Finished Product Formulation

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ABSTRACT

Rules of formulation are discussed. Some characteristic properties of raw materials and finished products can be instrumentally determined, others more empirically. Such approach applies to raw material interchangeability as well. Formulation problems will differ according to the type of finished product: margarines, shortenings, salad dressings, deep frying fats, specialty fats. They will also vary depending on the user: household, catering, manufacturer or food industry. Modern methods for formulation are then described.

OCCURRENCE OF FORMULATION

In food industries that deal with mixtures of several raw materials, formulation is done in new food product conception and at various steps in the management of the company. Formulation starts with the idea and market definition of use; continues in product development and is adapted to pilot plant and plant processing conditions. It is modified by many financial, production and cost considerations.

THE CONSTRAINTS IN FORMULATION

Whether the formulation of a product comes from innovation or management, it will undergo identified constraints and modifications imposed by raw material costs, competitive pressures and markets.

Such constraints are very important as raw materials account for about 50% of margarine cost. The benefit coming from a well managed formulation can easily be predicted through a time-projection of raw material costs.

HOW TO FULFILL THESE CONSTRAINTS

Economical Constraints

With computerization, especially with microcomputers, several methods will allow the optimizing of formulation cost or least-cost formulation.

The easiest method is selecting from the formula file. In order to follow fluctuations of raw material prices, new formulas have to be created in the margarine industry. Year after year, the number of formulas increases and gets too great to be processed manually. These formulas are put in computers that will sort out the least cost formula according to raw material prices. The final decision will depend on schedules and previous purchases of raw materials.

One can also create new formulas by minimization. These methods will optimize formula cost vs constraints. These constraints are based on the characteristics of finished products that can be made from the raw material characteristics. Among quantitatively measurable characteristics, we shall mention the solid fat contents vs temperature. These contents can be determined by dilatometry and nuclear magnetic resonance (NMR).

Production constraints relate to raw material properties, existing processes, new processes and productivity in the plant. Acutal production costs account for 20% of the margarine cost. "Other" costs are 30% of the total. A quantitative study on the effect of formulation is difficult. One will find essential to compare formulas and processes in order to improve productivity. Weighing errors or unsuitable formula will lead to recycling. This should be less than 0.1-0.2% of the total plant production.

Quality constraints relate to product specifications, fulfillment of these specifications and product consistency, expected technical performances, and scientific research on consumer health. Depending on quality control efficiency, recycling losses may reach 0.2-0.4% of the total production. They generally originate from problems with raw material quality.

Dilatometry is a time-consuming method. NMR has been much developed both in its methodology and its equipment (1-3). The parallel method is very fast. All sample tubes will together undergo crystallization and conditioning, then a direct distribution in several thermostatic baths preset to the specific measuring temperatures. The new microprocessors will allow direct data handling by microcomputers.

For identical manufacturing conditions, a direct relationship can be found between solid contents (from 5 to 45 C) and margarine properties such as consistency. We measure it by Instron penetrometer. Fig. 1 shows the relationship between % solid contents and Instron consistency in N. or Pascal.

We then have to know what relation there will be between the individual content and their mixtures'. This problem can be solved in two ways. First, let us summarize the determination of "statistical equivalents" presented by Haighton at AOCS Congress in 1976 and by L. Faur at ITERG session of "Journées de la Margarinerie" (4,5). Each component, according to its amount in the mixture, is supposed to contribute linearly to the solid content of the mixture. These "statistical equivalents" are determined by computer calculation of results measured on a great number of mixtures of known composition. This linearization, valid for limited variations in the composition, is the only published and presently usable method.

The other method would be a full study of the crystalline forms originating from the fatty mixtures. Despite the many publications from Unilever and other laboratories, these studies are far from being completed.

