Use of Fish Oils in Margarine and Shortening

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INTRODUCTION

In Europe, Canada, Japan, and other countries hardened whale oil has been used in margarine and edible fats for over 50 years. Hardened fish oil has likewise long been used in foods, although to a lesser extent, since until recently the amount of fish oil available was invariably smaller than that of whale oil. Many countries, however, have now greatly increased their fish oil production, whereas the whale-oil production has decreased.

The types of fish oil that are marketed change. Whereas 10 to 15 years ago it was mainly herring oil that was marketed in Western Europe, besides menhaden oil from the United States, at present it is chiefly anchovy oil from Peru. The latter oil is characterized by an exceptionally high iodine value.

Hydrogenation is a necessary process in making marine oils suitable for use in edible fats; with a view to the flavor, the highly unsaturated fatty acids must be removed or at least converted to less unsaturated ones. Polymerization might also be applied, were it not for serious objections to the use of polymerized fats in foods.

HYDROGENATION

General

Catalytic hydrogenation of oils was technically developed by Normann early in this century. Besides vegetable oils, it was mainly whale oil which was then selected for hydrogenation because large amounts became available on account of its being no longer needed for illumination. It appeared that a fat could be prepared from it which, with respect to its consistency, was well suited for use in margarine.

Whereas in the past, the primary objective of hydrogenation of fatty oils was the increase in melting point, at present it is the improvement of taste. Therefore, vegetable oils are sometimes hydrogenated in such a way that the liquid character of the oil is largely maintained. A similar hydrogenation of whale oil and fish oil does not, however, give oils possessing the high standards required for human consumption; the fishy taste is insufficiently removed.

Although the taste is improved as the melting point is raised, there is a certain limit to this rise in melting point, since the fat as such, or in combi-

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nations, must be capable of melting in the mouth. It should, however, be noted that the standards set on taste differ in various countries. In Japan, for instance, where whale meat is used for human consumption, fewer objections will be made to slight fishy taste than in Western Europe, with the exception perhaps of Norway where they are accustomed to the odor of whale oil.

In the hydrogenation process, three phases are present: liquid phase (oil), gas phase (hydrogen), solid phase (catalyst).

Liquid Phase (Oil)

If the free fatty acid content is higher than 0.1%, the oil must be neutralized and bleached before hydrogenation in order to avoid poisoning of the catalyst. These treatments are discussed in Chapter 15.

The sulfur compounds, however, which also poison the catalyst, cannot be removed by a normal refining process. Neutralized and bleached whale oil still contains ca. 30 ppm sulfur, fish oil 10–15 ppm.

Other properties of fish oil before hydrogenation will be discussed in the section on the keeping qualities of the hardened fat.

Gas Phase (Hydrogen)

Several procedures may be followed for the industrial preparation of hydrogen which is suitable for the hydrogenation of fish oil.

(a) Steam/Iron Contact Process.—This is one of the oldest and cheapest processes. Iron ore is reduced to iron or FeO; on treating with steam at 600°–800°C. hydrogen is formed. The iron is oxidized to Fe_3O_4 which is again reduced with, e.g., water gas prepared by passing steam over coke. As this hydrogen contains H_2S, purification, e.g., in a caustic scrubbing tower is necessary.

(b) Electrolysis of Water.—Electrolyzers which perform at normal or elevated pressure and produce oxygen as a by-product are commercially available. If a fat-hardening factory is in the vicinity of a plant where NaCl is electrolyzed, the hydrogen released by this process can readily be used for hydrogenation. Hydrogen obtained by electrolysis has a high degree of purity.

(c) Catalytic Steam/Hydrocarbon Process.—A hydrocarbon, e.g., propane, is passed with steam over Ni-catalyst at 800°–1000°C.; this gives H_2 CO, and CO_2. The propane is previously desulfurized by passing over bauxite catalyst at 370°C. Organic sulfur is then converted to H_2S which is removed with monoethanolamine by a scrubber. Removal of CO may be carried out by catalytic conversion into methane and water, using nickel catalyst at about 300°C.

For hydrogenations in the laboratory, electrolytic hydrogen from a cylinder can be used without further treatments.

Solid Phase (Catalyst)

Only those hydrogenation catalysts are discussed which are industrially applied. In Western Europe they are mainly nickel formate or nickel/guhr catalysts, in Russia also nickel/copper catalysts (in which copper serves to lower the reduction temperature of nickel oxide), while in Japan also nickel-free copper catalysts are used, or at least have been suggested.

Application of the nickel formate catalyst is relatively simple; it is, therefore, most attractive for small industries. The nickel formate is suspended in four times its weight of oil and reduced for 30–60 min. at ca. 204°C. (so-called wet reduction); a finely divided metallic nickel is then formed. If nickel copper formate is taken as starting material, the reduction temperature can be lower. Since 240°C. is far too high for unhardened fish oil, the nickel formate is best taken up in, for example, hardened fish oil. The hydrogenation activity of such a nickel catalyst is excellent, although the filtering properties are poorer than those of a nickel/guhr catalyst; this results in the filtering of black oil. After reduction, the catalyst suspended in fat can be stored or transported in the form of flakes.

