Report of the Cellulose Yield Committee, 1953-1954

During the past year three samples were sent out to 12 laboratories. Two of these samples were second cut linters, and one was hull fiber. The following table gives the average analysis of the three samples sent out:

Lab. No.	No. of Tests	A Linter	B Linter	C Fiber	Over-all Avg. for the Yr.
1	3	78.7	73.9	67.3	73.3
2	3	78.4	73.6	67.0	73.0
3	3	79.0	74.6	67.4	73.7
4	3	78.8	74.3	67.3	73.5
5	3	77.9	73.8	67.4	73.0
6	3	78.9	73.6	66.7	73.1
7	3	79.0	74.0	67.2	73.4
8	3	78.9	74.6	67.6	73.7
9	3	78.1	73.8	67.0	72.9
10	3	78.8	74.4	67.4	73.5
11	3	78.7	73.8	68.4	73.6
12	3	79.5	74.4	67.1	73.7
Average		78.7	74.1	67.3	73.4

With a few exceptions the check analyses were very good. In the case where a laboratory was a little out of line, attention was called to the poor test. As seen from the above table, the over-all averages of the analyses were very good.

During the past year several inquiries have been made in regard to the type of wire used on the screen on the yield washer. The standard method does not give details of the wire to be used so it is thought advisable to include the specific specifications of the wire which have been used from the beginning of this test. The screen wire used is a 60-mesh nickel screen with the following specifications:

Mesh, Tyler designation	60
Number of Bureau of Standards designation	60
A.S.T.M. designation (microns)	250
Opening, in.	.0097
Opening, mm.	.246
Diameter of wire, in.	.0070
Diameter of wire, mm.	.1778

The following tolerances are allowed:

Openings	4%
Diameter	10%

Recommendations

It is recommended a) that samples be sent out at least three times a year to all laboratories equipped to run the cellulose yield, and b) that the specifications of the wire used on the yield washer be included in the standard A.O.C.S. method. This can be considered a clarification of the present method as no new equipment is being used.

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Consistency of Fats Plasticized with Acetoglycerides[1]

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MODIFICATION of cottonseed, peanut, and similar oils by the introduction of acetic acid to produce a large proportion of diacetoglycerides results in unusual oil products (4). The melting, cloud, and pour-points are generally higher than those of the original oils, but plasticity at low temperatures is greatly increased. Increased plasticity results from the fact that low-melting compounds, like 1,2-diaceto-3-olein, melting point of —18.3°C., are formed, and that these and certain higher melting acetoglycerides solidify into a waxy or plastic form (1, 4, 5, 6, 7, 9, 10). The modified oils are more saturated than the original oils and hence should have a better keeping quality. Also they can be rendered flavorless and odorless by ordinary oil-processing techniques.

The acetylated oils, as they will be referred to hereafter, may have some important uses in the food field. However their use in foods must await the completion of feeding and other physiological tests now under way.

One potential use for acetylated oils is in the formulation of a margarine-like spread having an exceptionally long plastic range. Representatives of the armed forces have indicated the need for such an item in individual operational rations. Their requirements include physical and chemical stability at temperatures ranging from —40° to 100°F.(—40° to 38°C.), spreadability at temperatures between 40° and 100°F.(4° and 38°C.), appearance and acceptability comparable to margarine or butter, and a storage life of at least 6 months at 100°F.(38°C.). Experiments have shown that mixtures of acetylated oil, hard fat, salt, traces of antioxidant, imitation butter flavor, and butter color may meet the requirements.

A related use for acetylated oils might be in the plasticizing of commercial margarine oils to produce products having a moderately greater plastic range than those presently available. Some commercial margarine oils undergo great changes in consistency with small variations in room temperature.

A somewhat different use for acetylated oils might be in the plasticizing of hard fats which are sometimes used in the form of a chocolate type of coatings for ice cream bars and certain hard candies. Frequently, when such products are stored at low temperatures, the coatings become harder than desirable and tend to shatter.

[1]Presented at the 27th Fall Meeting of the American Oil Chemists' Society, Chicago, Ill., Nov. 2-4, 1953.
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To obtain a better indication of the performance of acetylated oils in the above-mentioned uses, various tests were made in which the consistency of mixtures containing acetylated oils and a hard fat or margarine oil, or the hardness of mixtures containing acetylated oil and hard fat were measured. The results of these tests are described in the present communication.

