popularity as driers. There has been a flurry of interest toward so-called odorless paint driers, a number of which are based upon vegetable oil fatty acids. At this time it is difficult to estimate the proportion of paint driers which will eventually be of this "odorless" variety.

Metallic soaps of tall oil have established themselves to some extent in the paint drier field *vs.* the naphthenates (see Table II). They will no doubt continue to grow in popularity in this and other applications as refiners of tall oils continue to make up-graded and well-defined fractions available and as the pressure for low material costs is reflected by customer buyer-resistance.

Summary

In this discussion we have attempted to cover pertinent factors concerning the production and applications of solid fatty acid soaps, with particular emphasis on how the fatty acid characteristics come into play. We have avoided reference to specific formulations because these must be kept in the realm of metallic soap manufacturers' "know how." Those interested in modifiers and their effect on metallic soaps can find reference material in past issues of the Journal of the American Oil Chemists' Society (for example, reference 9) and in the patent literature.

Reference to theoretical considerations of metallic soap structure has also been avoided as in this area the reader can again find reference material in the Journal of the American Oil Chemists' Society (for example, reference 10).

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Lubricating Greases

E. S. CARMICHAEL, Socony-Vacuum Laboratories, Socony-Vacuum Oil Company Inc., New York, New York

THERE was a time 20 years or so ago when some people believed that grease production had reached an all-time peak and production thereafter would decrease because of replacement of greases by lubricating oils. History has proved that belief to be wrong. In fact, the production curve for greases in this country has risen to the point where present-day grease manufacture is of the order of 1,200,000,000 lbs. on an annual basis. There is no immediate prospect that grease production will decrease appreciably.

E. S. Carmichael

Generally speaking, greases are recommended for all types of bearings in the following classes of service:

1. where mechanical design (sometimes accompanied by high operating temperatures) would result in excessive oil leakage, high oil consumption, and, in certain industries, contamination or staining of the finished product.
2. where simplicity of design is required, as for example, in in many of the aircraft applications.
3. where mechanical design fails to prevent the entrance of grit, water, or other contaminants into the lubricated areas. Correctly selected greases can provide an effective seal for bearings operating in dusty atmospheres, such as occur in cement mills and coal mines, and thereby prevent excessive wear.
4. where the application of a lubricant is infrequent, on account of the multiplicity or inaccessibility of the bearings. Such conditions are frequently encountered in line shafts, in conveyor systems, and in overhead cranes.
5. where low operating speeds and heavy loads may hinder the ready formation and continued maintenance of adequate lubricating films. These severe conditions are experienced in steel mills, as for example in the lubrication of roll-necks, as well as in various industrial plants where jaw- and roll-crushers are employed.

Structure of a Lubricating Grease

Basically, what is a lubricating grease? It is essentially a thickened oil in which particles of the thickening agent, usually soaps, are highly dispersed in the oil. Until recent years the highly dispersed particles were not visible microscopically because in size they were too small for resolution by the conventional light microscope. The usual type of conventional lime base grease, when viewed at a magnification of 1,000x, had the appearance as shown in Figure 1. Very little information was gained regarding the basic structure of the grease, using this technique.

With the advent of the electron microscope, procedures (1) were developed for viewing grease structures at magnifications of the order of 20 times greater than was possible with the light microscope. Under the high-resolving power of the electron microscope, dispersed soap particles of greases were readily made visible. An electron microscopic view of the lime base grease shown in Figure 1, examined at a magnification of 20,000x, is given in Figure 2. The dispersed soap particles, in this instance calcium tallow soap, are of the order of one micron in length and 0.1 micron in width. It is to noted that grease properties are not only dependent on the composition of the lubricant but also on the size and configuration of particles of the thickening agent.

