Uses of Fats, Fatty Oils, and Derivatives in the Petroleum Industry[1]

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THE petroleum industry, though not a major user of fatty materials when compared with the food or detergent industries, nevertheless affords a considerable market for these materials which is yearly expanding. Moreover, use by the petroleum industry of fatty materials of less than edible quality provides an outlet for materials which would require very expensive refining. It would be less economical to convert these materials into products suitable for the food and soap industries. In 1935 fatty materials of the values shown in Table I were used by the petroleum industry (1). Materials in amounts valued at less than $25,000 are not included.

Substantially all of this $22,704,900 worth of fatty products used in the petroleum industry entered into the manufacture of lubricants; however some quantities are used for the manufacture of paints, detergents, and other miscellaneous purposes. Generally speaking, any and all classes of lubricants may contain a fatty oil or derivative. Some fatty material or synthetic derivative may be incorporated in greases, steam cylinder oils, marine oils, soluble oils, cutting oils, gear oils, transmission oils, automotive and diesel oils, and other engine lubricants now on the market. While the various petroleum companies may not always be desirous of disclosing the amount, nature, or objective of the inclusion of a fatty material or a derivative in a specific lubricant, some general information is available on these three subjects.

Fatty materials contained in a lubricant may vary from as little as 0.1 per cent to as much as 50 or 60 per cent by weight. A lubricant consisting entirely of an animal or vegetable oil is not here considered as a product of the petroleum industry.

TABLE I

Value of Fats and Oils Used by Petroleum Industry

Material	Dollars Per Year
Acid, fatty distilled animal	$ 26,600
Acid, hydrogenated	2,800,000
Degras	987,000
Grease, yellow	1,142,000
Oil, corn	30,400
fish	415,600
lard	6,372,300
linseed	125,200
palm	79,000
rapeseed	415,100
soya bean	26,400
sperm	4,274,000
tallow	2,929,300
Tallow, prime	1,147,500
Total of fats and fatty oils	20,770,400
Naval stores and other oils	1,934,500
GRAND TOTAL	$22,704,900

TABLE II

Nature of Fatty Materials and Their Uses In the Petroleum Industry

											TYPE OF LUBRICANT													
											OIL										GREASES		
Fatty Material		Automotive Crankcase	Aviation Crankcase	Steam Cylinder	Diesel	Marine	Racing	Gas Engine	Compressor	Mill	Cutting	Turbine	Spindle	Air Tool	Quenching	Soluble	Break-in	Car	Wire	Brick	Textile	Gear Lubricant	Low Temp.	High Temp.
I Whole Fats and Fatty Oils																								
A Unmodified	Lard Oil			x	x			x	x	x	x	x	x	x	x					x		x	x	x
	Castor Oil						x		x													x		
	Rapeseed Oil								x					x										x
	Sperm Oil												x											
	Tallow Oil			x				x	x					x					x			x	x	x
	Degras			x	x			x		x				x						x		x	x	x
	Neats Foot Oil																				x			
B Halogenated		x	x																			x		
C Sulfurized											x													
D Voltolized		x	x				x																	
E Blown	Blown Rapeseed Oil					x			x					x										
II Fatty Acids																								
A Unmodified	Oleic			x	x			x	x	x	x	x		x		x		x	x	x	x	x		
B Halogenated	Chlorostearic	x																						
III Derivatives	Cottonseed																						x	
A Soaps	Stearates																					x	x	x
1. Unmodified	Tallow																					x	x	x
	Rosin																					x	x	
2. Halogenated	Calcium dichlorostearate				x																		x	
3. Substituted	Calcium phenylstearate				x																			
B Esters 1. Unmodified	Methyl ricinoleate	x																						
2. Halogenated	Methyl dichlorostearate	x	x		x		x	x	x	x			x	x			x	x				x		
3. Sulfurized	Sulf. Methyl Linoleate	x			x																			

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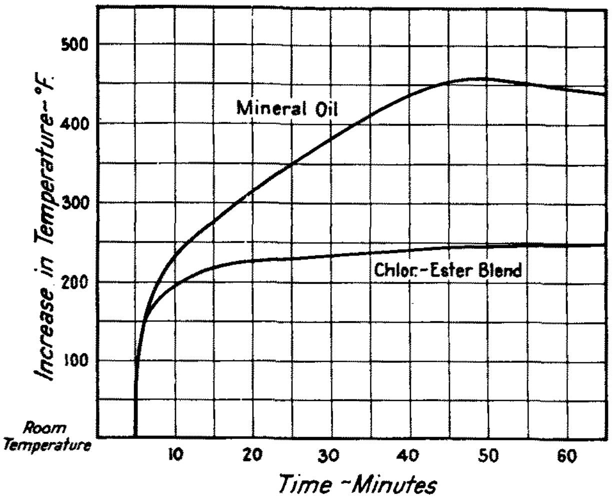

Figure 1 — Temperature Increase in Almen Bushings

In addition to the animal and vegetable fats and oils shown in Table I, a large number of derivatives of these basic molecules are used by the petroleum industry. While it is, of course, impossible to mention all the fatty materials which are or may be used, a few common examples are presented in Table II together with the type of lubricant in which the various fatty materials and derivatives may be incorporated.

Animal and vegetable oils and their derivatives are used in petroleum or hydrocarbon lubricants to accomplish numerous and diversified improvements in the physical and chemical character of the lubricants and to accomplish specific results in practical lubrication. There are three general properties of fats, fatty oils, and derivatives which account for their use in the petroleum industry:

I. Wetting and oiliness
II. Carrying agents for active elements
III. Thickening effect of soaps in lubricating greases

These modern objectives in adding fatty materials to petroleum lubricants have developed to their present widespread use slowly through long ages. Man has been attempting to overcome friction by means of lubrication since before the beginning of recorded history. For the major portion of the ages involved in recorded history, fats, fatty oils, and water were the only known lubricants. Petroleum was used as a lubricant on a very small scale prior to the drilling in 1859 of the first oil well in the United States.

With the turn of the century, more complicated machines were devised; and the problems of friction became more acute. Special lubricants were required for specific duties, and even today new lubricating duties and new lubricants are being developed for the satisfactory reduction of friction in special services. It is commendatory that the technical men of the fat industry, the petroleum industry, and the mechanical industry have been cooperating to develop commercially feasible answers to the various lubricating problems as they arise.

