from the difference in surface area of the two materials. (Vold and Phansalkar [11] give 1.64 m^2/g. for the specific surface of a cotton sheeting probably similar to that used in the present work, and the surface area of the carbon is given as 95 m^2/g. [15]). While the average level of sorption is much higher on carbon than on cotton, the difference between builders is less marked. For example, at 0.2% builder concentration, the highest sorption obtained on cotton (with S H M P) was about 43% higher than the lowest sorption (with T S P) whereas the corresponding figure for sorption on carbon was only about 14%. Within this comparatively narrow range there is considerable crossing of the curves so that it is not possible to establish any clear-cut order of effectiveness of the builders. It should be noted however, that at the highest sorption levels, *e.g.*, with 0.4% S H M P, about 90% of the available detergent has been sorbed. If a higher initial concentration of detergent had been used, it is possible that a greater differentiation between builders might have been obtained, *i.e.*, the maximum sorption is probably limited less by the action of the builder than the amount of detergent available for sorption.

Schneider's theory (10) that builder action is caused primarily by an increase in the rate of micelle dissociation is not substantiated by the data for sorption on carbon. The concentration of detergent was in all cases below the c.m.c., yet substantial increases in sorption were observed in the presence of builders. Furthermore it has been shown previously (8) that under the experimental conditions employed, equilibrium is established in less than 10 min. Hence an increase in the rate of sorption, unless also accompanied by a change in the equilibrium conditions, would not be expected to increase the total amount sorbed in 10 min. or longer. It is therefore concluded that, while an increase in the rate of micelle dissociation may be a contributing factor in those cases where it is applicable, the mechanism of builder action cannot be explained satisfactorily on this basis alone.

Summary

In the case of sorption on cotton there was an approximately linear increase in sorption of the detergent with increasing builder concentration. The effectiveness of the builders in this respect increased with increasing anionic charge and decreasing pH of the builder. In the case of sorption on carbon the addition of builder again led to an increase in sorption, but in this case the sorption was an exponential function of the builder concentration. The differences in effectiveness of the various builders in increasing sorption was less clear-cut than in the case of sorption on cotton, and there did not appear to be any consistent correlation between the amount of detergent sorbed and either the pH or the anionic charge of the builder.

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A Disk Rheometer Applicable to Measuring Shortening Flow-Properties

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THE RESOLUTION of the physiological concept of shortening "consistency" in a numerical system is a challenging problem. Shortening systems, being transitory in nature susceptible to changes by temperature, time, shear, and other variables, are not simple rheological systems to study. Some of the properties of shortenings have been measured by various applications of viscometry. Gravenhorst (4) applied a Brinnell type of ball penetrometer, using a relatively constant shear rate and measuring the stress variable. Clardy *et al.* (1) developed another version of the constant shear rate-variable stress approach by using an orifice and ring forced through the sample. The techniques of Rich (6), using the A.S.T.M. Grease Penetrometer, and of Feuge and Bailey (3), using the micropenetrometer test, are modifications of a constant-stress, variable-strain principle.

These tests contribute greatly to the measurements of shortening consistency but are limited to the application of one shearing action. Recognizing that shortenings are subject to changes by shearing or "working" and that the system is temperature-dependent, test equipment was designed and a method was developed which would determine the relative viscosities of shortenings under a single shear application; the change in viscosities of shortenings as a result of controlled repeated shearing or working; and the relationships of both of these properties as a function of temperature.

In addition to these fundamental objectives, consideration was given to sample dimensions so to facilitate sampling of pails, drums, cartons, and similar unit-sizes. The aspect of laboratory preparation of shortenings was not overlooked, and the sample shape was made compatible with laboratory chilling-techniques. Operator convenience and the speed of the test were studied to achieve the compromise of maximum test output per man-day and maximum interpretation. The method and equipment was designed to be universally adaptable to research, problem-solving, and routine quality-control.

