

Fats and Their Derivatives

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THE important place occupied by fats and oils in our economic structure can best be understood by inspection of Figure 1.

It will be seen that there are three major uses of fatty oils. The first, and by far the largest, is the use as food. The second use depends on surface action effect and the largest item in this class is, of course, soap. The third use is as coating material and depends on the property of certain oils to oxidize and polymerize, either with or without the addition of chemicals or heat, to a hard, non-tacky, impervious film for the protection of metals, wood, etc.

Miscellaneous uses cover many fields, such as cup greases, journal greases, candles, rubber accelerators, tin-plating fluxes, plasticizers, etc. While these products differ from either the detergent or the coating field, the use of glyceride oils or their component fatty acid is necessitated because of the same basic properties; namely, surface activity or film formation.

Figure 1 shows statistics as obtained from government bureaus (1). The method of charting was used by Gordon McBride in a recent article on fatty oils published in "Food Industries" (2). It shows clearly that we are in an excellent position in regard to sufficient domestic fats to cover our food requirements. The position of the soap industry is not so favorable, due principally to the need of coconut oil which is a very essential ingredient in producing free-lathering and readily soluble soaps.

In the paint and varnish industry the domestic production meets only about one-half our requirements. We have improved this situation somewhat in the last few years by increased domestic production of linseed oil. The production of linseed oil rose from 157 million pounds in 1938 to 387 million pounds in 1940, while during the same years imports decreased from 293

million pounds in 1938 to 225 million pounds in 1940. Given time and enough incentive, we could raise sufficient flaxseed to cover our linseed oil requirements.

The faster drying oils, such as perilla, oiticia and tung oil together with castor oil, which is made into a drying oil by dehydration, are practically all imported. These oils are the major and essential ingredients of varnishes and quick-drying paints and cannot be replaced by slower-drying oils such as linseed.

While domestic production has started on tung oil and is being investigated in the case of castor oil, it will be many years before we will be self-sufficient in either of these oils. Another approach to the solution is the production of synthetic materials through research. In order to produce a substitute it is not necessary to reproduce tung oil itself, but only the active ingredient. The only parts of the oil that determine its properties are the component fatty acids and their location on the glycerol radical. In the case of soap, even the position on the glycerol radical has nothing to do with the resulting soap because the glycerine is removed and the remainder is a mixture of sodium salts of the fatty acids themselves.

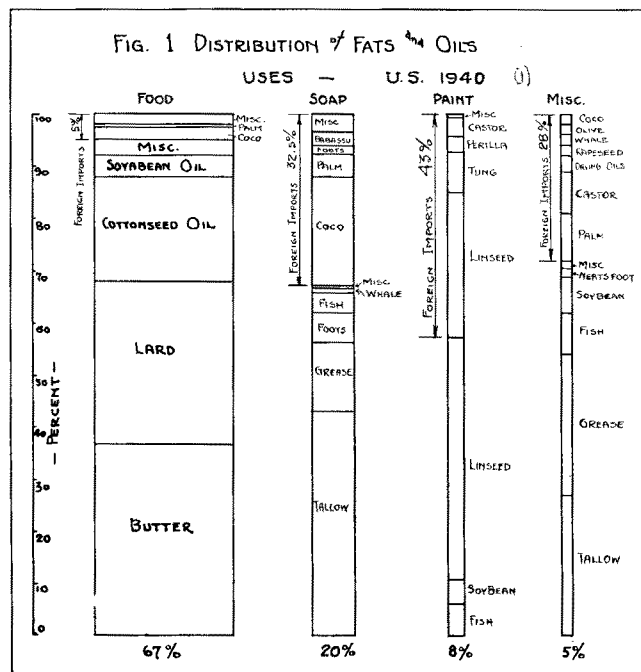
Vegetable or animal oils are used because of certain properties that are exhibited by the component fatty acids. Coconut oil is required by the soapmaker because it contains lauric acid as the principal ingredient; tung oil is required by the varnish-maker because of its high content of eleostearic acid; etc.

