

Fats and Fatty Acids for Lubricating Grease Manufacture *

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IN discussing the subject of fats and fatty acids for lubricating grease manufacture, perhaps the most pertinent questions might be itemized as "What?" "How Much?" and "How?" As to the questions of what fats, and how much are used by the Petroleum Industry, the reports of the Bureau of the Census are of interest.

TABLE 1
Approximate Annual Consumption of Vegetable Oils by Petroleum Industry

	lbs.
Cottonseed Oil.....	600,000
Rapeseed Oil.....	10,000,000
Linseed Oil.....	500,000
Castor Oil.....	700,000
Miscellaneous Vegetable Oils.....	600,000
Vegetable Oil Fatty Acids.....	2,000,000
	14,400,000

Table 1 shows an approximate summary of the annual consumption of vegetable oils by the Petroleum Industry, as summarized from Bureau of the Census Reports of the past few years. The consumption of vegetable oils by petroleum refiners and compounders is not large although the utilization of Rape Seed Oil and of vegetable oil fatty acids is noteworthy.

TABLE 2
Approximate Annual Consumption of Animal and Marine Fats by Petroleum Industry

	lbs.
Tallow and Tallow Oil.....	43,000,000
Greases and Lard Oil.....	40,000,000
Whale, Sperm, and Fish Oils.....	5,000,000
Wool Grease.....	2,400,000
Stearines and Foots Oils.....	2,300,000
Red Oil.....	2,600,000
Stearic Acid.....	4,300,000
Miscellaneous Fatty Acids.....	9,000,000
Total.....	108,600,000

Table 2 is a similar summary of the approximate annual consumption of animal and marine fats by the Petroleum Industry. The preponderant consumption of tallow and hog fats in relation to other fats and oils and the utilization of various types of fatty acids is of interest.

On account of the tremendous diversification of the petroleum industry, both as to the number of refiners, compounders and marketers and to the great variety of fat containing lubricants manufactured and sold, the Bureau of Census figures probably do not include a considerable poundage of the fatty materials actually used in lubricants. The total fat consumption by the Petroleum Industry is thus most probably considerably greater than indicated by Tables 1 and 2.

Fats and fatty oils are incorporated in a large variety of lubricants and specialty products such as steam cylinder oils, soluble oils, core oils, rust preventives, surface coatings, cutting oils, extreme pres-

sure lubricants, and so on, in addition to lubricating greases. The Bureau of Census figures include the fats used in all types of petroleum products and thus give only a general or approximate idea of the overall utilization.

Fairly accurate figures became available on fat consumption specifically for the manufacture of lubricating greases through the medium of reports which grease makers were required to file with the Petroleum Administrator for War (1).

TABLE 3
Lubricating Grease Production and Fat-Fatty Acid Consumption Second and Third Quarters

	1943	1941
	lbs.	lbs.
Total Lubricating Grease Manufactured.....	254,246,000	229,381,000
Total Fats Used.....	16,313,000	20,215,000
Total Fatty Acids Used.....	13,896,000	8,228,000

Table 3 is a summary of these PAW records. Since all but the smallest grease manufacturers were required to file reports with PAW, it is estimated that about 90% of the grease production in the United States is included therein.

It will be noted that the total production of lubricating greases in the United States in 1943 was of the order of 500,000,000 pounds annually and that some 60,000,000 pounds of fats and fatty acids were consumed in the manufacture of these lubricants—an average of about 12% total fatty materials in the finished grease lubricants produced.

Information available at the present time indicates that lubricating grease production is at least as great as, if not greater than the 1943 figures. The higher proportion of fatty acids in relation to fatty glycerides used in 1943 as compared to 1941 was the result of a Petroleum Administrator order requiring grease makers to use fatty acids wherever possible as a glycerine conservation measure. With the cancellation of this order it is probable that the fatty acid-glyceride ratio has returned more nearly to that of 1941.

