

was found at the equivalence point, *i.e.*, one mole of anhydride to one epoxide equivalent. The heat-distortion temperatures and moduli of elasticity are given in Table III.

The proper amount of accelerator was determined by fixing the following parameters: a) ratio of reactants at the equivalence point, b) temperature of cure at 160°C., and c) time of cure at 10 hrs., while varying the amount of benzyldimethylamine from 0.1 to 10% (based on the weight of all reactants). Maximum heat-distortion temperature was observed at the 2.5% level of accelerator. Other properties of these resins are given in Table IV.

TABLE IV
Effect of Varying Accelerator Concentration on the Properties of Epoxidized Soybean Oil/Phthalic Anhydride Resin

Accelerator ^a concentration	Heat-distortion temperature	Tensile strength	Elongation	Modulus of elasticity
weight %	°C.	lbs./sq. in.	%	lbs./sq. in. × 10 ⁻⁵
0.1	23	3,570	10.6	1.18
0.5	51	2,210	3.0	1.03
1.0	49	3,500	4.5	1.14
1.5	50.5	5,060	12.6	1.46
2.0	52	4,740	5.1	1.50
2.5	62	4,700	4.7	1.57
3.0	54	5,030	6.5	1.54
5.0	44	1,470	1.6	1.21
7.5	33	550	0.8	0.968
10.0	31	330	1.0	0.482

^a Benzyldimethylamine, cured at 160°C. for 10 hrs.

In another series the cure times were varied while the anhydride, epoxide, and accelerator concentrations as well as the temperature were held constant. In this case equivalent weights of anhydride and epoxide, 5% benzyldimethylamine, and 140°C. were arbitrarily chosen as the constants while the cure times were varied from 0.5 to 32 hrs. The heat-distortion temperature levelled off to 51°C. after four hours (Figure 2). For comparison, a similar series was made at 120°C. with cure times varying from 10 to 45 hrs. Again the heat-distortion temperature reached a maximum at 51°C., but 30 hrs. were required (Figure 2).

The final conditions established were: a) equivalent weights of epoxide and phthalic anhydride, b) 2.5% benzyldimethylamine, c) temperature of 150°C., and d) a cure time of 8 hrs. The temperature was chosen midway between 140° and 160° to insure a reasonable gel and cure time. Under these conditions the epoxidized soybean oil resin had a heat-distortion temperature of 49°C. All other resins except that from perilla oil were made by this procedure. The perilla oil resin was cured for 24 hrs. at 135°C.

Summary and Conclusion

Epoxy resins were made from phthalic anhydride and the following epoxidized fatty glycerides: neats-foot oil, lard oil, triolein, soybean oil, perilla oil, and trilinolein. Some physical properties of these resins were measured and tabulated.

It has been shown that heat-distortion temperature, tensile strength, and modulus of elasticity increase with the unsaturation of the glyceride precursor of the epoxy intermediate.

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Removal of Fatty Soil from Glass-Solvent System Mechanism

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IN HOME or commercial dishwashing, either by hand or machine, the indication of effectiveness most frequently used is the appearance of glassware: it should be clear and spot-free. A greasy or milky film may result either from inadequate cleaning, or from water hardness, and water spots from poor drainage.

The removal of soil from glass surfaces is such a commonplace operation that other than awareness that some compositions are more effective than others, little has been published regarding the real mechanism of soil removal involved. No attempt will be made to distinguish between soils except as they may be either dry or oily, and oily soils only in that a fatty soil was chosen for this work.

Glass

The physico-chemical properties of glass merit close attention for the marked effect they have as a substrate on soiling and soil removal. Glass is anything but a simple material. Formulas vary widely, and surfaces and chemical properties with them. Soda (or potash) glass has molecules of sodium in what appear to be free spaces in the surface described as wells (13) and from which they can be leached (3, 11). Dielectric properties indicate that sodium ions at the surface are mobile and migrate under the influence of an electric field (11, 26) and in dilute aqueous electrolyte solutions (17). Migration of the sodium ion from its original position to a neighboring "hole" or "well" produces a dipole effect; the open

structure of the glass offers alternative positions for the ions (26). Ordinary sheet glass is known usually to be deficient in sodium ions near the surface (13), and flaming even below the softening point effects a simultaneous volatilization of sodium (11) and diffusion of sodium within the glass structure (27). That sodium is lost by flaming was evidenced by immersing the flamed surface in a solution of radio-tagged sodium carbonate, where a much greater rate of sorption of Na ion occurred than with surfaces cleaned in water or solvent-degreased. It was suggested that flaming does not produce new reactive centers but uncovers more of the kind already available from usual cleaning (10). Thorough annealing which reduces dielectric losses (13), also relieves at least a portion of the interior and surface stresses suggested by Langmuir (18) as being formed by the atoms in rearranging themselves to minimize surface area.

A clean glass surface is assumed to consist of a silica network in which the units are held together by Si-O-Si bonds and in which there also are Si-OH, Si-ONa, and similar groups. A silica glass was suggested as an electrolyte which in the framework of SiO₄ groups is the highly viscous solvent while trace element cations, *e.g.*, sodium, are highly mobile like highly dilute aqueous solutions of electrolytes. Conversion of Si-OH bonds to Si-O-Si bonds occurs with water loss and shrinkage (11). A glass surface is conceived as one of negatively charged oxygen atoms; the positively charged Si atoms are located in small spaces between these: Si-O-Si. This explains why positively charged surfactants (cationics) can form a film on this surface. In contrast to nonadsorption of anionic surfactant by glass from a polar solvent, positive adsorption of surfactant occurs from nonpolar media (14).

Glass was believed by Langmuir to be amorphous and probably not arranged in a regular lattice structure such that an indefinite number of elementary spaces were present. Present-day thinking of the glassy state may have to be revised if Tilton's (24) concept of glass structure can be substantiated. He suggests that glass structure is based on the "vitron," a submicroscopic structural unit or cluster of pentagonal dodecahedra with subunits of silicon oxygen tetrahedra. These clusters are conceived as being joined loosely by "connective tissue" that have weaker bonds but greater densities than the vitron. This structural concept however does not necessarily change the concept of glass-surface characteristics.

