Storage locale (indoor, outdoor, sheltered, or unsheltered containers) and the exterior coating on the containers in exposed locations were found to be of less importance than protection of the stored oil from atmospheric oxygen.

The most pronounced effect of prolonged storage on tung oil is a shortening of the heat test (gel time at 282°C.).

Uncontaminated tung oil does not spontaneously isomerize during storage.

Acknowledgment

The authors wish to express their appreciation to R. T. O'Connor of the Analytical, Physical-Chemical and Physics Division, Southern Regional Research Laboratory, for analyzing the stored oil samples for beta-eleostearic acid, and to C. W. Goodyear Sr., of Bogalusa Tung Oil Inc., for supplying the oil used in this work.

REFERENCES

1. American Oil Chemists' Society, Official and Tentative Methods, 2nd Ed., edited by V. C. Mehlenbacher, Chicago, 1946, rev. to May 1951.
2. Anon., Natl. Paint Varnish Lacquer Asso., Sci. Sect. Circ., *651*, 15 pp. (1943).
3. A.S.T.M. Specification for raw tung oil, D12-48.
4. Eisenschiml, G., Am. Paint J.,*30*, (28) 76, 78, 80; Paint Oil Chem. Rev., *109*, (7) 16, 18 (1946); Official Digest Federation of Paint & Varnish Production Clubs, No. *255*, 170-2 (1946); C.A., *40*, 3621 (1946).
5. Gardner, H. A., Ind. Eng. Chem., *8*, 997-8 (1916); Paint Mfrs. Asso. U. S. Ed. Bur. Circ., No. *40*, 4 pp. (Nov. 1, 1916); C.A., *10*, 3168 (1916).
6. Gardner, H. A., Ind. Eng. Chem., *11*, 759-61 (1919); Drugs, Oils, & Paints, *35*, 9-10 (1919); C.A., *13*, 2139 (1919).
7. Gardner, H. A., Paint Mfrs. Asso. U. S. Circ. No. *205*, 12-24 (June, 1924); C.A., *18*, 2815 (1924).
8. Holmes, R. L., and Pack, F. C., J. Am. Oil Chem. Soc., *25*, 163-7 (1948); C.A., *42*, 4767 (1948).
9. Hopkins, F. W., Am. Paint Varnish Mfrs. Asso. Circ. *297*, 28-31 (1927); C.A., *21*, 658 (1927).
10. McClure, E. A., Lingnan Sci. J., *9*, (3) 233-65 (1930).
11. Munroe, C. L., Thesis, University of Illinois, 1913.
12. O'Connor, R. T., Heinzelman, D. C., McKinney, R. S., and Pack, F. C., J. Am. Oil Chem. Soc., *24*, 212-16 (1947).
13. Pack, F. C., A.S.T.M. Bulletin No. 191, TP 93 (July 1953).

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A Quick Dilatometric Method for Control and Study of Plastic Fats

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DILATOMETRY has been widely used for studying phase change. Its use on fats was apparently first reported by Normann,[1] and a detailed study of many fats and fat mixtures has been described by Hofgaard.[2] Various types of equipment and modes of application have been recommended. Bailey [3] has contributed to design and use of the method and has reviewed developments in some detail.[4] A particularly interesting discussion of dilatometry as applied to margarine is that of Andersen.[5]

For several years dilatometry has been employed in our research laboratories for fundamental study of fat phase behavior and in our factory control laboratories for plant hydrogenation control. An apparatus of considerable convenience, and its method of application to control procedures are described here. With the equipment here described, results of good reproducibility are obtained within two hours.

The dilatometers used in this work are of the volumetric type, in which the fat sample in a glass bulb expands against a confining liquid (mercury), free to move in a glass capillary. By measuring the changes in length of the mercury column, the volume changes can be calculated for the fat sample. It is necessary only to know the fat weight and the capillary calibration for the instrument. No stem correction for exposed capillary is necessary. The effects of mercury and glass expansion are eliminated by the process of taking "liquid" readings. The final determined value is put in terms of "solid content" as deduced from the rather general principle that complete solidification of most fats involves a change of 10% in specific volume upon total solidification — or 0.1% change upon 1% solidification. Details are presented later.

