Modification of Vegetable Oils.
I. New Products by Fractional Crystallization of Glycerides From Petroleum Naphtha

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Introduction

It has been recognized for some time that even the most painstaking fractionation by means of solvent crystallization cannot be expected to yield a quantitative separation of the complex glyceride mixtures existing in natural fats and oils. The most patient and laborious crystallizations, on the part of Boemer, Klimont, Amberger, and others yielded only meager qualitative data on the composition of certain fats.

It is possible that the shortcomings of the method as an analytical tool have adversely affected its acceptance as a means of preparing commercial products, in spite of the obvious fact that it is by no means necessary for commercial separations of glycerides to be quantitative for them to be highly useful. At any rate, such investigations of solvent crystallization as have been reported in the literature have been primarily concerned with the analysis of fats and oils rather than techniques for the preparation of new oil and fat products. Furthermore, the authors have no personal knowledge of any process in actual commercial operation which utilizes the principle of fractional solvent crystallization of fats and oils.

One of the effects of the present world war has been the creation of a marked scarcity of certain normally imported oils, such as coconut, palm, olive, tung and perilla oils, cocoa butter, etc. The development of new, artificial products from North American grown materials, to form substitutes for the imported oils, has become an urgent necessity.

In considering new techniques for the manufacture of such products, it has appeared desirable to investigate the possible applications of solvent crystallization, since this process seems particularly adapted to the purpose in certain cases. The investigations reported in the present communication had as their principal object the development of an olive oil-like product from peanut oil, although the experimental work also included the production of winterized cottonseed and peanut salad oils.

Laboratory Crystallization Apparatus

In order to be able to conduct the operations of both crystallization and crystal separation under strictly controlled conditions it was necessary to use specially designed and constructed equipment for the experiments. The construction of the special combined chiller and filter is illustrated in Figure 1, which shows the apparatus in vertical cross section. The oil-solvent mixture is contained in the cylindrical chilling chamber, *C*. The hollow shaft, *S*, which operates at 12 r.p.m., through a stuffing box at the top of the apparatus, is provided with scraper blades which bear lightly against the walls of the cylinder and thus prevent solidified material from adhering to the heat transfer surfaces.

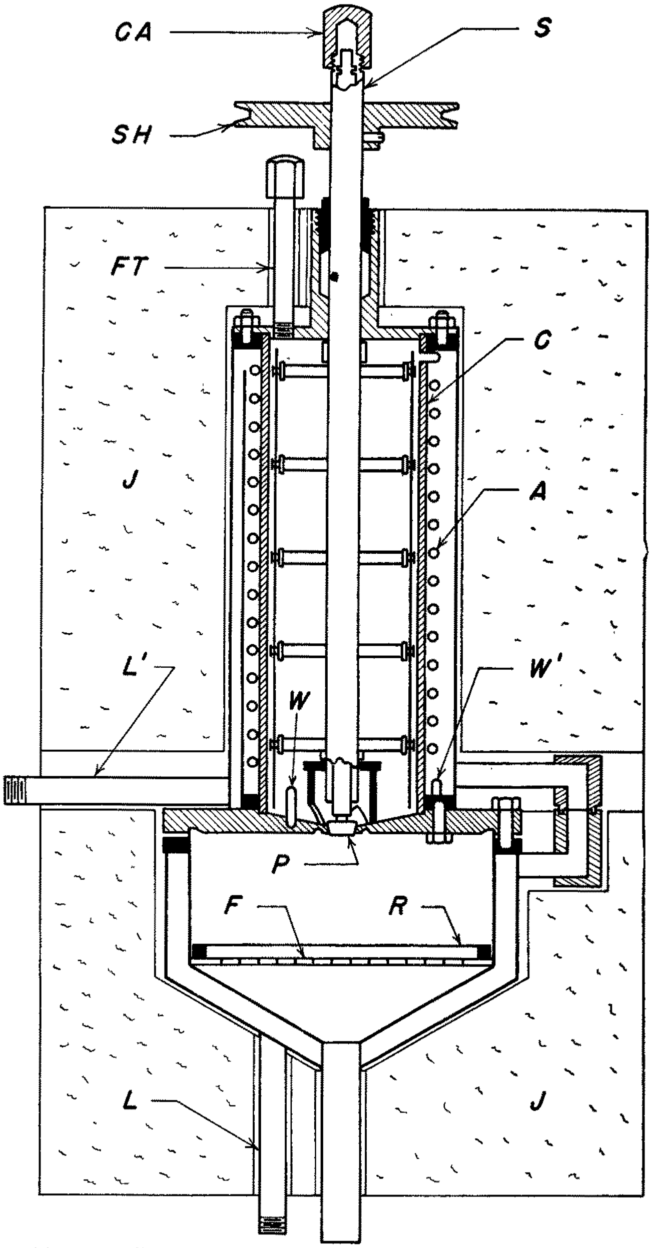

FIG. 1. Combined chiller and filter for low temperature solvent crystallization of fats and oils.