One suggestion is that glass should not be considered as having a porous surface though capable of adsorbing water. Here a solution process is suggested as occurring by which water molecules are combined by secondary valence forces with the atoms of the groups of atoms forming the glass (18). The thickness of the water vapor film adsorbed on fresh blown glass is said to be unimolecular but, on aging, becomes polymolecular (2). At 0.7 and 0.9 relative pressures the adsorption of water extends from 1 to 6.2 molecular layers in thickness (6, 20, 21), based upon measurements for Jena glass. Vacuum-dehydrated porous glass, when subjected to infrared spectral analysis, exhibited active centers for water adsorption (16). A plane surface is considered as limited to one molecular layer (18), but a glass surface either exposed to water vapor or washed in water no longer remained planar (8). The attack on most glasses by water results in

the liberation of alkali (9) with formation of a complex silicate (2), and even fire-polished glass stored in moist air shows a change in refractive index through leaching of the alkali (5). Ordinary glass, after exposure to moisture, was considered as structure of the glass offers alternative positions for covered with a spongy material in which the ratios of H₂O:SiO₂ and SiO₂:Na₂O were greater than in the depth of the glass. This normal surface-layer was said possibly to consist of silicic acid, which certainly differs chemically from the bulk of the glass, and protects it from contact with solution (27). The surface conductance of the film on glass approaches that of a silica gel film with a thickness of 0.005 μ (5).

A degree of physical change in glass surface-structure can be induced by rubbing it with cotton wool, paper, wool, wood, or a glass rod. The surface exhibits an apparent alignment of crystal structure in the direction of the rubbing. Such a surface when rinsed in 1% HF loses the directional surface alignment. Indications are that the oriented surface has an upper limit thickness of 0.3 μ (5). Marring of glass surface can result from combined chemical and mechanical action. Contact scratching of glass-to-glass surfaces is said to be caused by seizure and recombination of the glass surface in a disordered manner (25).

The foregoing descriptions of glass surfaces indicate that marked changes can occur and that "used" surfaces can become greater in area as the roughness is increased, and probably more reactive in nature.

Drinking glasses, tumblers, returnable bottles, and the like certainly are not discarded after the first use and are subject to leaching, abrasion, and other factors likely to make the surfaces less uniform and more porous and reactive. Inhomogeneity of a glass surface may result from lack of adequate mixing in manufacture or segregation on melting, but in properly manufactured products this seems unlikely. That glass surfaces show lack of uniformity in spite of care in manufacture is indicated in several ways. Sorbed radio-active Na ion is not uniformly distributed over the surface (27). A comparison of soft glass with fused silica shows that receptive sites must be available for adsorption to occur since at room temperature for 0.13 monolayer of sodium, only 0.04 of a monolayer occurs on fused silica. Sorption rate increases with temperature; a change of 40°C. increases the adsorption seven-fold to 0.87 monolayer (10).

Experimental evidence from evaporation experiments shows that monolayers of volatile adsorbate exist as patches on the surface. Evaporation takes place at patch edges (7). Similar experiments with long-chain fatty acids and a long-chain fatty amine adsorbed on glass, when subjected to vacuum evaporation, showed no change in film structure, indicating that the films existed as patches on the surface and that evaporation occurred from the patch edges. That monomolecular films of cerotic acid exhibited no change in structure during evaporation was taken as an indication that these films also existed as patches on the glass surface and that evaporation took place from patch edges (15).

Langmuir's concept (19) of a crystal surface in which the atoms are in checkerboard arrangement, forming a regular lattice plane structure, is probably illustrative of most surfaces. He proposed that crystal surfaces had a definite number of "elementary

spaces," each capable of holding one adsorbed molecule or atom, with frequent cases where two or three different kinds of spaces existed. A stepwise adsorption often encountered was attributed to the stronger force causing the initial adsorption; subsequent adsorption was slower for the lesser forces present. It was visualized that the molecular size of the adsorbate could be large enough to be unable to occupy adjacent elementary spaces, which then remained unsatisfied. Crowding of large molecules could result when their size was larger than the elementary space. The exact fraction of the elementary spaces covered was said to be dependent upon the shape and plastic properties of the molecules and their mobility on the surface.

Films are said to have a certain permeability which varies with the film packing and the nature of the molecule (4). Barium stearate-stearic acid films built up in the classic manner show that these films contain holes aggregating about 4% of the total surface (23) and that defects accumulate so that the second layer has 8% holes and so on. After 25 layer deposits the thickness was only 24 layers, showing that one layer was lost in filling up the holes in the other 24.

Presence of adsorbed layers of water on the glass surface may hinder the complete adsorption of a polar oily soil unless sufficient time, or time and temperature increase are observed, to permit oily soil adsorption.

Experimental Procedures

Glass Substrate

Composition. Soft glass microscope slides were chosen for this work for convenience and knowledge of their chemical analysis.

Preliminary tests showed that the polished surface as received did not retain soil sufficiently well to permit differentiation between cleaning compositions; and a frosted surface, with greater surface area, was chosen for this work. Tests demonstrated that the abrasive size chosen for frosting the smooth surface was not exceedingly critical, and a single grade of carborundum was used throughout.

Frosting Discs. Cut microscope slides to measure $1 \times 1\frac{3}{16}$ in. Grind corners so that discs will fit a $1\frac{1}{4}$ -in. circular counting pan. Transfer 0.03 g. of 320-mesh carborundum powder to a flat 4×4 -in. glass lapping plate. Place this plate on one pan of a lab beam balance (counter weigh with a 1,000-g. wt.). Add 4 drops of water to the carborundum and lap the prepared discs in a circular manner for 60 complete cycles. (Use sufficient pressure to balance the 1,000-g. counter weight.) Thoroughly rinse the carborundum from disc and lapping plate with distilled water. Repeat lapping until the disc is frosted over the entire surface. When restoring previously lapped surfaces, this procedure is repeated twice. Initial frosting of the discs may require considerably more lapping uniformly to level the surface.

