. The fabric was cut into 6.5 cm × 6.5 cm swatches with pinking shears. Swatches were soaked in a 10% (wt/vol) sodium chloride solution for 21 h to solubilize inorganic salts accumulated from previous handling and finishing. This was followed by a Soxhlet extraction with water for at least six cycles, air drying, a Soxhlet extraction with toluene for 12 h and air drying at 21°C. Samples were stored in envelopes lined with lint-free paper.

Soiling procedures. Aluminum weighing pans with 6-cm diameter were used to make soiling frames. The bottom part of each pan was removed. The fabric specimen to be soiled was mounted over the top of the modified weighing pan. An aliquot of the oily soiling solution was pipetted onto the center of the fabric held taut in the frame. When soiled fabrics were aged, the frames holding the fabrics were stacked, one on top of the other, providing a convenient method to handle many samples without the soiled fabrics touching each other.

Oleic acid, triolein and squalene were applied to swatches as a single oily soil or mixture of two or three oily soils. The 8% (wt/vol) soiling solution of each oil was prepared in toluene. An 80-μL aliquot of soiling solution was applied to the center of each swatch to give a soiling level of 6.4 mg of oil per 6.5 cm × 6.5 cm swatch. To make radioactive oily soiling solution, the 8% (wt/vol) nonradioactive soiling solution of each oil was combined with such an amount of each labeled oil that the activity per swatch was between 20,000 to 30,000 counts per minute. For example, 8 μL of ^{3}H triolein stock solution, which was commercially available at a concentration of 0.5 mCi/mL (1.11×10^{6} dpm/μL, because 1 mCi = 2.22×10^{9} dpm), was added to 10 mL of the 8% (wt/vol) soiling solution of triolein in toluene to give 888 dpm/μL soiling solution. Counts for an 80-μL aliquot ($888 \times 80 = 71040$ dpm) of this soiling solution on a Beckman LS-7000 Liquid Scintillation Counter® (Beckman Instruments, Fullerton, CA) corresponded to @ 28416 counts per minute because the counting efficiency of tritium is about 0.4. An 80-μL aliquot of soiling solution was applied to the center of each swatch to give a soiling level of 6.4 mg of oil per 6.5 cm

× 6.5 cm swatch [1.09% of fabric weight (owf)]. Labeled specimens were prepared simultaneously with unlabeled specimens. Samples soiled with nonradioactive oily soils were used for the color measurements, thin-layer chromatographic analysis and OsO_4 solution treatment, while the radioactive counterpart was used only for the radiotracer analysis.

For the mixed oily soil, an 8% (wt/vol) labeled soiling solution in toluene was prepared of triolein and oleic acid, respectively, with [9,10-^{3}H(N)]-triolein and [^{14}C(U)]-oleic acid at an activity of ^{3}H-isotope approximately four times stronger than that of ^{14}C isotope. A two-component solution of oleic acid and triolein was made by mixing identical volumes of these two single-oil soiling solutions. A three-component solution of oleic acid, triolein and squalene was prepared by adding a calculated amount of squalene into the two-component solution of oleic acid/triolein, such that the resulting weight-to-volume ratios of each of the three oils were the same. An 80-μL aliquot of each soiling solution was applied to the center of each swatch (6.5 cm × 6.5 cm) to give a soiling level of 3.2 mg for each of oleic acid and triolein (1.09% owf) and 3.2 mg for each of oleic acid, triolein and squalene (1.64% owf).

To study the effect of soiling level on soil removal for each of triolein and squalene as single soils, a series of oily solutions at different concentrations was made. An 80-μL aliquot of soiling solution was pipetted in the center of each swatch (6.5 cm × 6.5 cm). Soiling amounts for each oil were 1.6, 3.2, 6.4 and 12.8 mg/swatch.

Aging procedures. Soiled swatches were air-dried for 2 h and then aged in the dark at two different temperatures, simulating body temperature (40°C) and normal room temperature (21°C). At 40°C, samples mounted on the aluminum soiling frame were kept in a stack in a Blue M® mechanical convection oven with a Temp-master® (Blue Island, IL), which provides continuous monitoring of chamber temperature to within ±1°C. The other set of samples were kept on a shelf of a laboratory that had free flow of air and no light. The temperature and relative humidity of the laboratory recorded during the aging period were 21 ± 2°C and 50 ± 10%. After aging periods of 1, 2, 4, 8, 26 and 48 wk, chemical and color measurements were made.

Solvent extraction of aged squalene. The aged oil was removed from the fabrics by extraction. Squalene-soiled swatches, aged for 2 mon, were extracted with each of methanol, acetone, chloroform and a 0.175% (wt/vol) detergent solution. One fabric specimen was placed in a flask containing 20 mL of each solvent and was shaken on a Burell Wrist-Action® Shaker (Pittsburgh, PA) for 30 min. The further extraction of material still remaining on the fabric was conducted by a Soxhlet treatment with the same solvent for five cycles. Samples were removed and dried after each solvent treatment. Color measurements of the fabric were made before and after each solvent treatment.

Laundry procedures. A Terg-O-Tometer® (United States Testing Co., Hoboken, NJ) with an agitation rate of 100 cycles/min was used to wash the fabrics. Two sample swatches from four replicates were washed together in an individual Terg-O-Tometer® can with 400 mL of a 0.175% (wt/vol) detergent solution for 10 min at 44°C. Two 5-min rinses of four replicates together were carried out in 400 mL water at 44°C with the same agitation rate. All samples were air-dried at 21 ± 1°C and a relative humidity of 65 ± 2% for 24 h before analyses.

Color measurements. The color change, due to aging of oily soiled samples, was measured by reflectance with a Macbeth® 1500/Plus Color Measurement System (Newburgh, NY) (33). The CIELAB color coordinate system (Commission International de l'Éolairage, L, u, b, opponent, color corrdinates) with D65 daylight as the illuminant was chosen. The color plot of oil-soiled and aged swatches was drawn to see the location of the aged samples in color space relative to the standard, which was a cleaned and unsoiled fabric swatch. Readings at five locations (at the center of the fabric swatch and at four locations 2.5 cm radially distant from the center) on one fabric swatch were taken and averaged for each treatment. Changes in the "b" value were analyzed because positive values show an increase in yellowness.

Radiotracer analysis. Radiotracer analysis was used to determine the amount of oil on the fabrics before and after each treatment. This analysis was used to study the production and loss of volatile breakdown products during aging and to measure quantitatively the amount of oily soil remaining on each swatch after different aging times. The amount of oil removed was also determined by radiotracer analysis of labeled oily soils present before and after laundering.

For the soil removal experiments, three replicates of labeled specimens that had been aged at two different temperatures for different periods were analyzed before laundry to determine the amount of oil volatilized and the amount of oil present after aging and before laundering. Four replicates per treatment were washed, dried according to the laundry procedure and counted.

Liquid scintillation counting was used for quantitative determination of the radioisotopes. Each fabric swatch was folded and placed in a glass scintillation vial with 20 mL of Scintiverse LC® fluid (Fisher Scientific). Radioactivity of a fabric swatch was counted on a Beckman LS-7000® Liquid Scintillation Counter. For the single-labeled specimens, ^{14}C was counted on channel 1 of Beckman LS 7000® library program 4 (34). Tritium, ^{3}H, was counted on channel 1 of program 5. For the dual-labeled specimens, the activities were counted on channel 1, which is the lower energy window for tritium, and on channel 2, which is the upper window for ^{14}C, of program 8 (34).

Standardization of the counting system (counting efficiency determination) was accomplished by counting Beckman Quenched Standard Sets of ^{14}C and ^{3}H, with ^{137}Cs, a γ-emitting isotope, as an external standard. The specific activities of the ^{14}C and ^{3}H in dual-label experiments were calculated from a pair of simultaneous equations (35). The average disintegrations per minute and standard deviation (SD) were obtained from replicates of each treatment. The amounts of oil remaining on the fabric after several periods of aging were expressed in weight or weight percentage of the original amount by using Equations 1 and 2:

$$\mathrm{Wt}_{\mathrm{remaining}} = \mathrm{dpm}_{\mathrm{x,average}}/\mathrm{dpm}_{\mathrm{aliquot,average}} \times \mathrm{Wt}_{\mathrm{aliquot}} \qquad [1]$$

$$\%_{\mathrm{remaining}} = \mathrm{dpm}_{\mathrm{x,average}}/\mathrm{dpm}_{\mathrm{aliquot,average}} \times 100 \qquad [2]$$

where $dpm_{x,av.}$ = average dpm of three replicates of swatches soiled and aged for x wk; $dpm_{aliquot,av.}$ = average dpm of three replicates of swatches soiled but not aged; and $Wt_{aliquot}$ = weight of oil per aliquot.