In full viscous lubrication, a relatively thick film of lubricant separates the moving parts. At times, however, when pressures are high and rubbing speeds are low, the film of lubricant tends to be squeezed out. In boundary (not partial) lubrication, the distance between rubbing surfaces approaches molecular dimensions; and only an adsorbed film remains to protect the relatively moving parts. The resistance of this remaining film to rupture determines its lubricating value. As long as it is unbroken, the metal surfaces are fully protected. The presence of chemically combined active elements as components of the adsorbed film increases its resistance to rupture. Even when such a film does break, the active element serves to convert the metals to compounds which prevent fluxing and seizure. In the absence of such active elements, the adsorbed films are relatively weaker; and when they are broken, the metal surfaces weld and tear apart, thoroughly damaging the completely unlubricated metals.

In these two fields of viscous and boundary lubrication, the joint activity of the petroleum and the fatty oil industry is essential to the operation of modern machinery. The physical and chemical properties of the fats and their derivatives make them particularly suited for use in boundary lubrication and of value for special uses in viscous lubrication. Particularly to be mentioned is the wetting ability of the glycerides in steam cylinder and marine lubrication.

Whereas in the distant past animal and vegetable oils and fats were the lubricants in general use, a period followed during which time petroleum lubricants were favored to the exclusion of all others. This was a natural development when it is considered that the fats and fatty oils supply is limited and, compared with petroleum lubricants, much more expensive. Moreover, certain chemical properties of the petroleum oils make them better suited than fatty oils to meet the requirements of modern lubrication. In use, properly manufactured mineral lubricating oils do not resinify or gum as do fatty oils and do not thicken to anything like the same extent, nor do the mineral oils hydrolyze and form corrosive acids, causing damaging emulsions, and promote spontaneous combustion in handling.

The fatty materials were obviously not replaced for grease manufacture; and as the petroleum oils were increasingly more highly refined to overcome certain inherent characteristics, it was obvious that the fatty oils and their derivatives accomplished results in practical lubrication that could not be accomplished by petroleum lubricants. As a very common practical

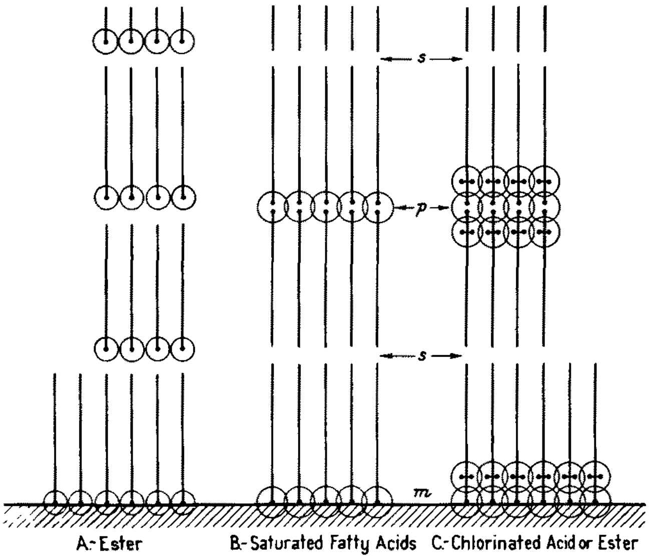

Figure 2 — Orientation of Molecular Types on Metals

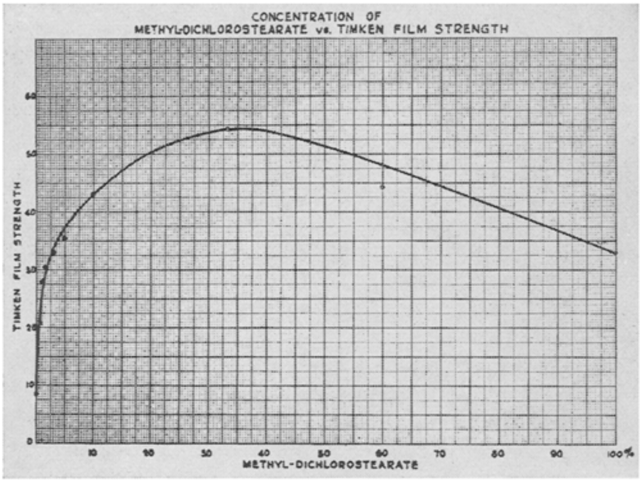

Figure 3 — Concentration of Methyl Dichlorostearate vs. Timken Film Strength

example, machines that were "running hot" were frequently benefited by the injection of a quantity of fatty oil in the lubricating system. The fatty oil reduced the friction, and the machine "cooled" to its normal operating temperature.

The physical and chemical aspects of the "cooling" or friction reducing properties of the fatty oils are commonly referred to as wetting or oiliness.

I

WETTING AND OILINESS

As a result of wetting, "the behavior of liquids in contact with solids varies greatly. A particular liquid does not, for instance, act towards all solids in the same way. Water will wet and spread over a clean sheet of glass; but when a drop of water is placed upon a sheet of solid paraffin, it draws itself up into a bead. Mercury will not wet any known solid with which it does not amalgamate, the mercury being torn off wholly when the bead is removed. The stray fields of the mercury atoms at the surface attract the solid less forcibly than the attraction of mercury atom for mercury atom. Fortunately, there are a large number of oily liquids and solids," like the fats, fatty oils, and derivatives, "which spread over and wet the surfaces of metals, etc., and they adhere so strongly that it is difficult to displace them. Liquid lubricants also wet such materials as cotton and worsted, and siphon through wicks made of them." (2)

Oiliness may be defined as the friction reducing effect referable to the chemical nature of a fluid and of the contacting surfaces. Oiliness is the result of the interaction of molecular and surface forces at the interface. The maximum effect of oiliness is reached when contacting surfaces are separated by an oil film of multimolecular dimensions. There is no oiliness effect in fluid film lubrication.

Wetting and oiliness thus are apparently synonymous in some respects but not necessarily in all respects. The physical and chemical forces causing the phenomena of wetting and oiliness are very similar in character if not identical.

There is some controversy as to the words which should be used in defining oiliness; but the polar character and residual chemical valence of the molecules of fat, fatty oil, or derivative become effective in practical lubrication, protecting metal surfaces by wetting and reducing friction and wear by oiliness.