During heating, the fatty crystals not only melt but also dissolve. The study of solubilization is fairly easy if the

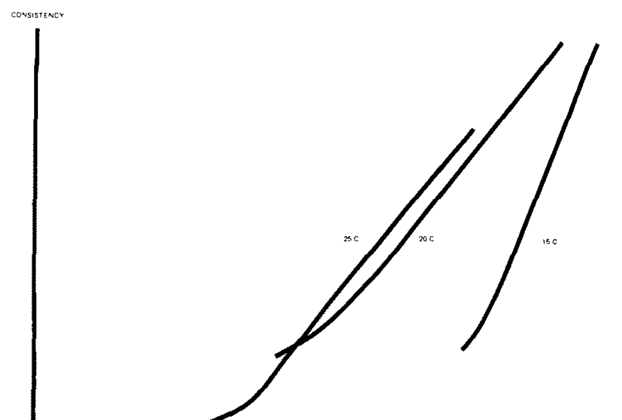

FIG. 1. Relation between percentage solid and consistency.

crystal system behaves as a continuous solid solution. This system is often found for monofat margarines such as sunflower margarine. Let us consider the mixture of a fluid vegetable oil with the same hydrogenated oil. Figure 2 shows the evolution of the solid contents of the hydrogenated fat vs its dilution in the same fluid oil. This picture tells us little about these mixtures' crystalline system. On the contrary, the drawing of isosolid lines (Fig. 3), comparable to Rossel's isodilatometric curves (6), provides more information.

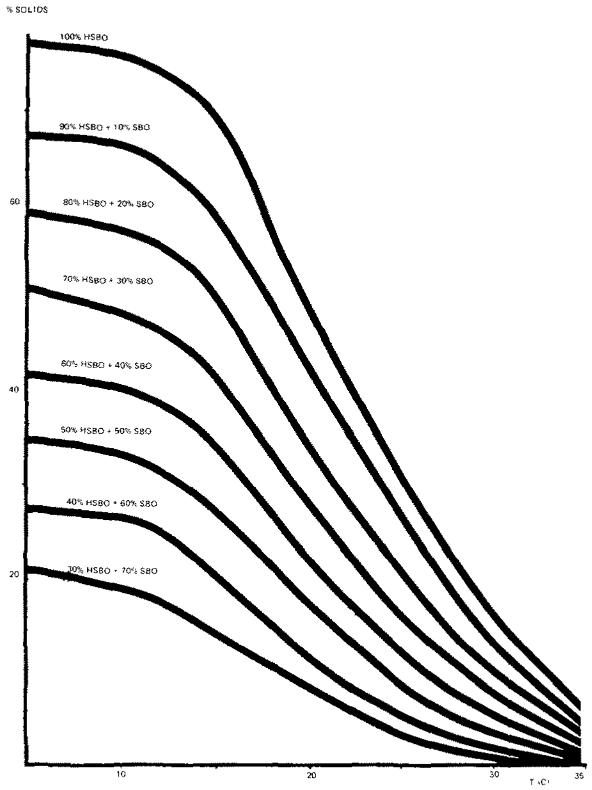

FIG. 2. Percentage of solids of HSBO in SBO.

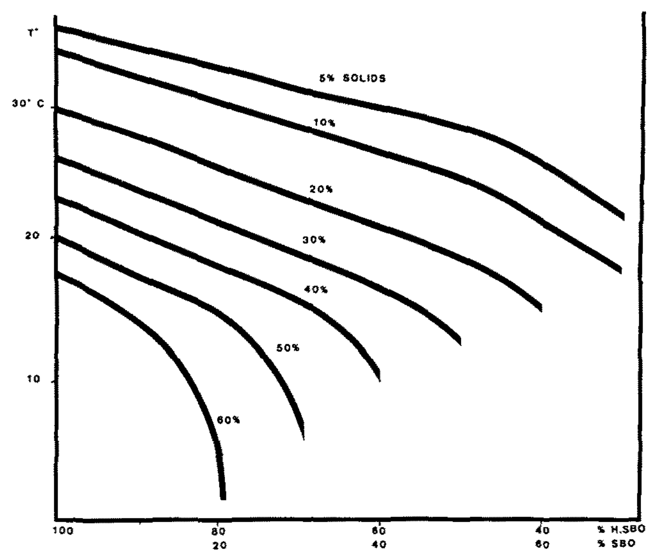

FIG. 3. ISO solid curves vs dilution.

A computer program has been published (7) in order to control the drawing of these lines. It provides for direct processing of NMR data into isosolid lines. A look at these curves shows that the mixture makes a continuous solid solution. The modified Clapeyron's Law is valid. The logarithm of the ratio fat/mixture is proportional to inverse temperatures in K and approximately to the temperature (Fig. 4). Such diagrams can be used to prepare sunflower or corn oil margarines, the fatty phase of which includes hydrogenated and interesterified fats.