Surface Area. The polished surface would have a roughness factor (ratio true to geometrical surface) approaching 1. Examination of the lapped or frosted surface indicated the roughness as hemispherical indentations, and calculation on this basis showed the new surface to have a roughness factor of 1.9. The roughness factor attained by several more precise methods is shown in Table I. The discrepancy in these values may be attributed to the adsorptive nature of glass and to peculiarities of the adsorbates used. It is believed that a more sensitive method would give roughness values in excess of 2.

TABLE I
Roughness (R) Factor for Frosted Glass
(Ratio of actual area/geometrical area)

Compound	Surface area per molecule— \AA^2	Method	R
n-Octadecane.....	88.0	Molecular model	1.525
Tristearin.....	61.5	Surface pressure (1) and radio-tagging	1.975
Calculation.....	Hemispheres	1.9
Methylene blue.....	130.0	(12)	6.5
	62.3	(22)	3.1
	43.0	Molecular model	2.14

Soil

The soil chosen for this work was tristearin C_{12} tagged in position 1, at an activity level of 1.73 mc/millimole (Nuclear Chicago). For use this was diluted with untagged C. P. recrystallized tristearin to 0.157 mc/millimole and applied from carbon tetrachloride solution.

Soiling Procedure

Preparation (in hood with exhaust operating). Place glass disc to which soil is to be added on a steel plate ($5\frac{1}{2} \times 9 \times \frac{3}{4}$ in., the edges insulated to reduce heat loss) preheated to 80°C . in an air oven (Figure 1).

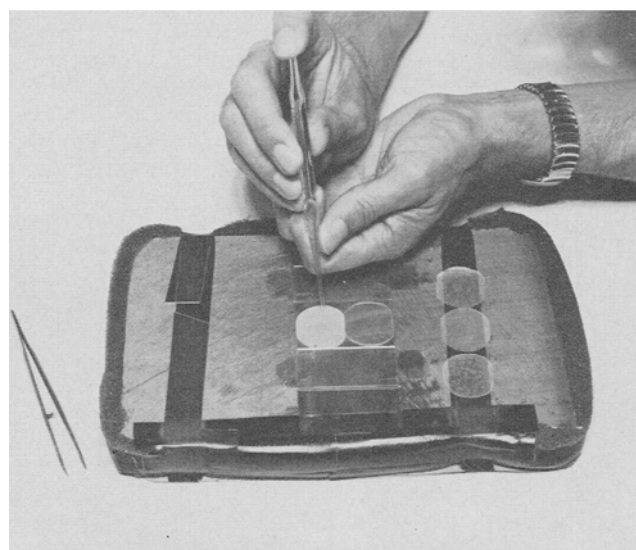


Fig. 1. Soil application.

Using an accurate micropipette (usually about 0.1 ml.) and a bulb or vacuum line, draw the solution of the radio-active soil above the calibration mark. Allow the solution to flow out to the calibration mark, and then commence incremental droplet additions to the frosted glass disc. Add in small individual portions (total incremental additions about 200) without allowing flow-together of separate additions before the solvent has evaporated (Figure 2). A sufficient number of droplet additions will have been made completely to cover the disc surface with a soil layer.

Aging of Soiled Disc. Place the soiled discs in an oven at 79 – 80°C . for 15 min. (This constitutes removal of surface moisture and permits adsorption of soil.) Remove and cool in a desiccator.

Counting Procedure

Equipment. Scaling unit, Nuclear Instruments, Model 182. Flow Counter, Nuclear Instruments, Model D46A. "Q" gas, Nuclear Instruments, self-quenching.

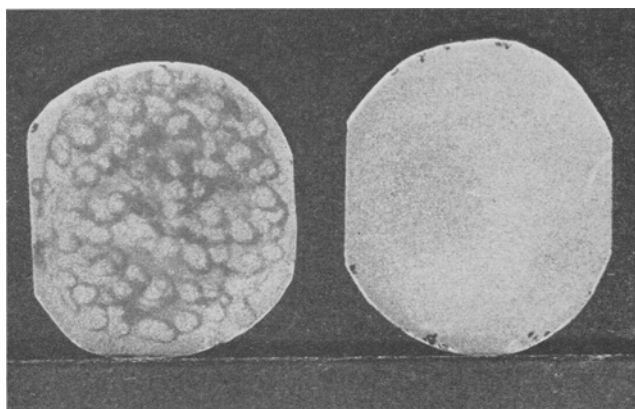


Fig. 2. Appearance of partially soiled and clean discs.

Procedure. Transfer the frosted glass disc to a 1¼-in. diameter counting pan and place in flow counter.¹ Two successive 5-min. counts should agree to a 98% level before accepting data. Average these readings, divide by five, subtract background radiation level per minute, and express results as activity in counts per minute (cpm).

Preliminary Cleaning

Removal of Organic Contaminants. Oil-soluble soils such as grease, tagged (C-14) fats, etc., are removed as follows. Heat 100 ml. of 100% nonionic surfactant² in a 400-ml. beaker to approximately 130°C. Using a pair of steel tweezers, immerse the frosted disc in the hot nonionic for 20 sec. Remove and rinse with a stream of ethanol until the nonionic is removed. Repeat three times. Vapor-degrease the sample by holding in vapor of boiling CCl₄ until condensation on disc ceases. Cool disc by a quick immersion in fresh ethanol, and repeat the degreasing step three times. The disc is now ready for removal of inorganic contaminants.

Removal of Inorganic Contaminants. Boil discs in a solution of HCl/water (5/95 volume) for 5 min. Rinse 3 times for 30 sec. each with 100 ml. of deionized water (room temperature). Boil in 0.1% sodium hydroxide for 5 min. Rinse three times again in deionized water. Blot dry with absorbent paper. Degrease with vapor of boiling CCl₄ for 10 sec. Apply soil immediately.