Materials and Testing Procedures

Materials. Most of the acetylated oils were prepared in the laboratory by interesterifying a refined and bleached natural oil with triacetin at a mole ratio of one oil to six of triacetin. The interesterification was conducted under dry hydrogen for 30 minutes at 50°C.; 0.2% of sodium methoxide, on an oil basis, was used as the catalyst. The interesterification procedure was the same in other details as that described by Eckey (2). The reaction product was washed with dilute acid to destroy the catalyst, washed with water, heated in a pot still under reduced pressure to remove most of the uncombined triacetin, stripped with steam while at a temperature of 200°C. and under a partial vacuum, and bleached with neutral activated clay and carbon. Two acetylated oils were obtained from a commercial firm which is producing them on a pilot-plant scale.

The aceto-olein product was prepared from commercial oleic acid (233 LL Elaine, Emery Industries[3]) essentially as described previously (4). The acid was further purified by distillation and converted into a mixture of mono-, di-, and triglycerides containing 64.8% of monoglycerides, the mixture was acetylated with acetic anhydride, and the reaction product was purified by removing unreacted acetic anhydride and acetic acid.

The properties of the various acetoglyceride products are described in Table I.

TABLE I

Properties of Acetoglyceride Products

Product	Acetyl, %	Iodine value	Linoleic acid, %	Hydroxyl value	Free fatty acids,[a] %
Acetylated cottonseed oil:					
A	14.1	82.2	24.5	0.0	0.05
B[b]	17.9	73.2	32.9	0.4	0.72
Acetylated peanut oil					
A	0.6	91.1	26.0	1.0	0.14
B	6.1	83.7	39.0	0.0	0.06
C	11.7	73.9	....	0.0	0.10
Aceto-olein product	14.9	62.8	1.4	4.0	0.87
Acetylated soybean oil	15.2	96.8	....	0.0	0.10
Acetylated lard[b]	19.8	42.0	6.0	0.4	0.92

[a] Calculated as oleic acid.
[b] Obtained from a commercial firm.

The hard fats were prepared in the laboratory by hydrogenating cottonseed oil (iodine value, 108.3) under moderately selective conditions. Four products were prepared having iodine values of 55.2, 39.8, 29.3, and 1.5, respectively.

The monostearin which was prepared by a commercial firm from relatively pure stearic acid, contained over 90% of monoglycerides. It had an iodine value of 5.3 and a melting point of 73°C.

[3] This product is named merely as part of the exact experimental conditions. Naming it does not constitute an endorsement of this product over those of other manufacturers.

The margarine oil was also obtained from a commercial source. The oil had an iodine value of 76.7, a linoleic acid content of 2.4%, and a melting point of 35.5°C.

The salt used in the margarine-like spread formulations was a chemically pure grade which had been ground to pass a 100-mesh sieve.

Testing Procedures. Consistency was measured by two different procedures. One used the micropenetrometer apparatus and technique described by Feuge and Bailey (3). This procedure comprises solidifying the melted samples in copper blocks chilled to 0°C., tempering the samples for 16 hours at 0°C., warming the samples slowly to the test temperatures, and measuring the depth to which a needle penetrates when dropped under specified conditions.

In the other procedure the cone penetrometer apparatus and technique specified in Method D 217-48 of the American Society for Testing Materials were used except that the weight of the cone and movable attachments was 50 g. instead of 150 g. The procedure, which was designed for testing petroleum greases, measures the depth to which the cone penetrates a sample in 5 seconds when the cone just touches the surface of the sample at the start of the test.

In the measuring of consistencies with the cone penetrometer each test sample was solidified at 7° to 10°C., worked at room temperature, held at the test temperature for a length of time sufficient to produce constant and reproducible results, and tested with the penetrometer which also had been heated or cooled to the test temperature. Necessary holding times at the test temperatures were found to be: 100 hours at —20°C., 20 hours between 0° and 20°C., and 4 hours at room temperature and above.

The effect of addition of acetoglycerides on the hardness of a fat was determined by means of the Shore durometer method described by Warth (11). For these tests the aceto-olein product and hard fat were mixed at 75°C., poured into a heated mold measuring 0.25 in. x 1.5 in. x 3 in., and then cooled to room temperature at a moderate and uniform rate, after which the block of solid fat was removed from the mold and held at the test temperature for 16 hours before measurements were made.

Acetyl contents were determined by the method of Matchett and Levine (8). Hydroxyl values were determined by the method of West *et al.* (12) except that the ratio of acetic anhydride to pyridine used was 1:3 instead of 1:7. All other determinations were made according to the Official and Tentative Methods of the American Oil Chemists' Society.

Margarine-Like Spread

One of the requirements of the spread desired by the armed forces is that it remain spreadable over the temperature range of 40° to 100°F. (4° to 38°C.). This means that the spread should have a consistency of about 160 at room temperature as measured by the cone penetrometer, and this consistency should be maintained about 20°C. above and below room temperature. A consistency of 160 is about that possessed by commercial margarine at 24°C.

