Measurement of the Consistency of Plastic Vegetable Fats

A Standard Micropenetration Technique

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Introduction

It is noteworthy that there is no standard and generally accepted method for evaluating the highly important property of consistency in plastic fats. It is still customary to describe the hardness or softness of fats in terms of their melting points, setting points, titers, etc. These characteristics are more or less related to consistency, but singly or combined, they fail by a good deal to give an adequate picture of the body of a fat over the entire range of temperatures at which it is to be stored or used.

Among shortening manufacturers it has become rather general practice to employ some mechanical device for testing the body of commercial products after the latter have been solidified and filled into packages. However, as recently pointed out by Rich (4), there is nothing approaching standardization of methods or instruments among the different manufacturers. The instruments in use, moreover, are adapted only to the examination of relatively large samples of material.

Experience has shown that the initial solidification of a fat must be carried out very rapidly, so that the solidified crystals are small, if the later consistency of the fat is to be definite and predictable at any given temperature. Rapid chilling is attained as a matter of course in the chill rolls or votators used in solidifying commercial products. However, it is extremely difficult to solidify a large sample of fat quickly in the laboratory. Consequently, the above-mentioned devices are unsuitable for the examination of experimental or partly finished products.

The consistency of a plastic product must necessarily be measured according to an empirical procedure and expressed in arbitrary units. Hence any method is suitable for its determination if it gives reproducible results over a reasonable range of values. From the standpoint of simplicity and ease of manipulation of the instrument, the penetration technique of consistency measurement has much to recommend it. This is particularly true if the penetrating device is actuated simply by the force of gravity, as it is, for example, in the Goddard-Hewes (2) penetrometer, which employs a falling needle.

Freyer (1) has devised a micro-form of the falling needle-type of penetrometer. The sample required by the Freyer instrument is very small, and is solidified with sufficient rapidity by being simply poured into a small hole drilled in a chilled copper block.

The apparatus and technique described by Freyer were admittedly only suggestive, and were not standardized in all particulars. However, with proper standardization they are capable of yielding results of rather remarkable precision. One of the authors has, over a period of years, had a considerable amount of experience in the use of a modified Freyer micropenetrometer to check the consistency of hydrogenated cottonseed oil products. The results of this experience fully justify the statement that, in the case of these products at least, the micropenetration curve of a fat (penetrations plotted against temperature) may be considered as definite and characteristic as its melting point, solidification point, or titer. Furthermore, there is a close correlation between the micropenetrations and the actual consistency of the finished product, as determined by macropenetrations or other methods.

Unfortunately, the micropenetrometers previously used, by the authors and others, have not been of a design that can be readily reproduced, so that it has been difficult or impossible to obtain comparable results with the instruments in use in different laboratories. Particular difficulty is experienced in attempting to standardize the penetrating needle, inasmuch as ordinary darning needles are customarily used, and these vary considerably in length, weight and taper, even amongst needles of the same nominal size.

The work reported here had the following objects: (a) The design of an improved micropenetration apparatus, capable of being reproduced in all essential details. (b) Investigation of the various factors influencing the consistency of micro-solidified fat samples, in order to determine standard test conditions applicable to different kinds of fat. (c) The recording of micropenetrometer data on a variety of fat products, including commercial shortenings and margarines.

Theory of Plasticity in Fats

Plastic fats, such as lard, shortenings, butterfat and margarine oils, are composed of a solid phase of fat crystals intimately mixed with a liquid phase of fluid oil. Body is given to the fat by the tendency of the solid particles to interlock. Technically, the fat is plastic so long as this interlocking effect is sufficient to enable it to resist completely small deforming stresses. With the application of increased stresses, a point is reached where the structure of the product abruptly yields, and plastic flow occurs. The consistency of a fat—its relative hardness or softness—is simply a matter of the stress or load required to cause plastic flow.