Soil removal for different aging times was calculated based on the amount of oil remaining before wash and after aging instead of the original amount of oil applied (Equation 3):

$$\text{soil removal (\%)} = (1 - dpm_{Af,x,av.}/dpm_{Bf,x,av.}) \times 100 \qquad [3]$$

where $dpm_{Bf,x,av.}$ = average dpm of three replicates of swatches soiled and aged for x wk, $dpm_{Af,x,av.}$ = average dpm of four replicates of swatches soiled and aged for x wk and washed.

In both cases, the error for measurement was calculated from Equation 4:

$$\sigma_{x/y} = (\sigma_x^{\ 2} + \sigma_y^{\ 2})^{1/2} \qquad [4]$$

where $\sigma_{x/y}$ = SD for f = x/y, σ_x = SD for x, σ_y = SD for y.

Thin-layer chromatography (TLC). Oleic acid, triolein and squalene as single-component soils were aged on TLC plates or fabric swatches. The 8% soiling solution of each oil was spotted three times on a 2.5 cm × 6.5 cm silica gel 60 F_{254}® TLC plate and aged. These samples were taken out after 0, 1, 2, 4 and 8 wk of aging and developed in a TLC chamber. Two fabric swatches, soiled according to the procedure in single oily soil application and aged, were placed in an Erlenmeyer flask with 20 mL of chloroform and methanol in a 1:1 vol/vol ratio and were shaken on a Burell Wrist-Action Shaker® for 30 min. The first extract was then decanted into a flask. Another 20 mL of chloroform and methanol was used to further extract the same fabric swatch by shaking for an additional 30 min. After the second extract was combined with the first, solvents were evaporated until the volume reached about 2 mL. The solution was then subjected to TLC analysis. The solvent systems adopted were *n*-hexane/diethyl ether/acetic acid (50:50:1) for aged oleic acid and *n*-hexane/chloroform/methanol (20:10:1) for aged triolein and squalene. Nondestructive detection of each band on the silica gel 60 F_{254}® TLC plate (EM Science Co.) was accomplished by the quenching of bands under an ultraviolet (UV) lamp at 254 nm. Bands still containing double bonds were detected by black color after hanging developed TLC plates in a dram bottle containing 2 mL of 2% OsO_4 solution.

To avoid the time-consuming extraction procedure at each aging period, TLC patterns of oils aged on TLC plates were substituted for aged oils on fabrics. TLC patterns of oils extracted from oily soiled fabric that had been aged two months were obtained for comparison.

Infrared (IR) spectroscopy. A 0.2-g sample of each oleic acid and triolein was weighed into a petri dish and aged at 40°C. After 0, 4, 8 and 24 wk of aging, a drop of each aged oil was placed between two NaCl IR plates. Transmission IR spectra of aged oils were taken on a Perkin Elmer-680® IR Spectrophotometer (Norwalk, CT) connected to a Perkin Elmer 3600® Data Station. A 5-g sample of squalene was aged in a petri dish at 21°C. After 24 wk of aging, a small amount of aged squalene (0.2 g) was removed and placed in another petri dish to increase the surface area contacting with air. After 0, 4 and 24 wk of aging of the original sample, and after 1, 2 and 8 wk of aging after the surface area in contact with air was increased, a drop of aged squalene was spread out between two NaCl IR plates and analyzed.

The OsO_4-tagging procedure. Aged fabric swatches were treated with 2% wt/vol aqueous OsO_4 for 3 h. Four to ten fabric swatches were treated at one time by laying them flat in the bottom of a 600-mL beaker and covering them with about 10 mL of OsO_4 solution. After 3 h of treatment, the osmium tetroxide solution was removed from the beakers. The sample swatches were then rinsed in 400 mL of distilled, deionized water for three 20-min periods. After air-drying at 21 ± 1°C and a relative humidity of 65 ± 2% for 24 h, the resulting color due to the reaction of OsO_4 with the double bonds of the unsaturated oils was recorded from visual observation.

Statistical analysis. With the Statistical Analysis System (SAS®) (Cary, NC) package (36), Duncan's multiple range tests were conducted on soil removal data for each oil in the single-soil systems and two kinds of mixed soil systems after 0 and 26 wk of aging at two temperatures, 21 and 40°C, to find significant differences among the nine means.

RESULTS AND DISCUSSION

Effect of aging on the visual appearance of oil-soiled fabric. Because unsaturated oils are known to cause yellowing of fabrics, changes in color of oil-soiled swatches after aging were measured with a Macbeth Color-Eye® System. Among the three unsaturated oily soils studied—oleic acid, triolein, squalene—yellowing was observed only when fabrics were soiled with squalene as single or mixed component.

Color plots of each measurement of oil-soiled swatches after 1, 2, 4, 8, 26 and 48 wk of aging (Fig. 2) revealed that

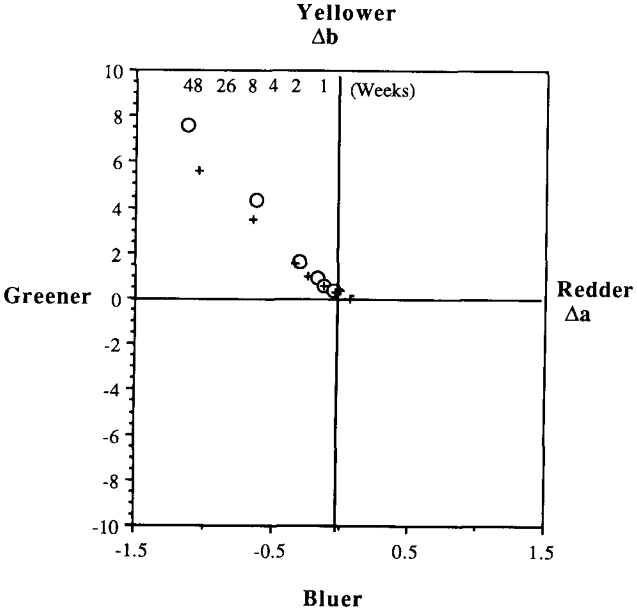


FIG. 2. Color plot showing the gradual yellowing of squalene-soiled fabric swatches during aging (increased Δb after 1, 2, 4, 8, 26 and 48 wk of aging). Symbols—O, aged at 21°C; +, aged at 40°C. Note that data for oleic acid- and triolein-soiled and aged samples are located inside the cross-hatched box.

fabric soiled with squalene became yellower with increased aging, while fabric soiled with oleic acid or triolein were in the tolerable region [−0.5 to +0.5 in Δb (33)]. For fabrics soiled with oleic acid or triolein, yellowing was not visually apparent, even after the longest aging period (46 wk). Yellowing of fabric soiled with squalene was noticed visually after aging for 2 wk (Δb = 0.6). This visual observation indicated that an instrumental difference of about 0.5 in Δb was likely to be visible to the eye.

The intensity of yellow color produced on squalene-soiled fabric is well described by changes in the b unit (Δb). The color produced by aged squalene also increased in the green color component, Δa (Fig. 2). More intense yellow color was developed when squalene-soiled fabric was aged at 21°C rather than at 40°C. This was probably due to more loss of squalene by volatilization during aging at 40°C than at 21°C, which will be discussed later in this paper.

Yellowing of fabric was also observed when squalene was applied as mixed soil with triolein and oleic acid (Fig. 3), while fabric soiled with a mixture of triolein and oleic acid did not become visually yellow, even after 26 wk of aging. Yellowing of fabric soiled with a mixture of squalene, triolein and oleic acid was not noticeable visually until after two months of aging, while it was observed after only two wk when squalene was applied alone (Δb = 0.6). Changes in yellowness after 26 wk in these two fabric specimens are presented in Figure 3. The lower degree of yellowness measured in mixed-component than single-component soiling may have resulted from the different amount of squalene applied (6.4 mg per swatch in a single soil, 3.2 mg per swatch in mixed soil) or from the presence of other soils, which might delay the formation of the yellow component.

