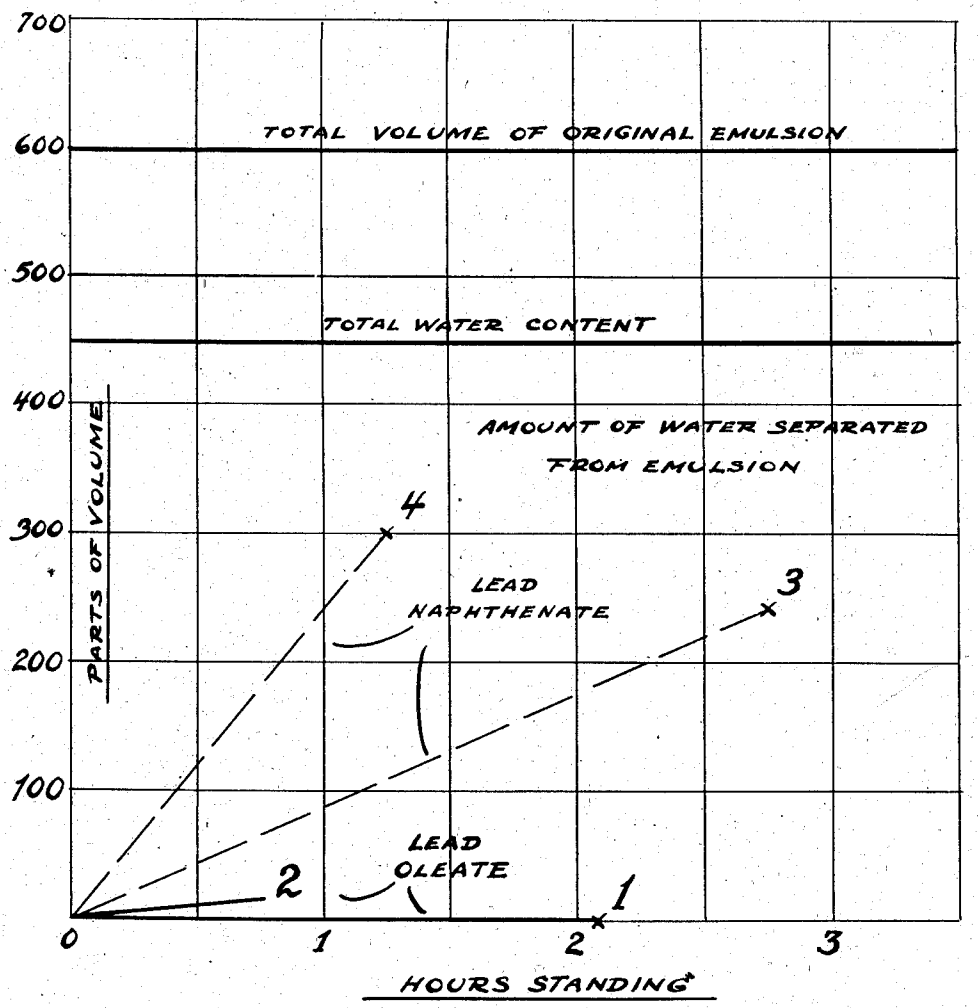
Oct. 30, 1945. M. RESWICK 2,388,083

LUBRICANT

Filed April 5, 1941



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Patented Oct. 30, 1945 2,388,083

UNITED STATES PATENT OFFICE

2,388,083

LUBRICANT

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Application April 5, 1941, Serial No. 387,008

6 Claims. (Cl. 252—37)

This invention relates to novel lubricants and to methods of preparing and using same.

There are many industrial uses for lubricants where the lubricating composition comes in contact with water or other aqueous fluids which tend to wash away the lubricant by emulsification or otherwise, thereby impairing lubrication performance. This is especially true, for instance, in steel mills where the approach tables on hot strip mills are subjected to a spray of high pressure water used for cleaning the scale off the hot rolled steel. This water gets into the roll bearings and gear cases and emulsifies with the lubricant, causing it to overflow and gradually become more dilute until eventually it is insufficient for lubrication.