However, Clapeyron's Law no longer holds if the crystal system behaves as a eutectic. In the following example, the coconut/palm oil mixture is diluted in a fluid oil. The isosolid lines (Fig. 5) show the formation of an important eutectic. The semilog drawing of solid contents vs temperature is not linear. One can hypothesize that the fluid oil participates in the eutectic formation.

The known or expected relationships between the characteristics of the components and their mixtures may be used to prepare programs for linear programming (8,9). These programs will minimize formula cost and simultaneously comply with several constraints representing the expected properties of the finished product. Some companies already use such programs (10).

Formulation and Production

Formulation improves production profitability. The profit resulting from good formulation is hard to evaluate. The formula has to comply with existing processes. Also one has

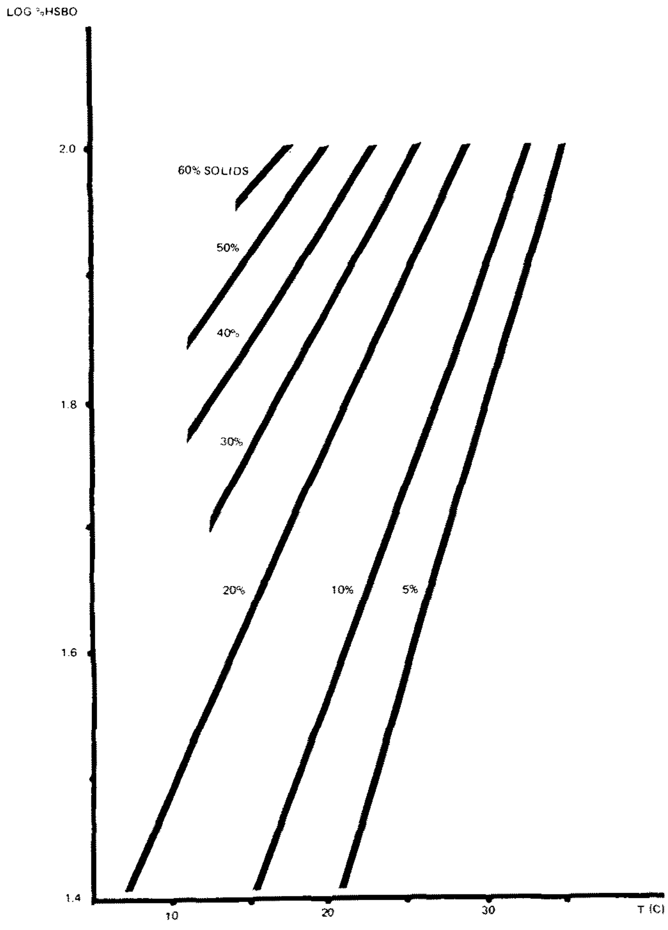

FIG. 4. ISO solid lines vs log %HSBO.

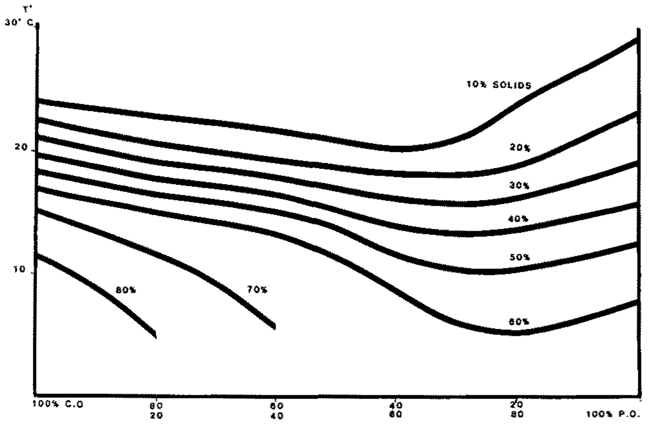

FIG. 5. Palm oil plus coconut oil ISO solid curves.

to modify formula in adapting with always more productive processes. Let us see how the process can control the formulation characteristics.

The simplified chart for margarine production includes the circulation of the emulsion through one or several scraped tubular exchangers (Fig. 6) called A units, then the more or less intensive kneading in a crystallizer called B unit.