Although oleic acid and triolein did not cause yellowing of fabric under the aging conditions used in this study, more vigorous aging conditions, including longer aging time, higher aging temperature, higher humidity and presence of clay, could cause yellowing of fabric, as observed by other researchers (16,18).

Effect of various solvent extractions on the measurement of yellow color. The yellowing caused by oxidation of squalene during aging persisted even after laundry (Fig. 3). Laundered fabrics with squalene alone or in a mixture and aged at either 21 or 40°C had Δb values larger than 1.2 when compared to clean, unsoiled fabric. Although the content of squalene in human sebum is about 10% (12), a smaller amount than the one used in this study, the gradual accumulation of the yellowing material may cause deterioration in fabric appearance in naturally soiled clothing.

Organic solvent extraction was used to remove the yellow material from squalene-soiled fabrics that had been aged for two months (Fig. 4). The result of extraction with 0.175% built powder detergent in water was compared with those with three organic solvents. The amount removed was estimated by changes in the "b" values, as measured on the MacBeth® color system, before and after each solvent extraction. Shaking of fabric swatches for half an hour in each of the solvents, methanol, acetone and chloroform, did not extract completely the yellow material. Even after subsequent Soxhlet treatment with the same solvent, the yellowing of fabric persisted with Δb = 0.97 for methanol extraction when compared to clean, unsoiled fabric.

Color measurement results after solvent extraction are presented in Table 1. Treatment with detergent solution had almost the same effect on color removal as methanol extraction, causing a decrease of 1.23 "b" units after 30-min shaking and an additional decrease of 0.43 "b" unit after one hour boiling (total decrease of 1.66 "b" units). The polarity of the solvent used in extraction is described by its dielectric constant (ε) (Table 1). The more polar solvents tended to extract more yellow materials from the fabric. The residual yellowing after solvent extraction could be due to the yellowing of the durable-press finished cotton/polyester fabric. From the data collected in these experiments, it is not possible to differentiate between the effects of aged oils and of aging of the durable-press finished fabric.

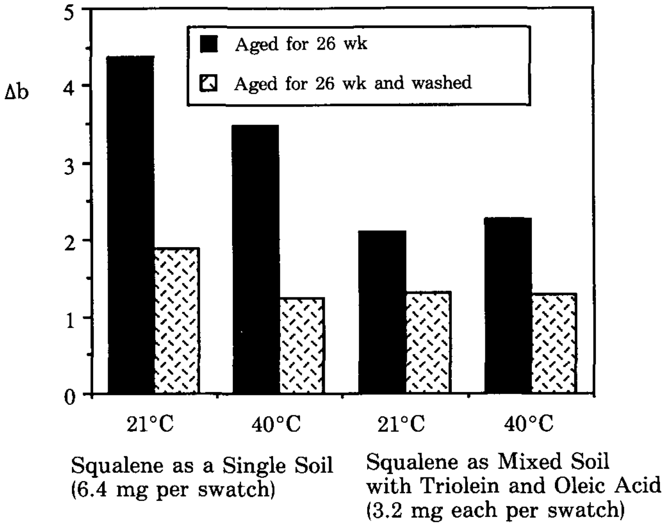


FIG. 3. Yellowing of squalene-soiled fabric after 26 wk of aging.

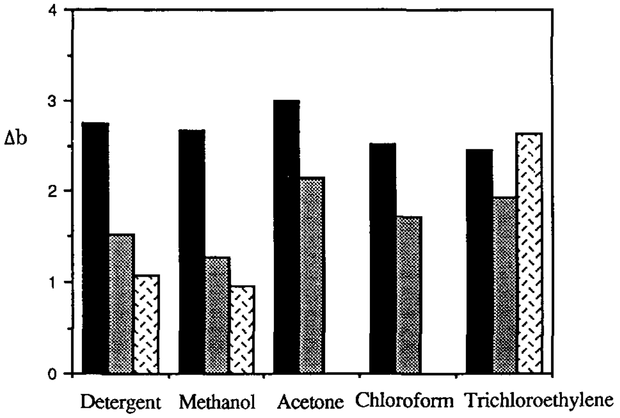


FIG. 4. Changes in yellowness after solvent treatment of squalene-soiled and aged fabric swatches. Symbols—solid bar: 2-mon aging at 40°C; shaded bar: 30-min shake; broken-line bar: 1-h boiling (detergent) or 3-cycle soxhlet (solvents).

TABLE 1

Relationship Between Decrease of "b" Unit After Solvent Extraction of Yellow Material and Solvent Polarity

Solvent	0.175% Detergent solution	Methanol	Acetone	Chloroform
Dielectric constant[a], ε	—	32.63 (25°C)	20.7 (25°C)	4.806 (20°C)
Δb[b] (after 30-min shaking)	−1.23	−1.39	−0.86	−0.8
Δb (3-cycle Soxhlet or 1-h boiling)[c]	−0.43	−0.30	—	—

[a] Data obtained from the *CRC Handbook of Chemistry and Physics*, 66th edn, edited by R.C. Weast, CRC Press, Inc., Boca Raton, 1985, pp. E 50–51.

[b] Δb = b (after treatment); −b (before treatment): (positive Δb is increased yellowing, negative Δb decreased yellowing).

[c] The specimens treated with detergent solution were boiled 1 h.

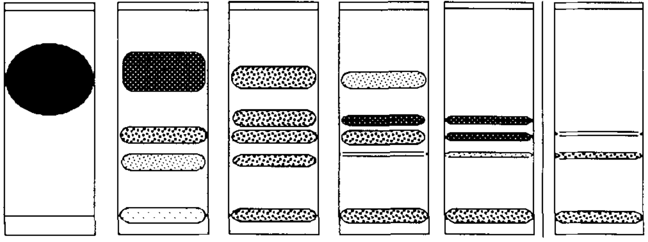
Chemical changes of single-component unsaturated oily soils after aging. TLC was used to study chemical changes in oils with aging. When oleic acid, triolein and squalene were aged at 40°C on TLC plates as single components, all of the three unsaturated oils exhibited common characteristics: the gradual disappearance of the original compound and the formation of various oxidation products with lower R_f values than the original compound (Fig. 5). Because the stationary phase (silica gel or water bound on the surface) is much more polar than the mobile phase (developing solvents), polar materials tend to stay near the bottom of the TLC plate while less polar materials move up the TLC plate in the direction of the developing solvent front. Thus, oxidation products with lower R_f values were more polar than the starting unsaturated oils. This is probably due to reactions of double bonds with oxygen from the air during aging.

Quantitation of each product on the TLC plates was not undertaken in this study. The amount of each product was described qualitatively in relative amounts with six rankings judged by the extent of quenching of each band under an UV_{254} lamp and the intensity of black color after reaction with OsO_4 vapor by visual observation.

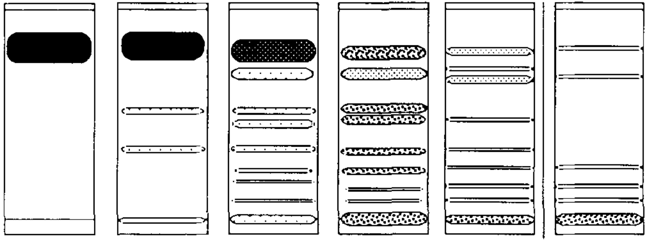
The original band, corresponding to the unaged oil, became thinner for all three oils upon aging, indicating a decrease in the amount of unreacted oil with time. When unsaturated oils were aged at 40°C on TLC plates, squalene and oleic acid disappeared after two and eight weeks, respectively, while a small amount of triolein still remained unreacted after eight weeks of aging (Fig. 5). With squalene, after only one week of aging, more than ten different oxidation products, including a yellow band in the spotting position, were observed. This indicates the rapid oxidation of squalene, which has also been recognized by other researchers (11,12,16). Reactivity of triolein seemed slower than that of oleic acid, probably due to the steric hindrance within the triolein molecule. But with time, triolein changed into various polar materials as observed for oleic acid and squalene. The use of more polar-developing solvent would probably further separate these materials.

When the sample of squalene aged two months on TLC plates was developed with a more polar solvent (methanol/chloroform, 1:1) to obtain information about the polar yellow material, three yellowing bands that had R_f values of 0.89, 0.54 and 0 appeared with traces of several other products. All three yellow bands were darkened when exposed to OsO_4 vapor, indicating the presence of double bonds in each TLC band. The TLC band with R_f = 0.89 was lightly colored, and the band at R_f = 0.54 was dark and broad. However, the possibility of the presence of the other products could not be excluded, because miscellaneous products from the original squalene might not be completely separated on TLC plates under these conditions.