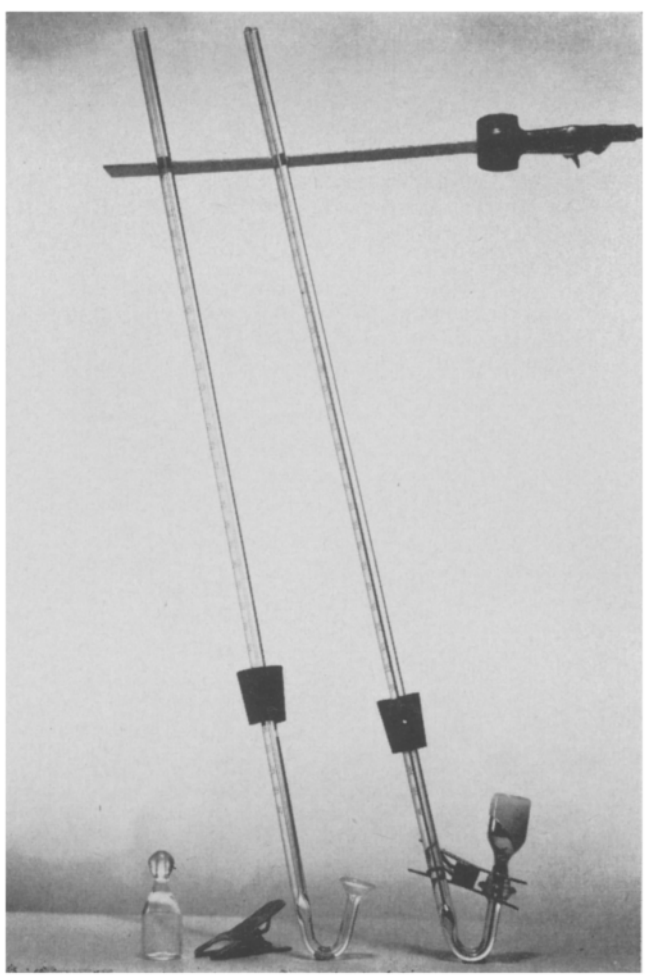

FIG. 1. Picture of unassembled and assembled filled dilatometers.

Apparatus

A picture of the dilatometer is given in Figure 1. The glass capillary as shown in the picture was of

precision bore tubing approximately 6-8 mm. OD and having a uniform, circular bore diameter between 1.02 and 1.07 mm. The capillary tube was graduated in centimeters and subdivided in millimeters starting exactly from the top edge. The graduations were carried through 40 cm. of length and the total length of capillary was not less than 55 cm. The graduated, precision bore tubing was purchased from Scientific Glass Apparatus Company Inc., Bloomfield, N. J., or from Ace Glass Inc., Vineland, N. J.; and the apparatus was fabricated in our own glass blowing shop.

The capillary was calibrated in order to obtain the exact volume per unit length at various points by filling it with mercury (using suction to avoid small air pockets), draining the mercury from the capillary in approximately 5 cm. increments through a special valve arrangement, and weighing each volume of mercury thus obtained on an analytical balance. From the specific volume of mercury at the temperature at which the calibration was performed, the volume per unit length of capillary at each point was calculated. For ordinary work the over-all average calibration value was used. For very precise work or where precision bore tubing was not used, calibration curves were drawn, from which could be obtained the exact volume per unit length of capillary corresponding to any point on a given tube.

The volume of the bulb for holding the sample was made so that the volume ratio of fat to confining liquid was between 3:1 and 4:1. For a 5-g. sample, which was normally used for stocks of low to medium hardness, the bulb size was about 7.3 cc. For firm stocks a 3-g. sample was used in a bulb of about 4.3 cc. volume.

The bulb was joined to the capillary by means of a ball and socket joint. For sealing the joint a small amount of stopcock grease, somewhat soluble in the usual organic solvents, was preferred. Experience showed that insoluble stopcock grease (of the silicone type) got into the capillaries and changed the calibration.

A constant temperature bath capable of holding a temperature in the range of 10°C. (50°F.) to 60°C. (140°F.) with an accuracy of ± 0.05°C. was used. Temperature variations of this order affected the height of the confining liquid in the capillary by about ± 0.017 cm., which was just perceptible to the eye.

