TABLE III

Transition and Melting Point Temp

	mp K	Transition temp K
n-heptyl thiolaurate	297	308.6
n-octyl thiomyristate	309	340.9
n-decyl thiomyristate	311	333
n-decyl thiopalmitate	316.5	339
n-butyl thiostearate	305	341.1

than the melting point temp. This explains why *n*-propyl thioacetate, *n*-undecyl thiomyristate, *n*-octadecyl thiomyristate, *n*-nonyl thiopalmitate and *n*-hexyl thiolaurate are adequately represented by Eyring's equation.

This phenomenon also occurs with water (9) and benzene (10). Rossini's viscosity data for hydrocarbons, when treated in the same manner, also shows this property. Because of this non-uniform change in viscosity throughout the entire liquid state, Eyring's equation is not valid for all temp. It does give satisfactory results when a different set of values for E_{vis} and pre-exponential factors are used for each liquid structure. The values are given in Table IV. Because of this alteration of liquid structure, the viscosity has been considered in two regions, one "near" the melting point and the other "far" from the melting point, each of which displays a linear relationship with reciprocal temp. (In this section is is not implied that the liquid structure will change precisely at one given temp. Because of mixing or entropy effects of two types of liquid structures co-existing at the same time, the transition may occur over a temp range of a few degrees or a few hundredths of a degree.)

Activation Energy. In the calculation of activation energy for viscous flow, the selected values were from those portions of the viscosity-temperature curves which showed one type of liquid structure.

Figure 2 is a plot of activation energy, E_{vis}, vs. the number of carbon atoms in the chain. Treating the data in this manner shows that the activation energy increases as the chain length increases; however, this is not a linear increase.

TABLE IV

Activation Energies for Viscous Flow and Preexponential Factor

Compound	A	A′	E_{vis}	E'_{vis}
n-propyl thioacetate	—1.619	....	2103	....
n-heptyl thioacetate	—1.771	—1.949	2733	3055
n-hexyl thiohexanoate	—1.99	....	2970	....
n-hexyl thiolaurate	—1.905	....	3718	....
n-heptyl thiolaurate	—1.940	—2.417	3845	4555
n-tetradecyl thiolaurate	—2.013	....	4383	....
n-hexadecyl thiolaurate	—2.04	....	4536	....
n-hexyl thiomyristate	—1.880	....	3898	....
n-octyl thiomyristate	—1.943	—2.301	4040	4599
n-decyl thiomyristate	—2.86	—2.36	....	....
n-tetradecyl thiomyristate	—2.05	....	4543	....
n-nonyl thiopalmitate	—1.994	....	4299	....
n-decyl thiopalmitate	—2.022	—2.446	4399	....
n-undecyl thiopalmitate	—2.05	....	4490	....
n-dodecyl thiopalmitate	—2.09	....	4630	....
n-tridecyl thiopalmitate	—2.08	....	4640	....
n-octadecyl thiopalmitate	—2.13	....	4952	....
n-butyl thiostearate	—1.94	—2.01	4080	4590
n-undecyl thiostearate	—2.054	....	4611	....
n-hexadecyl thiostearate	—2.17	....	5020	....

The prime values refer to that liquid structure "near" the mp.

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REFERENCES

1. Sasin, G. S., Richard Sasin and Nicholas Capron, J. Org. Chem. *21*, 852 (1956).
2. Sasin, G. S., P. R. Schaeffer and Richard Sasin, *Ibid.* *22*, 1183 (1957).
3. Sasin, Richard, W. F. Ashley, J. W. Manning, Jr. and Albert Paolini, Jr., JAOCS *35*, 192 (1958).
4. ASTM, "Standards on Petroleum Products and Lubricants" D445-53T part 6, p. 204. (1958).
5. Shrigley, J. W., C. W. Bonhorst, C. C. Liang, P. M. Althouse and H. O. Triebold, JAOCS *32*, 213 (1955).
6. Gros, A., and R. O. Feuge, *Ibid.* *30*, 213 (1952).
7. Rossini, F. D., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds." Pittsburgh, Pa., Carnegie Press, 1953.
8. Yarshni, Y. P., and S. N. Srivestana, J. Phys. Chem. *62*, 706 (1958).
9. Innes, K. K., *Ibid.* *60*, 817 (1956).
10. Hu, P. M., and R. W. Parsons, Proc. Phys. Soc. of London *72*, 454 (1958).