The internal strength of the material, or its capacity for resisting such stress, is determined by the number of points of contact between the crystal particles. If the crystals are very small, there will be more points of contact and the fat will be firmer than if the crystals are relatively large. With crystals of a given size, the consistency will be determined
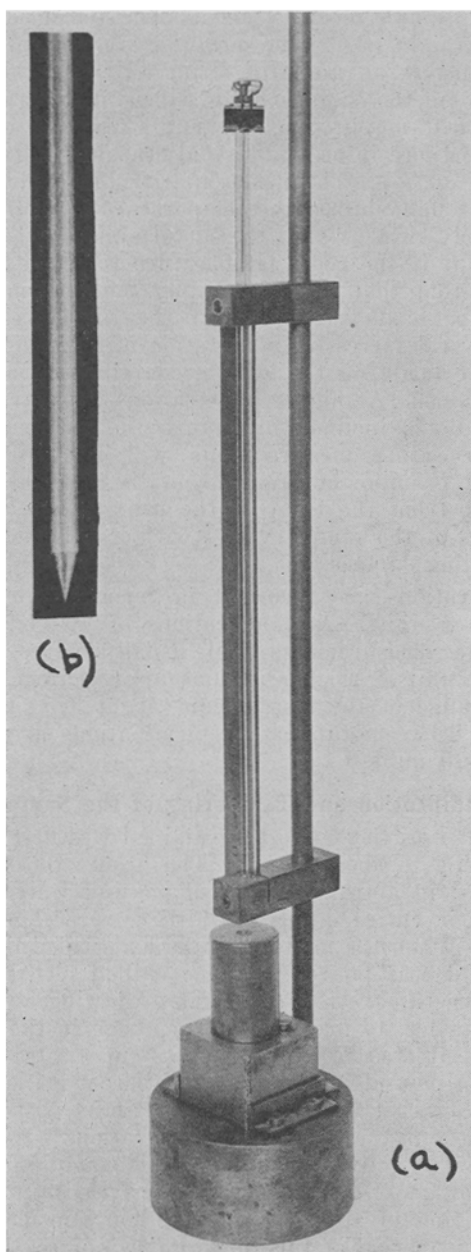
FIG. 1. Photograph of (a) micropenetrometer, and (b) point of micropenetrometer needle (enlarged).

FIG. 2. Dimensions and structural details of micropenetrometer.

by the number of crystals, or in other words, the relative proportions of fat existing in the solid and liquid states. These proportions are in turn determined primarily, but not entirely, by the temperature of the fat.

There are two factors which prevent the proportion of solids in a fat from being purely a function of temperature. One of these is the phenomenon of polymorphism, or the ability of fat crystals to exist in unstable modifications of low melting point. In order to insure that the crystals of a fat are small and uniform, it is necessary to form the crystals rapidly, by chilling the fat strongly. Unfortunately, rapid chilling also favors the formation of unstable crystal forms. The unstable forms are transformed irreversibly to higher melting forms of greater stability at temperatures below their melting point, but the transformation requires an appreciable time. The other factor which may lead to abnormal proportions
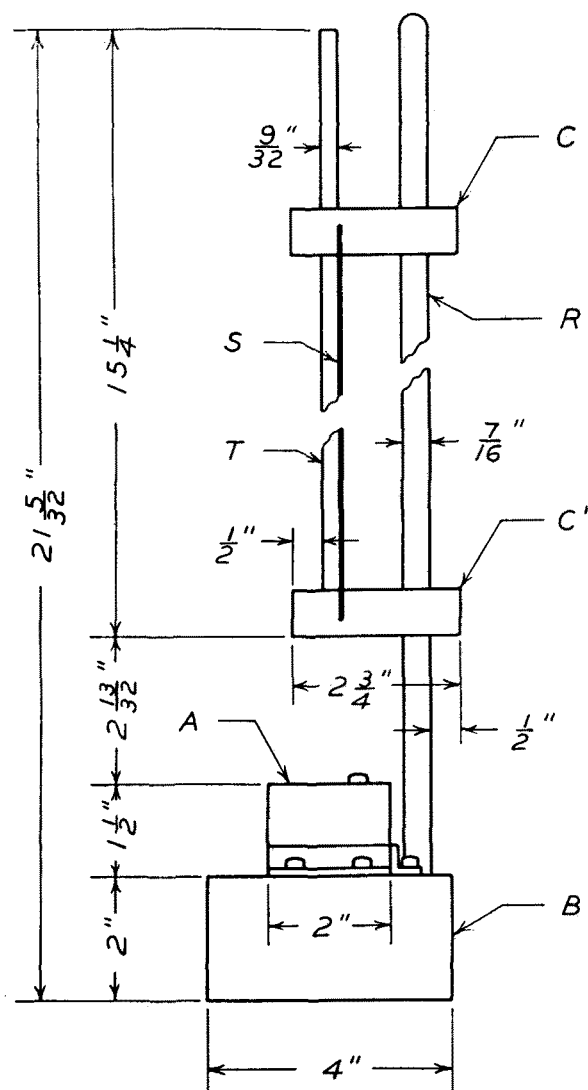
of solids and liquids is the pronounced tendency of fats to supercool in passing from a higher to a lower temperature. A fat which is in a supercooled condition contains, of course, an abnormally low proportion of the solid phase.

All of the foregoing considerations must be taken into account in the formulation of a standard micropenetration technique.

The Micropenetrometer

The design and construction of the micropenetrometer are shown in Figures 1 and 2.