A logical method of extending the plastic range of an acetylated oil-hard fat spread above room temperature is to employ a hard fat component having

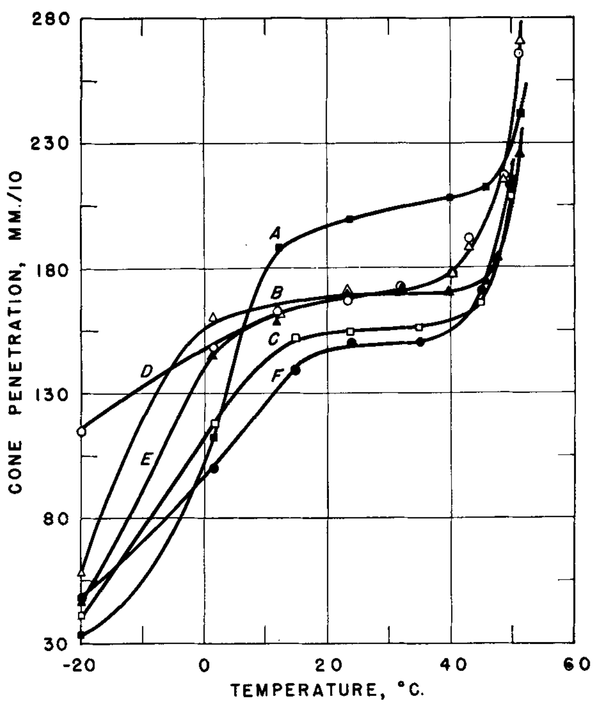

FIG. 1. Relation of consistency to temperature for mixtures containing 79% of acetylated oil, 18.5% of hydrogenated cottonseed oil (iodine value, 1.5), and 2.5% of salt: (A), acetylated lard; (B), acetylated cottonseed oil B; (C), acetylated soybean oil; (D) aceto-olein product; (E), acetylated cottonseed oil A; and (F), acetylated peanut oil C.

the highest possible melting point. The amount by which the plastic range is extended below room temperature depends in large measure on the composition of the acetylated oil.

To establish the effect of the latter, spreads were prepared with various kinds of acetylated oils. Each spread contained 79% of acetylated oil, 18.5% of hydrogenated cottonseed oil of iodine value 1.5, and 2.5% of salt. The consistencies determined for these samples are recorded in Figure 1.

All of the oils, with the exception of the aceto-olein product (curve D, Figure 1) produced spreads having consistency curves of a decided sigmoid shape, with the more nearly horizontal section of the curves being in the temperature range of about 0° to 45°C. Because the aceto-olein product was almost free of completely saturated triglycerides, the spread made with it had a fairly soft consistency even at —20°C. When comparing consistencies at room temperature, the acetylated lard produced the softest mixture even though it possessed the lowest iodine value (Table I). Part of the behavior of the acetylated lard-containing spread can be attributed to its high content of acetyl (19.8%), but other factors must also have been involved. Acetylated cottonseed oil B, which had an acetyl content of 17.9%, produced a spread of about the same consistency as that for acetylated cottonseed oil A, which had an acetyl content of 14.1%. Of course, the relative proportions of the long chain fatty acids in the two oils may have been different. The acetylated peanut oil produced the firmest spread, but this oil also contained the least amount of acetyl.

The effect of acetyl content on the consistency of a spread is better illustrated in Figure 2. Here are represented the consistency curves for spreads similar to those described above but in which the acetylated oils were all derived from the same peanut oil and differ from each other only in acetyl content. It is evident that the consistency becomes softer as the acetyl content increases. While a fully acetylated peanut oil, one consisting entirely of diacetoglycerides and containing 19-20% of acetyl, was not prepared and examined, undoubtedly, such an oil would be preferred for margarine-like spreads.

An important factor entering into the formulation of margarine-like spreads of wide plastic range is the proportion of hard fat used. The spread can be made softer or firmer at a given temperature by varying this proportion. However, as is evident from Figure 3, there is a definite limit to the range of variation.