Experimental Washing Procedure

Equipment. Terg-O-Tometer modified with test tube clamps (Figure 3). 400-ml. beakers. Constant-temperature bath.

Procedure. The Terg-O-Tometer was modified with test-tube clamps for holding the soiled discs. Figure 3 shows the washing assembly, including a temperature bath. The Terg-O-Tometer was operated at 75 cycles/minute, each cycle having a 380° angle of rotation. Place discs in test-tube clamps. Attach clamps to Terg-O-Tometer. Set cycles per minute as desired. Set timer for desired wash-period. A 20-

min. period was used in these tests unless otherwise indicated. After wash-period, remove clamp and washed disc (after wash). Place in 80°C. air oven to dry (10 min.). Recount radio-activity of disc. Express results as

$$\% \text{ Detergency} = \frac{(\text{initial} - \text{final count})}{\text{initial count}} \times 100$$

or

Amount of soil remaining in counts/min. (cpm).

Replication. Each test was made in triplicate; the three samples were cleaned in fresh cleaning solutions. The values given in this work have a 95% confidence level.

Carbon Tetrachloride Soil-Removal. The data of Figure 4 for tristearin removal in counts per minute (cpm) show that a soil monolayer level represented by about 400 to 600 cpm is attained very rapidly and that continued exposure to the solvent over an extended period reduces the level at best to about a half monolayer.

This strongly suggests that a relatively nonpolar solvent, such as carbon tetrachloride, acts by dissolving soil-from-soil, attacking, or weakening the soil cohesive forces until a layer of soil remains which must be held by another type of force, *i.e.*, adsorption. Upper soil layers (held by cohesive forces) were removed at a rate of about 9,000 cpm while the strongly held (adsorbed layer) was removed at about 1/6 cpm, a ratio of 54,000/1 in ease of soil removal under these conditions. Repeated tests with carbon tetrachloride always showed the same result, making a dip in this solvent an excellent test for determining the effectiveness of other cleaning agents in removing soil. It was used throughout this work for differentiation purposes. For the subsequent work at a monolayer (400 cpm) level, discs

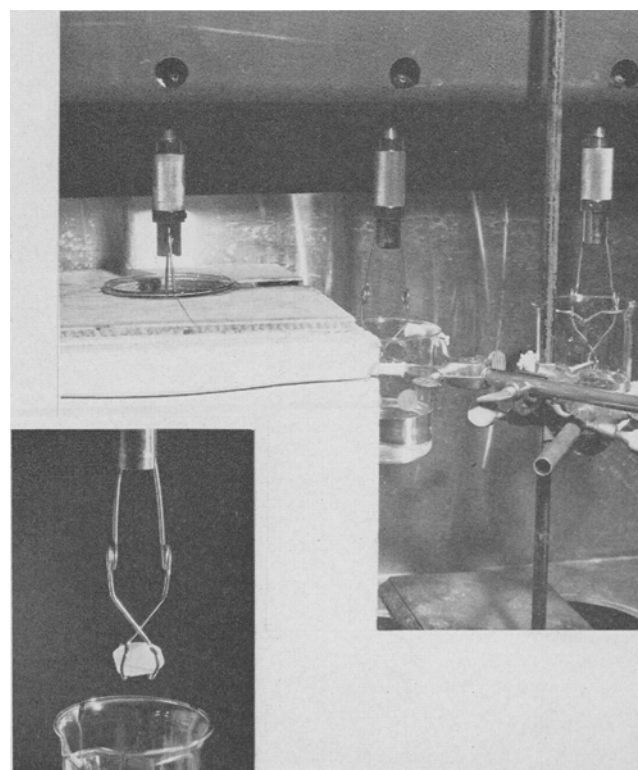
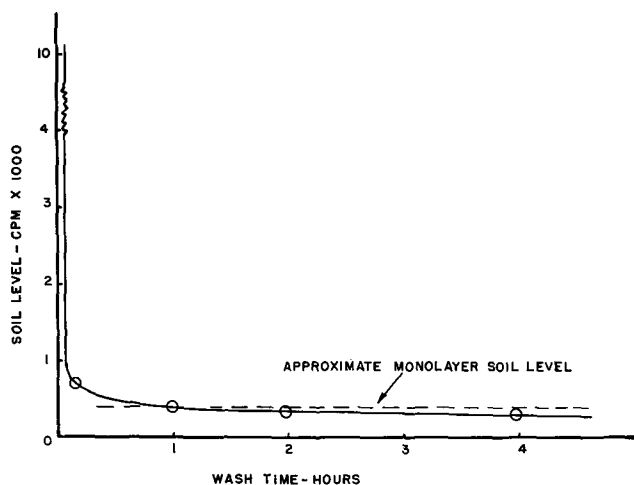


Fig. 3. Washing apparatus, modified Terg-O-Tometer.

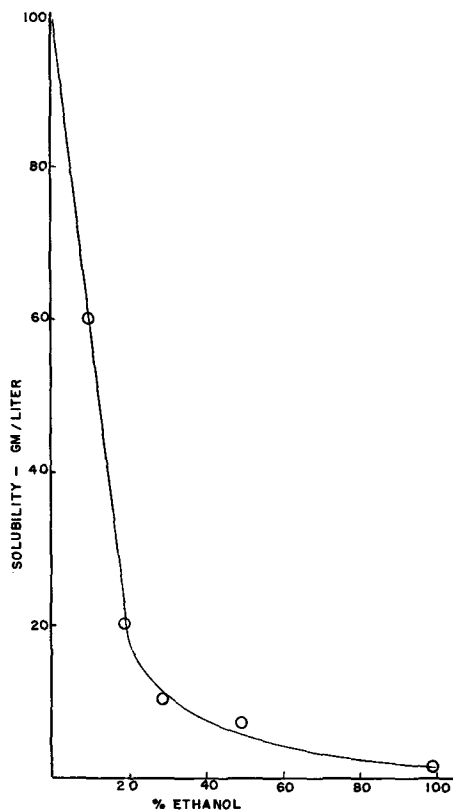
¹ Orientation of active samples in the flow counter should always be the same (before and after washing) as rotation in the counter will result in slight changes in the apparent level of activity. For maximum reproducibility the sample should always be oriented in the same way. This is accomplished by allowing one of the corners from the original rectangles (cut from microscope slides) to protrude slightly after grinding, using this for orientation purposes.