The base, B, of the instrument is turned from a 4-inch billet of machinable cast iron, and the removable sample block support A is cut from a 2-inch square bar of mild steel. The top and bottom faces of both the base and sample block support must, of course, be exactly parallel. Two fillister-head machine screws are set in the top face of the sample block support to fix the position of the sample blocks with respect to the support. The inner sides of the machine screw heads are flattened so that they will bear solidly against the sides of the sample blocks when the latter are placed in the instrument. Three guides fashioned from $\frac{1}{2}$ x $\frac{1}{2}$ x $\frac{1}{8}$ inch angle iron are fastened to the base with heavy machine screws to

maintain the moveable sample block support in a fixed position with respect to the other members of the instrument. The guides, which are slotted, are adjustable on the base. When the instrument is first assembled they are so adjusted that when the needle is dropped into the sample under test, its point will strike the surface of the latter 1.0 to 1.5 mm. from its outer edge.

The penetrometer needle is directed in its fall by a glass capillary tube T of 1.5-1.75 mm. bore. Care must be taken to select a straight piece of tubing and to mount it exactly perpendicular to the top face of the base B. The tube and the steel millimeter scale S, immediately behind it, are held in position by a single set screw in each of the front end faces of the clamps, C and C^1. The clamps are made from ¾-inch square bar stock. Larger set screws in the other end faces fix the supports on a cold rolled steel rod R. The scale S is graduated in 0.5-mm. divisions. A needle release is made from a binder clip, a machine screw and two nuts. The distance that the needle drops measures 330 mm. from the point of the needle to the surface of the sample.

The cylindrical blocks in which the samples are solidified are turned from 1½-inch billets of bearing bronze. The finished blocks are 1⅜ inches in diameter, 2 inches high, and have a vertical hole in the top surface ⁵⁄₁₆ inch in diameter and 1⅝ inches deep. The outside dimensions of all blocks must be identical, in order that the solidified samples will be in the proper position when the blocks are placed in the penetrometer. The holes in the blocks must be accurately bored and centered. Each block is stamped with an identifying number.

The penetrometer needles were made from number 18½ music wire. If a length of this wire is stretched, and then heated and quenched in the stretched condition, perfectly straight sections can be obtained. This treatment does not affect the diameter of the wire appreciably; the original diameter is 0.042 inch, and the diameter of the finished needles will be about 0.0419 inch. The ends of the straightened sections are ground to a 30° conical point with the aid of a small jig and power grinder. The points are then specially tempered and given a final grinding with a fine oil stone. The needles are then cut to the proper length and ground to a square surface on the unsharpened end.

The finished needles weighed 0.5000 gram each, were 1.06 mm. (0.0419 inch) in diameter, and were 73.6 mm. long. The points were sufficiently hard that when the needles were dropped through the instrument into a bronze surface two or three times there was no evidence of blunting. The three needles prepared were found to give identical penetrations.

The temperature of the tempering bath used in connection with the instrument must be carefully controlled if precise and reproducible results are to be obtained. The bath used in the present work consisted of a 12-quart insulated earthen crock, stirred by an electric motor. It was heated by means of a 500-watt knife-type heater controlled through a vacuum tube relay by a mercury filled thermoregulator. The temperature, which was read with a low titer thermometer, could be maintained within 0.05° C. of that desired.

Before the needle is dropped into the tempered sample, the surface of the latter is scraped off even with the sample block by means of a spatula or other sharp straight edge. The scraping edge is inclined so that it makes an angle of about 45° with the block surface on the side *toward* which it is traveling. Very hard samples must be cut away carefully, in small portions, in order to avoid cracking and pitting the cut surface. The heat capacity of the blocks is sufficient to maintain the temperature of the sample reasonably well while the determination is being made, but if the room temperature is markedly different from that of the sample, the determination should be made promptly. If the fat is relatively firm, several successive penetration measurements can easily be made on the sample contained in a single sample block. At higher penetrations the entrance of the needle is inclined to disturb the entire sample, and succeeding measurements will be erroneously high. It is important for the needle to strike 1.0 to 1.5 mm. from the edge of the sample hole, as the hardness of the sample varies with its distance from the chilling surface.

Penetrations are recorded in terms of one-tenth millimeter units. At penetrations of 100 or below, duplicate measurements will usually agree within about 2 units. At penetrations approaching the extreme range of the instrument (about 375) the difference between duplicate determinations may be as much as 5 units.

Solidification and Tempering of the Samples

In all cases the fat to be examined was first melted by heating to about 70° C. The bronze blocks were immersed in a tray of cracked ice and water to almost their entire depth until they were thoroughly chilled. When the melted sample had cooled to about 50° C., it was poured into the chilled blocks. Care was taken to have a drop of fat projecting above the block surface, to provide for shrinkage in the fat on cooling. It was found that the temperature of the fat when poured into the blocks was not critical, and could be varied within reasonable limits without appreciable effect on the micropenetrations.

Since it is convenient to allow the samples to chill overnight, most of the tests were carried out with a chilling time of approximately 16 hours in ice water. A chilling period of this duration is apparently sufficient to produce a condition of equilibrium in the fat. In some of the experiments, in order to investigate the feasibility of accelerating the test, the chilling period was considerably shortened.