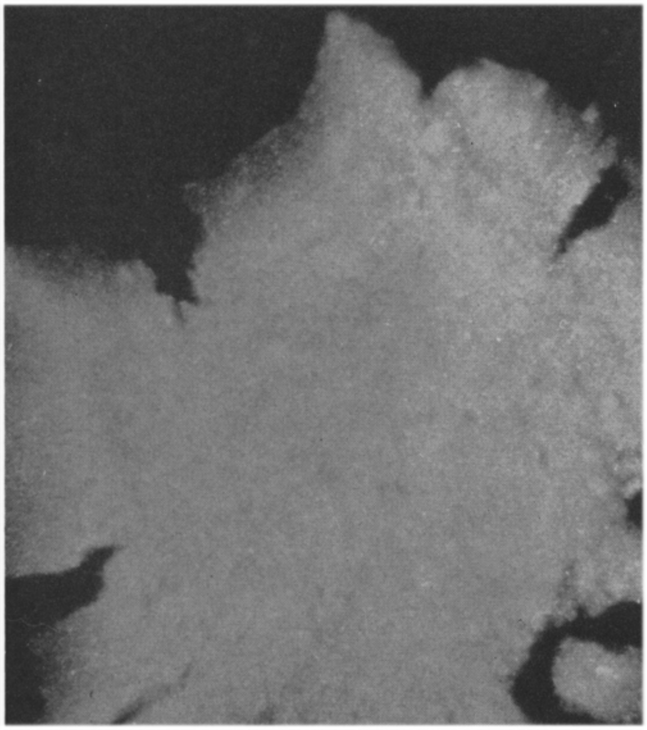

FIG. 1. Conventional lime base grease.
Light microscope
1000x magnification

Types of Greases and Suitability for Use at Elevated Temperatures

More than 90% of all greases manufactured today have soap as the thickening agent. In other words, most greases consist essentially of soaps and mineral oil, with or without small amounts of other materials being present, such as additives.

One way of classifying greases is by the metallic component of the soap that is used as the thickening agent. On this basis present-day soap thickened greases are for the most part: calcium, sodium, lithium, aluminum, and barium.

Conventional lime base greases are dependent upon a small amount of water, generally about 10% of the soap content, to maintain a smooth, buttery type of cup grease structure. In fact, if this water is lost or is reduced below a certain critical minimum value, depending on the composition of the particular grease, the lime soap will separate from the lubricant and a heterogeneous mixture of soap and oil will result. For this reason a conventional lime base grease should be used at temperatures at which no appreciable water will be lost, *i.e.*, at temperatures not exceeding 150°F. In this connection it should be pointed out that there are special types of lime base greases currently marketed, which are not dependent on water as a stabilizing agent. These products, in some cases, can be used satisfactorily at temperatures considerably above 200°F.

Although aluminum base greases require no water for stabilization purposes, a product of this type should not be used at temperatures much higher than 150°F. An aluminum stearate grease, the type generally marketed, usually will undergo structural changes at temperatures somewhat higher than 150°F. (at which soap begins to dissolve) and will not be reversible unless the grease is cooled very slowly with suitable mixing to room temperature. An aluminum base grease having a smooth, buttery structure, for example, may change to a rubbery type of product at about 200°F. or higher and, on cooling at a relatively rapid rate from that temperature level to room temperature, may become a coarse, hard, unsatisfactory lubricant. For that reason the structural change, resulting from high temperature treatment, limits the use of this type of grease to relatively low operating temperature conditions.

Sodium, lithium, and barium base greases, generally speaking, have reversible structures and can be employed at temperatures higher than 200°F. In other words, the soaps are not appreciably oil-soluble until temperatures well above 200°F. are reached. The suitability of greases of these types for continued use at high temperatures will, of course, depend on such factors as chemical stability, volatility of the mineral oil component, and the like.

Of the five types of soap base greases listed above, calcium and sodium base greases, in that order, are the two types most widely used at the present time and together account for approximately 70% of total grease production. The lithium base lubricant, a relatively new entry into the field, currently represents 10-15% of the soap base grease market.

