

using *Fatty Acids*

IN LUBRICATING GREASES

FATTY ACID DIVISION

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FATTY ACIDS IMPROVE UNIFORMITY

Soap composition can make or break a lubricating grease. However, the full effect of the fatty acid components upon grease performance is not yet scientifically defined. Many practical findings about fats and fatty acids guide the greasemaker, but they do not show up consistently in purchase specifications for these materials, even when intended for use in the same type of grease.

With the help of the electron microscope, we now know that the structural framework of a typical grease is composed of fibrous crystalline aggregates of soap, acting as a kind of colloidal sponge upon the mineral oil. This must retain its oil-retentive structure under shear, temperature change, and time. Still, two greases which appear quite different under the microscope, as well as in their composition, may prove to be equal in performance. There is no single optimum soap structure in grease. It is specifically interrelated to the other constituents, and to the type of service into which the grease goes.

Today's grease manufacturer, as he works to improve his product in a scientific way, faces the task of reducing the variables, so that the effect of any particular ingredient on performance can be predetermined. This will direct his choice of materials toward more completely purified and uniform composition. One of the important milestones on the road to scientific greasemaking is the increasing availability of fatty acids (and their pre-formed soaps) of well-defined and uniform analysis. Of course, there are many non-critical jobs for which minimum-price greases appear to be "good enough". But the whole trend of industrial design is tending to upgrade grease requirements, and to give enough payoff value to uniform performance to justify the higher cost of uniform raw materials.

Reducing The Variables

If lubricating grease performance is to be consistent, five or more variables must be kept in line:

1. Variation in the soap cation (metallic component)
2. Variation in the fatty-acid radicals
3. Variation in the petroleum oil
4. Variation in additives — free alkali, free fatty acids, water, glycerol, anti-oxidants, modifiers, etc.
5. Variation in the processing method and process control.

So far as base metals for soaps are concerned, their relation to structure and performance have been explored in great detail (1) and will not be reviewed here.

At the same time, the metal cation and the fatty-acid radical are so interrelated in their effects upon the soap structure that generalizations as to the effect of a particular metal (say, lithium) on performance also depend on the *particular* fatty acid combination with which it is linked. Some metal soaps are critically affected by the degree of saturation of the acid, others far less so.

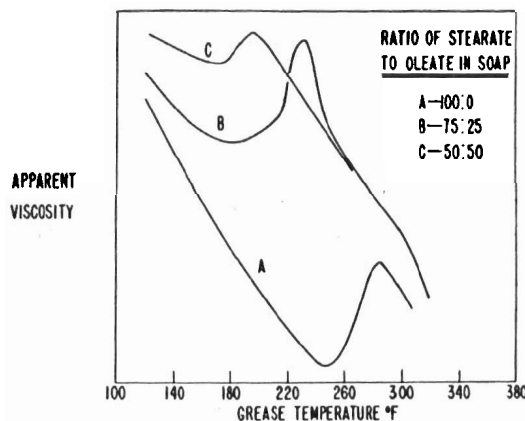


FIG. 1 — Effect of soap composition on apparent viscosity. (Moses and Puddington data)

A sodium base grease, for example, may be satisfactory when the ratio of stearate to oleate is, say, 50:50. Aluminum oleate, however, is not a satisfactory grease component, and saturated acids will be preferred when aluminum is the metal base. Two calcium-base grease formulations may have similar characteristics, despite wide variations in fatty acid polyunsaturant content or chain-length distribution. But two lithium-base greases will respond very critically to fatty-acid differences of the same order. In general, metals with a narrower tolerance to variations fatty-acid length and structure are being favored in high-quality greases.

Effect of Petroleum Oil Variations

Variation in petroleum oil composition, as it affects grease performance, is too broad and basic a matter for review here. Again, an intricate interrelationship with the soap phase exists. Physical characteristics of the oil, such as viscosity, are important to the strength and length of the soap fibers formed. In fact, the same soap may form an entirely different fiber structure as oil viscosity changes. Also, the structure of the fibrous soap network is affected by the chemical composition (cyclic vs. chain hydrocarbons) of the oil. C. J. Boner writes, "Until lubricating oils of more definite chemical composition are available, it will be difficult to draw rigid conclusions as to the effect on structure. . .". (2) This, of course, adds to our difficulty in relating the oil-retention and service of existing greases to their fatty acid composition, except where petroleum oils of identical composition are assured.