At the end of the chilling period the solidified samples were immediately transferred to a thermostatically controlled water bath for tempering to the proper temperatures for the actual penetration measurements. The usual procedure was to place the entire series of blocks in the bath at the lowest temperature employed (10° C.), and then increase the temperature of the bath step-wise, removing a block for measurement after a proper tempering period at each successively increasing temperature. In this way each sample examined was not only tempered at the temperature of examination, but was also subjected to corresponding tempering periods at each of the previous lower temperature levels. In some of the experiments, however, the samples were transferred directly from the ice bath to a water bath operating at the temperature at which the penetration was to be determined.

Measurements on All-Hydrogenated Products

A popular brand of all-hydrogenated vegetable oil shortening was tested under the different conditions listed in Table 1. After a chilling period of 16 hours, it was found that virtually identical penetrations

TABLE 1

Micropenetrations of an All-Hydrogenated Type Vegetable Oil Shortening Chilled and Tempered Under Different Conditions.

Test No.	AH-1	AH-2	AH-3	AH-4	AH-5	AH-6
Chilling time, hrs	16	16	16	1	16	16
Tempering time, min. at each temp	15	30	60	30	30	30*
Micropenetrations, mm./10:						
at 10.0°C	15	15	16	17	15	15
12.5°C	....	....	....	....	19	....
15.0°C	22	25	25	23	24	23
17.5°C	....	....	....	....	28	....
20.0°C	39	42	42	39	41	45
22.5°C	....	....	....	....	62	....
25.0°C	86	92	94	86	97	96
27.5°C	....	....	....	....	133	....
30.0°C	185	181	183	171	178	191
32.5°C	....	....	....	....	242	....
35.0°C	323	324	319	305	317	332

* Transferred directly from ice to water bath at temperature at which penetration was determined.

were obtained with tempering times of 30 and 60 minutes. The penetrations were inclined to be slightly lower at the lower temperatures with a tempering time of 15 minutes, and were also slightly lower at all temperatures when the chilling period was reduced to 1 hour. Slightly higher penetrations were obtained when the samples were transferred directly from the ice bath to water at the temperature at which they were to be examined, rather than being brought to this temperature gradually. Reducing the temperature intervals from 5.0° to 2.5° C. had no appreciable effect on the consistency of the samples examined with a chilling time of 16 hours and a tempering time of 30 minutes at each temperature.

It is apparent that in fats of the all-hydrogenated type variations in consistency due to polymorphism are not much in evidence, and that the procedure followed in tempering the samples is not, as a consequence, extremely critical.

Measurements on Blended Type Products

The fat selected as a representative blended product consisted of a mixture of 11 percent hydrogenated cottonseed oil with an iodine value of 12.5 and 89 percent unhydrogenated cottonseed oil with an iodine value of 108.6. Detailed results of the examination of this fat under different conditions are recorded in Table 2. With this fat, the micropenetrations were to a large extent dependent upon the conditions under

TABLE 2

Micropenetrations of Blended Type Vegetable Oil Shortening Chilled and Tempered Under Different Conditions.

Test No.	BS-1	BS-2	BS-3	BS-4	BS-5	BS-6
Chilling time, hrs	16	16	16	16	16	1
Tempering time, min. at each temp	30	60	120	240	30*	30
Micropenetrations, mm./10:						
at 10°C	30	30	30	31	30	35
15°C	37	42	42	43	39	36
20°C	61	70	76	85	62	50
25°C	113	118	125	131	108	91
30°C	176	173	184	179	165	145
35°C	253	236	222	203	275	232
40°C	300	272	245	218	Too soft	312

* Transferred directly from ice to water bath at temperature at which penetration was determined.

which the fat was tempered. After an overnight chilling period, the samples became progressively softer at the lower temperatures and firmer at the higher temperatures as the tempering time was increased from 30 minutes to 60, 120, and finally to 240 minutes.

Whereas a tempering time of 30 minutes sufficed to bring the consistency of the hydrogenated fat to a constant value, it is apparent that a comparable consistency cannot be attained in the case of the blended fat with any practicable tempering time. The conditions chosen for blended products must, therefore, be arbitrarily selected. Any conditions adopted for chilling and tempering hydrogenated fats would appear to be suitable also for blended products.

The progressive stiffening of the blended fat at the higher temperatures with increased tempering time is quite evidently due to polymorphic transformations. Some manifestation of polymorphism in such fats is to be expected from the relatively simple nature of their solid glycerides, and is in line with common experience in the solidification of blended shortenings in commercial equipment.

Obviously, any set of standard solidifying and tempering conditions must be rather carefully adhered to in examining blended fats, if consistent results are to be obtained.

