THE PREPARATION OF GREASE FROM THE
LIGHT METAL SOAPS OF NAPHTHENIC ACID TYPE
PETROLEUM DERIVATIVES

by

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preface</td>
<td>1</td>
</tr>
<tr>
<td>Lubricating Theory</td>
<td>3</td>
</tr>
<tr>
<td>Grease Preparation</td>
<td>6</td>
</tr>
<tr>
<td>The Evaluation of Greases</td>
<td>10</td>
</tr>
<tr>
<td>Naphthenic Acids</td>
<td>13</td>
</tr>
<tr>
<td>Experimental Preparation</td>
<td>16</td>
</tr>
<tr>
<td>Evaluation of the Aluminum-Magnesium Naphthenate Greases</td>
<td>26</td>
</tr>
<tr>
<td>Conclusions</td>
<td>37</td>
</tr>
<tr>
<td>Bibliography</td>
<td>39</td>
</tr>
<tr>
<td>Appendix</td>
<td>42</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.</td>
<td>Curve of Variation of Grease Viscosity with Oil Content</td>
<td>25</td>
</tr>
<tr>
<td>Figure 2.</td>
<td>Diagram of Evaluation Apparatus</td>
<td>27</td>
</tr>
<tr>
<td>Figure 3.</td>
<td>Final Evaluation Apparatus</td>
<td>28</td>
</tr>
<tr>
<td>Figure 4.</td>
<td>Prony Brake</td>
<td>29</td>
</tr>
<tr>
<td>Figure 5.</td>
<td>Curve of Variation of Temperature of Several Lubricants with Time</td>
<td>31</td>
</tr>
</tbody>
</table>
THE PREPARATION OF GREASE FROM THE LIGHT METAL SOAPS OF NAPHTHENIC ACID TYPE PETROLEUM DERIVATIVES

PREFACE

In the preparation of this thesis I have given a brief resume of the present theories of lubrication, accenting the phases which were particularly applicable to the research problem. I have also given a summary of the methods most commonly used at present for the preparation of lubricants. These summaries are naturally brief and I make no pretense that they are complete. It is hoped that enough material has been included on these topics to make the assumptions and methods of the experimental work understandable.

My experimental work has been entirely with the aluminum and magnesium soaps of the naphthenic acids. I first attempted methods of preparation that are in general use at present in the manufacture of greases. After finding that these methods were more or less unsatisfactory, I devised several methods of my own for the preparations.

It is believed that the methods using the basic salts of the metals as saponifying agents are completely original. These methods were found satisfactory and far superior to the methods which the literature indicates are common practice.
The research problem was fundamentally that of preparing the greases by improved methods, but it was felt that the work would not be complete without at least an effort to evaluate the greases that had been prepared. It would be a hopeless task, worthy of several theses, to evaluate accurately all of the greases prepared. I therefore decided to limit the evaluation to the greases which by their visible properties indicated that they were the most likely to be good lubricants.

By the evaluation method finally decided on, the greases which were tested proved superior to commercial lubricants marketed for the same use as is recommended for my aluminum-magnesium naphthenate greases. Apparatus to make complete tests was not available, but I believe that the indications given by my tests warrant a much more complete study of the greases.

It is believed that the aluminum-magnesium naphthenate grease composition is one that has never before been prepared and evaluated. A patent has been applied for on this grease composition.
The word "lubricant" has come into common usage as a word which means a substance that is capable of reducing friction between bearing surfaces in relative motion. Unfortunately, however, the factors that cause this reduction are not so easily defined. The first attempt to explain the principles of lubrication was made by Reynolds in 1886 (2, p.1-3). He was working with oils and bearings and came to the conclusion that the lubricating oil film might be of "sufficient thickness to enable the problem to be understood from a hydrodynamical standpoint..." Reynold's work was well done, and his theory was universally accepted as the explanation of all lubrication until comparatively recent times. This theory has come to be called the "hydraulic wedge theory." However, as machinery design became more and more complex, it was found that although Reynold's theory was a partial explanation of lubrication, there was much about the subject that was not clearly understood. In many lubrication problems, especially in connection with gears, it became apparent that the pressures on the bearing surfaces were so high that under such conditions the theory of hydraulic pressure maintaining an oil film in place was not tenable.

It was obvious that some force, much stronger and of a different character than hydraulic force was keeping
a layer of lubricant between the bearing surfaces in such cases. The logical corollary was that the force was an intermolecular force, that of adhesion or adsorption, which are closely related. Weiser states that, "The principle involved in lubrication consists in the maintenance of an adsorbed layer of an easily deformable substance... on each of the two solid surfaces so that they are prevented from coming into contact," (25, p.68). While most authorities do not believe that adsorption is the only factor in the efficacy of a lubricant, it is generally believed that adsorption along with the "hydraulic wedge" give a more or less complete picture of lubrication (23, p.10). It is apparent that the hydraulic force is the most important factor in bearing where the clearances allow the "hydraulic wedge" to operate, but that adsorption is the chief force in the maintenance of the oil film in gear lubrication.

