

The Commercial Solvent Separation of Fatty Acids*

R. E. KISTLER, V. J. MUCKERHEIDE and L. D. MYERS
Blaw-Knox Company, Pittsburgh, Pa.—Emery Industries Inc., Cincinnati, Ohio

PART I

Technical Aspects

THE early history of the fatty acid industry engaged in the production of commercial stearic and oleic acids is closely associated with the manufacture of candles. In the past century the producers of tallow candles recognized the need for improvement in their product. It was quite natural for them to attempt to use some modified form of the tallow to obtain a harder material for candles. The conversion of tallow into fatty acids and then the separating of the hard solid acids from the liquid acids was the most logical step. The solid acids obtained, known as commercial stearic acid, gave a vastly improved candle. The liquid acids obtained, known commercially as red oil or oleic acid, were then considered of very little value. The pressing method established at that time for the separation of the stearic and oleic acids has been the standard procedure up to the present.

For successful operation the pressing method depends on utilizing fatty acids in which the ratio of solid acids is such as to give a crystalline mixture in order that the liquid acids may be easily expressed during pressing operations. In stearic acid manufacture this ratio is approximately 45% stearic acid and 55% palmitic acid and as a result, commercial stearic acid is a crystalline mixture of stearic and palmitic acids with traces of unsaturated acids.

The pressing method consists mainly of hand operations and in consequence is slow and requires considerable labor. In practice, hot fatty acids are transferred into aluminum pans, allowed to solidify, and then cooled to a temperature of about 36° F. This requires about eight hours. The cakes of solidified fatty acids are then removed from the pans, wrapped in burlap cloths, and stacked in hydraulic presses where pressure is applied. This "Cold Pressing Operation" removes the greater portion of the liquid acids. The content of the solid acids in these liquid acids is dependent upon the temperature maintained in this pressing operation. The solid acids obtained are known as cold pressed cake, the liquid acids as red oil. In order to raise the melting point and lower the liquid acid content the cold pressed cake is melted and again allowed to solidify in aluminum pans at room temperature. These cakes are then placed in horizontal presses where they are subjected to a slight amount of heat and pressure, yielding single press stearic acid. Further hot pressing removes practically all of the liquid acids and produces a grade of stearic acid known commercially as double pressed stearic acid. In like manner double pressed stearic acid is made into triple pressed stearic acid. The liquid acids removed during hot pressing contain considerable quantities of the solid acids and

are blended with the original fatty acids in order that the solid acids may be removed by the cold pressing operation. It should be noted that there is a constant recycling of fatty acids during the pressing process which amounts to about 40% of the weight of the fatty acids in process. (Our company is 105 years old. Some of the original molecules are probably still going around and around.) Several disadvantages of the pressing method are:

1. Large labor requirements.
2. Limitations of fatty acids which may be handled.
3. Excessive product losses due to handling.
4. Cost of remelting and chilling.
5. Re-working.

FATTY acid processors, realizing these disadvantages, have recognized the need for an improved, less wasteful method of separating mixed fatty acids. In consequence an investigation to discover better methods of separating fatty acids was initiated by Emery Industries, Inc. Although methods of separation applicable to analytical testing are shown in the literature, no commercial method had been devised. The development of an economical commercial method capable of continuously effecting a 95% complete separation was found at times to be a very disheartening job. Investigation of previous attempts to affect a separation of solid and liquid acids were made, such as the use of solvents for extraction (1,2), or by the use of water in connection with an emulsifying agent (3). Also existing were the classical laboratory methods, for example, the Twitchell lead soap method, which is suitable for analytical procedures but unfortunately has no practical commercial use. The use of solvents to effect a separation of solid and liquid acids appeared to offer commercially feasible possibilities. Investigation of solvent methods revealed that a degree of separation could be obtained in a system wherein the fatty acids were maintained in a liquid state. Such methods are dependent on the selectivity of the solvent and to a larger extent the effect of mutual solubility of the fatty acids in each other. A method wherein the fatty acids are dissolved in a solvent and then by some means the solid acids are caused to separate in an insoluble state would overcome the disadvantage of mutual solubility. The most promising method of accomplishing this separation of acids in their solid state was by lowering the temperature of the solvent solution of mixed fatty acids. Under such conditions the solid acids are removed by filtration and the liquid acids remain in solution.