Nickel catalysts on carrier can be prepared by precipitation of nickel hydroxide from a solution of nickel sulfate containing waterglass or guhr, by means of soda. After washing and drying a storable green cake is obtained. Before use, this cake must be subjected to dry reduction with H_2 in, for example, a rotary-drum-type oven at 400°–500°C. The reduced catalyst is pyrophoric; it must, therefore, be kept in inert medium and be taken up in the oil to be hardened as soon as possible. If it is to be stored or transported, it must be taken up in a relatively saturated oil such as hardened marine soil.

The various hydrogenation catalysts commercially available nearly always consist of finely divided nickel, whether or not it is on carrier, taken up in fat. The nickel content is ca. 25%.

Apparatus

There are two types of apparatus for batch-hardening, those with and those without recirculation of the hydrogen. Hardening with the former type is called dead-end hardening. Hydrogenation is usually performed at an overpressure of ca. 1 atm. in order to prevent penetration of air into the hardening vessel and thus the danger of explosion.

For a smooth-running, dead-end hardening process, pure hydrogen is required. Since volatile substances will evaporate from the oil—some of which are catalyst poisons—the gas in the top of the apparatus must be let

off at intervals; this is, of course, uneconomic owing to the loss of hydro gen.

In the recirculation system, the gases from the hardening vessel are re turned via a scrubber. In laboratory experiments, the hydrogen may sim ply be passed through a vessel with oil, with intensive stirring, and let of in the open air.

In addition to batch-hardening, there is the continuous or semi-contin uous system which is sometimes used for vegetable oils. A slurry of oi and catalyst is pumped through a series of 3 or 5 hardening vessels through each of which hydrogen is passed. This system is applied ir Russia for the hydrogenation of sunflower oil (Sokol'skiĭ and Bolkhovi tina 1956; Sergeev et al. 1956, Okrugov and Kopylenko 1962). The semi continuous system only performs well if raw materials of constant qualit can be supplied. Since in Western Europe the quality varies widely, the batch system is generally also applied for vegetable oils.

As in the hardening process a heterogeneous system is involved, thor ough stirring being required in order to bring the three reacting phases into close contact.

Hydrogen Addition

Hydrogen addition is one of the three main reactions occurring in the hardening process. Since the aim of the process is to hydrogenate the highly unsaturated fatty acids and to leave those with one double bond unchanged, selective hydrogenation is required, in which high tempera tures must be applied. Should, however, the fish oil be heated to 180°C. after which the hydrogen is introduced, the temperature of the oil would rise too much. This would lead to a temporarily insufficient supply of hy drogen and consequently to excessive isomerization—particularly on har dening with poisoned catalyst—and formation of cyclic compounds, o which the physiological properties are as yet not fully known (Gottenbo and Thomasson 1965). It has been found that at extremely high harden ing temperatures aromatic fatty acids (bound to glycerol) may be formed To determine the amount of these aromatic acids the total fatty acids ar treated with urea. Aromatic acids do not form adducts. It has been ad vised (Coenen et al., to be published) to harden highly unsaturated fisl oils in two steps, first at relatively low temperature, e.g., 150°C., and after wards at higher temperature, preferably below 200°C.

Thorough stirring is required also here, because the reaction at 150°C must proceed as rapidly as possible.

In Fig. 42 the changes in highly unsaturated, diunsaturated, monoun saturated and saturated fatty acid percentages occurring during hydrogen ation with poisoned catalyst are given for three marine oils. These oil
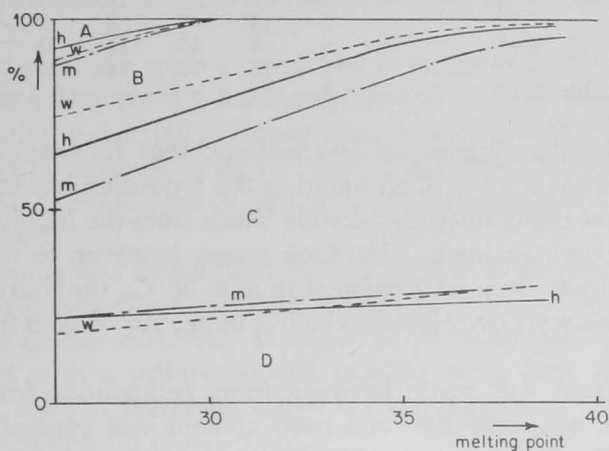
FIG. 42. COMPOSITION OF PARTIALLY HARDENED FATS
WITH DIFFERENT MELTING POINTS

h = Canadian Herring Oil
w = Whale Oil
m = Menhaden Oil
A = Highly Unsaturated Fatty Acid Region
B = Di-unsaturated Fatty Acid Region (not con-
jugable)
C = Mono-unsaturated Fatty Acid Region
D = Saturated Fatty Acid Region

behaved almost identically. The rise in saturated fatty acid is only *ca.*
1%/h (selective hydrogenation). Near m.p. 35°C. there is hardly any dif-
ference between the three oils with respect to their saturated, monounsat-
urated, and diunsaturated fatty acid percentage.