(a) Oleic Acid (*n*-hexane/ethyl ether/acetic acid = 10:10:1)



(b) Triolein (*n*-hexane/chloroform/methanol = 20:10:1)



(c) Squalene (*n*-hexane/chloroform/methanol = 20:10:1)

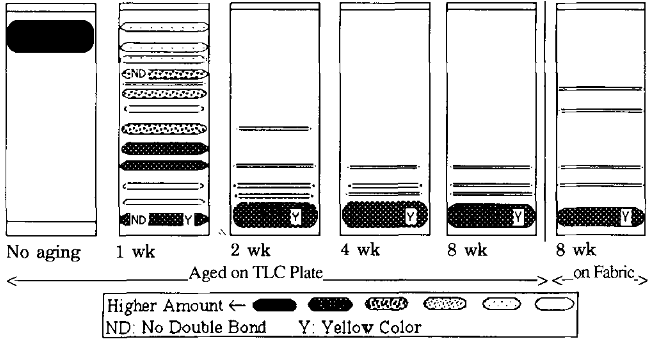


FIG. 5. Thin-layer chromatography (TLC) patterns show the formation of polar oxidation products during aging of unsaturated oils at 40°C on TLC plates and fabric.

In comparing oils that had been aged on fabric to oils aged directly on the TLC plates, it appears that the products formed during aging are similar (Fig. 5). The chemical changes in oils aged at 40°C for 8 wk on the fabrics were compared to oils aged directly on the TLC plates under the same aging conditions. After developing the thin-layer plates for oils extracted from aged fabrics and the oils aged directly on the TLC plates, little difference was observed in the patterns. Aging of the oils under these two conditions appears to result in similar, but not identical, aged products.

Formation of new functional groups. Neat bulk liquid each of oleic acid, triolein and squalene was placed in a petri dish and aged at 40°C. After 24 wk, oleic acid turned into a viscous, pale yellow liquid while triolein became a more viscous, transparent gel. Squalene was an intensely yellow solid after only 4 wk.

The IR spectra of oleic acid, triolein and squalene after 0, 4, 8 and 24 wk of aging are presented, respectively, in Figures 6–8. Common changes of IR spectra with increasing aging time observed for both oleic acid and triolein are: (i) development of new peaks in the region from 3000 to 3600 cm^{-1} for oleic acid and near 3450 cm^{-1} for triolein; (ii) changes from a sharp peak to a broad peak at 1715 cm^{-1} for oleic acid and at 1750 cm^{-1} for triolein; and (iii) changes in peak shapes in the region from 1100 to 1300 cm^{-1}. These absorption peaks are characteristic group frequencies of oxygenated compounds that are related to O-H, C=O and C-O stretching vibrations, respectively (37,38). These IR spectra support the formation of various polar oxidation products as demonstrated by thin-layer chromatographic analyses of aged oils.

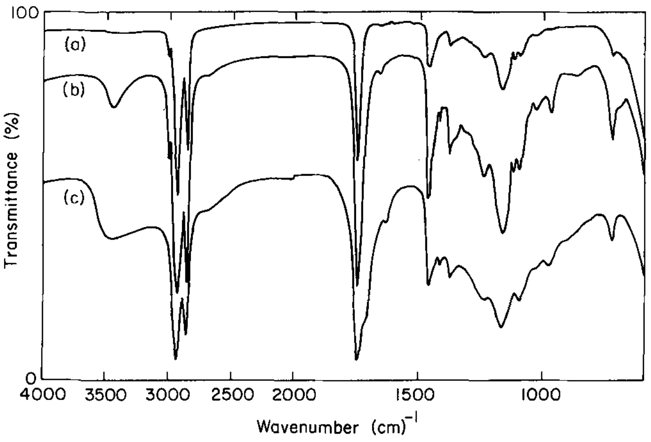


FIG. 7. The infrared spectra of triolein before and after aging at 40°C (neat liquid, NaCl plates): (a) without aging, (b) 4 wk, (c) 24 wk.

The spectra of squalene aged in a petri dish at 21°C, up to 24 wk, showed no significant chemical change (Fig. 8b–c). Following this, a smaller sample (0.2 g) of squalene was taken from the sample aged for 24 wk and spread out

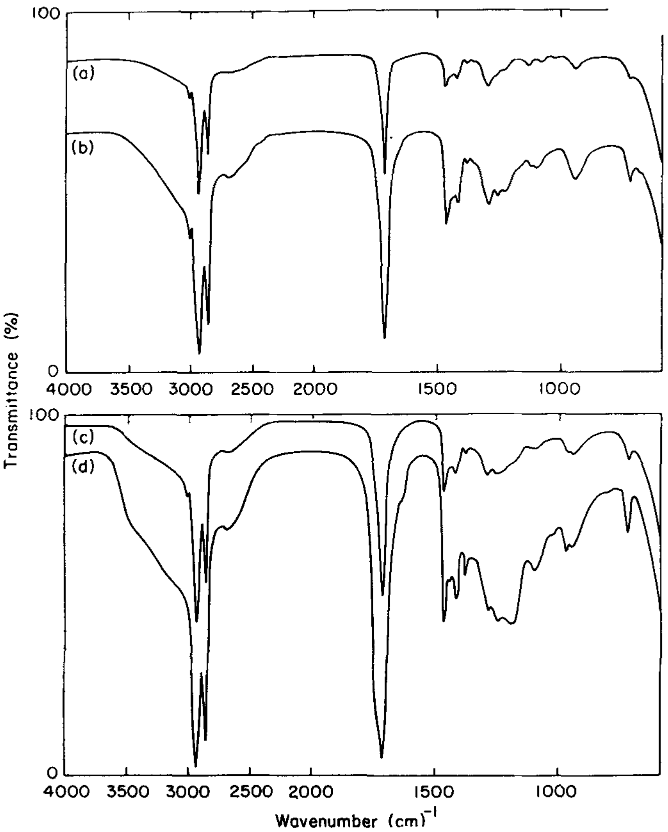


FIG. 6. The infrared spectra of oleic acid before and after aging at 40°C (neat liquid, NaCl plates): (a) without aging, (b) 4 wk, (c) 8 wk, (d) 24 wk.

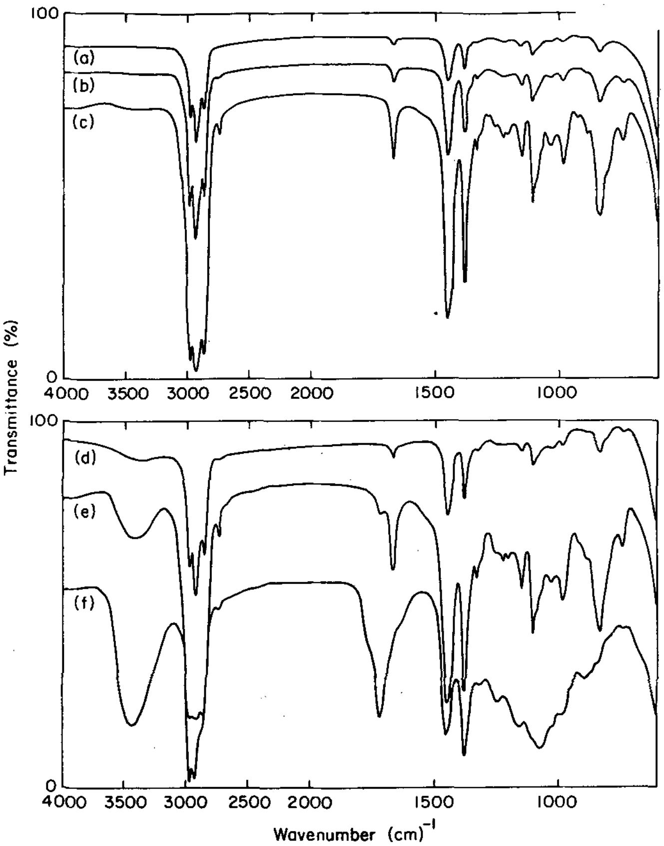


FIG. 8. The infrared spectra of squalene before and after aging at 21°C (neat liquid, NaCl plates): (a) without aging, (b) 4 wk, (c) 24 wk. Spectra after increasing the surface area and additional aging of (d) 1 wk, (e) 2 wk, and (f) 8 wk.

in a petri dish to increase contact with oxygen in the air. When the IR spectra of these twice-aged squalene samples were recorded, spectral changes, and therefore structural changes, were evident after one week of additional aging (Fig. 8d). The IR spectra of the samples after two weeks of additional aging and eight weeks of additional aging showed marked changes (Fig. 8e–f).

