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## LUBRICANT

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This invention relates to chemically resistant lubricants, and more particularly to nitration-resistant lubricants.

Experience has shown that the lubricants used on pumps handling concentrated nitric acid or blends of nitric and sulfuric acids usually eventually become nitrated with the result that explosions often occur. In an effort to correct this condition numerous lubricants have been tested and found comparatively ineffective for preventing this nitration or unsuitable for other reasons. The lubricant for such pumps should preferably have a consistency corresponding to that of a petroleum jelly (which may be considered as a mixture of petrolatum wax and mineral oil) ranging from a soft to a barely plastic texture; however, petroleum jelly itself is not sufficiently resistant to nitration, even when refined to U. S. P. quality. Mineral white oil and paraffin wax, also refined to U. S. P. quality, are likewise not sufficiently resistant to nitration and also do not have the consistency required for the lubrication purposes in question. Other types of lubricants containing soaps, stearic acid, etc., are even less effective than the hydrocarbons of the petrolatum or paraffin wax type.

The primary object of the present invention is to prepare satisfactory nitration-resistant lubricants and also to prepare such lubricants having the proper consistency for use either alone or when impregnated in a suitable packing material, for lubricating pumps which handle nitric acid or mixtures thereof with sulfuric acid.

It has now been found that a nitration-resistant lubricant of proper consistency can be produced by blending together a major proportion of mineral white oil, a highly refined petrolatum wax and a polyisobutylene having a molecular weight of about 10,000 to 100,000.

To illustrate the invention some experimental data are given on a number of different compositions containing various amounts of polyisobutylene having a molecular weight of 12,000, 60,000, or 80,000, as indicated in the table, and an artificial or synthetic petroleum jelly containing about 78% by weight of heavy mineral white oil, 18% by weight of a substantially colorless petrolatum wax having a melting point of about 150–160° F., which had been decolorized by filtering through bauxite, and about 4% of paraffin wax of about 122° F. melting point, together in certain instances with the addition of an acid-resistant graphite. For comparison, the artificial petroleum jelly and paraffin wax were also tested alone.

These various compositions were subjected to an acid-reaction test, using in some cases nitric acid alone (98% concentration) and in other cases a mixture of 80% nitric acid (98% concentration) and 20% fuming sulfuric acid, to see whether there was any discolorization, fumes, or any other apparent sign of reaction, and these compositions were also subjected to an explosion test in a steel bomb.

This bomb test consisted of mixing 40% by weight per volume of acid, either nitric acid alone or a mixture of 80% nitric acid and 20% sulfuric acid, with 60% by weight of the lubricant to be tested. The mixing was done with a spatula and the mixture then placed in a steel bomb which in turn was placed on top of a lead crushing block about 2½" high and 1¼" in diameter. A No. 8 detonating cap was then placed in the grease chamber which is open at the top of the bomb; then on top of this was placed a steel cover weighing 6½ pounds. The detonating cap was exploded and the height to which the cover was blown was measured, as well as the amount of compression of the lead crushing block. Unless the cover was thrown to a height of over 10 feet or the lead crushing block was compressed more than 0.10 inch for the 8-pound cap, in the tests with the nitric acid alone, it was considered that the mixture gave no dangerous reaction, except in such cases where the reaction had been so violent during the mixing of the acid and the grease that most of the reaction took place before the mixture could be put in the bomb.

The results of this series of tests are shown in the following table.