TABLE III
EFFECT OF OLEIC ACID ON OILINESS AS MEASURED BY HERSCHEL COEFFICIENT OF FRICTION

Oil Viscosity, S.S.U.		Mineral Oil			0.5 Per Cent Oleic Acid		
100° F.	210° F.	White Metal (200)	Brass (CWS)	Bronze (SAE 64)	White Metal (200)	Brass (CWS)	Bronze (SAE 64)
2,300 (Max.)	130	.079	.103	.118	.073	.059	.085
1,400 (Max.)	95	.087	.108	.120	.073	.078	.089
650 (Max.)	66	.102	.112	.123	.089	.096	.098
575	64	.122	.120	.185	.093	.116	.110
350	54	.130	.120	.170	.101	.099	.135
225	47	.150	.115	.182	.101	.102	.126

The primary purpose of adding fatty material to steam cylinder, marine, and other lubricants used under moist conditions such as those for air tools, vacuum pumps, and the like, is to obtain the metal-wetting effect of the polar fatty molecules. In some instances the polar material is carried to the metal surfaces in water emulsion. Boundary lubrication obtains under the conditions of use of all these devices and serves to protect the metal surface from wear, oxidation, and corrosion.

The greater oiliness of fatty materials has been recognized for many years; but controlled utilization of the property in conjunction with petroleum oils was accomplished by Wells and Southcombe, who at the same time avoided the inherent disadvantages of the straight fatty oils. Their discovery that the fatty acids were the active ingredient of fatty oils in lubrication led to world-wide patent protection (3) of the method.

Continental Oil Company acquired the North American rights to the patent in 1923 and blended 0.5 to 1.0 per cent of oleic acid with mineral oils to produce its "Germ Processed" lubricants from 1923 until 1934. Many millions of pounds of oleic acid were consumed in this first lubricant on the American market having added oiliness designed for specific lubricating duties.

Table III shows the effect of 0.5 per cent of oleic acid on the coefficient of friction of a mineral oil blended to decreasing viscosities as determined by the Herschel Oiliness Machine (4) when employing different types of metals. There is a marked decrease in coefficient of friction for all of these metals and for all viscosities.

Higher loads per unit of projected area imposed on bearing surfaces by the increased speed and power output of modern automotive engines necessitated the change in some instances from babbitt to cadmium-

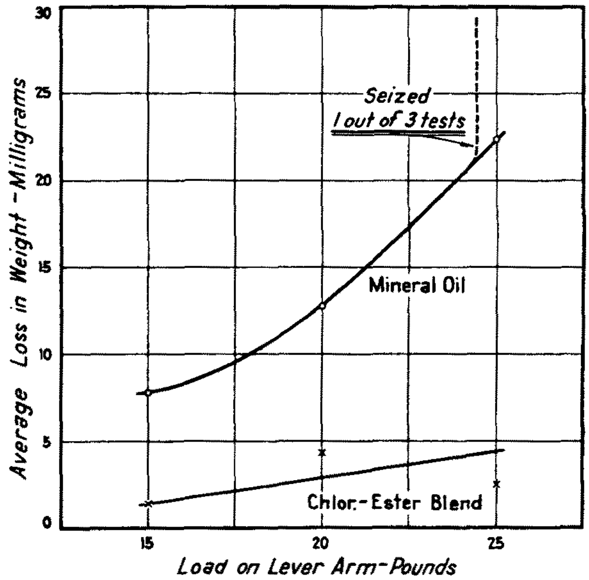

Figure 4 — Long Time Timken Wear Tests

TABLE IV
TIMKEN WEAR TESTS ON BEARING METALS

		Load on Beam — Pounds			
		20	40	60	80
Metal	Oil	Loss in Weight — Grams			
SAE 11	Mineral	0.0019	0.0040	0.0058	0.0091
	Chlorinated Ester Blend	0.0014	0.0026	0.0034	0.0071
Cadmium No. 50	Mineral	0.0026	0.0075	Seized	
	Chlorinated Ester Blend	0.0011	0.0056	0.0073	
Cadmium No. 51	Mineral	0.0025	0.0033	Seized	
	Chlorinated Ester Blend	0.0006	0.0030	0.0047	0.0062
Copper-Lead	Mineral	0.0013	0.0336	0.0390	Seized
	Chlorinated Ester Blend	0.0004	0.0035	0.0153	0.0316
Bronze No. F-1	Mineral	0.0129	Seized		
	Chlorinated Ester Blend	0.0021	0.0015	0.0046	0.0054

silver, or copper-lead bearing compositions. The same changes in automotive engine design have resulted in loads near the maximum capacity of petroleum lubricants with lead containing bearing materials. Automotive lubricants, because of this change in design, may not now contain any substantial amount of free fatty acid because of its corrosiveness to some of the newer bearing metals; and lubricants of higher load-carrying capacity are required in order to avoid damage under severe operating conditions.

II

FATTY MATERIAL AS AGENTS FOR CARRYING ACTIVE ELEMENTS

Lard oil contributes oiliness but is objectionable for many uses because of gumming. Converting the glyceride to the acid increases oiliness, but the acids are corrosive to some lead containing bearing compositions. Converting the acid to the monohydric ester creates a compound with high oiliness but without the gumming character of the glycerides and without the corrosive character of the acid. Added to a lubricant, the ester does not, however, contribute to the load-carrying capacity as defined below. Properly chlorinating the ester gives a material having all of the advantages of the unchlorinated ester and load-carrying capacity in addition.

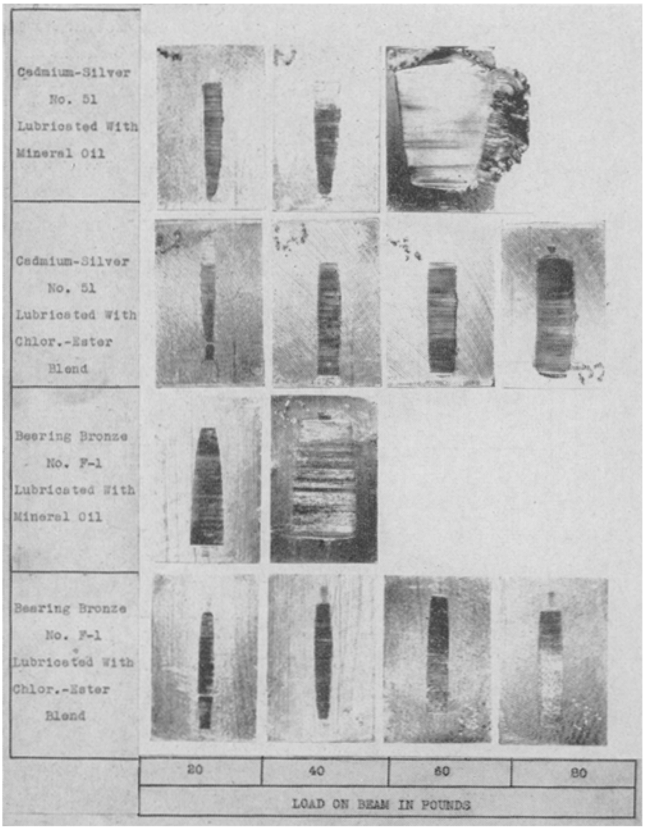

Figure 5 — Bearing Metal Blocks from Timken Wear Test

An example of the effect on practical lubrication of adding a small amount of a particular fat derivative is the use of methyl dichlorostearate (5). These effects may be summarized as follows:

1. Greater oiliness aids practical lubrication because it tends to reduce friction and results in lower operating temperatures. This in turn decreases engine wear, damage to the oil by oxidation, and requires the use of less fuel.

