

# Modification of Vegetable Oils. IX. Purification of Technical Monoglycerides<sup>1</sup>

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TECHNICAL monoglycerides almost invariably are prepared by the reaction of fat or fatty acids with glycerol in the presence of an alkaline catalyst (2, 3, 5). The end product of this reaction always contains substantial quantities of free glycerol, diglycerides, and triglycerides, in addition to the desired monoglycerides. In fact, the monoglyceride content of commercial products seldom exceeds 60 per cent, which limit is fixed by the solubility of glycerol in the glycerides which in turn is fixed by the maximum permissible temperature (4).

When technical monoglycerides are incorporated in edible goods for the purpose of emulsifying the fatty ingredients, the proportions of di- and triglycerides accompanying the monoglycerides is usually immaterial; and in instances where monoglycerides are used to impart staling resistance to breads, cakes, etc., the composition of the technical monoglycerides also may be of little significance. However there are present and potential uses where monoglycerides having purities greater than those generally available are desirable.

Where monoglycerides derived from natural fats are used as emulsifying agents for systems consisting of non-glyceride oils and water, any di- and triglycerides associated with the monoglycerides are completely inert and expensive diluents. Elimination of the di- and triglyceride components from the technical products would in most instances double or triple the surface activity of the monoglyceride portion and simultaneously provide raw materials for the production of more monoglycerides.

Relatively pure mono- or diglycerides are excellent chemical intermediates and, if they were available in large quantities, would often be preferred over the present technical products in the manufacture of detergents, special surface active agents, and oil-modified resins. The pure compounds also are potentially important in the preparation of "tailor-made" fats.

The present investigation was undertaken to determine how technical monoglycerides could be fractionated by relatively simple methods adaptable to large scale production. Several methods for removing free glycerol from the glycerides were examined, and attempts were made to fractionate the glycerides with the aid of immiscible solvent mixtures. The major emphasis however was placed on fractional crystallization from solvents.

## Materials and Methods of Analysis

**Monoglyceride Products.** All of the monoglycerides used in the experiments were prepared from U.S.P. glycerol and a high-grade refined and bleached cottonseed oil which had been hydrogenated to an iodine value of 0.7 and which contained 0.16 per cent of free fatty acids. The average molecular weight of

the combined acids was 279.2, calculated from their neutralization value without correcting for unsaponifiable matter.

Reactions between the fat and glycerol were carried out under hydrogen at atmospheric pressure using a glass vessel equipped with a stainless steel stirrer and heated by means of an electric heating mantle. The products containing approximately 40% of monoglycerides on a glyceride basis were prepared, using approximately 20% of glycerol on a fat basis and allowing the reaction to proceed for 3½ hours at 200°C. Those products containing approximately 60% of monoglycerides were made with 45% glycerol, using a temperature of 250°C. and a reaction time of 15 minutes. In all instances sodium hydroxide equivalent to 0.1% of the weight of the fat was used as a catalyst. Unless stated otherwise, at the completion of each run and before the temperature was reduced, the catalyst was destroyed by the addition of a phosphoric acid-glycerol solution sufficient to provide 0.75 mole of acid per mole of catalyst. Before being employed in fractionation experiments some of the end products were freed of uncombined glycerol by repeatedly emulsifying them with distilled water, cooling, and destroying the emulsion under agitation, and filtering to separate the water. The glycerol-free products were dried by melting and agitation under vacuum. The technical monoglycerides used in most of the experiments described hereafter are listed in Table I.

TABLE I  
Technical Monoglyceride Products Used for Fractionation

Product	Analysis of fatty portion			Free glycerol, %
	Mono-glyceride, %	Diglyceride, %	Free fatty acids, %	
M 3-5,9 <sup>a</sup> .....	38.9	46	1.87	0.00
M 6-8 <sup>a</sup> .....	59.7	35	1.11	0.00
M 10.....	43.6	44	.....	9.48

<sup>a</sup> Free glycerol was removed by washing with distilled water.

