Margarine Oil Formulation and Control[1]

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Abstract

The formulation and control of margarine oils and margarines is based on an understanding of the relation between various physical measurements and the composition of the oils and margarines. Solid-to-liquid-fat ratios are determined by dilatometry or by nuclear magnetic resonance spectroscopy. Oils are chosen for their crystal habit under conditions of processing and finishing.

Some margarine test methods involve appearance, oral melting characteristics, oil-off, slump or collapse, get-away, penetration, and spreadability. Many measurements are effective only when they describe conditions over a range of temperatures. These include dilatometry and consistency determinations which require multipoint measurements.

Introduction

THE CONTINUING INCREASED margarine production and per-capita consumption in the United States and around the world indicates the importance of margarine as a significant food item. This growing acceptability is attributable in large measure to the improved performance characteristics of today's margarine products as seen at the retail consumer level. Since certain important characteristics of finished margarines are dependent on the physical properties of the fats and oils used in these products, it is important to consider these factors and their behavior under processing, storage, and handling conditions when formulating a margarine oil blend.

This subject can be more easily approached by avoiding discussion of specific oil blends and formulations for specific margarines or margarine types and dealing rather with the principles and means for measuring those properties or characteristics about margarine which are needed in order to formulate and control its oil blends. Broadly, these have to do with oil blend, the finished margarine, the choice of components, and some orderly method of putting them together.

Until recently, margarine has been defined exclusively as a plastic product indicative of a fat composition with significant levels of solid or crystalline fat at normal environmental temperatures. The physical properties of margarines are therefore concerned with consistency, plasticity, and structure. These factors depend on the melting point of its component glycerides, the total solid or crystalline glycerides present at any given temperature, the distribution of these solid fats over a temperature range, and the polymorphic modification or crystal habit of the fat composition. The most important characteristic is their collective response to temperature and work applied by external forces.

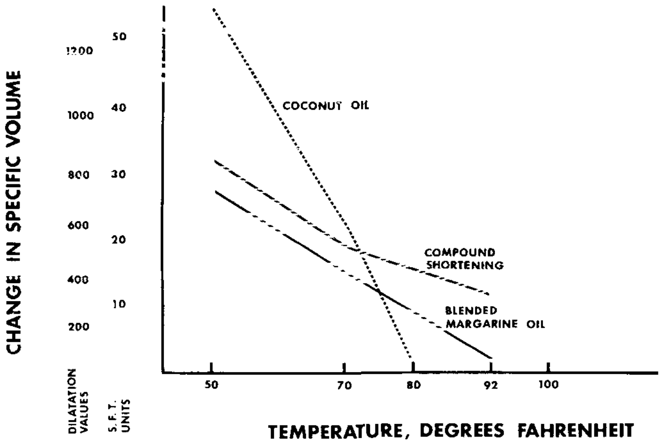

FIG. 1. Dilatometric curves of three different fats described in terms of their solid fat indices (Official AOCS Method) and dilation values.

The hardness of a fat is usually measured by its melting point. This however is quite empirical and does not distinguish well between fats even when several melting-point methods are used. For a fat or fat blend to be plastic it must consist of both a solid and a liquid phase. A ratio of these two phases determines its consistency, that is, the firmness or hardness characteristic of a fat composition. The most convenient and widely adopted method for characterizing this property of a fat or fat composition is dilatometry, the measured change in increased specific volume with increasing temperature owing to melting dilation (1). Dilatometric curves for three different fats are shown in Fig. 1 and are plotted in terms of their solid fat indices as determined by the Official AOCS method (2). These index values are not absolute terms and only refer to relative solids-contents at various temperatures. There are many methods used for measuring and reporting melting dilations, and therefore another scale representing dilatation values (3) has been included to illustrate a comparison of numbers.

The development of a broad-line Nuclear Magnetic Resonance (NMR) instrument offers a new approach to the determination of the solids in fats, blends, and shortenings (4–6). These determinations are reported in absolute terms and extend the measurement range of solids to more than 60%, thus allowing accurate solids levels to be determined in this higher range. The dilatometric procedures are not satisfactory for fats or fat compositions with SFI values over about 60 units at 50F. This has been demonstrated with comparative dilatometric and NMR plots for the same fat sample (4b), showing good agreement only at the lower range of solids measurement (Fig. 2). The further comparison of NMR and SFI values in Table I illustrates how empirical the SFI method can be. Although the NMR instrumentation is quite expensive, it will surely gain prominence in the future.