Standard Conditions for Chilling and Tempering the Samples

The foregoing results suggest that suitable conditions for conducting a standard micropenetration test would include an overnight chilling period of approximately 16 hours, followed by tempering periods of 30 minutes each at successively increasing temperatures at intervals of 5° C. All of the micropenetration determinations reported in subsequent portions of this article were made under these conditions.

Effect of Hydrogenation on the Consistency of Vegetable Oils

An indication of the rate at which the consistency of vegetable oils change with hydrogenation is furnished by the data represented in Figures 3, 4, 5, and 6. In Figure 3 are plotted the micropenetrations of a laboratory hydrogenated peanut oil at varying iodine values. Similar data for hydrogenated cottonseed and soybean oils are shown in Figures 4 and 5, respectively.

In Figure 6 the interpolated micropenetrations of the different hydrogenated oils at a temperature of 22.5° C. are plotted against their iodine values. It will be noted that the maximum deviation of micropenetration values from the smooth curves is about 2 units, which is approximately the limit of accuracy of the method. This corresponds to a reduction in iodine value of about 0.5 unit. The micropenetration method may thus be said to be sensitive to an alteration in the consistency of the fat equivalent to less than 1 unit change in iodine value.

The three hydrogenated oils are comparable with one another, inasmuch as they were hydrogenated under identical conditions and with the same catalyst. The micropenetration data illustrate the general principle that the hardness of a hydrogenated oil at a given iodine value is in direct proportion to the iodine value of the original oil. The original iodine values of
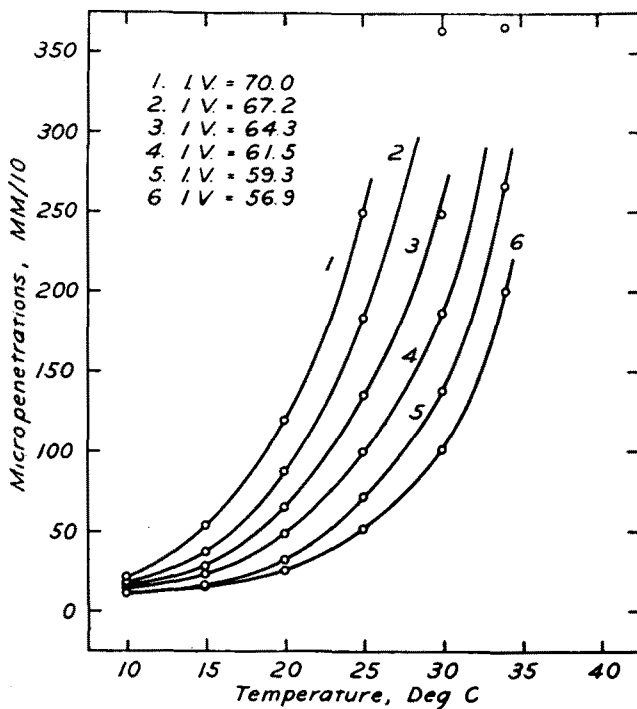
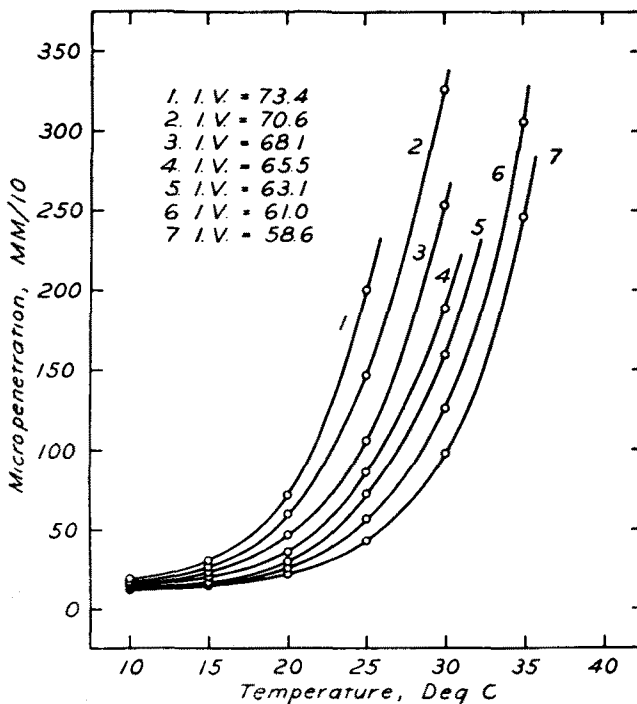FIG. 3. Micropenetration curves, peanut oil hydrogenated to varying degrees of hardness.

FIG. 4. Micropenetration curves, cottonseed oil hydrogenated to varying degrees of hardness.

the peanut, cottonseed, and soybean oils were 93.2, 108.6, and 133.3, respectively.