**Solvents.** The various alcohols used in the experiments were of reagent grade; unless they contained less than 0.1% moisture by actual test (9), they were brought to this condition by treatment with calcium oxide and then distilled. The acetone employed was an anhydrous commercial product of reagent grade which was treated with anhydrous calcium sulfate (Drierite)<sup>3</sup> and distilled before use. The commercial hexane (Skellysolve B)<sup>3</sup> was used as received. The other nonpolar solvents were chemically pure.

**Methods of Analysis.** Whenever samples were analyzed for monoglycerides, the periodic acid oxidation method as modified by Handschumacher and Linteris (6) was employed. The free glycerol in the reaction

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<sup>3</sup> This product is named as part of the specification of the exact experimental conditions and does not imply that this product is particularly endorsed or recommended by the Department of Agriculture over other products having the same or similar properties.

products was determined by applying this method to the samples before and after washing with water. Since one part of free glycerol is equivalent to 7.68 parts by weight of monoglyceride, the content of free glycerol could be calculated from the two monoglyceride determinations, making allowance for the change in weight produced by washing. Whenever it was required that solvents be removed from fat samples to determine yields, the products were spread over a relatively large surface area and heated under vacuum to 80°C. in order to minimize any tendency of the monoglycerides to decompose.

#### Removal of Free Glycerol

Settling and decantation is perhaps the simplest method of removing at least a portion of the free glycerol unavoidably present in technical products, at least when the content of monoglycerides is high. It has been shown (4) that in the preparation of a product such as the one from which sample M 6-8 was prepared, which contained about 60% monoglycerides on a glyceride basis, a minimum of 40% (on an original fat basis) of free glycerol must be employed in the interesterification. Only 38% of the added glycerol will combine chemically, leaving about 22% of free glycerol (on a final glyceride basis) at the completion of the reaction. Laboratory experiments have shown that in such an interesterification only about 10% of free glycerol (on a glyceride basis) is miscible in the glyceride portion of the end product after the catalyst has been destroyed and the product cooled to about 90°C. Hence about 55% of the 22% of free glycerol in the end product can be removed by decantation.

Evidence exists to indicate that this method of removing glycerol is used by some manufacturers, as a commercial sample of glycerol monostearate said to contain 60% of monoglyceride, was examined and found to contain about 10% of free glycerol.

When the end product of an interesterification contains less than approximately 10% of monoglycerides, it can be liquefied and successfully washed free of uncombined glycerol with a 20% solution of sodium sulfate in water. At higher monoglyceride levels stable emulsions form in spite of the sodium sulfate; and, if glycerol removal by water washing is desired, it is best to emulsify the product in pure water and destroy the emulsion by stirring and cooling below the solidification point of the glycerides.

It has been claimed (8, 9) that mixtures of pure mono- and diglycerides of fatty acids can be distilled without disproportionation and that free glycerol can be fractionally distilled from a mixture without decomposing the mono- and diglycerides if the alkaline catalyst used in the interesterification is destroyed by neutralization. However by employing a modified form of distillation, it was not possible completely to remove free glycerol without the occurrence of extensive decomposition, possibly because the mixtures were not sufficiently pure.

In one experiment an interesterification was conducted, using the materials and conditions employed in the preparation of product M 6-8. Before reducing the temperature at the end of the reaction, 0.75 mole of phosphoric acid per mole of soap in the reaction mixture was added, as usual. The mixture was distilled for 1 hour at a temperature of 200°C. and a pressure of 2 mm. of mercury. Free glycerol began

to evolve rapidly as the temperature surpassed 160°C. While the temperature was 200°C., a small amount of dry hydrogen was passed through the fat to strip out residual glycerol. After the distillation the monoglyceride content of the glycerides was found to be 24.5% instead of the original 61.0%. The resulting distillate was a milky fluid at room temperature and much too small in volume to contain the monoglycerides which were not found in the residue. Experiments with other monoglyceride products showed that the monoglycerides likewise decomposed when steam was substituted for hydrogen or when the catalyst was destroyed with acetic acid at a temperature of about 100°C.