Variation in Fats

Animal fats are estimated to constitute over 80 per cent of the fatty materials used in the production of lubricating greases. In this class, the biggest single component will be inedible tallow, totalling 40 million pounds or more per year. As a traditional material to which the art of the greasemaker has long accustomed itself, tallow makes up in familiarity what it lacks in uniformity. Particularly in the conventional lime-base and sodium-base greases, it can be "doctored" to produce greases of structural uniformity and reasonably good performance. But as one supplier was recently quoted: "All my business life I've supplied fats to your industry and wondered how you could possibly make uniform products. Your specifications could be met by hundreds of combinations of beef, pork, and sheep fats." (3)

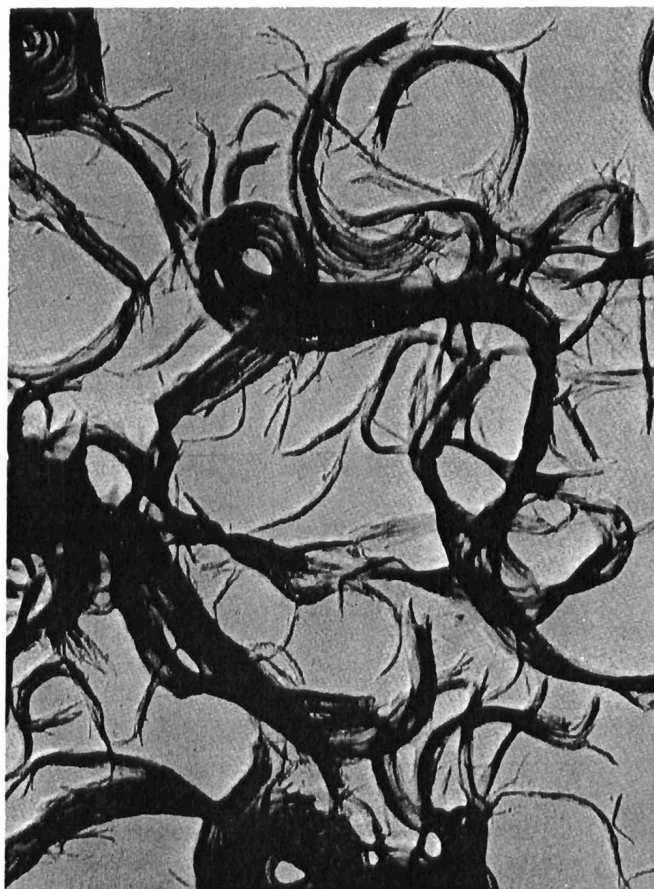


FIG. 2 - Structure of a lithium-calcium stearate type grease as shown by the electron microscope (10,000X)

Standard grades of tallows and animal greases are defined only in terms of solidifying point (titer), free fatty acids, M.I.U.*, and color, with no control over the particular combination of fatty acid radicals except that arising from the similar tendency of fats of particular animals to hold to the same proportions. There is also lack of control over water-soluble impurities such as proteins and gelatinous matter.

Even for the buyer of animal fats who limits his purchases to a single source to minimize these variations, the effect of seasonal and geographical factors and the time and temperature changes in movement of stock to market will still exist.

Will Greater Uniformity Pay?

It would be idle to contend that a grease manufacturer, having built a paying business on his skill in coping with such variable raw materials, should now abandon tallow and grease "across the board" for something higher-priced. At the same time, the

*Moisture, Insolubles, Unsaponifiable -- a "catch-all" classification of the valueless content of the fat.

exploration of the full possibilities of uniform raw materials on performance is now receiving wider study. One tendency has been to seek some inorganic or synthetic thickener which is inherently uniform. But it is proving even more rewarding to explore soaps and soap source materials freed from "unknowns."

There are technical as well as economic limitations to the degree that natural fats as such, particularly those of by-product origin, can be supplied with any assurance of chemical uniformity. But these limitations are much less severe when glycerides are hydrolyzed to fatty acids and glycerol. Distillation, solvent separation, fractional crystallization, and other processes such as hydrogenation, are more effectively applied to the fatty acids than to glycerides to alter or adjust their composition and to eliminate impurities. Source materials of different origin permit enrichment to arrive at a uniform composition of the desired chain-length distribution, degree of saturation, and — if necessary — molecular arrangement.

Even more strictly standardized fatty acids (or their pre-formed soaps) can be expected in the future. Their commercial development is technically possible. As the value of uniformity becomes more widely held, and thus improves the economics of their manufacture, the grease industry will have a much wider range of products to choose from to meet specific needs.

