# United States Patent [19]

**Souillard et al.**

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[45] ***Dec. 3, 1974**


[54] **LUBRICANT COMPOSITIONS**


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[ * ] Notice: The portion of the term of this patent subsequent to Aug. 21, 1990, has been disclaimed.

[22] Filed: **Sept. 18, 1970**

[21] Appl. No.: **73,572**

**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 555,050, June 3, 1966, abandoned, Continuation-in-part of Ser. No. 73,575, Sept. 18, 1970, Pat. No. 3,753,905, which is a continuation-in-part of Ser. No. 778.858, Nov. 25, 1968, abandoned.

[30] **Foreign Application Priority Data**

| | | |
|---|---|---|
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| Aug. 24, 1966 | Belgium | 23769 |

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[51] **Int. Cl...... C10m 1/40,** C10m 1/32, C10m 1/18

[58] **Field of Search**.......... 252/33, 32.7 E, 59, 33.4, 252/51.5 A



[56] **References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,227,692 | 1/1941 | Barnard | 252/59 |
| 2,304,874 | 12/1942 | Barnard | 252/59 |
| 3,004,837 | 10/1961 | Riemenschneider | 252/59 |
| 3,076,841 | 2/1963 | Hutchings et al. | 252/33 |
| 3,085,978 | 4/1963 | Mitacek et al. | 252/59 |
| 3,105,049 | 9/1963 | Voorhees | 252/33 |
| 3,158,572 | 11/1964 | Andress | 252/33 |
| 3,285,851 | 11/1966 | Dyer | 252/33.3 |
| 3,298,951 | 1/1967 | Guminski | 252/33.3 |
| 3,321,399 | 5/1967 | Versteeg et al. | 252/33 |
| 3,377,281 | 4/1968 | Gower | 252/33.3 |

FOREIGN PATENTS OR APPLICATIONS

| | | | |
|---|---|---|---|
| 940,143 | 10/1963 | Great Britain | 252/59 |



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[57] **ABSTRACT**

Lubricant compositions comprising:

a. 5–80 percent mineral oil
b. 10–75 percent liquid polybutene
c. 3–30 percent superbased alkaline earth metal sulfonate
d. minor amount of alkenyl succinimide.


