($N_I = 85.1$, $N_{OH} = 188$, $N_A = 188$) while the specific numbers equal the specific molecular constant ($\overline{N} = \overline{N}_I = \overline{N}_{OH} = \overline{N}_A = 3.35$). As is seen in Table I for oleic acid, linoleic acid, and linolenic acid, the specific iodine number ($\overline{N}_I$) is in the ratio of 1, 2, and 3, respectively, to the corresponding specific molecular constant ($\overline{N}$) for each compound.

When a complex mixture is being examined, the use of specific numbers will permit a more rapid interpretation and indicate in a more direct fashion the nature of the mixture. This is particularly true when the data are used in conjunction with modern instrumentation, infrared and ultraviolet spectrophotometers, vapor phase chromatography, etc.

Several examples of convenience of the new procedures with mixtures are given below:

**Example I**

Mixture of alcohol and acid:

*Conventional numbers*

Iodine number ($N_I$) = 63.2
Hydroxyl value ($N_{OH}$) = 83.6
Acid number ($N_A$) = 118

*Specific numbers (millimoles per gram)*

Specific iodine number ($\overline{N}_I$) = 1.49
Specific hydroxyl number ($\overline{N}_{OH}$) = 1.49
Specific acid number ($\overline{N}_A$) = 2.11

The identity of the specific iodine and hydroxyl numbers suggests the possibility that the unsaturated and the hydroxyl functions may be in the same molecule and that the acid is saturated. This information is readily available and not buried, as in the conventional numbers.

**Example II** (hypothetical case)

$$\text{Unknown triglyceride} \xrightarrow[\text{treatment}]{\text{enzyme}} \beta\text{-monoglyceride} + \text{mixture of acids}$$

| | Unknown triglyceride | β-monoglyceride | mixture of acids |
|---|---|---|---|
| *Conventional numbers* | | | |
| $N_I$ | 59.2 | 71.3 | 47.2 |
| $N_S$ | 196 | 157 | 209 |
| $N_A$ | 0 | 0 | 209 |
| *Specific numbers* (millimoles per gram) | | | |
| $\overline{N}_I$ | 2.33 | 2.81 | 1.86 |
| $\overline{N}_S$ | 3.49 | 2.81 | 3.71 |
| $\overline{N}_A$ | 0 | 0 | 3.71 |

The ratio of the $\overline{N}_S$ to $\overline{N}_I$ in the starting material is 3 to 2, indicating that, since this is a triglyceride, there are only 2 double bonds present. The ratio of $\overline{N}_S$ to $\overline{N}_I$ in the monoglyceride is 1, indicating that the beta-acyloxy group has one double bond and further that the molecular weight is $1/\overline{N}_S$ or 356. Since this is a monoglyceride, the acid residue must be monounsaturated $C_{18}$ (monoglyceride − glycerol + water = 356 − 92 + 18 = 282). The ratio of $\overline{N}_A$ to $\overline{N}_I$ in the acid mixture isolated is 2 and, since there were only 2 double bonds in the original triglyceride and one remains in the monoglyceride, the acid mixture has only one double bond. Combining this with the data for the tri- and monoglycerides leads to the conclusion that the acids isolated have a total carbon content of 34. None of this can be found using the conventional numbers without tortuous calculation.

The following points are to be stressed. The definition of the specific molecular constant provides a rational basis for reporting data in terms of the basic units, moles and grams. The specific numbers provide a more rapid and less cumbersome method of correlating data. The multiplicity of conventional numbers is replaced by a constant or an integral multiple of it, easily obtained from the molecular weight only.

It is suggested that, for an interim period, both the conventional numbers and the specific numbers be reported, and then only the specific numbers.