Fatty Acids vs. Glycerides

Aside from factors of uniformity and controllability of composition, purified fatty acids have been cited as being preferable to raw fats for the following reasons. (4)

1. Greater ease of saponification.
2. More complete saponification.
3. Greater yield of anhydrous soap (per 100 lbs. of component).
4. In the case of calcium soaps, a more translucent product.
5. More controllable stabilization against oxidation.
6. More controllable length of soap fiber (by regulating the titer and unsaturated content).
7. Direct control of glycerol content in the grease.

Against these advantages, the question of higher costs must be measured. The storage and handling of

fatty acids may require wider use of corrosion-resistant tanks and equipment. (5) Moreover, the point has been raised that the claim of greater uniformity for fatty acids has not always been substantiated in practice: Acids meeting the conventional test specifications as to titer, saponification value, iodine value and the like may still produce differences in performance.

During World War II, for example, regulations for glycerine recovery forced a shift to fatty acids on the part of grease manufacturers. Many of these "emergency" mixed acids had no more uniformity than the "bottom-of-the-barrel" type of fat available at that time. Experience with these mixed fatty acids can not be applied to the purified, specialty types available today.

Of course, since uniformity and reproducibility are obtained at some extra production cost, this brings us to a question of which particular fatty acid characteristics are worth paying for. Are we measuring and specifying the right things to produce a better product, in terms of actual grease service?

What price — composition analysis?

As shown in Table 1, seven conventional tests used to characterize fatty materials have gained acceptance, and are reflected in purchasing specifications of the grease industry. Some of these, taken together, establish the average composition of the material. For example, under certain conditions, the composition of stearic-palmitic mixtures can be calculated from titer (6).

It may be asked, should not these specifications be supplemented or replaced by a breakdown such as shown in Table 2? From the standpoint of research and product development, such composition analysis has justification despite the fact that analytically it is a complex task, calling for special experience and expensive equipment (see Note A). Most suppliers of fatty acids, when cooperating in a new product development with grease producers, are in a position to supply such data. As yet, however, the economic justification does not exist for composition analysis as a routine specification.

This can best be understood if we realize that some 30 or more man-hours of analytical time are involved in fractional distillation and spectrophotometric work to set up and run an analysis such as shown in

Table 2. Any simplification of the test, by combining certain groups of acids, at once reintroduces the chance that significant effects of minor constituents will be unrevealed.

Many generalizations are found in the literature as to the effect of fatty acid chain length on grease characteristics. Some (9) have held that only C_{16} and C_{18} Acids led to optimum results. Others state that increasing saturation of the fatty acid portion raises the thermal stability of the grease, as well as the dropping point. But the fact remains that specific formulations violating almost all such generalizations have been found desirable for one purpose or another.

One investigator, for example, cautions against the use of fats or fatty acids with an iodine value above 20. Others have set the limit as high as 70. Hydrogenated materials, particularly those derived from fish oils containing about 75% of C_{20} and C_{22} Acids, are favored for lubricants by some producers, but not others.

Many more grease performance tests, made with no variable except the fatty-acid chain-length composition, would appear to be necessary before *significant* differences can be clearly separated from *insignificant* differences. It may then prove to be possible to concentrate the analytical work on areas and degrees of uniformity vital to good grease.

In the meantime, experimental lots of fully-characterized fatty acids are being made available to grease manufacturers conscious of this long-range goal, as well as to manufacturers of pre-formed soaps, for study and development work.

Use of Pre-formed Soaps

Technical as well as historical reasons have favored separate preparation of metal soaps of aluminum and lithium. Similarly, metallic soaps of lead, zinc and other metals used as additives in mixed base greases are generally pre-formed.

Producers of metallic soap almost invariably use fatty acids, and have been in the forefront in seeking uniformity of fatty acids as a means of producing soaps of reproducible quality in the grease. They may employ direct reaction (fusion) or precipitation from a soluble soap solution.

Aluminum stearate, as a typical example, is reported (10) to alter grease characteristics depend-

ing upon: (a) the fatty-acid chain-length distribution, (b) the acid-to-base ratio (mono-, di- and tri-aluminum stearate percentage), (c) the particle size, (d) any impurities, such as sodium sulphate, moisture, etc.

Aluminum base soaps are compounded almost entirely with fully saturated acids, so that little tendency to oxidize, or other instability, will arise from a properly selected soap component.