² Sterox AJ-100, Monsanto Chemical Company.

Fig. 4. Tristearin removal—CCl₄.

soiled with the equivalent of 30 monolayers of soil were washed for an hour in carbon tetrachloride at room temperature to give reproducible 400 cpm residual counts.

Polar Solvent Soil-Removal. Relatively polar solvents, such as ethanol, are frequently used in cleaning glass surfaces, and experiments were performed with mixtures of these and carbon tetrachloride. Since solubility is important to removal of cohering soil, the solubility of tristearin in these various mixtures was determined (Figure 5). It becomes apparent that as ethanol alone is effective for soil removal the probability is great that it must act differently than by a dissolution mechanism because of its low solubility for tristearin.

Fig. 5. Solubility of tristearin in ethanol/CCl₄ mixtures.

A comparison of ethanol and carbon tetrachloride for removal of high soil levels is shown in Figure 6. These data show the rapid removal rate for the chlorinated solvent, but that the polar solvent can remove more soil, given a sufficiently long time.

To investigate the effectiveness of solvent mixtures, a monolayer of soil (no excess of free or cohering soil) was taken as the initial soil level and removal tests were made with several of the solvent ratios shown

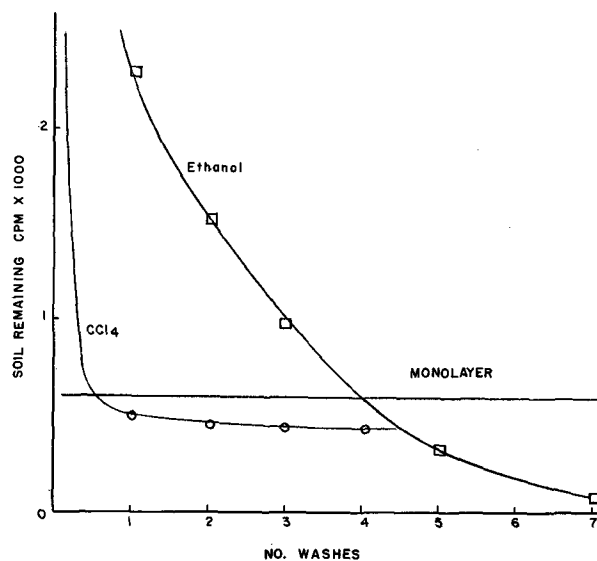


Fig. 6. High level soil removal.

in Figure 5. The data are plotted in Figure 7, showing that an increase in the polar character of the cleaning solvent markedly affects the removal of adsorbed soil. These data further suggest that the presence of a good soil solvent, even though ineffective for adsorbed soil removal, can prove beneficial, presumably by dissolving soil removed by the polar solvent, in which the removed soil is relatively insoluble.

Since increased polarity of solvent improved soil-removal, a series of solvents of varying polarity (using dielectric constant, ϵ , as the criterion) were evaluated, and the data are shown in Figure 8. These data indicate, as before, that simple solubility of tristearin is not a controlling criterion for complete removal but that increased rates and more complete removal are achieved by solvents of relatively high dielectric constant.

However dielectric constant is not necessarily a complete criterion since when two materials of the same ϵ are used, one of them containing a small proportion of highly polar solvent, the latter more effectively removes the tristearin (Figure 9).

On a dielectric constant scale, water is relatively polar but has a high interfacial tension value against tristearin in contrast with ethanol or carbon tetrachloride. Tests made with water/ethanol and ethanol/carbon tetrachloride mixtures for soil removal at the monolayer level are shown in Figure 10. These show that water removes some soil, suggesting that since soil dissolution could not occur, another means for soil attack must take place with polar materials.

The curves of Figure 8 suggest that once the relatively rapid initial removal has occurred, the differ-

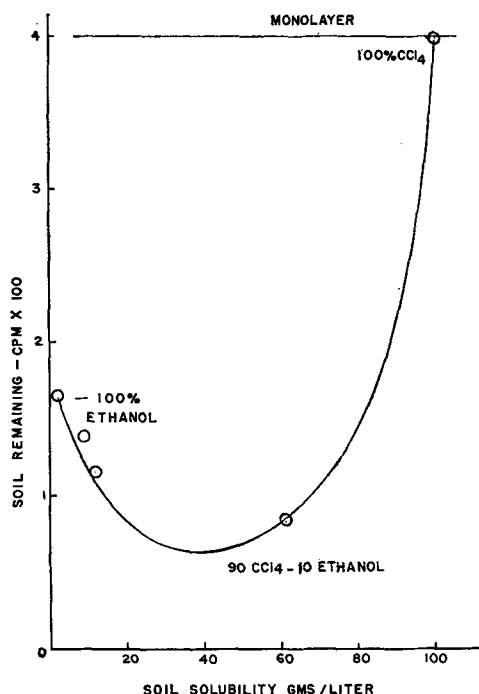


Fig. 7. Adsorbed soil monolayer removal by solvent mixtures.

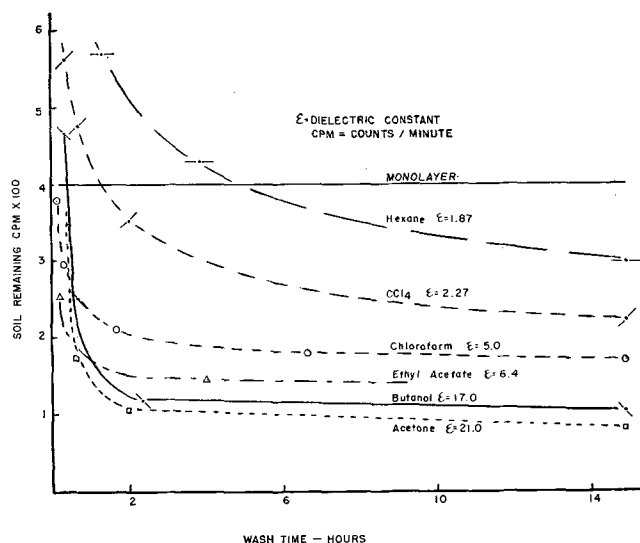


Fig. 8. Soil-removal efficiency of various solvents.

ence in rate from this point on may be attributed to one of three possible factors: physical inaccessibility of the soil, redeposition, and difference in mode or magnitude of soil bonding at various sites on the glass.