The present invention has for one of its primary objects the preparation of lubricants which have water-repellent properties which make them especially suitable for lubrication of machinery operated either in water, or in continuous or at least occasional, contact with water. Another object of this invention is to prepare lubricants not only having water-repelling properties but also having extreme pressure lubricant characteristics, by which is meant the ability to lubricate metal parts which move in contact with each other under extremely high pressure or heavy loads. Another object of this invention is to prepare lubricants of the above types which are especially resistant to water which contains high amounts of acid and mineral salts or other materials which normally promote emulsification of mineral oil and water, as, for instance, is the case with the water in the Monongahela River near Pittsburgh, Pennsylvania, which contains considerable amounts of iron and calcium and varying amounts of free acid (mostly sulfuric, probably from coal mining and steel pickling operations). Samples of Monongahela River water taken in the vicinity of Homestead, Pennsylvania, over a period of a year, show the following ranges in analysis (expressed in grains per gallon):

Total acidity	0.3 to [1] 3.1
$FeSO_4$	0.1 to 0.4
$Al_2(SO_4)_3$	0.1 to 2.3
Hardness	3.5 to 10.6

[1] In two instances when the total acidity was 3.1, the free acid was found to be 0.4 and 0.5.

Another sample of Monongahela River water analyzed more in detail as to mineral constituents showed the following analysis:

Iron, per cent (as Fe_2O_3)	0.009
Calcium, per cent (as CaO)	0.004
Magnesium, per cent (as MgO)	0.0005
Sodium, per cent	0.002
Sulfate ion, per cent	0.0132
(Equivalent as sulfuric acid, per cent)	0.0135
Chloride ion, per cent	0.0022

Broadly, the invention comprises a mineral lubricating oil base stock with a heavy metal naphthenate soap and a small amount of hydroxy aromatic compound. More specifically the invention may be illustrated by a lubricant comprising a major proportion of mineral lubricating oil, about 15% of lead naphthenate and about 2% of cresol.

The mineral lubricating oil base stock to be used may be obtained from any of the crude petroleum stocks normally used such as the paraffinic base oils, e. g., Pennsylvania crudes, naphthenic base oils, e. g., California and Venezuelan, and mixed base oils, e. g., West Texas and other Mid-Continent crudes. Although the viscosity index of the lubricating oil does not appear to be a critical factor as far as the present invention is concerned, the viscosity index should be between the approximate limits of 0 and 150, and usually between the limits of about 30 and 100. The particular stocks used may be separated from the crude petroleum by any of the methods commonly used including distillation, extraction with various solvents, e. g., phenol liquefied sulfur dioxide, etc., having a selective solvent action for aromatic and unsaturated hydrocarbons, etc., and the fractions obtained may be subjected to

any desired refining or purification steps such as acid-treating, soda washing, clay treating, etc. The proportion of the mineral oil in the finished lubricant will, of course, depend upon the amount of soap and other addition agents used and should normally range between the approximate limits of 70 and 98%, and usually between the limits of 80 and 95%. Suitable lubricating oil base stock fractions may have Saybolt viscosities ranging between the approximate limits of 35 to 200 seconds at 210° F., or about 100 to 10,000 seconds at 100° F.

The soap to be used should be one derived from a heavy metal such as lead, tin, barium, antimony, etc. Heavy metals selected from groups II, IV, and V of the Mendeléeff Periodic Table are preferred, and of all the metals included within the above scope lead is preferred as the most suitable. The acids to be used in preparing these heavy metal soaps should be naphthenic acids, preferably derived from petroleum stocks and they should preferably be obtained from fractions having a boiling range at least as high as that of kerosene or lubricating oil cuts, although in some cases one may use naphthenic acids obtained from lighter cuts, such as the naphtha fraction. The desired naphthenic acids are those containing at least one cyclic nucleus and preferably contain more than 8 carbon atoms. They are usually mono-carboxylic acids corresponding to the general formula $C_nH_xO_2$, where n is an integer between the approximate limits of about 8 and 23 and ranges between $2n$ and $2n-4$.

The soaps of the present invention, such as lead naphthenate, are quite different from the corresponding heavy metal soaps of high molecular weight, substantially straight-chained aliphatic carboxylic acids, such as lead oleate, as will be more fully discussed and illustrated later. The amount of heavy metal naphthenate to be incorporated in the lubricant according to this invention will vary according to the desired load-carrying capacity and the conditions under which the lubricant is to be used, but will ordinarily range between the approximate limits of 5 and 25% by weight of the finished lubricant and usually between the limits of about 5% to 20%. However, it should also be pointed out that if it is desired to have so-called extreme pressure lubricating characteristics in the lubricant, the amount of heavy metal naphthenate should be substantially over 10%, e. g., 12% or preferably 15%, although in some cases even 18 or 20% may be required to impart sufficient load-carrying capacity. Usually 12 to 15% of lead naphthenate in a mineral lubricating base stock will enable the compounded lubricant to carry a 43-pound load on the Timken lubricant testing machine.