One study favors a di-stearate-palmitate eutectic over either stearate or palmitate alone. Another has reported that hydrogenated marine acids, having some C_{20} and C_{22} chain-length acids, appear to contribute to smoothness and gel strength of aluminum stearate greases. Different lubricating oils apparently tip the scales toward different aluminum soap specifications.

Table II - Composition Analysis Of

A) TYPICAL ANIMAL FATTY ACIDS

	A	B
Myristic.....	2%.....	2%
Palmitic.....	23%.....	27%
Stearic.....	19%.....	17%
Oleic.....	47%.....	48%
Linoleic.....	8%.....	6%
Linolenic.....	1%.....	-

B) TYPICAL HYDROGENATED FISH ACIDS

Myristic.....	4%.....	7%
Palmitic.....	32%.....	31%
Stearic.....	22%.....	23%
Arachidic.....	23%.....	21%
Behenic.....	13%.....	13%
Oleic.....	6%.....	3%
Palmitoleic.....	-	2%

C) TYPICAL DOUBLE-PRESSED STEARIC ACID

Myristic.....	2%.....	-
Palmitic.....	51%.....	48%
Stearic.....	41%.....	46%
Oleic Acid.....	6%.....	6%

D) TYPICAL HYDROGENATED ANIMAL FATTY ACIDS

Myristic.....	1%.....	2%
Palmitic.....	29%.....	31%
Stearic.....	69%.....	66%
Oleic.....	1%.....	1%

Table 1 – Fat and Fatty Acid Specifications

NORMALLY DETERMINED BY ANALYSIS

	<u>Analytical Method</u>	
	Fats	Fatty Acids
1. Acid Value – (Free Fatty Acids).....	AOCS – Ca-4-25	L-1-55
2. Ash.....	AOCS – Ca-11-46	L-3a-55
3. Color.....	ASTM-NPA D-155-45T	
4. Iodine Value.....	AOCS – Cd-1-25	L-8a-55
5. Saponification Value.....	AOCS – Cd-3-25	L-7a-55
6. Titer.....	AOCS – Cc-12-41	L-6a-55
7. Unsaponifiable.....	AOCS – Ca-6a-40	L-4a-55
8. M.I.U. (fats only).....	AOCS – (Includes Ca-46)	

The use of pre-formed lithium soaps for production of lithium greases, whether produced by a separate supplier or by the grease manufacturer himself, puts even more stringent demands on the composition and uniformity of the fatty-acid employed.

According to one study, a lithium soap from stearic acid was preferred with a paraffin-base mineral oil, but for naphthenic oil, a palmitic acid soap is more stable (11). Another investigator favors a mixture of fatty acids containing 7.5% C₁₂; 12.1% C₁₄; 23.5% C₁₆; 54.8% C₁₈ and 2.1% greater than C₁₈.

The use of 12-hydroxystearic acid, both alone and in combination with highly purified stearic acid, has also been the subject of detailed performance tests in a lithium soap for grease usage.

Grease Production With Fatty Acids

In general, use of fatty acids rather than glycerides will simplify and increase the rate of saponification, but the degree of this advantage again will depend on the metal hydroxide or alkali employed. A sodium soap base, produced by the open kettle method using caustic soda solution, will follow the same general cycle with either fats or fatty acids. The time for saponification may be 1½ hours, but a "running up" time of 4 to 5 hours in the kettle to mill in the oil and develop the structure will be utilized.

Calcium base greases show more definite time and steam-saving advantages when made from fatty

acids. Saponification temperatures may be lower. Fatty acid-lime soaps may be formed in a much greater proportion of oil than are fat-lime soaps. Thus, a wide variety of methods of combining the ingredients may be employed. At least 5 such methods have recently been described, all offering benefits in saponification or hydration as compared to the use of fat. (12)

When lithium grease is prepared without the use of pre-formed soap in the open kettle procedure, the flexibility of the use of fatty acids is again emphasized. Fatty acids may be dispersed in 10 to 50 per cent of the total oil before lithium hydroxide solution is added. Thereafter, heating to some 400° F. provides for dispersion, following by cooling to form a gel and working of the gel to form the finished grease.

In the case of mixed-base lubricating greases, the soap may be formed in situ with fatty acids and a portion of the mineral oil, combined with the mixed metallic bases. Or, one or more pre-formed soaps, may be dispersed in the oil, or a second soap may be added following saponification of the fatty acids with one of the metallic bases. In each case, a more controllable rate of saponification, as well as of glycerol and water content, is attained.

The reasoning that fats are to be preferred to fatty acids because of the desired effects of glycerol in certain greases, is not complete. Some producers have found it advantageous to add glycerol as such – again on the basis that more flexibility and control justifies the higher first cost.