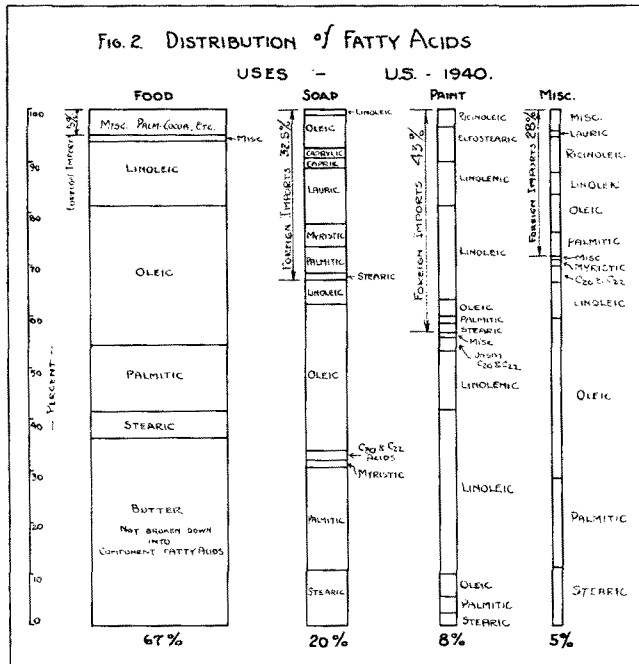
In every case the properties of the certain individual fatty acids are the controlling factors that dictate the selection of naturally occurring oils. The use of the natural oil forces the manufacturer to use varying amounts of fatty acids that are not only of no value for the specific purpose, but also in many cases are detrimental to the final product.

Figure 2 shows the same oils as charted in Figure 1, broken down into their component fatty acids. Butter has not been broken down into fatty acids because all butter enters the food industry. We would say in passing, however, that butter consists mainly of palmitic and oleic acids which are by far the principal fatty acids of food. It is interesting to note that the only fat that is synthesized by nature for the specific purpose of feeding its young consists mainly of palmitic and oleic acids. Inspection of the chart shows that we have an ample supply of palmitic and oleic acids. The large amount of linoleic acid shown in the food division is from cottonseed and soybean oils and for the most part is changed into oleic acid by hydrogenation.

Imports of food material are of minor importance and need not be considered because none of these materials are used for any special purpose and only appear at all because of economic reasons, and could be replaced by domestic fats without impairing quality.

In the soap industry one notices that the chief fatty acids are again oleic and palmitic acids. While these acids are the most desirable for soapmaking purposes, the use of naturally occurring oils containing them adds large amounts of stearic acid and other acids which produce more insoluble soap. To counteract the in-





solubility of sodium stearate the soapmaker must import large amounts of coconut oil which contains substantial quantities of acids, chiefly lauric, which produce very soluble sodium salts. Considerable oleic and palmitic acids are contained in imported oils. Their import would not be necessary if proper separation existed and provided a change could be made so that either the desired imported acid, namely, lauric, could be synthesized, or its use curtailed.

The chart shows that about the same amount of lauric acid is used as stearic acid. Now if pure lauric acid soap is prepared one finds that it will not be a satisfactory detergent. While it lathers profusely in cold water, it lacks the proper balance to remove the soil. A pure stearic acid is also a poor detergent because of its insolubility even in warm water. Our work to date has shown that the value of these two fatty acids for soapmaking purposes is dependent upon one another. If the stearic acid was removed from the soap kettle it would be possible to eliminate the lauric acid and still produce soap that would be quite satisfactory in the majority of cases.

Another example of the addition to the soap kettle of acids which do not belong there is the use of nearly 100,000,000 pounds of fish oil annually. It is because of this addition to soap that one finds strange fellows like C₂₀ and C₂₂ acids. These acids do not belong in the soap family. In the natural unsaturated condition they produce sticky, slimy, insoluble masses which oxidize rapidly, causing rancidity, discoloration and fishy odors. When partially or completely hydrogenated, as they usually are, they are changed into acids, the sodium salts of which are quite insoluble and are of no more value as soaps than the equivalent amount of sand.

The composition of sardine oil (3) as shown in Figure 3 leads one to believe that its value as a raw material for both the paint and the soap industry could be greatly enhanced if the individual fatty acids could be separated one from another. One will notice that 59 percent of the acids are C₁₈ chain length or lower and 41 percent are the unsaturated C₂₀ and C₂₂ acids. If we separate the acids into two groups by fractional distillation and hydrogenate fraction I, we produce a fine soapmaking composition with an iodine number