TABLE 1

| Test No. | Artificial petroleum jelly | Polyisobutylene | | | Paraffin wax | Graphite | No. 8 cap | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 20% $H_2SO_4$, 80% $HNO_3$ | | | | 98% $HNO_3$ | | | |
| | | 12,000 | 60,000 | 80,000 | | | Color | Fumes | Comp. | Height | Color | Fumes | Comp. | Height |
| | | | | | | | | | *Inches* | *Feet* | | | *Inches* | *Feet* |
| 1 | 100 | | | | | | Brown | | .015 | 10 | Yel | | .347 | 25 |
| 2 | | | | | 100 | | | | .050 | 12 | | | .30 | 30 |
| 3 | 90 | 10 | | | | | Sl | | .012 | 10 | Sl | | .061 | 10 |
| 4 | 99 | | 1 | | | | Yel | Few | .076 | 12 | Yel | | .046 | 10 |
| 5 | 95 | | 5 | | | | Yel | | .057 | 10 | Yel | | .012 | 10 |
| 6 | 85 | | 5 | | | 10 | | | | | Sl | | .040 | 10 |
| 7 | 95 | | | 5 | | | | | | | Sl | | .032 | 10 |
| 8 | 90 | | | 10 | | | Sl | | .076 | 10 | Sl | | .034 | 10 |
| 9 | 80 | | | 10 | | 10 | | | .011 | 10 | | | .003 | 10 |

The above test data indicate that whereas the artificial petroleum jelly alone was not satisfactory for resisting nitration, the addition of 1 to 10% of polyisobutylene having a molecular weight ranging from 12,000 to 80,000 made the artificial petroleum jelly sufficiently nitration-resistant to be satisfactory.

It should also be noted in connection with the above tests that since the increase in viscosity of the synthetic petroleum jelly is directly proportional to the amount of polyisobutylene added and also directly proportional to the molecular weight of the polyisobutylene, 1% of polymer having a molecular weight of 80,000 will increase the viscosity of the artificial petroleum jelly almost as much as 10% (actually about 7 or 8%) of a polymer having a molecular weight of 12,000. Now, it is desired to have a non-fluid lubricant, i. e., one which is not fluid, at ordinary temperatures and yet which is soft enough or plastic enough to be pressed into the pump shaft bearings, etc.; and, therefore, it is obvious that the constituents must be compounded in such proportions as to produce a composition falling within these limits of consistency, which may be measured by A. S. T. M. penetration and Saybolt viscosity at 210° F. The approximate limits of the A. S. T. M. penetration should be as follows: 100 to about 300 unworked at 77° F., and preferably from about 150 to about 250; and the Saybolt viscosity should be from about 100 to about 500 seconds at 210° F., and preferably from about 200 to about 400. Because of this reason and also because the amount of nitration-resistant property imparted to the composition appears to be directly proportional to the amount of polyisobutylene added, more or less independently of the molecular weight, providing it is not below the minimum desired limit of about 10,000, it is preferable to use 10% of the 12,000 molecular weight polyisobutylene rather than the slightly more than 1% of the 80,000 molecular weight polyisobutylene which would give equivalent increase in viscosity. Similarly, 20% of the 12,000 molecular weight polyisobutylene would produce much better nitration-resistance than about 4 or 5%, of 60,000 molecular weight polyisobutylene which would give substantially the same increase in viscosity.

The functions of the various constituents of the composition of this invention may be summarized briefly as follows. The polyisobutylene serves, as explained above, primarily for increasing nitration-resistant properties of the composition. The petrolatum wax, by which is meant the substantially oil-free petrolatum wax itself, is necessary to give proper body or consistency to the composition; other fluid acid-resisting lubricants have been made heretofore, but they are not satisfactory for the present purposes which require a plastic but non-fluid lubricant. Petrolatum is also a valuable constituent because of its protopet structure, by which is meant that it has the characteristic of helping to hold the oil in the composition, i. e., the petrolatum helps to prevent the oil from running out of the composition. Finally, the mineral white oil, which is the major constituent of the artificial petroleum jelly used in the above described test, is necessary in order to impart proper softening or plasticizing characteristics, i. e., to obtain the proper consistency.

To further illustrate the advantages of the present invention, the results of a series of tests are reproduced herewith in Table 2 where a number of different individual materials and mixtures thereof were submitted to a nitric acid test which consisted in mixing 4 grams of concentrated (98%) nitric acid with 6 grams of the material contemplated for use as a lubricant. The acid and lubricant were mixed together and the mixture watched for signs of reaction. In cases where the acid and lubricant are immiscible, the mere fact that no reaction occurred does not necessarily mean that the substance being tested is acid resistant, as perhaps the lack of reaction is primarily due to lack of miscibility.