Consistency vs. Hard Fat Content of Blended Products

A series of blended fats were prepared from cottonseed oil with an iodine value of 108.6 and hydrogenated cottonseed oil with an iodine value of 12.5. In this series the content of hydrogenated oil was varied from 8 to 13 percent, in increments of 1 percent. The micropenetration curves of this series of fats are

reproduced in Figure 7. In Figure 8 the micropenetrations at 22.5° C. are plotted against the hard fat contents of the mixtures. It will be seen that the micropenetration method is sensitive to an addition of hard fat of less than 0.5 percent.

Consistency of Commercial Products

The micropenetrations of the fat from a number of commercial fat products of different types are listed in Table 3.

A Quick Micropenetration Technique for the Control of Hydrogenated Products

A rapid modification of the standard micropenetration method may be used for controlling the
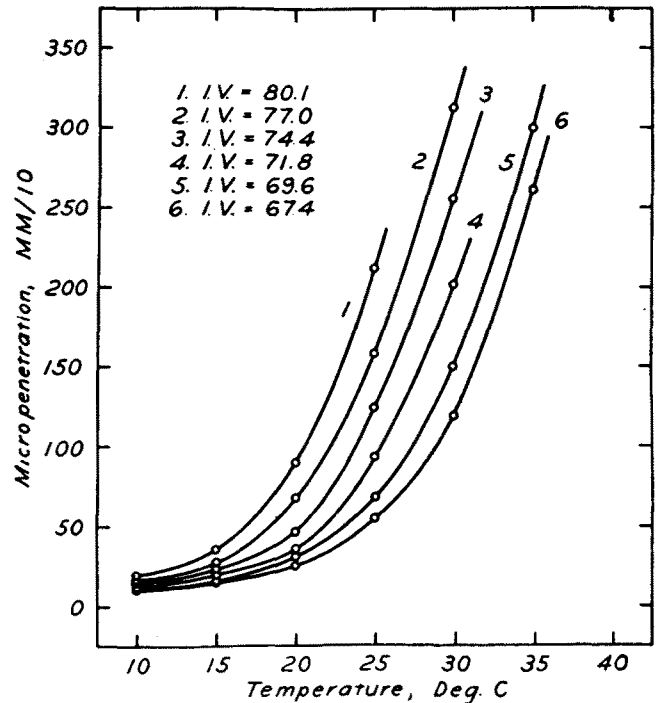

FIG. 5. Micropenetration curves, soybean oil hydrogenated to varying degrees of hardness.
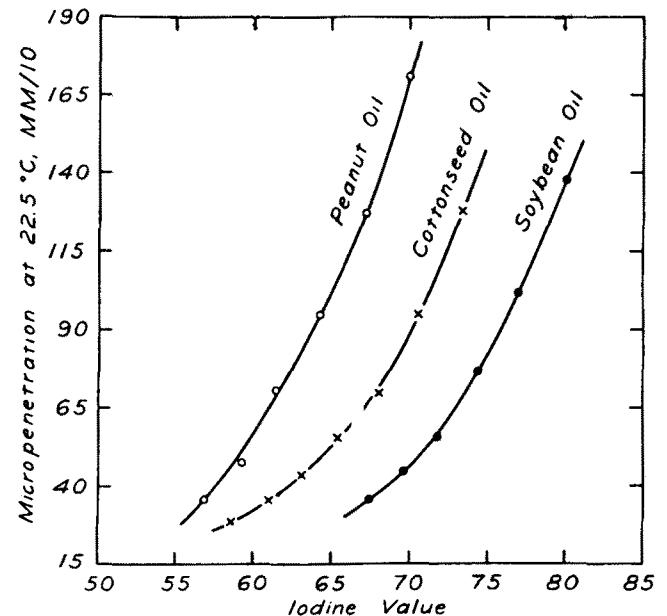