Laboratory tests were made on distilled animal fatty acids containing approximately 40% solid acids (stearic and palmitic) and 60% liquid acids with various solvents. The method evolved consisted of dissolving the fatty acids in the solvent and cooling to a temperature at which practically all of the solid

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acids were crystallized. These crystallized solid acids were filtered by vacuum and washed with solvent at the same temperature. Solvents such as petroleum, ether, acetone, 95% ethanol, 90% methanol, isopropanol, and others were tried. In the laboratory separations of solid and liquid acids of 85% to 95% efficiency were obtained; however it was noted that the various solvents behaved differently with respect to the following factors:

1. Type of the solid acid crystal obtained.
2. Temperature to which the solvent solution of fatty acids had to be cooled to effect a practically complete separation of the solid acids.
3. Stability of the solvent and the comparative ease of removal from the solid and liquid acids.

Translation of laboratory results into actual practice required careful consideration and further investigation of these factors.

Since the commercial success of a solvent method depended on a continuous process, it was quite evident that the crystals of solid acids should be of such a nature as to be easily filtered and readily washed of entrained solvent containing the liquid acids. Repeated crystallization of the solid acids would naturally accomplish a complete separation; however, such a procedure, although satisfactory in laboratory technique, is economically prohibitive for plant practice. The crystals of solid acids obtained by cooling a solution of commercial stearic in petroleum ether were beautiful, lustrous plates with a pearly finish, but unfortunately their filtration was very slow and washing of such flat plates was exceedingly difficult. Likewise the same conditions were obtained using other hydrocarbons and chlorinated solvents.

Solvents such as ethanol, acetone and methanol when used in the separation of stearic acid gave needlelike crystals which filtered and washed very readily. Numerous other solvents were investigated to determine the type of solid acid crystal obtained. The results obtained with some typical solvents are given in Table I.

TABLE I
Type Solid Acid Crystals From Some Typical Solvents

Solvent	Nature Cryst. Solids	Filtering Characteristics
85% Acetone.....	Granular needlelike	Good
Petroleum ether.....	Flat plates	Poor
Propylene dichloride.....	Plates	Poor
90% Methanol.....	Granular needles	Good

Above tests made using 10% of commercial stearic acid in the solvent.

THE next factor considered was the temperature to which the solvent solution of mixed fatty acids must be cooled to obtain a practically complete crystallization of the solid acids. From a commercial consideration this factor is most important since the refrigeration is one of major costs of operations in a solvent crystallization process. In laboratory tests the measure of the effectiveness of the separation of animal fatty acids was indicated by the iodine value of the stearic acid obtained and the titre of the oleic acid recovered. The titre of commercial oleic acid gives a fairly good indication of the extent of the solid acid removal. In general, it has been found that solvents such as 95% ethanol, 85% acetone, and 90% methanol do not require a very low temperature

to produce low titre oleic acid, whereas solvents such as petroleum ether require very low temperatures to insure complete crystallization of the solid acids. Table II shows the effect of temperature on the titre of oleic acid obtained from some of the various solvents tested. Tests were made using 20% concentration of distilled mixed animal fatty acids in the solvent.

TABLE II
Effect of Temperature to Which Solvent Solution of Mixed Fatty Acids Are Cooled on the Completeness of Separation.

Solvent	Temperature °C.	Titre Oleic Acid °C.
85% Acetone.....	-1.0	12.8
Petroleum ether.....	2.0	27.6
90% Methanol.....	-0.5	6.5
Ethylene dichloride.....	3.5	20.7

The solubility of the solid stearic acid in the solvent alone cannot be taken as a definite criterion in the separation of mixed fatty acids because the nature of the solvent is modified by the presence of unsaturated acids.

During these investigations the stability and ease of removal of the solvent was given utmost consideration. While it was perfectly satisfactory from a laboratory test to use such solvents as iso-propyl ether, carbon disulfide, and similar low boiling solvents, their use in a plant is undesirable from the standpoint of solvent loss and toxicity. When high boiling solvents were used the problem of their removal was complicated and vacuum evaporation was required to avoid subjecting the products to high temperatures. Vacuum evaporation of solvents was not economically feasible and contributed to high solvent losses. After evaluation of all of these factors the solvent finally selected was 90% methanol. Stability, low cost, availability, and relative ease of recovering were among the factors considered in making this selection. It was found necessary to devise a plant method of solvent removal which would not cause an esterifying reaction of the 90% methanol with the fatty acids. As in all reactions of this type, the effect of time and temperature are the controlling factors. The problem resolved itself into providing a method whereby the solvent would be removed in the shortest time at minimum temperature and at atmospheric pressure. The method finally developed consists of removing the bulk of the solvent at a low temperature and the removal of the remainder of the solvent by a stripping column. In the column, as the temperature increases, the alcohol strength decreases. Consequently when the temperature reaches a maximum, the amount of solvent present is very low. Under these conditions of solvent removal, esterification of the fatty acids by alcoholic solvents is avoided.

