extract containing ascorbic acid further enhanced protection in some cases (Stoloff *et al.*—*Food Inds. 20,* 1130).

Some of the newly patented antioxidants were an ethylene dichloride extract of soap stock (Buxton—U. S. 2,433,593), hydrogenated deodorizer scum (Hickman—*U. S. 2,440,606*), a mixture of N.D.G.A. and phosphoric acid (Kraybill & Beadle—*U. S. 2,451,748*), a mixture of phospholipids and fatty acid esters of ascorbic acid (Riemenschneider & Turer — *U. S. 2,440,383*), natural vitamins containing added ammonia (Buxton—*U. S. 2,434,790;* OPCO Chem. Co.—*Brit. 591,511*), divanillal acetone or isopropanol (Jarowski & Stiller—*U. S. 2,455,254*), diisoeugenol (Jarowski—*U. S. 2,455,256*), extracts from the leaves and stems of *Larrea divaricata* (Shipner—*U. S. 2,457,741*), polycyclic aromatic hydrocarbons of at least four condensed rings combined in the form of a pyrene nucleus (Evans *et al.*—*Brit. 572,458*), a mixture of an aliphatic hydroxy polybasic acid and an aromatic p-hydroxy monobasic acid (Penn—*U. S. 2,441,307*), hydrocaffeic acid and derivatives thereof (Elder & Levenson—*U. S. 2,437,731*), hydroxylamine (Scherr —*U. S. 2,441,547*), 5- pentadecyl resorcinol (Barnes —*U. S. 2,448,207*), organic sulfur compounds containing unsubstituted amino groups capable of enolizing to furnish sulfhydryl groups (Gyorgy *et al.*—U. S. 2,456,937) and biguanide p-tert-amylphenyl phosphates (Cook—*Brit. 591,836*). Lecithin was stabilized against rancidity by alkaline salts (Fitzpatrick—*U. S. 2,444,984*). Literature on the extraction of natural antioxidants included the concentration of N.D.G.A. (Gisvold — *U. S. 2,444,346*) and antioxidants from rice bran (Jarowski & Stiller—*U. S. 2,455,255;* Patterson & Williamson—*U. S. 2,455,083*), and peanuts (Banerji & Mukherji—*Indian Soap J. 13,* 6). Vitamin A was rendered more stable by converting it into an ester (Embree & Shantz — *U. S. 2,434,687;* Basu & Sen Gupta—*J. Am. Chem. Soc. 70,* 413). Antioxidants were added to marine vitamin oils in order to preserve the therapeutic properties during their concentration (Buxton — *U. S. 2,434,788-90*). Prooxidant metals were precipitated from oils with β-mercaptopropionic compounds (Gribbins —*U. S. 2,457,227*).

Flavor Reversion. A method for testing the reversion properties of hydrogenated soybean-oil shortenings was based on subjective organoleptic tests on samples that were heated to 140°C., rapidly cooled to ±5°C. and rewarmed to 80°C. (Handschumaker —*J. Am. Oil Chem. Soc. 25,* 54). Semi-quantitative values were realized in the test when samples were compared with blends made from hydrogenated soybean and cottonseed oils. Moyer & Marmor (*U. S. 2,454,937*) claimed that materials that cause reversion in soybean oils could be removed by treatment of the oil with magnesium oxide which had previously been heated to 350-500°C.

Dutton, Schwab, and others (*J. Am. Oil Chem. Soc. 25,* 57, 385) produced evidence that the protection accorded to the flavor of soybean oil by organic acids and polyalcohols was due to their role as metal scavengers, for this was compatible with their known metal complexing properties. In the course of this work a four-sample glass laboratory oil deodorizer was designed.

Martin *et al.* (*Ibid.* 113) qualitatively analyzed the volatile materials from reverted soybean oil. They believed the flavor was due in part to carbonyl compounds, one of which was identified to be α-heptenal.

The Adsorptive Capacity of Cotton for Sodium Oleate

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The retention of soaps by fabrics during washing and rinsing operations has long been of practical and theoretical interest to both the user and manufacturer of detergents. While the presence of a small amount of fatty matter is desirable as a fiber lubricant, the accumulation of lime soaps, especially in so-called "hard water" districts, makes white fabrics dingy and colors dull.

Several investigators (3, 6, 7, 9) have studied the adsorption of various detergents on wool, silk, and to a lesser extent on cotton, but insofar as the latter fiber is concerned, there appears to be little agreement regarding the nature of the adsorption mechanism or the character of the material adsorbed.

Thus Neville and Harris (9) have reported that while wool and silk exhibit a pronounced selective adsorption of alkali from sodium oleate solutions, cotton adsorbs equal and relatively small quantities of both alkali and fatty acid.

Colt and Snell (3), on the other hand, working with an 80% tallow to 20% coconut oil soap, found that 19.5% of the total soap present in a 0.10% solution was adsorbed on cotton and that the amount was "somewhat greater at lower concentrations than at higher concentrations which is as should be expected." They also noted that the solutions in contact with the cloth decreased in pH: evidence of selective adsorption of alkali.