**7 Claims, 5 Drawing Figures**

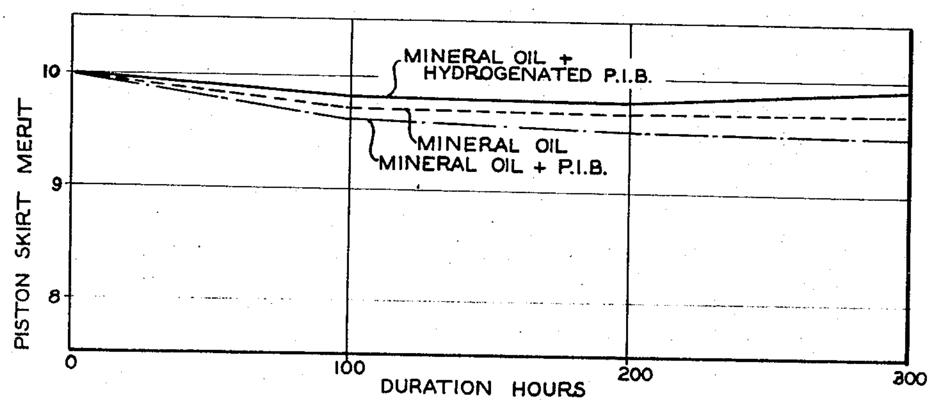


*FIG. 1*

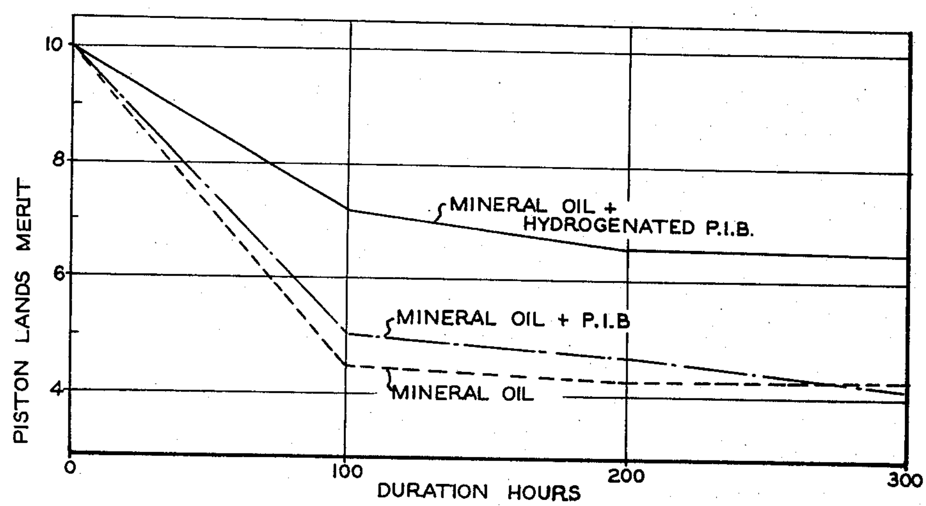


*FIG. 2*

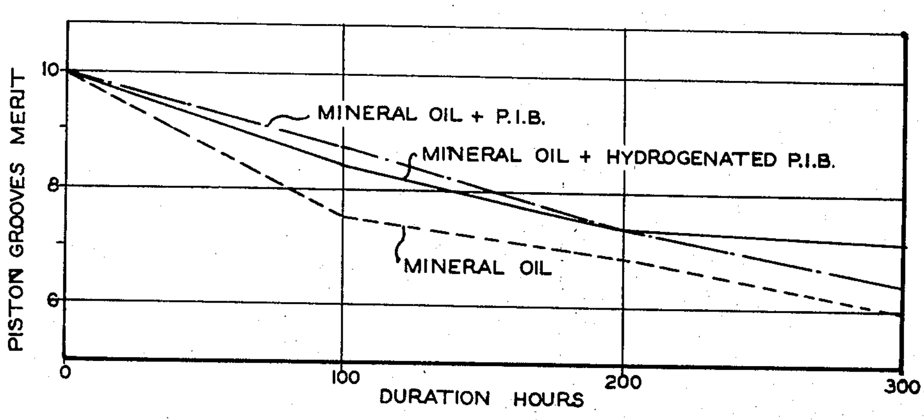


*FIG. 3*

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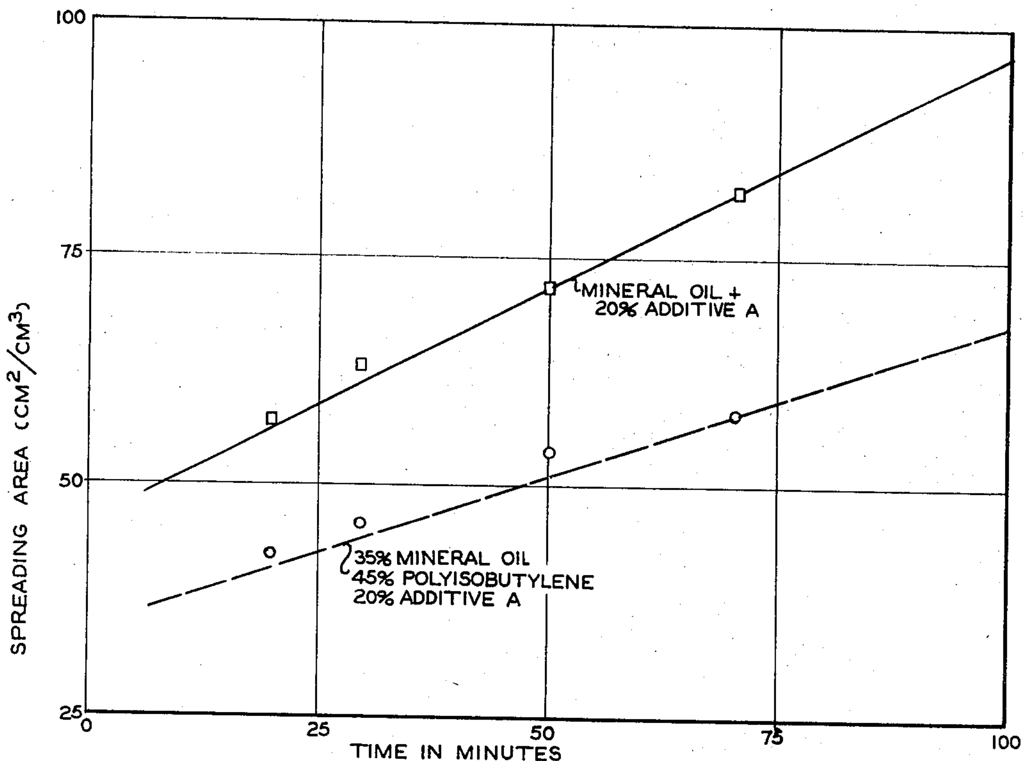
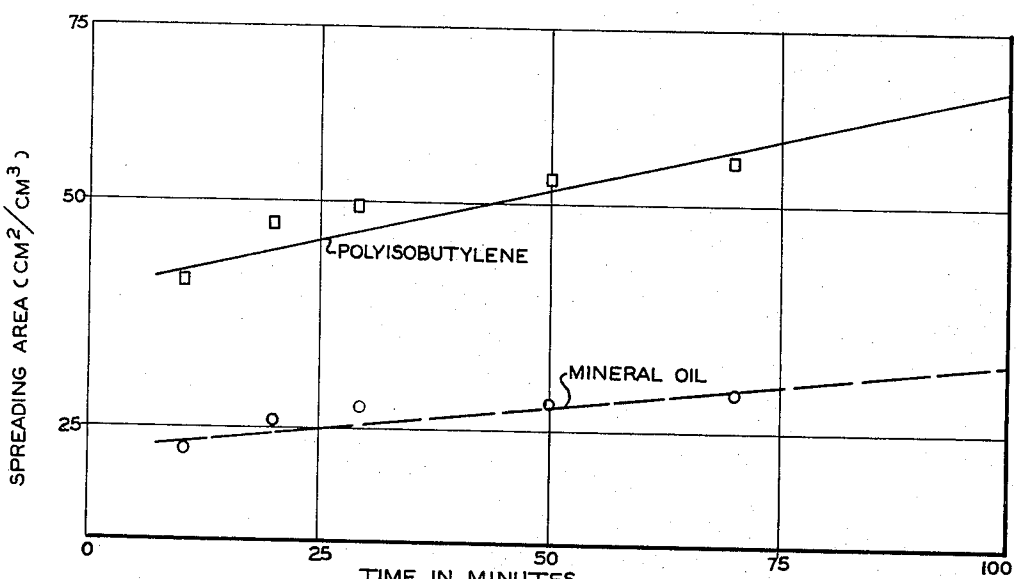