Solid Content Index (SCI) Theory

The definition of Solid Content Index can be simply developed from the schematic diagram for a hypothetical fat in Figure 2. At high temperatures, like actual fats, this fat is completely melted and its specific volume is linear with temperature. At low temperatures it is completely solid, and the important approximations are made that the specific volume is linear with temperature, runs parallel to that of the liquid fat, and is precisely 0.1 units lower in specific volume for a given temperature. When melting begins, the volume-temperature relationship follows the course indicated by the curved line of the diagram. At 70°F. (21.1°C.), for example, the specific volume of the partially melted fat is "X." The approximate amount of solids, expressed as percentage, at "X" is given by the simple relationship:

$$\% \text{ solids} \cong \frac{A}{B} \times 100$$

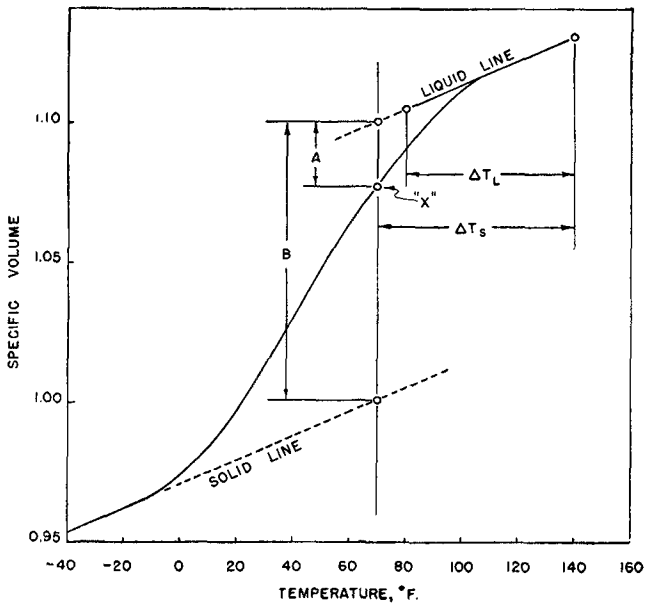

FIG. 2. Solid Content Index Theory.

Assuming B = 0.1 as previously indicated, SCI is defined by the equation:

$$\text{SCI} = \frac{A}{0.1} \times 100 = 1000A$$

Among actual fats it may be very difficult, experimentally, to realize the condition of complete solidity. This and reasons of simplicity justify the approximations made.

By confining the fat in a glass bulb and measuring its expansion against a confining liquid, such as mercury, in a glass capillary, the value of "A" at any desired temperature can be calculated from "liquid" and "solid" readings of the height of mercury in the capillary. Stem corrections are neglected since they are small and are essentially the same from one comparable case to another. The effect of volume changes due to glass and mercury is eliminated by the subtraction term in the equation for determining "A" which follows:

$$A = \frac{1}{1000}\left(R_s C_s - R_L C_L \frac{T_o - T_s}{T_o - T_L}\right) \times \frac{1}{W}$$

$$\text{SCI} = \frac{R_s C_s - R_L C_L \Delta T_s / \Delta T_L}{W}$$

where R_s = Solid reading, the distance in centimeters from the top of the dilatometer to the mercury at the temperature T_s at which the amount of solids is being determined.

C_s = Dilatometer calibration value in mm.³/cm. at R_s.

R_L = Liquid reading, the distance in centimeters from the top of the dilatometer to the mercury at the temperature T_L at which the sample is completely liquid.

C_L = Dilatometer calibration value in mm.³/cm. at R_L.

$\Delta T_s = T_o - T_s$, where T_o is the reference temperature at which the mercury level is even with the top of the dilatometer.

$\Delta T_L = T_o - T_L$.

W = weight of sample in g.

The SCI is a convenient arbitrary measure of the solids in a fat, precise and reproducible if not identical with actual % solid. It compares with percentage of free fatty acid expressed as oleic acid for a convenient arbitrary method of expressing the free fatty acid in a fat.

Sensitivity of the Instrument

Sensitivity is determined by the bore of the capillary and the sample size. There is an optimum sample size for each bore tube to utilize the full calibrated length of the capillary tube. The same sensitivity can be obtained with a large bore tube and a large sample or a small bore tube and a small sample. For a given bore tube, sensitivity can be improved by using a longer capillary tube and a larger sample.

The dilatometer used in this work had a sensitivity of about 1.7 SCI units per cm. reading on the capillary tube when a 5-g. sample was used or about 2.9 SCI units per cm. when used with a 3-g. sample. The maximum SCI which could be measured at 70°F. (21.1°C.) was 30 with a 5-g. sample and a 40-cm. capillary. For firmer samples, or if the SCI at temperatures less than 70°F. were desired, a 3-g. sample was used. With a 3-g. sample the maximum SCI which could be obtained with the 40-cm. capillary was 80 at 70°F. (21.1°C.).

The precision of the SCI determination with this equipment when using a 3-g. sample was obtained by making 15 repeated determinations of the SCI of a single sample of fat at several temperatures. The experimental results, expressed as standard deviation, are given in Figure 3. This represents about what can be expected in a single laboratory. Actual plant experience among several laboratories, mostly with 5-g. samples, in routine, factory, hydrogenation control analysis indicated a somewhat greater standard deviation at small SCI values, but smaller standard deviation at large SCI values.