The main features of the IR spectrum of fresh, unaged squalene are: (i) peaks at 1671 and 3052 cm^{-1} due to -C=C- and -C=C-H bonds, respectively; (ii) strong peaks clustered at 2971, 2926, 2860 cm^{-1}, attributable to aliphatic C-H bonds; (iii) peaks at 1450 cm^{-1} (CH_2 bending) and 1383 cm^{-1} (CH_3 bending); and (iv) a peak at 836 cm^{-1} for the -C-H out-of-plane bending (Fig. 8a).

The changes in IR spectra observed after one week of additional aging with increased surface area include: a broad absorption peak near 3437 cm^{-1} due to the O-H bond, and small peaks near 1230 cm^{-1} attributable to the C-O bond (Fig. 8d). The C=C stretching absorption at 1671 cm^{-1} is still present. After two weeks of additional aging (Fig. 8e), the peak near 3437 cm^{-1} due to the -O-H stretch is broad. The 1721 cm^{-1} peak due to the C=O bond is now sharp. Peaks at 1205 cm^{-1} and 1153 cm^{-1} are attributable to two different types of -C-O bonds; the former shifted to the left, perhaps because of conjugation with a double bond. A small peak attributable to aldehyde C-H is present at 2731 cm^{-1}. The shoulder at 3051 cm^{-1} due to C=C-H bonds is still present.

The longer-aged squalene with eight weeks of increased exposure of the surface to air resulted in distinct changes in the IR spectrum (Fig. 8f): (i) There is a strong, broad absorption peak at 3436 cm^{-1} due to hydrogen-bonded O-H groups; (ii) a strong C=O peak is present at 1719 cm^{-1}; (iii) the intensities of the peaks at 1450 cm^{-1} from CH_2-bending vibration and at 1383 cm^{-1} from CH_3-bending vibration are reversed from that observed for the unaged squalene; (iv) overlapping peaks coalesce in the 1000 to 1300 cm^{-1} region related to C-O bonds; (v) an aldehyde hydrogen peak is present at 2737 cm^{-1}; and (vi) the peak at 838 cm^{-1} attributed to C-H out-of-plane bending has disappeared.

The most valuable information for alkenes is obtained from the =C-H out-of-plane region, which extends from 650 cm^{-1} to 1000 cm^{-1}. For example, one band near 815 cm^{-1} is obtained for tri-substituted double bonds as present in squalene (22). Thus, the absence of a peak at 838 cm^{-1} proves the disappearance of double bonds upon aging. The decreased intensity of the peak at 1450 cm^{-1} suggests that oxidation of squalene occurred at the CH_2 group. All CH_2 groups in squalene are located adjacent to double bonds and make methylene hydrogens sensitive to the hydrogen abstraction reaction that is the initiation step of autoxidation of unsaturated oil (20). The resulting oxidation products contributed the absorptions at 3436 cm^{-1}, 1719 cm^{-1} and in the region from 1000 to 1300 cm^{-1}, which are related to O-H, C=O and C-O stretching vibrations. These IR spectra support the formation of various polar oxidation products as demonstrated also by thin-layer chromatographic analyses of the aged squalene.

From the spectral features summarized above, it is possible to conclude that, after two weeks of aging, hydroxyl and aldehyde groups are present in the structure of aged squalene, while some double bonds remain. After eight weeks of additional aging, the number of hydroxyl groups and aldehyde groups increased, as evidenced by an increase in the intensity of their respective peaks. These new structural features are in good agreement with the aging mechanism proposed later in this paper.

Loss of double bonds. The disappearance of double bonds was observed visually by looking at the resulting colors on fabric swatches after reaction with OsO_4 (Table 2). For all three oils, the amount of unsaturation was observed to decrease considerably as the aging periods increased. High temperature accelerated the disappearance of double bonds of the oils. Triolein-soiled and oleic acid-soiled swatches that had been aged at 40°C for four weeks were nearly colorless, indicating that few or no double bonds remained after aging. Some double bonds were still present after aging of squalene at 40°C for four weeks. A quantitative measurement of the loss of double bonds during aging by neutron activation analysis of unsaturated oil-soiled, aged and bromine-tagged swatches will be published in a subsequent paper.

Effect of aging on volatility and soil removal. The loss of oil by volatilization was evaluated after aging the soiled fabrics for 0, 1, 2, 4, 8 and 26 wk at temperatures of 21°C and 40°C. All of the three oils, oleic acid, triolein and squalene, applied on fabric swatches as a single soil showed volatility during aging. Figure 9 indicates the rate and temperature effect. The amount of oleic acid remaining on the fabric swatch decreased linearly during the entire 26 wk aging period when aged at 21°C. At the higher aging temperature, 40°C, more rapid volatilization was observed over the first 8 wk, and little further volatilization occurred during the remaining aging period. Little or no triolein was volatilized during the initial period of aging (about 8 wk at 21°C and about 4 wk at 40°C). After this initial period and by the end of 26 wk, significant amounts of triolein had been volatilized. Squalene volatilized rapidly from the fabric swatch during the initial period of aging, with little additional loss by volatilization during the remaining aging period. The

TABLE 2

The Resulting Color of Soiled and Aged Fabric Swatches After OsO_4-Solution Treatments[a]

Type of soil aging time	Oleic acid (21°C/40°C)	Triolein (21°C/40°C)	Squalene (21°C/40°C)
0 wk	Greenish black	Brownish black	Deep brown
2 wk	Gray>gray	Black=black	Pale brown>pale brown
4 wk	Gray/colorless	Gray/small trace of gray	Pale brown>pale brown

[a] Symbols: >, more intense color; =, the same darkness.

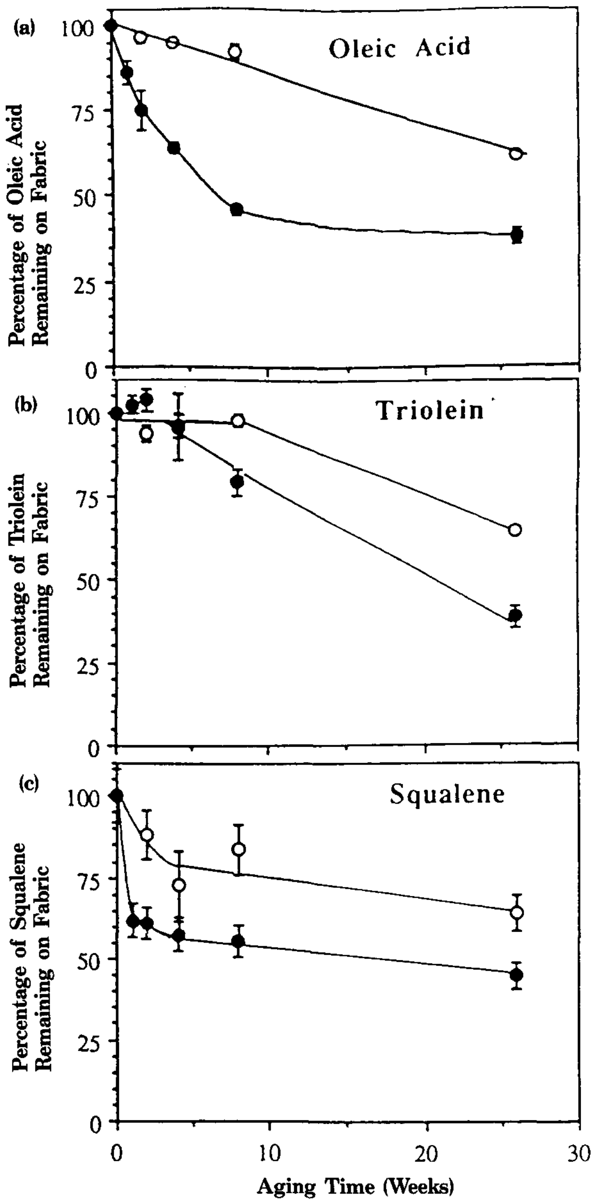


FIG. 9. Volatilization of unsaturated oily soils applied singly on fabric: (a) oleic acid, (b) triolein, (c) squalene. Symbols—○, aged at 21°C; ●, aged at 40°C.

same patterns were observed at the different aging temperatures, except that at 40°C more total squalene was lost by volatilization over a shorter time.