Equipment

The A.S.T.M. Grease Worker, used in conjunction with the penetrometer in A.S.T.M. Method D-217-49, is a device which can be used as a standard shearing-apparatus. The construction is such that it could be modified for use as a perforated disk viscometer similar to the viscometer described by Kinney (5). As with other viscometers of this type, either the technique of constant stress by a known weight can be employed or variable stress by different loadings may be used. Another approach is to apply a constant rate of shear and measure the resistance or stress by springs or a dynamometer. This was the approach chosen.

Figure 1 shows the grease worker modified for use as a viscometer sensing element. Six extra ¼-in. holes were drilled in the plate near the shaft to facilitate flow in this blank area. A plug was drilled and tapped into the bottom to facilitate loading of the cores of shortening. The slotted yoke used with motor-driven and hand-operated workers was removed, and a straight, connecting arm attached by two knurled bolts was substituted. An axle was attached to the bottom of the worker. This in turn fits into a bearing block and is secured by a 90° locking cam bar. Thus the axle is held in position but may oscillate.

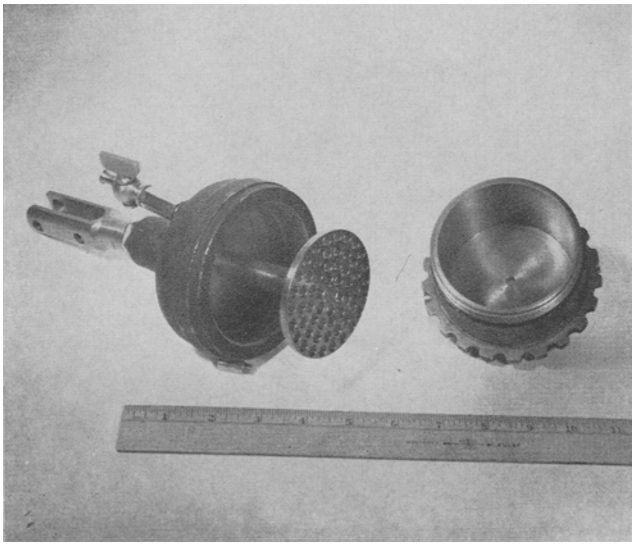

FIG. 1. The A.S.T.M. Grease Worker, modified with a vent in the bottom to allow loading of solid cores of shortening.

Figure 2 shows the worker in the operating position in the overflow, constant-temperature bath. The carbon string packing has been removed from the packing gland. The crankshaft is connected directly to the bearing of the cam of a motorized grease worker. The pivot axle and the directly connected crank shaft permit the driving of the perforated piston with a minimum of side-thrust resistance. The crankshaft and piston assembly are statically balanced by a counterweight attached to the back side of the cam.

The entire worker assembly is shown in Figure 2 connected to the recording, dynamometer-driving source. The dynamometer is known as a farinograph in the cereal field and as a plastograph in all other fields. Since commercial farinographs with the proper speeds were not available at the time of the investigation, an expedient was designed. The motor shaft of the farinograph was extended through the rear bearing-mount. With the motor electrically disconnected, the unit was driven by a Graham, variable-speed transmission. The high gear ratio used in the dynamometer (28.2 to 1) makes it possible to drive the shaft from an external source with negligible loss of indicated torque.