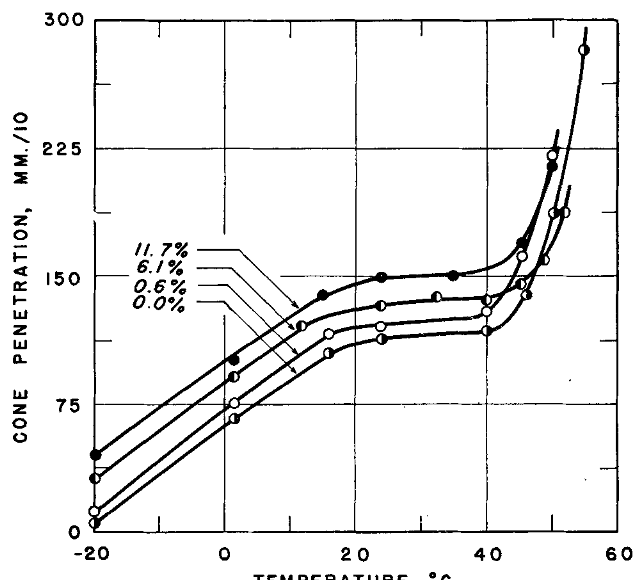

FIG. 2. Consistency curves showing the effect of acetyl content of peanut oil in mixtures containing 79% of peanut oil, 18.5% of hydrogenated cottonseed oil (iodine value, 1.5), and 2.5% of salt.

For spreads containing almost completely hydrogenated cottonseed oil and highly acetylated oils, it appears that the content of hard fat must be close to 18.5%. At this percentage the consistency curve has a fairly long almost horizontal section in the region of room temperature, indicating an almost constant consistency in this region, as is desired. Decreasing the percentage of hard fat to 9.25 eliminates the section of almost constant consistency, and increasing the percentage to 25 hardens the spread more than is desired.

The degree of hydrogenation of the hard fat used in a spread formulation would also be expected to influence the shape of its consistency curve. This effect is illustrated in Figure 4. The spreads represented in these curves differ from those represented in the preceding figures in that they contain no salt. It is evident that decreasing the degree of hydrogenation of the hard fat component softens the spread

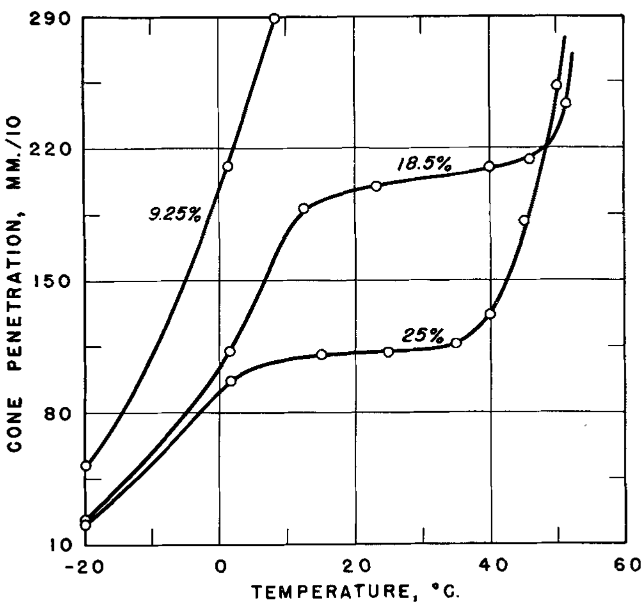

FIG. 3. Consistency curves showing the effect of amount of hydrogenated cottonseed oil (iodine value, 1.5) in mixtures containing acetylated lard, the hydrogenated cottonseed oil, and 2.5% of salt.

at all temperatures and lowers the temperature at which the spread loses its plastic properties. For all practical purposes a hydrogenated cottonseed oil cannot be used as the hard fat component if its iodine value is greater than about 55. However variations in iodine value from 1 to about 29 do not have a great influence on the consistency-temperature relationship.

Another factor which has an effect on the consistency of the margarine-like spreads is the amount

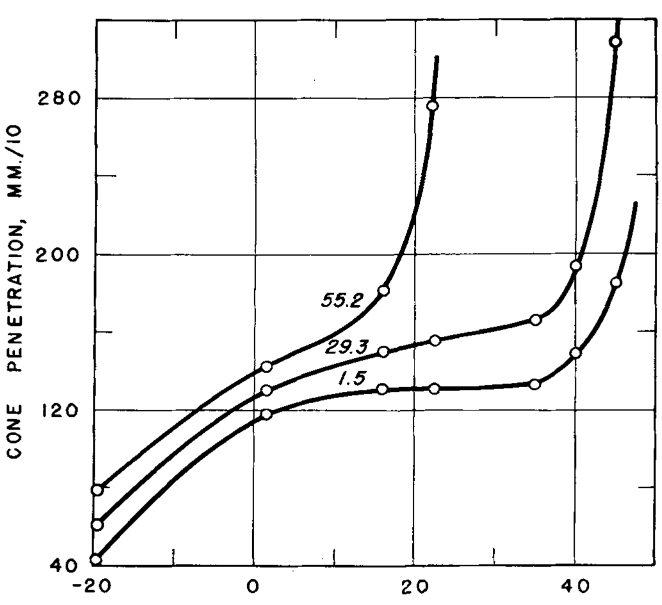

FIG. 4. Consistency curves showing the effect of the degree of hydrogenation, in terms of iodine value, of cottonseed oil when incorporated into mixtures containing 81.5% of acetylated cottonseed oil B and 18.5% of hydrogenated cottonseed oil.

of salt incorporated. From casual considerations it might be expected that the replacement of a portion of the liquid oil with salt would result in a firmer mixture. Actually the addition of salt softened the spread. The effect is shown quantitatively in Figure 5. No definite reason for the action of the salt can be given.