APPLICATION of the foregoing factors to plant operation required further investigation of certain points to insure continuous, trouble-free, and uniform operation of a commercial unit. These points included rate of cooling of the solution and the method of obtaining efficient heat transfer. For practical and economical reasons the chilling of the solution of fatty acids and solvent should be accomplished within a reasonable time so as to minimize the amount of total solvent required and the size of the chilling unit. For efficient heat transfer the cooling surface must be clean, consequently a scraping mechanism must be

used. Laboratory tests showed that very rapid rates of cooling caused precipitation of solid acids rather than crystallization and resulted in slow filtration.

Tests were made to determine the fastest rate of cooling permissible and still obtain filterable and washable crystals of fatty acids. Solvents were used which from previous tests produced easily filterable solid acid crystals. Cooling was accomplished using a jacketed metal container. The walls of this container were scraped by rotating blades. It was determined that the rate of heat transfer per unit area of surface had an influence on the formation of the solid acid crystals. The speed of scraping the crystals from walls of the container was of lesser effect. Too rapid scraping resulted in breaking the crystals whereas too slow scraping prevented efficient heat transfer. The translation of these results into a plant tubular jacketed crystallizer was particularly difficult in that the scraping mechanism had to be specially designed to prevent any blockage of flow and deposition of crystals on the scrapers.

The foregoing principles were also used to fractionate solid acids such as commercial stearic acid. The factors of crystal formation, rate of cooling and temperatures to which the solvent solution of fatty acids is chilled are important in obtaining a product high in stearic acid content.

Briefly some of the most important factors have been presented which were considered in translating laboratory data on the solvent separation of fatty acids to practical plant operation. The commercial plants which resulted are discussed in Part II of this paper.

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PART II

Commercial Application

THE information given in Part I of this paper was used as the basis for the design of a pilot plant. The successful operation of this experimental plant led to enlarging it so that the procedure could be practiced on a semi-commercial scale. Experience gained from this unit, together with the lessons learned from its operation, subsequently led to the construction of two commercial sized plants. The first one was built in 1942 and has been in continuous operation. During the years of commercial operation changes and improvements were made in the design of the equipment and were incorporated in the second plant which has recently been constructed and placed in operation. These have increased the efficiency and lowered the operating costs. Each plant fractionates 30 tons of mixed fatty acids daily. Separation of the mixed fatty acids is controlled to produce several grades and qualities of stearic and oleic acids.

The process, known as the Emersol process (1), operates on the principle of controlled crystallization of solid fatty acids from a polar solvent and removal of the solid acids by filtration. A sharp separation is obtained in a single-stage. The solvent is distilled from the stearic and oleic acids, then condensed and recycled for re-use. In practice the distilled fatty acids are dissolved in 90% concentration of methanol. In some lots of mixed fatty acids it has been found

that adding a small percentage of neutral fat will assist in crystallization and provide for better washing of the filter cake. The solution is chilled in a multi-tubular agitated crystallizer, which results in a slurry of solid acids in suspension. This slurry is separated into the solid and liquid portions on a continuous vacuum rotary filter. The solid acids are washed with cold alcohol to remove the entrained liquid acids.

The process requires that the following operations be performed continuously and under controlled conditions to achieve economical separation and the desired quality of product:

1. Preparation of Feed
2. Crystallization
3. Refrigeration
4. Filtration
5. Solvent Recovery.

1. Preparation of Feed

The preparation of the feed stock for the commercial plant is very important since it has a considerable effect on the quality of the fatty acids obtained. However, it is not necessary to maintain the critical palmitic-stearic acid ratio as required in the pressing method. In the operation of this process impurities in the form of color, odor, neutral fat and unsaponifiable material are not eliminated but appear in one or the other of the product fractions. Therefore, it is essential that the mixed fatty acids be distilled before subjecting them to this treatment. Although it has not been proven commercially, it may be possible to split very high grade fats by the autoclave technique and then separate the acids without distillation.

