

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.

LITERATURE CITED

1. Soap and Sanitary Chemicals, 1942, 18, 59; Soap, Perfumery and Cosmetics, 1942, 18, 306; Oil and Soap, 1941, 18, 239; all being abstracts or references to the original paper by B. Tjutjunnikov, Z Pleshkova and A. Chernichkina, Seifensieder-Ztg., 1941, 68, 193-4. 205-6, 215-16, 227-8, 237.

 See H. Kröper in Hefter-Schönfeld "Chemie und Technologie der Fette und Fettprodukte," Band IV, page 378, published by Julius Springer, Vienna, 1939.

3. W. D. Richardson, J. Am. Chem. Soc. 1908, 30, 414.

4. J. Alexander, Chem. and Met. Eng. 1918, 19, 631.

5. A. de Bretteville, Jr. and J. W. McBain, The American Mineralogist 1942, 27, 215.

A. de Bretteville, Jr. and J. W. McBain, Science 1942, 96, 471. J. W. McBain, A. de Bretteville, Jr., and Sydney Ross, J. Chem. Phys. 1943, 11, 179.

Phys. 1943, 11, 179. A. de Bretteville, Jr. and J. W. McBain, J. Chem. Phys. 1943, 11, 426.

 426.
 J. W. McBain, O. E. A. Bolduan and Sydney Ross, J. Am. Chem. Soc. 1943, 65, 1873.

Soc. 1943, 60, 1873. O. E. A. Bolduan, J. W. McBain and Sydney Ross, J. Phys. Chem. 1943, 47, 528.

6, R. H. Ferguson, F. B. Rosevear and R. C. Stillman, Ind. Eng. Chem. 1943, 35, 1005.

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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by Roller (7), comparatively little has been published concerning the improvement in the stability of lard brought about by the direct addition of vegetable oils. A number of patents, however, reveal that some practical work has been done along these lines. These refer to the addition to various fats and oils of small amounts, usually from 1 to 10 percent, of crude soybean oil (8), hydrogenated refined soybean oil (9), hydrogenated sesame oil (10), crude cottonseed oil (11), hydrogenated kapok oil (12), and cacao butter (13). Most of these patents stress the use of crude or hydrogenated vegetable oils. In view of recent knowledge concerning the antioxygenic action of tocopherols, including the concept of synergism proposed by Olcott and Mattill (1) and further studied by others (5) (14), it was considered desirable to review and investigate further the effect of adding vegetable oils to lard.

Experimental Results and Discussion: The antioxidant effect produced by the addition of small amounts of some of the more common vegetable oils to lard is shown by the results in Table I. These data were ob-

 TABLE I

 Effect of Small Quantities of Tocopherol-Containing Vegetable

 Oils ¹ on the Stability of Lard

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Lard Substrate	Vegetable Oil	Concen- tration of Added Vege- table Oil	Stability (A.O.M.)	In- crease in Sta- bility	Stabil- ity Factor ²
		percent	hours	hours	
	None	Control	3.0		
Steam-	Wheat germ	0.5	7.5	4.5	2.5
Rendered	Wheat germ	1.0	12.5	9.5	4.2
(F-2)	Peanut, refined	1.0	3.5	0.5	1.2
	Peanut, crude	1.0	4.5	1.5	1.5
	None	Control	6.0		
	Corn, refined	1.0	10.5	4.5	1.7
	Corn, refined	2.5	15.0	9.0	2.5
	Soybean, refined	2.5	14.0	8.0	2.3
	Cottonseed, refined	2.5	11.5	5.5	1.9
Steam-	Mixture of corn, soy- bean, peanut, and cottonseed	1.0	10.0	4.0	1.7
Rendered (W)	Same mixture as above	2.5	13.5	7.5	2.2
(,, ,)	Hydrogenated vegeta- ble oil (A)	1.0	9.5	3.5	1.6
	Hydrogenated vegeta- ble oil (A)	2.5	12.5	6.5	2.1
	Hydrogenated vegeta- ble oil (B)	2.5	15.0	9.0	2.5
	Hydrogenated vegeta- ble oil (C)	2.5	13.5	7.5	2.2
	None	Control	4.0		
	Cottonseed. refined	1.0	7.0	3.0	1.7
Steam- Rendered (F-1)	Cottonseed, refined	5.0	13.0	9.0	3.2
	Cottonseed, refined	10.0	15.5	11.5	3.9
	Hydrogenated vegeta- ble oil (A)	1.0	7.0	3.0	1.7
	Hydrogenated vegeta- ble oil (A)	5.0	15.0	11.0	3.7
	Hydrogenated vegeta- ble oil (A)	10.0	22.0	18.0	4.5
Drip- Rendered (V-2)	None	Control	3.0	••••	
	Corn, refined	1.0	6.0	3.0	2.0
	Corn, neutralized and washed Corn, crude	1.0 1.0	7.0 7.5	4.0	2,3 2,5
				4.5	

¹ All hydrogenated vegetable oils used were commercial shortenings of the all-hydrogenated type.

² Stability factor = stability of treated lard ÷ stability of control.

tained by using the Active Oxygen Method (A.O.M.) (15) with certain modifications, which have been described elsewhere (16). In all stability values reported in this paper, the time required for development of a peroxide value of 15 millimoles per kilogram of fat has been taken as the stability time. It has been found in this laboratory that this value agrees well with organoleptic assays when lard is the substrate.