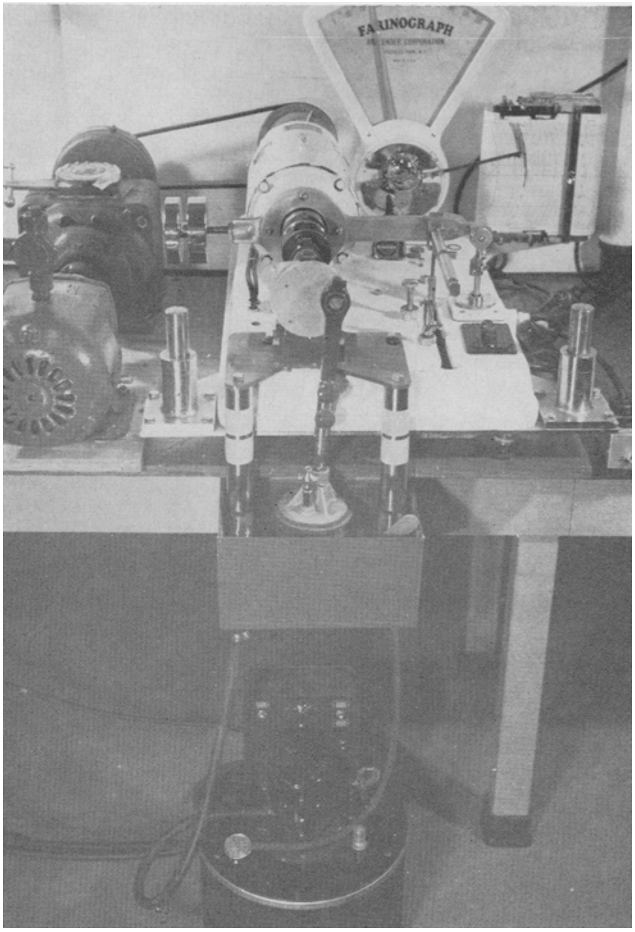

FIG. 2. The modified grease worker with connecting rod, balanced cam, and circulating water-bath, adapted to a modified farinograph which is driven by a stepless variable speed transmission.

The position of the piston shown in Figure 2 is at 90° from top dead center, the point of maximum velocity or shear rate. The perforated disk has traversed approximately one-half the distance from top to bottom. The shear rate application is therefore in the form of a sine wave going from zero to maximum and falling to zero in each half cycle. The shear rate maximum depends upon the velocity of the cam, being variable by means of the transmission. The relative shear rate can be expressed as velocity of the piston but for simplicity is expressed as r.p.m. The resistances appear on the chart as compressed sine waves; the peaks correspond to the maximum shear rate of any half cycle. The envelope of each half cycle is in reality a rheometer curve of the sample. The change in peak heights at any given speed indicates the degree of viscosity change by shearing. The diameter of the worker is 3 in. and the depth, 2½ in. Number 301 x 411 (No. 1 Tall) cans were cut to have 2½ in. of depth inside. By removing the bottom or punching an air-vent hole, cored samples can be taken from drums, pails, or cartons. For experimental work these samples were placed in constant-temperature cabinets for a minimum of 24 hrs. to establish equilibrium. A square of wax paper served as a dust cover.

The samples were loaded by cutting out the bottom of the can and transferring the sample to the worker with a piston. Figure 3 shows the sample form over the worker about to be transferred with the piston. The bottom is then inverted, the air plug replaced, and the top screwed onto the lower half. Wrenches are provided for easy opening. After the first downward stroke the thermometer hole and air-vent are closed to prevent aeration.

FIG. 3. An illustration of the shortening sample about to be transferred to the grease worker by means of a piston.

Calibration

To test the performance of the worker as a perforated disk viscometer, a modified approach of Kinney's (5) was used. An instrument constant was calculated for the worker when used with Newtonian fluids.

From Newton's fundamental law of viscous flow comes the following general expression

1. $\eta = K_1 F t$
η = coefficient of viscosity
F = shearing force
t = time for a constant amount of shear (1/v when v = velocity of shearing planes)
K_1 = constant.

For the shortening rheometer the equation can be expressed on

2. $F = K_2 B$ where B = maximum metergrams torque recorded for any single stroke (Brabender Units)
K_2 = constant
If $t = K_3/R$ where R = shear rate in r.p.m. and K_2 is a dimensionless constant, then equation 3 is developed:
3. $\eta = K_4 B/R.$

Since all shortening tests to be described were made at 4 r.p.m., the shearing velocity will be a constant, repeated at the maximum velocity point of the cam (90° from top dead center), and the equation can be reduced to

4. $\eta = KB.$

Any Newtonian oil should follow a typical shear stress line where the slope is a function of $\triangle B/\triangle R$; $\triangle B$ refers to shear stress and $\triangle R$ to shear rate. R and B being equivalent to statistical yx

5. $A = \triangle B/\triangle R$ where A = slope.