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Worksoftening of Margarine and Shortening

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Abstract

Margarine and butter have a certain yield value which is mainly determined by the fact that the fat crystals do not move in respect of each other but are fixed in a tridimensional network. The permanent network greatly contributes to the total hardness (60–80%). This contribution can be determined by kneading the sample isothermally and by measuring the hardness before and after kneading. The decrease in hardness is called the "structural hardness" and the relative decrease the "worksoftening." These values give a certain impression of the plasticity of the product at a certain hardness, while the Spreadability Index, which can be calculated from the structural hardness and the worksoftening, is a good measure for spreadability.

Introduction

DETERMINATIONS of the consistency of butter, margarine and shortenings serve mostly to obtain a relative comparative value for hardness or spreadability. It is almost impossible to calculate from these values quantitative data for the internal structure of the samples. The hardness of the products mentioned is, as will be known, for the greater part caused by the presence of a network of fat crystals. Hardness determinations before and after isothermal kneading can give an impression of the nature and strength of the bonds in the crystal lattice. For routine hardness determinations such as are carried out in margarine factories, simple apparatus giving reproducible results is required.

Procedures and Data

Network Structure of Crystals

In a rapidly cooled fat, most glyceride crystals are so small that it is often difficult to perceive them microscopically (<1 μ) (1). The number of crystals/cm^3 is so large that their mutual distance is only slight (0.01 μ). For this reason the mutual attraction (Van der Waals—London attraction) is so strong that the crystals move rapidly towards each other and flocculate. As a result of this flocculation, long chains with many ramifications are formed. This phenomenon has been intensively studied in e.g. clay suspensions and printing inks (2,3).

The attractive forces keeping the network intact are weak and the network can be disturbed by slight stirring. However, the old situation can be re-estab-

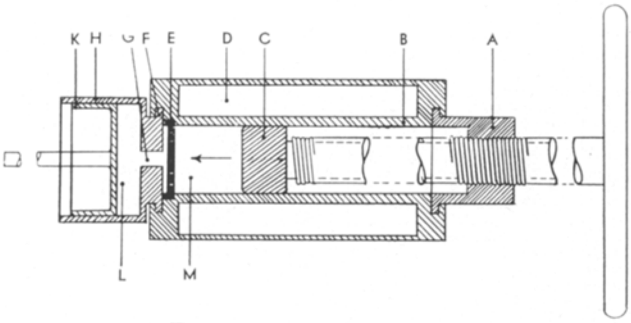


FIG. 1. Kneading apparatus.

lished again very easily by formation of many new bonds between the crystals. These so-called "secondary" bonds are therefore characterized by their weakness and reversibility.

The network of mobile crystals described, accounts for only part of the hardness of the fat and of other properties. Hardness must therefore also be the result of other factors. The weak network of secondary bonds may be strengthened at various places by other types of bonds, if the fat crystals grow together at some places. Such bonds are fairly strong, but if they are broken, they will in most cases not re-establish again at the same place and in the same way. A characteristic property of these "primary" bonds is therefore a relative strength and a certain irreversibility. By a combination of primary and secondary bonds, the crystals of the plastic fat form a tridimensional network of a certain strength. Various phenomena during plastification in the factory, or properties of the fat on use, can be explained better if more quantitative data are available as regards the network in the fat.

The same is valid for margarine. Besides fat crystals, many small water droplets (<6–$10\ \mu$) are present. The contribution of these droplets to the firmness of margarine is very slight. The product owes its hardness in the first place to the network of the fat crystals. The influence of the viscosity of the oil phase can also be neglected. This viscosity ranges from 50–80 cP., but that of plastic material from 10^6–10^{10} cP.