Isomerization Reactions

Besides hydrogen addition, two other reactions occur, viz. migration of
double bond and *cis/trans* isomerism. These reactions are promoted by a
low hydrogen coverage of the catalyst or by poisoning of the catalyst with
sulfur. No systematic investigation has been made into these reactions,
but an idea about the extent to which they occur can be given.

Herring oil with the double bond mainly in the 9-position was partially
hardened in the presence of sulfur-containing nickel catalyst at 180°C. to
m.p. 33°C. The position of the double bond in the hardened fat was de-
termined by oxidation with $KMnO_4$.[1]

Counting from the COOH-group, the position of the double bond was
as follows:

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[1] With acknowledgement to Mr. J. G. Keppler of Unilever Research Laboratory,
Vlaardingen, for these experiments.

Position	5	6	7	8	9	10	
% of double bond	6	8	13	18	18	14	
Position	11	12	13	14	15	16	17
% of double bond	8	6	←		8.5		→

From these values it must not be concluded that, for example, the entire percentage of the double bond found in the 5-position has migrated from the 9th carbon atoms since also double bonds from the highly unsaturated fatty acids have remained. Migration seems, however, to have occurred to a large extent. In a fat hardened to m.p. 38°C., the maxima at the 8- and 9-positions were even lower, which is indicative of even further migration.

No distinction was made between *trans* compounds from monoene, diene, triene, etc.; only the total *trans* content was consiedred. It was found that initially it rose very steeply; in a hydrogenation process of 2 h, 80% of the final *trans* content was obtained after only $^1/_2$ h, and 100% after 1 h.

It is supposed that after one hour approximately as large an amount of new *trans* compounds is formed as disappears by hydrogenation (or as is isomerized back to the *cis* form). Marine fats hardened with fresh nickel catalyst contain *ca.* 40% *trans* compounds, those hardened with sulfur-containing nickel catalyst 55–65%.

Selectivity

For selective hydrogenation both the process conditions and the nature of the catalyst are of importance (Coenen 1960). With respect to the former it is desirable that the hydrogen coverage of the nickel catalyst is low; this can be achieved by not too high a hydrogen pressure, a high catalyst concentration, and a relatively high temperature. A low hydrogen coverage of the catalyst unavoidably leads to strong conjugation, which results in migration of the double bond and formation of *trans* compounds.

The catalyst must have pores wider than 25 Å (Coenen *et al.* 1964). This allows a glyceride molecule to move rapidly. Suppose a glyceride molecule, containing one highly unsaturated fatty acid and two monounsaturated ones, is situated in a catalyst pore, on the nickel surface of which the highly unsaturated fatty acid is hydrogenated. If the molecule is not capable of diffusing out as a result of too narrow pores, the monounsaturated fatty acids will then also be hydrogenated, so that a trisaturated glyceride is formed. In view of the high melting point this is undesirable.

Coenen *et al.* (1964) have found that especially nickel catalysts with pores of 20–25 Å cause nonselective hydrogenation. Pores smaller than 20 Å are likewise undesirable because they are too narrow for triglycerides and do not, therefore, participate in the hydrogenation process.

The pore distribution in catalysts can be determined by gas absorption at ca. −200°C. The melting point at a specific refraction or iodine value may serve as a measure of the selectivity of a hardening process. Under selective conditions this melting point will be lower than under nonselective ones; the difference may be as much as 20°C. This primarily depends on the pore structure of the (nickel) catalyst and only in the second place on the process conditions.

Sulfur poisoning of a nickel catalyst mainly leads to cis-trans isomerization. A sulfur-poisoned catalyst is often said to be more selective than a fresh one, but on the selectivity as meant above sulfur has no influence. Fats prepared with a sulfur-poisoned catalyst have, however, a higher trans content, and are, therefore, firmer at room temperature as a result of a higher content of solid phase.

Practical Hydrogenation of Marine Oils

A fresh catalyst is first used for hydrogenation of marine oils to m.p. 42°–45°C. For the first three batches an amount of 0.1% nickel calculated on the oil is sufficient for hardening at a final temperature of 180°C. As the degree of poisoning increases the catalyst becomes less active, so that larger amounts are required. If these amounts become too large, e.g., 0.5% nickel, the catalyst is used for another type of hydrogenation, so-called steep-hardening. This also takes place at a final temperature of 180°C., but the oils are hardened to a melting point of only 35°–37°C. Gradually the catalyst becomes less and less active so that by the end of the processing even as much as 2% nickel must be used.

Only 10–15% of the fat obtained from hydrogenation with fresh catalyst can be used in margarine, since a higher percentage would affect the oral response. This fat is especially suitable for the preparation of margarine, because it initiates crystallization.