The instrument constant can be expressed as

6. $K_4 = \eta/A.$

A Bureau of Standards oil P with a viscosity of 444.2 poise at 30°C. was chosen for calibration of the instrument. The rheometer bath was adjusted to 30°C., the cup was filled with the oil and tempered in the bath until equilibrium had been attained. The drive was operated at several different r.p.m. settings. The repeated stresses formed a series of identical envelopes. As the speed or shearing rate was increased, the maximum heights increased. A slight difference between upstroke and downstroke resistances was noted.

Figure 4 shows the results of three calibration tests on the same oil and different days. The repeated maxima points at each speed were plotted against

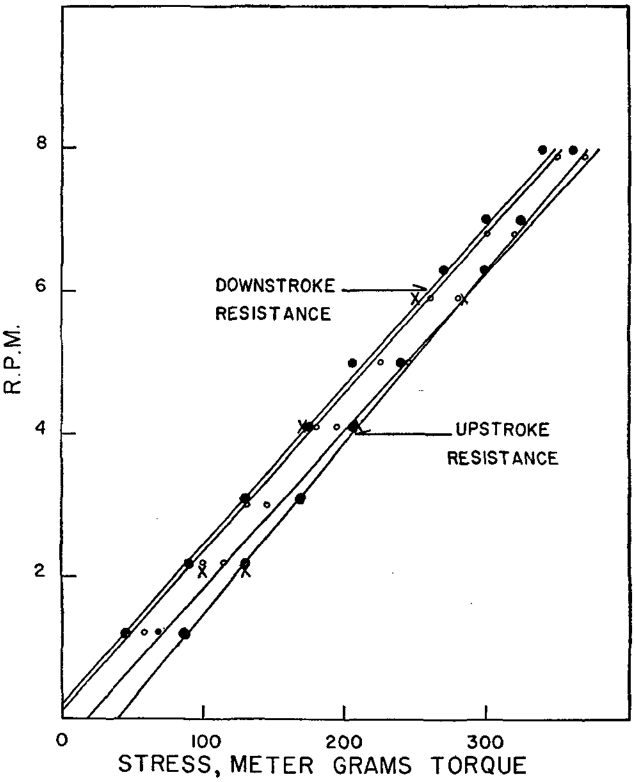

FIG. 4. The flow curve of Bureau of Standards Oil P in the viscometer. Solid dots, circles, and crosses indicate results obtained on separate days. The values indicated were taken from the repeated maxima at 90° and 270° from top dead center.

the shearing stress. The results were repeatable, and the differences were within normal physical-test experimental error. The downstroke curves extrapolate very close to the origin of the axes, indicating agreement with Newtonian flow in the rheometer.

The divergence of upstroke values was traced to a frictional force operative in one direction only. It involves the alignment of bearings which can be eliminated in successive models.

From the equation of the regression line of the downstroke values it was found that $A = 43.8$. The intercept was within analytical error of zero. Using equation 6,

$$K_4 = 444.2/43.8 = 10.1.$$

From equation 3 the instrument constant at 4 r.p.m. can be calculated as

$$\text{poise} = 10.1/4\ B \text{ or } 2.5B.$$

It is understood that this is the instrument constant, assuming Newtonian flow conditions and is only cited for orientation purposes to establish a magnitude reference for the stress values obtained with the machine.

Preliminary Experiments

Since shortenings are susceptible to change by shearing, it is conceivable that the change of viscosity under controlled conditions would exhibit some form of a decay curve. Figure 5 shows this typical decay of resistance to shearing at 4 r.p.m. The peaks occur at 90° and 270° from top dead center. The chart speed has been increased to 2.34 cm. per minute to increase readability. Preliminary investigations revealed that this hyperbolic curve was evident with all shortenings over a wide temperature range. The shape of the hyperbola varied significantly between different shortenings, particularly during the early shear stresses. The distorted hyperbolas, though satisfactory for ordinary comparison, are not adaptable to comparison of many results and not easily characterized in simple values for specifications, product descriptions, or reports. For these reasons transformation of raw curves is made by a modification of the technique which Dempster *et al.* (2) used in dough measurements.