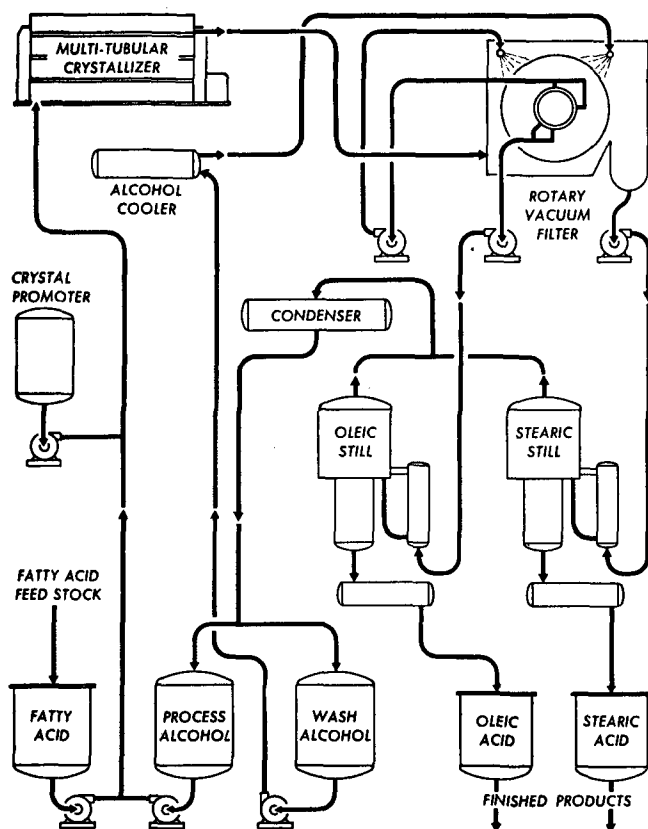
2. Crystallization

The mixed fatty acids and solvent are proportioned by positive displacement pumps discharging through flow meters to the crystallizer. The crystallizer consists of a series of jacketed horizontal tubes, through which the feed is passed for a sufficient time for the saturated fatty acids to crystallize from solution in a suitable form that can be readily filtered. Each tube is fitted with a slow moving scraping agitator. Cold anti-freeze solution is pumped counter-currently through the crystallizer jackets to reduce the temperature of the feed mixture and absorb the heat evolved during crystallization. The inherent solubility relation of stearic-palmitic and oleic acids is such that with the crystallizing conditions employed the stearic-palmitic acid is precipitated and the oleic acid remains in solution.

The crystallizer is the heart of the process for it is here that the desired fatty acid separation occurs. However, the other steps—preparation of feed stock, refrigeration, filtration, and solvent recovery—are essential if the process is to be operated economically and separated fatty acids of the desired quality are to be obtained.

3. Refrigeration

Refrigeration is supplied by a two-stage ammonia compressor driven by a steam turbine which is equipped with a variable speed control device. This type of drive permits a variation in refrigeration which effects a control over the titre of the oleic acid. Exhaust steam from the turbine is discharged at approximately 10 psi gauge and is utilized in the stills



EMERSOL PROCESS - SIMPLIFIED FLOW SHEET

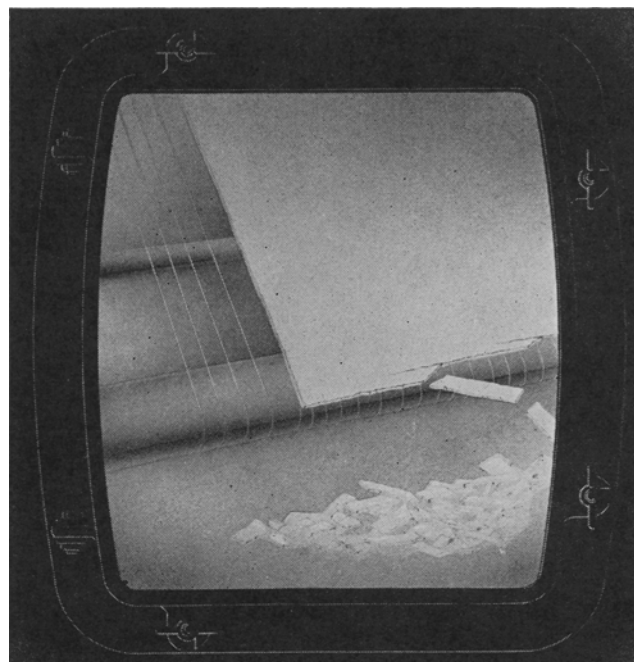
for solvent recovery. Thus steam is used both for power and process heating to achieve high thermal efficiency. Economy in refrigeration is achieved by heat exchanging the cold filtrate with the anti-freeze solution from the crystallizer. Through this arrangement approximately 75% of the total refrigeration is recovered.