The lubrication of bearings has ceased to be a great problem. Excellent lubricating oils are now on the market for all types of bearings. The more recent advancements in oils have been to improve the lasting properties, ability to operate at high temperatures, detergent properties etc., rather than actually improving the quality of lubrication.

The case is not the same, however, when it comes to gear lubrication (9, p.134; 27, p.162+; 28, p.28).
The introduction of the hypoid gear in recent years has caused a great flurry among grease manufacturers in a search for satisfactory lubricants. In hypoid gears, individual pressures as high as 400,000 pounds per square inch with a sliding velocity of 1800 feet per minute have been noted (26, p.206). It is apparent that the lubrication of this gear will require a lubricant which is very strongly held to the tooth surfaces and which will stand up under very extreme conditions in general. For the lubrication of this type of gear, highly complex mixtures of soaps, oils, and inorganic compounds have been introduced by the various manufacturers. These have come to be called extreme pressure lubricants. Some of the compounds added have been sulfur chloride, chlorinated wax, thioether, tricresyl phosphate, naphthalene tetrachloride and others (17, p.138). However, work has only begun on this phase of lubrication and there remains much to be desired to improve the performance of hypoid gear lubricants.

From the foregoing it may be concluded that there is a need for improved extreme pressure lubricants. It appears certain that they must be of a composition that is strongly adsorbed by the gear teeth. Since hydrocarbon oils are not strongly adsorbed (25, p.69), some sort of grease composition is indicated as the solution of the problem.
GREASE PREPARATION

Lubricants can be arbitrarily divided into two classes, oils and greases. Most lubricating oils are derived from petroleum and are more or less complex mixtures of the various saturated hydrocarbons. Additives of many types have been used to improve the properties of these oils. Greases are usually considered to be mixtures of the hydrocarbon oils with soaps. The greases are usually a gel formation with a lower melting point than the oils. As it is the latter with which this thesis deals, it is considered desirable that the methods generally used in grease manufacture be discussed.

For many years the manufacture of greases was considered an art rather than a science (9, p.129), and, even at the present time, many of the grease formulas are trade secrets that have never been published or patented. In general, greases are a mixture of mineral oil and a soap of one of the higher molecular weight fatty acids. Stearic acid is the most commonly used (9, p.134).

When greases were first made, it was for the purpose of putting oil in a more solid form (9, p.132) so that it could be applied to surfaces which would be difficult to lubricate by oils because of their fluidity. Little thought was given to the nature of the thickening
agent, the soap. It is unfortunate that even at present many grease consumers still retain their old idea that grease is nothing but an oil in a more solid form. Actually many greases have desirable lubricating properties that are derived from the constituent soap rather than the oil (6, p.R589-R590). Weiser (25, p.68) has presented a formula which he claims estimates the value of a lubricant. His formula is based entirely upon the adsorption theory. Its constants are derived from the degree of adsorption of the lubricant. He states that fatty acids and other polar compounds such as soaps are much more strongly adsorbed than are paraffin hydrocarbons. Hence from Weiser's formula one could claim that the oil in the grease has little effect on the value of the lubricant, but that the nature of the soap is all-important. While Weiser's theory is not used extensively in grease preparation, the truth of the matter remains that the nature of the soap is a very important consideration in the preparation of a grease.

In spite of these facts, the majority of the greases on the market are currently made from the soaps of stearic acid or its homologs. Most of the research in the field of grease preparation has been with the cation of the soaps rather than the acid (9, p.129). There is no doubt but that the various metals do impart many varying properties to greases in which they are
incorporated. They affect the viscosity, the temperature coefficients, the solubility, the stability, and many other properties of the grease. Little work has been done using the various acids which would theoretically be of great importance in regulating the properties of the grease. Naphthenic acids, which will be discussed more fully later, have been used in a few cases in grease manufacture, (16, p.127-133, 180-181) but comparatively little work has been done with them.

