

be run simultaneously by one analyst. Sufficient quantities of the separated glycerides are obtained so that characterization by chemical analysis can be made. The method is applicable to mixtures containing mono-, di-, and triglycerides and glycerine.

Summary

Monoglyceride concentrates are quantitatively separated into mono-, di-, and triglyceride components on silica gel columns by an adsorption chromatographic technique. The separated glycerides are determined gravimetrically. The adsorption on silica gel is dependent on the number of hydroxyl groups in the molecule, and the influence of unsaturation and chain length is minimized. Combinations of benzene and ethyl ether are used for elution, thus preventing isomerization, which frequently results when polar solvents such as alcohols are used.

The procedure for the chromatographic separation is simple and straightforward. The equipment used is easily obtainable. The silica gel adsorbent requires

only adjustment of its water content before use.

Mixtures of both saturated and unsaturated glycerides and those having different fatty acid chain length have been separated. Known mixtures have also been analyzed. For a known mixture containing 15% tripalmitin, 45% distearin, and 38% monopalmitin the average deviations from the calculated values were 0.4%, 0.2%, and 0.6%, respectively.

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An Instrument for Measuring the Hardness of Fats and Waxes^{1,2}

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APPARENTLY a really satisfactory method of measuring the hardness of fats has heretofore not been described in the literature. The needle and cone penetrometers, together with their various modifications, are suitable for measuring the consistency of plastic, semi-solid fats but are not suitable for measuring the hardness of solid or substantially solid fats. Instruments which do measure hardness are commercially available but leave something to be desired when used on products like cocoa butter and confectionery fats.

The Shore Durometer is currently in wide use to measure the hardness of wax-like products. It consists essentially of a frustoconical indenter, a spring to force the indenter into the test sample, and a scale-and-pointer arrangement to indicate the depth of the indentation. Among the undesirable features of this instrument are the variation of load with depth of indentation, the use of a fatigue-susceptible spring to supply the load, an arbitrary scale (0-100), and a limited range. The latter results in readings of 100 for different samples of quite hard materials, which obviously do not have the same hardness.

A survey of other instruments and procedures which might be used with hard fats and waxes indicated that a modified Brinell hardness test would be most likely to meet all requirements. The Brinell test (A.S.T.M. Method E 10-54 T) has been used for many years to determine the hardness of metallic materials. Confectionery fats, which may consist of 75% or more of hard crystals at room temperature, and completely solid fats and waxes have a number of properties in common with metal crystals.

Tests of the Brinell types consist of pressing a perfectly round ball onto the test surface until there is

obtained an impression, the diameter of which is equal to a fraction of that of the steel ball. Sometimes the impression is so slight that it is barely visible to the naked eye. Under such slight deformation of the test surface the results tend to be removed from the realm of empiricism and placed on a more or less fundamental basis. The hardness units tend to be related to well-defined physical properties. It has been demonstrated (2), both theoretically and experimentally, that when a ball of given diameter under a given force penetrates an elastic, isotropic material, the depth of indentation is determined solely by the elastic modulus of the material, provided the strain is small. While solid fats and waxes are not elastic, isotropic materials, they would be expected to behave to some degree like such materials.

There appears to be no published evaluation of the adaptation of the Brinell test to determining the hardness of solid or substantially solid fats. Ravich and Volnova (1) used one adaptation of the test to measure the hardness of mixtures of tripalmitin and tristearin but did not report all of the conditions under which their tests were made. Also they were not concerned with the effect of operating procedures on the hardness values. Von Rosenberg (2) described a test procedure for determining the hardness of waxes which embodied some of the principles of the Brinell test. He devised an instrument for forcing a plunger, which measured 5 mm. in diameter and had been ground to a hemispherical point, into the test sample; the force was such that the depth of penetration was usually less than 0.5 mm. With the load on the plunger the penetration was measured in 0.001-mm. units. Then the load was removed, and the penetration was again measured. From these values the elastic and permanent deformations were calculated, and the latter was then used to calculate a hardness index.