Fatty Materials Used in Lubricating Greases

If it is assumed that the average lubricating grease contains 15% soap, a quantity of fats and fatty acids of the order of 180 million lbs. (90,000 tons) is used yearly in products of this type. The fatty materials

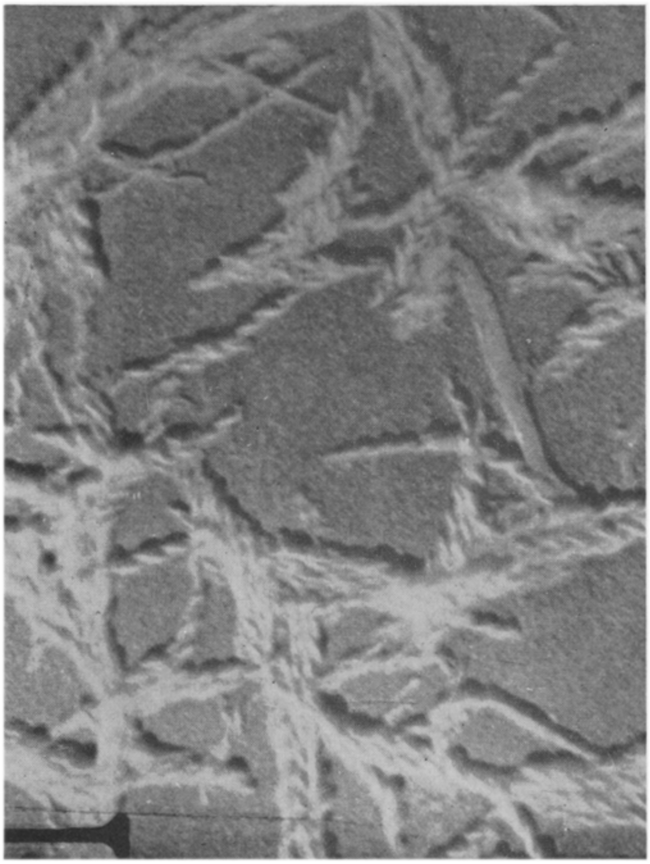

FIG. 2. Conventional lime base grease.
Electron microscope
20,000x magnification

most extensively employed for this purpose are tallow and tallow fatty acids, including hydrogenated varieties of both. These particular fats are used in large volume because of their relatively low cost and availability, also because the molecular weight range and degree of unsaturation of the acids make them suitable for many grease applications.

Broadly speaking, the fats most commonly used in grease manufacture are those that are listed in Table I. These fatty materials are employed in both the glyceride and fatty acid forms.

TABLE I
Fatty Materials Used in Grease Manufacture

Animal	Vegetable	Marine
Tallow	Hydrogenated castor oil	Hydrogenated fish oil
Hydrogenated tallow	Hydrogenated soybean oil	Hydrogenated sperm oil
	Hydrogenated cottonseed oil	

It is to be noted that, in the processing of the above fats and others, stearic and oleic acids, as such, are obtained which are employed to some extent in grease manufacture.

With respect to the fatty materials used in the production of specific types of greases, Table II may be of interest.

TABLE II
Fatty Materials Used in Specific Type of Greases

Type of Grease	Principal Type or Types of Fatty Material Commonly Used
Calcium	Saturated and unsaturated glycerides and fatty acids Glycerides of C_{16} and C_{18} acids most important volume-wise
Sodium	Saturated and unsaturated glycerides and fatty acids Glycerides of C_{16} and C_{18} acids most important volume-wise
Lithium	C_{16} and C_{18} saturated fatty acids. 12-Hydroxy stearic acid important volume-wise
Aluminum	C_{16} and C_{18} saturated fatty acids
Barium	Essentially the same as for calcium

Soaps of fatty materials, other than those previously mentioned, are sometimes employed, together with regularly used soaps, to confer desired properties to lubricating greases (2). For example, soaps of lower molecular weight fatty acids, such as lauric and myristic, and soaps of higher molecular weight fatty acids, such as the dimer acids, can be used for this purpose. Volume-wise however, consumption of these types of fatty materials in lubricating greases is relatively small.