Taking Wiedermann's phase diagram (11), we shall have temperature a at A unit outlet (Fig. 7). The emulsion is poorly crystallized and the first crystals have the composition a′. Crystallization is intense in unit B. Both the heat of crystallization and the mechanical work raise temperature in the emulsion to value b. The crystal composition will slowly move from a′ to b′ or from x_1 to x_2.

The scale-down of plant parameters to our pilot plant shows a temperature deviation of 1.1-1.2 C for soft margarines and of 2-3 C for pastry margarines high in fat solids. Beside these temperature variations, the rate of crystallization plays an obvious role for the above-mentioned reasons. This phase diagram does not hold for eutectic mixtures.

We have just seen that both formulation and process will control the amount and composition of crystals. In addition, the mechanical work given to the emulsion will control some properties of the finished product.

Industrial parameters were simulated in our pilot plant. The assembling diagram, temperatures, rotational speeds of A and B units and the composition of formulas were kept constant. Only the flow rates varied from 233 to 275 liter/hr. The temperature differences at the outlet did not exceed 1.6 C, due to large scraped exchange surfaces. However, important differences in consistency have been observed after a 4-day tempering at 15 C. Results in diagram form (Fig. 8) show that 5 C is the ultimate limit for spreadability.

One can hypothesize that crystals were formed before or early in B unit when a low flow rate was set. The important kneading lead to a fine crystallization and the destruction of the intercrystal bonds of the primary type. With a higher flow rate, crystals appeared late in B unit and partially during packaging. Crystallization was then coarser and intercrystal bonds were only slightly damaged.

These examples and the number of parameters they involve show how difficult it is to make general quantitative rules about industrial fat crystallization. All is still based on experience.

The process parameters have to be strictly observed in order to adapt formulas, showing the importance of con-

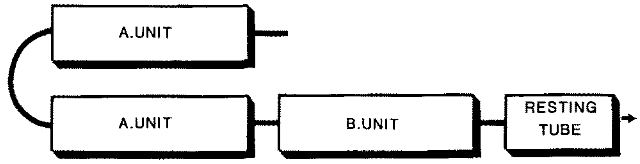

FIG. 6. Simplified chart for margarine production.

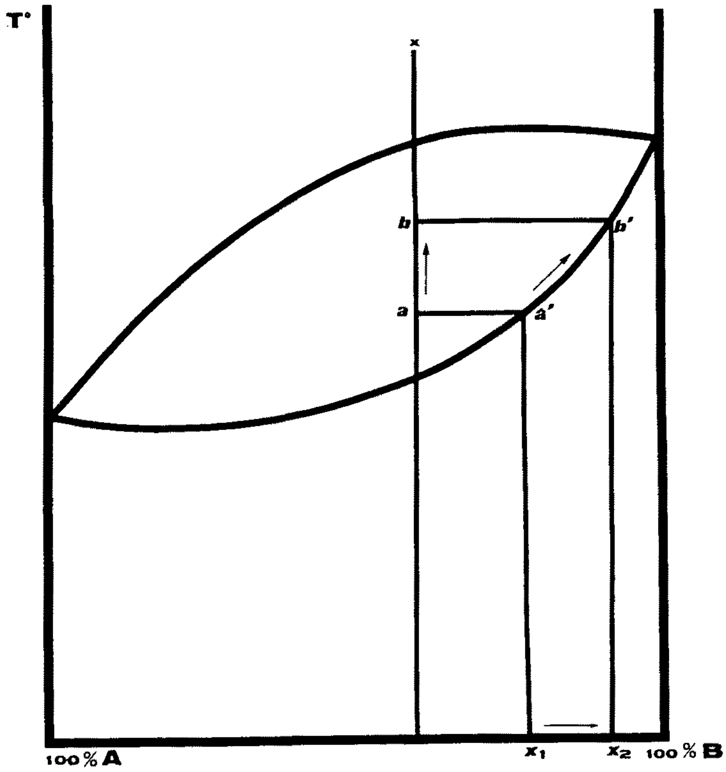

FIG. 7. Simple phase diagram of solid-state formation.

trol, especially on-line control. The development of microelectronics lets us guess at the possibility of full automatization. However, one will not find many specific sensors in our industry. We are not yet able to measure continuously water and salt contents. The viscosity sensors are not sophisticated enough. The flow rates and temperature measurements may be used as direct and indirect control tests (12-15).