The shear stress of a given stroke multiplied by the stroke number forms the ordinate, and the stroke number forms the abscissa. This transformation results in essentially straight lines, which can be compared easily by utilizing the origin or first-stroke resistance and the slope of the line. A practice has been established in this laboratory of expressing the slope of the line as the tangent of the angle formed by the curve and an abscissa drawn from a one-inch line down from the curve at the eighth stroke.

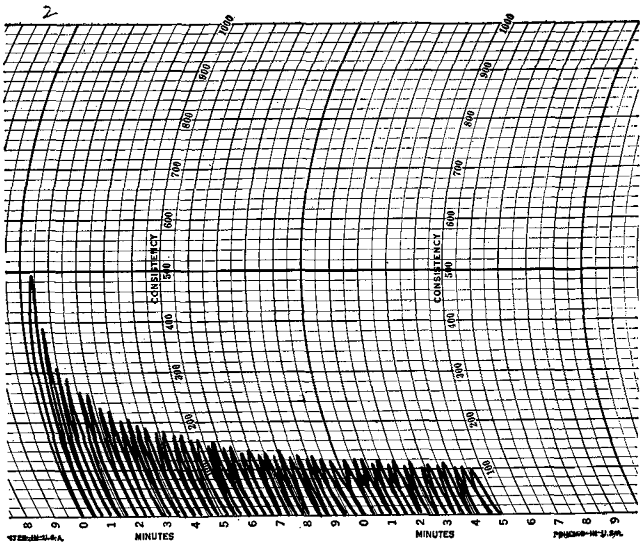

FIG. 5. *A typical curve of shortening showing* hyperbola formed by the decay of maximum resistance as shearing is repeated. The speed of the driving cam was 4 r.p.m., and the units of resistance are metergrams torque. Chart speed was 2.34 centimeters per minute to expand the sine wave form.

Plastic range can be expressed as the ratio of the tangent values found at any two temperatures. Many of the results in this report are expressed as tangents of curves made at 72° and 86°F. (22.2° and 30.0°C.). The ideal plastic range value would be unity where no difference in slope exists at the two temperatures.

Two shortenings, modified lards, considered to be functionally interchangeable were employed to test the discrimination ability of the test. A hydrogenated vegetable shortening with monoglycerides was included to test the range of change, realizing that this sample would be softer at high temperatures and harder at lower temperatures than the modified lards.

Figure 6 shows the transformation curves of the three shortenings. Modified lard No. 1 was considerably harder than No. 2, as designated by the origin and slopes of the tests made on samples tempered

