(2) We have prepared the following new substances from aldehyde and substituted amines: 8-Nitro-2,6-dimethylquinoline; 6-chlor-2-methylquinoline; 5- (or 7) chlor-2-methylquinoline; 8-chlor-2-methylquinoline; 6-brom-2-methylquinoline.

(3) We have prepared one derivative of quinaldine, 8-chlor-2-methylquinoline, from an aromatic amine and glycol, using arsenic oxide as the oxidizing medium.

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# REVIEW.

## Lubricating Greases.[1]

BY P. H. CONRADSON.

A SATISFACTORY examination or analysis of lubricating greases is, to say the least, tedious and complicated, even in a laboratory suitably equipped for this class of work, and I can readily appreciate the feeling of practical chemists, whose main chemical work around this section of the country is anything but greasy, when your manager sends you a tub of "grease," asking you to analyze the same, and tell him what it is made of, and if it is good for anything, and perhaps how it is made.

Before entering upon the chemical analysis and discussion of suitable methods, it might be well, as a practical introduction, to say a few words about greases in general, so as to acquaint you with the multitudinous materials or substances that enter, and are more or less used in compounding the numerous kinds and classes of lubricating greases found in the market.

The market price for these greases varies all the way from 1½ cents up to 15 cents per pound, and naturally the grease manufacturer uses, and has to use, very cheap or inferior materials to enable him to manufacture and sell at a profit, at such low figures, as the prices of the cheapest grades indicate; hence, the materials used for such cheap compounds are, to a large extent, waste materials or residues from petroleum distillation, mixed with waste fatty substances, and cheap inert mineral matter of all kinds and descriptions. On the other hand, the more expensive greases are generally compounded from good, pure materials suitable for the purpose. However, it should be borne in mind that a cheap grease, that is, the price of the grease, may not be any indication whatsoever as to the suitability of the grease for certain work any more than it follows that a more expensive grease would be any more suitable for certain kinds of work.

[1] Read before the Pittsburg Section of the American Chemical Society.

In making an examination of a lubricating grease, a chemical analysis alone does not enable the chemist to form a proper conclusion as to the lubricating value of the grease as such, or in comparison with other greases, and that is just exactly what the practical manager wants us to tell him. Therefore, to make an intelligent and practical report, a further study of the grease in question is necessary. Some knowledge of the compounding or manufacturing greatly facilitates one in judging the quality of the grease. I will, therefore, briefly touch upon a few points that may be of interest or of value to you.

The lubricating grease question, when it comes to the comparative lubricating value of the various compounds in the market, is a rather difficult one to answer intelligently, unless one knows the special work or kind of machinery for which the grease or greases in question are intended. Like everything else, one kind or grade of grease cannot be made that would be equally good or suitable for all kinds of work or machinery; hence, to make fair comparisons between two greases, the essential point to bear in mind is primarily, "For what kind or class of machinery, to be lubricated, is the grease intended"?

Without going into any lengthy details as to the various kinds or classes of machinery for which the multitudes of greases, now in the market, are used, it will suffice to mention as extremes, the slow-running, heavy, hot, rolling machinery in iron and steel mills, and the comparatively light and fast-running electric motors. Naturally, a grease suitable for hot-neck journals in a rolling mill would not do at all for electric motors, and *vice versa*. Therefore, as said above, to give an intelligent opinion as to the lubricating value of any grease in comparison with another grease or set of greases the kind or class of machinery and work must be known and taken into account as a basis for comparison, together with the chemical composition and physical properties or behavior of the grease or greases.

The various greases on the market may be divided, as regards chemical, physical and mechanical composition, into four main groups or classes, and each one of these in as many more subclasses or divisions: First, greases made with alkali soaps, as hardener or solidifier; second, greases made with fatty oil lime soaps; third, greases made with rosin oil lime soaps; fourth, greases made both with alkali and lime soaps.

Besides these there are greases containing magnesia, zinc, alumina and lead soaps. The greases in each of these main groups vary greatly in composition, both in kind, quality and percentages of the various ingredients entering into the compounds. They may contain from "none" up to 50 or 60 per cent. of bad, good or indifferent mineral matter, such as clay, chalk, soapstone, graphite, lime, talcum, etc.; from practically no *water* up to 20 or

30 per cent.; from 4 or 5 per cent. up to 50 or 60 per cent. of soaps; from no free fatty oils up to 40 or 50 per cent. petroleum oils of better or poorer quality, petroleum residues, rosin oils, coal-tar oils, etc.

The grease in consistency may be soft, medium, or hard, with softening- and melting-points varying from 90°-100° to 400°-450° F. From the above you will readily appreciate the variety of greases or solid lubricants now for sale on the market, some good, some indifferent, and some unsuitable for the purpose for which they were intended.