Formulation and Quality Management

Raw materials. As we know, management of quality requires the fulfillment of specifications and the regularity of properties of mixture. The desired specifications are obtained when formulas are made for raw materials of standard quality. This quality has to be maintained.

In the case of lack of integrated refinery and margarine plant, the raw materials are bought on the market with a great number of suppliers. It requires increased control of raw materials and stabilization of manufacturing parameters (16).

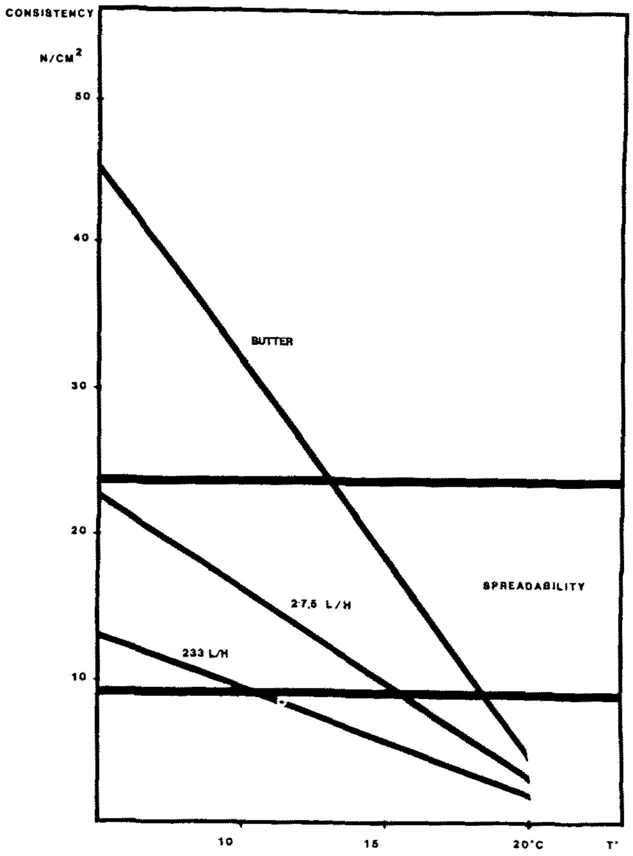

FIG. 8. Flow rate and consistency of tub margarine.

All this makes necessary the creation of specifications acceptable by a great many suppliers; the selection of suppliers according to the fulfillment of these specifications and to their consistent manufacture; and the setting-up of a rapid system for control and correction of formulas.

The raw materials control may easily become burdensome. A 1000-ton yearly production corresponds to 40 deliveries, hence the need to computerize these control data. More than 20,000 data are processed likewise each year in our plant. Whenever possible, the direct data handling of these results will be a real improvement (1,17).

The continuous improvement of productivity on the part of the suppliers will cause a permanent reevaluation of the specifications. The data processing and the formula changes sometimes necessary require great experience on the part of the formulation specialist.

In the case of an integrated refinery, the raw materials characteristics are generally obtained in the refinery (10). This allows an easier selection of the refining products depending on their use. The control in the plant will essentially bear on the production parameters and on finished products examination.

Elaborated products. The user will require that the characteristics specified for the finished product be in adequate for the intended applications. These characteristics vary upon use. Spreadability or consistency at using temperature are important for household margarines; for bakery and industrial margarines, the textures will vary considerably, depending upon use.

We know that consistency may be indirectly measured from NMR solids, from penetrometer or from cone/plate rheometer (18,19). This method is advantageously dynamic and can be used for soft margarines. In other instances, the crystal lattice is partially destroyed during the cone introduction. Also, some textural characteristics will not appear due to a constant and highly important torque at the cone surface (in standard conditions for sample preparation, a good relationship is observed between Instron consistency and the static yield value). The dynamic yield value is related to resistance against working for puff pastry margarines (5).

The organoleptic and performance controls are usually done by special taste panels according to the factory's standard tests.

We have briefly described the experimental methods for measuring of margarine characteristics. Now let us examine how these characteristics may be modified.

Table I summarizes the operating conditions change factors that affect texture:

Some parameters have been previously reviewed: formulation vs liquid/solid ratio, and formulation and production parameters vs composition, size and amount of crystals. Progress was made in the study of influence of glyceride composition on crystallization and properties of finished products. Research has dealt with the initial crystallization rate and rates of polymorphic changes.