In this series of tests the white oil used was a viscous white oil having a viscosity of approximately 340 seconds at 100° F. The paraffin wax was an ordinary refined paraffin wax having a melting point of about 125° F. Two different kinds of petrolatum wax were used, of which the light colored one had a high melting point (about 150 to 160° F.) and was relatively oil-free (contained not more than 2 or 3% of oil); whereas the dark petrolatum had a melting point of about 155–165, an A. S. T. M. penetration of about 60–70, and contained about 10% of oil. The results of this series of tests are as follows:

TABLE 2

*Nitric acid reaction tests*

| Test No. | White oil | Paraffin wax | Light petrolatum | Dark petrolatum | Polyisobutylene | Remarks |
|---|---|---|---|---|---|---|
| 10 | 100 | | | | | Poor contact—no reaction. |
| 11 | | 100 | | | | Do. |
| 12 | | | 100 | | | Slight reaction. |
| 13 | | | | 100 | | Violent reaction. |
| 14 | 80 | 20 | | | | Poor contact—no reaction. |
| 15 | 80 | | 20 | | | Reaction. |
| 16 | 80 | | | 20 | | Extremely violent reaction. |
| 17 | | 50 | | 50 | | Violent reaction. |
| 18 | 67 | 8 | 25 | | | Do. |
| 19 | 67 | 8 | | 25 | | Extremely violent reaction. |
| 20 | 61 | 22 | 7 | | 10 | No reaction. |
| 21 | 61 | 22 | 7 | | 10 | Do. |

From the above table of data, it is noted that the dark petrolatum gave violent reaction, the light petrolatum gave a slight reaction, and the white oil and paraffin wax were inconclusive because they gave poor contact with the nitric acid. A mixture of 80% of white oil and 20% of paraffin wax likewise gave poor contact. On the other hand, a mixture of 80% of white oil and 20% of light petrolatum gave a reaction and a mixture of 80% of white oil and 20% of dark petrolatum gave an extremely violent reaction. A mixture of equal parts of paraffin wax and dark petrolatum gave a violent reaction. A three-component mixture (test 18) containing 67% of white oil, 8% of paraffin wax and 25% of light petrolatum gave a violent reaction; and replac-

ing the light petrolatum with dark petrolatum in that composition resulted in an extremely violent reaction, thus showing again that the dark petrolatum was much more reactive than the light petrolatum. A comparison of test 13 where 100% of dark petrolatum gave a violent reaction, with test 16 where only 20% of dark petrolatum mixed with 80% of white oil gave an extremely violent reaction, seems to indicate either that the white oil per se would be very reactive with the nitric acid if it were miscible therewith or that the white oil would permit much better contact between the dark petrolatum and the acid, which would mean that the fluidity of the mixture and the compatibility of the components are important factors if any one constituent is at all reactive. Likewise, by comparison of tests 13 and 17, it is observed that the replacement of half of the dark petrolatum by paraffin wax did not substantially reduce the intensity of the reaction. Finally, it is observed that in tests 20 and 21, compositions containing a major proportion of white oil and also about 22% of light petrolatum and a small amount of paraffin wax, together with 10% of polyisobutylene gave no reaction (in spite of the fact that the materials were miscible with nitric acid). This shows the powerful acid-resisting or nitration-resisting properties of the polyisobutylene.

*Test 22*

A nitration-resistant lubricating grease was made with the following proportions of materials, in per cent by weight:

| | |
|---|---|
| Viscous white oil | 70 |
| Light petrolatum wax | 16 |
| Paraffin wax | 4 |
| Polyisobutylene [1] | 10 |

[1] Having an average molecular weight of about 12,000 to 15,000.

This composition was found to have the following physical properties:

| | |
|---|---|
| A. S. T. M. penetration unworked (at 77° F.) | 227 |
| Saybolt viscosity at 210° F. seconds | 347 |
| Viscosity index | About 127 |

*Test 23*

Another composition was made similar to that described in Test 22, except that slightly less oil was used and the composition was found to have an A. S. T. M. penetration of 163.