This degree of precision has been satisfactory for consistency control of shortening and margarine oils. More precise instruments can readily be designed by increasing the sample size and lengthening the dilatometer capillary; however the longer the capillary, the more awkward to handle and the greater the breakage.

The following information may prove helpful in designing an instrument to meet some particular requirements of sensitivity (SCI/cm.), sample size or length or bore of capillary. In Figure 4 the effect of capillary size on sensitivity is shown. In Figure 5 the value of the solid reading, R_s, at 70°F. (21.1°C.) (which determines the length of the calibrated portion of the dilatometer) is indicated as a function of sensitivity for various hardnesses of fat. In Figure 6 the sensitivity is given as a function of the probable percentage error in SCI. From these curves the

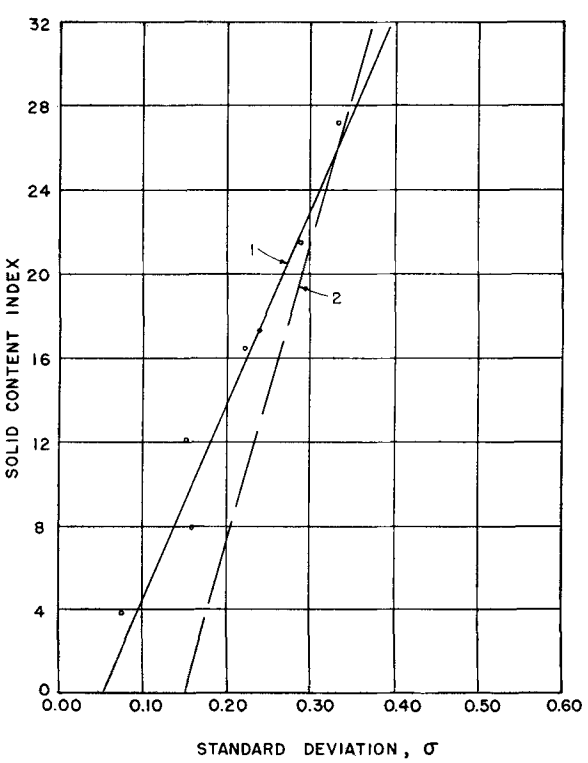

FIG. 3. Precision of Solid Content Index measurements; (1) single laboratory, (2) eleven laboratories.

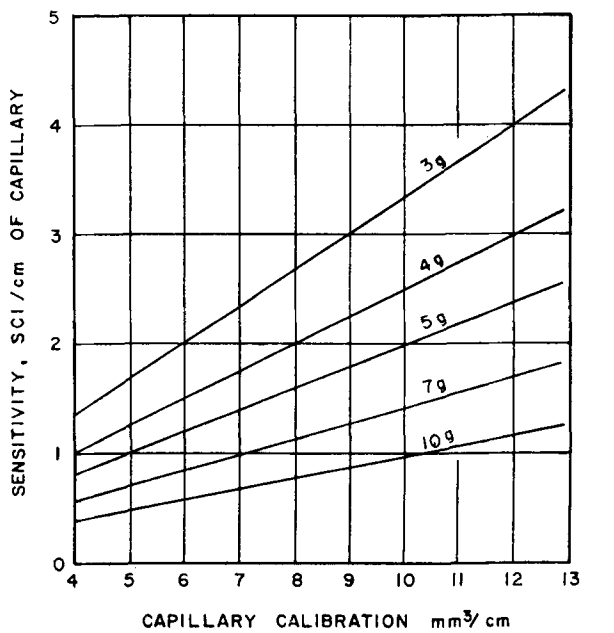

FIG. 4. Effect of capillary size on sensitivity for various sample weights.

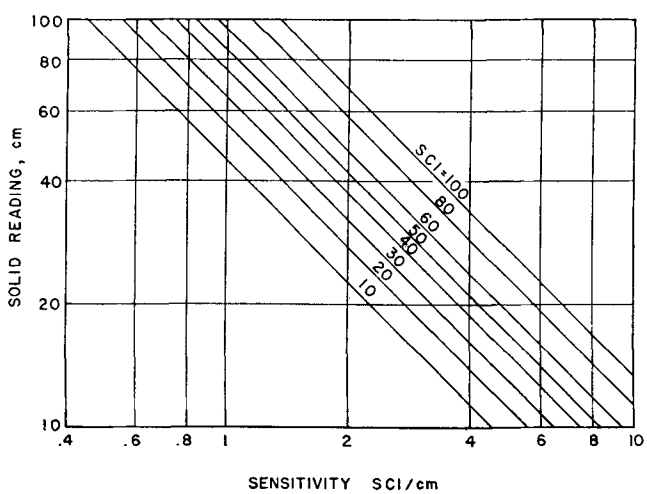

FIG. 5. Variation of solid reading at 21.1°C. (70°F.) with sensitivity.