The present report will be concerned with the

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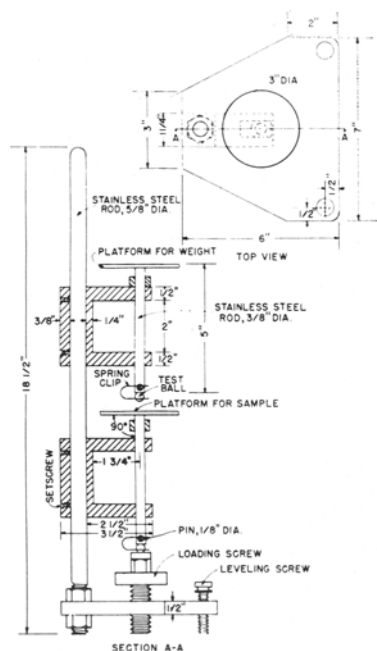


FIG. 1. Dimensions and structural details of hardness tester.

description of an instrument and technique, adapted from the Brinell test, which can be used to determine precisely the hardness and softening characteristics of fats and waxes.

Hardness Tester

The hardness tester which was designed and built is depicted in Figure 1. This instrument is believed to be simplified to the greatest extent possible without sacrificing the accuracy of the determinations to be made with it. All parts can either be purchased or readily made in a machine shop.

The steel ball used to make an impression in the test sample rests in a conical recess in the end of the $\frac{3}{8}$ -in. stainless steel shaft attached to the 3-in. platform for the weight. A spring clip held in place by a removable pin through the shaft holds the steel ball in the recess. This arrangement make it simple to change the size of the ball used in the test. The total weight of the platform, shaft, collar, pin, spring clip, and a $\frac{3}{8}$ -in. ball is 200 g., which is the minimum weight that can be put on a test sample.

The assembly of platform, shaft, etc., for supporting the sample to be tested is identical with the assembly for holding and weighting the test ball.

A loading screw is used to push the test sample upward until the test ball and all the weight on the ball rests on the sample. In order not to impart any circular motion to the test sample a single-row radial bearing has been mounted on a steel nut by cementing the outer race of the bearing to the nut; and this unit has been inserted between the loading screw and the $\frac{3}{8}$ -in. ball at the bottom of the shaft supporting the test sample. The 10 small ball bearings in the single-row radial bearing provide a relatively friction-free connection.

The shafts supporting the test ball and sample are, of course, carefully aligned with each other and with the center line of the loading screw.

Two levelling screws mounted in the base plate are employed to align the instrument so that the $\frac{3}{8}$ -in.

shafts supporting the test ball and sample are exactly vertical.

With the exception of the base and the two C-type supports clamped to the $\frac{5}{8}$ -in. stainless steel rod, the various parts of the instrument are made of stainless steel. The base and supports are made of brass.

The test balls are Grade 1 ball bearings in diameters of $\frac{1}{8}$, $\frac{3}{16}$, $\frac{1}{4}$, $\frac{3}{8}$, and $\frac{1}{2}$ in. These ball bearings are available in either carbon or stainless steel. In carbon steel they are spherical to within ± 0.000025 in.

Test Procedure

Hardness tests of the type under discussion must be conducted at a constant, known temperature. The test data which will be reported below were obtained by operating the instrument in a constant temperature cabinet made of transite and wood and measuring 2 x 2 x 2 ft. The cabinet was equipped with a glass window and two hand holes, enabling the operator to make measurements as easily as if the instrument had been on a laboratory bench.

The test sample need not have a particular shape. One of the few requirements is that the sample rest solidly on the sample platform and that the surface on which the test is to be made is perfectly horizontal and remains so throughout the test. Other requirements are that the thickness of the sample at the point of the indentation is at least 10 times the depth of the indentation and that the distance of the center of the indentation from the edge of the sample or edge of another indentation is at least two and one-half times the diameter of the indentation.

In determining the hardness values reported below the fat or wax generally was melted and poured into a steel dish measuring 40 mm. in diameter by 8 mm. deep. After solidification the top side of the test sample was smoothed by rubbing it over fine sand paper mounted on a flat surface. The sample then was placed on the sample platform of the hardness tester with the smoothed face downward, and the test was made on the molded face.