For the purposes of lubrication for which the compositions of this invention are primarily intended to be used, the A. S. T. M. penetration, unworked (at 77° F.) should usually be between the approximate limits of 100 and 300, and preferably about 150–250; and the viscosity expressed in seconds Saybolt Universal at 210° F. should usually be between the approximate limits of 100 and 500, preferably about 200 to 400. Usually the V. I. (viscosity index) should be above 110 and preferably it should be above 120.

Although polyisobutylene was used in all of the above described examples, it is believed that other substantially saturated aliphatic hydrocarbon polymers having an average molecular weight of at least 10,000 can be used instead thereof, as for example, polymerized 2-methyl-butene-1, polyethylene, or aliphatic hydrocarbon copolymers, such as an isobutylene-ethylene copolymer made from a mixture containing about 60% or 70% of isobutylene and the balance ethylene.

As indicated above, the petrolatum to be used should be refined to make it light-colored as by clay filtering, and if desired may also have received an acid treatment, e. g., by the use of concentrated or fuming sulfuric acid, and preferably should be substantially oil-free (i. e., contaning not more than about 2% of oil), if it has not received an acid treatment. The white oil used should be, as is commonly meant by that term, petroleum oil which has been strongly acid treated, i. e., with concentrated, or preferably fuming, sulfuric acid.

It is believed obvious to those skilled in the art that the proportions of the polymer, petrolatum and white oil (together with paraffin wax, if any is used) may be varied substantially without departing from the fundamental principles of the invention, and the following table is given to show the general scope of the invention:

*Composition ranges (Per cent by weight)*

| | |
|---|---|
| Polymer, average mol. wt.: | |
| 10,000 | 10–25 |
| 12,000 | 8–20 |
| 30,000 | 7–15 |
| 80,000 | 5–10 |
| White oil | 50–85, preferably 60–80 |
| Petrolatum (substantially oil-free) | 10–50, preferably 15–30 |
| Paraffin wax | 0–10 |

In the above table it is to be understood that only one type of polymer is necessary in any particular composition, but the table showing four different molecular weights is given so that the proper proportion to be used may be determined according to the molecular weight of the polymer being used; if the polymer to be used has an average molecular weight, intermediate the various ones shown, the amount to be used may readily be determined by interpolation. Ordinarily, the mathematical product of the percent of polymer multiplied by the average molecular weight thereof should be at least 100,000, and preferably at least 120,000.

It is not intended that this invention be limited to any of the particular examples which have been given for the sake of illustration nor unnecessarily by any theories as to the operation of the invention, but only by the appended claims in which it is intended to claim all novelty inherent in the invention as broadly as the prior art permits.

We claim:

1. A chemically-resistant lubricant having approximately the following composition in percent by weight:

| | Percent |
|---|---|
| Mineral white oil | 50–85 |
| Petrolatum (light oil-free) | 10–50 |
| Paraffin wax | 0–10 |

and an amount of substantially saturated aliphatic hydrocarbon polymer selected according to its average molecular weight, indicated by the following table:

| Average mol. wt. of polymer | Per cent |
|---|---|
| 10,000 | 10–25 |
| 12,000 | 8–20 |
| 30,000 | 7–15 |
| 80,000 | 5–10 |

2. Lubricant according to claim 1 containing polyisobutylene, the mathematical product of the percent of polymer times the average molecular weight thereof being at least 120,000.

3. Lubricant according to claim 1 which when subjected to the bomb explosion test described, does not crush the lead supporting block more

than 0.1 inch when tested with concentrated nitric acid alone and a No. 8 detonating cap.

4. A nitration-resistant lubricant having approximately the following composition in percent by weight:

| | Percent |
|---|---|
| Polyisobutylene having an average mol. wt. of 12,000–20,000 | 10–15 |
| Mineral white oil | 65–80 |
| Light petrolatum | 15–30 |
| Paraffin wax | 0–10 |

5. A lubricant packing material suitable for pumps handling nitrating acids, which comprises chiefly acid-resistant Blue African asbestos impregnated with a nitration-resistant lubricant defined in claim 1.

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