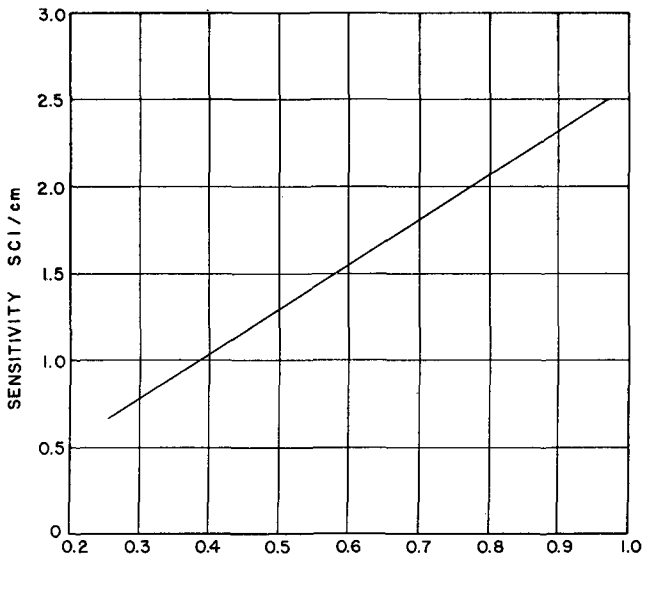

FIG. 6. Relations of error in SCI to sensitivity.

length and bore of the dilatometer capillary and the sample size required to meet a desired precision of measurement can be obtained. The recommended bulb volume for a given size sample can be calculated from the equation:

$$V = 1.45\ W$$

where V = bulb volume in cc.
W = sample weight in g.

Dilatometric equipment of this design has been used successfully for several years for factory control of the hydrogenation of edible fats. The degree of uniformity in consistency of finished products has been substantially improved over that obtained by iodine value or other methods of control.

Details of the Analytical Procedure

An appropriately sized sample (3.00 to 5.00 g. depending on the expected SCI of the oil tested) of clear melted oil was introduced into a tared dilatometer bulb by means of a small pipette with an elongated tip. The exact sample weight was obtained by reweighing the bulb and fat on an analytical balance to ± one mg. Sample weights were adjusted to exactly 5.00 g. for SCI expected to be 25 or less; to 4.00 g. for SCI expected to be between 25 and 40, and to 3.00 g. for SCI expected to be over 40 by adding or removing drops of oil from the bulb. Such sample size adjustment assured good accuracy by permitting nearly a maximum reading on the 40 cm. dilatometer, and it simplified the final calculations.

The dilatometer tube was joined to the bulb with a small quantity of stopcock grease to lubricate the joint. The open end of the dilatometer tube was attached to the mercury supply with a short piece of rubber pressure tubing. A tubing clamp insured a tight joint. The mercury supply consisted of a small cup of mercury closed at the bottom by a three-way stopcock. One arm of the stopcock was connected to the dilatometer, and the other arm was connected in series to a trap to catch back-flow of mercury, to a second trap pocketed in dry ice to remove moisture and solvents, and finally to a vacuum pump equipped with a manometer.

The bulb of the dilatometer was supported in a beaker of hot water (80 to 100°C.) and the dilatometer evacuated to less than 6 mm. pressure. When bubbles were no longer visible in the fat, the bulb was immersed for one minute in a dry ice-alcohol bath to freeze the fat. To insure complete removal of the dissolved gases, the fat was remelted in the hot water bath. It was often necessary to turn off the vacuum during remelting to avoid spattering. When all additional gas bubbles were removed (at 6 mm. pressure), the fat was refrozen in the dry ice-alcohol bath.

Mercury was introduced into the capillary and bulb by turning the three-way stopcock of the supply vessel. When mercury completely filled the capillary and bulb, the stopcock was turned to a neutral position, the dilatometer was disconnected from the mercury supply and carefully turned upright so that the inevitable, small air bubble moved around the bend in the capillary. A "mercury catcher" consisting of a one-hole cork stopper inserted in a 1¼-in. piece of 18 mm. glass tubing was placed on the end of the dilatometer tube. The small bubble in the capillary was removed by inserting a piece of clean nichrome wire into the capillary. Overflow of mercury displaced by the wire was caught in the cup on top of the dilatometer tube formed by the "mercury catcher."