The hydroxy aromatic compound which is added according to the present invention for improving the water-resistant or water-repellent properties of the lubricant, should preferably be a hydroxy aromatic hydrocarbon and should preferably be a hydroxy aromatic compound having a water-solubility less than about 5 grams per 100 cc. of water at 20° C. This limitation distinguishes phenal (which may be considered the simplest member of the hydroxy aromatic class) from cresols and other higher molecular weight members of the class having a more complicated chemical structure. Phenol is ordinarily too soluble in water for the best operation of this invention although under some circumstances, as for instance with some particular type of mineral oil base stock and with some particular type of heavy metal soap of some particular fraction of naphthenic acids, or perhaps where the conditions of use tend to prevent solubility in water, as for instance under low temperature operating conditions, phenol itself may be utilized. Ordinarily, however, one or more of the cresols (ortho-, meta- and para-) are preferred. The para-cresol is the best from the point of view of lowest solubility in water, but from a practical point of view a commercial mixture called "tricresol," which contains derivatives of benzene having one methyl group and one hydroxyl group by having them in different positions around the benzene nucleus, is preferred because it is available on the market at relatively low cost. If desired, other hydroxy aromatic compounds may be used such as alpha-naphthol or beta-naphthol or other alkyl, e. g., methyl, ethyl, propyl, butyl, amyl, etc., derivatives of hydroxy aromatic compounds containing one, two, or more cyclic nuclei which may be either condensed nuclei as in naphthalene or linked through a single bond as in the case of diphenyl. Such compounds may also contain two or more hydroxy substituents provided that the water-solubility and oil-insolubility are not so high as to prevent the desired water-repellent characteristics desired for the present invention. These compounds may, if desired, also contain other known hydrocarbon substituents, for example, amino groups as in the case of para-amino phenol, benzyl para-amino phenol.

The amount of hydroxy aromatic compound to be used for imparting the desired water-repellent properties according to this invention will depend upon a number of factors, such as the kind and amount of heavy metal naphthenate used and the particular type of chemical structure of the hydroxy aromatic compound itself, as well as upon the type of mineral lubricating oil base stock and the operating conditions under which the lubricant is to be used. Ordinarily, however, the amount required would be between the approximate limits of 0.1% and 5% and usually between narrowed limits of 0.5% and 3%.

Although the three above-mentioned ingredients, namely, mineral lubricating oil, heavy metal naphthenate soap and hydroxy aromatic compound are the three primary constituent lubricants prepared according to this invention, minor amounts of other addition agents known to the art may also be incorporated. For instance, thickeners may be used, especially such as high molecular weight solid polyisobutylene, which has the additional advantage of improving the adhesiveness of the lubricant, or in other words, of imparting additional stringiness. Other dyes may be used, and also small amounts of oxidation inhibitors may be added, although the hydroxy aromatic compounds used according to the present invention for the purpose of obtaining desired water-repellent properties, may also have oxidation inhibiting characteristics.

The products of this invention are useful for many different industrial applications. For instance, in addition to lubrication of the hot strip mill approach tables mentioned previously, they may also be used for lubricating the bearings in a cold roll mill for fabricating steel products, as well as for other uses such as submerged gear and bearings in marine vessels, paper mill machinery, etc.

That the present invention obtains unexpectedly useful results is indicated by the fact that it

has been known for many years that lead oleate will substantially improve the load-carrying capacity of mineral lubricating oils for use in lubricating gears and bearings operating under heavy load pressure (but it has been known that lead oleate lubricants will absorb moisture and form an emulsion with water to a substantial degree and that this characteristic, although desirable in some instances, is a disadvantage in most cases). The prior art has, therefore, generally recommended that when using a lead oleate lubricant of any type, one should make sure that it will not come in contact with water. ("Iron Age," September 24, 1931, page 816).

On the other hand, it has already been suggested in the prior art, in Patent No. 2,031,986, to use a small amount of phenolic substance in a lubricating oil containing 1 to 10% of a heavy metal fatty acid soap, such as lead oleate, as a solubilizing or stabilizing agent to prevent such soaps from settling out after long standing. For that purpose the phenol is much more effective than higher molecular weight phenolic compounds, such as cresol, xylenol, or alpha-naphthol, because to stabilize 4% of lead oleate in a certain lubricating oil stock having a viscosity index of 85, only 1.5% of phenol was required whereas 2% of cresol and 3% of either xylenol or alpha-naphthol were required.

