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Effect of Composition and Polymorphic Form on the Hardness of Fats[1]

R. O. FEUGE and WILMA A. GUICE, Southern Regional Research Laboratory,[2] New Orleans, Louisiana

HARDNESS is an important consideration in the performance of confectionery fats. Ordinarily fats are desired which are relatively hard and brittle at room temperature yet soften and melt at slightly higher temperatures. Conceivably a measurement of hardness also can be used to determine whether or not a fat-containing confection has been tempered properly (2).

The hardness of confectionery fats, which may contain 80% or more of solids at room temperature, should not be regarded as being identical with the consistency of plastic, semisolid fats like shortening and margarine oil, which generally contain less than 20% solids at room temperature. The general property of hardness has been variously defined as resistance to local penetration, scratching, cutting, wear or abrasion, and yielding. The multiplicity of definitions indicates that hardness is not a fundamental property but rather a composite one including yield strength, work hardening, true tensile strength, and modulus of elasticity.

On the assumption that a mass of fat crystals resembles in certain important respects a mass of metal crystals, it might be expected that a modification of the Brinell test for metals should be well suited for measuring the hardness of solid or substantially solid fats. Apparently tests bearing any resemblance, even remotely, to the Brinell test for metals have been used very infrequently with fats. Ravich and Volnova (3) applied such a test to tristearin-tripalmitin and stearic acid-palmitic acid mixtures. Von Rosenberg (4) described a test procedure for fats and waxes which embodied some of the principles of the Brinell test. Recently in our laboratory an instrument and test procedure were devised and found to be satisfactory in testing fats and waxes (2).

In our modification of the Brinell test a perfectly round steel ball having a diameter as small as 0.1250 in. or as large as 0.5000 in. is pressed for 1 min. with a force of 0.2 to 6.0 kg. into the surface of the test specimen. The applied force is selected so that the diameter of the impression ranges between 15 and 45% of the diameter of the ball. The hardness index is calculated from the formula:

$$H = \frac{P\,(100)}{\frac{\pi D}{2}\,(D - \sqrt{D^2 - d^2})}$$

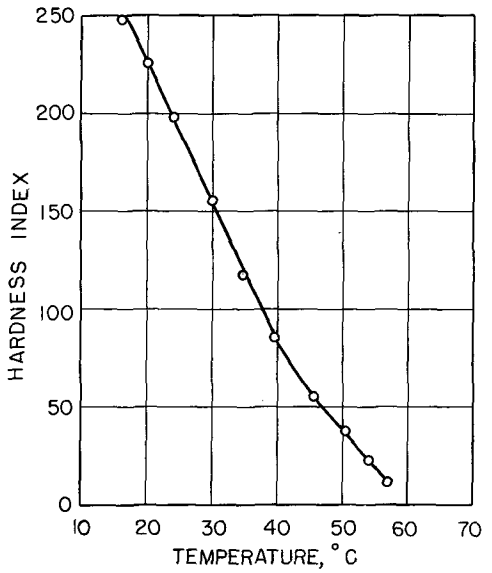

FIG. 1. Hardness curve for completely hydrogenated cottonseed oil melted and heated to 90°C., solidified at 26°C., and stored for several months at 26°C.

where H is the hardness index, P is the weight on the ball in kilograms, D is the diameter of the ball in millimeters, and d is the diameter of the impression in millimeters. The denominator of the above equation represents the curved area of the impression, while the factor 100 in the numerator reduces the dimensions of the hardness index to kilograms per square centimeter. The index is practically independent of ball size and test load if the other test conditions are confined to certain ranges (2).

This communication presents data on the effect of composition and polymorphic form on the hardness of fats. It should provide new information useful in the production of better fat products and also should provide a background for the evaluation of any new test data obtained with the instrument and technique.