The filter, *F*, is similar to an ordinary Buchner funnel, and, like the chilling chamber, is fully jacketed for circulation of a refrigerating liquid. The filter is used in conjunction with an ordinary filter paper, which is held in place by the retaining ring, *R*.

The opening between the chilling and filtering chambers is closed by the ground-in plug, *P*, which is lubricated with a glycerol-starch lubricant (5).

The plug is operated from the exterior of the apparatus by means of a rod extending through the hollow shaft; thermocouple wells, *W*, *W′*, are inserted in the chilling chamber and its liquid jacket.

An air delivery tube, *A*, made of nickel is wound in the annular space between the walls of the chilling chamber and its liquid jacket and hence is immersed in the refrigerating liquid. One end of this tube communicates with the interior of the chilling chamber near the top of the latter, while the other end extends without the apparatus.

All parts of the apparatus are made of nickel or stainless steel. The entire apparatus is enclosed in a heavily insulated stainless steel jacket, *J*. It is so constructed that after removal of the sheave, *SH*, the upper part of the jacket may be lifted off, after which the chilling chamber may be disconnected and removed, exposing the filtering chamber and the filter.

In operation, the apparatus is charged with the oil-solvent mixture through the filling tube, *FT*, the refrigerating liquid lines, *L*, *L′*, are connected, the operation of the scraper is started, and chilled ethylene glycol-water is circulated through the cooling jackets until the desired separation of crystals is attained. The rate at which cooling is conducted and the time allowed at the minimum temperature for final crystallization are, of course, predetermined, and accurately controlled.

After crystallization is complete, the outlet tube from the filtering funnel is unsealed, a receptacle is placed under it for the filtrate, and the charge is dropped to the filter by raising the ground-in plug, and locking it in a raised position. That part of the apparatus above the filter paper is then sealed by tightening the cap, *CA*, the scraper is stopped and air pressure is admitted through the refrigerated air tube to force the liquid through the filter. Throughout the filtering operation the entire apparatus is, of course, maintained at the minimum crystallizing temperature by continued circulation of cooling liquid through the jackets.

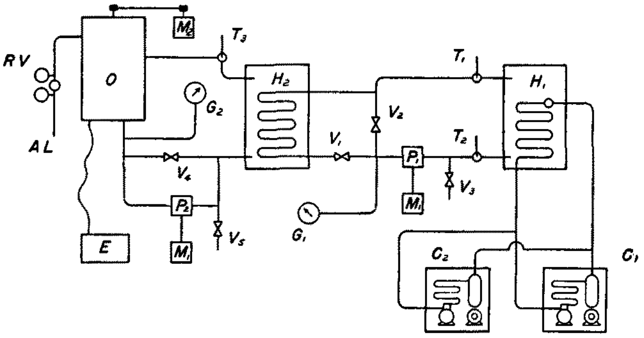

FIG. 2. Flow diagram, complete laboratory solvent crystallization apparatus. C_1, C_2, Freon compressors; E, potentiometer; G_1, G_2, pressure gages; H_1, H_2, heat exchangers; M_1, M_2, electric motors; O, chiller and filter; P_1, P_2, refrigerant pumps; T_1-T_3, thermometers; V_1-V_5, valves; AL, compressed air line; RV, reducing valve.

A somewhat elaborate cooling system is required for accurate temperature control of the apparatus. The lay-out of the complete refrigerating system is outlined in Figure 2. It consists of three individual cooling circuits, interconnected by heat exchangers. The primary source of refrigeration consists of the two one-third h.p. Freon compressors, C_1 and C_2, which are connected in parallel to the tube side of the first heat exchanger, H_1. The cooling jackets of the crystallizing apparatus are connected to the shell side of the second heat exchanger, H_2; rapid circulation of cooling liquid in this part of the system is obtained with the pump, P_2, so that the temperature of the liquid is substantially the same in all parts of the circuit. The rate at which the liquid in this circuit is cooled is controlled by varying the flow of liquid from the shell side of H_1, through the tube side of H_2. This is accomplished by by-passing a variable portion of the output of pump P_1 back to the shell side of H_1. As P_1 is a positive displacement pump, the extent to which the by-passing is accomplished is controlled by settings of the valves V_1 and V_2, and is indicated by the pressure on the gage, *G*. By manual operation of the valves it was possible to maintain the temperature within a range of 0.5°F., or less, at any desired value. The complete apparatus is shown in the photograph of Figure 3.