One of the more attractive methods of removing free glycerol on a large scale would involve mixing the technical product with a solvent which dissolves the glycerides but in which glycerol is practically insoluble. Other desirable features of such a solvent would include cheapness, wide availability, chemical inertness, and a low boiling point. Commercial hexane answers these requirements to a reasonable degree.

In one experiment product M 10 was mixed with commercial hexane in the ratio of 25 parts of product to 100 parts of hexane. The flask containing the mixture was heated to 55°C. to liquefy completely the fatty portion; afterwards it was thoroughly mixed and then immersed in a water bath where it was held overnight at a temperature of 55°C. The next morning the clear hexane soluble portion was withdrawn and analyzed. In similar experiments various small amounts of distilled water were added before heating and mixing and different concentrations of product M 10 also were used. The results obtained are recorded in Table II.

TABLE II  
Effect of Glycerides and Moisture on the Solubility of Uncombined Glycerol in the Hexane Phase for Systems Product M 10<sup>a</sup>-Commercial Hexane-Water, at 55°C.

Experiment No.	Ratio of water to glycerol	Conc. of M 10, g./100 g. hexane	Glyceride-glycerol fraction from hexane phase	
			Apparent monoglyceride content, <sup>b</sup> %	Free glycerol content, %
25a.....	0.36:1	50.0	56.0	1.57
26b.....	0.36:1	25.0	55.1	1.46
26d.....	0.36:1	12.5	54.9	1.43
26c.....	0.00:1	25.0	59.6	2.05
26d.....	0.36:1	25.0	55.1	1.46
26a.....	1.10:1	25.0	50.7	0.90
28d.....	2.20:1	25.0	46.5	0.36

<sup>a</sup> Product M 10 contained 9.48% free glycerol and 39.5% monoglycerides.

<sup>b</sup> On analyzing for monoglycerides 1 part of free glycerol is equivalent to 7.68 parts of monoglycerides.

It is remarkable that a 4-fold increase in the fat in the system resulted in such a slight increase in the solubility of free glycerol. Monoglycerides have solvent properties quite different from those of hexane, and a substantial change in the proportions of the two could conceivably have a marked influence on the behavior of the combination.

When a substantial quantity of water is added to a monoglyceride-commercial hexane solution, very stable emulsions are formed. If however free glycerol is present and the ratio of added water to glycerol is similar to those shown in Table II, the aqueous phase settles rapidly and the emulsion breaks. In the ex-

TABLE III  
Distribution of Monoglyceride Product M 3-5,9 Between Commercial Hexane and Aqueous Solutions of Methanol and Ethanol

Experiment No.	Temp., °C.	Conc. of M 3-5,9 in hexane, g./100 g. hexane	Wt. ratio of aqueous alcohol to hexane	Type of alcohol	Conc. of aqueous alcohol, wt. %	Glycerides in alcohol solution		
						Yield of glycerides, %	Mono-glyceride content, %	Yield of monoglycerides, %
20b.....	40	7.5	1:1	Methanol	95	46.1	72.5	85.9
20a.....	40	15.0	1:1	Methanol	95	44.0	66.4	75.1
18c.....	40	30.0	1:1	Methanol	95	9.7	.....	.....
19a.....	30	30.0	1:1	Methanol	98	0.0	.....	.....
18a.....	30	30.0	1:1	Ethanol	80	16.2	80.8	33.7
17a.....	40	30.0	1:1	Ethanol	80	18.7	68.3	32.9
18b.....	40	30.0	2:1	Ethanol	80	48.6	62.4	77.9

periments summarized in Table II the volumes of the aqueous solutions always were nearly equal to the combined volumes of the free glycerol and water in the system.

#### Distribution Between Immiscible Solvents

Several exploratory experiments were made to fractionate monoglyceride product M 3-5,9 by allowing it to distribute itself between two immiscible solvents. The mixtures always were prepared in the late afternoon and allowed to come to equilibrium overnight while being kept at a constant temperature. The data obtained are reproduced in Table III.