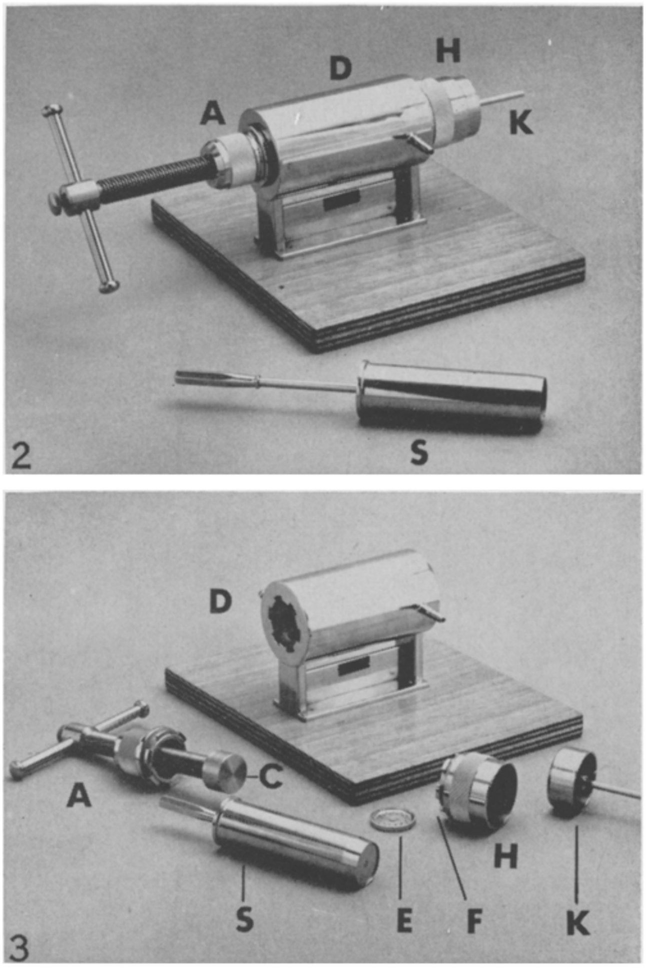
Worksoftening

The plasticity of margarine and fats is largely determined by the ratio in which the above-mentioned types of bonds occur. When the network is very strong on account of many primary bonds the product is hard and brittle. The network is disrupted by kneading and the product becomes very soft.

An impression of the strength of the crystal network can be obtained from hardness measurements carried out on the fats before and after kneading. An early attempt to evaluate the softening of fats by kneading was made by the oil industry, in connection with research work on lubricants.

The Institute of Petroleum standardized a "grease worker" which was adopted by the American Society for Testing Materials (4). The ASTM has described a cone for determining hardness but the relationship between hardness and penetration depth obtained by the cone in question is so complicated that there is little point in calculating a "worksoftening."

For a correct assessment of the worksoftening, the hardness or firmness must be expressed in a linear scale. The yield value or C-value determined with a suitable cone penetrometer (5) fulfills this condition. If this value for the unworked fat is assumed to be C_u and after working C_w, the worksoftening (W) (by definition the decrease in hardness, caused by kneading and expressed in percentages of the initial hardness) is then:



FIGS. 2 and 3. Kneading apparatus for margarine or fat with sampletaker(s).

$$W = \frac{C_u - C_w}{C_u} \times 100\%$$

Using the relationships between cone penetration and yield value we may also express the worksoftening in terms of the penetration depth (p) (5)

$$W = \left[1 - \frac{p_u}{p_w}^{1.6}\right] \cdot 100\%$$

p_u = penetration depth of cone in unworked sample

p_w = penetration depth of cone in worked sample

(p_u and p_w determined with the same penetrometer)

Kneading

Apparatus. Besides the use of a correct method for the determination of hardness, a suitable kneading apparatus is necessary by which the determination can be carried out quite quickly.

The sample must be kept at a constant temp and the heat of friction generated during kneading must be removed quickly. Care should be taken that no air can penetrate the sample on kneading. The apparatus should be simple and easy to clean. Since the grease worker recommended by the ASTM is not suitable for carrying out such determinations, an apparatus of the extrusion type has been developed by us. This apparatus consists of a metal inner tube B (Fig. 1–3) (blue prints are available on request); length 120 mm; diam 32 mm. This tube is surrounded

TABLE I

Decrease of Hardness of Sample on Repeated Kneading

Sample	C_u g/cm²	After working (C_w)			Worksoftening		
		1x	2x	3x	1x	2x	3x
Margarine I 15C	1090	195	165	140	82.1	84.8	87.1
Margarine II 15C	760	245	230	......	67.8	69.8	......
Special purpose shortening 20C	2300	1300	1190	910	43.4	48.2	60.3
Special purpose shortening 20C	2250	1120	1060	970	50.3	52.9	56.9

by a water mantle D. In tube B a plunger C can be moved by means of a rod with screw thread. The closing cap A is connected to B by means of a bayonet catch. On the other side is a kneading plate E being a disk with 24 holes (diam 1.5 mm). This disk is kept in its place by cup H which is connected to the kneader by means of bayonet catch. All the parts of the kneader are chromium-plated. The sample is introduced into B by means of sampler S which consists of a hollow tube with piston.

If the screw is screwed in, the non-kneaded sample M is pressed through the holes E and flows through the opening G into cup H. This cup is completely filled because the kneaded material L presses the piston K forward. The capacity of sampler S is equal to that of tube B. The capacity of cup H is somewhat smaller so that K is completely pressed from the cup. If the cup is completely filled, K is removed and the cup disconnected. After the flat back of the cup has been cleaned and the front has been smoothed by means of a knife the cup is placed under the cone of a penetrometer for the C_w determination.