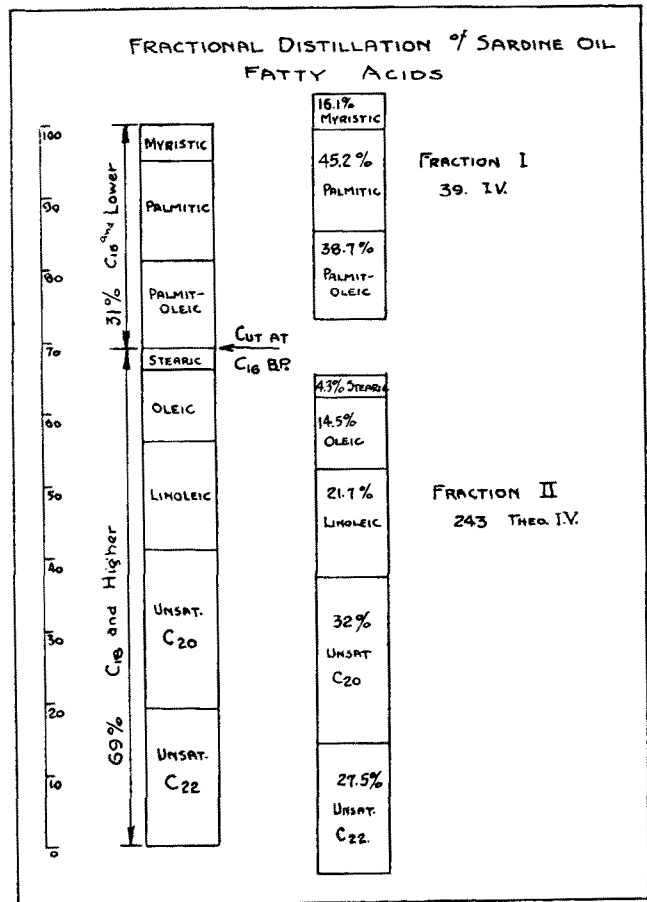


Fig. 4

of 39, the same as tallow. The calculated iodine value of fraction II is 320. In practice, however, some polymerization occurs which causes the iodine number to drop somewhat, although we have obtained fatty acid having an iodine number of 290.

If it is desired to produce a larger paint oil fraction we can change our cut as shown in Figure 4. It will be noticed that now we obtain a 38 iodine number soapmaking fraction that could be used without hydrogenation and the remaining 69 percent has an iodine number of 243, which is a better paint vehicle than the higher iodine fraction shown in Figure 3.

These examples show the importance of separation as a tool for using our fat and oil supplies at maximum efficiency. Separation can be obtained by several methods which depend upon different physical properties. Acids having widely different melting points can be separated by the well known crystallization and pressing operations. A second method is dependent upon the different boiling points of the various fatty acids which are shown in Table 1. One can see that separation according to carbon chain lengths is quite possible. Both methods fail in their ability to separate acids of similar chain lengths having varying degrees of unsaturation.

TABLE 1.

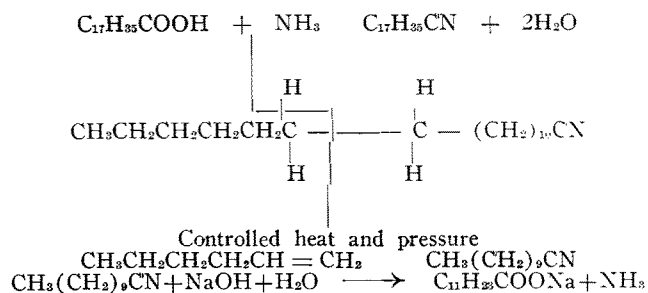
Acid	Boiling Points of Fatty Acids (4)	
	B.P. (760 mm.) °C.	B.P. (5 mm.) °C.
Stearic	383	208
Palmitic	352	191
Myristic	333	176
Lauric	301	158
Capric	268	141
Caprylic	232	113
Caproic	203	89
Oleic	206.5
Linoleic	205

While the above methods are the only ones practiced commercially, other means, such as selective solvents, changing the fatty acid to another derivative which in turn would have different physical or chemical properties and thereby lend itself to separation, are known.

One can readily see that even though economical means of separation were developed so that all pure acids were available, certain fatty acids would still be in demand. With our adequate supply of oleic and palmitic acid we could synthesize a very fine shortening, more desirable than lard or hydrogenated cottonseed oil. Less hydrogenation would be required because some of the domestic linoleic acid now being hardened would be more than ample for our paint requirements. Stearic acid could be produced in quantities far in excess of our demands.

The soap industry likewise would have ample palmitic and oleic acids. When the lower molecular weight acids of coconut oil are required we might investigate a process, the experimental work with which has indicated that low molecular weight acids can be obtained from the higher acids by pyrolytic cracking of the corresponding nitriles (5). This process is best illustrated by the following chemical equations:

Lauric Acid from Stearic Acid:



Stearic acid is treated with NH_3 at high temperature to form stearonitrile. The nitrile behaves very similarly to a hydrocarbon in that the chain will break to form a lower molecular weight nitrile and an unsaturated hydrocarbon.