4. Filtration

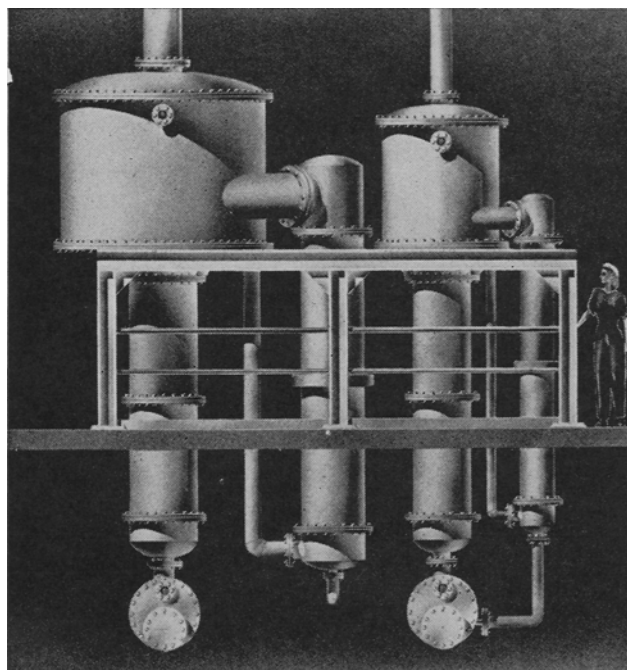
The slurry mixture from the crystallizer is delivered to the continuous rotary vacuum filter where the precipitated fatty acids are removed from the mixture. The liquid acids remain in solution. A continuous rotary vacuum filter is ideally suited for this purpose because of the bulkiness of the filter cake. During filtration the solid fatty acids are continuously washed with fresh solvent to remove mother liquor containing liquid acids. The rate of flow and temperature of the wash solvent is automatically controlled. This wash assures production of commercial stearic acid of high quality. The solid acids are discharged as a solid filter cake, the liquid acids are withdrawn separately from the filter.

5. Solvent Recovery

It is essential that the solvent recovery percentage be high. Since the solid acids discharged as a filter cake retain approximately 50-60% solvent and the liquid acids are dissolved in a large volume of solvent, provision must be made for its recovery. This is accomplished by a uniquely designed still incorporating a preliminary evaporator in conjunction with a plate type stripping column. The temperature of the evaporator and stripping column are automatically controlled.



Stearic acid cake discharged from the vacuum filter as seen through observation door.



Solvent is removed from stearic and oleic acids for re-use in Emersol process.

The solvent-saturated fatty acid cake discharged from the filter is melted and fed into the still, where the solvent is recovered overhead and condensed. The molten acid is then pumped through a cooler to a product storage tank.

The solvent-soluble acid solution from the filter after passing through a heat exchanger is fed to a preheater before going to a separate still where the solvent is recovered overhead and condensed. The preheater functions as a partial condenser for the vaporized solvent and effects an economy in steam requirements. The solvent free oleic acid is then pumped through a cooler to the product storage tank.

Emersol Processed Mixed Fatty Acids

Fatty Acids	Titre	Iodine value	Product	Yield %	Titre	Iodine value
No. 1 tallow.....	42.4° C.	52.2	Stearic acid.....	51	129.5° F.	6.0
			Oleic acid.....	49	2.0° C.
White grease.....	38.7° C.	62.5	Stearic acid.....	38	128.7° F.	6.0
			Oleic acid.....	62	2.0° C.
Yellow grease-stearine.....	45.2° C.	44.7	Stearic acid.....	52	129.5° F.	6.0
			Oleic acid.....	48	2.0° C.
Garbage grease.....	37.5° C.	68.4	Stearic acid.....	35	127.6° F.	6.0
			Oleic acid.....	65	2.0° C.
Linseed oil.....	185.0	Solid acids.....	14	44.7° C.	87.0
			Liquid acids.....	86	195.0
Soya Bean oil.....	129.3	Solid acids.....	15	48.5° C.	50.0
			Liquid acids.....	85	144.0
Sardine oil.....	160.0	Solid acids.....	25	30.0
			Liquid acids.....	75	201.5

The products are discharged from the stills at about 218° F., and the coolers reduce the temperature to about 170° F. This prevents most of the deleterious heat effect on the products, especially when they are exposed to air. The condensed solvent from both stills is recycled, to be mixed again with fresh feed to the crystallizer.