It appears that other normally solid materials may have an unexpected influence on the consistency of spreads. In an attempt to extend the plastic range of margarine-like spreads, monostearin was substituted for the almost completely hydrogenated cottonseed oil. The monostearin was higher melting and less soluble than the hydrogenated oil. Contrary to

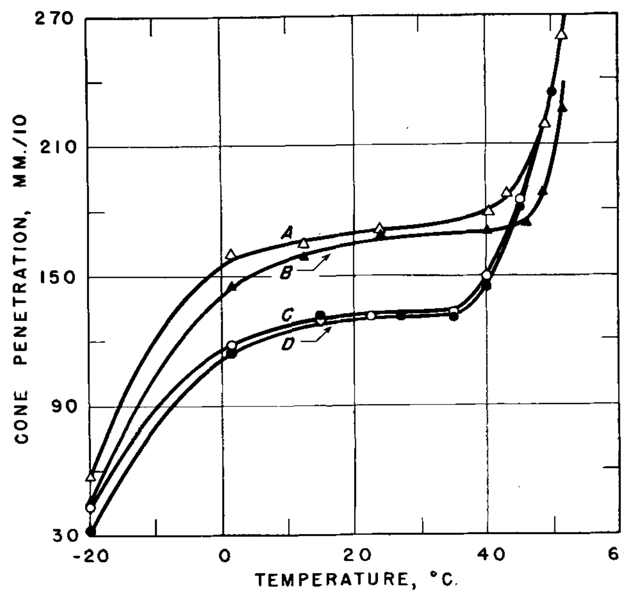

FIG. 5. Effect of salt on the consistency curves of mixtures containing acetylated cottonseed oils and 18.5% of hydrogenated cottonseed oil (iodine value, 1.5): (A), 79% of acetylated cottonseed oil B and 2.5% of salt; (B) 79% of acetylated cottonseed oil A and 2.5% of salt; (C) 81.5% of acetylated cottonseed oil B and no salt; and (D), 81.5% of acetylated cottonseed oil A and no salt.

expectations, substitution resulted in a spread which was softer and became fluid at a lower temperature, as is shown in Figure 6.

Unlike the phenomena observed with salt, that with monostearin appears to have a logical explanation. The monostearin solidified in a relatively grainy mass which tended to bleed. Undoubtedly the crystals were of a larger size and different shape than those formed from the hydrogenated cottonseed oil under similar conditions, and the proportion of liquid oil enmeshed by the monostearin was relatively smaller.

Modified Margarine Oil

When commercial margarines are stored at low temperatures (5° to 15°C.), they generally become quite firm. At room temperatures (about 25°C.) small increases in temperature result in relatively large softening effects. These characteristics are considered to be a direct reflection of the properties of the oils used in their formulations.

Tests were made to determine if addition of the aceto-olein product to a commercial margarine oil would result in the latter being somewhat less firm at 10°C., which is about the temperature at which margarine is stored in a domestic refrigerator. At such a temperature margarine oil already contains a liquid phase. A moderate increase in its amount would not be expected to produce a marked change in the physical properties of the margarine oil unless the added component had a marked effect on the viscosity of the liquid phase or the characteristics of the crystals in the solid phase. The results of the tests shown in Figure 7 indicate that addition of the aceto-olein product did soften the margarine oil at