2. Greater load-carrying capacity tends to prevent metal-to-metal contact by maintaining a lubricating film under higher operating pressures. In conjunction with oiliness, it reduces engine wear, maintenance, oil deterioration, and frequency of oil changes. It is also of great value in engine design by permitting higher loads per unit of projected bearing area.

Oiliness

The frictional heat characteristic associated with oiliness may be demonstrated by determining the rise in temperature at a rubbing surface lubricated with a mineral oil as compared with the temperature rise under identical conditions with the same mineral oil containing an oiliness agent. Thus Figure 1 shows the increase in temperature of the Almen (6) bushing at 600 r.p.m. and 2,000-pound load over a period of one hour. The temperature was measured with a thermocouple buried in the bushing at the bearing surface. The methyl dichlorostearate blend shows 44 per cent less increase in temperature than the mineral oil. Since the room temperature was 75 degrees F. when the data of Figure 1 was obtained, the maximum temperature reached with the mineral oil was 540 degrees F. Similar results may be obtained with the Sibley oil testing machine, which in addition may be used to test load-carrying capacity.

In many hundreds of thousands of miles of technically controlled road work, there has been a definitely lower operating temperature as measured by the differential increase in water temperature, temperature of oil from the bearings, and the oil-sump temperature for the blended oil as compared with the mineral oil under comparable operating conditions. As an example, in Chevrolet fleet tests, where the comparisons were carried out under conditions as nearly

TABLE V
CYLINDER AND PISTON RING WEAR

	Amount of Wear With Chlor.-Ester Blend	Amount of Wear With Mineral Oil	Per Cent Greater Wear With Mineral Oil
Buick Test Fleet — 15,000 Miles			
Oil-ring wear, g.	0.1311	0.1795	37
Compression-ring wear, g.	0.1666	0.3692	121
Total ring wear, g.	0.2977	0.5487	84
Average clyinder wear, in.	0.00021	0.00029	38
Ford Truck Test Fleet — 12,500 Miles			
Oil-ring wear, g.	0.0753	0.1119	48
Compression-ring wear, g.	0.0791	0.1275	61
Total ring wear, g.	0.1544	0.2394	55
Average cylinder wear, in.	0.00018	0.00029	62
Chevrolet Test Fleet — 30,000 Miles			
Oil-ring wear, g.	0.2621	0.4664	78
Compression-ring wear, g.	0.3522	0.3828	9
Total ring wear, g.	0.6143	0.8492	38
Average cylinder wear, in.	0.00019	0.00023	21

TABLE VI
FIBER LENGTH AND CHARACTERISTICS OF GREASES — DATA OF FARRINGTON AND DAVIS (18)

Classification	Fiber Length Microns	Remarks
Long Fiber	100 or more	Fibrous and ropy. Soda base greases. Chasis lubricant made with soda soap.
Medium Fiber	10 to 100	Clinging and slightly rough. Milled soda base greases, soda base greases made at high temperatures, wheel bearing grease.
Short Fiber	1 to 10	Slightly rough and short fiber. Soda base greases. Driving journal compound, ball bearing grease, paper mill dryer roll bearing grease.
Microfiber	1 or less	Smooth, unctuous or buttery. Lime base cup greases, aluminum base greases, and lead base greases.

identical as possible, the average sump temperature of the cars on the chlorinated ester blend ran 8 - 10 degrees F. below those on mineral oil.

Probably the best example we have of this characteristic was made at the Indianapolis speedway, where a Studebaker racing car was under test at 104 m.p.h. Switching from mineral oil to the same oil containing 0.7 per cent methyl dichlorostearate and back showed an average lower sump temperature of 20 degrees F. under identical driving conditions.

Studies of esters, acids, halogenated esters or acids, and blends of these materials in mineral lubricating oil by diffraction of an X-ray beam, static and kinetic coefficients of friction, interfacial tension, capacitance, oil adhesion, heat of wetting, and observed phenomena of such lubricants in service all indicate a molecular arrangement on a metal surface as portrayed schematically in Figure 2. The vertical lines represent the hydrocarbon chains; the dots at the ends of the lines, the polar groups. The circles are used to designate the interlocking fields of force. In the primary film the polar groups are directed toward, and firmly attached to, the metal surface, m, by virtue of their marked affinity for it. The hydrocarbon chains are arranged parallel to one another. When a first layer has been formed on the metal surface, a more or less homogeneous surface is produced by the free ends of the adsorbed molecules, which serves as a foundation for the formation of a second layer of attracted polar molecules. In this way many layers of adsorbed molecules are indicated to be formed on a metal surface, although the force which serves to bind the molecular layers decreases progressively as the distance from the surface increases. The polar groups standing opposite each other are bound firmly in consequence of their strong affinity. In the planes of the methyl groups, the mutual forces of attraction, as previously shown, are very slight on account of the small affinity between these groups. In these planes, therefore, sliding can result with minimum friction.

The polar compound may act in a number of different ways in building this film. Figure 2-A shows how a long-chain weakly polar compound, such as a glyceride or methyl stearate, may build a film with the polar end of the first layer of molecules attached to the metal surface and all the single molecules in the succeeding layers oriented in the same direction. Molecules of fatty acids, such as stearic acid, seem to orient as shown in Figure 2-B with the first layer arranged monomolecularly on the metal surface like the ester. The succeeding layers are built with double molecular units formed by the association of two molecules because of the high polarity of the carboxyl groups. These molecular arrangements are referred to as single and double, respectively.