The process is flexible, in that product specifications can be varied in accordance with the demand. Operating costs are approximately 65% less than the pressing method. A comparison of the operating costs for the two procedures is shown in the following tabulations:

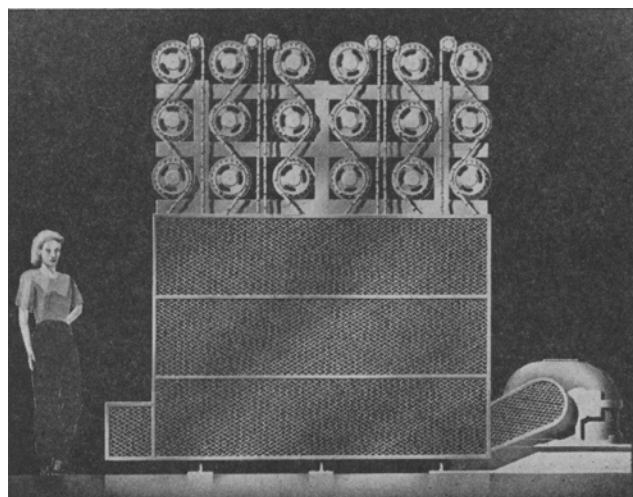
Operating Cost for Separating Single Pressed Stearic Acid and 4 Titre Red Oil

	Cost per 1,000 pounds	
	Pressing method	Emersol method
Labor.....	\$2.82	\$.67
Supervision.....	.15	.14
Maintenance.....	1.30	.42
Sulphuric Acid.....	.04
Press Cloth Replacement.....	1.11
Hair Mat Replacements.....	.75
Miscellaneous Supplies.....	.06	.11
Steam.....	.60	1.20
Power and Light.....	.51	.23
Water.....	.04	.04
Acid Boiling and Filtering Red Oil.....	1.26
Methanol.....23
Total.....	\$8.64	\$3.04

Operating Cost for Separating Double Pressed Stearic Acid and 4 Titre Red Oil

	Cost per 1,000 pounds	
	Pressing method	Emersol method
Labor.....	\$3.47	\$.80
Supervision.....	.17	.17
Maintenance.....	1.30	.50
Sulphuric Acid.....	.04
Press Cloth Replacement.....	1.21
Hair Mat Replacement.....	.90
Miscellaneous Supplies.....	.06	.11
Steam.....	.64	1.40
Power and Light.....	.55	.23
Water.....	.04	.04
Acid Boiling and Filtering Red Oil.....	1.33
Methanol.....27
Total.....	\$9.71	\$3.52

Emery research chemists have developed a laboratory technique for separating fatty acids by which plant operations can be predicted. The results can be interpreted to indicate those materials which can be profitably fractionated by the commercial process. It is also used for a close processing control over plant operations. The following tabulation illustrated the results that have been obtained on typical fatty acids.



Multi-tubular crystallizer with variable speed chain drive.

The Emersol process, although designed for the separation of fatty acids, is also adapted to the separation of fatty glycerides. Tank car lots of inedible greases have been processed through the semi-commercial plant, producing oil and stearine of the following analyses:

Oil		Stearine	
Yield.....	75%	Yield.....	25%
Pour Point (ASTM).....	37.0° F.	Moisture.....	0.45%
Cloud Point (ASTM).....	50.0° F.	Insoluble.....	0.00%
Free Fatty Acid.....	4.7%	Soluble Mineral Matter....	0.01%
(as oleic)			
Iodine No.....	75.0	Unsaponifiable.....	0.26%
Saponification No.....	194.0	Titre.....	45.8° F.
Titre.....	33.0° C.	Free Fatty Acid.....	1.9%

Original white grease had the following analysis:

Moisture.....	0.4%
Insoluble.....	0.15%
Soluble Mineral Matter.....	0.01%
Unsaponifiable.....	0.47%
Titre.....	38.8° C.
Free Fatty Acid (as oleic).....	4.0%

The Emersol process is practicable for separating other fats and oils, such as tallow, sardine oil, sperm oil, and all vegetable oils into solid and liquid portions. Vegetable oils can be winterized by this process to produce salad oils with an excellent cold test.

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