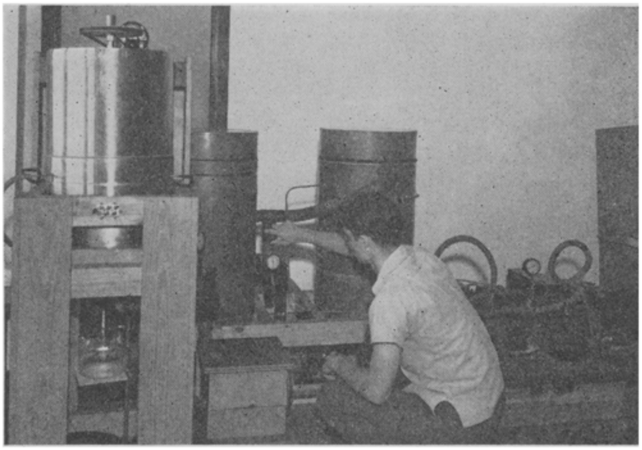

FIG. 3. Complete solvent crystallization apparatus in operation.

Choice of a Solvent

The present experiments, which may to some extent be regarded as preliminary in nature, were carried out with the use of a commercial petroleum naphtha consisting essentially of hexane (Skellysolve B) as the sole solvent.

A solvent of this type has the advantage of being cheap, stable, and easily recovered from the oil, and is available in practically unlimited quantities. It is, of course, inflammable and there is a certain hazard of fire and explosion attendant upon its large scale use. Experience in recent years with such processes as the solvent extraction of oilseeds has demonstrated, however, that such hazard may be reduced to a negligible factor in a well designed and well operated plant.

Modification of Peanut Oil to Simulate Olive Oil

Olive oil is distinguished from all other common vegetable oils, with the exception of teaseed oil, by its very high content of oleic acid and its consequent low content of saturated and linoleic acids. Because of its unusual composition it has a much lower iodine value than other liquid vegetable oils. Consequently, it combines the property of liquidity at low temperatures with great stability, both with respect to the development of rancidity and tendency to gum or polymerize. Its unique properties are considered essential in certain industrial applications, particularly in the field of textile processing.

For the preparation of an artificial olive oil-like product, a batch of peanut oil was first hydrogenated, under conditions conducive to a maximum formation of normal oleic acid (3), until its liquid unsaturated acids consisted of approximately 8 per cent linoleic acid and 92 per cent normal oleic acid.

The higher melting portions of the hydrogenated oil were then removed by fractionally crystallizing the oil from petroleum naphtha at a low temperature, and filtering off the liquid fraction. Most of the solvent was distilled from the filtrate, and the residue of modified oil was finished by steam deodorizing it at 450°F. under a pressure of 1 mm. of Hg.

All operating details in the preparation of a typical batch of oil are given in Table 1.

TABLE 1

Operating Data. Modification of Peanut Oil to Produce an Olive Oil-like Product

Hydrogenation of the oil (HPO-27-30):	
Temperature, °F.	350
Hydrogen pressure, p.s.i. gage	27
Nickel (catalyst), percent	0.05
Speed of agitator, R.P.M.	408
Size of oil charge, pounds	16
Iodine value of finished oil	70.2
Hydrogenation time, minutes	25
Crystallization of the hydrogenated oil (WHPO-64):	
Ratio, solvent to oil (by wt.)	3:1
Minimum temperature, °F.	3
Cooling time, hours : minutes	3:30
Holding time (at min. temp.), hours : min.	00:30
Filtration Time, hours : minutes	00:20
Total time, hours : minutes	4:20
Filtration pressure, p.s.i. gage	1-2
Yield, finished oil, percent	78.1

Characteristics of the New Product

Analytical data on a typical lot of modified oil, at different stages in its processing are given in Table 2. In the same table are recorded the characteristics of typical samples of olive oil and refined cottonseed oil.

The modified oil does not deposit crystals or solidify except at near freezing temperatures. Its cloud and pour points are considerably above those of olive oil, but below those of ordinary peanut oil and approximately the same as those of cottonseed oil. Thus, although its iodine value is lower than that of any natural vegetable oil, the modified oil is completely liquid at all ordinary temperatures.