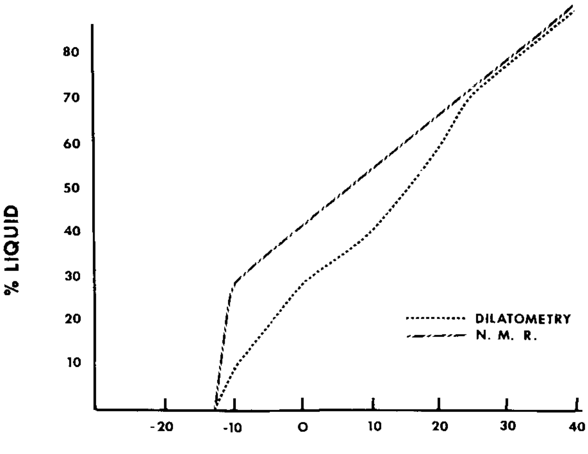

FIG. 2. Percentage of liquid by NMR; variation in liquid/solid content of margarine oil by NMR and dilatometry (4).

The level of solids in most margarine oils falls within a satisfactory range of measurement by the SFI procedure, and the NMR method would have only particular

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• *Margarine Oil . . .*

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TABLE I

Comparison of NMR-SFI Values[a]

	50	70	80	92	100°F
NMR	83.5	74.5	63.0	48.2	33.0
SFI	53.0	44.7	40.2	28.2	17.8
NMR	51.1	40.9	24.0	15.0	7.8
SFI	40.3	27.0	21.5	8.7	1.0
NMR	25.2	21.4	15.9	11.1	8.5
SFI	20.9	14.7	12.6	9.2	5.0
NMR	35.5	17.9	14.3	9.9	5.8
SFI	27.5	18.5	16.9	16.1	9.0
NMR	45.3	30.5	14.2	5.9	3.5
SFI	46.8	21.0	14.1	3.2	0.3

[a] Reported (6) for various vegetable and animal fats.

advantage in the monitoring of its higher melting components. Since, as seen by the comparative data in Table I, there is little basis for comparing one fat blend with another at the same solids level, the NMR procedure would be useful in establishing at least an initial correlation between absolute solids levels and the relative solids levels as indicated by the SFI or other dilatometric procedures.

Both the SFI and NMR procedures require the use of anhydrous fat samples and therefore do not give actual solids present in the finished fat product at a particular temperature. The oil has first to be separated from the product, and the resulting solids values are a measure of the characteristic response of the separated fat to a subsequent, controlled chilling and tempering procedure. The only reasonably close determination of the solids-fat in a margarine, as it exists in the market place, is a method of Hellman and Zobel (7). They employed high-speed centrifugation to plastic fats, and although the method was not entirely satisfactory, it did offer some basis for limited application. The method depends on the collapse of structure under the forces of gravity to release the oil where it can be measured above the solids. It is obvious that high solids-content materials would not lend themselves to such a separation.

The usual guidelines for developing plastic fat compositions, in general, are applicable to the formulation of margarine oils. Since vegetable oils, as opposed to animal fats, are primarily used, hydrogenation plays an especially important role in the preparation of margarine oils. Other oil treatments, as shown in Table II, are sometimes employed.

By far the most common practice for the preparation of margarine oils is direct blending by using hardened oil components. The treatment of oils other than hydrogenation and blending seems unnecessary, and there is no particular advantage to be gained by these treatments in our normal practices. These other preparative approaches are however warranted in regard to oil cost and availability and where somewhat different melting properties are sought. The patent literature cites numerous examples of such practices, some of which have been included in Table II.

Through the use of these processing techniques the means of developing fatty compositions with an extremely wide range of physical properties are available. However, before subjecting a fat or blend to one of these treatments or processing procedures, something should be known about the crystal habit of these fats. In Table III a listing of primarily vegetable oils has been made according to their characteristic crystal habit. Here the fats and oils have been separated into the *beta* and the *beta prime* types. The desirable characteristic of margarines and shortening compositions is described by the *beta prime* type of crystallization. The degree to which each of these oils or fats will exhibit either *beta* or *beta prime* properties will increase with increased hardness, e.g., hydrogenation.