TABLE I

Operating Conditions and Texture

Operating conditions	Factors affecting texture
Formulation	Liquid/solid ratio
Temperature, flow rate, mechanical work	Size, composition amount of fat crystals
	Surfusion and rate of crystallization
Storage	Crystal form and polymorphism

The crystallization rates of raw materials and their mixtures were studied during self-cooling (20,21). For the mixtures, one finds as much complexity in the study of crystallization rates as in the study of solid content additivity.

Monoglycerides speed up the crystallization (22). The action of diglycerides is more complex. For palm oil, they decrease the α-form lifetime. At concentrations above 6%, they reduce the amount of crystallized solids (23,24). These data may appear high, yet palm oils originating from unbruised ripe fruits will contain 5% diglycerides while free acidity is only 0.3% (25).

We have cooled down and then reheated a neutralized palm oil with a constant temperature gradient. We simultaneously continuously monitored the density difference between partially crystallized palm oil and liquid palm oil (extrapolated density). Our hypothesis is that the density difference between the fat crystal and its liquid equivalent is 0.1 g/cc. We get the following curve (Fig. 9) similar to SFI curves obtained by dilatometry. An important overcooling can be observed for palm oil. The same palm oil has been filtered through an alumina column to get rid of monodiglycerides and other polar substances. Crystallization is then quite fast. Neither the solid content nor the fusion curve were modified after stabilization.

New rapeseed oils low in erucic acid were examined, too. Hydrogenated oils show a rapid transition towards

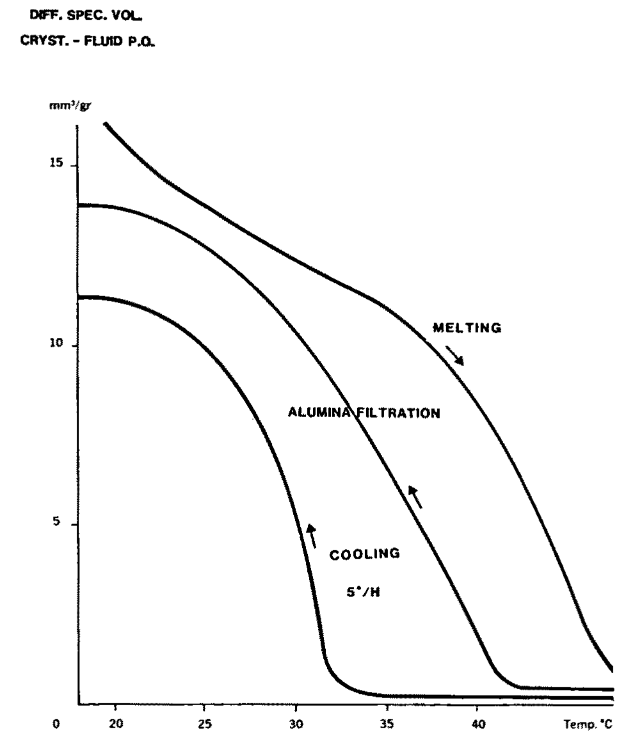

FIG. 9. Crystallization of palm oil.

β forms involving sandy margarines. The addition of 2.5-5% 1-3-diglycerides stabilizes importantly the β' phase (26). The author does insist on the technical interest of this discovery. Other stabilization methods for the β' phase are: the incorporation of more than 20% of β'-fats in the mixture (11); interesterification, and low temperature of storage. The transition rate also depends on the cooling rate and the mechanical work (27,28).

In the margarine industry, the β' forms are generally desired because such crystal lattices ensure the plasticity of the product. Some industrial products, such as liquid shortenings and coating fats, sometimes require the β form. The β crystals are transformed into coherent film resisting to high pressures. Their original consistency is easily recovered after storage (29).

Through these various studies, one notes the influence of glyceride composition on the physicochemical properties of mixtures. For the future, one can hope to see formulations based more on functional properties of different glyceridic groups than on present criteria about raw material groups (30-31).

The results of research on influence of food consumer health play an important role in formulation. A good review of this research can be found in Bruxelles 1979 Congress Report on Lipids and Lipoproteins and in München 1982 DGF Symposium Reprot. The influence of this research on formulation will be further examplified in the "Health Margarine" development.