Method of Kneading. The kneading is carried out by pressing the sample through the holes in E and by changing the flow-direction several times. Plate E fits closely to the wall of the cooling water mantle in order to remove rapidly any generated heat. It is recommendable that the temp of the cooling water is ca. 0.5C below that of the sample.

When all the operations are carried out quickly, it is not necessary to carry out the determination in a specially tempered room, provided the sample and the sample taker are in a constant temp cabinet. It is recommended that worksoftening determinations be carried out in samples which are not too soft. Mostly temp between about 5 and 15C are chosen. For hard bakery fats (pastry, e.g.) the temp may be higher (20C).

Intensity of Kneading. It is almost impossible to destroy the network structure of a sample completely. Micro particles of the network will always remain intact. If an already kneaded sample is kneaded again in the apparatus, a further although slight decrease in C_w will be observed in hard samples. This value decreases further if the sample is kneaded for a third time (Table I). In such experiments it is almost impossible to avoid local increases in temp of some 0.1C in the kneading holes.

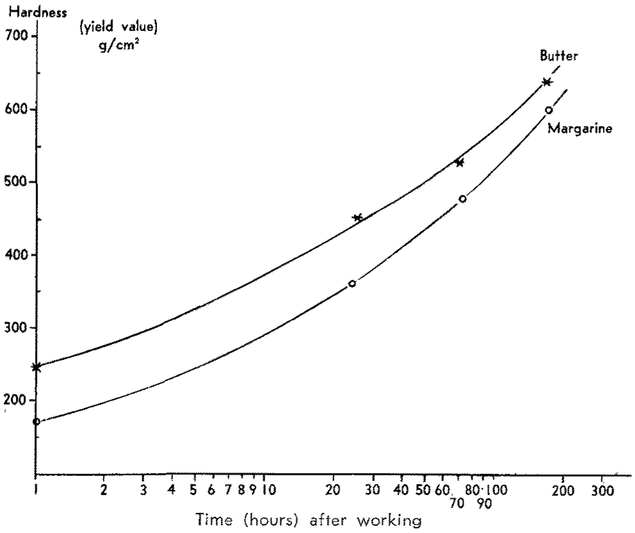


FIG. 4. Solidification of margarine and butter at 15C after kneading (15C).

Solidification after Kneading. If after the determination of C_w the filled cup is stored at a constant temp for some time, the contents will harden again immediately. The degree and rate of solidfication can be followed by hardness determinations. The hardness mostly increases with the log of the time (Fig. 4,5). This solidification is due to a slow renewal of the crystal lattice of secondary bonds. At the beginning there are loose crystal chains slowly forming ramifications which thus form a secondary network, but later on primary bonds are slowly formed again by melting and precipitation of insoluble glycerides reinforcing the lattice.

Accuracy of the Determination

The accuracy of the determination of W depends on the accuracy of C_u and C_w. The accuracy of the cone yield value measurement is exactly known but it is not constant. If the standard deviation, for homogeneous samples, is expressed as percentage of the yield value, an almost constant value of 2–3½% is found. This variation coefficient can be attributed to experimental and instrumental error. Larger deviations are generally found especially for C_u. These deviations are caused by irregularities during plastification such as small and repeatedly occurring variations in the cooling temperature, the throughput, in the state of nucleation in the votator cooler etc.

Applications

Control of Votator Process. It is rather easy to make a fat which has a desired Solid Fat Index, but this is no guarantee that the final product also has a certain desired hardness. If there is too much undercooling in the votator, and postcrystallization takes place in the packing, the product becomes hard and crumbly. In this case the worksoftening values increase to more than 80%. If too much crystallization occurs, the product becomes too soft and the worksoftening values decrease below 70%.

Influence of Temperature Fluctuations. A fat or margarine may have an excellent plasticity when leaving the factory, but on account of temp fluctuations

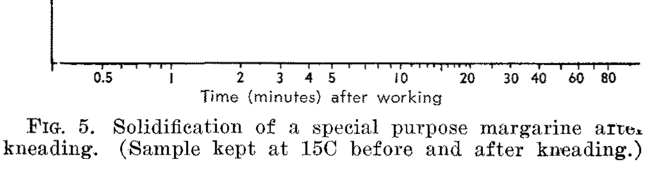


FIG. 5. Solidification of a special purpose margarine after kneading. (Sample kept at 15C before and after kneading.)

during transport the plasticity may disappear completely. Certain fat compositions are more sensitive to this than others. By means of worksoftening determinations the plasticity can be followed.