Physical Inaccessibility. If the solvent molecule were too large in physical dimensions to reach the soil molecules deep in small crevices of the substrate, removal rate would slow at that soil level. In Table II molar volumes are listed for each of the cleaning solvents, and molar volume is directly proportional to the single-molecule volume. The table shows that in some cases larger molecules are better cleaners. Also the soil molecule is much larger than those of any of the cleaning solvents. In view of these molecular-size relationships and because removal rates correlate so well with polarity of the solvent molecule,

there is little justification for considering physical inaccessibility of the soil as a controlling factor in these studies.

Redeposition and Preferential Adsorption Sites

Redeposition. This may be defined as readsorption of soil which has already been removed in the cleaning process.

In Figure 8 six different solvents were compared for cleaning effectiveness *versus* time of wash. Each solvent showed very rapid soil-removal in the first few minutes, followed by an extreme slowing of removal rate, yet the amount of soil remaining on the substrate when removal rate declined varied for each solvent. Table II shows the approximate amount of soil left on the substrate after the removal rate had become very slow.

According to Figure 11, two hours of washing in butanol gave a slow tristearin removal rate. The problem to be solved was whether some sites on the glass surface permitted release of original soil, then readsorbed a soil molecule from solution, or whether no release of soil actually occurred at these sites.

TABLE II

Some Fundamental Properties of Solvents Compared as to Their Cleaning Efficiency

Solvent	ϵ^a	Molar volume	Remaining soil (cpm) after 7-hr. wash
Hexane.....	1.87	130	365
CCl ₄	2.27	97	260
CHCl ₃	5.0	80	180
Ethyl acetate.....	6.4	97	140
n-Butanol.....	17.0	83	115
Acetone.....	21.0	74	97
Tristearin soil.....	1,030

^a Dielectric constant.

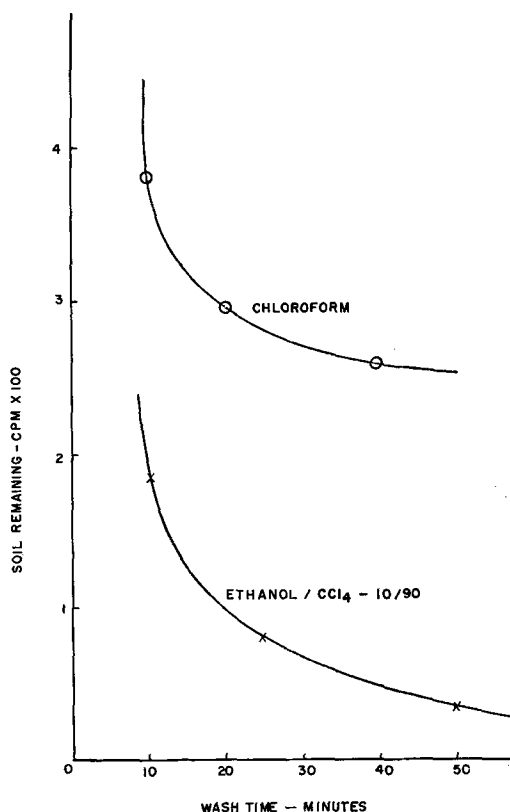


Fig. 9. Solvents with same dielectric constant.

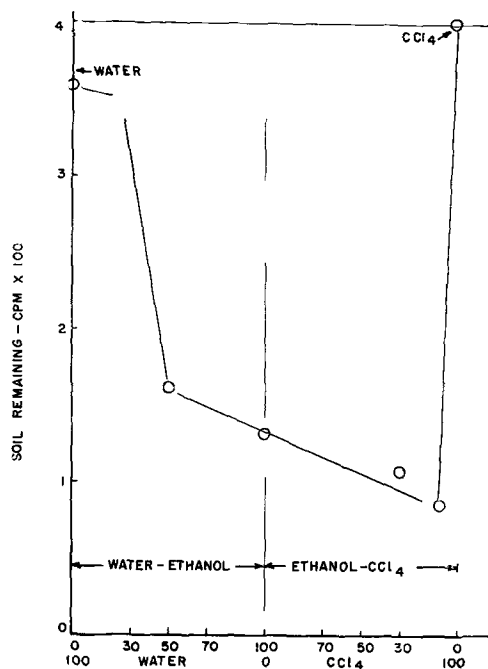


Fig. 10. Monolayer removal by solvent mixtures.

By using radio-active soil for molecule (1) of Figure 12 and nonradio-active soil for molecule (2), a sharp drop in radio-activity of the sample should occur during washing, if interchange or redeposition occurred. If however the removal rate did not in-

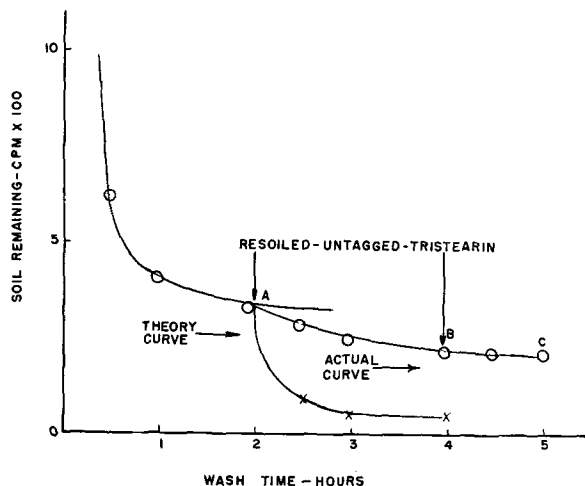


Fig. 11. Redeposition effect.

crease, it is indicated that the residual tagged soil was strongly adsorbed, not interchangeable, and not redeposited.

