Raw Materials for Soap. Saturated and Unsaturated Fats

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THE glycerides which are the principal raw materials for soap are the animal fats (e.g., tallow and grease), the lauric acid oils (e.g., coconut oil, babassu oil, palm kernel oil), the oleic-linoleic acid oils (e.g., cottonseed oil foots, palm oil), and the marine oils (e.g., hydrogenated whale oil). To this might be added soybean oil foots as a representative of the linolenic acid oils.

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Nearly two billion pounds of fats, oils, rosin, and tall oil were used in soap manufacture in the United States in 1950. The figures (14) are 1,873,389,000 pounds of fats and oils, 42,780,000 pounds of rosin and 13,233,000 pounds of tall oil. Of the oils and fats, tallow and grease were used in by far the largest amount, followed by coconut oil and babassu oil, vegetable oil foots and palm oil, and finally hydrogenated whale oils.

The glycerides react with sodium hydroxide (or similarly, potassium hydroxide) according to the equation shown, using tripalmitin as an example:

$$\begin{array}{lcl} CH_3(CH_2)_{14}CO_2CH_2 & & CH_2OH \\ \quad\quad\quad\quad\quad\quad\;| & & \;| \\ CH_3(CH_2)_{14}CO_2CH + 3NaOH & \longrightarrow 3CH_3(CH_2)_{14}CO_2Na + & CHOH \\ \quad\quad\quad\quad\quad\quad\;| & & \;| \\ CH_3(CH_2)_{14}CO_2CH_2 & \text{Na palmitate} & CH_2OH \\ \text{Tripalmitin} & & \text{Glycerol} \end{array}$$

Actually the natural fats and oils are composed mainly of mixed glycerides. The structure of the glycerides, whether simple or mixed, however does not greatly concern the soap maker. The structure of the fatty acids does affect the properties of the soap. The glycerides may be hydrolyzed by water alone in a high pressure reaction, or by acid hydrolysis catalyzed by the Twitchell reagent, to produce the fatty acids and glycerol. The fatty acids, which may be distilled and partially separated, may then be converted to soap by neutralization with sodium carbonate. Thus it is important to think of the fatty acids, either as such or in combination as glycerides, as the essential raw materials.

The fatty acid composition of one representative of each of four classes of glyceridic raw materials is shown in Table I. Beef tallow, coconut oil, cottonseed oil, and Antarctic whale oil are representatives of the animal fats, the lauric acid oils, the oleic-linoleic acid oils, and the marine oils, respectively. The four fats represented have iodine numbers of 49.5, 8.0, 105.0, and 108.0, respectively.

Beef tallow (1) is principally composed of the glycerides of oleic, palmitic, and stearic acids in that order with smaller amounts of myristic and linoleic acid.

TABLE I

Fatty Acid Composition of 4 Fats
Weight, %

Acid	Beef Tallow	Coconut Oil	Cotton-seed	Antarctic Whale
Caprylic		5.4		
Capric		8.4		
Lauric		45.4		
Myristic	6.3	18.0	1.4	9.2
Palmitic	27.4	10.5	23.4	15.6
Stearic	14.1	2.3	1.1	1.9
Oleic	49.5	7.5	22.9	(37.2)
Linoleic	2.4		47.8	( )
C_{20} unsaturated	(0.3)			12.0
C_{22} unsaturated	(0.1)			7.1

Linolenic and arachidonic acid are also found in tallows in amounts under 1% (9, 13). Recently it has been shown that even more highly unsaturated acids

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INDEX

having 20 to 22 carbon atoms and 5 double bonds are present in animal fats to the extent of about 0.1% (3).

Coconut oil (10) is principally a glyceride of lauric, myristic, and palmitic acids with smaller amounts of caprylates, caprates, and oleates. In addition to the fatty acid composition shown, there is present 0.8% caproic, 0.4% arachidic, and 1.3% hexadecenoic acids. The only unsaturated acid present to any important extent is oleic acid.

Cottonseed oil (5) is mainly a glyceride of linoleic, oleic, and palmitic acid. In addition to the small amount of myristic and stearic acid tabulated, the oil contains 1.3% arachidic, 0.1% tetradecenoic, and 2.0% hexadecenoic acids.

Whale oil (6) is principally a glyceride of oleic, palmitic, myristic, and polyunsaturated 20 and 22 carbon acids. The value 37.2% represents mainly oleic acid. The 20 carbon and 22 carbon acids contain on the average 3 and 4 and 4 and 5 double bonds, respectively. Whale oil also contains 0.6% arachidic, 2.5% tetradecenoic, and 13.9% hexadecenoic acids. It is apparent that glycerides from the four fats differ considerably in their fatty acid composition. Several fatty acids from caproic (C_6) to C_{22} unsaturated acids have now been mentioned as constituents of the four glyceridic raw materials.