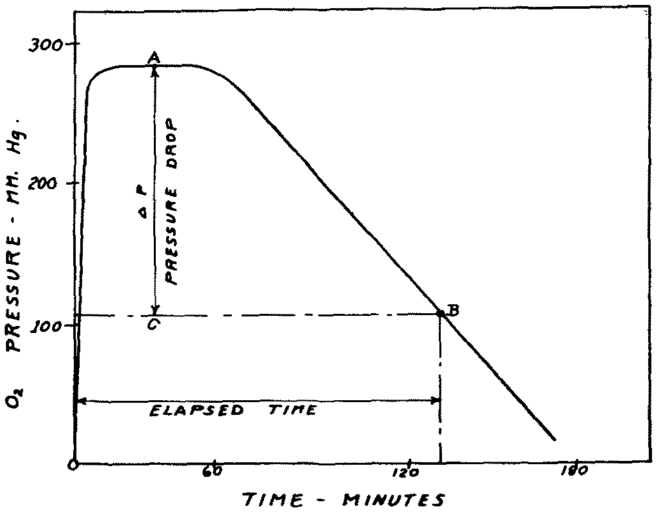

Figure 6 — Oxygen Absorption Curve

The type of film formed by chlorinated esters is shown in Figure 2-C. The circles on each of the hydrocarbon chains near the carboxyl end represent the fields of force of the two chlorine atoms on the alpha carbon. These fields of force magnify the total degree of polarity of the molecule. By the introduction of the two chlorine atoms, the weakly polar ester becomes more active physico-chemically and displays a double molecular arrangement similar to stearic acid.

TABLE VII
OXYGEN ABSORPTION OF FATTY MATERIALS

No.	Description	Time in Minutes To Drop 60 mm.
1	Cottonseed fatty acids	20
2	Cottonseed fatty acids	40
3	Cottonseed fatty acids	44
4	Oleic acid	45
5	Hydrogenated cottonseed fatty acids	72
6	Prime tallow	82
7	Stearic acid	196

TABLE VIII
OXYGEN ABSORPTION OF GREASES

Sample	Appearance	Oven Test 72 Hours @ 150° F.	Time in Minutes To Drop 60 mm.
EHQ	Badly oxidized	D	34
EIU	Badly oxidized	C	39
EQT	Oxidized	B	43
CXP	Good	A	59
EWL	Excellent	B	69

Load-Carrying Capacity and Wear

Figure 3 shows the effect of methyl dichlorostearate on the Timken (7) film strength of a good quality petroleum lubricant which has an original Timken film strength of 8.5 pounds on the loading arm. From this curve it is obvious that only a very small (0.5 to 1.0 per cent) amount of methyl dichlorostearate trebles or quadruples the load-carrying capacity of a good mineral lubricant.

A series of wear tests of thirty-minute duration were made on various bearing metals, and the weight loss in grams of the bearing block as shown in Table IV was used as a measure of the rate of wear. A new polished cup was used for each metal and oil; but the same cup was used for the various beam loads, i. e., 20, 40, 60, and 80 pounds. The oils used were an acid-treated, paraffin-base Mid-Continent SAE 30 mineral oil and the same oil plus 0.7 per cent methyl dichlorostearate. It is interesting to note that although the mineral oil will carry relatively high loads on some of the bearing metals, the resultant rate of wear

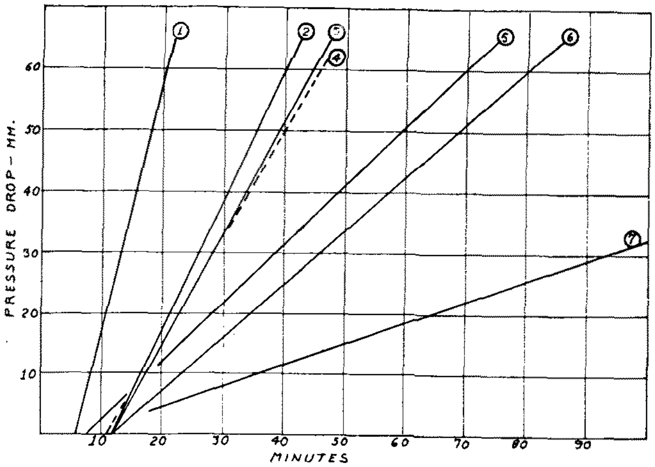

Figure 7 — Oxygen Absorption Tests on Grease Components Shown in Table VII

is materially higher than when the same oil carries a satisfactory addition agent.

In order to counteract any possible effect of differences in the cups, a series of six-hour runs was made with the same cup on cadmium-silver blocks at sufficiently low loads that the cup was not changed appreciably during the series. The average results of several runs are charted in Figure 4. In the case of the mineral oil at 24-pound load, failure occurred in one run out of three.

This shows that at high load but definitely below the seizure point or film strength of either oil, the methyl dichlorostearate blend will result in less wear than the mineral oil. Similar studies have been made with other compounding agents; and in general it can be said that, if the product has the highly polar film-forming characteristics which give oiliness and is not corrosive on the bearing metals or copper, the rate of wear will be low.

Photographs of the wear-test blocks for the cadmium-silver No. 51 and the bronze No. F-1 are given in Figure 5. The failure of the cadmium-silver with mineral oil at a load of 60 pounds is particularly interesting because it indicates a possible reason for the failure of these bearings in severe service. The mineral oil failed to maintain a lubricating film, and the resultant frictional heat was sufficient to melt the surface of the metal which was "wiped" out of the bearing. The methyl dichlorostearate blend, even under 80-pound load, maintained a sufficiently low friction to protect the bearing from failure. In the case of the bronze, the mineral oil under 20-pound load allowed twice the wear that resulted with the chlorinated ester blend under 80 pounds.

The significance of the laboratory data in practical lubrication is shown by carefully controlled fleet tests. The results of three such tests are given in Table V. The actual ring wear as determined by loss in weight is substantial and in all cases shows a materially greater wear for the mineral oil than for the chlorinated ester blend.

In all cases the cylinder wear is surprisingly low. All test runs were made in the open country at 50 m.p.h. under high-temperature conditions. There were relatively few starts and stops for mileage covered, and therefore the low wear measured is added proof that corrosion under starting conditions is the cause of the major portion of cylinder wear.

The cylinder-wear figures are the average of six measurements for each cylinder. Very accurate measurements were taken at the top, middle, and bottom of each cylinder and both lengthwise and across the block at each point. Measurements before and after runs were made at identically the same points, and sufficient readings were taken accurately to "bracket" the true reading. All measurements were corrected for temperature.

The differences in cylinder wear, although small, show substantially in favor of the chlorinated ester blend. The average wear with the mineral oil is 40 per cent greater than with the compounded oil. Using the wear figures for the top of the cylinders, the difference becomes greater; thus, in the case of the Buick fleet, the average top-cylinder wear with the mineral oil was 48 per cent greater than that for the lubricant containing the methyl dichlorostearate. An independent operator of a fleet of transcontinental busses found substantially the same relationship in over one and one-half million miles of shop-controlled operation.