The method of preparation of greases varies with the type of soap that is to be used (16, p.114). The lime and sodium soap greases are usually made by a separate preparation of the soap base and the later addition of the mineral oil. Aluminum greases are usually made by the following process (3, p.781-784; 4, p.R424-R427). The acid is saponified with sodium hydroxide, the oil is added and this mixture brought to a temperature slightly below the boiling point of water. A solution of aluminum equivalent to the sodium hydroxide is added all at once. This mixture is cooked until the aluminum grease has separated from the water in the vat. The mixture is cooled and the grease repeatedly washed to remove the inorganic salt formed in the metathesis. The water is then removed from the grease by evaporation. It can be seen that in many cases, especially where emulsions are formed, that the removal of the inorganic salts presents
quite a problem (5, p.46). Other insoluble soaps are often made by this method, although they are sometimes made by direct saponification with the metallic bases (8, p.1). The chief difficulty in the latter process is that many of the hydroxides are very insoluble and others are difficult to prepare.
THE EVALUATION OF GREASES

The evaluation of greases was a difficult problem at the beginning of the science of lubrication and remains a problem today. Although hundreds of devices to evaluate lubricants have been invented and used (6, p.215-234; 26, p.206-229), the fact remains that the only reliable test is the actual use of the lubricant in the machinery for which it was designed (3, p.781-784; 14, p.465).

It was not until 1938 (24, p.25-26) that any real attempt to classify greases was made. At that time the National Lubricating Grease Institute adopted the standard penetration test for the consistency of greases. The A.S.T.M. now has a complete set of standards for classifying greases (1, p.1-574). These include penetration, which shows the consistency of the grease; drop point, which is an indication of the melting point of the grease and other standard tests which are used for evaluation of petroleum products such as color, flash point, corrosion etc. However, it is evident that these classification tests give no indication of the actual lubricating properties of the grease (14, p.R465).

Some of the evaluation methods attempt to classify greases by the temperature rise of the bearing or gear in operation (21, p.22). Others measure amount of wear
and still others measure the amount of the grease consumed. Some methods attempt to incorporate all of these measurements in the same test.

The fact remains that no apparatus has been designed that will accurately predict the performance of a grease under different conditions (20, p.501; 26, p.226-229). The four ball machine was highly lauded for some time as an accurate method for evaluating gear lubricants, but exhaustive tests have shown that some very good gear lubricants fail in this test, while other comparatively poor lubricants pass the test (43, p.R551; 26, p.226-229). With any of the extreme pressure evaluation devices, the Almen, Timken, S.A.E. and others, the results are the same.

The Army, Navy and other big grease consumers have practically abandoned laboratory tests for evaluation of greases and have turned to actual service conditions as the only reliable procedure (20, p.501+).

In conclusion, the following statement is quoted from Kraus (16, p.111-112), "... it is now obvious why such lubricants can be passed on as to their suitability by means of the practical shop test. This conclusion, arrived at as a result of long experience, is not intended to deprecate in any way the part of importance of testing machines occupy in the laboratory.... Instruments will reveal characteristic tendencies and bring
out behavior of such lubricants in a manner which will often furnish leads towards the subsequent improvement of such greases."
NAPHTHENIC ACIDS

Naphthenic acids are cyclo-monocarboxylic acids found in most crude petroleum oils. They occur in various American crudes in quantities ranging from 0.03% to 0.30% (10, p.1063). The naphthenic acids are recovered as a by-product of petroleum refining in the acid wash process and in some of the solvent refining processes (10, p.1064; p. 1066).

At least eight different naphthenic acids have been identified (19, p.770-777). They are 2-methyl cyclopentane carboxylic acid, 3-methyl cyclopentane carboxylic acid, 2-3 dimethyl cyclopentane acetic acid, cyclohexane acetic acid cis 2,2,6 trimethyl cyclohexane carboxylic acid, cyclopentane carboxylic acid, cyclopentane acetic acid, and 3-methyl cyclopentane acetic acid. There are undoubtedly a much larger number of these acids, but their similar chemical structure makes them difficult to separate and identify. They are commonly marketed simply as "naphthenic acid" with the acid number specified. In this experimental work, various commercial naphthenic acid mixtures were used. Specifications for the acids used are given in the Appendix.

The naphthenic acids obtained from different crude oils vary considerably in physical and to some extent chemical properties. Those used in this work varied from
light oily fraction with an acid number of 174 to a solid tar-like fraction with an acid number of 97. The acid used in the final preparation had an acid number of 163.

All of the naphthenic acids studied were readily saponifiable. Their saponification reactions were not materially different from those of the high molecular weight fatty acids.

Naphthenic acids have been used for a variety of purposes, the most important being in the manufacture of emulsifiers (9, p.127), detergents (9, p.127), waterproofing compounds (10, p.1088) and greases (9, p.127). Only the sodium and lead soaps have been used to any extent in the preparation of greases.

The aluminum soap is a brown rubberlike compound. It has been used as a rubber extender (3, p.783). It is miscible in all proportions with ordinary lubricating oils with which it forms a very stable gel (5, p.400-401). The aluminum naphthenate lubricating oil gel has been used as a lubricant (6, p.1).