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# The Measurement of the Hardness of Margarine and Fats with Cone Penetrometers

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At present the "hardness" of margarine, fats, etc., is measured with various types of instruments, but the results obtained are not directly comparable. Consequently much time is wasted in correlating these data. In spite of the differences between the instruments the measurements made with them all depend on the same rheologically defined quantities, such as yield value, viscosity, and elastic modules. In order to overcome these difficulties, an attempt was made to express the hardness unambiguously in one rheologically defined quantity. For this purpose the elastic modulus is unsuitable because it is not decisive for the hardness. As the viscosity and the yield value are closely related,[1] either of these quantities is sufficient rheologically to define the system, but, because of its simplicity, the yield value was chosen. A reliable instrument for the rapid measurement of this yield value is the cone penetrometer, various types of which are described in the literature (1–5).

[1] It can be derived (Figure 1) that the products of $P_1 \tan \alpha_1 = P_2 \tan \alpha_2 = constant$. (The angle $180 - \alpha_1°$ represents the viscosity.)

### The Yield Value

As margarine and fats have to be considered as quasi-plastic materials when subjected to deformation, their behavior during flow can be established from a shear stress/velocity gradient curve (Figure 1). In

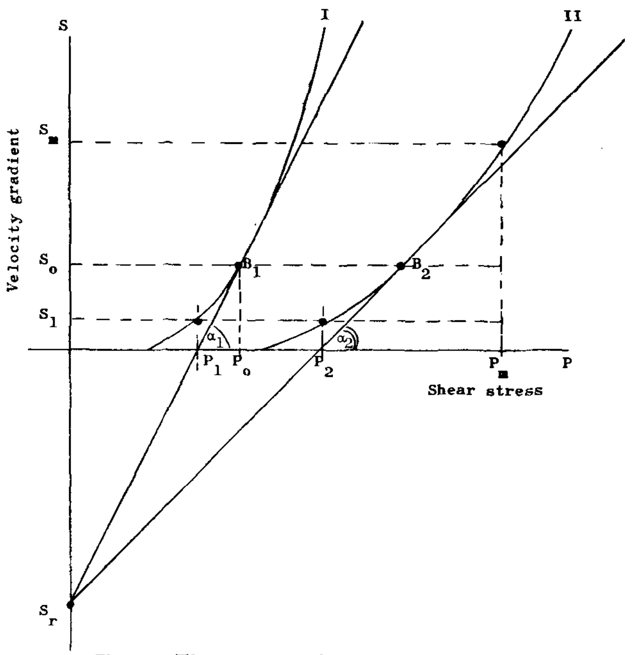


FIG. 1. Flow curves of margarines and fats.

double logarithmic plot, straight lines are obtained. From the results of a great number of measurements with rod penetrometers and by measuring the flow through capillaries (6) it appeared that these lines run practically parallel so that they can be represented by the general formula: $\log S = \log F + n \log P$; $(S = F.P^n)$.
in which:

$S$ = velocity gradient
$P$ = shear stress
$F$ = fluidity (reciprocal viscosity)
$n$ = parameter (constant)

So these flow curves are determined by F. For purely practical considerations however, use is often made of points $P_1$, $P_2$, etc., on the abscissa (Figure 1), which are called the "yield values."

These points are obtained by drawing a tangent through points $B_1$, $B_2$, etc., lying on the same but arbitrarily chosen height $S_o$ of the curves. Mathematically it can be proved that these tangents intersect each other in one point $S_r$ on the ordinate, and the abscissa in $P_1$, $P_2$, etc., in accordance with the general formula:

$$\text{Yield value} = K.\frac{P_m}{\sqrt[n]{S_m}} \qquad \text{g/cm}^2 \qquad (1)$$

in which

$$K = \frac{n-1}{n}\sqrt[n]{So}$$

and $P_m$ and $S_m$ are the coördinates of one point on the curve chosen at random. In practice $n$ appears to be reasonably constant. At a definite value for $S_o$, K becomes a constant and the yield value can then be calculated from only one measurement.

It should be borne in mind that margarine and fats become softer when kneaded or when other deformations take place. In order to avoid these deformations during the measurement or at least to reduce them to a minimum, the hardness has to be measured at low-velocity gradients.

### Yield Value Determined with Cone Penetrometers

With cones the rate of deformation will be great at first, but the cone is soon retarded, and so ultimately the hardness is measured at low-velocity gradients.