Diesel Lubricants

The development of an outstanding lubricant for modern diesel engines depended on the use of a fatty derivative to carry active elements. The use of mineral oils alone in this service leads frequently to difficulties due to ring sticking, scuffing, excessive wear, and bearing failure. The first of these is usually associated with lacquer-like deposits which prevent sealing of the rings against the cylinder wall and thus cause blow-by. The difficulty often starts with the top compression ring and spreads rapidly to the others. Perhaps as a result of overheating due to blow-by, metallic particles are torn from the rings, pistons, and cylinder walls and cause scratches on these parts.

Wear is a relative term, but as an absolute example a cylinder wall wear of 0.015 inch per 1,000 hours of operation in a 100-h.p. automotive type diesel engine should be considered excessive.

Babbitt-lined bearings lose considerable of their crushing strength at high temperatures, and this is the immediate cause of failure of such bearings. New alloy bearings have more resistance to impact at high temperatures but are more susceptible to corrosion by the oil, and failure in this type of bearing is frequently due to this cause.

In order to avoid these difficulties as far as possible a diesel lubricating oil should have high film strength, high oiliness, detergency, low carbon-forming tendency, oxidation stability, and noncorrosiveness toward the metals involved. The improvement in a mineral oil in these characteristics by the addition of 1 to 1.5 per cent of calcium dichlorostearate (8) is marked. The Timken film strength of this blend is 30 pounds, or about four times that for the mineral oil alone and for other diesel oils. By protecting the surfaces from metal-to-metal contact, this blend reduces scratching and wear. Wear is also reduced by the increased oiliness of the blend. Friction and torque are reduced as may be demonstrated by various machines. In turn, reduction of friction tends toward reduced operating temperatures and lengthens bearing life.

Detergency is the ability to keep sludge, soot, and resins in suspension so that they do not accumulate behind rings and in other critical places. Soap blends show a high degree of detergency and thus aid in the prevention of ring sticking.

Carbon and soot are formed from all lubricating and fuel oils. Some is hard, tends to cake, and is abrasive. The use of calcium dichlorostearate with a suitable oil gives a particularly soft carbon which does not pack tightly and is readily dislodged and suspended in the oil.

The properties of stability and noncorrosiveness of a blended oil are functions of the oil itself and of the addend, together with the effect of each on the other. Calcium dichlorostearate blends are as satisfactory in these respects as the base oil alone.

Fat Derivatives as Carriers for Other Active Elements

Large volumes of fatty material are used for carrying sulfur in various forms in lubricating compositions. Cutting oils, gear lubricants, transmission oils, and textile oils may contain fatty materials which have been treated with sulfur or a sulfur compound. Chemically combined sulfur in a lubricating oil acts in some respects like chemically combined chlorine, but in other respects it is entirely different. Small quantities of certain sulfur-bearing compounds in crankcase oils serve to stabilize them against the formation of sludge and other oxidation products. Use of larger quantities in hypoid gear lubricants, particularly in conjunction with lead soaps or with chlorinated organic compounds, serves to improve load-carrying capacity.

For some purposes the sulfurized glycerides are not wholly suitable due, for example, to the viscosity increase which invariably accompanies sulfurization. For these purposes the mono and dihydric esters of fatty acids from unsaturated fatty oils are especially advantageous for sulfurization (9), since they are not as viscous and do not thicken in use as much as the glycerides. For example, the methyl esters of the acids of corn oil or soya bean oil may be sulfurized until they contain 12 to 18 per cent of sulfur, which is more than can be introduced into the corresponding glycerides without obtaining products too viscous for most uses. These sulfurized esters are superior in that blends containing them do not become cloudy in storage, are non-corrosive to the common bearing metals, and resist oxidation in use.

A fatty oil derivative containing phosphorus has been recommended for the improvement of the load-carrying capacity of lubricating oils. The compound is derived by splitting the whole oil into the fatty acid, reducing the fatty acid to the alcohol by hydrogenation, and finally treating the alcohol to form the alkyl ester of phosphorus or phosphoric acid. Tri lauryl phosphate is an example of this class of compounds.

Some other synthetics derived from fatty materials which have been suggested for this use are halogenated esters of fatty acids and cyclic hydroxy compounds (10) which may at the same time have pour test depressing properties, halogenated fatty acid condensation products with fatty and nonfatty materials (11), halogenated fatty alcohols (12), and halogenated amides of fatty acids (13). Nonhalogenated fatty derivatives which have been added to lubricating oils for increasing film strength or for other purposes include hydroxy-fatty acids (14), nitriles (15), and ketones (16).

The electrically treated oils known as voltolized oils should be mentioned as addition agents for lubricating oils. These are mineral, vegetable, or animal oils subjected to the action of electrical discharge whereby they become considerably more viscous but not darkened in color. Recommended blends of 5, 10, or 15 per cent of the treated fatty oil in mineral oils are claimed to have higher viscosity, higher viscosity index, lower pour points, and greater oiliness. Voltolized oils have been widely used in Europe, particularly for airplane lubrication. These oils have received considerable discussion in this country but are not commercially available.

Substitute Fatty Materials from Petroleum

Petroleum contains quantities of saturated aliphatic hydrocarbons which may be converted by suitable oxidation processes into organic acids and organic compounds with other characteristic chemical groupings, but thus far no derivative of petroleum has seriously threatened to commercially replace the fats, fatty acids, and their derivatives in this country.

III

THICKENING EFFECT OF SOAPS IN LUBRICATING GREASES

Probably the most commonly known use of fats, fatty acids, and derivatives by the petroleum industry is in the manufacture of greases. In the field of practical lubrication an unending number of special problems may arise. Many of these problems may be solved by means of liquid lubricants, but a solution of some involves the use of a grease. It is necessary to use a grease when it is impossible to hold a liquid lubricant at the point being lubricated, or under certain conditions of temperature, squeezing pressure, dust, and the like.

Greases on the market today invariably comprise mineral oil and a salt of an organic acid. The organic acid is usually a fatty acid or substituted fatty acid, notable exceptions being those greases that contain naphthenates or abietates. Soaps are used in greases to obtain a suitable consistency, but the mineral oil is the lubricant. The quantity of soap in a grease may vary between as little as 0.25 per cent in certain textile lubricants to as much as 60 per cent in some railroad driving journal compounds. This wide soap variation provides lubricants of vastly different physical properties. By definition, all greases are lubricants containing soap and mineral oil, but the mere placing of a soap in a mineral oil does not necessarily make a lubricating grease.