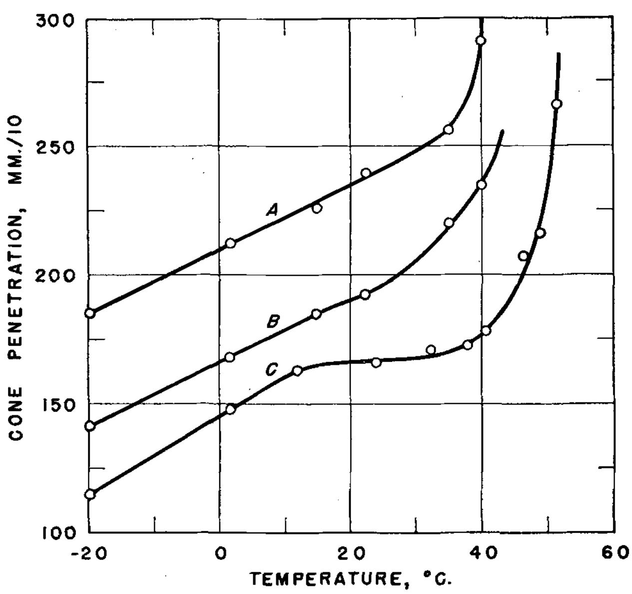

Fig. 6. Relation of consistency to temperature for mixtures in which hydrogenated cottonseed oil (iodine value, 1.5) has been replaced all or in part by monostearin: (A), 79% of aceto-olein product, 18.5% of monostearin, and 2.5% of salt; (B), 79% of aceto-olein product, 9.25% of monostearin, 9.25% of hydrogenated cottonseed oil (iodine value, 1.5), and 2.5% of salt; (C), 79% of aceto-olein product, 18.5% of hydrogenated cottonseed oil (iodine value, 1.5), and 2.5% of salt.

the lower temperatures but softened it even more at the higher temperatures.

Another way in which an acetoglyceride might be incorporated in margarine oil would be as a mixture with hard fat. The percentage of the mixture to be added would depend upon the consistency-temperature characteristics desired. The curves in Figure 8 show such a use may be desirable. However, relatively large proportions of the mixture would be required. In practice, care would have to be exercised in the choice of a hard fat so that the final product would not produce a waxy sensation in the mouth.

Possibly the best use of acetoglycerides in margarine oil would be in the preparation of a blended type of product consisting of a hard fat and a normally liquid oil which has been acetylated to a limited extent. An indication of what might be accomplished with such a mixture is illustrated in Figure 9. Over

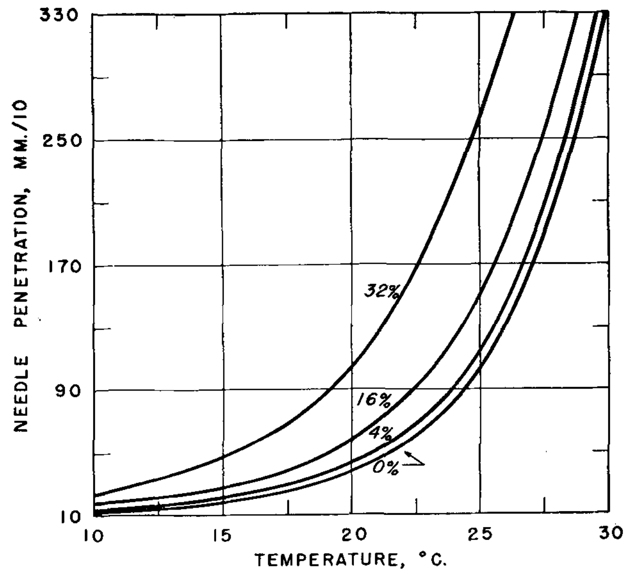

Fig. 7. Effect of aceto-olein product on the consistency of a commercial margarine oil. Percentages on the curves indicate the content in weight percentage of aceto-olein product.

the temperature range of 10° to 30°C. the change in consistency for such a mixture is less than that for a mixture containing the unacetylated oil and hard fat. Both of the mixtures undergo less change in consistency than does a commercial margarine oil.

It should be emphasized that the curves in Figure 9 are only an indication of what can be accomplished. In practice, it probably would be desirable to sacrifice some of the good plastic properties of the acetoglyceride-containing mixture for other considerations like good mouthing qualities.

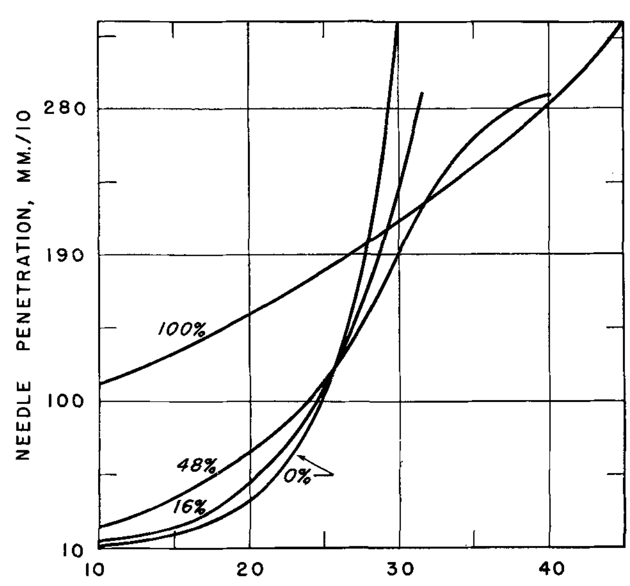

Fig. 8. Consistency curves showing the effect of adding a mixture of 86% of aceto-olein product and 14% of hydrogenated cottonseed oil (iodine value, 1.5) to commercial margarine oil. Percentages on the curves indicate proportion of the mixture on a total weight basis.