Various investigators have used the cone penetration for the determination of hardness of materials, such as pitch, paraffin, wax grease, etc.

Mohr (1) derived a formula for the yield value measured with a cone penetrometer, which was improved by Rebinder and Semenenko (2) and later by Agranat (3).

This formula is expressed as follows:

$$\text{Yield value} = K' W/p^2 \qquad \text{g/cm}^2 \qquad (2)$$

in which $K'$ is a constant, only dependent on the angle $\alpha$ of the cone, W is the weight of the cone (kg) and p is the penetration depth (cm). The derivations are intricate, and the calculation of $K'$ is complicated. For margarine and fats the derived formula (2) cannot be used in the same form as various complications with this material arise. Factors which influence this yield value and must be taken into account are:

a. *smoothness of the cone*—It is necessary to clean the cone in order to reduce the influence of friction as much as possible.
b. *sharpness of the cone tip*—A reduction factor should be introduced when working with nonideally sharp cone tips. The actual depth becomes $p + p'$, in which $p'$ is the height of the truncation.
c. *structural hardness and work hardening*—On calculating the yield value from equation (2), Agranat starts from the assumption that the material is ideally plastic. This is certainly not the case with fat and margarine.
d. *duration of the penetration*—Generally the cone comes to a standstill after 2–3 seconds, but under unfavorable conditions (soft samples and small cone angles) the penetration can go on for hours. For routine determinations however a time of 5 seconds gives reproducible results and was therefore chosen as the standard time.
e. *kinetic energy of the cone*—It should be borne in mind that the penetration depth of a given cone is not only de-

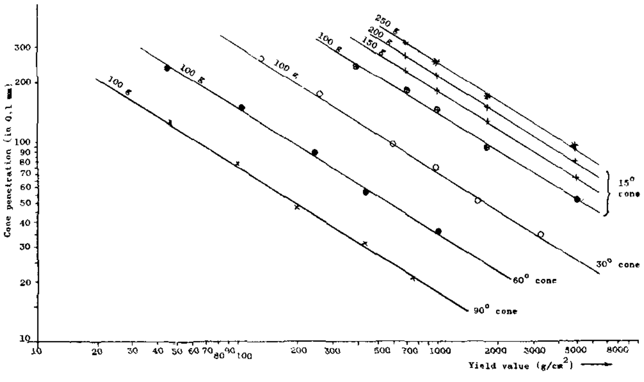


FIG. 2. Yield values as a function of cone penetration, measured with cones of various angles and weights.

pendent on its weight but also on the kinetic energy of the moving cone, which was neglected in the formula derived by Agranat (3).

### Calculation of the Yield Value from the Penetration Depth of a Cone

Yield values $P_1$, $P_2$ (Figure 1) have only a relative value because they represent the force necessary to cause a certain, though small, deformation $S_1$. As stated in the foregoing section, equation (2) is not quite valid because these above-mentioned factors are not fully taken into account. An empirical formula has been found by plotting yield-values, as measured with other instruments, against the cone penetration depths $p$, in a double logarithmic graph. Figure 2 shows a number of parallel lines for various cones. The slope and distance of the lines are indicative for the relationship:

$$\text{Yield value} = KW/p^n \qquad g/cm^2 \qquad (3)$$

From a great number of measurements with margarine fats and shortenings $n$ appeared to be 1.6.

The penetration depth p is measured in 0.1 mm. W is the weight of the cone, and the K-value, which depends only on the angle of the cone, is a constant. The mean K-values found empirically for cones, with angles increasing by 5°, are given in Table 1. Part of these values are obtained by graphic interpolation.

TABLE I

K for cone angles of 15 to 90° graphically determined partly by interpolation

| Cone angle $\alpha$ (degrees) | K (mean value) |
|---|---|
| 15 | 30700 |
| 20 | 19000 |
| 25 | 13000 |
| 30 | 9670 |
| 35 | 7400 |
| 40 | 5840 |
| 45 | 4700 |
| 50 | 3900 |
| 55 | 3300 |
| 60 | 2815 |
| 65 | 2350 |
| 70 | 2000 |
| 75 | 1700 |
| 80 | 1425 |
| 85 | 1250 |
| 90 | 1040 |

When extremely soft and extremely hard samples are used, the scattering in the (mean) K-values is great. To avoid this the angle and weight of the cone should be adapted to the sample to be investigated.