Temperature Effects

Temperature has a marked influence on the hardness of a solid fat, even when polymorphic transformations, changes in crystal size, and partial melting are not involved. The decrease in hardness as the temperature increases is relatively gradual, even for a pure triglyceride, and is not an abrupt phenomenon like the melting of a pure compound. In fact, over the temperature range at which fats are commonly utilized

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[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

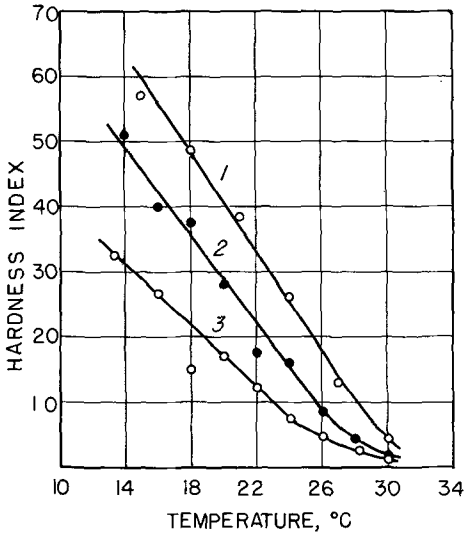

FIG. 2. Hardness curves: (1) illipe butter, heated almost to point of complete melting, solidified by cooling to 10°C., and stored at about 25°C. for 1 day, (2) Cocoa Butter A, bars molded by manufacturer and stored at room temperature (24-28°C.) for several months, and (3) Confectionery Fat A, lauric acid type, Wiley m.p. 117.5°F. (47.5°C.), melt seeded and cooled to 26°C., tempered for 2 days at 26°C.

the hardness is more or less inversely proportional to the temperature.

Hardness *vs.* temperature curves for four fat products are reproduced in Figures 1 and 2. It is evident that the hardness index of solid and substantially solid fats can vary widely at a given temperature, and the amount of softening per degree of increase in temperature also varies. For the linear sections of the four curves, the decrease in hardness ranges from 2.4 to 7.2 per degree of increase in temperature. The hardness *vs.* temperature curves for fats resemble those of metals. The hardness of the latter also usually decreases in a relatively linear manner as the temperature increases.

Polymorphic Form

In the course of the earlier investigations (2) it was found that the hardness of cocoa butter was affected to a marked degree by the thermal history of the test specimen. When the melted cocoa butter was seeded during solidification and tempered for 5 hr. at 27°C., the test specimen was approximately twice as hard as one which was obtained by simply solidifying the melt and quickly cooling to 5°C. This difference was noted at test temperatures at which both specimens were substantially solid, hence the difference observed could not be attributed to a difference in the content of liquid fat.

Subsequently two samples of commercial chocolate, which were identical except that one was tempered and the other untempered, were examined. The tempered sample was found to be approximately twice as hard as the untempered sample. Four additional samples of commercial chocolate, which were identical except that they had been cast off and molded at slightly different temperatures, were found to have the following hardness indices:

Temperature at which sample was cast off and molded, °F.	Hardness index at 80.2°F. (28.8°C.)
84	1.81
86	1.80
88	1.50
92	1.26

These indices, which show a real difference, were obtained several days after the molding operation and after the samples had been shipped a considerable distance. If the tests had been conducted immediately after molding, larger differences undoubtedly would have been observed.

Tests carried out with illipe butter indicated that its hardness also can be increased by tempering. Increases as large as four-fold were encountered.

Further evidence that tempering increases the hardness of fat products is presented in Figure 3. The

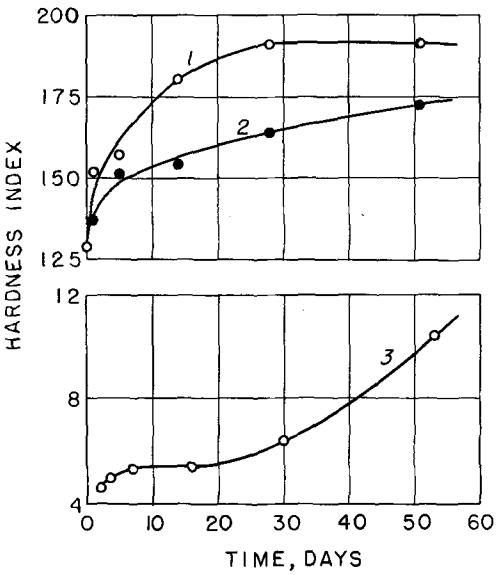

FIG. 3. Effect of aging on hardness: (1) completely hydrogenated cottonseed oil, melt solidified by cooling to 25°C., (2) tristearin solidified by cooling to 25°C., and (3) Cocoa Butter B solidified by cooling to 15°C., held for 2 days at 21°C. All samples were stored at room temperature, about 25°C., and all tests were made at 25°C.

products represented were melted completely, solidified under moderate conditions, and then stored at room temperature. The cocoa butter was still increasing in hardness after 53 days of storage; the hardness index at this time was 10.4. The ultimate hardness of the butter under these conditions was approximately 12. From an investigation carried out with the major components of cocoa butter (1) it is known that tempering these components to higher melting polymorphs is a relatively slow process, particularly in fat mixtures. Obtaining the highest-melting polymorphs in cocoa butter by tempering at 25°C. should require several months.