Importance of Fatty Component of Soap with Respect to Grease Performance Properties

Grease development is sometimes said to be an involved undertaking because numerous factors influence the characteristics of the finished product. These factors, for the most part, are:

1. metallic component of the soap
2. fatty component of the soap
3. presence of free alkali or free fatty acid
4. presence of water
5. presence of additives (antioxidants, structure modifiers, etc.)
6. nature of mineral oil
7. processing, including temperature cycles, homogenization, etc.

All of the above factors influence the characteristics of the finished grease because they either a) affect the size and shape of the dispersed particles, or b) affect the solubility relationship between the soap particles and the oil.

The scope of this paper will not permit a review of the inter-relationship of the seven factors listed. Instead three examples only will be cited to illustrate the importance of the fatty component of the soap with respect to performance characteristics of the lubricating grease.

Example No. 1. An aluminum base grease can be prepared by dispersing 10% of aluminum stearate in mineral oil, with suitable additives present, which will be a clear, smooth, adhesive lubricant of an approximately No. 3 NLGI consistency grade. No way has as yet been found to produce a similar type grease from aluminum oleate. In the latter case a fluid product results.

Example No. 2. The effect of varying the ratio of sodium stearate to sodium oleate on the viscosity of a particular sodium base grease, over a 200°F. temperature range, is shown in Figure 3 (3). It will be apparent that wide differences in viscosity resulted when the ratio of sodium stearate to sodium oleate was changed from 100:0 to 50:50. In more practical terms the grease represented by Curve A would be expected to show excessive leakage from bearings at elevated temperatures as compared with the greases represented by Curves B and C.

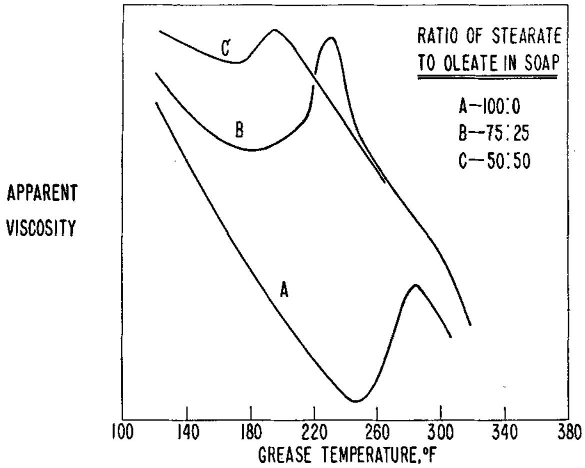

FIG. 3. Effect of soda composition or apparent viscosity. (Moses and Puddington Data)

As a matter of interest, it will be noted that the hump in the viscosity-temperature curve occurred at lower and lower temperatures as the amount of sodium oleate in the soap mixture was increased. The position of this hump with respect to the ordinate is a function of the temperature at which the soap particles begin to dissolve in the oil.

Example No. 3. The effect on the viscosity of a special type of lime base grease at elevated temperatures, which resulted from the presence of highly unsaturated fatty acids, namely, linoleic and linolenic acids, is shown in Figure 4. The two fats used in these greases were supplied by different companies. Although both fats showed the same total amount of unsaturation, as indicated by iodine number, differences in the types of unsaturated molecules gave a

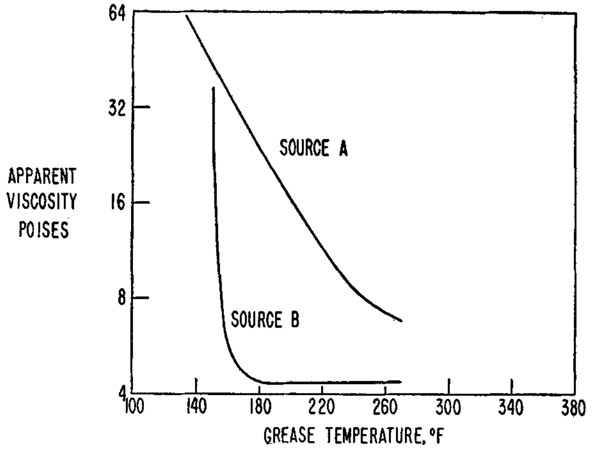

FIG. 4. Variation of apparent viscosity with source of fat in soap.

marked difference in the high temperature viscosity characteristics of the two greases that were prepared.