The second type, viz. the steep-fat, is characterized by a relatively steep dilatation line as a result of a relatively high trans content. Both types of fat are used for the preparation of margarine.

The still relatively high melting point of the above fats may be a drawback with respect to melting in the mouth, but hydrogenation to a lower melting point does not sufficiently remove the fishy taste.

It has been suggested to add small amounts (<0.1%) of organic nitrogen compounds (e.g., acetamide or benzylamine), soybean lecithin or dimethylpolysiloxane (Ogami et al. 1962; Shimamura et al. 1964) during hydrogenation. This would lead to hardened marine oils which, at a relatively low melting point, taste better than the corresponding fats obtained without these additives. The effect of such additions, however, largely

depends on the surface and structure properties of the hydrogenation catalyst.

Control of Hydrogenation Process

The simplest method of controlling a hardening process is by determination of the refraction and melting point. If, for example, a fish oil is to be hardened to m.p. 35°C., a trial hardening may be made in the laboratory with 200 gm. oil. Samples are drawn at regular intervals and the refraction of the desired fat is determined. During the industrial hardening process, samples are drawn for control of the refractions and, if necessary, the melting points.

The most common method of determining the melting point is by way of the slip point; this is the temperature at which the amount of solid phase in the melting fat has become so low that an air bubble is forced upward in an open capillary filled with the fat. This takes place when there is only 3–5% solid phase present.

Besides the slip point, determinations may also be made of the complete melting point, the Wiley melting point, the softening point, the critical temperature of dissolution, the aniline point, etc.

The melting point only indicates at what temperature the fat is completely melted; it does not give information about the consistency of fat at temperatures below the melting point. In order to know whether we are dealing with a "steep" or a "flat" fat, we must know the amount of solid phase present at different temperatures. This can be determined by dilatometry as well as calorimetry. Since dilatometry is generally applied for checking the hydrogenation process and since it is of great interest in the preparation of margarine, some more attention will be paid to it in the next section.

DILATOMETRY[2]

If a fat is cooled to complete crystallization and subsequently heated gradually, the volume increases as a result of the expansion of the solid fat. At a specific temperature, when the fat begins to melt, the volume increases relatively more. If it is melted completely, another gradual although smaller expansion occurs due to expansion of oil.

These expansions are diagrammed in Fig. 43. Line RS represents the melting expansion of 100% solid fat, R being the volume of undercooled oil at temperature T_1 and S the volume of solid fat at the same temperature if the melting process could be retarded at B. PR is called the dilatation:

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[2] Boekenoogen 1964.

it is normally expressed in mm³/25 gm. fat. The percentage of solid phase at T is roughly RP/RS × 100%.

This is not quite exact because not all the glycerides from the fat have the same melting dilatation; it depends on the unsaturation and polymorphism of the glyceride. For partially hardened marine oil with m.p. ca. 35°C. the melting dilation for 100% solid fat at 0°C. is 1500–1700, dependent on the manner of cooling. For partially hardened marine oil with m.p. 42–45°C. it is 1800–2000. This value is increased by ca. 100 mm³/ 25 gm. per 10°C. temperature rise.

The dilatation of hardened fish oil (m.p., 37°C.) at 20°C. (D_{20}) is 1100, i.e., the amount of solid phase at 20°C. is ca. 1100/19 = ca. 60%. If D_{30} is 625, the amount of solid phase at 30°C. is ca. 625/20 = ca. 30%. In hardening industries just as in margarine factories it is unusual to convert dilatation values into percentages of solid phase. Hardened fats and margarine compositions are characterized by dilatation values.

As stated above, we distinguish between steep and flat fats. Examples of steep fats are cocoa butter and coconut fat, as well as the fat obtained from hydrogenation of marine oil with sulfur-poisoned nickel catalyst. The fat owes its steepness at a relatively low melting point to a high content of *trans* compounds. Fats hardened with fresh nickel catalyst also contain *trans* compounds, but during the hydrogenation also saturated fatty acid is formed which gives fats with higher melting points.
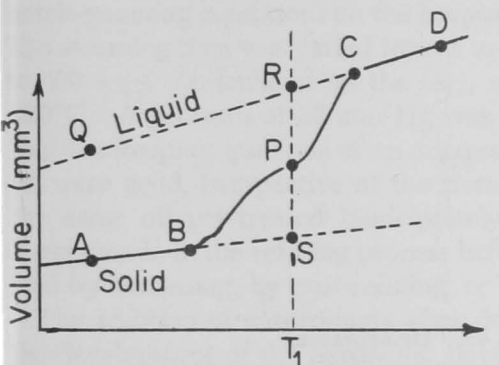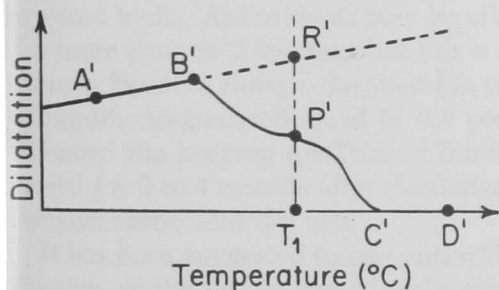

FIG. 43. VOLUME-TEMPERATURE AND DILATION-TEMPERATURE DIAGRAMS

Flat fats of good taste and m.p. below 40°C. can be prepared from vegetable oils by hydrogenation with fresh catalyst. Corresponding hydrogenation of marine oil does also give a flat fat, but its taste is unsatisfactory. In addition, the catalyst absorbs sulfur from the marine oil and forms *trans* compounds, so that on repeated use of the catalyst a steep fat is obtained.