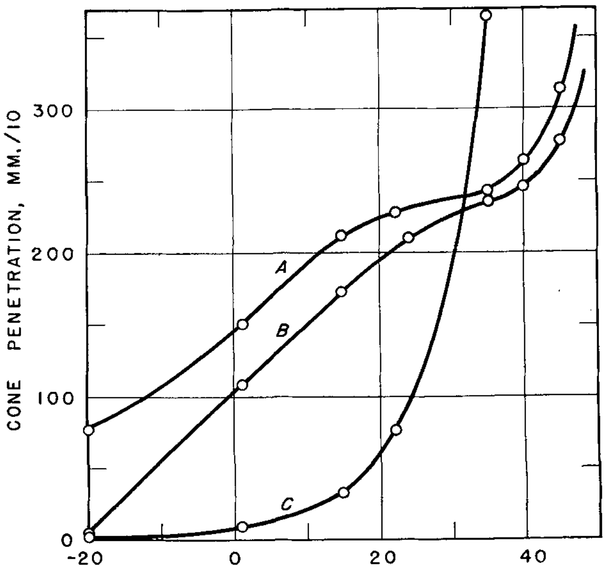

FIG. 9. Relation of consistency to temperature: (A), 91% of acetylated peanut oil B and 9% of hydrogenated cottonseed oil (iodine value, 1.5); (B), 91% of peanut oil and 9% of hydrogenated cottonseed oil (iodine value, 1.5); and (C), commercial margarine oil.

Modified Hard Fats

Slabs of fat consisting of a hydrogenated cottonseed oil and varying percentages of the aceto-olein product were prepared. The hardnesses of these slabs were then tested at different temperatures to obtain an indication as to whether or not acetoglycerides are effective in reducing the brittleness of hard fats when stored at low temperatures. In these tests it was assumed that hardness was directly proportional to brittleness. The results are summarized in Figures 10 and 11.

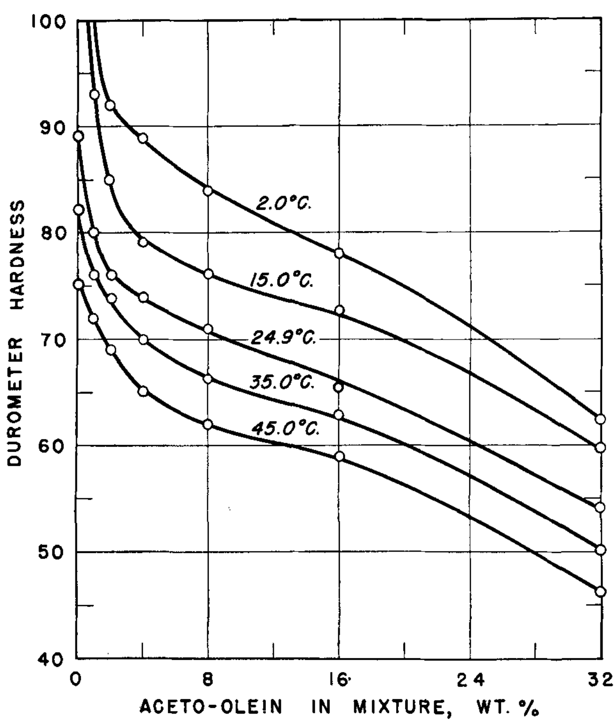

FIG. 10. Relation of the hardness of hydrogenated cottonseed oil of iodine value 1.5 to content of aceto-olein product, measured at the temperatures indicated.

It is indicated by the curves that small amounts of acetoglycerides in hard fats would be useful in reducing brittleness at low temperatures. At 2°C. (Figure 10) the hydrogenated cottonseed oil was too hard for measurement but, as small amounts of aceto-olein product were incorporated, the hardness decreased rapidly. As more and more aceto-olein product was added, the relative effect of each percentage unit of increment decreased.

In tests at another temperature, 24.9°C., the hardness of the hydrogenated cottonseed oil (Figure 10) was 89 units. When 2% of aceto-olein product was incorporated, the hardness was reduced 13 units. An additional 2% of aceto-olein decreased the hardness only an additional 2 units.