The thermal history of a sample of fat or wax has

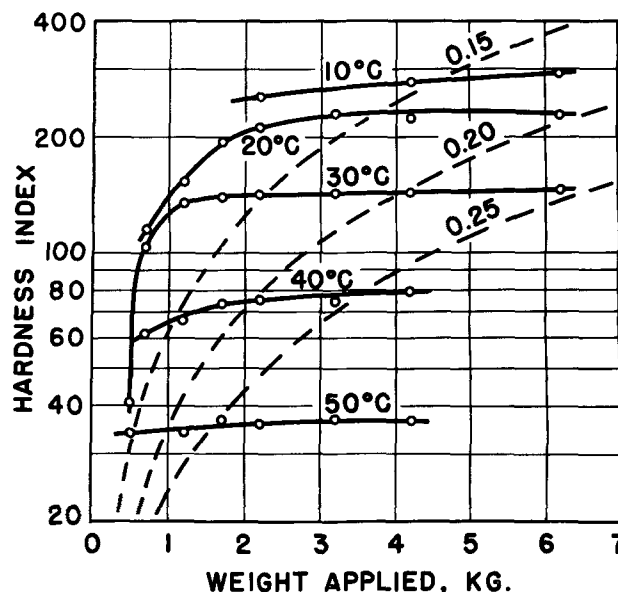


FIG. 2. Effect of applied weight on hardness index of highly hydrogenated cottonseed oil at different temperatures, using a $\frac{3}{8}$ -in. ball and applying test load for 1 min. Dash lines are constant value curves for d/D .

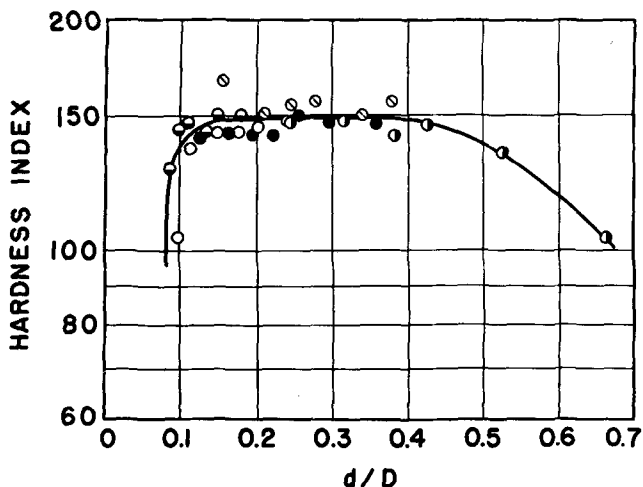


FIG. 3. Hardness index vs. d/D for test balls of different diameters: side-filled circles, $\frac{1}{8}$ in.; divided circles, $\frac{3}{16}$ in.; solid circles, $\frac{1}{4}$ in.; open circles, $\frac{3}{8}$ in.; bottom-filled circles, $\frac{1}{2}$ in. Tests made on highly hydrogenated cottonseed oil at 30°C ., load applied for 1 min.

an important bearing on its hardness. Some aspects of this factor will be discussed below. Concerning the immediate testing technique, a sample measuring about 40 mm. in diameter and 6 mm. in thickness should be at the test temperature at least one hour before the test is made. Preferably the sample is stored at a lower temperature just prior to testing. Because no evidence has ever been found that crystals of fat can be superheated, the suggested sequence of temperatures should put the sample in thermal equilibrium. On the other hand, if the sample is cooled down to the test temperature, there is danger that any liquid components of the fat will supercool and not solidify.

For most tests with hard fats it is recommended that a ball $\frac{3}{8}$ in. (9.525 mm.) in diameter be used. The weight applied to this ball should be such that, for the tests to be made, the ratio of the diameter of the impression d , to the diameter of the ball D , ranges between 0.15 and 0.45. When the ratio d/D falls outside of this range, the weight on the ball should be changed. If the available weights do not yield ratios within the suggested range, a ball of either a smaller or larger diameter should be used.

The impression in the test sample is made by turning the loading screw (Figure 1) until the weighted test ball is supported entirely by the sample. Timing is begun the moment the entire load is supported, which can readily be determined by watching the point at which the load rests on the upper C-type support. After exactly one minute the loading screw is turned backward, and the sample is lowered until the test ball no longer touches it.

The diameter of the impression is measured with the aid of a cathetometer or a magnifying glass with a built-in scale. It is desirable that this measurement be accurate to within 0.02 mm. A movable lamp can be used to advantage to bring into sharp definition the edges of the impression. Two diameters of the impression can be measured at right angles to each other, and their average value can be used in calculating the hardness, though, if the instrument has been built as described, the two measurements have nearly always been found to be equal.

The hardness index is calculated from the formula:

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

where H is the hardness index, P is the weight of the ball in kilograms, D is the diameter of the ball in millimeters, and d is the diameter of the impression in millimeters. In the above equation the denominator is the curved area of the impression in terms of the diameters of the impression and ball while the factor 100 in the numerator reduces the dimensions of the hardness index to kilograms per square centimeter.