In spite of characteristic patterns, such as gradual volatilization of oleic acid, slower initial volatilization of triolein and rapid leveling out of squalene during the early period of aging, the amount of each oil remaining on fabric after 26 wk fell in similar ranges, 61% (oleic acid), 65% (triolein) and 64% (squalene) at 21°C, and 38% (oleic acid), 39% (triolein) and 45% (squalene) at 40°C. Volatilization was accelerated at the higher aging temperature for all three oils.

Volatility during aging is more likely due to loss of various oxidation products, such as hydrocarbons, aldehydes or ketones with shorter chainlength (23,24), than from volatilization of whole molecules. This is supported by the fact that oleic acid, triolein and squalene have high boiling points. Because volatilization of triolein occurred after several weeks, the volatilization of whole molecules seems unlikely. This suggests that triolein, being a large molecule, will remain on fabric unless significant changes in the chemical structure occur. The volatility pattern of squalene during aging indicates that volatile oxidation products are produced initially, and probably resinous products with higher molecular weights are formed over time. The formation of resinous material was confirmed by observation of increased rigidity of the soiled and aged fabric.

Volatility of unsaturated oils during aging must be considered when studying the soiling and cleaning of fabrics. The volatility observed during aging may be the source of unpleasant odor from unwashed, soiled garments. Contrary to this, higher soil removal of unsaturated oily soils can be achieved by machine-drying or drying under the sun than by air-drying due to enhanced volatilization. In detergency experiments, little attention has been given to the volatilization of unsaturated oils, and the original amount of oil applied has been used in the calculation of soil removal. In this research we have observed that the actual soiling level decreases with increasing aging time due to volatility of the oil. Therefore, the percentage of soil removal was calculated based on the amount of oily soil remaining after aging and just before washing, rather than on original soiling amount.

The amounts of soil removal for oleic acid, triolein and squalene without aging were 82, 24 and 32%, respectively. Figure 10 shows how these values changed during aging at two different temperatures for each of the oily soils. Soil removal of oleic acid was almost the same over the 26 wk of aging at 21°C. But, it tended to decrease gradually during the entire period of aging at 40°C (Fig. 10a). Soil removal of triolein aged at 21°C remained the same for the first 8 wk of aging, about 24% (no aging), and increased to 53% after 26 wk of aging. Triolein aged at 40°C exhibited higher soil removal after only one week of aging and continued to increase, resulting in soil removal after 26 wk that is as high as that observed for the smaller and more polar oleic acid. Overall, under these experimental conditions, longer periods of aging and higher aging temperature contributed to better soil removal of triolein (Fig. 10b). For squalene, increases in soil removal with aging were even more dramatic than observed for triolein. Large increases in soil removal were observed at both aging temperatures after only one week of aging (20% increase at 21° C and 41% increase at 40°C). The trend of better soil removal for longer periods of aging at higher temperature was the same as that observed in triolein. The amount of squalene removed by laundering was similar (86%) after 8 wk for both aging temperatures (Fig. 10c).

Before aging, the order of oily soil removal, from most difficult to least difficult was: triolein (24%) > squalene (32%) >>> oleic acid (82%). According to their melting points [oleic acid (16.3°C), triolein (-5.5°C), squalene (<−20°C)], the three oils were in a liquid state both at room temperature and at wash temperature, thus excluding the effect of melting points of the oils on their ease of removal. The roll-up mechanism has been confirmed

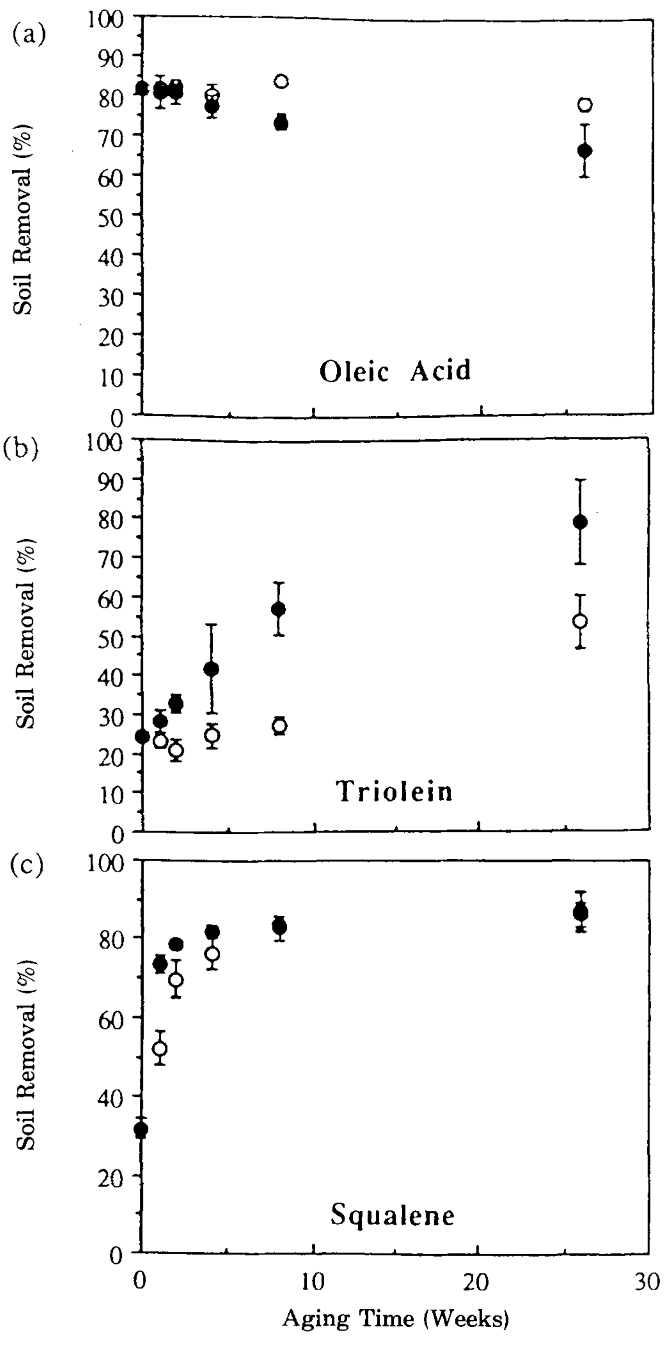


FIG. 10. Effect of aging on soil removal of unsaturated oily soils applied singly on fabric: (a) oleic acid, (b) triolein, (c) squalene. Symbols—○, aged at 21°C; ●, aged at 40°C.

as the major mechanism for the removal of oily soil from hydrophilic and hydrophobic fibers by anionic, cationic and nonionic surfactants (39,40). Solubilization of oily soil by a surfactant solution in the hydrocarbon interior of the micelles also has been shown to be an important mechanism in the removal of oily soil (41). Detergency removed more oleic acid, which is a small polar molecule, than triolein, which is a large, less polar molecule. This is in agreement with previous results that have shown oil removal to be dependent upon molecular size and polarity (42). Another factor contributing to the large difference between removal of oleic acid and triolein is the use of a built detergent in this experiment. Builders increase the alkalinity of a detergent solution (43). According to Scott (43), fatty acid removal increases as the pH of the detergent solution increases due to soap formation. Soap formation was an operative removal mechanism for oleic acid under the wash condition used as well as the roll-up and solubilization mechanisms. Soap formation was probably not as effective a mechanism for removal of triolein (44).

Formation of mesomorphic phases was proposed by Lawrence (45) as a mechanism for removal of oily soil. It is based on the penetration of aqueous surfactant solutions into oily soil to produce mesomorphic phases, the dispersion of the mesomorphic phases in water by the osmotic influx of water and its dissolution by the surfactant (39). This mechanism favors the removal of the most polar soil because surfactants form mesomorphic phases with fatty acids and alcohols but not with triglycerides and hydrocarbons (39). Thus, oleic acid might be removed by this mechanism as well as soap formation, solubilization and rolling up, while triolein and squalene were removed mainly by solubilization and rolling up.