Lubricating greases consist of two phases, an oil phase and a soap phase, both exhibiting colloidal properties within themselves and very pronounced colloidal properties when properly associated with each other. In a lubricating grease, the mineral oil acts as the discontinuous phase and the soap as the continuous phase.

Practically every type of mineral lubricant and practically every animal and vegetable saponifiable fat and oil have been used or recommended for use in the production of lubricating greases. According to Klemgard (17), many metals have been suggested for forming soaps with the fatty materials for grease manufacture. Probably more than 95 per cent of all commercial greases are made with sodium, calcium, aluminum, or lead soaps. Fillers of both inorganic and organic nature have been mixed in with lubricating greases for various purposes. Some of the inorganic fillers are graphite, mica, Jefferisite, asbestos, talc, zinc oxide, powdered lead, copper, and zinc. Organic fillers include wool yarn, horse hair, goat hair, ground cork, sawdust, and flake naphthalene. The use of nonlubricating fillers is decreasing.

To the foregoing list of materials which may be used in grease manufacture should be added a rather imposing number of different perfuming substances and coloring substances which are used to mask the use of poor quality materials or for identification purposes. It is apparent without further amplification that a lubricating grease may have a diversified chemical composition.

It must be clearly understood that mere chemical analysis does not explain the properties of a lubricating grease. The manufacture of an acceptable grease requires close control of the character of the ingredients, conditions of temperature, time and agitation in blending, order of incorporating the components, cooling conditions, and a number of other items which may appear to the inexperienced to be minor details but which in fact may be the difference between success and failure in the finished product. Many of these points are mentioned by Klemgard (17), but experience is a very essential factor in commercial grease manufacture.

The entire manufacturing process must be controlled to obtain the proper colloidal dispersion of the soap in the oil. This distribution of the soap in the oil is sometimes referred to as the micelle or space lattice structure. Farrington and Davis (18) studied the distribution of the soap in various greases by means of photomicrographs taken with dark field illumination. These workers found that a continuous decrease in fiber length of the dispersed soap takes place as the texture of the grease becomes smoother and that this characteristic is sufficiently nonvariable to serve as a basis for a recommended classification of greases. Table VI, taken from Farrington and Davis (18), shows the relationship between fiber length and character of the grease.

Obtaining and maintaining the fiber structure or consistency of a grease is fairly difficult under commercial conditions. To obtain the desired structure may necessitate the controlled incorporation of a certain amount of water or the inclusion of a carefully controlled percentage of glycerine of the order of 0.5 to 0.75 per cent. Small amounts of another soap such as 0.75 per cent of aluminum stearate in certain soda base greases serve to control fiber character. Maintaining fiber structure requires close control of minor details. For example, straining a grease through a screen may be totally damaging to consistency. The difference in agitation resulting from filling one-pound grease cans and 100-pound grease pails has been known to damage the consistency (fiber structure) beyond acceptability.

Lubricating grease manufacturers develop grease formulas and manufacturing procedures adequate for the commercial production of various greases. Lubricating grease compositions have not been standardized; therefore manufacturing procedures are not standardized. Representatives of the fatty material industry may well be amazed at the difference in preferences of petroleum companies for particular fatty materials for the manufacture of a given lubricating grease. For example, one petroleum company may purchase cottonseed fatty acid for the production of a certain grease while another petroleum company requires a high-grade stearic acid. There is considerable difference of opinion regarding the use of hydrogenated and nonhydrogenated fatty materials. A detailed study of these differences might disclose the reasons and provide justification for the differences, but this will not be attempted here.

Disregarding the decreasing number of grease manufacturers who knowingly manufacture and sell lubricating greases of inferior quality, there is a growing tendency to use high quality fatty material in the production of all greases. It is doubtful that edible fats of the very highest quality fatty material would produce superior greases. Certainly the increase in quality would not justify the increased price of the highly selected and refined fats, fatty oils, and derivatives.

Continental Oil Company's practice is believed to be representative of that of other petroleum companies which produce high quality lubricating greases. Continental carefully avoids purchase of cheap fatty materials that are available from desiccating companies, reclaimers of refuse fatty material, recovered garbage "grease," and the like, all of which are often referred to as "yellow grease." There are very sound reasons for not using these materials in grease manufacture, namely:

1. The finished grease would not be acceptable to a discriminating purchaser because of odor, color, and appearance.
2. The successive purchases are so variable in quality that the laboratory and process department must conduct a comprehensive research program on each batch of fatty material to establish product specifications and manufacturing procedures.
3. The expense of sales resistance, cost of complaint adjustments, and extraordinary costs as indicated above nullify the apparent economy of using a poorer quality, cheaper fatty material than is required for the production of a quality product.

Continental Oil Company's present grease manufacture consumes whole fats and fatty acids in the ratio of about one to nine, respectively. Cottonseed oil fatty acid is satisfactory for the production of many greases, whereas stearic acid is more suitable for others. The soaps of these two types of fatty acid are different in character and contribute different character to lubricating greases. By hydrogenation, the chemically unsaturated fatty materials are converted into suitable substitutes for chemically saturated fatty materials used in grease manufacture. For reasons not wholly understood, it is not always possible to substitute a hydrogenated material for a fatty material that is naturally chemically saturated. It is customary to investigate the feasibility of such changes in the chemical laboratory, then in semicommercial grease manufacturing equipment. Before commercialization, product specifications and manufacturing procedures must be prepared and accepted by the laboratory, process, and sales departments. Special technical supervision of the initial commercial batches is necessary with new product specifications and new manufacturing procedures.

The authors' experience has been that an investigation of all these steps must be made in substituting a given fatty product obtained from one manufacturer for the same product from another manufacturer. Sometimes such substitution may be made without any difficulty; but again, for reasons not wholly understood, it is not always possible. These difficulties probably arise due to a lack of complete understanding of all of the factors involved in manufacturing the fatty material and the significance of variable characteristics in employing the fatty material for grease manufacture. The problem is an important one, since most purchasing agents want at least three sources of supply of any commodity purchased. Continued cooperative effort between the technical men of the two industries should ultimately lead to a solution of mutual advantages to both industries.