The experiment was performed as follows. The detergency rate curve was determined (left curve of Figure 11) for butanol. This curve represented the

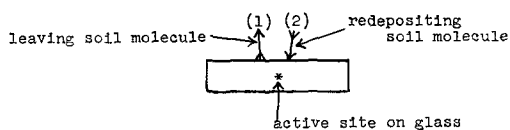


Fig. 12. Redeposition.

true rate of removal of tristearin from glass by butanol from zero time through two hours.

The remaining soil was tested for interchangeability. At point ("A") in the wash curve, the glass plate was resoiled, but with nonradio-active soil. This addition returned the soiled substrate to the zero-time condition; the only difference was that the relationship of radio-activity to actual soil level had been shifted. Washing of this plate should have shown a detergency rate curve identical with the original curve if redeposition were the primary cause of the plateaus of Figure 8. This theory curve (assuming redeposition) is shown in Figure 11 as the ("X") curve. After continued washing however the "A" to "B" curve was obtained. As can be seen, the theory curve and the curve experimentally found after resoiling ("A" to "B") do not coincide, proving that redeposition was not the controlling factor in causing the plateaus found for the solvents of Figure 8. It can be observed however that a more rapid drop in radio-activity did occur from "A" to "B" than would have been predicted from an extension of the original wash curve. The resoiling was therefore repeated at point "B" in the curve and on continued washing to point "C," a smooth extension of the "A" to "B" curve was obtained. This conclusively shows that redeposition was not a significant factor under the experimental conditions. This leaves only one conceivable factor to account for decreasing soil-removal rates observed throughout the solvent experiment work, namely, that certain sites on the glass release soil more slowly than others, the third possibility already suggested.

Temperature Variable in Detergency. The literature notes that the existence of adsorptive forces in soil removal phenomena are best verified by showing that soil-removal rates vary with temperature. This procedure is applicable in eliminating physical entrapment of soil as a prime factor in soil-removal rates obtained from wash data. An insensitivity to temperature could however be interpreted to indicate that the soil was physically entrapped or that the temperature range studied was inadequate to provide measurable changes in desorption rates.

Although temperature can influence a great many phenomena in a cleaning system (*i.e.*, surfactant solubility, soil solubility, soil viscosity, etc.), careful design of experimental conditions can reduce its influence to that of affecting desorption rates.

Data of Figure 13 show marked changes in desorption rates as a function of temperature. This is offered as further support that removal of tristearin monolayers from frosted glass is primarily a desorption phenomenon as opposed to physical entrapment and supports earlier conclusions.

Discussion

Soiled substrate before and after partial or complete cleaning may be visualized as shown in Figure 14.

Langmuir (18) believed that adsorption on surfaces occurred at sites which were relatively selective in nature. In our case the relatively polar tristearin very probably was adsorbed, polar-end to glass-receptive site, and in the case of nonpolar solvent tristearin removers, such as carbon tetrachloride, only soil-to-soil bonds were effectively detached. A higher energy level or more polar solvent was required for removal of adsorbed tristearin.

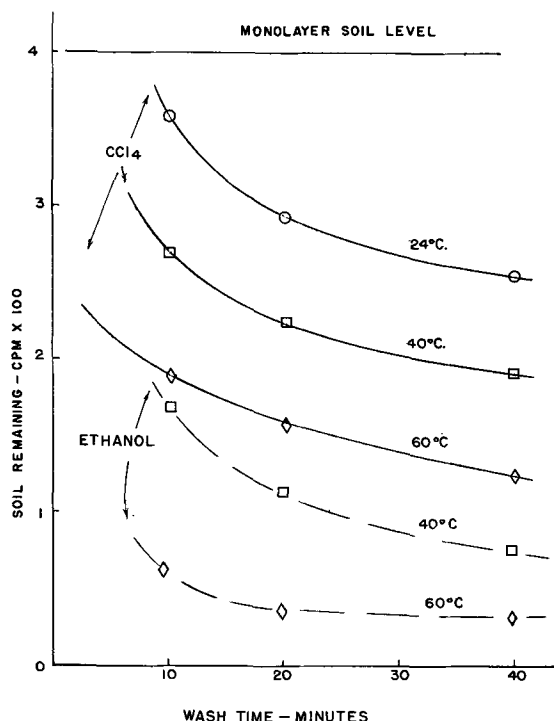


Fig. 13. Temperature effect.

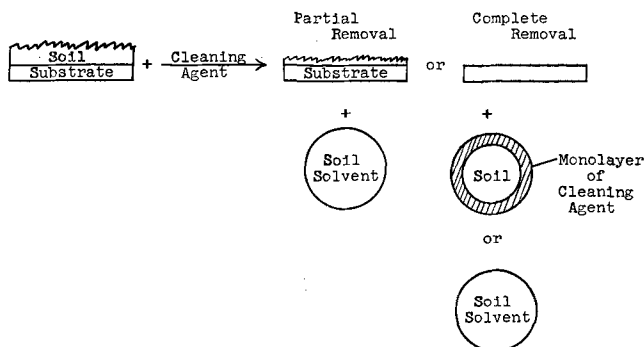


Fig. 14. Soiled substrate before and after cleaning.

One mechanism of soil removal of tristearin from glass, as with carbon tetrachloride, has been described. This mechanism of removal may be termed dissolution and occurs as in Figure 15(a).