Test Data and Discussions

It has been the experience of metallurgists that hardness as measured by the Brinell method is relatively independent of the size of ball and weight used in the measurement. To check the effect of these factors when measurements are made on a fat, test samples were prepared from highly hydrogenated cottonseed oil. All of the samples or test disks were molded at one time and tempered as a group to ensure uniformity.

The effect of changes in the test weight on hardness values determined at different temperatures, using a $\frac{3}{8}$ -in. ball, is indicated in Figure 2. As is evident from these curves, when the ratio d/D begins to exceed 0.15, the hardness index becomes practically independent of the applied weight. Because the maximum test load used in this series was 6.2 kg., the ratio d/D for the various determinations was always below 0.45. The highest ratio obtained was approximately 0.40 for one of the tests made at 50°C .

In Figure 3 are shown the effects of varying the size of the test ball and varying the load on the ball; the latter is expressed in terms of d/D . The data indicate that varying the size of the ball does affect the hardness value but not to an important degree between d/D values of about 0.15 and 0.45. Deviation from an approximately average value is generally a matter of a few percentage units.

The hardness index has been found to vary with the length of time that the test weight is applied, and

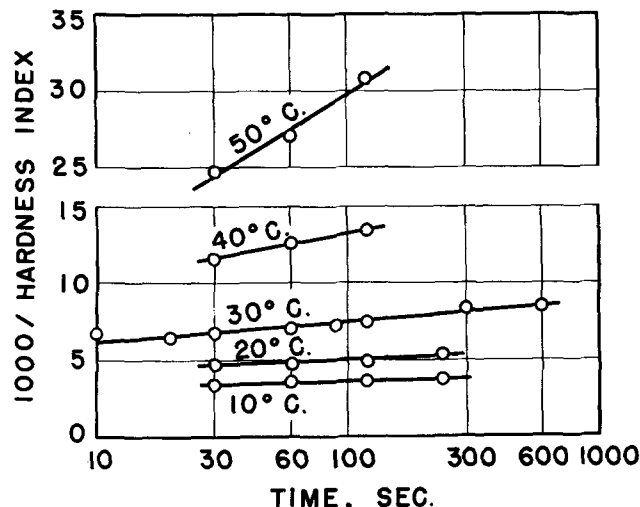


FIG. 4. Variation of reciprocal of hardness index with length of time test load is applied. Data obtained with highly hydrogenated cottonseed oil and $\frac{3}{8}$ -in. ball.

this variation can be significant when the time factor varies several-fold. For example, the hardness index of the highly hydrogenated cottonseed oil when tested at 30°C., using a 4.2 kg. weight and a 3/8-in. ball varied as follows:

Hardness index	Time, sec.
155	20
146	30
145	60
136	120
120	300

When the reciprocal of the hardness index is plotted on an arithmetical scale against the time on a logarithmic scale, the plotted points fall along a straight line. Such plots are reproduced in Figure 4.

Working with waxes, Von Rosenberg found a similar straight line relationship on plotting the reciprocal of the hardness index *vs.* the logarithm of the time.

The effect on the hardness index of varying the test weight, ball size, and length of time the weight was applied was investigated, using other fats and waxes. The results obtained with samples of cocoa butter, sugar cane wax, and ceresin wax are summarized in Tables I, II, and III, respectively.

TABLE I
Test Data for Cocoa Butter A

Ball size	Wt. applied	Duration of test	<i>d/D</i>	Hardness index
<i>inches</i> 3/16	kg. 0.2	sec. 10	0.252	17.4
	0.2	60	0.294	12.7
	0.2	120	0.294	12.7
1/4	0.2	60	0.228	11.9
	0.4	10	0.268	17.3
	0.4	60	0.315	12.4
	0.7	60	0.441	10.8
3/8	0.2	60	0.168	9.8
	0.5	10	0.210	15.8
	0.5	30	0.220	14.3
	0.5	60	0.262	10.0
	0.5	120	0.262	10.0
	1.2	60	0.409	9.6
1/2	0.7	60	0.228	10.3
	1.2	60	0.307	9.9
	1.7	60	0.346	10.8