Magnesium naphthenate is a hard, dark brown amorphous solid. It is soluble in all proportions in mineral oils. It has been studied and used to very little extent.

The method commonly used for making aluminum and magnesium greases from naphthenic acids is the same as that previously described for aluminum greases in general.
It is extremely difficult to remove the inorganic impurities from aluminum naphthenate or aluminum naphthenate greases prepared in this manner (5, p.400-401).

Since it is generally accepted that high molecular weight compounds are more strongly adsorbed than low molecular weight compounds and that branch chains and molecular complexity also increase the adsorption (25, p.68-76), it follows that naphthenic acid soaps should be especially desirable in the preparation of lubricants. Unfortunately the strong gel that the aluminum naphthenate forms with lubricating oils makes this mixture undesirable as a general purpose gear lubricant. If, however, an additive can be used that inhibits the gel formation without adding undesirable properties, an excellent gear lubricant should result.
EXPERIMENTAL PREPARATION

The method first attempted to prepare aluminum naphthenate was essentially the same as that commonly used to prepare aluminum greases. A quantity of lubricating oil and naphthenate in a ratio of about three to one was heated in a casserole to about 140°F. Three normal sodium hydroxide solution was then added until the pH of the mixture was approximately six. The saponification took place immediately. This mixture was then heated to about 215°F and a quantity of three normal aluminum chloride solution, exactly equivalent to the sodium hydroxide, added all at once. The mixture was cooked for about five minutes during which an aluminum naphthenate, oil, and water emulsion separated from the bulk of the solution. It is believed that the following equation explains the reaction:

\[ 3 \text{ROO} \text{Na} + \text{AlCl}_3 = (\text{ROO})_3 \text{Al} + 3 \text{NaCl} \]

The emulsion formed in this preparation was a sticky mass not unlike used chewing gum in appearance. The water in the emulsion carried with it part of the sodium chloride formed in the metathesis, necessitating removal of the bulk of the water by some means other than evaporation. The only method previously used to eliminate the salt was "thorough washing" (5, p.400-401). It was first attempted to wash the gluey emulsion by
repeated agitation with large amounts of water. After
the washing was completed the emulsion was broken by
heating in an oven at 120°C for twelve hours. It was
found that no reasonable amount of washing by this method
would remove all of the sodium chloride. It was found
that washing by this method for three hours with re-
peated quantities of fresh water about four times the
volume of the grease did not remove enough of the sodium
chloride to make the resulting grease usable. Various
types of agitation, such as stirring, beating, shaking,
and agitation with air, were used with no effect on the
results. It thus appeared that washing with water was
impractical.

The next purification method which was attempted
was extraction with carbon tetrachloride, in which the
grease was soluble. The method satisfactorily removed
the water and sodium chloride, but all of the carbon
tetrachloride then in the grease could not be removed,
therefore this method was abandoned also.

The next method tried was electrodialysis. This
proved impossible because the water in oil emulsion
would not pass any measurable current even with poten-
tials as high as 500 volts.

It was then attempted to break the emulsion in
a centrifuge. When centrifuged for periods of five hours
at 18,000 RPM, the emulsion did not break although about
one-half of the water in the emulsion settled out.
Finally the centrifuge was used in four-hour stages.
The sodium chloride solution which settled in each stage was removed by decantation and replaced with pure water.
After four such stages, enough of the sodium chloride had been removed so that the decanted solution gave a very weak chloride test. This washed emulsion was heated in an oven at $120^\circ\text{C}$ for 12 hours. The resultant grease was not entirely free of sodium chloride, but it was believed that enough of the salt was removed to prevent any damage by it in the grease. This method was so laborious and expensive that it would probably be impractical as a commercial process.

A search was then in order to find a method of preparation which would introduce no foreign material that could not be easily removed.

A method that has been used is the direct saponification with a slurry of freshly precipitated aluminum hydroxide (8, p.1). This was attempted with slurries of aluminum hydroxide in both water and oil, using exactly the theoretical amount of aluminum hydroxide. Saponification did occur, but an appreciable quantity of the aluminum hydroxide aggregated into visible granules and did not react with the acid. No method was found to keep the particles from aggregating. It was found impossible to remove the granules of unreacted aluminum hydroxide.
Any filter fine enough to remove the particles was too fine to allow the gelatinous grease to pass.

Direct saponification of the naphthenic acid with the normal aluminum salts was found impossible.