In addition to the fact that highly unsaturated fatty materials at times have an adverse effect on grease structure, the oxidation stability of these unsaturated fats is poor. Since grease life and performance properties are dependent to a large extent on the resistance which a product possesses against deterioration, chemical stability of greases has received considerable attention during recent years. In fact, improvements in greases in this respect have been largely responsible for the trend toward the adoption of factory prepacked anti-friction bearings, which cannot be serviced without disassembling the machine or equipment. The improvements effected in chemical stability have been accomplished primarily through the use of better grade fatty materials, more stable mineral oil stocks, and highly effective oxidation inhibitors.

It will be apparent from the above examples that performance properties of lubricating greases are dependent to a considerable extent on the chemical nature of the fatty component of the soap. In some cases, differences in fat composition can be compensated by the method of processing or the use of additive materials. However on a grease production basis, where a particular grade of fatty material has been adopted for use, appreciable differences in fat composition cannot be permitted by the grease manufacturer. Such differences may lead to serious customer complaints on grease performance.

It is, of course, up to the grease manufacturer to define as precisely as possible his needs to suppliers of fats and fatty acids because he knows better than anyone else the fatty acid compositions best suited for his particular greases. The use of relatively pure fatty acids, rather than mixtures of glycerides, provides the grease-maker with greater assurance of uniformity from shipment to shipment. It is to be noted that the composition of purchased acids may be satisfactorily controlled by specifications that are based on distillation of methyl esters of the fatty acids.

Use of Fats in Greases Other Than for Preparation of Soaps as Thickening Agents

Unsaponified glycerides are sometimes incorporated in certain types of greases, in small percentages, to improve their lubricating properties. Twister ring greases, for example, are used in the textile industry and occasionally, when requirements justify, will contain free fatty material.

Likewise sulfurized fat is often used in heavy duty greases, such as are employed in steel mills, to improve their load-carrying ability. Sulfurized fats are generally prepared from lard or sperm oil and, when film strength requirements are high, may be used in conjuction with lead soaps. In this case the lead soap is not present as a thickening agent but is employed primarily as a film strength-improving material. It also enhances rust-preventive properties.

The quantity of fats used for purposes indicated under this heading is small when compared with that consumed in the manufacture of soaps as thickening agents.

Greases Other Than Those Thickened with Soaps

Five per cent or less of the greases marketed at the present time are thickened with materials other than soaps. Materials of the non-soap type include modified bentonite, attapulgite, and finely-divided silica. To aid in dispersing thickeners of this general type and to provide water-resistance, organic compounds are either adsorbed or reacted on the surfaces of the thickener. For example, in the case of bentonite high molecular weight amines are reacted with the clay surfaces (4). Like soap base greases, lubricants prepared from a given inorganic thickener can vary widely in performance properties, depending on factors, such as degree of dispersion, nature of the fluid component, and presence of additives.

In some respects greases prepared from the inorganic thickeners have properties not found in soap-base greases. For example, since the inorganic materials are not soluble in the oil as temperature is increased, the products do not show a "melting" point. Furthermore lubricants of this type exhibit good resistance against structural breakdown under conditions of shear. Soap-base greases vary widely in this respect.

It should be pointed out that the somewhat higher cost of the "inorganics" and certain characteristics thereof have limited the use of greases of this type up to the present time. These characteristics, not all of which apply to any given grease, include incompatibility with most soap-base greases, unsatisfactory protection against corrosion, poor oxidation stability, and failure to be water-resistant.

Synthetic Greases

Another class of lubricating greases, known as "synthetic greases," is used in special applications where greases of the above described types are not suitable. Greases in this category contain a synthetic fluid, such as a silicone, which replaces the mineral oil of the soap-base grease, and are thickened either by a soap or other type of gelling agent. In general, lubricants in this class are designed for extremely high or low temperature applications, or both.