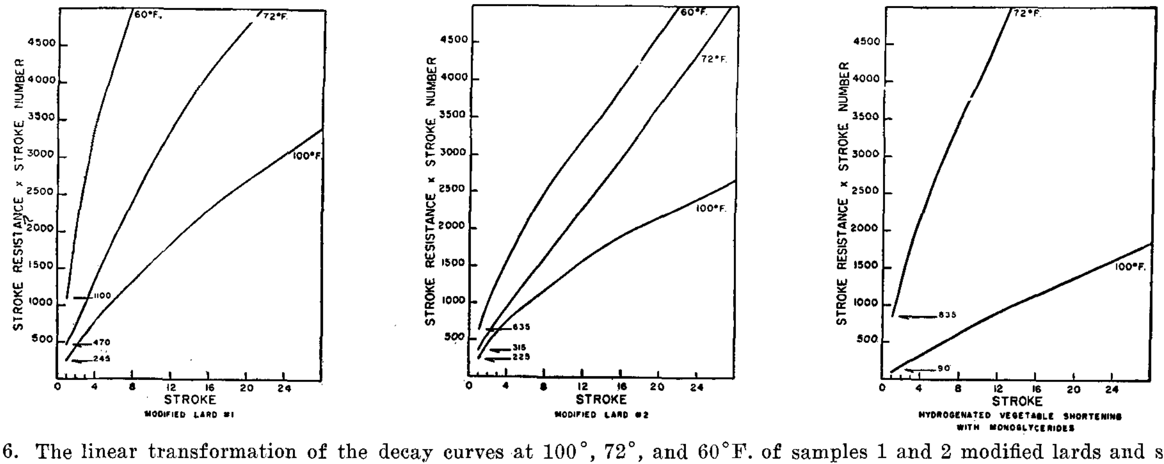

FIG. 6. The linear transformation of the decay curves at 100°, 72°, and 60°F. of samples 1 and 2 modified lards and sample 3, a hydrogenated vegetable shortening with monoglycerides. Sample 2 exhibits a better plastic range than sample 1, changing less with temperature. Sample 3 exhibits a poor plastic range, being very soft at 100°F. and very hard at 72°F.

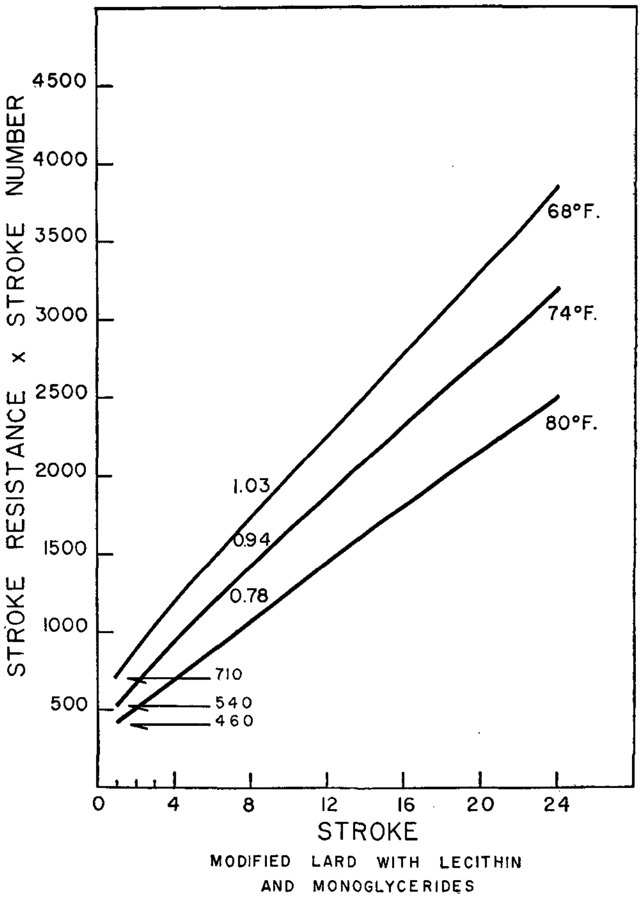

FIG. 7. The linear transformation curves of a modified lard with lecithin and monoglycerides at 68°, 74°, and 80°F.; these curves illustrate the sensitiveness of the test to relatively small changes in temperature. Slope or tangent values at the eighth stroke illustrate the simple expression of consistency. The ratio of any pair of these numbers can be used to express the plastic range in the respective temperature limits.

and tested at 100°, 72°, and 60°F.(37.7°, 22.2°, and 15.6°C.). The difference in slopes of any pair of curves indicate that sample No. 2 had a better plastic range. Transformation curves were made for samples 1 and 2 as low as 45°F. Several strokes were necessary to soften the shortening to the 1,000-metergram resistance range.

The third sample, hydrogenated vegetable shortening with monoglycerides, exhibited a great response to temperature, becoming very hard at 72°F.(22.2°C.). The large change in slope and origin between these two temperatures indicates a poor plastic range when compared with the modified lards. Tests could be made as low as 60°F.(15.6°C.) with considerable strain on the machine and many repeated strokes to soften the shortening below the 1,000-metergram torque mark. At 45°F.(7.1°C.) the shortening was very hard and would not flow through the disk.