TABLE II

Margarine Oil and/or Component Treatments

	Patent references
Hydrogenation (selective)	8
Hydrogenation (nonselective/selective)	9
Interesterification[a]	10
Co-Randomization[a]	11
Directed interesterification[a]	12
Fractionation (topped) component	13
Blending	14
Blending directly, natural fat and liquid oil	15

[a] Can be hydrogenated, either before or after treatment.

TABLE III

Classification of Fats and Oils According to Their Crystal Habit

beta Type	*beta prime* Type
Soybean oil	Cottonseed
Safflower seed oil	Palm
Sunflower seed oil	Rapeseed
Sesame	
Peanut	Herring
Corn	Menhaden
Olive	Whale
Coconut	Tallow
Palm kernel	
	Milk fat (butter oil)
Lard	

A characteristic of these oils, which is responsible for their exhibiting a particular crystal habit, is their palmitic acid content. As a rule, the *beta* type oils contain relatively low, approximately 10% palmitic acid whereas the *beta prime* type fats contain at least twice that level of palmitic acid. The exceptions to this are lard and tallow, both with 25 to 30% palmitic acid contents. Here the *beta* characteristic of lard is attributed to the high concentration of palmitic acid in the *beta* position of the glycerol molecule. Distribution therefore of the palmitic acid on the glycerine moiety is also important in providing the necessary effective concentration of the *beta prime* type of glycerides.

Coconut and palm kernel oils have a high concentration of short-chain fatty acids whereas the marine and fish oils have high concentrations of longer-chain fatty acids. These two fats have, as a result of their peculiar compositions, lower titers and are therefore not as high melting as other vegetable oils for similar iodine values or degrees of unsaturation.

Another important aspect for predicting or choosing an oil for use in margarine formulation is its response to interesterification. Of the *beta prime* type fats, only palm oil remains unchanged in its crystal habit on interesterification. Of the oils grouped under the *beta* classification, no change in crystal habit is observed with interesterification or co-randomization. It can be noted that milk fat (butter oil), is a *beta prime* former, which becomes *beta* on interesterification.

Another requisite need for margarine manufacture is some testing procedures to evaluate what has been formulated and processed. Some typical evaluation methods employed in practice today are grouped in Table IV.

The use of these test methods results occasionally in anomalous observations. For example, in the comparison of two margarines, it may be obvious in a subjective test that one is softer than the other; however an instrumental reading, e.g., penetrations, will indicate the opposite. The reason is not that the method is in error or that the individual has not made a proper judgment but rather that the two observations are not comparable in this instance. The difficulty is that the actual penetration measurement is only a single-point determination that reflects a limited response of the system. These single-point measurements are referred to as apparent measurements and suggest that the apparent penetration does not adequately describe the actual hardness of the product. This is further demonstrated by the two consistency curves in Fig. 3.

These curves visualize the flow response to the changing pressures applied to the two margarines or plastic fat compositions, A and B. An extrapolation of these curves to the abscissa gives rise to points a and b as yield values, representing the minimum force necessary to initiate product flow. If a force X is arbitrarily applied to each of these fats, their flow responses (single point) would be similar. If a force less than X had been applied instead, it would be concluded that product A is softer than B; and if a force greater than X had been applied, the opposite conclusion would have been made. In all three instances the interpretations would have been in error. The only correct way of measuring the flow characteristics of these two fat compositions would be to measure their response over a range of pressures. This would result in the complete consistency curve, the slope of which would be characteristic of each, and these would then be comparable product characteristics.

The importance of the philosophy of multiple-point measurements was demonstrated earlier when melting-point characteristics (single-point measurements) of a fat were abandoned in favor of dilatometry, a variable melting response over a range of temperatures. This can be extended to the oil-off procedure, where instead of only making comparisons at, for example, 85F, one would better use a two-temperature measurement, at 80 and 85F, and, from the slope of a line connecting these two points, obtain a response characteristic of the margarine product. The concern for a multipoint response has not been entirely neglected, and a few attempts to improve this situation have been reported. Some of these methods are grouped under rheological properties for determining hardness and spreadability (Table IV). The primary difficulty has been that sophistication of instrumental design for the measurement of these rheological properties lags far behind the need. However there are several approaches that deserve additional evaluation in laboratories today.