The fatty acids which are really desirable in soap making however are only five: lauric, myristic, palmitic, stearic, and oleic acids. The sodium salts of caproic, caprylic, and capric acids are too low in molecular weight to have true soap-like properties, and they are believed also to contribute to skin irritation. Salts of the polyunsaturated acids such as linoleic acid are soft in consistency, give an undesirable "greasy" lather, appear to be too hydrophilic to have characteristic soap-like properties except at low temperatures, and are too susceptible to oxidation for many uses. They nevertheless have some application, for example as a component in liquid soaps, highly built alkaline laundry soaps, and superfatted soaps for floor washing. The marine oils in particular can be hydrogenated to advantage, converting the unsaturated 20 and 22 carbon acids to arachidate and behenate. The latter soaps are really too insoluble to be useful except with careful blending.

Solubility and the Blending of Raw Materials. The four types of glyceridic raw materials are seldom used individually. Very often they are blended. This is notably true in the making of toilet soap from blends of tallow and coconut oil in the ratio of about 4:1, respectively. The need for blending can be realized from a consideration of the properties of the individual soaps of lauric, myristic, palmitic, stearic, and oleic acids. One very important property is solubility.

Table II shows the approximate solubility in percentage, in the presence of a small amount of alkali to depress hydrolysis, taken from the curves of McBain and Sierichs (11).

TABLE II

Solubility of Individual Soaps, %

	Temperature °C.				
	25	40	50	60	70
Na laurate	2.5	15.0	f	......	......
Na myristate	0.1	1.0	8.0	f	......
Na palmitate	i	......	1.0	4.0	22.0
Na stearate	i	......	0.2	......	2.5
Na oleate	15.0	f	......	......	......
K laurate	f	......	......	......	......
K myristate	f	......	......	......	......
K palmitate	8.0*	f	......	......	......
K stearate	......	......	26.0	f	......
K oleate	f	......	......	......	......

* at 30°
f = freely soluble
i = almost insoluble

Of the sodium soaps only the laurate and oleate are reasonably soluble at room temperature, sodium myristate is slightly soluble, and sodium palmitate and sodium stearate are almost insoluble. Solubility, of course, increases with increasing temperature, and at high enough temperatures even sodium stearate is adequately soluble.

Sodium laurate has a quick and profuse lather but not a lasting suds in solution and has inferior detergency. Sodium palmitate and sodium stearate are very good detergents at higher temperatures. Sodium oleate has good foaming, deterging, and solubility properties but lacks some of the firmness of the soaps of the saturated fatty acids and is more susceptible to oxidation. Sodium myristate, of these five sodium soaps, appears to have all of the desirable properties near the optimum, but of course no common soap raw material contains an adequate amount of myristic acid as the glyceride.

The potassium soaps are much more soluble than the sodium soaps. The sodium soaps of the saturated acids make what are called "hard" soaps from their firmness and slower rate of solution in water. Potassium soaps in general and the sodium soaps of unsaturated acids are "soft" soaps. Because of the more rapid rate of solution of potassium palmitate and potassium stearate they can simulate the properties of the sodium soaps of the coconut oil acids. Potassium soaps which give clear solutions and are easily soluble are used to make liquid soaps.

Improvement in solubility, foaming characteristics, and other properties is achieved by blending the raw materials. To some extent the desirable properties of a myristate soap can be approximated. It is a matter of experience that the less soluble palmitates and stearates are solubilized by laurates and myristates. It has been shown, for example, that 1:1 mixtures of sodium stearate with either potassium stearate or sodium laurate have lower solution temperatures than sodium stearate alone (12). Thus blends of tallow and coconut oil give a mixture of soaps with complementary properties, having the right hardness, correct solubility, and greater usefulness.

It is now of interest to describe briefly representative glyceridic raw materials: tallow, grease, coconut oil, cottonseed oil foots, soybean oil foots, palm oil, and hydrogenated whale oil.

Tallow

More tallow is used in soap making than any other single fat. Almost entirely it is the inedible grade of tallow that is selected. Inedible tallows and grease produced by meat-packing houses may contain either hog or beef fat and are defined in terms of titer rather than origin. A fat with titer over 40°C. is a tallow, a fat with titer below 40°C. is a grease.

Tallow is usually rendered by a steam-rendering process. Waste material from slaughter houses, meat shops, hotels, and restaurants is digested with steam under pressure. The fat forms an upper layer above the water and is separated.

The more common grades of tallow are defined in terms of titer, free fatty acids, color and MIU (moisture, impurities, and unsaponifiable matter) as represented in Table III.