It was finally attempted to saponify the naphthenic acid with basic aluminum acetate powder. The theoretical amount of the basic aluminum acetate was added to a quantity of naphthenic acid. This mixture was heated. Saponification started at a temperature of about 75°C. The heating was continued until a temperature of about 103°C was reached. At this temperature the water formed in the reaction boiled off. Heating was continued to about 130°C at which temperature all of the acetic acid and water had boiled off. It was found advisable when using crude mixtures of naphthenic acids to heat the mixture to about 150°C to make certain that any volatile impurities in the original acid were removed.

The reaction described above could be carried out either with or without the presence of the lubricating oil. In making greases it was found advisable to add the mineral oil before saponification. The grease prepared in this manner was homogeneous and free of impurities other than those present in the original naphthenic acid. It is believed that the reaction is according to the following equation.
\[ 3\text{ROOH} + \text{AlAc}_2\text{OH} = (\text{RO}_3\text{Al})_3 + 2\text{HAc} = \text{H}_2\text{O} \]

It is not definitely known that the tribasic aluminum naphthenate is formed in the above reaction. MacBain and McClatchie state that tribasic aluminum soaps do not exist (18, p.3257). They believe that, "Aluminum soaps are commonly a mixture of uncombined free fatty acid with either a monobasic or a mixture of mono- and dibasic soaps." It is believed that the tribasic aluminum naphthenate is formed in the above reaction because although the theoretical amount of the salt to form the tribasic soap was used, there was no evidence that unreacted salt remained in the grease. If any was present it was in such minute particles that it could not be observed. One explanation of the apparent disagreement with MacBain's extensive work is that his work was with the straight chain fatty acids from which he made the generalization for all aluminum soaps. Although the reactions of naphthenic acid are similar to those of the fatty acids, it is possible that the naphthenic radical is enough different in character to account for this difference. It is quite difficult to determine analytically the extent of the saponification (9, p.184) and no further efforts were made to clarify the point. The question is academic in any case.

It was found that by mixing a commercial three and one-half per cent aluminum naphthenate with oil,
greases exactly like those prepared in the above manner would result. Greases prepared by the two methods were used interchangeably in the tests with no difference in the results. The procedure used to prepare the grease from the commercial aluminum naphthenate was as follows:

The weighed aluminum naphthenate was broken into small pieces, the desired amount of mineral oil added, and the mixture heated to about 150°C and stirred thoroughly. A homogeneous clear mixture resulted after about five minutes of stirring at the elevated temperature.

In the preparation of magnesium naphthenate greases a similar procedure was followed. There are no commercially available magnesium naphthenates. The magnesium naphthenate was first prepared by the addition of a solution of a normal magnesium salt to a heated mixture of sodium naphthenate and mineral oil. Again it was found practically impossible to remove the inorganic salt formed in the metathesis. The grease prepared by direct saponification of the acid with a slurry of magnesium hydroxide again contained aggregates of the hydroxide that could not be removed.

It was found that basic magnesium carbonate would saponify the naphthenic acid directly. The reaction follows:

\[ 3\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 3\text{H}_2\text{O} + 4 \text{ROOH} = 4 (\text{ROO})_2\text{Mg} + 3 \text{CO}_2 + 6 \text{H}_2\text{O} \]

The carbon dioxide and water were completely expelled by
heating the mixture to 100°C. In practice this mixture was heated to about 160°C to remove any volatile impurities that may have been in the original naphthenic acid.

The magnesium naphthenate was a brown amorphous solid when cold. When heated it became an extremely sticky plastic mass. It was completely insoluble in water.

When the magnesium naphthenate was mixed with lubricating oil, there resulted sticky grease rather than the strong gel which the aluminum naphthenate formed.

All of the aluminum naphthenate greases prepared were very gelatinous and apparently not very satisfactory for any general type of lubrication. The magnesium greases were rather sticky and the indications were that it also would be of no particular value as a lubricant. Since the properties of the two greases were so different, it was decided to mix the two greases to see if there was any chance of the undesirable properties nullifying each other.

When mixed together in practically any proportions, a decided difference was noted in the grease. It was found that the gelatinous structure of the aluminum grease was somewhat broken, and the stickiness of the magnesium grease was not apparent in the mixture. The mixture was a clear, highly viscous liquid, very oily in feel and possessing all of the properties considered
desirable in a lubricant of the semi-grease type.

Since the composition of this grease would indicate that it would be strongly adsorbed to metal surfaces and since its viscosity could be easily adjusted to that of the commercial hypoid lubricants it was decided to attempt to evaluate this grease as a gear lubricant.

It was decided that neither the aluminum grease nor magnesium grease alone had as many possibilities as did the mixture. Neither would probably be of any value except for very special applications. As evaluation under even ordinary conditions is difficult, it was decided to limit the evaluation to the mixture.