The filled dilatometer was placed in the reference temperature bath at 60.0° ± 0.05°C. (140°F.) so that the bulb was about 1 in. below the surface of the water. When expansion of the fat and mercury stopped (in about 20 minutes), the mercury on top of the dilatometer tube was removed by scraping with a straight edge so that the meniscus was flush with the top of the capillary tube. The dilatometer was removed from the 60°C. constant temperature bath, and after the mercury had receded a few mm. from the top of the capillary, the "mercury catcher" was stripped off into a container of mercury for reuse.

The dilatometer was then placed in a second constant temperature bath maintained at 26.7° ± 0.05° C. (80°F.). The drop in mercury level was followed by means of a small metal clip until the mercury level remained constant. Equilibrium was reached in 7-10 minutes. The distance from the top of the capillary to the mercury meniscus was measured to the nearest 0.01 cm. and recorded as the liquid reading, R_L. At this point in the determination the sample had to be still completely liquid. If a cloud formed, the sample was remelted at 60°C. (140°F.) and held at a higher temperature (as 100°F.) to obtain the liquid reading.

After the liquid reading was obtained, the fat was solidified by immersing the bulb in an ice water bath at 0-2°C. (32-36°F.) for a minimum of 5 minutes. For very hard stocks 10 minutes were used. The fat was then tempered by immersing the bulb in a constant temperature bath held at 26.7 ± .05°C. (80°F.) until the mercury level remained constant. Approximately 30 minutes were usually required. For stocks which melted at 26.7°C. (80°F.) a lower temperature was used, *i.e.*, 21.1 ± 0.05°C. (70°F.).

If the Solid Content Index was to be determined at 26.7°C. (80°F.), the distance to the nearest 0.01 cm. from the top of the dilatometer to the mercury

level was measured and recorded as the solid reading, R_s.

To determine the Solid Content Index at temperatures below 26.7°C. (80°F.) the fat was rechilled for 5 minutes in the ice bath and then put in a constant temperature bath at the temperature of interest. If measurement were to be taken at a series of temperatures on a given sample, the measurement had to be taken at the lowest desired temperature first and then at each succeeding higher temperature. If the solid fat approached a constant temperature from the high side, misleading results were obtained due to super cooling. Correct results were obtained only by remelting the fat in the bulb and repeating the chilling, tempering, and rechilling cycle. The Solid Content Index was calculated from the readings, using the general formula previously described.

After completing the determinations, the dilatometers were cleaned in the following fashion. The spherical joint was opened and the mercury poured into a container for salvage. The fat in the bulb was melted on a steam or hot water bath and poured out of the bulbs. The bulbs were washed several times with ethyl ether and air dried.

The tubes were cleaned by sucking successively through the capillary ethyl ether, alcohol, distilled water, concentrated nitric acid, distilled water, alcohol, and ethyl ether by means of a water aspirator. Precautions had to be taken to prevent the nitric acid from coming in contact with the alcohol during this cleaning sequence.

The mercury was cleaned after each use with successive washes with 10% potassium hydroxide, 15% nitric acid, and distilled water and filtered through an adhesion type of filter according to a recognized general procedure for cleaning mercury. The criterion for cleanliness of the mercury was that it must not hang up in the dilatometer capillary during contraction of the mercury column.

Normal precautions were taken to avoid mercury poisoning by keeping the working area well ventilated and cleaning up spills immediately.

Discussion

The tempering period at 80°F. (26.7°C.) after solidifying the fat, before making the solid reading, is perhaps the principal difference between the present dilatometric method and other methods. This step was introduced for two reasons. First, a major field of interest was the phase behavior of shortenings which are usually tempered for some hours at a temperature near 80°F. after being packed. In seeking a method of hydrogenation control it was natural to assume that better correlation with final product consistency could be obtained if the test sample and the product were both subjected to nearly the same temperature history. Second, it was demonstrated experimentally that better precision was obtained and less time was taken over-all for the test when the 80°F. tempering step was included in the method. Without tempering the solid reading tended to drift, sometimes for hours, before an approximately steady state was established.