FIG. 6. Variation of the consistency of various oils with hydrogenation as measured by micropenetrations at 22.5°C. by the standard method.
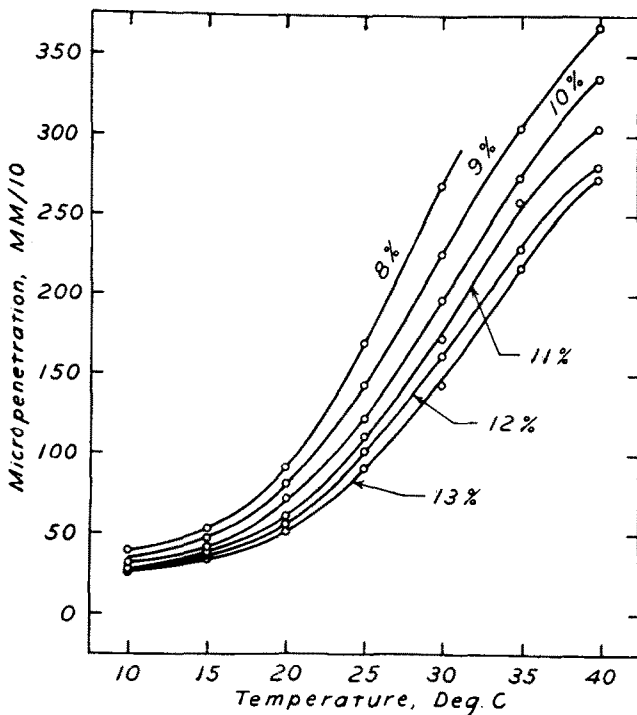
FIG. 7. Micropenetration curves, cottonseed oil containing varying percentages of hard oil.
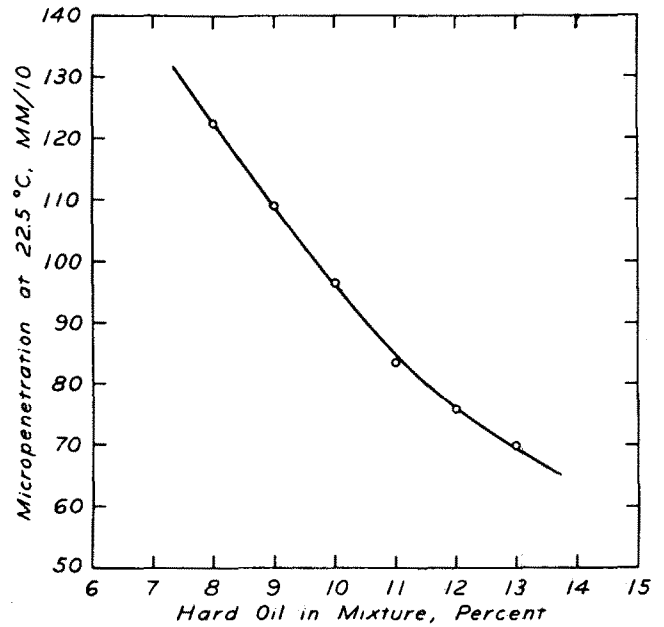

FIG. 8. Variation of the consistency of cottonseed oil with the addition of hard oil, as measured by micropenetrations at 22.5°C. by the standard method.

hydrogenation process. It has been found that consistent micropenetrations can be obtained on hydrogenated oils of the approximate consistency of shortening or margarine, in the temperature range of 20 to 25° C. if the chilling and tempering times are reduced to 15 minutes each.

The so-called "quick" micropenetrations thus obtained are not identical with the regular micropenetrations, but they bear a definite relationship to the latter. The relation found between regular and quick micropenetrations at 22.5° C. in the case of different hydrogenated oils is shown graphically in Figure 9. The variations which occur in the quick micropenetrations at 22.5° C., as the different oils are hydrogenated, are shown in Figure 10.

In practice, it will be found that the position of a curve representing micropenetrations vs. iodine value will vary somewhat from one hydrogenation run to another, even with careful control of the variables of temperature, pressure, concentration of catalyst, etc., during hydrogenation. Differences in the consistency of products hydrogenated at different

times are apparently due to unavoidable variations in the nature of the catalyst and the composition of the raw oil. Therefore, if plots are made of a number of different hydrogenations of the same kind of oil, a family of curves will result, similar in appearance to those of Figures 6 or 10.

The procedure to be followed in applying the quick micropenetration method to hydrogenation control may be best illustrated by a specific example. Let it be supposed that cottonseed oil is being hydrogenated to produce a shortening of the all-hydrogenated type. The average consistency of good shortenings of this type at 22.5° C. is equivalent to a regular micropenetration of about 65, which corresponds in turn to a quick micropenetration of 55. The oil is hydrogenated until its iodine value approaches but does not reach the approximate value desired in the final product. Hydrogenation is then interrupted, and a sample is drawn and its quick micropenetration at 22.5° C. determined. At the same time its iodine value is also determined by a quick method (3). The point corresponding to this penetration and iodine value is plotted amidst the family of curves referred to previously. After this is done it will be readily apparent just how much farther the hydrogenation

TABLE 3

Micropenetrations of Fat From Various Plastic Commercial Products.
(Determined under standard conditions, chilled overnight and held 30 minutes at each temperature.)