Figure 43 can also be used for representing thermal measurements by plotting the heat content on the vertical axis. The slope of *AB* then no longer represents the expansion coefficient of solid fat but its specific heat, and the slope of *CD* now represents the specific heat of oil. Line *RS* is no longer the melting expansion but the heat of fusion. Thus the same data on, e.g., the percentage of solid phase in a hardened fat can be obtained by calorimetry, although in a more complicated way. Moreover, calorimetry requires a much more complex apparatus than dilatometry.

A dilatometer is shown in Fig. 44. The glass bulb contains *ca.* 5 gm. fat and is connected with a calibrated capillary which contains a sealing liquid, e.g., water, or a solution of calcium chloride.

Dilatation figures of hardened marine oils vary. They depend on the properties of the relevant oil, such as iodine value, place of origin, pretreatment of the oil, properties of the hardening catalyst, etc. When hardened to melting point 33°–37°C., D_{20} varies between 800 and 1200, D_{30} between 300 and 700, D_{35} between 0 and 300.

FIG. 44.   DILATOMETER

Of a hardened marine oil with a melting point of about 45°C., D_{20} is 1400–1600 and D_{30} 1200–1400.

POST-REFINING AND DEODORIZATION

After hydrogenation and filtration the fat is post-treated at about 100°C. with a weak alkaline solution (0.1 N) to remove traces of fatty acid and hardening catalyst. As to the use of active or inactive bleaching earth in the subsequent bleaching process opinions differ. Our experiments showed that in the hardened fish oil post-bleached with active bleaching earth a hardening flavor developed more rapidly during storage than in the same oil post-bleached with inactive bleaching earth. When using nickel guhr catalyst with good filtering properties the remaining nickel content in refined, hardened fats is zero or at any rate lower than 0.5 ppm.

After bleaching, the fat is subjected to steam-deodorization under reduced pressure (e.g., 10 mm Hg). For removal of the volatile components the fat may also be stripped with an inert gas, but the ultimate results obtained by steam-deodorization are better. Steam probably exercises a hydrolytic action on some flavor precursors, as a result of which the keeping qualities of fats treated with steam are in most cases bettter than those of fats stripped with nitrogen.

In our laboratory an investigation was made into the influence of the batch-steaming conditions on the keeping qualities of hardened marine oil. The steaming time was varied from 1 to 23 h, the amount of steam from 25 to 400 wt.% (calculated on the fat), and the temperature from 150° to 220°C. A pressure of 10 mm Hg was invariably applied. It was found that the keeping qualities of an adequately pre-treated, hardened marine oil were good, irrespective of the steaming conditions, and that those of the same oil pre-treated inadequately could in no way be improved. Errors made in the refining process before hydrogenation cannot be rectified by hardening, by post-refining, or by deodorization.

The addition of antioxidants after deodorization has little effect, since the development of the hardening flavor in the deodorized fat cannot be arrested by it. Antioxidants may be effective if the fats have to be stored for more than ca. 3 months., but this is generally not the case with margarine; in Western Europe the shelf-life of margarine is much shorter.

Nordihydroguaiaretic acid in the presence of citric acid favorably influenced the keeping qualities of hardened marine oils which had been stored for 3 to 4 months after deodorization, whereas dodecyl gallate and dehydroacetic acid did not.

It has been suggested to add antioxidants to the fish oil during the production of the oil, so immediately after processing, which sometimes is done on the high seas, deterioration of the oil would be prevented prior to

the refining process, where the added antioxidants are removed. It is not known whether this method is being applied successfully. Working up the oil to a hardened fat immediately after processing seems to be preferable (Pringuet 1964).

The hardened fat should be deodorized immediately before being worked up to margarine.

FLAVOR AND KEEPING QUALITIES OF DEODORIZED HARDENED FISH OIL

On storage of a hardened marine oil which immediately after deodorization is tasteless, an off-flavor develops. In daylight this flavor develops within a few hours, but also in the dark the fat acquires a certain off-taste.