Figure 7 shows the effect of 80°F. tempering time on the SCI-temperature relationship of a commercial shortening. The plot of SCI *vs.* temperature has been customarily made as shown because of the similarity of the curve when plotted this way to the normal

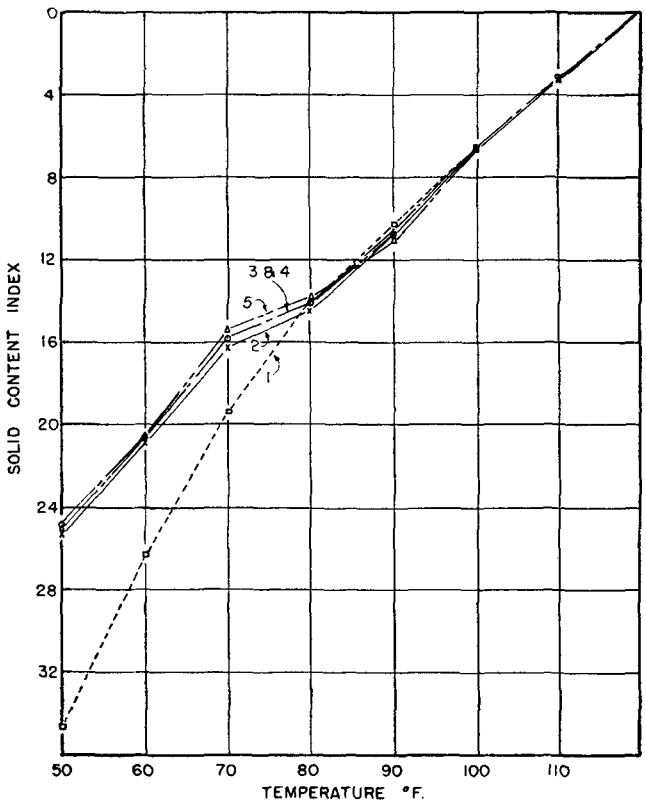

FIG. 7. Effect of tempering: (1) not tempered, (2) tempered ½ hour at 26.7°C. (80°F.), (3) tempered 1 hour at 26.7°C., (4) tempered 4 hours at 26.7°C., (5) tempered 24 hours at 26.7°C.

penetration *vs.* temperature curve, showing shortening consistency. The effect of tempering is to decrease the amount of solids at temperatures less than the tempering temperature. In this particular example, tempering equilibrium was not established in ½ hour at 80°F. but was achieved substantially in one hour at 80°F. Softer stocks, such as hydrogenated shortening base or margine oil, normally are completely tempered in ½ hour at 80°F.

A study of the SCI *vs.* temperature curve of a shortening or other fat can reveal valuable information with regards to its composition of intermediate melting and trisaturated glycerides. The intercept at zero SCI is, of course, the complete melting point of the stock.

Summary

A dilatometric method is presented which is of considerable convenience and reliability in application to commercial fats, notably shortening and margarine. The instrument is of volumetric type with mercury as confining fluid. The simplified calculations give results in terms of "Solid Content Index," which is an approximation to the true % solid. The apparatus is applicable not only to basic study of composition and processing but is adaptable to hydrogenation control where it has been used with notable success for several years. With shortenings, for instance, the method cuts substantially the deviation from normal consistency encountered with the best thermal methods. Despite the high precision the determination can be completed in about two hours. Part of the reason for the combined precision and speed is a "tempering" step introduced to expedite approach to a steady state prior to final measurement.

REFERENCES

1. Normann, W., Chem. Unschau Gebiete, Ole, Wachse us. Harge, *38*, 17-23 (1931).
2. Hofgaard, K., Dilatometriske Fedstof-Undersogelser, J. Jorgensen, Copenhagen, 1938 (English Summary).
3. Bailey, A. E., and Kraemer, E. A., Oil & Soap, *21*, 251-253 (1944).
4. Bailey, A. E., pp. 91-105, "Melting and Solidification of Fats," Interscience Publishers Inc., New York (1950).
5. Andersen, A. J., Inst. Chem. Engrs. (London) and Soc. Chem. Ind. (London) Chem. Eng. Group, Advance Copy (1944), 2-11; also in Food, *13*, 37-42 (1944).
6. Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, Cleveland, Ohio.