A second mechanism of removal, in this case giving the more perfectly cleaned surface, is a stripping or displacement action, Figure 15(b). Combinations of both modes of attack generally are more effective than (a) alone, and can have obvious advantages over

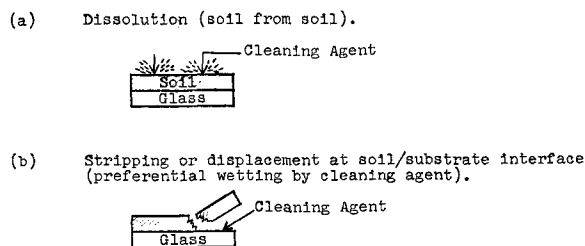
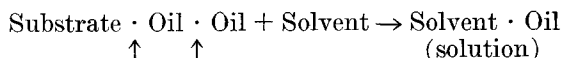


Fig. 15. Mechanisms of soil removal.

(b) in some situations. These may be further characterized as:

Dissolution (cleaning forces acting against cohesion)



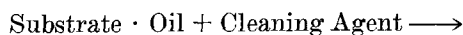
↑ ↑
Adsorption Cohesion

Substrate · Oil (monolayer)

↑
Adsorption

Outlying oil was removed by the solvent while the last monolayer of oil (the adsorbed monolayer) was not removed because the solvent did not preferentially wet the substrate to release the soil.

Stripping or Displacement (cleaning forces acting to desorb soil)



↑
Adsorption

Substrate · Cleaning Agent
(preferential wetting)

Soil · Cleaning Agent
(soil suspension or solution)

Complete cleaning of the glass surfaces on which adsorbed tristearin was present could be accomplished only when a sufficiently polar solvent was used. In multimolecular layer systems of soil, any soil-adsorptive sites would seem to be fairly well covered, but since soil-to-soil attractions are fairly easily displaced, the relatively strongly adsorbed monolayer can be uncovered. Since nonpolar solvents fail to remove significant portions of the adsorbed layer, it must be concluded that they are insufficiently polar and have lower energy of displacement than the soil. That more highly polar compounds can displace the adsorbed soil monolayer indicates their higher energy but further infers that since dissolution does not remove the adsorbed soil, they must gain entry to the glass surface through sites on which soil is not adsorbed, in effect at soil-patch edges, and preferentially wet the glass (adsorbed preferentially by it) to release the soil by a stripping or displacement action.

Since there appear to be preferential adsorption sites for tristearin on glass, leaving other unoccupied sites, the calculation for glass roughness factor given for this compound in Table I very probably is in error, and is low. This difference in apparent surface area has no significant effect on this work since the 400 cpm value was so repeatedly obtained as to suggest only that another, more applicable method for general surface area measurement should be used.

Summary

One of the glass surface-characteristics pertinent to the present research is its ability to adsorb multilayers of water. Soil becomes adsorbed when these layers of water are removed, as in the elevated-temperature aging of the soil. Another characteristic has been described as possession of "elementary spaces" which are selective in adsorptive capacity.

Fatty and other substances adsorb on glass as "patches," and evaporation occurs at patch edges. If the adsorbed molecule is large enough, it may cover but not sorb on other sites similar to its primary adsorption site, leaving these free to sorption by mole-

cules polar enough and small enough to penetrate these essentially porous, adsorbed films.

The present data prove that tristearin soil at the monolayer level is held by adsorption forces while cohesive forces are active at multimolecular soil thicknesses. The adsorption appears to be operative through the soil polar groups, and adsorbed soil is released only by more polar materials. Access of solvent molecules to the glass substrate surface presumably occurs through voids in the packed soil monolayer or at soil patch edges. Soil removal in these solvent systems takes place by dissolution of coherent soil and by stripping or preferential sorption mechanism at adsorbed soil patch edges. Non-polar or weakly polar solvents act by dissolution of coherent soil, and polar solvents through preferential sorption and stripping and detaching at adsorbed soil sites. Combinations of polar and nonpolar solvents prove more effective in some instances than polar solvent alone.

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Separation and Chemical Assay of Lipide Classes¹

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THE INTEREST in human diseases which may be accompanied by abnormalities in lipide metabolism has greatly stimulated the development of methods for separation and micro-analysis of lipide classes. It therefore should be worthwhile to consider methods for micro-determination of cholesterol and its esters, triglycerides, and phospholipide constituents. The material has been restricted mainly to include those methods with which the author has had experience.

Determination of Total Cholesterol in Serum

The desire for convenient analysis of small quantities of cholesterol and its esters in serum and some tissues is evidenced by the great number of modifications of the basic chemical procedures. In material where sterols other than cholesterol can be expected, such as adrenals or intestinal contents, the determination is very tedious. For cholesterol assay in serum, four different colorimetric methods are in use, including, in order of increasing specificity: direct addition of the color-forming reagents to a sample of serum (1, 2); addition of the reagents to the lipides isolated from serum (or tissue) by solvent extraction (3); application of the reagents for color development to the unsaponifiable fraction (4); and precipitation

with digitonin of nonesterified 3 *beta* hydroxy steroids from a saponified lipide extract and subsequent addition of the reagents to the sterol digitonide (5).

Development of a Colored End-Product. Three different color producing reactions are suitable: the reaction with acetic anhydride and sulfuric acid to produce a blue to blue-green color (Liebermann-Burchard reaction), reaction with ferric chloride which forms a purple complex (2), and reaction with zinc chloride-acetyl chloride for cherry red (Tschugaeff reaction) (6). The Liebermann-Burchard (L.B.) reaction is the most widely used. It actually yields two colored components, one having an absorption maximum at 625 $m\mu$ and a more stable product which can be conveniently determined at 430 $m\mu$ (7). The latter wavelength can be used only if no related steroids and bile acids are present to give interfering green-yellow to yellow reaction products.

In the L.B. reaction, chloroform may be used as the solvent (8) although acetic acid is preferred. Free and esterified cholesterol have different absorption characteristics, but this difference is much less when the reaction is carried out in acetic acid than when chloroform is used as the solvent (Table I). For that reason alone it is best to use acetic acid rather than chloroform when the esters have not been saponified. Another disadvantage of chloroform as the solvent is the instability of the reaction product at 625 $m\mu$ (7, 9). At 25°C. the maximum develops within 6-8 min. for esterified cholesterol and within 10-12 min. for free cholesterol, then declines at a rate of 2½-

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