As an intermediate class of lubricants, between the real solid greases and fluid lubricants (oils), we may consider the so-called solidified oils; they have or should have a soft jelly-like consistency, which should not vary much, if any, within reasonable temperature ranges, that is, they should retain their normal solid consistency within practical working temperature limits.

Having in the above briefly called your attention to the rather complex compounds that you may be called upon to examine, I will now proceed to describe the method or methods I use in my work, and find to be more or less satisfactory from a practical and technical point of view. I say practical and technical, because to make a complete and accurate chemical analysis of some of the greases would be a very thankless and very tedious task, unless you were requested to make a grease exactly similar in composition and behavior.

I generally submit lubricating greases to the following tests and analyses, which enables me to form a pretty good idea about the quality and composition of the same.

### PHYSICAL TESTS.

(1) Consistency of the grease, soft, medium or hard.

(2) Color, dark or light, etc.

(3) Odor, tarry or asphaltic or resinous, etc. Oftentimes the odor of the grease gives quite an indication as to the nature of at least some of the materials that may be present, principally tarry matter and rosin oils.

(4) Softening-point, the temperature at which the grease begins to become soft, when carefully warmed or heated.

(5) Incipient melting-point, the temperature at which the grease begins to partially melt, oftentimes with separation of the oil or fatty matter from the soap and mineral matter.

(6) Melting-point, the temperature at which the grease is completely melted.

(7) Flashing-point, the temperature at which inflammable vapors are given off, indicated by applying a small flame.

(8) Burning-point, the temperature at which the grease begins to burn, when flame is applied.

(9) Note if the grease foams or swells and spatters during heating; this indicates the presence of more or less water.

Some greases, when heated to make the above tests, foam or swell much, until the water is driven off; others remain quiet and melt uniformly; others again partly melt at a comparatively low temperature, with the separation of the soaps in solid lumps, or the settling out of the mineral matter to the bottom of the vessel.

It is well to carefully note the behavior of the greases in these respects, as the practical value of a lubricating grease to a large extent depends upon how it acts when heated, or when coming in contact with hot boxes, journals or brasses, or how high a temperature it will stand before it begins to decompose or separate out.

A grease that stands a good or high temperature, before melting or separation of the ingredients or compounds, is naturally much better adapted for some work than a grease that separates readily when warmed or heated, other things being equal.

## CHEMICAL TESTS.

(1) Put 10 grams grease into a 300 cc. wide-necked Erlenmeyer flask, add 50 to 75 cc. 88° Bé. gasoline, break up or disintegrate the grease with a glass rod, then add 200 cc. more gasoline, shaking well at intervals several times; allow to stand and settle, pour off or siphon off the clear, supernatant liquid without disturbing the precipitate, and, if necessary, filter; to the remaining contents in the flask add 100 to 125 cc. 88° gasoline, shake, allow to stand and settle, pour off the clear liquid, transfer the insoluble portion in the flask to a sufficiently large filter, let drain, rinse out flask with 88° gasoline, and wash contents on filter a couple of times, or until the gasoline goes through practically colorless, and allow to drain.

(2) Evaporate the mixed gasoline extracts, best in an ordinary tinned iron drinking-cup, to small bulk, transfer to a small weighed beaker, evaporate on steam- or water-bath until practically constant weight. The residue in the weighed beaker will contain all the oils in the grease.

(3) The insoluble contents on the filter from the above gasoline treatment, after draining off the gasoline (keep funnel covered), but before beginning to dry, is transferred to a weighed dish, in case the residue has a light color, *i. e.*, appears to be free from tarry or asphaltic matter, insoluble in the gasoline, and dried to practical constant weight, as described later in (4). If the residue is dark and contains tarry matter, transfer it back to the Erlenmeyer flask, and add a mixture of 20 cc. strong ethyl ether and 10 cc. chloroform, digest at ordinary temperature with frequent

shaking, transfer contents in flask to same filter, allow to drain and rinse out the flask with some of the ether and chloroform mixture, allow to drain.

(3*a*) Evaporate the ether-chloroform extract in a weighed dish on a steam- or water-bath. This will contain the tarry and asphaltic matter insoluble in gasoline, and possible traces of soaps.

(4) Transfer the insoluble portion from the ether-chloroform treatment to a weighed dish, dry first at low temperature on top of the air-bath, then in the air-bath with gradual rise of temperature, from 200° to 250° F., until practically constant weight. The dried residue contains all the mineral matter, if any is present, and the insoluble soaps.