With respect to the matter of stability, the modified oil is outstanding. Various samples prepared in this laboratory have had keeping qualities by the Swift method ranging from 30 to 40 hours. As previous experience has demonstrated that commercially prepared fats, carefully protected from oxidation, invariably keep much better than equivalent fats hydrogenated in the laboratory, it is believed that stabilities of not less than 60 or 70 hours may be expected from large scale operation of the process. Samples of the product were tested in the laboratories of two different manufacturers of textile finishing oils. Both reported that it produced a satisfactory sulfonated oil, and one expressed the opinion that it was an entirely adequate substitute for olive oil.

The new product, unlike olive oil, is extremely light in color, and is completely neutral in flavor and odor. Although the new oil was formulated with the intention of duplicating olive oil, it is evident that it is in many important respects far superior to any natural liquid oil.

Solvent Winterization of Cottonseed Oil

Following the successful application of solvent dewaxing in the treatment of lubricating oils from petroleum, many vegetable oil technologists have speculated upon the possibility of applying a similar process to replace the present slow and inefficient winterization process for cottonseed oil. One group of investigators (1) reported preliminary experiments in the winterization of cottonseed oil, with the use of a self-refrigerating solvent, but made no mention of the yield or properties of the finished product.

Excellent results have been obtained in the solvent-winterization of cottonseed oil in the experimental apparatus described above.

The operating and analytical data obtained in the preparation of a typical batch of solvent-winterized cottonseed oil, in comparison with similar data applicable to a winterized oil produced by present commercial methods, are given in Table 3.

It is evident from the data recorded in Table 3 that solvent-winterization will produce a much better product, in a higher yield, in a small fraction of the time required by the conventional method. Disadvantages of the method are, of course, the necessity of chilling and recovering a considerable volume of solvent, and the relatively low temperature required for crystallization.

Solvent Winterization of Peanut Oil

Because of the gelatinous nature of the portions which separate when peanut oil is chilled, it has heretofore been impossible to produce a winterized peanut

TABLE 2

Analytical Data, Modified Peanut Oil at Different Stages of Processing, in Comparison with Olive and Cottonseed Oils

Sample	Untreated Refined Peanut Oil	Hydrogenated Peanut Oil (HPO-27-30)	Finished Modified Peanut Oil (WHPO-64)	Olive Oil	Cottonseed Oil (Refined)
Iodine value	97.7	70.2	75.8	84.9	107.6
Thiocyanogen value	71.3	65.7	71.0	78.7	69.6
Composition of acids.					
Saturated, percent	19.2	23.5	17.3	8.5	22.4
Iso-oleic, percent	......	12.9	11.0	......	......
Normal oleic, percent	48.3	58.6	66.3	84.4	30.9
Linoleic, percent	32.5	5.0	5.4	7.1	46.7
Cloud point, °F. (ASTM)	40	64	36	22	38
Solid point, °F. (ASTM)*	34	50	28	14	28
Titer, °C.	31.3	32.4	28.0	23.0	36.2
Stability, hours (Swift method, to peroxide value of 75).	8	40	35	20	......
Color (Lovibond)	10Y-1.1R	10Y-1.2R	5Y-0.7R	70Y-3.0R**	......
Flavor and odor	Characteristic	Characteristic	Neutral	Characteristic	......

* Modified by examination of the sample at intervals of 2° rather than 5° F.

** Approximate color. Greenish color of oil made red and yellow color determination difficult.

TABLE 3

Comparison of Operating and Analytical Data, Solvent-Winterization and Conventional Winterization of Cottonseed Oil

Method	Solvent-Winterization (WCO-7)	Conventional Winterization
Iodine value of original oil	107.6	103-110
Ratio, solvent to oil (by wt.)	1:1	....
Minimum temperatures, °F.	2	42
Hrs. to reach min. temp.	5.5	24-96
Hrs. held at min. temp.	1.0	12-24
Filtration rate, lbs. oil per hour, per sq. ft. filtering surface	20	0.2-2.0
Maximum filtering pressure, p.s.i. gage	1	20
Yield percent	77.1	65-75
Cold test,* hrs.	Over 72	5-15
Cloud point °F., (ASTM)	20	24-26
Solid point °F., (ASTM)**	18	20-22

* Time required to cloud, at 32° F.

** Modified by examination of the oil at intervals of 2° rather than 5° F.

oil by the methods in current use for winterizing cottonseed oil.