Table I gives a summary of representative greases made of the aluminum-magnesium naphthenate mixtures.

It was found that mixtures with a ratio of aluminum naphthenate to magnesium naphthenate of about two or three had the best apparent properties. Lubricating oil was used in various amounts to control the viscosity of the lubricant. Figure 1 is a curve of the viscosity of the two to three mixture versus the per cent of SAE 30 lubricating oil.
<table>
<thead>
<tr>
<th>Grease</th>
<th>Aluminum Naphthenate</th>
<th>Magnesium Naphthenate</th>
<th>SAE 10 Mineral Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>40.0%</td>
<td>9.5%</td>
<td>50.5%</td>
</tr>
<tr>
<td>II</td>
<td>32.5%</td>
<td>16.5%</td>
<td>51.0%</td>
</tr>
<tr>
<td>III</td>
<td>25.0%</td>
<td>25.0%</td>
<td>50.0%</td>
</tr>
<tr>
<td>IV</td>
<td>13.2%</td>
<td>13.2%</td>
<td>73.6%</td>
</tr>
<tr>
<td>V</td>
<td>10.0%</td>
<td>18.0%</td>
<td>72.0%</td>
</tr>
<tr>
<td>VI</td>
<td>9.5%</td>
<td>14.0%</td>
<td>76.5%</td>
</tr>
<tr>
<td>VII</td>
<td>6.6%</td>
<td>8.4%</td>
<td>85.0%</td>
</tr>
</tbody>
</table>
FIG. 1. VISCOSITY OF 2-3 AL-Mg GREASES

VISCOSITY - SAYBOLT SECONDS UNIVERSAL

PER CENT SAE 30 OIL

50 76 78 80 82 84 86 88 90 92

100 150 200 250 300
It has been previously stated that it is difficult if not impossible to make laboratory tests to evaluate lubricants accurately. In order for the tests to be of value they must approximate actual service conditions.

The apparatus finally decided on is diagrammed in Figure 2 and illustrated in Figures 3 and 4. An Ohio speed reduction gear of the worm type was coupled by means of a V belt to an electric motor. The gear was a 20:1 reducer with a rated capacity of one-half horsepower. The worm of the reduction gear was made of steel and the bull gear of bronze. For the first trials a one horsepower motor was used, but later it was exchanged for a two horsepower motor.

It was decided to compare the aluminum-magnesium naphthenate greases with a commercial hypoid gear lubricant and with a light, SAE 10, lubricating oil. The former should be the best commercially available grease for the gear, and the latter should be a comparatively poor gear lubricant.

The first comparisons attempted were the measurement of the comparative temperature rise of the various lubricants in the operating gear. The gear was first run at no load with each of the lubricants. It was found that the data obtained by this method was extremely
FIG. 2 DIAGRAM OF EVALUATION APPARATUS

A WATT METERS
B 2 H.P. MOTOR
C RECORDING THERMOMETER
D OHIO 20:1 REDUCER
E PRONY BRAKE
FIG. 3 EVALUATION APPARATUS
FIG. 4 PRONY BRAKE
erratic. During some runs the light oil came to a final temperature lower than that of either of the other lubricants, while other runs with apparently the same conditions would reverse the results. All efforts to obtain reproducible results were to no avail.

The gear was then loaded to capacity by means of a Prony brake and the temperature rise measured in the same way. Again it was found impossible to correlate the data or reproduce results. With runs under identical conditions at times each of the lubricants including the light oil appeared to be the best. After extensive attempts to correlate the data with no success, the method of evaluation by temperature rise was abandoned. Data from various typical runs are plotted in Figure 5.

It was then decided to use the same apparatus and attempt to measure the extent of wear of the gear with the various lubricants. It appeared that this method should give an accurate indication of the lubricating efficiency. The best lubricant should allow the least wear on the gear. It was impractical to weigh the gears after each run; therefore, it was decided to analyze the various lubricants for copper after runs under identical conditions. The bronze gear, being the softer, should wear most rapidly and the amount of copper in the lubricant after the run should be proportional to the amount of wear of the gear during the run.
FIG. 5 GEAR TEMPERATURE AT 350W LOAD

1-SAE 10 Oil
2-Hypoid 90 Lubricant
3-Hypoid 90 Lubricant
4-Al-Mg Lubricant
5-SAE 10 Oil
Watt meters were put in the electrical circuit to determine any difference in power input between the runs. The Prony brake was adjusted for identical gear loads while using the several lubricants.