(5) The weight of this (4), with the weight of the asphaltic matter, if present, and the oils found in No. 2, added together and subtracted from 100 gives the amount of water present by difference (also, of course, any small amount of oil volatilizing at 212° F., a temperature necessary to use to drive off the last of the gasoline from the oils).

(6) *Mineral Matter.*—In stirring up the grease in No. 2 with the gasoline and giving the contents in the flask a rotary motion, it is very easy to see if any free mineral matter is present, as the soaps generally are quite flocculent and stay suspended in the gasoline some little time, while the heavy, dense, mineral matter settles quite rapidly, so that a good idea as to the kind and amount can readily be formed. If the amount of mineral matter noticed be very small, merely a trace, it comes from the slaked lime or soda used in compounding the grease, and can be neglected.

(7) If mineral matter be present in a larger amount, put 5 grams grease into flask, add 100 cc. of a mixture of 30 cc. spirits turpentine, 30 cc. 74° Bé. benzine and 70 cc. alcohol. This mixture becomes perfectly clear and uniform when warmed a little. Put flask on steam- or water-bath, connect with return condenser, boil gently, shaking occasionally until the grease is dissolved, except the mineral matter. This mixture will dissolve by gently boiling all the soaps, fats and oils. Lower the heat so as to stop boiling, allow to stand a few minutes, then filter rapidly while hot into another flask, transfer insoluble matter to filter, wash once or twice with the above mixture (hot).

(8) The insoluble portion on the filter contains all the free mineral matter; finish off the washing with some benzine, and, lastly, with some alcohol, dry and weigh, and, if so desired, determine the character of the mineral matter. Add the benzine-alcohol washings to 9 after the soaps are decomposed.

(9) The filtrate in the flask contains all the soaps and oils in the grease. Put the flask on steam- or water-bath, connect with return condenser, heat until the liquid becomes clear, then add 2 or 3 grams oxalic acid, either in dry form or dissolved in a

little alcohol, boil, and shake well for some time; the oxalic acid will decompose the soaps, forming insoluble oxalates with the oxides, which thus can be readily separated and determined by well-known methods.

(10) In case the grease is free from mineral matter, then, of course, this procedure can be omitted, and the dry soaps (4) from the first gasoline treatment carefully ignited, and the bases determined.

The flashing- and burning-points of greases will indicate whether a high-fire test oil is used. The consistency of the separated oils will indicate whether a thin, fluid, or heavy, thick petroleum oil is used. In so-called cup greases, neutral light-colored petroleum oils or paraffin oils are generally used; in cheap mill greases, dark-colored or black petroleum oils or residues are generally used.

(11) The above-described method is simple enough, and for all practical purposes answers quite well; however, for a more accurate and complete analysis some additional work is necessary.

First, in the gasoline treatment a little of the lime and magnesia soaps will generally disoslve (the soda soaps are practically insoluble),and if zinc, aluminum and lead soaps should be present, a considerable amount of these would dissolve; however, as a rule, these three latter soaps would hardly occur, except in special greases; therefore, the separated and weighed oils will usually only contain a little lime and magnesia soaps.

Second, the separated oils from the gasoline treatment, after weighing, should be saponified to determine the amount of free fatty oils, if any, whether rosin oil is present or not, tar oil, and the quality of petroleum oils used.

Third, in some alkali soap greases free caustic and carbonate of soda may occur, even though free saponifiable fats are found.

If present in larger amounts than negligible, they should be determined.

(12) The separation of oils from the small amount of soaps, dissolved in the gasoline treatment, may be effected either before or after the separated oils are weighed.

In the former case, evaporate the gasoline mixture (2) down to 50 or 75 cc., transfer to a conical glass-stoppered separatory funnel, add 0.5 to 1 gram dried oxalic acid, dissolved in 10 cc. strong alcohol, shake repeatedly for some time, allow to stand and settle. If any soaps should be present, a precipitate of oxalates will form; add 20 cc. water to the funnel, shake well, allow to settle, draw off the watery liquid, and wash the contents in the funnel two or three times with water, add the washings to the first watery liquid, and evaporate to dryness and determine the amount and kind of oxides in the oxalates, and then calculate the amount found to corresponding soaps, using oleic acid as a standard factor, and add this amount to the weight of insoluble soaps from the first gasoline treatment.

(13) Transfer the remaining gasoline liquid in the separatory funnel to a small weighed beaker, evaporate on steam- or water-bath until constant weight, this gives the percentage of oils plus the free fatty acids from the decomposed soaps.

(14) Transfer the weighed oils, after noting the consistency, color, etc., of the same, by means of 88° gasoline to a 300 cc. saponifying flask, and add 50 cc. neutral strong alcohol, and a few drops phenolphthaleïn, neutralizing with standard potash solution, noting the number of cubic centimeters used, from which the amount of free fatty acids, due to the decomposed soaps, can be calculated, and subtracted from the weight of the oil in the beaker.