No one apparently has investigated the possible conversion of the adsorbed materials to lime soap in a hard water rinse or the effects which such conversion has on further adsorption. Since it was believed that the adsorption of sodium soaps and the "in situ" conversion of these to lime soaps during rinsing is largely responsible for the accumulation of the latter material, a further study of the mechanism by which a detergent is attracted to and maintained upon the fiber surface seemed desirable.

Materials and Methods

The sodium oleate employed for this investigation was prepared by saponifying the fractionated methyl ester with NaOH. The product was thoroughly dried and stored in tightly stoppered bottles. Only after

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approximately 18 months' storage could any rancidity be detected. Portions of the dried material were used as required.

The cotton fabric was AA sheeting with a thread count of 97 warp and 90 fill and a weight per yard of 3.02 ounces. Adsorption and other tests were made upon the cloth as received from the finisher and after a thorough scouring, which consisted of washing with a commercial soap followed by rinsing in several changes of *boiling* distilled water. As will be shown, this boiling water rinse removes all soluble adsorbed soaps.

The amount of soap adsorbed from solution was determined from the difference in concentration of the solution before and after immersion of the cloth. The small changes in concentration were measured by means of a differential refractometer modeled after that described by Rau and Roseveare (10). The actual instrument used is shown in the photograph, Figure 1, and comprises, from left to right, a sodium lamp, collimating telescope, prismatic cell for water and solution with constant temperature air bath, 1° analyzing prism with vernier scale and magnifier, and finally the viewing telescope. The instrument differed from that of Rau and Roseveare principally in the addition of the air thermostat which permitted measurement at elevated temperatures.

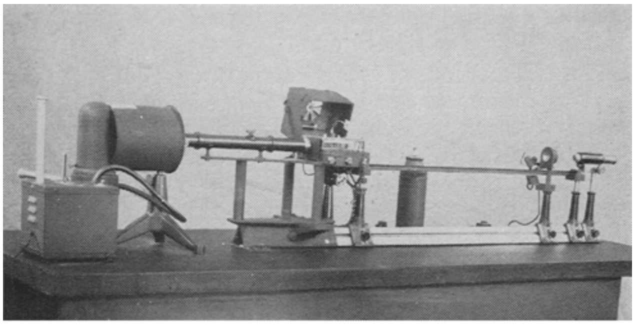

Fig. 1

For the purposes of this investigation it was sufficient to draw a calibration curve in which displacements of the analyzing prism were plotted against the concentrations of carefully prepared solutions. In the adsorption tests the concentration of the solution before and after immersion of the cloth were read from this curve. The sensitivity of the refractometer was such that a 1.0 mm. displacement of the prism represented a change of 0.0015% sodium oleate. Settings were reproducible to within 0.2 mm. and hence the soap concentrations could be read to within ± 0.0003%.

The test solutions were prepared by carefully weighing a portion of the soap into a 125-cc. Erlenmeyer flask and adding sufficient distilled water to make the volume 115 cc. The flask was stoppered and the mixture homogenized by heating in an oven at 120-125°F. until all the solid had dissolved. A 15-cc. aliquot was then removed and the concentration determined in the refractometer with the cell containing the solution being maintained at 92°F. An approximately 5-gram sample of cotton sheeting was weighed and immersed in the solution and the flask was again stoppered and placed in the oven at 120-125°F. After a sufficient period of time (usually 3-4 hours) to assure the attainment of equilibrium, a second and final aliquot was removed and the concentration again determined. Throughout the test care was taken to keep the flask stoppered and contact of the soap solution with air at a minimum to avoid precipitation of acid soap by atmospheric carbon dioxide. The flask was occasionally shaken to liberate air bubbles trapped in the fibers, but at no time during the test was the cloth removed from the solution.

Adsorption Data for Sodium Oleate

The per cent soap, as sodium oleate, adsorbed on unwashed cotton sheeting is plotted in Figure 2 as a function of the original concentration of soap in the solution. A nearly identical curve was obtained for cotton sheeting which had been prewashed and rinsed in boiling distilled water.

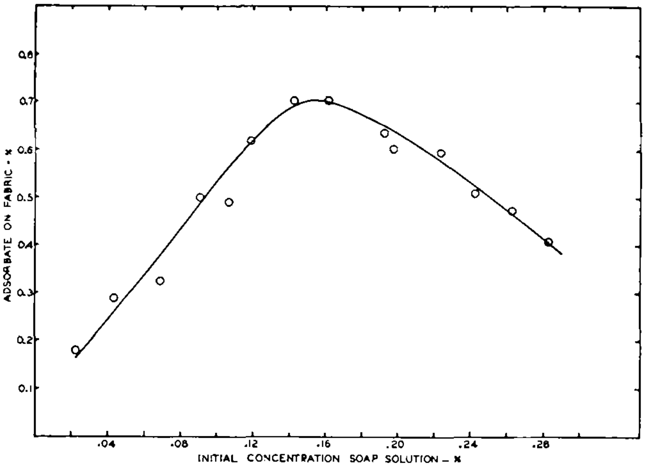

Fig. 2. Adsorption curve for sodium oleate.