All these characteristics of formulated products are instrumentally or experimentally determined. One has to process the data through modern methods of quality management. The time has gone when the importance of quality control was related to the size of the control laboratory. Results must be processed by computer in order to obtain the validity of sampling, statistical tolerances or reliability. Studies on the buyer/supplier relationship or on aftersale quality can also be included (32,33).

RECENT DEVELOPMENTS IN FORMULATION

Soft Margarines

Many patents have been published about soft margarines. A great deal of these involve palm oil fractions or palm kernel oil fractions. These fractions or their mixtures are sometimes hydrogenated or interesterified (34-45). By-product utilization is necessary for fractionating plants in order to improve process profitability (46-48).

A patent (49) advises interesterification for margarines containing low erucic acid rapeseed oil so that the β' phase should be stabilized.

The usual sunflower margarines are always sucessfully sold. They generally contain a hydrogenated and interesterified hard phase (50,51). Characteristics of sunflower margarine formulation are shown in Figure 10.

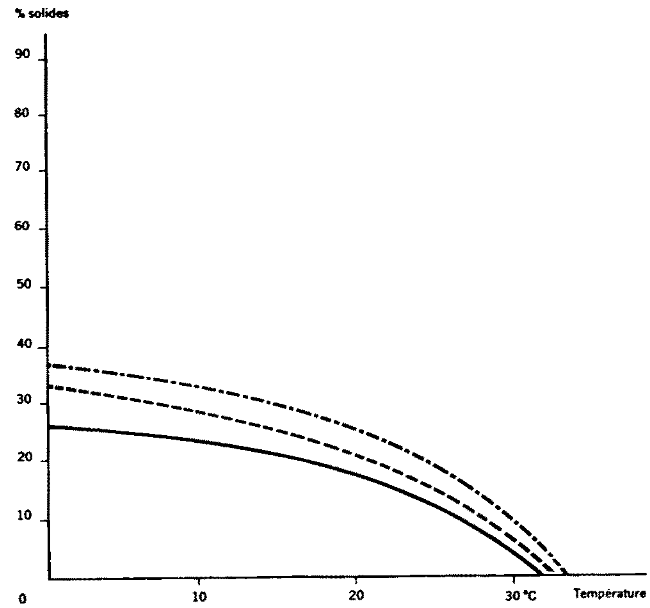

FIG. 10. Composition of sunflower margarine. —·—·— 2/3 hydrogenated sunflower oil 39° + 1/3 sunflower oil; – – – – interesterification; ——— 80% interesterification + 20% sunflower oil.

"Health Margarines" Rich in Polyunsaturated Fatty Acids (PUFA)

These margarines include 15-20% of a fully hydrogenated and interesterified hard phase, containing a mixture of palm oil (or a hydrogenated fluid oil) with a lauric fat (52,53). When sunflower is the fluid oil, the linoleic acid content of the lipid phase is limited to 50-55%. For higher contents, safflower oil is sometimes used.

Parson tried to prepare a concentrate of PUFA by selective extraction of the linoleic rich triglycerides from sunflower oil (54). Other authors studied a different process. Through directed interesterification they tried to separate the 10-12% saturated fatty acids of sunflower oil as S_3 or S_2U. The saturated triglycerides will act as the hard phase in the margarine (55,56). The fully saturated hard phases do not contain *trans* isomers. A zero *trans* isomer margarine based on soybean oil has been described, too (57).

Low Fat Margarines

These products contain only 40-41% fat, including vegetable or dairy fat. Three main tendencies may be observed:

- The water phase is a milk protein concentrate. Keeping properties are limited due to the instability of these proteins (pH and pasteurization temperature) (58-61). One patent advises the use of soybean protein (62).
- The water phase contains stabilizers or gums (63-66).
- The product is prepared with both an emulsifier system and an adequate process. The emulsifier system generally includes a mixture of saturated and unsaturated monoglycerides with lecithins (67-71).

Pastry and Industry Products

One can hardly draw general rules for such products. The characteristics for margarine and shortening will vary regionally, depending on habits, climate, working conditions, etc. Differences can even be found in the recipes in which these products are incorporated, depending on the country.

Some studies on emulsifier systems have been recently published and may help to formulate such products (72-79). Excellent reviews on these topics have been presented (80-82).

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