We now come to certain acids that are used by the paint industry, which have very desirable properties. They are the essential ingredients of spar varnishes and quick-drying enamels. Linoleic acid will not answer the requirements nor will linolenic acid. These acids in the form of their glycerides dry rapidly and yield tough elastic films.

We have shown how it is possible to obtain very highly unsaturated acids from fish oils. While these acids dry quite rapidly, the films are too brittle and are at best only in part a substitute for eleostearic acid found in tung oil. Eleostearic acid is important when a rapid drying, tough, flexible film is required. It is evident, therefore, that if we are to be self-sufficient in supplies of this fatty acid we must do one of three things: (1) Grow tung trees; (2) produce eleostearic acid synthetically; (3) discover and produce other fatty acids that have properties similar to eleostearic acid.

The first method, that of raising tung trees, will not be discussed here because it does not require the services of a chemist.

The chemist will have more work solving the second and third problems. If we inspect the formulas of linolenic and eleostearic acids we find that they are identical except for the position of the double bonds:

Linolenic acid:

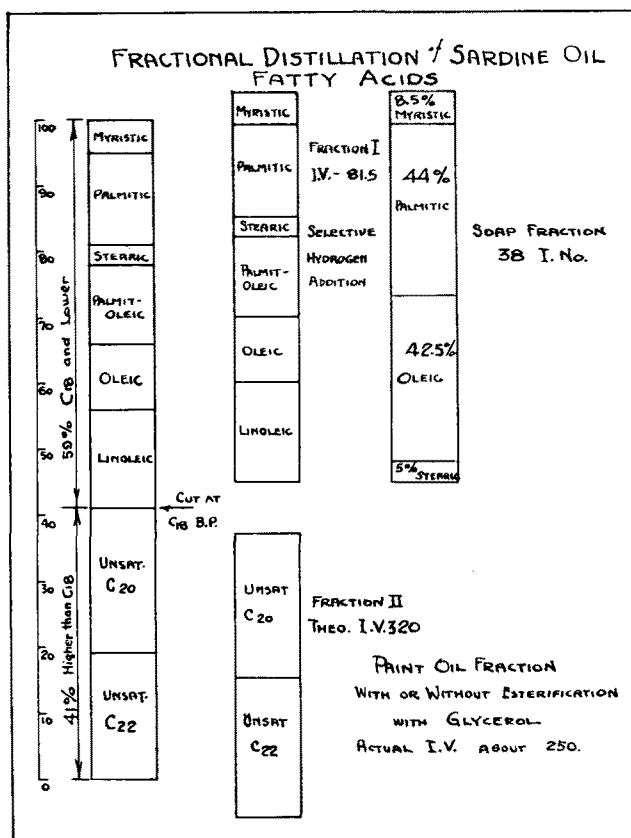
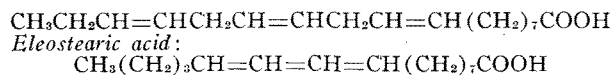


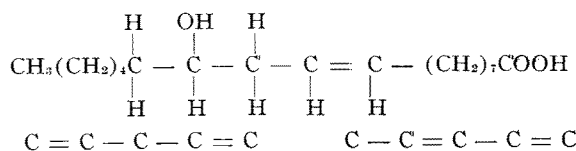
Fig. 3



Several investigators have reported that we can shift the position of the double bond. With the development of economical plant processes it might be possible to produce eleostearic acid.

Inspection of the formula and the mechanism of the polymerization reaction shows that only a pair of conjugated C atoms can enter the reaction and it is entirely possible that a good drying oil would be obtained with a conjugated di-olefinic acid. This has been borne out by the work that has been done with castor oil. The chief acid of castor oil is a mono-olefinic mono-hydroxy C_{18} acid.

Dehydration of Ricinoleic Acid:



Mixture of non-conjugate and conjugate

It has been found that upon heating under certain conditions water is removed forming a 2-double bond acid, with the unsaturated groups mainly in the conjugated position. The paint industry has accepted dehydrated castor oil and, although it is an imported oil now, there is a good chance that castor beans can be grown in this country without too much difficulty.

Another method of producing a conjugated linoleic acid is by treatment of linoleic acid itself in such a manner that we cause the double bond to shift into the conjugated position. Success of this process will place soybean and cottonseed oil in a position to compete in the paint oil field.