### Some Particulars of Cone Penetrometers

Various suitable penetrometers with changeable cone are on the market. Most of them are provided with a scale on which the penetration depth in 0.1 mm. can be read off. Some of them are provided with an automatic arresting device for a penetration time of at least 5 seconds. To this latter type belongs for instance the Hutchinson penetrometer, which is used in our laboratory. The original calibration in 0.1 mm. is however replaced by a scale from which the yield value can be read off directly. (Figure 3). The cone, which we made of aluminum, has a shaft and a cone tip of hard steel. The cone angle is 40°, and the total weight of cone and moving parts is 80 g. The measuring range can be extended by introducing an extra weight of 80 g. The yield value is then found by doubling the scale reading.

In the Institute of Petroleum penetration method (I.P. 49/46 and 50/48) use is made of a special

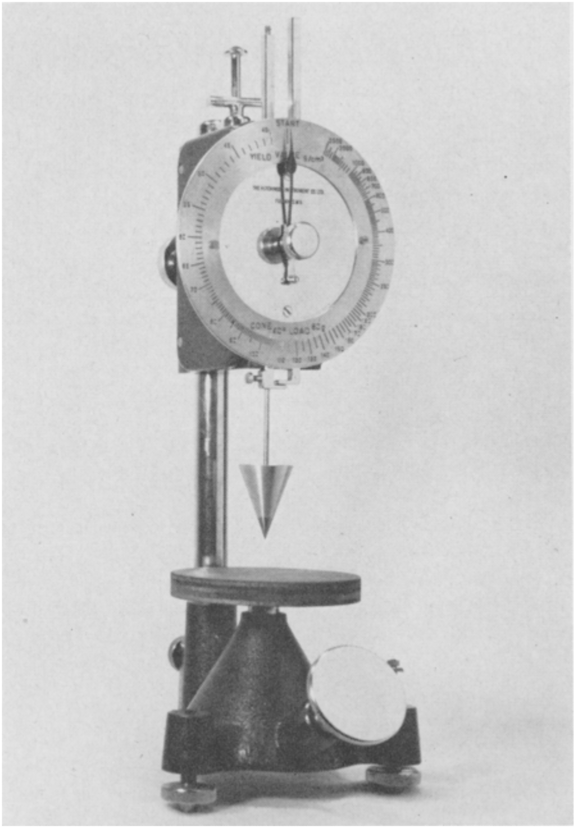

FIG. 3. Penetrometer with scale for reading yield value directly.

"grease cone," which is in fact a double cone. In Figure 4 the dimensions of this cone are given.

This cone is often used in the determination of the hardness of soft greases, petrolatum, and fats (4). However the expression of the hardness in the penetration depth as such is, in our opinion, not justified because its relationship with the yield value is complicated (Figure 4). The break in the curve occurs

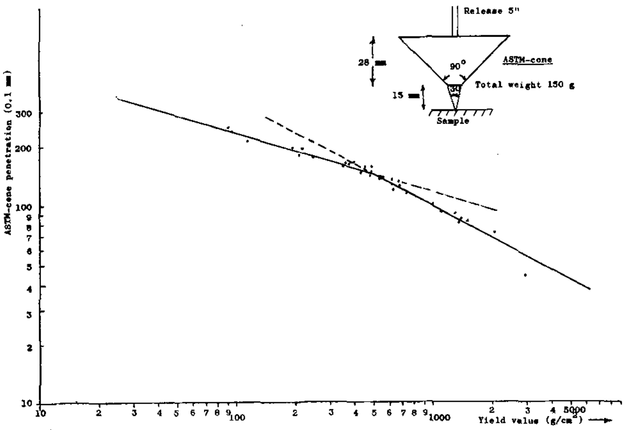


FIG. 4. Penetration depth of an *ASTM cone* as function of the yield value of margarine and fat samples of various hardness.

at a penetration depth of 150 scale units (0.1 mm.) and occurs at the place where the cone of 30° changes into that of 90°.

