The Structure of Transparent Soap

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Attention has recently been directed to the so-called glassy condition of transparent soaps (1). The best known example of such commercial soap is Pears Soap (2). This is said to be tallow-rosin soap of high soap content made with alcohol and containing some glycerin. The alcohol is evaporated during the process of manufacture, but the soap remains permanently transparent. In addition to being transparent it is full of amber or port-wine light, producing a dichroic effect against the olive green tinge of the edges. The bar has a glassy fracture. Following a well known paper by W. D. Richardson (3), transparent soap has been regarded as an undercooled liquid or solution. This is supported by later writers, such as Alexander (4), who found in the ultramicroscope that slow cooling could produce large distinct crystals in a clear matrix. The soap thereupon becomes opaque, due to irregular scattering by the large randomly arranged crystals and clefts between them (1).

In recent years it has been amply demonstrated that soap boilers' neat soap at elevated temperature is not an ordinary solution but is a solution in the form of anisotropic liquid; that is, transparent or at least translucent crystalline liquid, doubly refracting between crossed Nicols and exhibiting characteristic "conical" appearances, which however do not represent actual boundaries. Normally, upon slow cooling, the soap boilers' neat soap crystallizes to a solid mass of intermeshed fibrous crystals whose size depends upon the slowness of cooling, as for example in a frame. The crystalline nature of the various forms that appear have been studied by means of X-rays in a number of laboratories in the United States and Germany.

The Soviet investigators (1) used a polarizing microscope to find that the glassy condition of the transparent soaps might be attributed to inhibition of the usual crystallization and that such soap should represent a metastable system resembling an undercooled melt—thus reaffirming the original conception of Richardson. They concluded that these transparent soaps are in a glassy, amorphous condition.

It has seemed worth while to test the accepted conception that transparent soaps exist in an amorphous glassy condition, by submitting them to X-ray examination. Two samples of Pears Soap were investigated. The first was a sample made in England twenty years ago and the second was one of recent manufacture, purchased in the United States. The two look very similar in spite of the great difference in age.

Both the old and new bars of Pears Soap gave an X-ray pattern that immediately proves that they are definitely crystalline. They are not even merely liquid crystalline as far as the main material is concerned.

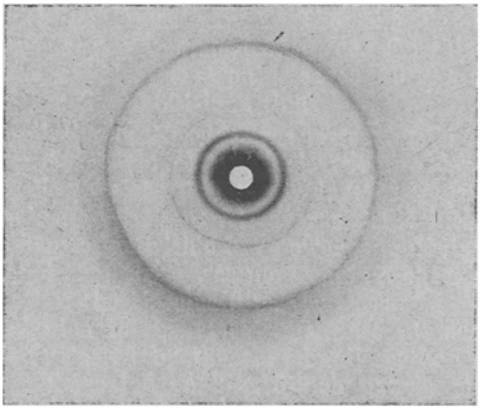

FIG. 1. X-ray diffraction photograph of Pears Soap, twenty years old. Cu K α radiation. Crystal to plate distance 50.0 mm.

Figure 1 shows the X-ray photograph of Pears Soap taken after the soap has been kept at room temperatures for twenty years. At least eight lines of very different intensities are visible, and the photograph is a typical powder diagram.

In order to provide a ready comparison of the patterns of the two samples of Pears Soap, microphotometer tracings are recorded in Figure 2, one placed conveniently below the other. Also included in Figure 2 is a microphotometer record for a control X-ray photograph of pure glycerine, showing two broad halos only, as shown by the two rounded elevations in the microphotometer curves. This glycerine pattern is that of a typical liquid, or amorphous glass or undercooled melt. These halos are in the neighborhood of about 4.3 A and 8.4 A and are distinctly observable also in the patterns from Pears Soap.

The Bragg spacings for the Pears Soap are listed as follows:

Intensity	Bragg spacing in A u	Remarks
s.	14.1 × 3 = 42.3	Long spacing
v. w.	10.7 × 4 = 42.8	Long spacing
m.	8.5 × 5 = 42.5	Long spacing
s.	4.65	Side spacing
Outer halo	Around 4.3	Glycerine halo
s.	3.95	Side spacing
v. w.	3.25	Side spacing
m.	2.85	Side spacing

These Bragg spacings resemble those established in previous papers from this laboratory for the most stable crystalline form of a sodium salt of a fatty acid at room temperature (5). This we have called the gamma form* since 1940.