| Sample No.	S-1	S-2	S-3	S-4	S-5	S-6	M-1	M-2	B-1
Product	Shortening	Shortening	Shortening	Shortening	Shortening	Shortening	Margarine	Margarine	Butter
Brand	Spry	Crisco	Dexo	Jewel	Vegetole	Scoco	Parkay	Nucoa	Cloverbloom
Type	All-hydrog. veg. oils	All-hydrog. veg. oils	All-hydrog. veg. oils	Blended animal and veg. oils	Blended animal and veg. oils	All-hydrog. veg. oils	All-hydrog. veg. oils	All-hydrog. veg. oils	....
Iodine value	72.2	74.1	75.4	87.2	74.6	67.9	72.9	72.3	33.2
Micropenetrations, mm./10:									
at 10°C	15	16	16	26	21	14	12	13	11
15°C	25	24	25	41	31	19	18	19	17
20°C	42	45	43	71	56	27	35	41	43
25°C	92	101	102	124	112	63	87	117	145
30°C	181	212	203	196	172	136	252	357	367
35°C	324	336	315	270	258	252	Too soft	Too soft	Too soft
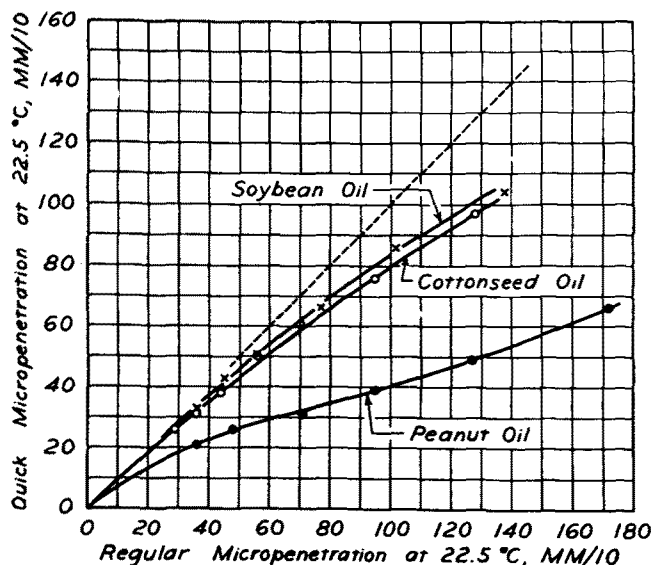
FIG. 9. Relationship between regular (standard) micropenetrations and quick micropenetrations of different hydrogenated oils at 22.5°C.

FIG. 10. Variation of the consistency of various oils with hydrogenation, as measured by micropenetrations at 22.5°C. by the quick method.

must be continued to reach the penetration desired in the final product.

Suppose that the iodine value and quick micropenetration of the sample are found to be 72.0 and 85, respectively. Reference to the curve for cottonseed oil in Figure 10 will reveal that the iodine value must be further reduced to about 66.7 in order for it to have a quick micropenetration of 55. Hydrogenation is then resumed until the oil has absorbed an amount of hydrogen equivalent to a reduction in iodine value of 72.0 to 66.7. By the careful application of this technique it is possible to hydrogenate oil to any desired consistency with a high degree of accuracy.

Summary

1. An improved micropenetrometer is described, by means of which it is possible to measure the consistency of fats with a high degree of precision.

2. The intelligent use of a micropenetration method requires some consideration of the theory of plasticity in fats. This theory is briefly discussed.

3. The influence of various factors on the consistency of solidified fats has been investigated, and as
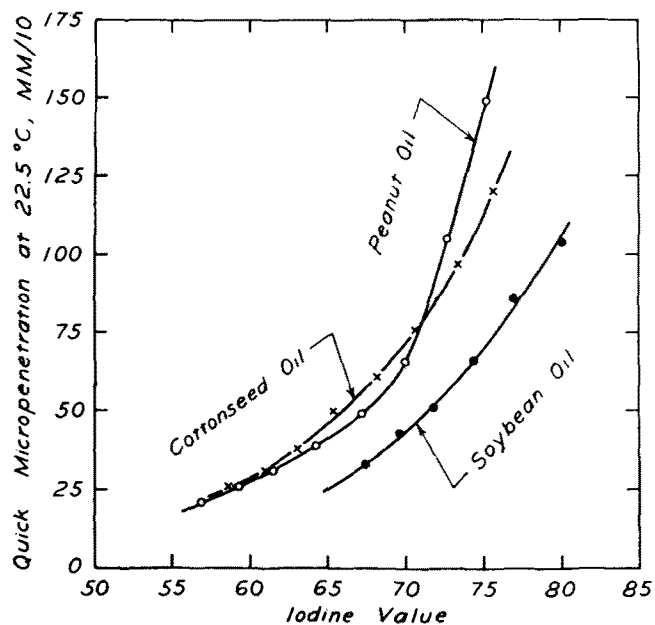
a result of this investigation a standard technique for making micropenetration tests is proposed.

4. Micropenetration data are recorded on cottonseed, peanut, and soybean oils hydrogenated to different degrees, on cottonseed oil blended with various proportions of highly hydrogenated oil, and on various commercial samples of shortening and margarine.

5. A quick micropenetration method, applicable as a control in the hydrogenation of fat products, is described.

Acknowledgment

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