In these tests the alcohol phase exhibited a strong tendency to disappear into the hexane phase as the amount of glycerides in the system was increased or the water content of the alcohol was decreased. As the water content of the alcohol was increased, its dissolving power for monoglycerides decreased rapidly. While some of the results obtained appeared promising and while this method is potentially valuable in the development of continuous fractionation processes, the method was not investigated further because better results were obtained with fractional crystallization procedures.

#### Fractional Crystallization from Solvents

Because of the fact that mono-, di-, and triglycerides of given fatty acids differ greatly from each other with respect to average molecular weight and because the number of polar groups per molecule varies from none for triglycerides to two for the relatively low molecular weight monoglycerides, purification processes utilizing fractional crystallization from solvents should be ideally suited for accomplishing the intended objectives. The separation of mixtures of mono-, di-, and triglycerides by fractional crystallization from ethanol-water solutions has been employed as an analytical tool (7), and numerous investigators have used this procedure to purify small quantities of monoglycerides, but it appears that no quantitative data on this type of fractionation have ever been published.

In the present experiments the fatty product was always weighed into a glass-stoppered Erlenmeyer flask and the desired quantity and type of solvent added. Then the fatty product was liquefied by immersing the flask in water maintained at 60°C. or at a temperature just slightly below the boiling point of the solvent if the solvent boiled below 60°C. After complete liquefaction the fatty product and solvent were mixed well, and the flask was placed for an hour in an oven maintained about 10° above the desired crystallization temperature. The flask was then immersed almost completely and left overnight in a thermostatically controlled water bath set at the crystallization temperature. The following day a sintered

glass filter was placed in the bottom of the flask and, without removing the flask from the bath, the clear filtrate was forced into a second Erlenmeyer with the aid of dry nitrogen which had been adjusted to the crystallization temperature and was maintained under a slight pressure. Filtration was discontinued when the first bubbles of nitrogen gas passed through the filter. Most of the solvent was evaporated from the filtrate and the residue then was placed in a vacuum oven held at 80°C. From the weight of the filtrate and the weight of fatty material in the filtrate the yield of glycerides was calculated by taking into consideration the amount of filtrate which was not actually removed from the cake; *i.e.*, the yields of glycerides given are the quantities actually soluble under the conditions of crystallization. The fatty material obtained from each filtrate was analyzed for monoglyceride content (purity); and this value, the corrected yield of fatty material, and the total quantity of monoglycerides in the system were used to calculate the yield of monoglycerides.

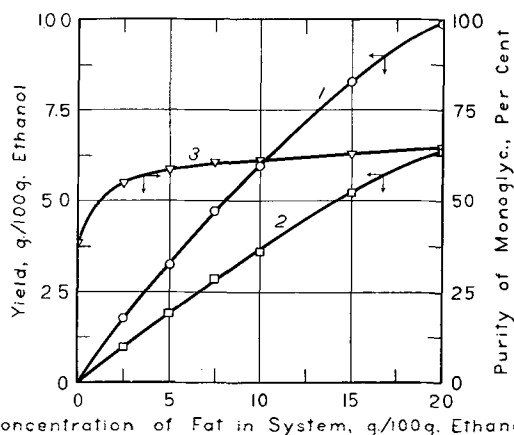


FIG. 1. Yields and purity of alcohol soluble fatty material obtained by cooling solutions of ethanol and glycerol-free technical monoglyceride M 3-5,9 (38.9% monoglycerides) to 30°C.: (1) Yield of fatty materials; (2) yield of monoglycerides; (3) monoglyceride content of the filtrate fraction.