This preliminary series established that the test has discrimination and a range sufficient to cover different shortenings over a wide temperature range.

Application Experiments

The equipment and method have been applied to many problems concerned with the cause and extent of flow property changes. A few are described here, plus illustrations of the flow properties of typical shortenings.

Figure 7 shows the transformation curves of a modified lard with lecithin and monoglycerides made at temperatures plus and minus 6°F. from a normal room temperature, 74°F.(23.3°C.). The samples were drawn from a drum by the technique previously described, placed in constant temperature cabinets for 24 hrs. or more before the test.

The values near the curves above the eighth-stroke abscissa point are the tangent values previously described. Significant changes in flow properties are distinguishable when the temperature has changed in the normal range of usage. The simple application of the first stroke resistance and a slope value are all that is needed completely to describe the consistency and stability to shear at any temperature.

Figure 7 also illustrates the use of a master curve for testing a sample at any temperature to determine uniformity. This is important to the quality-control application of the test method. It would not be desirable to adjust small temperature differences between day-to-day sampling by storing at a constant temperature for 24 hrs. The alternative is to establish the desirable limits within a realistic temperature range. With knowledge of the consistency vs. temperature of the standard and the temperature of the unknown, a test can be made on the sample at its "as is" temperature by quickly adjusting the bath.

It is also possible to apply the test to determine the effect of a process step involving shear on the consistency of a shortening. To illustrate the measurement of such change a sample of hydrogenated vegetable shortening with lecithin and monoglycerides was pumped at 72°F.(22.2°C.), using a Moyno pump. Samples of the unpumped and pumped material were put in the molds, tempered for 24 hrs., and tested at 72°F. Figure 8, which shows the decay curve formed by connecting each stroke at maximum resistance, indicates that one pass through the pump is approximately equivalent to 24 strokes of the grease

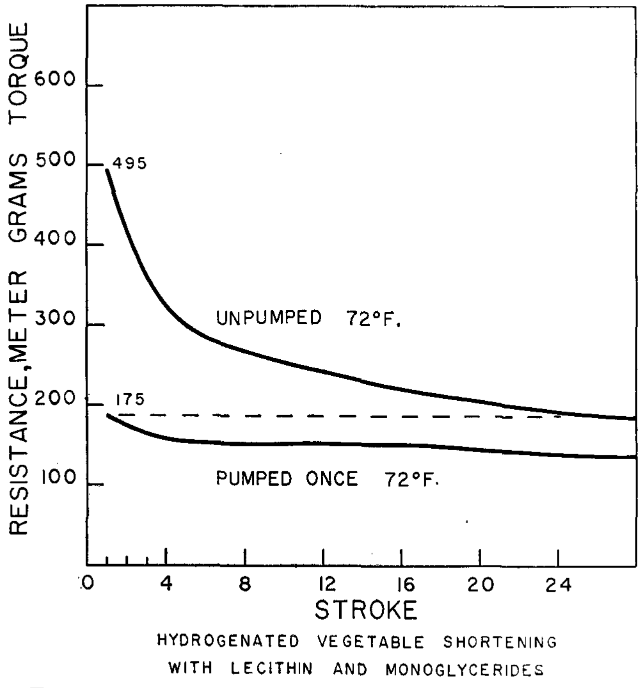

FIG. 8. Simplified decay curves, showing the effect of pumping on the flow properties of a shortening. The effect of one pumping approximates the effect of 24 shearing strokes in the grease worker.