While accurate information is not available, it can be said that the bulk of fatty glycerides used for grease manufacture are tallow and hog greases. The fatty acids used are largely stearic acid, hydrogenated fish oil acids, and acids distilled from animal oils. Cotton seed oil fatty acids are used to a considerable extent in times when vegetable oils are more available.

Properties of Lubricating Greases as Related to the Fat Constituent

In considering the question of how fatty oils and acids are utilized in the preparation of lubricating greases, a brief description of greases and of manufacturing procedures is in order. A detailed discussion is impossible in a paper of this length, and only the "high spots" as related more particularly to fat utilization can be mentioned.

* Presented at the 20th annual fall meeting of the American Oil Chemists' Society, Oct. 29-Nov. 1, 1946, Chicago, Ill.
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Lubricating greases may be considered to consist of lubricating oils absorbed in a metal soap matrix, this matrix or base being responsible for the plastic and non-fluid characteristics of this type of lubricant. Greases may accordingly be described as fluid lubricating oils which have been converted to a semi-solid or plastic consistency by incorporation of metallic soaps. It has been stated further that it is the mineral oil constituent of greases which provides the lubricating value and that the soap constituent serves the primary purpose of maintaining the oil in a non-fluid state so that it will adhere to and resist leakage or seepage from lubricated parts or mechanisms.

The particular lubricating oil and the particular metal soap used in preparing a given grease depends upon the specific application for which the grease is intended. Table 4 outlines some of the properties imparted to grease type lubricants by different metal soap bases. Calcium, aluminum, and sodium soap base greases constitute the great bulk of those now manufactured and used. Lithium and barium soap greases as well as soaps of certain other metals are relatively new developments, and their use has so far been restricted to rather specialized applications partly because their higher costs of raw materials and processing.

TABLE 4
Effect of Metal Soap Bases on Properties of Lubricating Greases

Soap Base	Grease Structure	Approximate Grease Melting Point	Resistance to Emulsification by Water
Calcium	Smooth, buttery	200°F.	Good
Aluminum	Smooth, buttery	200°F.	Good
Sodium	Short to long fibre	Over 300°F.	Poor
Lithium	Smooth, buttery	Over 300°F.	Good
Barium	Short to medium fibre	Over 300°F.	Good
Mixed Base	Short to medium fibre	Over 300°F.	Fair to Poor

Calcium and aluminum base greases are characterized by smooth, buttery textures, relatively low melting or dropping points, in the order of 200°F., and good water resistance. The term water resistance is generally used to denote the resistance of greases to emulsification and washing on exposure to water or wet operating conditions.

Sodium base greases are characterized by a spongy or fibrous texture, high melting or flow points, usually exceeding 300°F., and poor resistance to emulsification by water. Accordingly, calcium or aluminum base greases are preferred in applications where water exposure is anticipated and where operating temperatures are moderate and well below 200°F. Sodium base greases are preferred where wet operating conditions are not involved and where operating temperatures are likely to be high, such as automobile wheel bearings, electric motor bearings and the like.

Mixed base greases customarily refer to mixtures of soda and aluminum soaps or soda and calcium soaps. The properties of such mixed base greases are quite similar to straight sodium base greases since soda soaps are usually predominant.

The newer types of soap base greases, such as lithium and barium, combine the desirable properties of high melting point and good water resistance and have sometimes been referred to as "all purpose" greases since they do not have the respective limitations of calcium, aluminum, or sodium base lubricants. It is possible, accordingly, that greases of the

lithium and barium soap types may find wider application in the future, particularly if their raw material and processing costs can be reduced to be more nearly competitive with the more common types.

Grease Texture

The texture of lubricating greases is customarily classified as smooth or buttery, or as fibrous or spongy. The fibre type greases are further divided into general classes of short, medium, and long fibre (2). Figure 5 illustrates typical examples of buttery texture, and short, medium and long fibre greases, from left to right respectively. As mentioned previously, calcium, aluminum, and lithium soap greases are characteristically of smooth, buttery texture, while sodium, barium, and mixed soap base greases are of the fibrous type.