In Figure 1 are shown the yields and purity of the monoglyceride-rich product from the filtrates obtained when solutions of ethanol and glycerol-free technical monoglyceride were cooled to 30°C. It is evident from this figure that both the monoglyceride and total glycerides in the filtrate increase in a roughly linear manner with the total fat content of the system, and the net result is that over most of the range shown the monoglyceride content or purity of the fatty material from the filtrate remains relatively constant. Calculations show that over the given range of concentration most but not all of the

monoglycerides in the system appear in the filtrate. Percentage yields of monoglycerides are 98.6, 93.4, 89.5, and 82.1 when fat concentrations in the system are 5.0, 10.0, 15.0, and 20.0 g. per 100 g. of ethanol, respectively. These results indicate that after an appreciable quantity of fatty material has been forced out of an ethanol-technical monoglyceride solution by decreasing the temperature, any further decreases in temperature will result in a mixture of monoglycerides and non-monoglycerides being separated from the solution in a relatively constant proportion.

Determination of the hydroxyl value of the fatty portion of the filtrate obtained when the concentration of the fat in the system represented in Figure 1 was 20 g. per 100 g. of ethanol revealed that the glycerides in the filtrate consisted entirely of mono- and diglycerides.

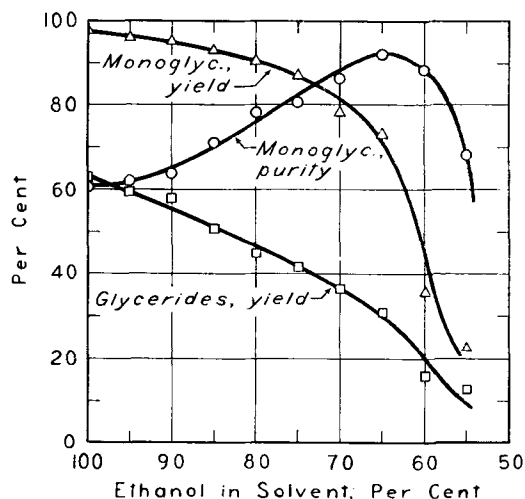


Fig. 2. Yields and purity of soluble fatty material obtained by cooling to 30°C. ethanol-water solutions containing 7.50 g. of glycerol-free technical monoglyceride M 3-5,9 per 100 g. of solvent. Monoglyceride content of technical product, 38.9%.

Figure 2 shows the solubility of a technical monoglyceride in an ethanol-water solvent as the concentration of ethanol in the solvent decreases. The concentration of monoglycerides in the soluble fraction increases fairly rapidly as the concentration of the ethanol decreases, and when the ethanol concentration reaches 65%, the fatty portion of the filtrate contains 92% of monoglycerides. At this point only 31% of the glycerides in the system are in solution, but 74% of the monoglycerides in the system are soluble. As the concentration of the ethanol decreases below 65%, the dissolving power of the solvent decreases rapidly below the range of practical significance, and rapid filtration becomes more difficult because the solids separate out of solution in finer and finer particles. When the ethanol concentration reaches 55%, the system represented in Figure 1 has a milky appearance and some of the solids will pass through coarse filter paper.

Since the fatty acids combined in the technical monoglycerides used in these experiments consist of approximately 75% stearic and 25% palmitic, it might be supposed that when a relatively small amount of monoglyceride-rich material is separated by fractional crystallization the average molecular weight of the acids in the monoglyceride-rich frac-

tion would differ from those in the technical product. However determination of the average molecular weight of the combined fatty acids in several such fractions showed that the lowest molecular weight was 274.8 for a fraction (from product M 6-8) obtained in a yield of 34.8% and containing 83.3% of monoglycerides. Since the average molecular weight of the combined fatty acids in the technical monoglycerides is 279.4, the change in average molecular weight can be neglected for all yields of practical significance.