After one separates the fatty acids and investigates their special properties it is a natural step to see what some of their derivatives will be like. Just as the major uses of fatty acids are divided into two general classes, namely, soap—in which surface activity is the chief factor—and paint—which involves oxidation and polymerization of the alkyl chain, the derivatives can also be classified into the same groups. Reactions involving the carboxyl group are typified by such compounds as alcohols, aldehydes, nitriles, amines, amides, ketones and the like; and those in which the alkyl chain is involved, such as hydroxy acids, resins, polymerization products, halogen addition products, and the like.

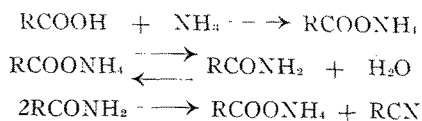
The most successful research along the line of reactions involving the carboxyl group is typified by the production and promotion of the sodium salts of fatty alcohols for detergent purposes. These products are superior to soap in their ability to resist precipitation in hard water and in neutrality of their solution. In regard to reducing our consumption of imported fats, however, the alcohols are not very helpful because lauryl alcohol is the one selected as having the best solubility and detergent balance.

Of the many derivatives that we have investigated, the amine group of derivatives has been put through the various paces of research and pilot plant development to the point where they will become full-fledged plant products within a few months.

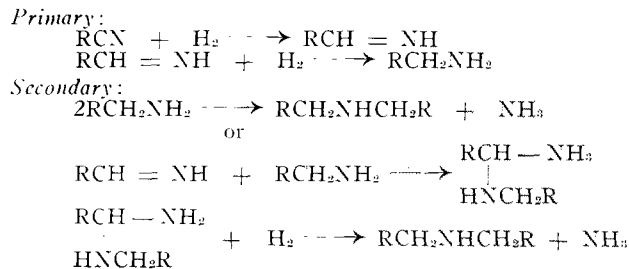
The fatty amines have for several years indicated surface active properties that are particularly suited for many types of flotation work. Until a few years ago they were chemical curiosities, produced by reacting fatty acids with ammonia to form nitriles and then subsequent hydrogenation by means of metallic sodium in an alcohol solution. After the preliminary laboratory work and the evaluation of samples for specific uses the primary amines of the common fatty acids, such as oleic, palmitic, and stearic acids, were chosen as the subjects for pilot plant development.

Three years have elapsed and during that time we have built a number of units for the purpose of contacting and reacting ammonia and fatty acids. The present unit has received our approval after it has operated 7 days a week, 24 hours per day since last fall, producing about one-quarter million pounds of nitriles.

The reactions involved in the manufacture of nitriles are shown by the following equations:



The hydrogenation of the nitriles to amines proceeds as indicated by the following equations:



The chemical engineers didn't relish the thought of tossing several tons of metallic sodium around any more than the cost accountants did the thought of adding the price of it to the amine costs, so we had to set out to do the job by more familiar methods. Our first attempts were not very successful. The nitriles failed to hydrogenate and when they did, we produced as much secondary amine as we did primary. After several years we are now able to produce a product containing about 90 percent primary amines. The hydrogenations work quite similarly to cottonseed oil hydrogenations, the amount of hydrogen required being the same as though pure linoleic acid (iodine number 180) were reduced to zero iodine number.

For most purposes it is only necessary to filter out the catalyst to obtain a satisfactory material. If a pure primary amine is desired it is necessary to distill under vacuum. The primary amines have a somewhat lower boiling point than fatty acid and much lower than the corresponding secondary, so it is not difficult to furnish products which analyze close to 100 percent primary amine.

In another month or two our large installation will be complete. The pilot plant personnel will move in with their centigrade to fahrenheit conversion tables, start up a few pumps, tune up some of the automatic controls, and remove others which appeared indispensable but prove to be excess baggage. About two of the many temperatures that will be recorded on the potentiometer will be carefully watched and necessary adjustment made. For several weeks everything will be in a turmoil, then suddenly when you are just about ready to junk the whole thing the entire set-up will start to operate. The operating department will take over, someone will produce a batch having 95 percent primary amines, the sales department will insist on it all being like that one batch even though it was a freak or the analysis was in error, the plant operators won't be able to remember their Greek and n-octadecyl amine will become tallow amine or garbage grease amine, drums will roll out and tank cars will be loaded and pulled out two days late, and n-octadecylamine will become just another commodity.

LITERATURE

- (1) Chem. & Met. 48, 4-120, April, 1941.
- (2) Food Industries, 13, 4, 46-47, April, 1941.
- (3) Hilditch, T. P., "The Industrial Chemistry of Fats & Waxes."
- (4) Armour & Co., Laboratory Data.
- (5) U. S. 2,033,536, Ralston, Pool & Harwood, Mar. 10, 1936.