The curve is unusual in that it does not resemble the classical adsorption isotherm but instead shows a falling off in the concentration of adsorbate after a maximum is reached at an initial solution concentration of about 0.15%. This adsorption behavior may best be explained on the assumption that the specific material adsorbed from solution first increases and then decreases in amount as the total soap concentration increases.

McBain and Jenkins (8) have published a composition diagram for aqueous sodium oleate solutions which shows the proportions of each constituent such as acid soap, simple ions and molecules, neutral colloid and ionic micelles present at any particular soap concentration. From this diagram it appears that the concentrations of acid soap, simple oleate ions, and simple sodium oleate molecules first increase and then decrease with increasing total soap concentration. Therefore it might be expected that any of these is the material adsorbed from solution by cotton.

If the material adsorbed by the fabric is an acid soap resulting from hydrolysis, the addition of sodium hydroxide should decrease the concentration of acid soap in solution and decrease the amount adsorbed. To test this point a solution containing 0.14% sodium oleate with 0.0175% free sodium hydroxide and another containing 0.14% sodium oleate with 0.035% free sodium hydroxide were made up.

Using the procedure previously outlined, changes in concentration of the solutions (as sodium oleate) resulting from adsorption on cloth, were estimated.

In both cases this amount proved to be much smaller than previously found and, expressed as percentage of adsorbate based on the weight of cloth, was less than 0.10%. This contrasts with the figure of 0.70% from a solution of the same concentration of oleate without added alkali.

In view of the fact that the method of measurement will detect the removal from solution of any material contributing to the refractive index, the small apparent change in concentration indicates that NaOH was not adsorbed to any appreciable extent. This agrees with the findings of Neville and Harris (9) to the extent of their conclusion that alkali is not preferentially adsorbed by cotton from detergent solutions.

As a further check on the nature of the material adsorbed by cotton from sodium oleate solutions, several samples which had adsorbed about 0.70% of "soap" were extracted with hot neutral ethyl alcohol. Analysis of the extracted substance indicated it to be an acid soap of composition 1 NaOl : 1 HOl.

McBain and Jenkins assigned the formula 2 NaOl : 1 HOl to the acid soap present in dilute solutions but the investigations of Ekwall (4) and Stauff (12) prove that the 1 : 1 product exists under conditions similar to those of the present tests.

Nature of the Adsorption Phenomenon

The strong affinity of the cotton fiber for acid soap is demonstrated by the fact that repeated rinsing in *boiling* distilled water was required to remove the adsorbed material. After this treatment the cloth would again adsorb acid soap to the same extent as originally. If a sample of cloth containing acid soap were rinsed in warm or even hot distilled water and again immersed in oleate solution, no appreciable adsorption took place.

When cloth containing adsorbed acid soap was first rinsed in warm distilled water to which a small amount of calcium chloride had been added and then in cold distilled water, the adsorptive capacity for acid soap was restored to approximately its original value.

It was further found that this cycle of adsorption and conversion to lime soap could be repeated indefinitely with the accumulation of substantial quantities of the latter material on the fabric. Although it is known that calcium oleate freshly precipitated in the presence of an excess of sodium oleate "adsorbs" some of the latter material, when precipitated and dried calcium oleate was added to a sodium oleate solution, no change occurred in the concentration of dissolved soap, thus ruling out the possibility that calcium soaps may serve as the adsorptive surface for fresh quantities of acid soap.

These facts indicate that when adsorbed soaps react with hard water constituents, the active groups of the cotton fibers are freed and that the resulting lime soaps are held in place by mechanical or weak cohesive forces.

It is, of course, obvious that in practical laundering operations additional quantities of lime soap are formed by precipitation, in the rinse, of dissolved sodium soaps from the solution with which the cloths are saturated. Much of this is flushed away with the rinse water but a fraction is no doubt retained in the cloth along with that formed directly on the fibers from the adsorbed acid soap. In any event, insofar as sodium oleate is concerned, adsorption must be a major factor in the accumulation of lime soap.

Harkins, Mattoon, and Corrin (5) have indicated that soaps in close packed arrangement occupy an average cross sectional area of about 27Å^2 per molecule. From this value and an average value for the diameter of cotton fibers it has been calculated that 20 double layers of acid sodium oleate would have to cover the surface to account for the adsorption of 0.7% acid soap. The term "double layer" is used here to designate a monomolecular film of the 1 NaOl : 1 HOl acid soap.

Although Sheppard and Newsome (11), Berkley and Kerr (2) and Aiken (1) have shown that intermicellar adsorption of water by cotton does take place, it appears unlikely that the structure of the fiber is sufficiently open to accommodate any substantial part of the adsorbed acid soap within the fiber itself.

Summary

The adsorption of soap on cotton from solutions of pure sodium oleate has been investigated. The adsorbate has been shown to be an acid soap of the composition 1 NaOl : 1 HOl. The addition of free sodium hydroxide represses hydrolysis and reduces the adsorption. The acid soap may be removed from the fabric by repeated boiling distilled water rinses or the adsorptive capacity for fresh acid soap may be restored by converting the adsorbed material to lime soap by rinsing in hard water. The resulting lime soap is largely retained by the fiber and on repeated washes accumulates in substantial amounts.

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