The fact that peanut oil will not produce a winterized salad oil, suitable for storage in domestic refrigerators and for mayonnaise manufacture, has not been a serious disadvantage in its over-all utilization in the past, because of the relatively small amount of peanut oil produced. Under present conditions, with the production of peanut oil tending to approach that of cottonseed oil in the United States, the unsuitability of peanut oil for this purpose may be expected to prove somewhat more disadvantageous.

It was found possible to produce a winterized peanut oil of good quality, in a satisfactory yield, by solvent-crystallization. A certain amount of difficulty was encountered in filtration, however; times of 3 to 5 hours were required for filtering each batch, as compared with times of 20 minutes or less for equivalent batches of cottonseed oil.

In an effort to break up the particular configurations of glycerides responsible for the formation of difficultly filterable crystals, several batches of peanut oil were subjected to molecular rearrangement reactions. In some cases the method of Bailey (2) was used for effecting rearrangement (with glycerol as a catalyst); in others that of van Loon (6) was used (with a metallic catalyst). All of the rearranged oils filtered readily and yielded well winterized products.

Following is the procedure employed in carrying out a typical rearrangement (RPO-3); 1,500 gms. of peanut oil were reacted with 0.5 per cent glycerol and 0.05 per cent sodium hydroxide with stirring, under an atmosphere of hydrogen at 220°C.(428°F.) for 3 hours. After the batch was cooled, the sodium soaps formed during the reaction were removed with phosphoric acid according to the method of Eckey and Clark (4).

TABLE 4

Operating Data. Solvent-Winterization of Peanut Oil

Experiment No. Oil Used	WPO-11 Peanut Oil	WRPO-44 Rearranged Peanut Oil (RPO-3)
Iodine value, original oil	97.7	97.7
Ratio solvent to oil (by weight)	3:2	2:3
Minimum temperature, °F.	5	2
Time to reach minimum temperature, hours : minutes	5:08	6:10
Time held at minimum temperature, hours : minutes	1:00	1:00
Time to filter, hours : minutes	3:00	00:20
Total time, hours : minutes	9:08	7:30
Maximum filtering pressure, p.s.i. gage	28	15
Yield, percent	80.2	68.8

The operating data on the preparation of typical batches of winterized oil from both rearranged and un-rearranged peanut oil are given in Table 4.

Analyses of typical finished (winterized and deodorized) oils, in comparison with the original peanut oil, are given in Table 5.

TABLE 5

Analysis of Peanut Oil and Solvent Winterized Peanut Oils

Sample	Original Oil	Winterized Oil (WPO-11)	Winterized Rearranged Oil (WRPO-44)
Cold test,* hours	1	26	26
Cloud point, °F. (ASTM)	40	28	26
Solid point, °F. (ASTM)**	34	26	24
Iodine value	97.7	98.8	100.5
Thiocyanogen value	71.3	72.3	73.8
Saturated acids, percent	19.2	18.1	16.2
Oleic acid, percent	48.3	49.6	51.2
Linoleic acid, percent	32.5	32.3	32.6

* Time required to cloud, at 32° F.

** Modified by examination of the sample at intervals of 2° rather than 5° F.

Significance of the Results

The experimental results demonstrate that low temperature fractional crystallization from solvents under commercially feasible conditions, can be used to produce a variety of useful new products from cottonseed and peanut oils.

Particular attention is directed to the fact that all of the products reported were prepared under conditions which can be economically duplicated on a commercial scale. Low ratios of solvent to oil were used, crystallization was carried out at only moderately low temperatures, and the solvent used was one which is cheap and easily obtainable in large quantities. The crystallization process was, furthermore, carried out in an agitated mixture of solvent and oil, under conditions similar to those which would apply in commercial equipment. There is an obvious constructional similarity between the short chilling cylinder of the laboratory apparatus, and longer and larger cylinders, suitable for use in large scale continuous operation.

The new olive oil-like product should be suitable for use in replacement of olive and teaseed oils in industrial applications where a liquid oil of high stability is required, as for example, in the textile industry. In addition, the light color, neutral odor, and superior stability of the new product should make it suitable for certain uses for which olive oil cannot be used, as in the manufacture of cosmetics, and for certain edible purposes. It also seems probable that it might serve as a suitable substitute for certain other oils of low iodine value, including neatsfoot and lard oil.

The success of the solvent process in producing winterized cottonseed and peanut oils is noteworthy in view of the rapidly increasing production of peanut oil in the United States.

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