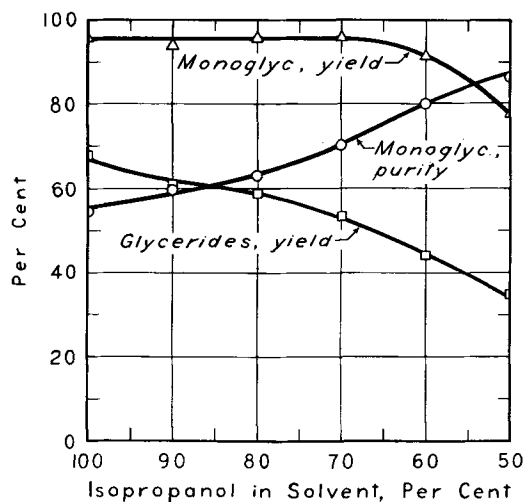


Fig. 3. Yields and purity of soluble fatty material obtained by cooling to 30°C. isopropanol-water solutions containing 7.50 g. of glycerol-free technical monoglyceride M 3-5,9 per 100 g. of solvent. Monoglyceride content of technical product, 38.9%.

The systems shown in Figures 3 and 4 are identical with that represented by Figure 1 with the exception that isopropanol, methanol, and acetone have been substituted successively for ethanol.

Inspection of these systems reveals that ethanol, isopropanol, methanol, and acetone can be made equivalent to a fair degree, insofar as the fractional crystallizations are concerned, if the water content of each is adjusted to the proper level. The dissolving power of methanol is most sensitive to a change

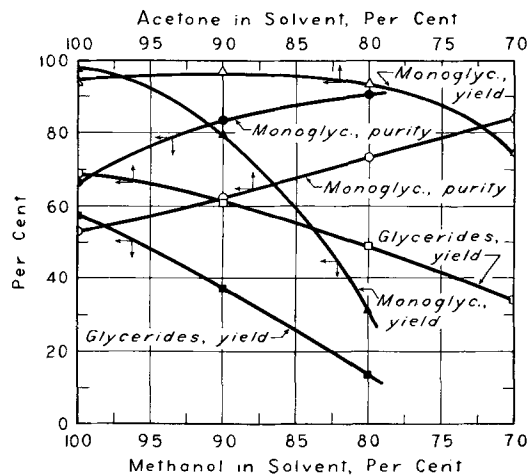


Fig. 4. Yields and purity of soluble fatty material obtained by cooling to 30°C. methanol-water solutions and acetone-water solutions each containing 7.50 g. of glycerol-free technical monoglyceride M 3-5,9 per 100 g. of solvent. Monoglyceride content of technical product, 38.9%.

TABLE IV  
Influence of Temperature and Concentration of Total Glycerides on the Composition of the Soluble Glycerides in Various Systems of Technical Monoglyceride-Solvent

Variable	Mono-glyceride product	Solvent	Crystallization temp., °C.	Concentration of glycerides in system, g./100 g. solvent	Glycerides soluble, %	Mono-glycerides in soluble glycerides, %	Yield of mono-glycerides, %	Yield of other glycerides, %
Temperature.....	M 3-5.9	65% Ethanol	30	7.5	31.1	92.0	73.6	4.1
			35		35.5	86.1	78.6	8.6
			40		38.2	82.6	81.1	10.8
Temperature.....	M 6-8	70% Ethanol	30	7.5	55.4	88.7	82.3	11.3
			35		61.6	83.4	86.1	21.3
Temperature.....	M 6-8	70% Isopropanol	30	25.0	53.1	80.1	71.3	26.2
			40		65.0	68.5	74.6	50.8
Temperature.....	M 3-5.9	Hexane	30	15.0	36.8	9.9	9.4	54.3
			40		59.8	17.9	27.4	80.0
Concentration.....	M 3-5.9	65% Ethanol	40	7.5	38.2	82.6	81.1	10.8
				15.0	42.5	78.4	85.6	15.0
				22.5	24.8	81.4	51.9	7.6
Concentration.....	M 6-8	80% Ethanol	30	7.5	59.4	83.2	82.8	24.7
				15.0	34.8	83.3	48.5	14.4
Concentration.....	M 3-5.9	Ethanol	30	5.0	63.3	58.7	98.6	44.1
				20.0	49.6	64.4	82.1	28.9
Concentration.....	M 6-8	70% Isopropanol	30	15.0	63.6	79.6	84.7	32.3
				25.0	53.1	80.1	71.3	26.2
Concentration.....	M 3-5.9	Hexane	30	7.5	56.8	9.8	14.2	84.0
				15.0	36.8	9.9	9.4	54.3
Concentration.....	M 6-8	Hexane	30	7.5	31.8	18.7	15.2	64.1
				15.0	31.1	24.4	12.7	58.3

in water content while that of isopropanol is least sensitive. Ethanol and acetone are of intermediate and almost equal sensitivity.