Referring again to the X-ray diagram, the uniform circular pattern proves the complete randomness of the crystallites in the transparent soap. The degree of sharpness of the lines shows definitely that the crystallites are of fine ultramicroscopic dimensions and they are apparently of unchanged size after twenty years, as if practically the whole mass consisted of such small crystalline particles.

Hence the difference between ordinary opaque or semi-opaque soap and transparent soap consists es-

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* Ferguson, Rosevear and Stillman in a recent paper (6) have used the term omega when referring to gamma.

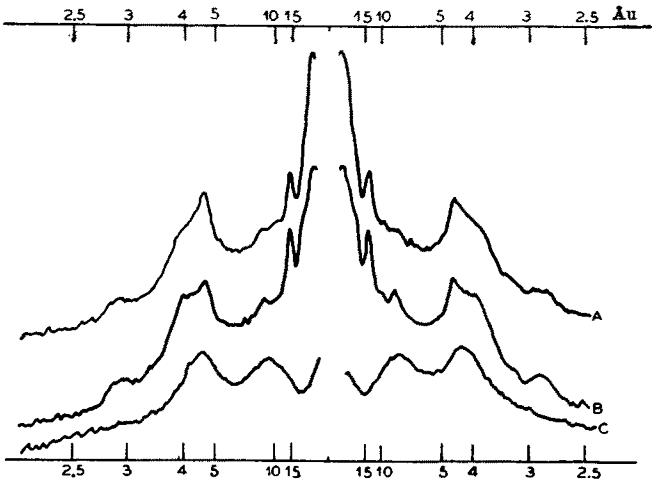

FIG. 2. Microphotometer records of X-ray diffraction photographs: A is Pears Soap, recently manufactured.
B is Pears Soap, twenty years old.
C is liquid glycerine, U.S.P.

sentially in the very much finer size of the crystalline particles of the latter. The bar is transparent because the extremely small crystalline particles are too small to provide optical discontinuities when compared with the wave length of ordinary light.

Summary

The classical conception of transparent soaps as amorphous undercooled liquids has been tested by means of X-rays. A transparent soap, such as Pears Soap, is shown to consist of a mass of fine ultramicroscopic crystallites, scattering light and arranged completely at random. Keeping for twenty years at room temperature does not appreciably affect this structure.

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Improvement Produced in the Stability of Lard by the Addition of Vegetable Oils*

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Blending animal and vegetable fats to produce compound shortenings and substitutes for butter is a well-known practice. This practice originated in attempts to provide materials similar to certain natural fats from cheaper and more readily available oils and fats. The natural products were simulated in regard to consistency, texture, and in so far as possible, flavor. The exact composition of these blended products, i.e., the particular vegetable oils and animal fats used and their relative proportions, has varied considerably from time to time, depending on their relative availability and price. In recent years, however, owing to wide acceptance of hydrogenated vegetable oils as shortening and cooking fats, a favorable market and price for vegetable oils have been created. At present there is probably no economic advantage in marketing compound shortenings containing a high ratio of vegetable oil; more likely, there would be an economic advantage in blends containing a low proportion of these oils.

Since commercial interest in these compounded fats has centered around their economic advantages, sufficient attention may not have been given to the possibility of improving the keeping quality of animal fats by admixture with relatively small percentages of certain vegetable oils. It is known that, in general, shortenings prepared by hydrogenation of vegetable oils are somewhat more resistant to rancidification than are animal fats. Previous work (1) (2) has indicated that at least some of the common vegetable oils owe their stability chiefly to the presence of naturally occurring tocopherols. Wheat-germ oil contains from about 0.3 to 0.5 percent of tocopherols (3) (4), whereas cottonseed, corn, and soybean oils have from 0.1 to 0.2 percent. Considerable variation, of course, may be expected in different specimens. Moreover, refining treatments usually reduce the tocopherol content of an oil. It has been shown (1) (5) that the addition of as little as 0.01 to 0.001 percent of tocopherol produces a significant increase in the stability of lard. Concentrations of that magnitude can readily be introduced into the lard by direct admixture with relatively small amounts of tocopherol-rich oils.

Although in 1926 Anderegg and Nelson (6) reported evidence indicating that wheat-germ oil protected highly unsaturated fats in prepared dietary mixtures and these findings were confirmed in 1931

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