TABLE II
Test Data for Sugar Cane Wax

Ball size	Wt. applied	Duration of test	<i>d/D</i>	Hardness index
<i>inches</i> 3/8	kg. 0.7	sec. 60	0.202	216
	1.2	60	0.265	213
	2.2	60	0.350	221
	4.2	60	0.479	218
	6.2	60	0.589	204
3/16	2.2	60	0.231	228
	4.2	10	0.298	260
	4.2	30	0.302	252
	4.2	60	0.309	242
	4.2	120	0.315	232
	6.2	60	0.390	219
1/4	4.2	60	0.249	210
	6.2	60	0.301	211
3/8	4.2	60	0.163	221
	6.2	60	0.202	211

As indicated above, the temperature at which hardness is determined and the thermal history of the test sample have a pronounced influence on the hardness value obtained. From Figure 5 it is evident that the hardness of cocoa butter B changed significantly with temperature. As the test temperature increased from about 12 to 20°C., the hardness index decreased about 50%. Obviously, in this particular case, the obtaining of accurate results required controlling the tem-

TABLE III
Test Data for Ceresin Wax

Ball size	Wt. applied	Duration of test	<i>d/D</i>	Hardness index
<i>inches</i> 3/16	kg. 0.2	sec. 60	0.214	24.4
	0.4	60	0.298	24.6
	0.7	10	0.336	33.8
	0.7	60	0.395	24.2
	0.7	120	0.407	22.7
1/4	0.4	60	0.230	23.6
	0.7	60	0.298	24.4
	1.2	60	0.389	24.1
3/8	0.7	60	0.203	23.8
	1.2	10	0.225	33.0
	1.2	30	0.245	27.8
	1.2	60	0.262	24.0
1/2	1.2	60	0.205	22.4
	2.2	60	0.266	24.0

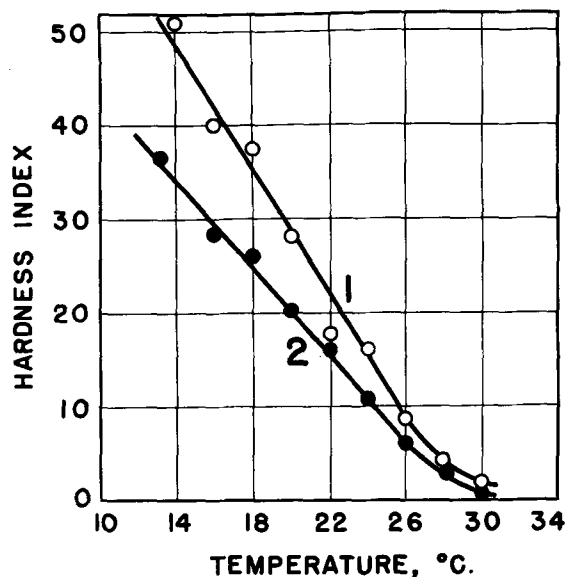


Fig. 5. Hardness curves for cocoa butter B: 1) bars molded by manufacturer and stored at room temperature (24–28°C.) for several months before testing; and 2) test samples obtained by melting some of the bars, seeding the melt as it resolidified, and tempering the resolidified cocoa butter for 24 hrs. Tests made with a 3/8-in. ball and load applied for 1 min.

perature to within a small fraction of one degree. Apparently the great change in hardness between 12 and 20°C. can be attributed to a softening of the fat crystals and not to partial melting. It has been found (4) that over this range the liquid content of cocoa butter changes by about 2 or 3 percentage units.

Practically all fats and waxes are able to exist in two or more polymorphic forms, hence their hardness at a given temperature is affected by the amount of tempering each sample received prior to testing, where tempering refers generally to holding a sample a few degrees below its melting point for a period of time. Seeding a fat with crystals of its highest melting polymorphic form as the fat begins to solidify and aging the solidified fat for extended periods of time also tend to temper it. Invariably the best tempered samples are the hardest.

Of the several fats and waxes which were investigated, cocoa butter was found to be the most sensitive with respect to the effect of tempering on hardness. By varying the thermal history, differences in hardness varying over sevenfold could be brought about. The differences in hardness observed under a specific set of test conditions are recorded in Table IV.