TABLE III
O.P.A. Standard Grades of Tallow and Grease

	Minimum titer °C.	Maximum FFA %	Maximum FAC Color	Maximum MIU %
	TALLOW			
Edible	41.5	1	5	1
Fancy	41.5	4	7	1
Choice	41.0	5	9	1
Prime or Extra	40.5	6	13 or 11B	1
Special	40.5	10	19 or 11C	1
No. 1	40.5	15	33	2
No. 2	40.5	20	37	2
No. 3	40.0	35		2
	GREASE			
Choice white	37.0	4	13 or 11B	1
White A	37.0	8	15	1
White B	36.0	10	19 or 11C	2
Yellow	36.0	15	37	2
House	37.5	20	39	2
Brown	38.0	50		2
Garbage	34.0	60		3

In the manufacture of toilet soap and light colored flakes for fine laundering it is necessary to produce as white a product as possible, and it is often necessary to bleach the tallow before saponification. Although tallow is normally blended with other stocks, principally coconut oil, soaps with special application are made from tallow alone, for example soaps for commercial laundries which can take advantage of the detergent properties of tallow soaps at the higher temperatures.

Grease

Grease, the softer inedible animal fat, ranks next to tallow in the volume of animal fats used by the soapmaker. Some greases are made by steam rendering and others by solvent extraction. The more common grades of grease are defined in Table III.

A "Choice White" grease has been found to have the following analysis and fatty acid composition:[2] iodine number 64.7, 48.9% oleic, 11.3% linoleic, 0.9% linolenic, 0.3% arachidonic, and 38.6% saturated acids. This grease differs from the tallow in Table I principally in containing a larger amount of linoleic acid. In general, greases have higher iodine numbers than tallow and may be partially hydrogenated more nearly to resemble tallow.

Soaps made from greases lack the body of those made from tallow and produce a slow-forming but durable lather. Greases are almost always blended with other fats in making soap. The lower grades of grease, for example garbage grease, cannot be used directly in the soap kettle but are split into fatty acids and distilled before use. Greases are seldom used in toilet soaps because of their instability and odor characteristics but find their chief uses in the manufacture of yellow laundry soap, soap powders, cleansers, and industrial soaps.

Coconut Oil

Coconut oil is the most important vegetable oil used in soap making. It is obtained by crushing the pulp of the fruit of the coconut palm and is imported into this country either as the dried copra prior to crushing, or as coconut oil, usually from the Philippine Islands.

Coconut oil is a soft white fat melting at about 24-7°C. The grades used in soap making have an iodine number of 9-13, a free fatty acid content of 2-6%, and a characteristic odor attributed to the volatile free acids. When used alone, as in cold-process soaps, coconut oil produces a firm, white, soluble soap with a rapid-forming fluffy lather which breaks down quickly. Coconut oil is usually blended with tallow or hydrogenated oils.

The babassu oil of Brazil and the palm kernel oil of West Africa can be substituted for coconut oil. Fatty acid compositions of the three glycerides are compared in Table IV.

TABLE IV
Lauric Acid Oils
Fatty Acid Composition, %

Acid	Coconut Oil (10)	Babassu Oil (8)	Palm Kernel Oil (2)
Caproic	0.8	0.2	
Caprylic	5.4	4.8	2.7
Capric	8.4	6.6	7.0
Lauric	45.4	44.1	46.9
Myristic	18.0	15.4	14.1
Palmitic	10.5	8.5	8.8
Stearic	2.3	2.7	1.3
Arachidic	0.4	0.2	
Hexadecenoic	1.3		
Oleic	7.5	16.1	18.5
Linoleic		1.4	0.7

There is a remarkable similarity. The lauric acid content is about the same for the three glycerides, but babassu oil and palm kernel oil are more alike and have a higher oleic acid content than coconut oil.

Cottonseed Oil Foots

The edible grade of cottonseed oil is not used to any great extent in soap making. However cottonseed oil foots, or soapstocks, from the alkaline refining of crude cottonseed oil, is an important raw material for the soap maker. Soapstock contains soap, entrained oil, nonfatty organic substances, and water. Compared to cottonseed oil, it is low in cost on a fatty acid basis. The constituent acids, palmitic, oleic, and linoleic, are in the same proportion as in cottonseed oil, approximately 1:1:2, respectively. Raw soapstock may be processed with caustic soda and brine much like a full-bodied soap to give a "boiled-down" or a "settled" soapstock, used in the manufacture of high alkali soap powders and highly built yellow laundry bar soap. Alternatively, raw soapstock may be processed to yield distilled fatty acids which can be made into soaps. In this case hydrolysis of the entrained unsaponified oil is completed, and the mixture is heated with sulfuric acid to convert the soaps to the fatty acids. The fatty acids can be fractionally distilled to give relatively pure palmitic acid and a mixture of oleic and linoleic acids, which can in turn be hydrogenated to stearic acid.