The principal deterrent to extending the use of synthetic greases is their relatively high cost. Extensive development work is under way on lubricants of this type at the present time, and increased use will in time undoubtedly effect some reduction in raw material costs. However these greases will most likely continue to remain at a high cost level as compared to that of petroleum greases and will therefore be restricted to specialized applications. In other words, it is believed that synthetic greases will continue to supplement petroleum greases and will be employed primarily in those applications where extremes of temperature are encountered.

Summary

A brief review has been given of the principal types of lubricating greases and of the fatty materials used therein. No attempt has been made to include a discussion of all conditions which may affect grease structure. However it has been indicated that various factors, as far as the grease itself is concerned, influence performance because they either affect the size and shape of the dispersed particles of the thickening agent, or affect the solubility relationship between the dispersed particles and the oil.

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Applications of Fatty Acids and Derivatives in Alkyds and Other Polyester Coating Resins

K. A. EARHART, Jones-Dabney Company, Louisville, Kentucky

IN THE surface-coatings field, to which this paper is directed, fatty acids are used principally in the following types of products: alkyd resins, epoxy resin esters, *in-situ* varnishes, maleinized oils, and polyhydric alcohol esters.

While the fatty acids that are available commercially vary in composition, depending upon the oil from which they are derived, the coating chemist is primarily interested in the following key fatty acids:

Drying Types	Carbon Atoms	Non-Drying Types	Carbon Atoms
Clupanodonic	22	Ricinoleic	18
Arachidonic	20	Lauric	12
Eleaostearic	18	Capric	10
Licanic	18	Pelargonic	9
Linolenic	18	Caprylic	8
Linoleic[a]	18		
Oleic	18		

[a] and conjugated isomer.

The higher saturated fatty acids, such as myristic, palmitic, and stearic, are of little interest to the coating resin chemist except that they act as diluents in the oxidative type of fatty acids essential to the drying processes involved in effecting dried resinous films.

The fatty-acid derivatives of most interest to the coating chemist are as follows:

Name	Carbon Atoms	Carboxyls	Combining Weight
Dimer Acid	36	2	300
Soybean and Fish Oil F.A. Alcohols	18-22	0	......
Sebacic Acid	10	2	101
Azelaic Acid	9	2	94
Pelargonic Acid	9	1	158

For the sake of completeness in tabulating the tools with which the surface-coating chemist works, the following are the more important oils from which fatty acids are (or may be) derived:

Castor
Coconut
Corn
Cottonseed
Dehydrated Castor
Fish (Menhaden, Sardine)
Linseed
Safflower
Soybean
Sunflower
Tall Oil
Walnut-Seed

K. A. Earhart

From a commercial viewpoint the fatty acids from cottonseed, soybean, and coconut oils are used in the greatest volume. Since cottonseed, corn, and soybean soapstocks are large-volume by-products of the food industry, fatty acids, with approximately 10 iodine value steps ranging from approximately 100 to 140, are available because of modern fractional distillation and crystallization techniques.

If it were not for the fatty acids available from these soapstocks, fatty acids would not be used in alkyds in competition with oils in view of the economic advantage of the latter.

The principal properties of the fatty acids which define their use in surface coatings are the iodine value, molecular weight and characteristic groups, and position and number of the unsaturated bonds.

The iodine value gives us an idea of the degree of unsaturation and a rough approximation of whether the particular fatty acid can be considered a drying or non-drying type for a particular application. Recently, the author has been applying the concept of functionality to the iodine value, along with the functionality of the dibasic acid, polyhydric alcohol, etc., involved. For example, if the basic polymer to which a fatty acid is attached is of low molecular weight, a high iodine value will be necessary in order to obtain acceptable drying speed. If the basic polymer is of higher molecular weight, a fatty acid of lower iodine value will suffice as long as the iodine value is due in great part to linoleic acid, which oxidizes sufficiently fast to effect cross-linking in a reasonable period of time.

The molecular weight of fatty acids is important only for differentiating the long chain drying acids