TABLE IV
Effect of Tempering on Hardness of Cocoa Butter C^a

Sample	Wt. applied	d/D	Hardness index
	kg.		
Bars tested as received from manufacturer	0.7	0.181	29.8
	1.2	0.229	31.7
Cocoa butter melted by heating to 38°C., melt seeded on solidification, tempered for 5 hr. at 27°C., cooled for 10 min. at 5°C. to release from mold.	0.7	0.181	29.8
	1.2	0.232	30.8
Cocoa butter melted by heating to 50°C., solidified, and held for 5 hr. at 5°C.	0.2	0.134	15.6
	0.7	0.252	15.2
	1.2	0.331	15.0

^a Tests made at 15°C., 3/16-in. ball used, and load put on ball for 60 sec.

Even well tempered samples of cocoa butter tended to show differences, as is evident from the curves in Figure 5.

Several of the conditions recommended in carrying out the hardness tests were not investigated extensively. The recommendation that the thickness of the test sample at the point of indentation be at least 10 times the depth of the indentation is based on the observation that this thickness always yielded reproducible results with the fats and waxes which were tested. It appears to be larger than necessary. The thickness recommended is a convenient one; also it conforms with the specifications of the A.S.T.M. test for determining the Brinell hardness of metals.

On the basis of considerations similar to the above it was recommended that the distance of the center of the indentation from the edge of the sample or edge of another indentation be at least two and one-half times the diameter of the indentation.

With regard to the reproducibility of results, hardness values obtained under identical conditions have generally been found to deviate no more than two or three percentage units from an average value. For example, successive measurements of the hardness of sugar cane wax, made at 30°C. and using a 3/16-in. ball, 4.2 kg. weight, and a test time of 60 seconds, gave the following hardness values: 235, 238, 245, 242, and 242. The average for the series is 240, and the maximum deviation is 2.1%.

To show the versatility of the instrument which has been described, hardness values determined for a variety of fat and wax products are recorded in Table V. It is believed that this is the first time that the hardness of these compounds has been shown on a common scale. Unless noted otherwise, the hardness of each sample was determined after heating it to a

TABLE V
Hardness Values of Several Fat and Wax Products^a

Product	Test temperature	Hardness index
	°C.	
Rosin.....	30	860
Carnauba wax.....	30	420
Sugar cane wax.....	30	320
Crude candelilla wax.....	30	250
Rice bran wax.....	30	210
Tristearin.....	30	170
Hydrogenated cottonseed oil.....	30	140
Hydrogenated jojoba wax.....	30	65
Ceresin wax.....	30	25
Paraffin.....	30	24
Chocolate liquor.....	25	19
Beeswax.....	30	17
Cocoa butter (aged).....	25	15
Commercial candy fats other than cocoa butter.....	25	4-12

^a Ball and load sizes varied to suit the individual products. Test load applied for one minute in all cases.

few degrees above its melting point, pouring the melt into the mold, cooling the sample to room temperature, and then determining the hardness.

Summary

Heretofore a good method for measuring the hardness of fats and waxes has not been available. Instruments currently used to measure hardness (not consistency) are relatively inaccurate and give results based on an arbitrary scale.

A new instrument and technique have been devised for measuring the hardness of fats and waxes. They are essentially an adaptation of the Brinell hardness test used for metal and alloys. In determining the hardness of a fat or wax, a perfectly round steel ball having a diameter as small as 0.1250 in. or as large as 0.5000 in. is pressed with a force of 200 g. to about 6 kg. onto the surface being tested. The hardness index, in terms of kilograms per square centimeter, is determined from the slight impression produced. The index is relatively independent of ball size, test load, and other test conditions, provided these are confined to certain ranges.

Hardness indices have been determined for products ranging from poorly tempered cocoa butter to rosin. Differences in hardness observed have varied over 1500-fold. The hardness of cocoa butter has been found to vary over seven-fold, depending on thermal history.

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Ion Exchange Resin Catalyst Stability in in-situ Epoxidation¹

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THE expanding epoxide applications within the last decade as plasticizers and chemical intermediates have sparked the development of improved epoxidation processes. Evidence of this development is the use of a solid ion exchange resin catalyst in the *in-situ* epoxidation process. Vital to the success of this process is the stability of the resin catalyst to physical breakdown when exposed to the highly oxidizing conditions of epoxidation.

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Factors affecting resin catalyst stability have been evaluated in our laboratory in an effort to extend resin life, thereby making this process more attractive for epoxidation. This paper presents a method for evaluating resin stability and shows how metal contamination and cross-linking of the ion exchange resin, the concentration of hydrogen peroxide, the operating temperature, and the use of a complexing agent affect resin stability. The epoxidation process will first be reviewed briefly to provide background