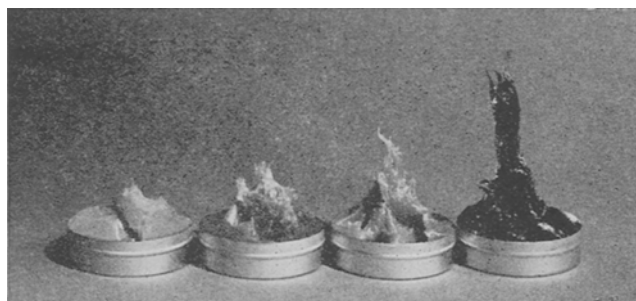


Fig. 5.

Grease Consistency

Grease lubricants vary in stiffness or consistency from semi-fluid products quite similar to viscous oils, up to very hard greases which must be cut into blocks for handling and application. The degree of stiffness or plasticity of a given grease is dependent upon the concentration of the metallic soap base therein. Small percentages of soap base, in the order of 1 to 5%, produce soft, semi-fluid type greases whereas soap concentrations in the order of 25 to 40% produce the hard, block type greases.

As shown in Table 3, it is interesting that the overall average soap content of all greases produced is in the order of 12%.

Calcium Soap Greases

Calcium base greases are prepared by saponifying the selected fat with hydrated lime, usually in the presence of sufficient mineral oil to maintain the soap base in a plastic condition capable of ready mixing and agitation. Saponification under pressure of 15 to 100 lbs. per square inch is frequently used to insure complete reaction in minimum time. After the so-called soap base is formed, the selected mineral oil is then worked into the base so that a thorough dispersion of the soap in the mineral oil results. Water in concentrations of from a fraction up to several percent must also be present in finished calcium greases since the calcium soap-oil system is essentially an emulsion wherein the water acts as a stabilizer or coupling agent.

In general, calcium soap greases are made from fats of fairly low titre and moderately high iodine number to secure the best texture and physical stability. Tallow and yellow greases are examples of preferred fats. High titre, saturated fats tend to produce calcium base greases of grainy texture and of poor stability as to separation and bleeding of oil.

It is also preferred practice to utilize a preponderance of fatty glycerides in preparation of calcium soaps since the glycerine liberated acts as a stabilizer of the calcium soap dispersion in the mineral oil.

Sodium Soap Greases

Sodium base greases are made similarly to calcium soap lubricants and the fats are saponified with an aqueous solution of sodium hydroxide. Since the saponification is rapid, open kettles are generally used and pressure saponification is not customary.

The soda soap base is usually processed at high temperatures to drive off the water, after which the mineral oil is worked into the base. Soda soap greases are thus usually substantially anhydrous, and water is not needed as a stabilizer, as is the case with calcium greases.

The type of fat used to make the soda soap base is an important factor in the fibre structure or fibre length of the finished grease. Low titre, unsaturated fatty oils and acids produce finished soda greases of the long fibre type, the fibre structure tending to be tough and elastic. High titre, saturated fats and acids tend to produce greases of the short fibre type. The widest range of fatty materials is accordingly used for soda base greases, with the fats or acids, and very often mixtures of these selected to produce the particular type of fibre structure desired for the given finished grease. It is generally preferable to use at least a portion of the total fats as glycerides since the liberated glycerine serves as a stabilizer of the soda soap-oil structure. However, many of the very hard, block type greases as utilized for mill and railroad lubrication and, where a grease of very short fibre and very high melting point is desired, are made with soda soaps of straight saturated fatty acids, such as stearic or hydrogenated fish oil acids.

The texture or structure of soda base greases is also affected materially by the details of processing, and manufacturing variations are numerous. These include steam kettle or direct fired kettle preparation, finishing by cold agitation, pan cooling, milling, homogenizing, etc.