The method used for the copper analysis was as follows. The grease was drained from the gear and the gear washed out completely with a measured amount of carbon tetrachloride, the washings being added to the sample. An aliquot part of the sample was taken, precautions being taken that a representative sample was obtained. The sample was diluted with a large amount of tetrachloride to facilitate filtering. The diluted sample was then filtered through a thick asbestos mat. The asbestos mat was then treated with about ten milliliters of concentrated nitric acid. This solution was neutralized with an excess of ammonium hydroxide and then boiled to remove the excess ammonia. About fifteen milliliters of glacial acetic acid was then added and the solution brought to the boiling point, after which it was cooled to room temperature. About fifteen milliliters of 30% potassium iodide solution was then added. The solution was allowed to stand for several hours and then titrated with a solution of sodium thiosulfate, previously standardized with copper foil that had been carried through the same process used for the grease.
This method of evaluation proved successful. Sample data are given in Table II. In all cases the greatest wear was observed when the light oil was used. This was as might have been expected. In all cases the least wear took place when the aluminum-magnesium naphthenate lubricant was used. The differences in wear between the commercial hypoid lubricant and the aluminum-magnesium naphthenate lubricant were in general small, while much greater wear was observed when the light oil was used.

This proved that the aluminum-magnesium naphthenate lubricant was superior to the commercial hypoid lubricant for use in the gear in question. It indicated but did not prove that the aluminum-magnesium naphthenate grease would be superior in general as a gear lubricant. In order to prove the latter it would have been necessary to run extensive tests in a commercial hypoid gear.

The runs made for the above tests were of three hours' duration with a constant load of approximately 300% of the rated capacity of the gear. No appreciable differences in input power were noted with the different lubricants. One twenty-four hour run was made with the commercial hypoid lubricant and with the aluminum-magnesium naphthenate grease. Samples from these runs were tested for change in viscosity and change in color. The change in color is often used as an indication of the
TABLE II

REPRESENTATIVE DATA FROM GREASE EVALUATION TESTS

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Gear Load</th>
<th>Duration of Run</th>
<th>Lubricant Tested</th>
<th>Grams Copper in Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2 H.P.</td>
<td>3 hrs.</td>
<td>Hypoid #90</td>
<td>0.00099</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SAE 10 Oil</td>
<td>0.00135</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Grease VII</td>
<td>0.00090</td>
</tr>
<tr>
<td>2.</td>
<td>1 1/2 H.P.</td>
<td>3 hrs.</td>
<td>Hypoid #90</td>
<td>0.00033</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SAE 10 Oil</td>
<td>0.00120</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Grease IV</td>
<td>0.00030</td>
</tr>
<tr>
<td>3.</td>
<td>1 1/2 H.P.</td>
<td>24 hrs.</td>
<td>Hypoid #90</td>
<td>0.00240</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Grease VI</td>
<td>0.00207</td>
</tr>
</tbody>
</table>

Note: Analyses of greases IV, VI, and VII are given in Table I.
ability of the grease to stand up without sludge formation. The viscosity of the commercial hypoid lubricant changed from 16.6 to 15.2 seconds Saybolt Furol at 212°F. The viscosity of the aluminum-magnesium naphthenate grease changed from 35.8 to 36.2 seconds Saybolt Furol. The color of the commercial hypoid lubricant changed from 4+ diluted twice to 6 diluted twice by the ASTM Union Colorimeter test. The color of the aluminum-magnesium naphthenate lubricant remained unchanged at 7+ diluted once. These changes in physical properties indicate that the extreme conditions of the test changed the aluminum-magnesium naphthenate lubricant no appreciable amount, while the commercial hypoid grease was changed somewhat by the conditions of the test. These tests confirmed the wear test in indicating that the aluminum-magnesium naphthenate lubricant was superior to the commercial hypoid lubricant under the conditions of the test. Time did not permit comparison with other commercial brands of hypoid lubricant.
### TABLE III

**1. A.S.T.M. tests of aluminum-magnesium naphthenate greases.**

<table>
<thead>
<tr>
<th></th>
<th>Aluminum naphthenate-%</th>
<th>Magnesium naphthenate-%</th>
<th>SAE 30 mineral oil-%</th>
<th>Viscosity at 210° F- SSU</th>
<th>Color (Union Colorimeter)</th>
<th>Flash point (open cup)</th>
<th>Fire point (open cup)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.6</td>
<td>5.5</td>
<td>7.1</td>
<td>9.5</td>
<td>7 dil.</td>
<td>375</td>
<td>460</td>
</tr>
<tr>
<td></td>
<td>5.3</td>
<td>8.0</td>
<td>10.4</td>
<td>14.0</td>
<td>6 dil.</td>
<td>375</td>
<td>460</td>
</tr>
<tr>
<td></td>
<td>91.1</td>
<td>86.5</td>
<td>82.5</td>
<td>76.5</td>
<td>5 dil.</td>
<td>375</td>
<td>460</td>
</tr>
<tr>
<td></td>
<td>138.8</td>
<td>164.2</td>
<td>203.8</td>
<td>298.6</td>
<td>7 dil.</td>
<td>375</td>
<td>460</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**2. A.S.T.M. tests of unused lubricants compared with tests of same lubricants after twenty-four hour test run.**