Now the heavy metal naphthenates of the present invention are unexpectedly superior to the oleates referred to above, because they are soluble in practically all mineral lubricating oils, regardless of the viscosity index, whether high or low, and needs no addition agent either to solubilize or stabilize blends thereof, as required in the case of lead oleate, particularly with high viscosity index oils. It should also be noted that when increasing amounts of lead oleate are used, the amount of solubilizing or stabilizing agent must likewise be substantially increased, but on the other hand, when the lead naphthenate of this invention is used, increasing the amount thereof apparently does not require any hydroxy aromatic compound to stabilize solution in the oil but also actually works better than smaller amounts thereof for the purposes of the present invention, namely, as a water-repellent lubricant, in the presence of a given small amount of hydroxy aromatic compound.

The objects and advantages of the invention will be better understood from a consideration of the following examples, which are given for the purpose of illustration and without the intention of limiting the invention specifically thereto.

Example 1

A gear lubricant was prepared using the following proportions and materials by weight:

	Per cent
Lead naphthenate	5.00
Heavy mineral oil A[1]	69.75
Light mineral oil B[2]	23.25
Cresol	2.00

[1] Viscosity about 170 seconds Saybolt at 210° F., viscosity index about 35.
[2] Viscosity about 60 second Saybolt at 210° F., viscosity index about 70.

The lead naphthenate used was prepared from naphthenic acids derived from a light lubricating oil fraction of California crude petroleum. A small sample of the above composition was churned with water in a laboratory mixing apparatus and after settling for about 24 hours, it was found that nearly all of the water picked up by the lubricant during the churning had dropped out as a separate layer, thus showing that the lubricant had very substantial water-repellent characteristics. Accordingly a larger sample of this product was used for lubrication of the roller bearings and gears on one of the approach table drives on a hot strip mill in a large steel plant and it was found to shed water effectively, which was automatically drained off by differential gravity, "water legs," or valves. Further experiments on a laboratory scale showed that 1% of cresol in the above composition was effective as a water-repellent agent.

Example 2

Another gear lubricant was prepared using the following compositions or materials:

	Per cent
Lead naphthenate	15
Cresol	2
Heavy mineral oil A	70
Light mineral oil C[3]	13

[3] Viscosity about 40 seconds Saybolt at 210° F., viscosity index about 28.

This compounded lubricant had a viscosity of about 110–120 seconds Saybolt at 210° F., and was found to shed water very satisfactorily when used as a gear lubricant on a hot strip mill, the same as in Example 1, and had the additional advantage of extreme pressure lubricating characteristics.

Example 3

In order to demonstrate the unexpected superiority of lead naphthenate, as compared to lead oleate, the following test results are set forth.

A series of four lubricants were prepared by using a mineral oil base stock having a viscosity index of about 40 and a viscosity of about 70 seconds Saybolt at 210° F. Test No. 1 contained 10% lead oleate as the soap ingredient but no cresol. Test No. 2 contained the same amount of lead oleate but contained 2% of cresol; this composition, therefore, corresponds to that recommended in the patent previously referred to, namely, Patent No. 2,031,986 (although the patent states that ½% of phenol is better for solubilizing and stabilizing purposes than 2% of cresol, and, in fact, with an oil of the viscosity index used here no addition agent is necessary for solubilizing or stabilizing the lead oleate. Test No. 3 contained 5% lead naphthenate and 2% of cresol, and Test No. 4 contained 12½% of lead naphthenate with 2% of cresol. The procedure followed in these tests was to weigh 150 grams of each lubricant in a one-liter breaker and add 150 cc. of Monongahela River water three times at intervals of five minutes, the mixture being churned in a Mix-master at approximately 900 R. P. M.

Through out the tests observations were made as to the thickening of the mixture, any change of color, and also whether the added water was absorbed by the lubricant (by which is meant, becoming emulsified, or, at any rate, so finely divided and dispersed within the lubricant that it had the appearance of a true emulsion). After the third addition of water had been churned into the lubricant, the sample was permitted to stand for a substantial length of time to determine the amount and rate of water separation from the emulsion.

The results of the above tests are tabulated in the following table and the amount of water separated is shown graphically on a chart in the accompanying drawing.

Table

Test No.	Percent soap: Oleate	Percent soap: Naphthenate	Cresol, percent	1st 150 cc.: Thickening	1st 150 cc.: Color change	1st 150 cc.: Water absorption	2nd 150 cc.: Thickening	2nd 150 cc.: Color change	2nd 150 cc.: Water absorption	3rd 150 cc.: Thickening	3rd 150 cc.: Color change	3rd 150 cc.: Water absorption	Standing time: Hour	Standing time: Minutes	Water separation
1	10	------	----	Slight	None	All	Appreciable.	Brown after 2½ min.	All	Heavy emulsion.	No further change.	All	[1] 2	5	None.
2	10	------	2	None	do	do	Slight after 3 min.	Brown after 3 min.	do	Heavy after 3½ min.	do	do	------	44	Only slight.
3	----	5	2	Began to thicken.	Brown	do	----------	----------	Not taken up.	----------	do	Not taken up.	2	45	2 layers: top 60% lub. bot. 40% water.
4	----	12½	2	None	Dark brown	do	Stringy	Lighter	Partly taken up	----------	do	do	1	15	2 layers: top 50% lub. bot. 50% water.