The completely hydrogenated cottonseed oil, iodine value below 1, represented in Figure 3 was softer than the tristearin; but after several days it was the harder of the two. A maximum value was attained after about 25 days.

The tristearin was still increasing in hardness after 51 days and was far from the maximum value. Tri-

stearin commonly is believed to crystallize in polymorphs melting at about 54.9, 64.0, and 72.5°C. Apparently storage at 25°C. did little toward producing the highest-melting form.

The effect of storage temperature and time on the hardness of tristearin is further illustrated in Figure 4. At 40°C. no increase in hardness was noted in 240 min. At 50°C. the hardness at first increased rapidly with time, reaching a value of 277 in 225 min. However further storage at 50°C. resulted in an increase at a slower rate; the hardness reached 282 in 285 min. and 294 in 465 min. At a temperature of 53°C. the maximum hardness of 326 was attained in about 170 min. Extended storage at 53°C. or storage at temperatures above 53°C. decreased the observed hardness below the maximum of 326. As will be explained below, this decrease is believed to be associated with changes in crystal size.

The tempering data suggest the possibility that hardness can be used to measure the degree of conversion of the components of a fat to higher-melting polymorphic forms. However it has not yet been established that the hardness of a triglyceride is a linear function of the degree of conversion of one polymorphic form to the next higher form, and the hardness indices of the different polymorphs of the various triglycerides have not yet been measured.

Composition and Crystal Size

Ravich and Volnova (3) found two marked maxima in the hardness curve for mixtures of stearic and palmitic acids. The maxima occurred at about 35 and 55% stearic acid. On the other hand, no maxima were observed for the tristearin-tripalmitin system; this was attributed to the formation of solid solutions. In our investigation increasingly larger additions of one fat to another were found more or less gradually to increase or decrease the hardness, provided the mixtures were not subjected to heat treatments which partially melted one of the components and allowed it to recrystallize.

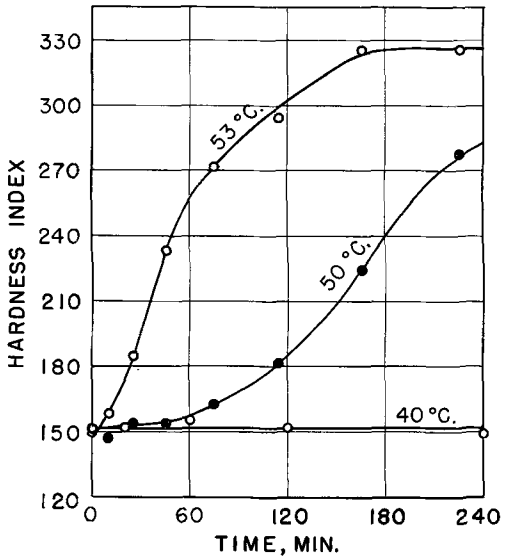

FIG. 4. Hardness-time curves for tristearin stored at the indicated temperatures. The tristearin samples were melted, heated to 90°C., poured into molds, quickly chilled to 10°C., and kept for 30 min. at 28°C. before each series of tests was begun.

In Figure 5 are reproduced hardness curves for mixtures of tristearin and tripalmitin. The hardness of the untempered mixtures usually increased as the content of tristearin increased. Tempering these mixtures for 4 hr. at 40°C. increased their hardness moderately. When the mixtures were tempered at 56°C. instead of 40°C., the hardness decreased in practically all instances. At 56°C. only the hardness of the pure tristearin increased. In the case of the mixtures, thrusting the quickly chilled samples suddenly into an oven at 56°C. apparently resulted in the partial melting of the tripalmitin fraction, which presumably was present in its lowest-melting polymorphic form. Subsequently, this fraction resolidified in relatively coarse crystals, which resulted in a softer matrix.