<table>
<thead>
<tr>
<th></th>
<th>Hypoid 90</th>
<th>Hypoid 90</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>New</td>
<td>Used</td>
</tr>
<tr>
<td>Viscosity at 212° F- SSF</td>
<td>16.6</td>
<td>15.2</td>
</tr>
<tr>
<td>Color (Union Colorimeter)</td>
<td>4+ diluted twice</td>
<td>6 diluted twice</td>
</tr>
<tr>
<td></td>
<td>Grease IV</td>
<td>Grease IV</td>
</tr>
<tr>
<td></td>
<td>New</td>
<td>Used</td>
</tr>
<tr>
<td>Viscosity at 212° F- SSF</td>
<td>35.8</td>
<td>36.2</td>
</tr>
<tr>
<td>Color (Union Colorimeter)</td>
<td>7 diluted</td>
<td>7 diluted</td>
</tr>
</tbody>
</table>
CONCLUSIONS

In the progress of the research the following have been accomplished.

1. The methods generally used for the preparation of aluminum and magnesium greases were thoroughly investigated in the preparation of greases of aluminum and magnesium naphthenates. All of these methods were found to be unsatisfactory.

2. A new method of preparing aluminum naphthenate grease by saponification of naphthenic acid with solid basic aluminum acetate was developed.

3. A new method of preparing magnesium naphthenate grease by saponification of naphthenic acid with basic magnesium carbonate was developed.

4. It was discovered that the mixing of aluminum and magnesium naphthenate greases produced a lubricant that was different in its properties from either of its constituents, and apparently superior to both.

5. The aluminum-magnesium naphthenate grease mixture was tested in an apparatus that closely approximated actual service conditions. It was found to be superior to a commercial hypoid gear lubricant which should be the best commercially available lubricant for the apparatus on which the test was made.

The methods of saponification of the acid directly
by the use of the basic salts of the metals is believed to be new and not previously reported in the literature. The composition of a mixture of the aluminum and magnesium naphthenates as the soap constituent of a grease is also believed to be original. No work has previously been published in regard to this composition.

The methods of preparation of the new lubricants previously mentioned are believed to be economically feasible. The raw materials are comparatively cheap and no expensive apparatus is required for the process.

It is believed that further research in the field of naphthenic lubricants would be fruitful. The soaps of many of the other metals with naphthenic acids should be investigated as possible constituents of lubricants. The field is very new, and practically none of the naphthenates except sodium naphthenate have been investigated to any extent.
BIBLIOGRAPHY


APPENDIX

SPECIFICATIONS OF NAPHTHENIC ACIDS

I. Acids obtained from Oronite Chemical Co.

<table>
<thead>
<tr>
<th>Naphthenic Acid</th>
<th>D</th>
<th>H</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Number, Oil-included</td>
<td>174</td>
<td>100</td>
<td>97</td>
</tr>
<tr>
<td>Acid Number, Oil-free</td>
<td>190</td>
<td>177</td>
<td>186</td>
</tr>
<tr>
<td>Unsaponifiable Content (Wt. %)</td>
<td>9</td>
<td>43</td>
<td>47</td>
</tr>
<tr>
<td>Color (ASTM)</td>
<td>Black</td>
<td>Black</td>
<td>Black</td>
</tr>
<tr>
<td>Water Content (Wt. %)</td>
<td>Trace</td>
<td>Trace</td>
<td>0.4</td>
</tr>
<tr>
<td>Viscosity at 100°F, SSU</td>
<td>800</td>
<td>1200</td>
<td>-</td>
</tr>
<tr>
<td>Specific Gravity, 60°F</td>
<td>0.98</td>
<td>0.97</td>
<td>1.00</td>
</tr>
</tbody>
</table>

II. Acid obtained from Union Oil Co.

<table>
<thead>
<tr>
<th>Crude Naphthenic Acid</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Number, Oil-included</td>
<td>163</td>
</tr>
<tr>
<td>Unsaponifiable Content (Wt. %)</td>
<td>27.0</td>
</tr>
<tr>
<td>Oil Content (Wt. %)</td>
<td>22.7</td>
</tr>
<tr>
<td>Water Content (Wt. %)</td>
<td>4.3</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.96</td>
</tr>
</tbody>
</table>