The possibility of employing 1,4-dioxane in fractional crystallizations also was investigated. Pure 1,4-dioxane proved to be an excellent solvent but possessed little value for fractionation at 30°C. while water solutions of 1,4-dioxane were inferior to alcohol solutions and exhibited a tendency to separate into two liquid phases.

Among the several nonpolar solvents tested commercial hexane yielded the best results and was also the most desirable from the standpoint of such secondary considerations as low boiling point, relative toxicity, chemical inertness, availability, and price.

When a nonpolar solvent is used on a mixture of mono-, di-, and triglycerides, the triglycerides are dissolved preferentially. The extent of this preferential solubilization is illustrated by the following example: A solution containing 7.5 g. of technical monoglyceride M 3-5,9 per 100 g. of commercial hexane was cooled to 30°C. At this temperature 56.8% of the glycerides still remained in solution, but the monoglyceride content of the glycerides in solution was 9.7%. Since the monoglyceride content of product M 3-5,9 was 38.9%, only 14.2% of the monoglycerides originally dissolved remained in solution while 84.0% of the non-monoglycerides remained.

Data presented earlier in connection with the partial crystallization of glycerides from technical monoglyceride-ethanol solutions showed that the monoglyceride content of the soluble fraction was relatively unresponsive to changes in the quantity of technical monoglycerides in the solvent or in the solvent and solid fraction combined. The data in Table IV show that the same is true but in a more marked degree than in other solutions of technical monoglycerides. The data in this table also show the influence which changes in the temperature of crystallization have on the quantity and composition of the glycerides in the solvent fraction. The data presented in Table IV are

of an empirical nature and were obtained with products derived from cottonseed oil stearine; however they can probably be applied with little or no error to products prepared from other hard fats in common use.

### Summary

Methods of purifying technical monoglycerides produced from cottonseed oil stearine by interesterification were investigated.

It was found that the concentration of uncombined glycerol in technical monoglycerides could be reduced to about 0.4% by dissolving the technical product in commercial hexane, adding water equivalent to twice the amount of free glycerol, and separating the hexane solution. The formation of stable emulsions was largely avoided by this procedure.

Technical monoglycerides containing 38.9% monoglycerides were purified by distributing them between two immiscible liquid phases (commercial hexane and an aqueous solution of methanol or ethanol). Products containing as much as 80% of monoglycerides were obtained in this manner.

On fractionally crystallizing a solution of the same technical monoglyceride from aqueous ethanol, a glyceride fraction having a purity of 92% and containing 74% of the monoglycerides in the technical product was obtained.

It was found that by addition of proper amounts of water ethanol, isopropanol, methanol, and acetone could be made nearly equivalent for fractionating mixtures of glycerides. Methanol is most sensitive to a change in water content while isopropanol is least sensitive.

When commercial hexane was used in the fractional crystallization of technical monoglycerides, as much as 84% of the non-monoglycerides was retained in the liquid phase, and the glycerides from this phase were found to have a monoglyceride content of 9.8%. The solids obtained by crystallizations from hexane were found to simulate the filtrates obtained with the polar solvents.

When a mixture of technical monoglycerides was partially crystallized from a solvent, the composition of the glycerides remaining in the solvent was relatively unaffected by changes in the concentration of the glycerides originally present in the solution.