Mixed Base Greases

Mixed base greases are manufactured similarly to straight sodium base lubricants, the essential difference being that mixtures of soaps such as calcium and sodium, or aluminum and sodium are formed as the base. In most instances, the soda soap predominates in the mixture and the resultant greases accordingly have properties substantially similar to straight soda soap lubricants. The primary intent of mixed base greases is to secure a very short fibre structure, approaching as closely as possible a smooth or buttery texture while retaining the high melting point properties of straight soda base lubricants.

Aluminum Soap Greases

Aluminum soap greases are generally manufactured by dispersing or dissolving commercial aluminum stearate in the selected mineral oil at temperatures in the order of 300° F. The hot soap-oil mixture is then cooled under carefully controlled conditions down to or close to room temperature, after which the cooled grease is usually milled or worked to break down the gel structure into the smooth, buttery texture characteristic of aluminum base greases.

Aluminum stearate used for grease manufacture is prepared by the familiar double decomposition method, involving treatment of a water solution of sodium stearate with a solution of aluminum sulfate or chloride, followed by washing and drying of the precipitated aluminum soaps. Due to the tri-valency of aluminum, three forms of aluminum stearate are possible. Grease making aluminum stearates are usually mixtures, with the mono and di stearates predominating, although commercially pure forms of the mono, di, and tri stearates are available (3).

Commercial stearic or hydrogenated fish oil acids are favored for manufacture of aluminum stearates, since high titre, saturated acids provide optimum oil gelling properties and hence form the best and most stable types of aluminum base greases. Aluminum soaps of unsaturated acids, such as oleic, have poor gelling properties and tend to form soft, unstable greases.

It is possible to prepare aluminum soaps by direct reaction of a hydrous aluminum hydroxide gel with the selected fatty acid, but the utilization of finished soaps specifically prepared for grease making by the double decomposition method has been the more general practice.

Lithium Soap Greases

Lithium soap greases are made similarly to aluminum base lubricants except that higher temperatures, in the order of 400° F., are required to dissolve or disperse the lithium soap in the mineral oil (4). Saturated, high titre acids are used almost exclusively in preparing lithium soaps, and stearic acid and hydrogenated fish oil acids are preferred (5).

Lithium soaps are prepared either by the double decomposition method or by direct reaction of lithium hydroxide with the selected fatty acid. The latter method of preparation is becoming more general because of the lower manufacturing expense.

The use of lithium soap greases has been restricted to rather specialized applications, such as aircraft lubricants and greases for extreme low temperature service, on account of the high cost of lithium. However, the very high melting point and good water resistance properties of lithium base greases offers advantages over calcium, aluminum and soda base greases, which may well lead to expanding usage.

Barium Soap Greases

Barium soap greases are made similarly to sodium base lubricants although the processing is more complex (6). As with lithium greases, barium base lubricants involve higher costs of raw materials and manufacture, but their combined properties of high melting point and good water resistance may well lead to expanding use.

Future Trends in Lubricating Greases

Lubricating greases are a relatively young class of lubricants, and it is only a matter of 20 or 30 years from the days of simple axle greases to today's tremendous variety of grease lubricants, each specifically formulated and processed to do a particular type of lubricating job.

Over this period of time grease lubricants have expanded from an insignificant and unimportant part in the petroleum lubricants field to the point they are now a material and indispensable factor. At the same time grease manufacture has developed from a secret

and sometimes mysterious art to an increasingly exact science capable of precise physical and chemical control from raw materials to finished lubricants.

Grease lubricants are primarily used in those applications where oils are unsatisfactory because of seepage and leakage. Because greases possess the characteristics of better adherence and resistance to seepage or leakage, they are also becoming increasingly preferred to oils in many applications wherein frequent replenishing is necessary when oil is used, but where such relubrication is inefficient or impractical. Greases are accordingly finding increased applications where performance for long periods without attention for shut-downs and relubrication is desired.