Remarkable increases in soil removal of triolein and squalene after aging probably resulted from the formation of various oxidation products (Fig. 5). These products may be polar enough for extensive mesomorphic phase formation (39) in addition to roll-up and solubilization. Higher temperature accelerated the reaction between double bonds of unsaturated oils and oxygen into the more polar oxidation products, resulting in higher soil removal for triolein and squalene. After 26 wk of aging, the soil removal for triolein and squalene were similar to that of oleic acid (Fig. 10).

The volatility pattern of triolein suggested that volatile smaller molecules might be produced after 4 to 8 wk of aging (Fig. 9b). Such changes in molecular size could be another important factor in the observed increase in soil removal. The possibility of the leveling-off of the amount of the triolein remaining on fabric between 8 to 26 wk of aging cannot be excluded because no measurement was made during this period. Therefore, formation of higher-molecular weight species of triolein on fabric, as observed from aging of bulk triolein, was possible. Even though the possibility exists for the formation of dimers, trimers or oligomers of triolein, increased removal of triolein with aging suggests that increased polarity of the molecular species is the overriding factor in removal of triolein, rather than the formation of bigger molecules that would decrease soil removal.

The volatility pattern of squalene (Fig. 9c), however, indicated the possibility of rapid formation of polymeric materials. Squalene, which is normally in the liquid state, becomes viscous and finally turns into a solid after aging in bulk. This agrees with the result obtained by Powe (12), who found that 70% of squalene became a resinous, brown, polar material, and none of the original squalene remained after 14 d when aged at 25°C in the dark. Despite the possible formation of oxidation products of bigger molecular size, total soil removal of squalene increased immediately with aging (Fig. 10c). This confirmed the importance of the formation of more polar compounds after aging. Despite the increase in total soil removal, aging of squalene is a problem due to the retention of yellow color (Fig. 3).

Although oleic acid also produced oxidation products (Fig. 5), its soil removal did not increase with aging (Fig. 10a). This is probably related to the fact that removal of oleic acid is relatively high even without aging. The decrease in soil removal after 26 wk of aging at 40°C could be due to the formation of bigger molecules, such as dimers, trimers or oligomers of oleic acid. The observation of viscous oleic acid after 24 wk of aging at 40°C, as discussed in the IR section, and no further volatilization of oleic acid between 8 wk and 26 wk of aging at 40°C (Fig. 9a) supports formation of higher-molecular weight species of oleic acid. The increased polarity after aging did not play a role in better removal of aged oleic acid as it did in triolein and squalene.

Because the loss of unsaturated oils from fabric by volatilization was observed with aging, the soiling level on the fabric also decreased with aging. To exclude the possibility of the effect of decreased soiling level during aging on soil removal of unsaturated oily soil, soil removal of triolein and squalene as single soils were determined with different soiling levels of 1.6, 3.2, 6.4, 9.6 and 12.8 mg on 6.5 cm × 6.5 cm swatches, before aging. Differences in removal of triolein were small between the different soiling levels (Fig. 11). Soil removal of squalene increased slightly with increased soiling level. Thus, the marked effect of aging on soil removal of unsaturated oily soil observed in this research resulted from chemical structural changes during aging, not from decreased soiling level due to volatilization with aging.

Effect of interaction of oily soils on removal after aging. The removal of oleic acid and triolein in mixed soils was studied by simultaneously, following two components, ^{14}C-labelled oleic acid and ^{3}H-labelled triolein. In the two-component soil system, equal amounts (3.2 mg) of oleic acid and triolein were deposited on each fabric swatch. In the three-component soil system, an additional equal amount (3.2 mg) of nonlabelled squalene was added to this two-component system to evaluate any effects of rapid oxidation of squalene on the removal of the other oils.

Without aging, mixing triolein and oleic acid caused increased removal of triolein (24 to 54%) while removal of oleic acid varied slightly (82 to 87%) (Table 3). This result supports Scott's conclusion (43) that the amount of nonpolar oil removed increases in the presence of a polar oil.

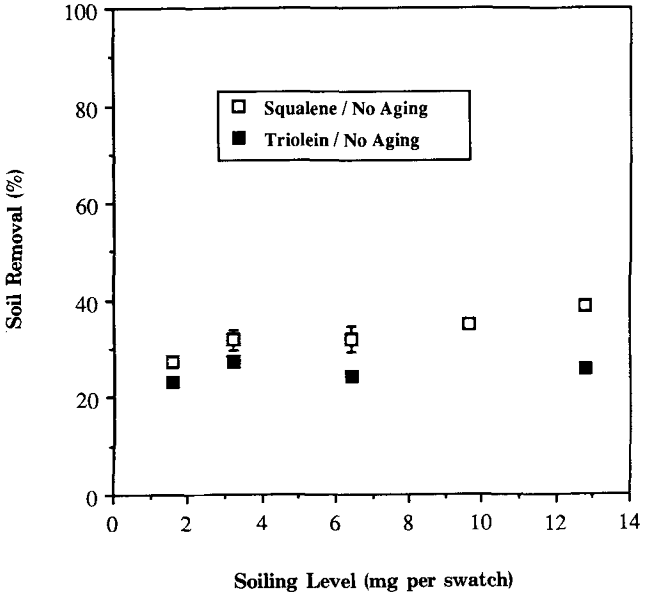


FIG. 11. Soil removal with varying soiling levels for each of squalene and triolein without aging.

However, in previous research (42), the presence of oleic acid did not affect the detergency of tristearin. This was explained based on the fact that the oils studied were in different physical states (tristearin, m.p. = 71.5-72°C and oleic acid, m.p. = 16.3°C) when washed at 38°C. Thus, the physical states of oils during washing seem to be an important factor in the effect of one oil on removal of another oil.

The effect of mixing on the removal of oleic acid after aging is shown in Figure 12. Removal of oleic acid from the two-component (Fig. 12a) and three-component (Fig. 12b) soil systems decreased gradually with aging. Removal of oleic acid decreased after aging, regardless of whether it was applied as single or mixed soil and whether it was aged at 21 or 40°C (Fig. 10a and Fig. 12). The results of Duncan's multiple T-test on soil removal of oleic acid in single and mixed soils after 26 wk of aging are presented in Table 3. Aging temperature did not cause differences in final soil removal of oleic acid from mixed soil as in the case of oleic acid as a single soil or for triolein in all cases. Because of the built detergent and the unique properties of oleic acid (small, polar and low melting

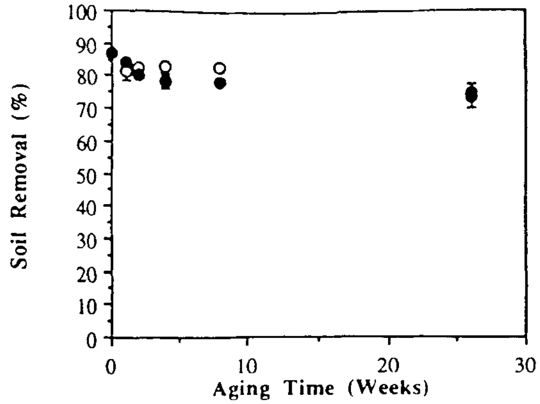
TABLE 3

Effect of Aging on Detergency of Oleic Acid and Triolein in Single- and Mixed-Component Systems (after 26 wk of aging)[a]

	Oleic acid removed (%)			Triolein removed (%)		
		Aged 26 wk			Aged 26 wk	
Soil system	No aging	21°C	40°C	No aging	21°C	40°C
Single soil	82 ± 2 (B[a])	78 ± 2 (C)	67 ± 7 (E)	24 ± 1 (Z)	53 ± 7 (X)	79 ± 11 (U)
Mixed soil Oleic acid + triolein	87 ± 3 (A)	75 ± 1 (D)	74 ± 4 (D)	54 ± 2 (W)	49 ± 11 (X,Y)	68 ± 3 (V)
Mixed soil Oleic acid + triolein + squalene	87 ± 6 (A)	78 ± 1 (C)	81 ± 3 (B,C)	55 ± 2 (W)	48 ± 6 (Y)	79 ± 1 (U)

[a] Means with the same letter group (A, B, C, D, E, F for oleic acid; U, V, W, X, Y, Z for triolein) are not significantly different at the 95% confidence level (based on Duncan's multiple T-test) with 24 degrees of freedom for each of oleic acid and triolein.