[1] 4th 150 cc. added but was not all absorbed after 5 min. additional churning.

These four tests show that both of the samples containing lead oleate not only absorbed all of the water in all three additions, but also the resultant emulsions which were so stable that little or no water was separated therefrom during the period of observation. A comparison of tests Nos. 1 and 2 indicates that the 2% of cresol was not effective in preventing the water absorption and had only very slight effect in accelerating the separation of water from the resultant emulsion. On the other hand, in both tests Nos. 3 and 4 where lead naphthenate was used instead of lead oleate only the first addition of water was completely absorbed, the third addition was not at all absorbed in either case, and the second addition of water was only partly taken up in test No. 4 containing 12½% of lead naphthenate but not at all taken up in test No. 3 containing 5% of lead naphthenate. Likewise, tests Nos. 3 and 4 both showed a fairly rapid separation of water when the mixture was allowed to stand, since in test No. 3 after 2¾ hours of standing two layers were formed, consisting of a bottom water layer representing 40% of the total volume and an upper lubricant layer representing 60% of the total volume; whereas, test No. 4 showed a still more rapid separation, namely, a 50% water and 50% lubricant separation after only 1½ hours. The chart showing these water separation test results demonstrate graphically the very great superiority of the lead naphthenate in tests Nos. 3 and 4 as compared to the lead oleate in tests Nos. 1 and 2.

In all of the examples discussed above, the lead naphthenate used was prepared from naphthenic acids obtained from a California (naphthenic base) petroleum fraction falling within the gas oil boiling range. The cresol used in all of the above examples was a semi-refined commercial product called "tri-cresol" which consists of a mixture of the ortho-, meta-, and para- forms of cresol. In each case the lead soaps were first added to the mineral oil and the cresol added last.

Although the invention has been found applicable to cases where the lubricant had to come in contact with water containing fairly large amounts of acids, mineral salts, etc. which tend to promote emulsification, it is conceivable, of course, that there may be limits to the amount of such emulsification-promoting impurities which can be counteracted or overcome by the use of the water-repellent extreme pressure lubricants of this invention.

In the appended claims the expression "heavy metal naphthenate" is intended to mean a naphthenate of a metal at least about as heavy as tin.

It is not intended that the invention be limited to any of the specific examples given nor unnecessarily by any theory as to the mechanism of the operation of the invention, but only by the appended claims by which it is intended to claim all novelty inherent in the invention.

I claim:

1. A lubricant comprising a major proportion of mineral lubricating oil, about 5–25% by weight of a lead soap of naphthenic acids containing at least one cyclic nucleus, and a small amount of a hydroxy aromatic hydrocarbon having a water-solubility less than about 5 grams per 100 cc. of water at 20° C.

2. Lubricant according to claim 1 containing about 0.1 to 5% of cresol.

3. An extreme pressure lubricant comprising a major proportion of mineral lubricating oil, more than 10% by weight of a lead naphthenate and a small amount of a hydroxy aromatic compound having a water solubility less than about 5 grams per 100 cc. of water at 20° C.

4. An extreme pressure lubricant comprising a major proportion of mineral lubricating oil, more than 10% of lead soap of naphthenic acids containing at least one cyclic nucleus and derived from a petroleum fraction having a boiling range at least as high as kerosene, and about 0.5 to 3% by weight of cresol, the amount of the latter being sufficient to make the entire compounded lubricant substantially water-repellent.

5. The method of lubricating moving metal parts where the lubricant must at least come in contact with water, which comprises using as the lubricant a composition comprising a major proportion of mineral lubricating oil, at least 5% of a lead naphthenate and a small amount of hydroxy aromatic compound having a water solubility less than about 5 grams per 100 cc. of water at 20° C.

6. The method of lubricating moving metal parts which contact each other under extreme pressure and where the lubricant must at least occasionally come in contact with water, which comprises lubricating said metal parts with a composition comprising a major proportion of mineral lubricating oil, more than 10% by weight of lead naphthenate and about 0.5 to 3% by weight of cresol.

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