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Tall Oil Studies. III. Bactericidal Activity of Polyethenoxy Tallate Ozonides. Identification of the Active Principle

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IN the preceding article (1) it was shown that polyethenoxy tallates (tall oil-ethylene oxide condensates) could be successfully decolorized with ozone. We have shown herein that completely ozonized polyethenoxy tallates can be prepared and that these substances are bactericidal nonionic detergents. It was further noted that polyethenoxy tallate ozonides containing a larger proportion of fatty acid were more effective bactericides than those containing more rosin acid. Polyethenoxy oleate ozonide was then prepared and showed greater germicidal activity than the corresponding tall oil derivatives. Up to this point the fat-soluble, water-soluble ozonides had been assumed responsible for the germicidal activity. However it was soon found that decomposing the ozonides to their corresponding acids (*e.g.*, by hydrogen peroxide in aqueous acetic acid) not only increased bactericidal activity but that the active principle could be separated from the residual polyethenoxy esters by steam distillation. The activity was volatile with steam. The steam distillate was investigated and found to contain pelargonic acid (I)

$$CH_3—(CH_2)_7—COOH \qquad (1)$$

a known decomposition product from the ozonization of oleates. Pure pelargonic acid was then obtained, and its bactericidal activity was ascertained. It soon became evident that the active bactericidal principle was essentially pelargonic acid and that the activity varied with the pH of its solution. In connection with these results the effect of pH on the germicidal activity of the fatty acids in the 9- to 12-carbon range was studied and undecylic acid exhibited the highest activity (2). Figure 1 illustrates the bactericidal activity of pelargonic acid *vs.* pH.

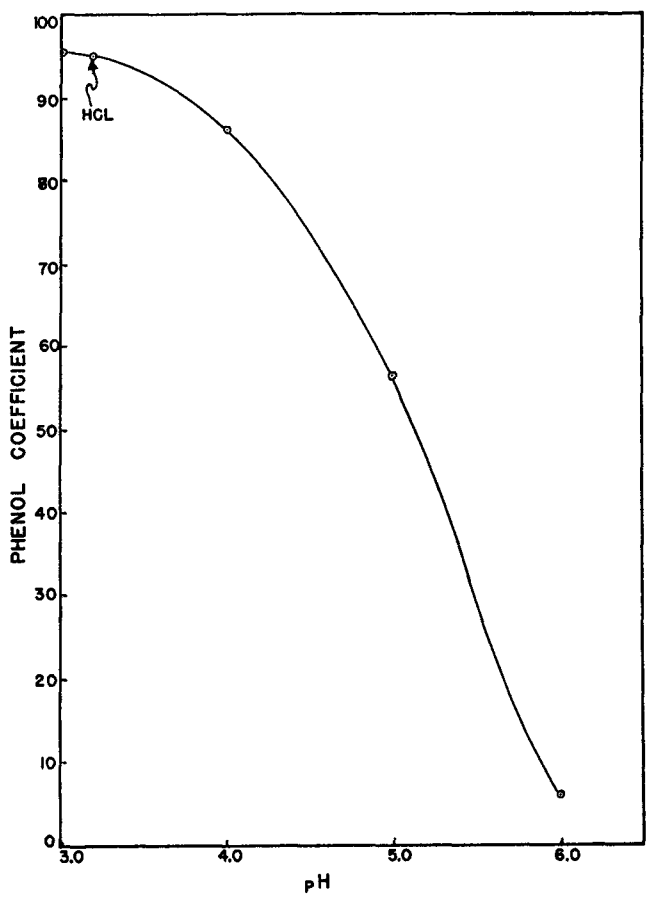

FIG. 1. Variation in "phenol coefficient" of pelargonic acid with pH.

Experimental Details

Preparation of Polyethenoxy Oleate Ozonide. Polyethenoxy oleate was prepared by condensation of pure oleic acid with 13 moles of ethylene oxide as described in a preceding article (3). Ozone, generated by the apparatus described in our previous report (1), was passed into 100 g. of polyethenoxy oleate until the gas was no longer absorbed. A total weight of 5.9 g. of ozone was absorbed by the ester giving polyethenoxy oleate ozonide as a water-soluble, light yellow oil with detergency values (*i.e.*, soil removal and whiteness retention in hard and soft water) comparable to the original polyethenoxy tallates (4). The ozonide possessed a phenol coefficient of 11 without acidification. Similar ozonides prepared from polyethenoxy tallates possessed considerably lower phenol coefficients. It was noted that the phenol coefficient decreased with increasing rosin acid content of the original tall oil.

Decomposition of Polyethenoxy Oleate Ozonide with Hydrogen Peroxide. The polyethenoxy oleate ozonide (20 g.) prepared above was dissolved in a mixture consisting of 100 ml. of water and 25 ml. of glacial acetic acid. Ten ml. of 30% hydrogen peroxide was added to the mixture, which was allowed to reflux for 1½ hours. A further quantity of hydrogen peroxide (2 ml.) was added with an additional reflux of 1½ hours. The product was then concentrated to a light yellow residual oil weighing 22 g., which was