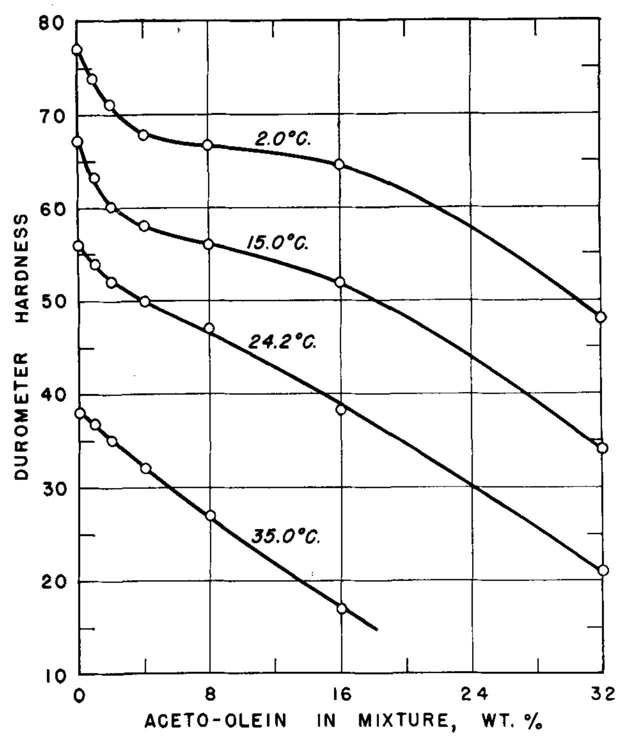

FIG. 11. Relation of the hardness of hydrogenated cottonseed oil of iodine value 39.8 to content of aceto-olein product, measured at the temperatures indicated.

As the temperature at which the mixture was tested increased, the degree of softening accomplished by incorporation of 1 or 2% of aceto-olein product decreased.

The curves in Figure 11 show the same effects but to a lesser degree. The hydrogenated cottonseed oil represented in Figure 11 was originally softer than that represented in Figure 10. Hence it must be concluded that small amounts of aceto-olein product show their greatest softening effect when used with the harder or more highly hydrogenated fats. This is logical because the less highly hydrogenated fats usually contain a small amount of liquid fat, and a small increase in this amount would not produce a marked effect. However acetoglycerides because of their low-melting components might be considered desirable as ingredients in coatings containing relatively soft fats if they are to be handled at low temperatures.

Summary

Several normally liquid, natural oils were modified by ester interchange or glycerolysis and acetylation to produce acetoglycerides. An aceto-olein product was also prepared from commercial oleic acid. These products together with two similar products obtained from a commercial firm were tested to determine their ability to plasticize fats.

Plastic mixtures of the acetoglycerides and hydrogenated cottonseed oils, in which the former predominated, were prepared by cooling and simultaneously stirring solutions of the two components. Usually, finely ground salt was added as a third ingredient. Consistency measurements were made to determine whether or not the mixtures could be used in margarine-like products which would remain spreadable over a wide temperature range.

Results of the measurements indicated that margarine-like products of wide plastic range could be prepared by acetylating lard and cottonseed, soybean, and peanut oils to an acetyl content ranging from about 12 to 20%. As the acetyl content increased, the consistency characteristics of the mixtures improved, that is, the spreads became softer at room temperature and still possessed a very wide plastic range. The latter extended generally from 15°C. to above 40°C.

The proportion of hydrogenated cottonseed oil required for the margarine-like spreads was determined to be about 18.5%. Variations of a few percentage units resulted in marked changes in consistency. Increasing the iodine value of hydrogenated cottonseed oil to about 30 lowered the upper limit of the plastic range only moderately. Increasing the iodine value to about 55 lowered the upper limit markedly.

The substitution of 2.5% of finely ground salt for an equal proportion of the liquid, acetylated oil in the margarine-like products resulted in a softer spread. The substitution of monostearin for all or part of the hydrogenated cottonseed oil also resulted in a softer spread.

Tests were made to determine whether or not acetoglycerides could be used to improve the plastic properties of commercial margarine oil. It was concluded that simple addition of acetoglycerides to margarine oil does not result in any improvements. Addition of an acetoglyceride-hard fat mixture improved the plastic range, provided addition was at a level of about 50%. A mixture of hard fat and peanut oil acetylated to a limited degree was found to have a much longer plastic range than did commercial margarine oil, and the consistency of the mixture was relatively constant over the temperature range of 15° to 30°C.

Small amounts (1 to 8%) of aceto-olein product incorporated in highly hydrogenated cottonseed oil were effective in reducing the hardness of the latter when it was cast in block form. The effect of the aceto-olein product decreased as the temperature increased and the degree of hydrogenation of the hard fat decreased.

Acknowledgment

The authors wish to express their appreciation to members of the Analytical and Physical Division of this Laboratory for determining some of the analytical values reported here; to Distillation Products Industries for furnishing the monostearin and two of the acetylated oils used in the investigation, and to the Southern Cotton Oil Company for the sample of margarine oil.

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