Published information concerning the tocopherol content of these oils indicates a rough relationship between the tocopherol content and the stabilizing effect produced. Wheat-germ oil has the highest tocopherol content and also the greatest stabilizing effect. Refined corn, cottonseed, and soybean oils contain appreciably less of the tocopherols than wheat-germ oil and have somewhat less stabilizing effect when added to lard. Considerable caution must be exercised, however, in interpreting the data of Table I, particularly if one is considering the quantitative aspects of the results. It must be recognized that these oils contain alpha-, beta-, and gamma-tocopherols in different mixtures and proportions and that analytical methods for determining tocopherols do not distinguish between these different forms. These various forms of tocopherol are reported to differ considerably in antioxygenic activity. The need for caution in interpreting the results is shown by the fact that 1 percent of wheat-germ oil added to lard F-2 resulted in a stability factor of 4.2, whereas 2.5 percent of refined corn oil, presumably containing about the same amount of tocopherol, when added to lard W resulted in a stability factor of only 2.5. The increased stability in hours was about the same in each case. Consequently, direct comparison of stability factors should be confined to those experiments conducted on the same substrate.

When varying amounts of a given oil or fat up to 10 percent were added, there was a tendency for the antioxidant effect to reach a maximum. This finding is in accordance with reports in the literature that the efficiency of tocopherols as antioxidants decreases with increasing concentration (14) (17).

The melting point of lard is usually lowered by the addition of vegetable oils. This can be compensated for by several means. Stearines, or fat of either animal or vegetable origin hardened by hydrogenation, may be incorporated to raise the melting point. Also the blend of lard and vegetable oils can be hardened to the desired extent by hydrogenation. These methods, particularly the latter, produce a further material increase in stability.

In another series of tests, some of the less common vegetable oils were added to lard in 1-percent concentration. These results are given in Table II. None of these oils showed any outstanding action, and only tomato seed oil and apple seed oil showed a degree of

 TABLE II

 Effect of Miscellaneous Vegetable Oils¹ in 1-Percent Concentrations on the Stability of Lard

Lard Substrate	Vegetable Oil	Concen- tration of Added Vege- table Oil	Stability (A.O.M.)	In- crease in Sta- bility	Stabil- ity Factor
	None	percent Control	hours 3.0	hours	
	Apple seed, crude	1.0	6.0	3.0	2.0
	Tomato seed. crude	1.0	7.0	4.0	2.3
Steam-	Safflower, crude	1.0	4.5	1.5	1.5
Rendered	Grape seed, crude	1.0	4.0	1.0	1.3
(F-2)	Walnut kernel,	1.0	4.0	1.0	1.3
(1-2)	crude	1.0	4.0	1.0	1.5
	Sunflower seed, crude	1.0	4.0	1.0	1,3
	Cocoa butter	1.0	4.0	1.0	1.3
	Orange seed, crude	1.0	3.5	0.5	1.1
	Avocado, crude	1.0	1.5	1.5	0.5

¹All these oils except the cocoa butter were furnished by Dr. L. B. Howard of the Western Regional Research Laboratory. action approaching that of the more common oils, such as soybean, corn, and cottonseed oil.

Since it has been shown (5) that pure alphatocopherol added to lard along with commercial soya lecithin and fatty acid esters of ascorbic acid greatly enhance the stability, it seemed of interest to determine whether the tocopherol requirements of such a synergistic composition would be readily furnished by the direct addition of certain vegetable oils. With this objective a series of experiments was carried out, the results of which are given in Table III. In the first

TABLE III					
Effect of Certain	Synergistic Mixtures	on	the	Stability of Lar	đ

Lard Substrate	Additive	Concen- tration of Addi- tive	tration of Stability Addi- (A.O.M.)		Stabil- ity Factor
	None Crude corn oil	percent 5.0	hours 5 23	hours 	4.6
	Crude corn oil alpha-Tocopherol	$^{5.0}_{.005}$ }	24	19	4.8
Steam- rendered and 5%	Crude corn oil Soy phospholipids	5.0	25	20	5.0
lard flakes	Crude corn oil	5.0 }	45.	40	9.0

certain other additives to delay the onset of rancidity in lard. The addition of such oils in sufficient quantity to incorporate 0.01 percent tocopherols along with 0.06 percent d-isoascorbyl palmitate increased the stability of lard approximately tenfold. The fact that addition of soy phospholipids exerts relatively little effect when added to mixtures containing crude corn oil or wheat-germ oil, which are probably themselves rich in phospholipids, indicates that the activity of phospholipids, like that of tocopherol, may fall off after reaching certain critical concentrations. Care must be exercised in such a presumption, however, because it is not certain that accelerated methods are satisfactory for measuring the antioxidant activity of phospholipids.

Since different samples of the same type of vegetable oil may vary appreciably in tocopherol content and in composition generally, the data presented here are not intended as an accurate comparison of the antioxygenic values of the vegetable oils but rather are given to show that many of the common vegetable oils when added to lard increase its stability.

Summary and Conclusions: An appreciable increase in the stability of lard as measured by the Active Oxygen Method may be effected by the addition of rela-

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