The future trends in grease lubricants may accordingly be summarized as:

1. Increasing importance in the over-all field of lubrication.
2. Development of improved greases having combined properties of high melting points, good water resistance, and exceptional stability for long service under severe conditions of load, temperature, and environment.
3. Improved methods of production including continuous rather than batch manufacture, mechanical homogenization and dispersion, etc.
4. Emphasis on the purity, composition, and stability of the fats and fatty acids utilized in making the metal soap bases.

With further respect to the fatty materials used in lubricating greases, it is well known that trace impurities of iron, copper, nickel, and lead in fats or fatty acids will act as active oxidation catalysts in greases exposed to elevated temperatures. Since oxidation stability of grease lubricants is receiving much attention, increased interest in fats containing minimums of catalytic impurities is indicated.

Because of the emphasis on temperature stable and oxidation resistant greases, much attention is also being given to oxidation inhibitors and similar addi-

tives. Study of the natural inhibitors present in many natural fats and the development of improved or stabilized fats is accordingly of much interest to grease manufacturers.

Lastly, grease chemists are paying considerable attention to metallic soaps prepared from substantially single component fats or fat acids instead of the heterogeneous mixtures existing in natural fats. There thus seems to be a fertile field for cultivation in fats and acids of more uniform and definite composition than the natural fats and roughly fractionated constituents therefrom.

The grease industry will certainly be interested in developments and improvements in fat technology along the lines mentioned and will welcome the cooperation of fat processors in the constant effort to produce better lubricants.

Acknowledgment

The authors wish to acknowledge the cooperation and assistance of the following members of the National Lubricating Grease Institute Technical Committee in the preparation of this paper:

H. L. Moir and L. B. Stevens, Pure Oil Company.
N. J. Gothard, Sinclair Refining Co.
T. G. Roehner, Socony-Vacuum Oil Co.
L. C. Brunstrum, Standard Oil Co. (Indiana).
Gus Kaufman, The Texas Company.

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Report of the Glycerine Analysis Committee October, 1946

THE Glycerine Analysis Committee has conducted collaborative analyses by three methods on three samples of glycerine and two types of organic impurities most frequently found in commercial glycerine products. The analytical methods investigated were:

1. Apparent Specific Gravity—Pycnometer Method 25°/25°C.
2. Moisture by Karl Fischer Method.
3. Determination of Glycerol by Oxidation with Periodic Acid.

As a result of these studies your committee recommends adoption of the procedures listed above, and herein described in detail, as tentative methods of the Society. The specific gravity method includes the table prepared by Bosart and Snoddy for conversion of apparent specific gravity into percent glycerol.

Preparation of Samples

Sample 1-A was a commercial C. P. glycerine distilled from selected salt crude and believed to be of high purity. Samples 1-B and 1-C were prepared from 1-A by dilution with about 5 and 12% distilled water.

Sample 2-A was a commercial trimethylene glycol. Such a product may be expected to contain normally about 1% glycerol. Sample 2-B was a crude polyglycerol, chiefly the dimer. From the mode of preparation, and data collected during the process, it was believed to contain about 20% glycerol. Samples 2-C and 2-D were prepared by addition of 80% 1-A to 20% 2-A, and 80% 1-A to 20% 2-B, respectively.

Periodic Acid Method

A summary of the analyses reported by eight members of the committee is shown in Tables I and II. No difficulty was reported in the analysis of samples 1-A, 1-B, and 1-C. Samples 2-A and 2-B gave some trouble, chiefly in selection of proper size of sample. Polyglycerols apparently are oxidized to some extent by periodic acid, but without production of formic acid which results from the oxidation of glycerol. Trimethylene glycol reduces periodic acid, but to a somewhat smaller extent. In the presence of considerable oxidizable impurities insufficient periodic acid may be left to accomplish the desired oxidation of glycerol itself unless the sample size is held to a smaller weight than is indicated by note 6 of the method. This trou-