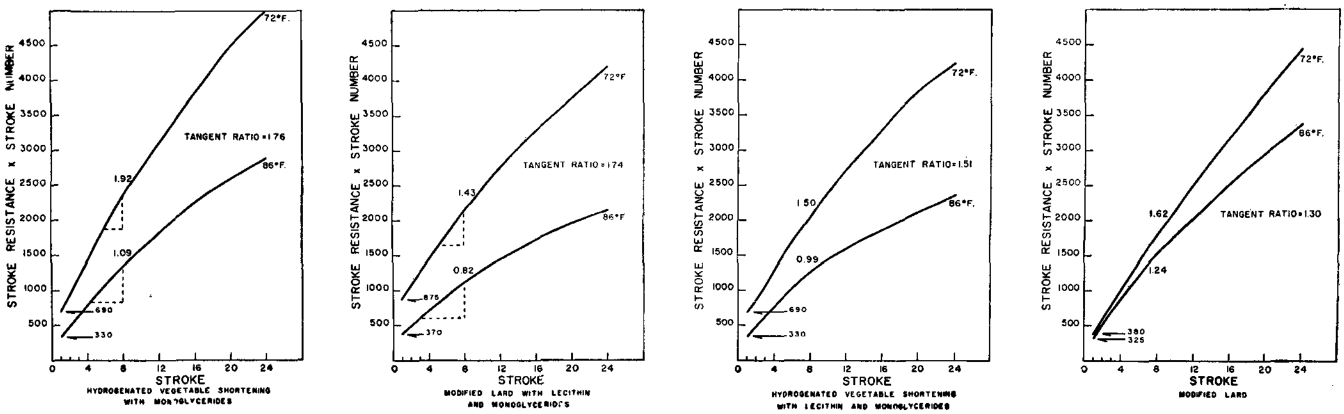

FIG. 9. The linear transformation curves of a) a hydrogenated vegetable shortening with monoglycerides, b) a modified lard with lecithin and monoglycerides, c) a hydrogenated vegetable shortening with lecithin and monoglycerides, and d) a modified lard.

worker. There is evidence of some structure re-establishment in the pumped sample after 24 hrs. as indicated by the slightly different arc at the initial strokes as compared with the end of the worked control.

Many kinds of shortening have been tested, but illustrations of these results would be of limited interest. A few of the typical curves are reproduced in Figure 9 to show differences which can be detected by the instrument. The temperatures used for such testing are 72° and 86°F.(22.2° and 30°C.) only because they are compatible with laboratory schedules and equipment. Any other two temperatures in the approximate range would serve equally well.

Discussion

The shortening rheometer described can be used to determine the flow properties of shortening. The test will establish the following: relative viscosities of shortenings under a single shear application; the change in shortening viscosities as a result of controlled repeated shearing or working; and the relationship of both of these properties as a function of temperature, this providing a simple number index of plastic range.

The test method provides a rapid and accurate method of achieving these results. Duplication is good; repeated tests fall within ± 1 to 5%. The technique is applicable to research, production problems, and quality control. Test output compared to other methods is very high for the amount of information produced. Depending upon the amount of shear given, from two to six minutes are the normal elapsed time of a single determination. With two interchangeable grease workers, the limiting factor is the speed at which the operator can remove, clean, and dry the sensing element. The test is convenient, being self-recording, and requires little or no operator attention. Errors because of operator fatigue are virtually eliminated.

The sample size and shape permits sampling of drums, pails, or cartons by use of open-end molds, from which the sample can be transferred directly to the grease worker. With appropriate segment-forms, chilling molds can be made for laboratory preparation of shortening for tests.

The transformation of the flow-property curves to simple values of initial consistency and tangent ratio at 72° and 86°F.(22.2° and 30°C.) is but one form of describing the flow properties of shortening. Future use of this testing method promises new information unattainable before because of the high cost of analysis and limited interpretation. Standardization of temperatures and sample preparation would establish a common communicative method to describe and control shortening rheological properties.

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Fat Splitting by the Twitchell Process at Low Temperature[1]

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In the usual Twitchell fat-splitting procedure the reaction is performed at about 100°C. under atmospheric pressure with vigorous stirring. For kinetic studies of the stepwise nature of the hydrolysis a slower rate of reaction was desirable. It seemed possible that this might be achieved if the reaction were performed at room temperature with no shaking or stirring. No data could be found in the literature. Accordingly experiments were conducted to determine the degree of fat splitting at 35°C. without agitation of the mixture. Also determined were the effects of dissolving the catalyst in the water layer or in the oil

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