We found that on storage in the dark the content of free aldehydes and ketones in hardened herring oil and whale oil may rise to ca. 5 ppm within two months. For most aldehydes this value is far above the threshold value (Meijboom 1964). The peroxide value generally increases to a value of ca. 1 within two months. In a few cases, however, it drops again after an initial slight increase. The content of bound aldehydes, which is 100–200 ppm immediately after deodorization, increases to 200–300 ppm within two months. Since, however, freshly deodorized oils are tasteless, it is assumed that the bound aldehydes do not contribute to the flavor. It may be expected that on storage of hardened marine oils various aldehydes are formed, each having a different threshold value. One of these aldehydes, 6-trans-nonenal, has an extremely low threshold value, viz. 0.0003 ppm. This aldehyde was isolated from hardened linseed oil and hardened soybean oil, where it is the carrier of the typical hardening flavor (Keppler et al. 1965). In our opinion, this compound is also responsible for the hardening flavor of hardened marine oils. However, when hardened marine oils are tasted indoors, the hardening flavor is sometimes not perceived provided it is present in a relatively low concentration. On inhaling outside air (even half on hour after tasting) it is experienced as an offensive taste in the throat. The sensitivity to this flavor varies individually.

Hardened whale oil and herring oil with a relatively low melting point (e.g., below 30°C.) almost invariably possess this hardening flavor. It can be largely removed by hardening the oils to m.p. 33°C. But even after hardening to m.p. 35°C., highly perceptive tasters will observe this flavor. Highly unsaturated fish oils, such as menhaden and pilchard oil, have to be hardened to an even higher melting point; hardening to a melting point below 40°C., generally is ineffective.

Although herring oil and whale oil hardened to m.p. 35°C. may be free from this particular hardening flavor, they as well as any other oil may de-

velop a certain off-taste during storage. These off-tastes are less objectionable because they can probably be masked when the fats are worked up into margarine (Meijboom 1964).

The content of so-called bound aldehydes, which occur particularly in unhardened marine oils, can be determined by the color reaction with fuchsin/sulfurous acid (Schiff's reagent). The color obtained is compared with that of standard solutions of heptanal and expressed as γ heptanal/gm. The values thus found have only relative significance, because one aldehyde may give a stronger coloration than another. On comparing the aldehyde contents of different marine oils, it should also be borne in mind that the aldehydes formed during autoxidation need not necessarily be all of the same type. For one type of marine oil, however, it may be assumed that the values found are indeed a measure of the aldehyde content of this oil and that, although the concentration may differ, invariably the same compounds are measured.

In the case of unrefined marine oils it was generally impossible to determine the aldehyde content due to the strong color of these oils. As regards bleached oils, it may be observed that the content of bound aldehydes rapidly increases when air is passed through at 70°C. or on exposure to sunlight. Thus, in the case of herring oil the aldehyde content rises from 2 to 14 mg./gm. when air is passed through for three h, and after two hour's exposure to sunlight the total aldehyde content has increased from 2 to 17 mg./gm.

A normally bleached marine oil contains ca. 1–5 mg. aldehyde/gm. The aldehyde largely disappears on hydrogenation; after hydrogenation only ca. 0.5 mg./gm. is left. As already mentioned, after deodorization only 0.1–0.2 mg. aldehyde/gm. oil is recovered. A correlation seems to exist between the content of bound aldehydes in the oil at the stage just before hydrogenation and the quality of the hardened oil. This is, in any case, true of whale oil and herring oil. As for fish oils with a higher iodine value, such as menhaden and pilchard oil, insufficient data are available.

The rate of hydrogenation, too, correlates with the aldehyde content. Herring oil, for instance, required a very long hydrogenation time after air had been passed through at 70°C. or if it had been exposed to sunlight, both processes giving rise to a high aldehyde content.

The correlation between the aldehyde content and the quality of the hardened fat appears from the values given in Table 34.

A careful pre-treatment of marine oil before hydrogenation, as was said before, is required for the preparation of a hardened fat with good keeping qualities.

Although hardly applicable in practice, it should in this connection be observed that molecular distillation of herring oil (normal quality) gave

TABLE 34

RELATIONSHIP BETWEEN ALDEHYDE CONTENT OF UNHARDENED
OIL AND FLAVOR OF HARDENED OIL

Type of Oil	Clarit (%)	Total Aldehyde in Un- hardened Oil (Mg./Gm.)	Harden- ing Time (H)	Assessment of Hardened Fat, 4 Weeks after Deodorization
Herring oil	0.5	4.2	2.25	Fairly good
Herring oil	3	1.7	2.25	Good
Herring oil	5	0.7	1.25	Good
Herring oil	5	0.7	1.25	Good
Whale oil 3 (bad quality)	2	10.0	3	Poor
Whale oil 3 (bad quality)	5	4.0	2.5	Rather poor
Whale oil 3 (bad quality)	10	1.1	2.5	Fairly good
Presstran[1]	0.5	>5.0	3.25	Very poor
Presstran[1]	3	2.3	2.5	Fairly good
Presstran[1]	5	1.3	2.5	Good

[1] Mixture of fish oils, mainly herring oil.

an oil with particularly good color. This oil could be hydrogenated rapid-
ly to m.p. 33°C.; after deodorization it had extremely good keeping quali-
ties. Molecular distillation of Norwegian herring oil, 30% f.f.a., first gave
a top fraction of 31%; after raising the temperature of the rotor from 110°
to 230°C. (pressure $<10^{-3}$ mm Hg/cm.^{2}) the oil itself distilled. This oil
also could be hydrogenated rapidly and gave a good fat, although not as
good as that obtained from herring oil of good quality.