The most recent publication describes an instrument for determining the level of work-softening of margarines and shortenings (22c). The plasticity of margarine and shortening compositions is largely determined by the ratio in which its internal bonding forces are affected when external work is applied to the system. These bonding forces can be divided into two groups. The secondary of these are the weaker forces, described by Van der Waals-London attraction, and are associated with a high degree of reversibility, thixotropy. The primary forces are relatively strong, exhibit a high degree of irreversibility, and are associated with the direct bonding which contributes most significantly to the structural hardness of the fat composition.

Reversibility and irreversibility refer to the capacity of these bonds (internal forces) to redevelop after being broken down by some external work force. The two methods use an ASTM grease worker to provide this external work force (22b, c). In one instance, the change in pressure (internal stress response) with continued work is recorded, and in the second the penetrations before and after working are recorded. The former actually represents a proper measuring procedure consistent with the change in product consistency whereas the latter is only a more sophisticated measurement of an apparent property. Since the regenerative forces in plastic systems continue to increase after the external force has been released, the greatest danger is determining how soon after work-softening the penetration measurement should be made.

The determination of the yield value through the application of penetrometer measurements (20 b) also results in an apparent observation. As seen from Fig. 3, the characteristic of either curve A or B is determined

TABLE IV

Evaluation of Physical Properties of Margarine

Testing techniques	References
Appearance	....
Oral melting characteristics	16
Oil-off, bleeding	17,16b.
Slump, collapse	16b.
Get-Away	19
Penetrations	17,18
Spreadability	16b.
Rheological properties . . . determining hardness and spreadability	
A. Penetration	20,21
B. Extrusion	19,22,23
C. General	24

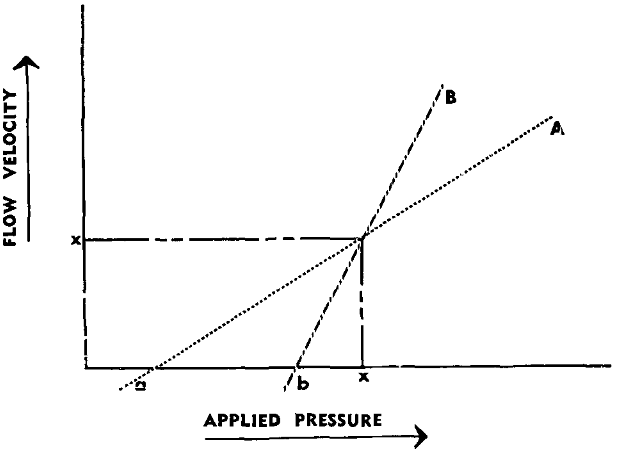

FIG. 3. Consistency curves of two plastic fats or shortening compositions.

by more than just its intercept with the abscissa (yield value). The instrument of Prentice (22a), in which an extruder is used for estimating the spreadability of plastic materials, appears to avoid this dilemma. Of all the methods, the application of extrusion techniques to a plastic fat composition seems to be the best way to approach the measurement of its spreadability. Since textural properties manifest themselves under dynamic conditions, texture measurements should not be performed under static conditions. Hardness therefore as a discrete property is not particularly important as its measurement is implicit in the spreadability determination. Or to put it another way, the hardness of a fat composition is not a property as important as its rate of deformation under an external load, which in reality describes spreadability.

Without sacrifice of sound philosophy, it is recognized that quality-control needs are less demanding than product development work, and routine testing methods can therefore be more empirical. Rate and type of force application and temperature should be optimized in order to obtain response measurement which will correlate with product functional properties and eating qualities.

The next step is to put an oil blend together and process it into a finished margarine. Although oil blending still reflects a fair amount of art at times, requiring some experience and familiarity with the interaction of different oil components, there are some guidelines that should be followed. Since most margarine oil blends are formulated on the basis of their solids content, the equation in Fig. 4 can be useful. This states that the oil blend SFI at any temperature T° is equal to the summation of the solids contribution of its component parts at that temperature (T°) times a constant k. The constant is usually a positive value, and, although not indicated as temperature-dependent, it is always smallest at temperature extremes (50 and 100F). A little experience will develop an appreciation for its place in SFI calculations.

Given a set of oil components and their individual SFI values, the formula can be used to determine what level of each component will be needed to meet a specific SFI requirement for the total oil blend, or it can be used to predict finished oil-blend SFI values. The use of soft or liquid oil components will, of course, increase the solubility of solids and depress calculated values at any particular temperature.