Soybean Oil Foots

Soybean oil foots are similar to cottonseed oil foots in their technology. The oils differ however in their glyceride classification. Cottonseed oil is an oleic-linoleic acid oil while soybean oil is a linolenic acid oil. These classifications are of course reflected in their fatty acid compositions. A soybean oil, iodine number 132.6, has the following fatty acid composition, in

[2] Analysis by S. G. Morris, Eastern Regional Research Laboratory.

weight percentage (7): myristic, 0.4; palmitic, 10.6; stearic, 2.4; saturated C_{20} and above, 2.4; unsaturated C_{16} and below, 1.0; oleic, 23.5; linoleic, 51.2; linolenic, 8.5. The principal differences from the cottonseed oil of Table I are a lower content of palmitic acid, a slightly higher content of linoleic acid, and the presence of linolenic acid in an appreciable amount.

Palm Oil

Palm oil is extracted from the fruit of the palm tree on plantations in the Netherlands East Indies, Malaya, and the Belgian Congo. It is an oleic-linoleic acid oil, orange in color, and semi-solid at room temperature. The constituent acids of a Malaya plantation oil (4) iodine number 53.8, are as follows in weight percentage: myristic, 2.5; palmitic, 40.8; stearic, 3.6; oleic, 45.2; linoleic, 7.9. It is considerably different from cottonseed oil, being mainly a glyceride of oleic and palmitic acid with considerably less linoleic acid than in cottonseed oil (7.9 compared to 47.8). The oleic and linoleic acid content promotes solubility; the oleic and palmitic acid content promotes detergency; and the palmitic and stearic acid content supplies firmness. Palm oil may be used alone or in blends with tallow and coconut oil.

Hydrogenated Whale Oil

Whale oil is usually extracted at sea by cutting up the blubber and boiling with water or heating in autoclaves. The oil must be hydrogenated to an iodine number of about 50 to prevent reappearance of odor on storage. The hardened fat which results from the saturation of the 20 and 22 carbon polyunsaturated components is not suitable for soap making alone but can be blended with softer oils or with coconut oil.

Summary

Four classes of glycerides have been discussed as raw materials for soap. They are the animal fats, for example tallow and grease; the lauric acid oils, for example coconut oil and babassu oil; the oleic-linoleic acid oils, for example cottonseed oil foots and palm oil; and the marine oils, for example hydrogenated whale oil. Soybean oil foots is still another class, representing the linolenic acid oils. No single fat has a fatty acid composition which would make it generally useful in soap making, and it is the usual practice to blend the raw materials.

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The Pretreatment of Soap Stocks

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IN the manufacture of soap in this country the basic fat stocks used for saponification are the various grades of tallow, greases, nut oils, such as coconut and babassu, marine oils (whale and menhaden), and soap stocks and acid oils produced by the refining of edible oils such as cottonseed, corn, peanut, soybean, etc. Formerly a fair quantity of palm oil was available, but since World War II imports of this stock have been, for all practical purposes, limited to that required for the manufacture of tin and tern plate. Tallow, greases, and nut oils form by far the greater proportion of soap stocks used today.

E. M. James

Tallows as produced by the packers or the renderer are graded according to their content of free fatty acid, FAC color, m.i.u. (moisture-insoluble-unsaponifiable), and titre (the solidification point of the fatty acids). In addition, choice or fancy tallows are graded according to the Lovibond color of a sample of the stock after caustic refining and earth bleaching in the laboratory.

These standards for the different grades of tallow are important for the following reasons. The percentage of free fatty acid has a direct bearing upon the glycerine yield when the stock is saponified, the m.i.u., particularly the m and i, represent non-fatty constituents which are lost in saponification and hence reduce the yield of soap. Hardness of the finished soap depends upon the titre, and the color of the original stock is reflected in the whiteness of the finished soap or in its brightness when a colored soap is produced.

The greases in general have higher limits for free fatty acid, m.i.u., and FAC color, and lower limits for titre. However choice white grease, which is usually an inedible lard, has limits on color, free fatty acid, and m.i.u. similar to those of the better grades of tallow.

The marine oils are usually bought on a basis of free fatty acid and m.i.u. Soap stocks are purchased on the basis of total fatty acid content (35% minimum) and acid oils on the same basis (85% minimum).

The higher grades of tallow and choice white grease are, as produced by the packers, often of edible quality. To prevent their use in edible products the gov-