Fatty Acid Soap vs. Non-Soap Gels

As previously mentioned, advances in grease-making are not being confined to the field of those using fatty-acid soaps. Silica gel, and new organic esters of silica, are effective colloidal agents for thickening oil. Others include organophilic bentonite and colloidal attapulgite, which are modified clays. Phthalocyanine blue is an effective grease-thickening pigment with wide-range temperature stability. Aromatic thioureas, used with silicones, open up another new class of lubricating agents.

Currently, the estimate for total use of non-soap thickeners is about 5 per cent of the market(13). They have several unusual advantages from the standpoint of temperature and oxidative stability. While they have been advanced as the ultimate answer to the search for an "all-purpose grease", their acceptance is limited on several counts. The silica gel and bentonite types depend on water-proof surface coatings of the particles, and these have temperature limits in the 250-300° F. range, according to recent observations (14).

From the standpoint of cost, effectiveness of additives, compatibility, and acceptance, the non-soap thickeners also have some serious limitations. Because they absorb but do not dissolve in the oil, they have limited "oiliness" (15). Ignoring cost, it is possible to make a case that they are superior to fats, but not necessarily to fatty acids, from the stability standpoint. Soap greases have been reputed to be less oxidation stable than the soap or oil from

which they are made, due perhaps to the catalytic effect of certain fat impurities on the oil, or vice versa. The inorganic thickeners neither increase nor decrease oil stability. However, if we select purified fatty acids from the same "specialty" view-point as some of the new thickeners, particularly with respect to unit cost, we open up the economic possibility of high stability with fatty-acid soaps as well, particularly because the effect of anti-oxidants will apply to both the oil and soap components.

The same "quality-mindedness" that is attracting attention to non-soap gels can, if applied to upgrade fatty-acid soaps, produce even greater gains for the buyer of greases.

Application Service Expanded

Expanded use of purified fatty acids has been variously estimated at from 30 to 45 per cent of the total fatty materials used. Unfortunately, accurate statistics on this point are unavailable to reveal the extent of the trend. But throughout the fatty-acid industry, the past ten years have seen a wide expansion in laboratory and development work. Several companies have enlarged their research staffs two or more times in this period. The trend to develop and supply fatty acids matched to the need of the lubricating grease producer, or the producer of preformed soaps for such use, is certain to continue. What is needed to assure benefit to all concerned is a closer tie-in between fatty acid *possibilities* and lubricating *abilities* in tomorrow's improved line of greases.

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Note A - Procedures for Composition Analysis of Fatty Acids

The procedure for determining fatty-acid chain-length by a combination of distillation and spectrophotometric methods has been outlined in detail (7). It calls for a fractionating column with a minimum of 15 to 20 theoretical plates and nearly perfect adiabatic conditions. Podbelniak columns are frequently used. Normally, the methyl esters are distilled. The distillation is most effective in determination of shorter chain saturated acids, such as capric, myristic, palmitic. Molecular distillation is also sometimes applied, particularly for separating stearols and other impurities and for the fractionation of unsaturated acids.

Fractional crystallization as an analytical method to separate saturated from unsaturated acids is frequently employed (8). The individual unsaturated acids in a given fraction are then determined by spectrophotometric procedure. A recent summary of the procedure appears in *Oil, Paint and Chemical Review* (July 14, 1955):

"The three most common unsaturated acids in the C_{18} fraction are oleic, linoleic and linolenic acids and these have one, two and three double bonds respectively. Oleic acid with its one double

bond cannot absorb in the ultraviolet region and accordingly, it is determined by difference. Linoleic and linolenic acids also do not absorb in the ultraviolet region but they can be made to do so by converting them to their conjugated forms. Thus, these acids are heated with alkali under specified conditions to shift the double bonds from an unconjugated to a conjugated position. Thereafter, the conjugated linoleic acid will absorb at 233 mu whereas the conjugated linolenic acid will absorb at 268 mu. A tetraenoic acid, which is present and which has been conjugated will absorb at 350 mu.

Because of these absorption characteristics, the transmission is determined at the appropriate wave length and this transmission is a direct measure of the quantities of each of the conjugated polyunsaturated acids present. An appropriate blank is also run. Oleic Acid, as indicated above, is calculated by difference.

If some conjugated acids are present initially in the acid mixture, the absorption of these may be determined directly. Subsequently, the conjugation procedure is carried out in order to determine the total quantity of each of the polyunsaturated acids."

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