One of the potential defects in margarine texture is graininess (25,28). The higher melting triglycerides melt out of their nongraining condition (solid solution) and crystallize as large, discrete particles, hence the term sandy margarines. The problem can be resolved by a proper choice of hard component(s) or a multiplicity of components. Earlier work demonstrated that this graining was attributable to polymorphic transformation with the formation of triglycerides in the *beta* form (26). Since the blending practice at that time was to use two-component systems, a hard and a softer component blend, and since extremes in hardness will accentuate grain formation (28), one obvious cure would be to use a strong *beta prime* type fat as the harder component. It is also obvious from the equation (Fig. 4) that the use of a third component of intermediate hardness will, for constant SFI values, reduce the hardness contribution of the hard component and thereby help stabilize the oil blend toward the prevention of grain formation. If a third component is good for the system, a fourth will be better, and this approach leads to today's practices with the wider availability and choice of oil components. The use of multiple components not only controls grain formation but, more importantly, leads to improved product-consistency control and product flexibility.

$$(\mathrm{SFI})_{T^0} = \sum \left[(\%)_i \left(\mathrm{SFI}_{T^0}\right)_i \right]_k \times k$$

FIG. 4. Equation for calculating SFI values of either blend or component parts at any temperature; k is a variable factor dependent on system and temperature.

Margarines are usually processed by quick chilling through a swept surface heat exchanger, followed by quiescent solidification prior to molding or forming. Where specific body characteristics are desired, a treatment similar to that employed in shortening manufacturing is applied, namely, the use of a working "B" unit after super-cooling. Thus it is a usual practice to feed an emulsion of the fat and aqueous phases directly to a crystallization unit (15). A number of patented procedures exist for processing margarines in which the process differs somewhat from this normal practice, and special product properties have been claimed for these processes. One is the use of a double emulsion, an oil-in-water-in-oil system, in which the dispersed phase is an oil-in-water emulsion, e.g., a cream, for which is claimed a finished product of longer plastic range (29). Improved melting (eating) characteristics are also claimed for precrystallization and milk injection processes (30). The whipping of margarines up to 50% over runs will also increase the hardness (allowing the use of softer oil blends) and change the texture of the finished products (31). The rate of cooling the emulsion, the type of working during and subsequent to chilling, and the condition of the emulsion to the chilling unit all have a marked effect on the finished product. Processing therefore is equally important at times as the oil-blend describing the physical and eating properties of margarines.

Some typical SFI values for various United States margarines have been included in Table V. The first four are representative of margarines available in the retail market and illustrate the wide range of solid contents which are employed today. Oil formulations can be used to satisfy the marketing requirements for eating and physical properties. The last three margarines are the bakery type of products. The bakers, and roll-in margarines are usually prepared by blending a standard stick margarine oil formulation with added hard fat and/or monoglycerides. The puff-paste product will require, because of its specialized application, a special tempering step to develop a high level of malleability.

The SFI values shown in Table V are generally representative of year-round distribution. The practice of using summer and winter specifications is rapidly disappearing with the increased availability of refrigerated

TABLE V

Typical SFI Values for U. S. Margarines

	10	21.1	26.7	33.3	37.8 °C
	50	70	80	92	100 °F
Stick (3-component system)	28	16	12	2–3	0
80% Liquid oil print	15	11	9	5	2
Cup products	13	8	6	2	0
Liquid oil + 5% hard fat	7	6	6	5.4	4.8
Bakers'	27	18	16	12	8
Roll-in	29	24	22	16	12
Puff paste Veg/A-V	25	24/21	23/20	22/16	21/15

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• *Margarine Oil . . .*

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storage and distribution facilities. This is particularly true in the United States. Where climatic conditions indicate other practices, the margarine formulations would be guided again by end-product or finished margarine testing methods.

Health margarines are still of some concern to the public today. In the past the American Heart Association has defined the health margarine as one with 25% maximum saturated acids and 25% minimum polyunsaturated acid contents. The American Medical Association has described a health margarine as one with a polyunsaturated saturated ratio of 1.2. These definitions rely on the gross fatty acid analyses of the oil blend, without any consideration for isomeric configurations of the unsaturated moieties, and on an assumption that monoenes (oleic acid) are neutral substances. The only established health condition of fats and oils is one that describes its essential fatty acid content, *cis,cis*-9,12-octadecadienoic (linoleic) acid (32). Content and supply of this fatty acid are adequately available in today's margarines even if they were to represent the sole source of fat supply in the diet (33).

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