It is worth mentioning that the same inferior Norwegian herring oil
(30% f.f.a.) could be purified by percolating a solution of the oil in techni-
cal hexane through a silica column. The partially hardened fat (I.V. 33)
subsequently prepared did not develop a hardening flavor until two
months after deodorization.

By steam-deodorization of fish oil before hydrogenation, the quality of
the oil can also be greatly improved, which results in relatively rapid hy-
drogenation.

On ascertaining whether a relationship exists between the content of
mucilage, phosphorus, and nitrogen in crude oil and the quality of har-
dened fat, it appeared that these substances are removed by a normal re-
fining process. So there is no relationship between these contaminations
in the crude oil and the hardening flavor of hardened marine oil.

MARGARINE AND SHORTENING

Margarine is at least 80% a fat/oil mixture, in which 16% water or
milk has been emulsified, using 0.25% soybean lecithin, calculated on the
oil, as emulsifier. A further 0.25% of a mono, di, and triglyceride mixture,

obtained from glycerolysis of, for example, hardened marine oil, is added. The mixture contains ca. 40% monoglycerides which bind the water and prevent the margarine from exuding moisture, which otherwise may give rise to the growth of mold on the wrappers.

Further ingredients are: coloring materials (annatto or carotene), flavors (chiefly diacetyl or some specific lactones), vitamins A and D, salt and a preservative (e.g., benzoate). In Western Europe the ultimate aim is to manufacture a salt-poor, nonpreserved margarine. This can be realized provided the water dispersion is sufficiently fine, i.e., if the emulsion droplets are ca. 5μ; at any rate no larger than ca. 12μ. In these small droplets the bacteria cannot multiply.

For the manufacture of margarine and shortening (Heesch 1963) mainly two procedures are followed, viz. the churn-drum process and the votator process. In the churn-drum process an emulsion (w/o) of fat, oil, and milk or water is prepared in a churn, which is a closed vessel equipped with a rapidly rotating stirrer. The emulsion is then brought onto a rotating drum which is cooled by cold brine. The fat in the emulsion crystallizes and, in the form of flakes, is scraped from the drum by a knife. The flakes are collected in trolleys and after a resting period during which the fat crystallization can proceed, they are kneaded by a crusher or a so-called plodder, which is a tube with a narrowed outlet. Kneading may be applied under vacuum, so that an air-free margarine is obtained, which promotes the keepability. After being kneaded, the margarine is immediately wrapped automatically. A drawback of this method is that the margarine can be infected rather easily.

In modern factories, therefore, a continuous closed system (Votator process) is used. For special shortenings the churn-drum process is still applied, since this system gives fats with a better plasticity than the closed system.

In the Votator system, the fat and water phase, whether emulsified or not, is led through cooling cylinders, so-called A-units, which are cooled by liquid ammonia. Crystallization takes place on the inner wall of the cylinders. The fat is scraped off by knives and fed to a so-called crystallizer, in which the partially crystallized margarine is subjected to a mechanical treatment. This treatment is necessary in order to give the margarine or the shortening its plastic consistency. On leaving the crystallizer, the margarine is again passed through one or more A-units, after which it enters a B-unit, a long resting tube, in which the margarine continues its stiffening process. As soon as it is sufficiently firm, it is packed automatically.

In order to prevent post-crystallization, which makes the margarine crumbly and hard, several methods may be applied, such as variations in

the cooling process. Each fat composition has its own optimum processing conditions.

Besides reducing the danger of infection, the closed system (with its many variations: Votator, Kombinator, Perfektor) has some further advantages, such as requiring smaller floor area and less labor force, and cooling more effectively.

A margarine factory must be extremely clean. The strictest hygiene must be observed. Frequent scrubbing and cleaning are first requisites, just as is air-conditioning. If required, the apparatus must be sterilized with a chlorine-containing bleaching agent.

Very important is the consistency of table margarine (Haighton 1959, 1963, 1965), especially its spreadability at room temperature. A rapid method has been developed to determine the hardness at different temperatures, which is expressed as C-values in gm./cm.^{2}. A margarine is spreadable between $C = 150-800$ gm./cm.^{2}, although this is also dependent on the firmness of bread. In winter, as well as for northern countries, the spreadability range is lower than in summer and for southern countries. Further it is important to know whether the margarine is to be stored in a refrigerator, in which case it must be spreadable from ca. 5° C.

The spreadability is chiefly determined by the solid phase/oil ratio. The work-softening and the size of the fat crystals indeed also influence the spreadability, but of primary importance is the amount of solid phase, of which the dilatation is a measure.

Dilatation figures of margarine depend on many factors, e.g., time of the year, climatic conditions of the relevant country, packaging material (tub or wrapper), way of storage (refrigerator or not), etc.