Adding 5 to 10% of a relatively hard fat, like completely hydrogenated cottonseed oil, to a soft fat, like cocoa butter, increases the hardness of the latter only slightly. The increase is considerably less than 5 to 10% of the difference in hardness of the two fats.

The addition of liquid oil to a hard fat, even in small amounts, greatly decreases the hardness. The effect of adding cottonseed oil to completely hydrogenated cottonseed oil is shown in Figure 6. The addition of cottonseed oil until the mixture contained 10% reduced the hardness at 26°C. from 153 to 68. Under the conditions represented in Figure 6 the cottonseed oil dissolved practically none (less than 0.2%) of the completely hydrogenated oil, hence the decrease in hardness cannot be attributed to solubility effects. Tests made with the mixtures indicated that none of the liquid oil was occluded by the hard fat; all of

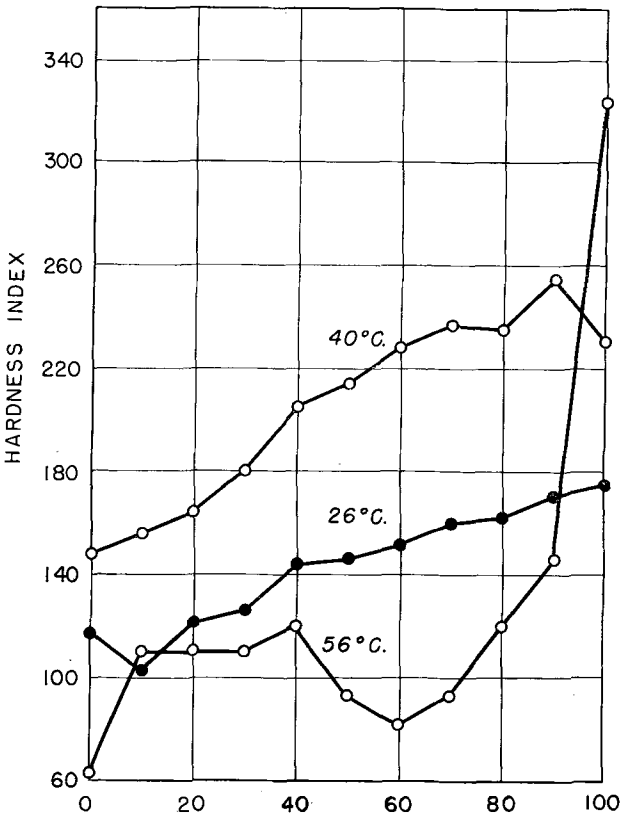

Fig. 5. Hardness of tristearin-tripalmitin mixtures at 26°C. Tempering temperatures are indicated on the curves. Tempering time was 5 hr. for sample tempered at 56°C. and 4 hr. for sample tempered at 40°C. All samples kept at 26°C. for approx. 24 hr. before testing.

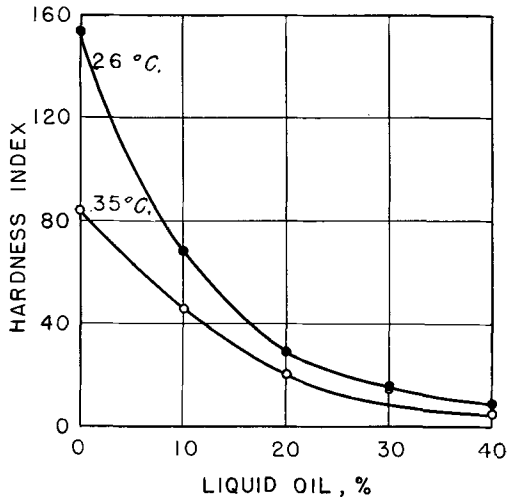

FIG. 6. Reduction in hardness on adding liquid oil (cottonseed oil) to a solid fat (completely hydrogenated cottonseed oil). Melted mixtures were solidified by cooling to 26°C., then tempered for 1 hr. at 50°C. and 2.5 hr. at 60°C. Samples were held over-night before being tested at the indicated temperatures.