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## Palm Oil Substitutes for Hot Dip Tinning<sup>1</sup>

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THE steel industry of the United States consumes annually appreciable quantities of palm oil, about 7,500 tons, in making hot dip tin plate. Over a period of years the price has fluctuated considerably, for example, rising from 3½¢ a pound before World War II to as high as 40¢. Furthermore the quality of oil has been uncertain; it has contained variable amounts of water and foreign matter and has been received in various degrees of rancidity. In addition, all this oil is now imported over long shipping routes such that the United States is in a strategically unfavorable position should an emergency arise which might imperil shipping lanes. In view of these factors a study of palm oil substitutes was instigated at the Armour Research Foundation of Illinois Institute of Technology under the sponsorship of the American Iron and Steel Institute.

### Requirements of a Tinning Oil

In the making of hot dipped tin plate, sheets of pickled steel are passed by means of rolls through a flux into a bath of molten tin and up through an 18-inch layer of hot (460°F.) palm oil floating on the tin. Three sets of rolls, operating in the oil, smooth and thin the tin coating (Fig. 1).

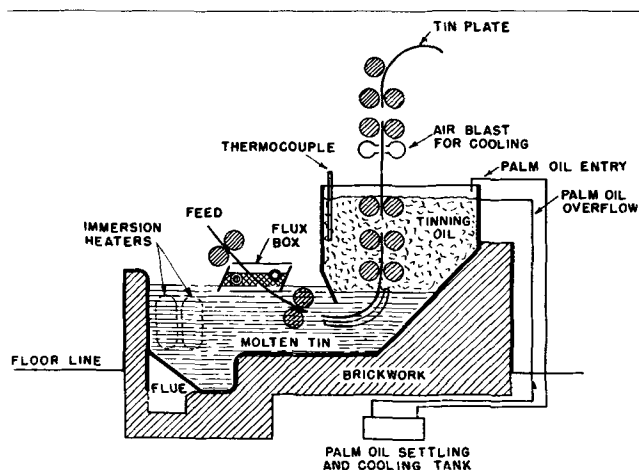


FIG. 1. Diagram of hot dip tin pot.

In order that an oil may operate properly in a tin pot, it should possess at least the following characteristics:

1. It should make smooth, bright, good quality tin plate.
2. It should drain rapidly and freely from the sheet.
3. It should be of low volatility.
4. It should have high flash and fire points.
5. It should neither oxidize nor polymerize readily.
6. It should be cleaned from the sheet readily.
7. It should be of low viscosity at 100 to 200°F. so that it may be pumped or poured without difficulty.

If a thin layer of oil is allowed to remain on the sheet, this oil affects the end use of the sheet. Consequently the oil should possess the following features:

1. It should be non-toxic, odor-free, and preferably edible.
2. It should not become rancid during storage.
3. It should not interfere with lithographing or lacquering procedures.
4. It should not interfere with soldering.
5. It should retard atmospheric corrosion.
6. It should assist handling in fabrication.

Finally, the oil should meet the following important economic requirements:

1. It should be readily available, preferably from domestic sources.
2. It should be inexpensive.

Palm oil has been and is a commercially satisfactory tinning oil; it has however several deficiencies. Its flash and fire points are low enough to create a fire hazard; it is quite volatile at tin pot temperatures and tends to increase in viscosity with time at tin pot operating temperatures. A primary disadvantage is its foreign source, and the strategic and financial problems which thereby arise.

### Survey of the Problem

The actual operations of making tin plate have always been more of an art than a science, with the lore of the tin house being passed from one operator to the next without ever being recorded. Much of the information on tinning oil is available only in the memories of the operators, and the important details have been closely guarded by the individual. Only comparatively recently has information been made available on tinning oils, and much of that has been from British sources. In virtually all the literature little space has been devoted to evaluating or explaining the mechanism of the tinning oil action; most of the research has been devoted principally to simulated service tests.

A review of the information gained in interviews of tin house operators revealed the following points of agreement:

<sup>1</sup> Presented at the 23rd annual fall meeting, American Oil Chemists' Society, Chicago, Oct. 31-Nov. 2, 1949.