(a) Mixed Soil System of Oleic Acid and Triolein



(b) Mixed Soil System of Oleic Acid, Triolein and Squalene

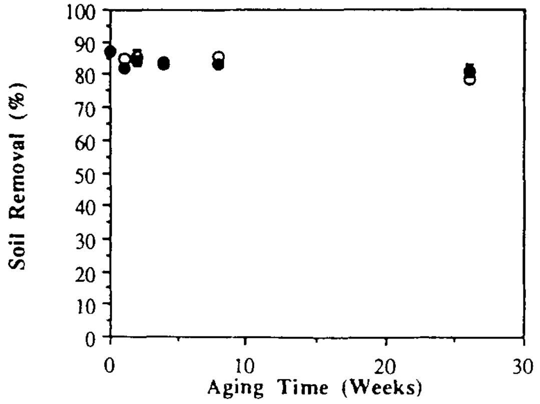
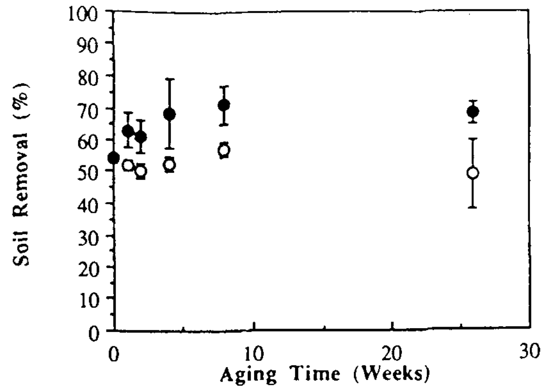


FIG. 12. Effect of aging on removal of oleic acid in mixtures with (a) triolein, and (b) triolein and squalene. Symbols—○, aged at 21°C; ●, aged at 40°C.

(a) Mixed Soil System of Oleic Acid and Triolein



(b) Mixed Soil System of Oleic Acid, Triolein and Squalene

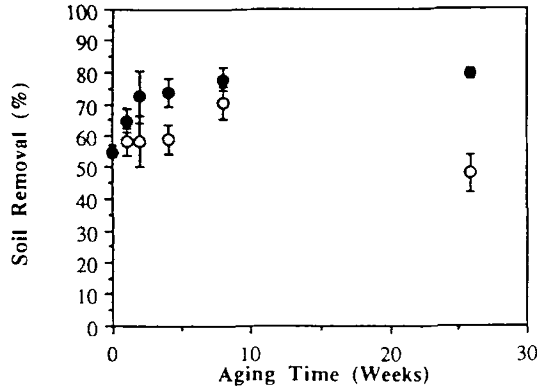


FIG. 13. Effect of aging on removal of triolein in mixtures with (a) oleic acid, and (b) oleic acid and squalene. Symbols—○, aged at 21°C; ●, aged at 40°C.

point), which result in high removal by laundering, the effects of aging on removal of oleic acid were not as obvious as for triolein. The use of a nonbuilt detergent in the washing process might be helpful in studying the effect of aging on the removal of oleic acid.

The effect of mixing on the removal of triolein after aging is presented in Figure 13. Removal of triolein from the two-component (Fig. 13a) and three-component (Fig. 13b) soil systems increased gradually during the first two months of aging; however, no further increase in the removal of triolein was observed when soils were aged for 26 wk and washed. A decrease in triolein removal was observed between 8 wk and 26 wk of aging for the three-component soil system when aged at 21°C. Higher aging temperature aided removal of triolein in the mixed soil system as in the single oil system (Fig. 10b). The presence of squalene also increased removal of triolein after aging at 40°C. But, it did not affect removal of oleic acid or triolein when washed without aging (Table 3). In the single-oil experiment, the percentage of triolein removed by detergency increased about 29 and 55% when aged at 21 and 40°C, respectively. Increases in the removal of triolein after aging at 40°C were not as large in the mixed-component systems (14% increase in two-component and 24% increase in three-component soils). Moreover, in the mixed oils aged at 21°C, the percentage of triolein removed by detergency decreased about 5 to 7% compared to that without aging.

The difficulty in the removal of aged oily soils had been demonstrated previously by Brown *et al.* (31) and Wentz *et al.* (32). They both used commercially available mixed oils, such as heavy and light lubricating oils, olive oil, vegetable cooking oil and sebum-type oil alone or mixed with linseed oil. The removal of these oils decreased after three weeks (31) or one month (32) under similar aging conditions as in our study. The opposite result of marked increases in soil removal of triolein and squalene after aging obtained in single-oil experiments indicated that the presence of other chemical classes of oils is an important factor in the effect of aging on oil removal.

In mixed soils, aging could cause the formation of oxidation products with high molecular weight, resulting from the interaction between different oils as well as from reaction with oxidation products in a single oil. The same oxidation products of triolein or squalene that contributed to greater removal of a single oil after aging may react with other oils present in a mixture, resulting in soil that is more difficult to remove. This was probably one of the reasons why removal of triolein increased less during

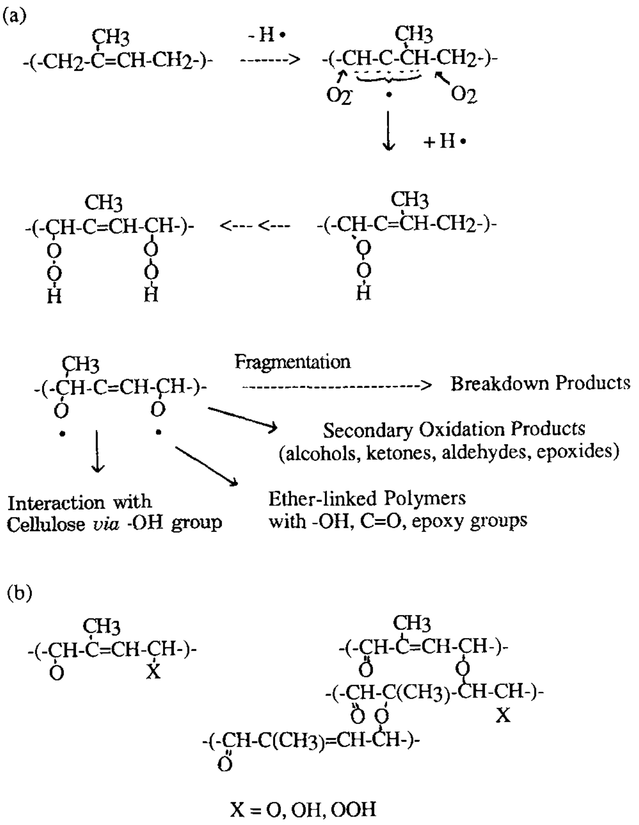


FIG. 14. (a) A proposed mechanism for the rapid oxidation of squalene in air and (b) proposed structures of oxidation products of squalene causing yellowing of fabric upon aging.

aging in the mixed soil system than in single soil. With mixed oils, the longer aging period at 21°C resulted in the decreased removal of both oleic acid and triolein (Table 3). This could be the result of chemical reactions between the oils and their oxidation products, when present together in a mixture.

Chemical changes in squalene affecting fabric yellowing. Our research showed that squalene aged in bulk liquid state turned into viscous, yellow material. The yellowing of squalene-soiled fabric occurred from the well-known rapid oxidation of squalene to a resinous, brown, polar material (10,12,17). The formation of yellow polar material from squalene was proven by thin-layer chromatographic analysis (Fig. 5). Yellow materials contain at least three different compounds. The polarity of aged squalene was also supported by its IR spectrum (Fig. 8). The yellow oxidation products of squalene remained on the fabric without further volatilization, indicating that they are also resinous on fabric (Fig. 9), and they became more intensely yellow upon further aging (Fig. 2).

A mechanism for various processes in the rapid oxidation of squalene is proposed (Fig. 14a), based on the results of chemical analyses of aged squalene and the well-established autoxidation of unsaturated lipids in the area of food chemistry (20,22,23,46). Among the oxidation products, secondary and polymeric products with conjugated C=O groups are suggested to be the source of yellowing qualene-soiled fabric upon aging (Fig. 14b). Difficulty involved in removing yellow materials (Figs. 3 and 4) may arise from the interaction of oxidation products of squalene with the fibers (Fig. 14a) as well as the formation of resinous materials.

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