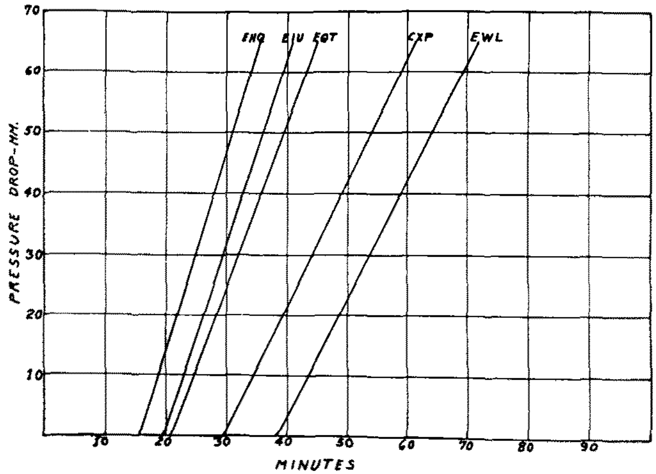

Figure 8 — Oxygen Absorption Tests on Greases Shown in Table VIII

Oxidation Stability

An immediate problem to which the technical men of both industries may devote some attention is the stability of greases.

One of the most important characteristics of a grease is its stability in storage and service. One of the prime factors is the resistance of grease to the action of atmospheric oxygen under the conditions of storage and use. Greases may oxidize only slightly in use but during storage acquire a brown crust which is objectionable both in service and sales. Since it is desirable to know in advance what this behavior will be, numerous accelerated oxidation tests have been devised (19). A simpler, faster oxygen absorption test which may be applied to fats, fatty oils, and finished greases is here presented for the first time. As in all such tests, it is to be remembered that the conditions are accelerated and hence never those of actual storage and use. Caution is therefore necessary in applying the results to predictions of future behavior.

The apparatus consists of a Sligh (20) flask used for testing the oxidation characteristics of lubricating oils modified by the substitution of a standard taper female joint at the top so that the flask over-all is 200 mm. high. Five grams of the grease to be tested are introduced into the flask by means of a glass tube filled with the grease and having a close-fitting glass rod serving as a plunger to deliver the grease into the bottom of the flask. Water is removed by means of a vacuum at as low a temperature as possible. Air is replaced by oxygen, and a manometer is attached by means of springs. The manometer is of the open type, having a standard taper male joint at the bottom and a capacity of about 350 mm. of mercury pressure. The assembly is immersed in a constant temperature bath. The pressure is read and recorded at five-minute intervals. Figure 6 shows how the pressure changes with time. It rises to a maximum of about 300 mm. due to the thermometric effect and after a time begins to drop as the oxygen is absorbed. The test is continued until the pressure drops 60 mm. from the peak pressure developed.

The constant temperature bath is best held at a temperature depending on the materials under investigation. In order to obtain time periods suitable for comparisons, a temperature of 300° F. for greases and 210° F. for fats and fatty oils may be used. The tests on fatty components of greases shown both in Fig. 7 and Table VII were run at 210° F.

Sample No. 1 was normal in the usual physical tests but gave considerable difficulty in manufacture and in appearance and yield of the finished grease, but Nos. 2 and 3 were satisfactory. All three of these samples were submitted as equivalents by three manufacturers.

Oxygen absorption tests on greases run at 300° F. are shown in Fig. 8 and Table VIII. Greases requiring less than 50 minutes to show an oxygen pressure drop of 60 mm. in this test or less than B in the oven test have been unstable in storage and unsatisfactory in use because of darkening and crust formation.

The oven stability test has been employed for grease stability studies for a number of years but has never proved entirely satisfactory. From Table VIII it will be noted that this test failed to point out a product that did oxidize and underrated an excellent batch of grease.

Conclusion

The use of fats, fatty oils, and derivatives is extensive in the petroleum industry to improve its lubricants in their wetting ability or oiliness. Fats and their derivatives serve to carry active elements such as chlorine, sulfur, and phosphorus for the improvement of load-carrying capacity, resistance to oxidation, inhibiting corrosiveness, and preventing wear during use. Greases are compounded from whole fats and fatty acids which serve under suitable conditions to gel lubricating oil and thus fulfill lubricating requirements which the liquid oils cannot themselves satisfy. Greases and their components may be tested for skin hardening in storage by means of an oxygen absorption test which distinguishes between satisfactory and unsatisfactory ingredients and products.

REFERENCES

1. Thompson, National Petroleum News, **28,** No. 6, 29 (1936).
2. Archbutt and Deeley, "Lubrication and Lubricants," Fifth Edition, Charles *Griffin and Company, Limited,* 1927, p. 17.
3. Wells and Southcombe, British Patent, 130, 377 of February 5, 1918; U. S. Patent 1,319,129 of October 2, 1919; Mexican Patent 18,915 of February 5, 1918; Canadian Patent 196,215 of January 20, 1920.
4. Herschel, Bull. 112, Am. Instrument Co. (1929); Chem. and Met. Eng., 28, 302 (1923).
5. Lincoln and Henriksen, U. S. Patent 1,994,941 of January 30, 1934.
6. Wolf and Mougey, Proc. A.P.I., **13,** (III) 118 (1932).
7. Wooler, J. Soc. Automotive Engrs., **35,** 229 (1934).
8. Lincoln and Henriksen, U. S. Patent 2,087,803 of July 20, 1937; Bray, More and Merrill, Oil and Gas Journal, 37, No. 5, 47 (June 16, 1938).
9. Lincoln and Steiner, U. S. Patents 2,113,810-1 of April 12, 1938.
10. Lincoln and Byrkit, U. S. Patents 2,157,078-9 of May 2, 1939.
11. Lincoln and Henriksen, U. S. Patents 1,939,979 and 1,939,993-5 of December 19, 1933; 2,074,338 of March 23, 1937; and 2,157,134 of May 9, 1939.
12. Lincoln, Steiner and Henriksen, U. S. Patent 2,137,777 of November 22, 1938.
13. Lincoln and Henriksen, U. S. Patent 1,959,054 of May 15, 1934.
14. Lincoln, U. S. Patent 1,945,614 of February 6, 1934.
15. Ralston, Pool and Harwood, U. S. Patent 2,053,045 of September 1, 1936; Ralston, U. S. Patent 2,125,851 of August 2, 1938.
16. Ralston and Christensen, U. S. Patent 2,033,543 of March 10, 1936.
17. Klemgard, "Lubricating Greases: Their Manufacture and Use," Reinhold, New York, 1937.
18. Farrington and Davis, J. Ind. Eng. Chem., **28,** 414 (1936).
19. Wright and Lutz, Product Eng., 7, 210 (1936).
20. Clayden, Proc. A.S.T.M., Thirtieth Annual Meeting, Part 1, page 460 (1927).