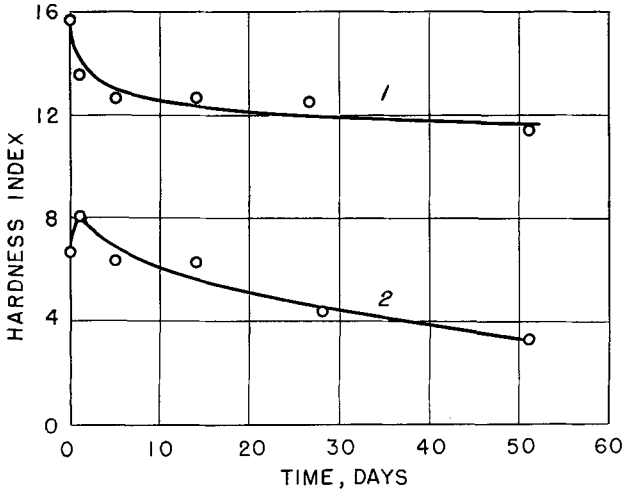

FIG. 7. Effect of aging on hardness: (1) Confectionery Fat B, lauric acid type, Wiley m.p. 113.7°F. (45.4°C.), and (2) Confectionery Fat C, derived from domestic oils, Wiley m.p. 103.0°F. (39.4°C.). Samples were solidified by cooling to 10°C., stored at room temperature, about 25°C., and tested at 25°C.

the liquid oil could be extracted with petroleum ether at room temperature.

As mentioned above, crystal size has an effect on the hardness of a fat or fat mixture. Not only was the hardness of tristearin-tripalmitin mixtures reduced when tempering was carried out at too high a temperature, but tempering tristearin alone at too high a temperature did not produce a particularly hard specimen. Quickly chilling melted tristearin and then plunging it into a water bath at 60°C. and holding it at this temperature for 2 hr. produced a test specimen having a hardness index of 250 at 28°C. When the temperature of the water bath was reduced to 53°C. and the other conditions remained the same, the hardness index of the tempered sample which was obtained was 303 at 28°C. Presumably at 60°C. the lowest-melting polymorph, obtained by quick chilling, melted and then resolidified in larger crystals.

In the course of tests with tristearin it also was found that reducing the temperature at which the melt was chilled (forming smaller crystals) increased the hardness of the solidified sample. A reduction from 26°C. to 8°C. produced an increase of about 10 units.

Further tests were carried out with pure 2-oleodistearin. When melts of this triglyceride were solidified by cooling at temperatures of 15 and 28°C., the hardness indices, measured at 15°C., were found to be 56 and 35, respectively. In other words, the more rapidly solidified sample, which contained the smaller crystals, was found to be the harder. Both samples were conditioned at the test temperature for 30 min. before measurements were made. This temperature treatment should have converted both test specimens to the next-to-highest-melting polymorph (1).

Crystal growth apparently is a factor in the changes in hardness occurring in some confectionery fats on storage. Two confectionery fats, B and C, having Wiley melting points 113.7°F. (45.4°C.) and 103.0°F. (39.4°C.), respectively, and containing sizable proportions of liquid oils at room temperature, were solidified and stored at room temperature. Both fats became progressively softer on extended storage (Figure 7). It is believed that this progressive softening was caused by the fine crystals dissolving in the liquid components of the fats and then resolidifying in larger crystals.

Summary

Hardness is an important index in the performance of confectionery and other fats.

Using an instrument and technique which were essentially a modification of those used in the Brinell test as applied to metals, the effect of composition and polymorphic form on the hardness of fats was investigated.

It was found that the hardness of a given sample of fat was influenced by the degree of tempering to which the sample had been subjected. Hardness always increased as the components of a fat were converted to higher-melting polymorphs. However the hardest test specimens were not obtained with the highest tempering temperatures. Presumably the use of too high a temperature in tempering melted some of the lower-melting polymorphs and allowed them to resolidify in larger crystals producing a softer matrix.

Adding progressively larger amounts of one fat to another generally increased or decreased the hardness of the mixture in a more or less uniform manner. Adding small amounts of liquid oil to a hard fat greatly decreased the hardness index.

Apparently the hardness index of a given fat decreases as the crystal size increases. It is believed that fats containing a sizable proportion of liquid component will become softer on prolonged storage because the presence of the liquid component makes possible a gradual increase in crystal size.

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