The amount of solid phase does not determine only the spreadability; it also determines the melting away in the mouth. In order to achieve rapid melting, the dilatation values at 30°–37°C. must be as low as possible, although not too low since otherwise oil exudes from the margarine; so a compromise must always be found.

It should be noted that the operator can easily modify the processing conditions and make the margarine firmer or softer; dilatations are, therefore, not the only standard.

Once the dilatation requirements for a margarine composition have been established, it is still very complicated to determine the ultimate composition since requirements other than the consistency must be fulfilled, such as taste, keepability, unsaturated fatty acid content, etc. Then there are types of margarine in which no animal fat may be worked up, and others which may not contain hardened fats. For all these reasons and on account of the fact that the prices of the different fats vary constantly, modern factories in Western Europe now calculate with the aid of

a computer what composition fulfills the various requirements most economically.

The dilatation values for hardened whale oil and hardened fish oil can be handled in the same way as those for other fats. With a view to the hardening flavor which is to be expected, the percentage of hardened whale oil and fish oil may be limited for certain types of margarine. Moreover, as was said before, people in one country are more sensitive to hardening flavors than in another country.

Something remains to be said about the rates of crystallization in the preparation of margarine. In Western Europe, usually 5–15% hardened fat, m.p. 42°–45°C. is used in the fat composition. This fat does not undercool in the Votator or on the cooled drum and, therefore, initiates crystallization. Instead of hardened vegetable oil also hardened whale oil can be used for this purpose. There are, however, some hardened fish oils, notably menhaden oil, which crystallize slower and are, therefore, less suitable. If hardened menhaden oil of say m.p. 35°–37°C. is used, the processing conditions may have to be modified, such as cooling to a lower temperature or circulation in the Votator.

Margarines prepared from hardened vegetable oils sometimes recrystallize on storage. Especially fats with C_{18}- fatty acids, such as soybean and sunflower oil tend to do so. This is caused by the fact that the glycerides which on storage crystallize into the metastable β'-modification, after some time partly pass to the β-modification. Fats with a greater variation in chain length do not display this phenomenon. Since whale oil and fish oil have a widely varied chain length, viz. from C_{14} to C_{22}, margarines with an excellent plastic consistency which is not lost on storage can be prepared from them, e.g., margarines consisting of 70–80% partially hardened whale or herring oil (m.p. 33°–35°C.) and 20–30% liquid vegetable oil. In many countries, however, the taste of this margarine is not considered excellent.

Shortenings and bakery margarines must have other properties than table margarine. Several types can be distinguished, viz. those used for puff pastry, cake, piped doughs, biscuits as well as those used for shallow frying and deep frying.

Fats used for making puff pastry may not intersperse with the dough, because the fat and dough layers must remain separate in order to give a light pastry consisting of many layers. Generally, hardened vegetable fats are more suitable for the preparation of a pastry fat than hardened fish oil. Fats used for pastry are characterized by higher dilatation values than those used for making normal household margarine.

Fats for cakes (pound cakes or high-ratio cakes) must readily take up

air and have good creaming property. For these fats, hardened marine oils can be used. These are also suitable for being worked up in biscuit fats.

For shallow frying, e.g., of fish, usually liquid oils are used. Fats used for deep frying must remain stable on repeated use and they must have a sufficiently high smoke point and not foam out of the frying-pan. In most cases a low smoke point is caused by the presence of fatty acid or traces of glycerol which disappear in a good refining process.

Hardened marine oils, if hydrogenated properly, are relatively foam stable. In connection with the taste stability, marine oils must be hydrogenated to over 40°C., which, however, on cooling may give rise to the formation of a fat film on products prepared from these fats.

An ever-increasing amount of pumpable shortening is produced for use in industrial bakeries. These fats are transported to the consumer by tank trailer and collected in vessels which are provided with a stirrer. Also in these pumpable fats, hardened marine oils can be used.

For the preparation of a confectionery fat—as a substitute for cocoa butter—the fractionation of hardened marine oil from solvent has been suggested. In this way a fraction can be obtained with melting properties approximately similar to those of cocoa butter, but on mixing a steep drop in melting point occurs.

SUMMARY

Hardened whale oil has been used in margarine for more than half a century. Fish oils, of which the available quantities increase in contrast to those of whale oil, can also be used for this purpose. Just as is the case with whale oil, there are good and bad batches of fish oil. For good stability of hardened margarine oil, it is necessary to process the oil as fresh as possible and to refine it adequately before hydrogenation. There are no essential differences between the qualities of hardened herring oil and hardened whale oil. The lower the initial melting point and the higher the iodine value of the nonhardened herring oil, the better. Menhaden oil and pilchard oil, which are characterized by a high iodine value and a relatively high initial melting point, must be hardened as high as the oral response permits. Even then the hardening flavor cannot be entirely eliminated. These fish oils with a high iodine value should be hardened in such a way that the temperature does not rise too much, since this leads to undesirable isomerizations.

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