(15) Saponify the oils in the flask (14) with standard alcoholic potash, according to any of the well-known methods, such as described in Allen's and Lewkowitsch's "Chemical Analyses of Fats, Oils and Petroleum." After separating and determining the amount of saponifiable fats present, the quality and kind of non-saponifiable oils can be examined according to methods also described in the above works.

(16) To determine free caustic and carbonate of soda in greases, methods described under soap analyses by Allen and Lewkowitsch can be followed.

I find the following simple method quite satisfactory in most cases: Extract 5 or 10 grams of the grease with 88° gasoline, as described under No. 1; dry the insoluble residue containing the free alkalies, if any, in the same flask in which the extraction was made, to free from water. Add 50 to 100 cc. strong neutral alcohol and warm until the alkali soaps are dissolved, filter, and wash with strong, warm neutral alcohol. Add phenolphthaleïn to the united alcoholic solutions and, if alkaline, titrate with fourth-normal hydrochloric acid, calculate the amount of free caustic alkali from the number of cubic centimeters of acid used. Treat the insoluble residue from the alcoholic treatment with water, and filter. Add methyl orange to the filtrate; if alkaline, titrate with fourth-normal hydrochloric acid, and calculate the amount of alkali carbonate from the number of cubic centimeters of acid used. If the grease should also contain lime soaps, it is well to ascertain if free caustic lime is present.

### QUALITATIVE TESTS FOR ROSIN OIL.

I have found the following simple method quite satisfactory to ascertain whether or not rosin oil is present in greases.

To 10 grams grease in a wide-necked flask add 25 cc. strong alcohol, break up the grease completely with a glass rod, and digest for a while at a gentle heat (80° to 90° F.), with frequent shaking; allow to settle, pour off the liquid on a dry filter, and add 25 cc. more strong alcohol to the flask, and repeat the treatment.

To the united, filtered alcoholic extracts add a little phenolphthaleïn as indicator, and add one-fourth normal potassium hydroxide in slight excess. Evaporate down to expel all the alcohol, stir up the residue with 25 to 30 cc. 88° gasoline, allow to settle, pour off the clear supernatant liquid, or filter, evaporating the clear liquid to free the same from gasoline. The residue will contain most of the rosin oil, if present, with a little mineral oil, and can readily be used for necessary identification tests for rosin oils, as described by Allen and Lewkowitsch, and others, such as (1) *Renard's Test.*—Rosin oil, 10 to 12 drops, treated with anhydrous stannic chloride or stannic bromide (1 drop), develops a beautiful violet coloration.

(2) *Liebermann's Test.*—Some of the above residue is shaken with a little acetic anhydride at a gentle heat; after cooling, the acetic anhydride is drawn off by means of a pipette, and tested by adding 1 drop of strong sulphuric acid. If rosin oil be present, a fine violet coloration is produced. Besides these tests, the gravity, taste and odor, especially on warming the residue, readily give evidence of presence of rosin oil. Of course it is always well at the same time to make a comparative blank test, using mineral oil somewhat similar in nature to the mineral oil found in the grease.

ANALYSES OF SAMPLES OF GREASES.

| | No. 1. | No. 2. | No. 3. |
|---|---|---|---|
| Color | Dirty yellow | Dark | Dirty yellow |
| Odor | Rosin | .... | Rosin |
| Consistency | Very soft | Hard | Medium |
| Softening-point | .... | 225° F. | 160° F. |
| Melting-point | Flows at 85° F. | 415° F. | 250° F. |
| Flashing-point | 385° F. | 540° F. | 350° F. |
| Burning-point | 450° F. | ...... | 400° F. |
| Soda soaps | ...... | 53.17 % | ...... |
| Lime, magnesia soaps | 5.68 % | ...... | 13.12 % |
| Mineral or hydrocarbon oils | 91.95 % | 32.32 % | 84.90 % |
| Water | 2.37 % | 14.51 % | 2.00 % |
| Gravity of separated oil | 23.5° Bé. | ...... | 23.0° Bé. |
| Free mineral matter | ...... | Little graphite. | Trace lime |

*Behavior on Heating.*—Greases foam some on heating. Nos. 2 and 3 have a tendency to separate into oil and lumps of soap.

The mineral oil in No. 2 is a thick, heavy, at ordinary temperature nearly solid, dark-colored oil.

Mineral oils in Nos. 1 and 3 were yellow-colored. These two latter greases are compounded with rosin oils.

FRANKLIN, PA., February 1, 1904.