### General Remarks

The consistency range between very soft and very hard samples lies between yield values of approximately 25 and 2,000 g./cm². This range can be covered by three cones (each of 100 g.) with angles of 30, 60, and 90°, respectively. The penetration depth can then easily be kept between 75 and 250 scale units necessary for a good reproducibility. If necessary, the weight of the cone is doubled. For the correct interpretation of yield values the following table may be used as a guide:

TABLE II

Assessment of Margarines and Shortenings by Means of a Great Number of Thumb Tests as Compared with Yield Values

| Yield value (g./cm²) | Assessment |
|---|---|
| < 50 | Very soft, to just pourable |
| 50–100 | Very soft, not spreadable |
| 100–200 | Soft, but already spreadable |
| 200–800 | Satisfactory plastic and spreadable |
| 800–1,000 | Hard, but satisfactorily spreadable |
| 1,000–1,500 | Too hard, limit of spreadability |
| > 1,500 | Too hard |

In the following table the "usability range" of some fat products, by which is understood the hardness limits at which a product is just usable for a special purpose, is given. It is not possible to give universal limits. They have to be established for a specific country and a specific product by statistical evaluation.

TABLE III

Usability Range of Some Products in Yield Values (g./cm²)

| | |
|---|---|
| Table margarine | 200–1000 |
| Puff-pastry margarine or fat | 800–1600 |
| Soft shortening for shortcake | 50–300 |
| Normal shortening (cake, etc.) | 200–700 |
| Hard bakery fats | 300–900 |
| Fats for dough, etc. ("warm" bakery) | 150–600 |

In the procedure for the hardness measurement of margarine and fats the thermal history of the product and the pretreatment (tempering) of the sample should be taken into account.

## Procedure for Determination of Penetration Values of Margarine and Fats

*Principle.* The hardness is measured by allowing a metal cone of known angle (15 to 90°) and weight (75 to 250 g.) to penetrate into a sample for 5 seconds. The cone is clamped into an apparatus with which the penetration depth can be determined, calibrated in 0.1 mm. or directly in yield values.

*Tempering.* To avoid undercooling the samples are placed in a refrigerator for some hours and subsequently at the measuring temperature for 24 hrs. or longer when samples of more than 250 g. are used. As is true for dilatation measurements with fats, previous cooling has proved to be the most satisfactory to get the best reproducible results in hardness measurements.

*Measurement.* Carefully smooth the surface on the spot where the penetration will be carried out. Place the sample rapidly under the cone and tip accurately upon the smooth surface. Allow the cone to penetrate into the sample for 5 seconds. Read the penetration depth in 0.1 mm. or in yield values. If the penetration depth is < 7.5 mm., the measurement is repeated with doubled weight of the cone or a smaller cone angle is chosen.

*Calculation.* The yield value is calculated from the penetration depth by means of the general formula:

$$C = KW/p^n$$

in which C = yield value in g./cm²
W = weight of cone and all parts belonging to it (= total cone weight in g.)
n = 1.6 (for margarine, butter, shortenings)
p = penetration depth in 0.1 mm.
K = factor dependent on the cone angle (Table 1)

## Summary

In order to be able to compare the results of hardness measurements on margarine, fats, shortenings, etc., measured both with cone penetrometers and other rheological instruments, several measurements have been made with various cones and samples. The results obtained showed that the yield value can be calculated from the following formula:

$$C = KW/p^{1.6}$$

in which C = yield value
K = factor dependent on the angle of the cone
p = the penetration depth in 0.1 mm. at a penetration during 5 seconds
W = the weight of the cone (grams)

This formula appeared to apply for cones with angles between 15 and 90° over a very wide hardness range (between 45 and 8300 g./cm²) for margarine, fat, shortening, and butter.

The advantages of the proposed procedure for determining the yield value are that is is an objective measure instead of a "thumb test;" results obtained with various cones can be compared; and this method is highly suitable for standardizing.

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