Shortenings. Especially when these fats must be worked intensively, not only a correct hardness before kneading, but also after kneading is important.

Spreadability of Butter and Margarine. In an earlier publication (5), the correlation between the yield value and the spreadability on bread was mentioned. This correlation is only valid if the products have all more or less the same worksoftening (70–75%). If this is not the case, the situation is quite different, which becomes especially manifest if the spreadability of butter and margarine is compared. Butter mostly has a lower worksoftening (50–55%) as compared with margarine (70–75%). If the hardness before kneading of the two products is the same, test panels will mostly assess margarine as being more easily spreadable than butter, since the hardness of margarine decreases to much lower values during spreading than butter. In such cases in which the spreadability of samples with different worksoftening values must be compared, C_u and C_w as such are less useful.

Excellent results are obtained if a Spreadability Index (S.I.) is calculated from C_u and C_w.

$$\text{S.I.} = C_u - 0.75\,(C_u - C_w)$$

The factor 0.75 was derived by comparing the results obtained with the apparatus with those of panel tests. In this way a high correlation coefficient (>0.95) was found between S.I. and the assessment by panels of housewives.

REFERENCES

1. Haighton, A. J., Fette Seifen Anstrichmittel *65*, 479–482 (1963).
2. Temple, M., van den, J. Colloid Sci. *16*, 284–296 (1961).
3. Lucassen-Reynders, E. H., "Stabilization of Water-in-Oil Emulsions by Solid Particles," Thesis, Utrecht 1962, Chapter IV.
4. American Society for Testing Materials, 5-25 and D 217-52 T, Philadelphia, Pa.
5. Haighton, A. J., JAOCS *36*, 345–348 (1959).

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A Light Test to Measure Stability of Edible Oils

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Abstract

The effect of light on the flavor of edible oils and of various fat-containing foods is reviewed to show its importance in food studies and the need for a method of evaluation. Such a test, in which fluorescent light is used in an easily assembled unit, has been developed, and the parameters for its use have been determined. Identical samples of soybean oil exposed on 10 different days and organoleptically evaluated show the method to be reproducible with a standard deviation of 0.79 with a scoring system of 1–10. This method was then applied to soybean, cottonseed, safflower and hydrogenated-winterized soybean oils, and a light-exposure value was determined for each oil based on a comparison with accelerated storage procedures ordinarily used. Advantages of this light test over current procedures are the short time required for completion, the reduction of variation by a controlled light source, reproducibility of results and its adaptability to related food products.

Introduction

THE DELETERIOUS EFFECT of light on the flavor stability of edible oils and various fat-containing foods is well known (5–9, 12–14, 16,17). However much of the work was done between 1930 and 1947; since then, few studies have been reported (21,22). The increased consumption of soybean oil, as well as the recent emphasis on the use of liquid oils in the diet, has renewed interest in the subject. In the fall of 1963 a survey of five local supermarkets showed that for the 15 brands of salad oil represented (5 cottonseed, 4 corn oil, 4 safflower, 1 soybean, 1 peanut) all were bottled in clear glass. Some of these oils previously had been marketed in brown glass bottles or in cans only.

In the past, grocery stores were small and products were received in corrugated cartons; a few items were removed at a time and placed on the shelves only as needed. This resulted in a relatively quick turnover (3). The small store of the past was not as intensely lighted as the modern supermarkets and the problem of oils and other food products developing off flavors while on the shelf because of exposure to bright fluorescent lighting arises under today's methods of merchandising.

Coe and LeClerc (4,9) studied the effect of light on the peroxide development of oils and showed that oils protected by black or green wrappings developed no rancidity even though the peroxide value was high. Golumbic et al. (11,12) investigated light reversion in fats exposed to IR and to UV radiation. IR exposure produced rapid reversion that resulted in well-defined flavors, such as grassy or haylike, easily recognized and described by all; the UV exposure produced samples difficult to describe and characterized by a drying sensation in the roof or back of the mouth. McConnell and Esselen (16,17) conducted light tests and found amber glass, which excluded most of the incident light below 500 mμ, effective in retarding off-flavor development in edible oils exposed to diffused light. However, amber glass afforded less protection when samples were exposed to direct sunlight. Gudheim (15) also found amber glass more effective than green, blue or opal glass in retarding off-flavor development in shortenings and liquid oils, and he reported that flavor and odor changes were not characteristic of rancid fat. Romani and Valentinis (21) showed that both the Kreis and peroxide values of fresh and aged edible oils increased on exposure to light. Higher viscosities and increased acetyl numbers resulted when Ryspaev (22) exposed fats to UV radiation.

Research on light effects has not been limited to

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