*SPREADING OF MARINE MINERAL OILS ON POLISHED CAST IRON VERSUS TIME*

*FIG. 4*




*SPREADING OF BASE OILS ON POLISHED CAST IRON VERSUS TIME*

*FIG. 5*

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# LUBRICANT COMPOSITIONS

This application is a continuation-in-part of my copending application, Ser. No. 555,050, filed June 3, 1966, and now abandoned; a continuation-in-part of our copending application, Ser. No. 73,575, filed Sept. 18, 1970, now U.S. Pat. No. 3,753,905, issued Aug. 21, 1973; in turn a continuation-in-part of application Ser. No. 778,858, filed Nov. 25, 1968, and now abandoned.

This invention relates to lubrication of high and low speed four-stroke, spark-ignition and compression-ignition engines, and two-stroke marine diesel engines which operate by having the lubricant directly injected into the cylinders, and particularly to a lubricant comprising a mixture of a liquid polybutene, mineral oil and a lubricant additive; and to operation of such four-stroke and two-stroke engines with this lubricant.

The known lubricating compositions are not fully satisfactory for lubrication of the present modern engines of these types which impose more severe requirements.

It is also common to run two-cycle marine engines, and especially the low-speed diesel engines, with low-priced fuels which contain important quantities of asphalts and sulfur, products which directly or indirectly cause rapid wear of the cylinders. Such low-grade fuels burn in these engines with production of sulfur oxides which by condensing on the cylinder walls lead to the formation of corrosive sulfurous and sulfuric acid which not only shortens the life of the engine because of their corrosive action, but also increases the quantity of deposits formed during combustion which also promotes engine wear. The amount of deposits formed during the combustion of the fuel increases with the asphalt content of the fuel.

Still another cause of premature wear of the piston and the cylinder walls is due to the lubricating system, which is by injection for the two-stroke marine diesel engines. In these engines, increasingly high pressures exist between the cylinder walls and the piston rings and also larger spacing of the lubrication inlets on the cylinder walls, the size of which are now designed larger and larger, causes the injected lubricant to spread thereover with greater difficulty. This hinders uniformity and complete lubrication and, therefore, leads to an abnormal wear of the engine. The use of a high base content lubricant for the neutralization of corrosive acids formed during the combustion of the fuel, does not meet the other causes of wear such as the abrasive deposits and the great need for spreading of the lubricant injected into the cylinder with this type of marine engine.

The high-speed running of four-stroke engines with every-day higher specific outputs and power-to-weight ratios, leads to increasing maximal temperatures. When the known lubricants are submitted to such temperatures, they tend to decompose excessively with formation of objectionable products. At the high temperature conditions, the decomposition products polymerize, forming deposits (varnish and so-called "lacquer" deposits) on and between the moving parts, particularly on the cylinder head, the piston skirt and grooves which often results in low and high temperature seizure. Moreover, deposits in the combustion chamber and on the cylinder head disturb the fuel ignition pattern so that ignition is caused not only by the spark plug, but at random from the numerous hot spots created by the deposits. The result is a completely abnormal, often smokey, combustion of lower efficiency and reduced engine life; and for spark-ignited engines, high octane requirements. Such conditions are exaggerated by recently required forced gas recycle for crankcase ventilation which increases the deposits on the inlet valves and in the combustion chamber, and increases the corrosion problems encountered with conventional four-stroke lubricants.



The present lubricant is superior to other common lubricants in that occasional contact with water or glycol from the cooling system will not result in precipitation of additives which remain homogeneously suspended despite such aqueous contact and contamination.

According to one aspect of the invention, a crankcase lubricant for four-cycle engines, spark-ignited as well as compression-ignited engines, markedly superior to solve the lubrication problems listed, is provided by a composition comprising 10 to 24 percent liquid polybutene, 5 to 80 percent mineral lubricating oil and 1 to 15 percent, preferably 3 to 15 percent, additive as defined below, the proportions being by weight.

The polybutene hereof is a light liquid polybutene or polyisobutylene or mixtures thereof; the polybutene is preferably hydrogenated.

The polybutene preferably has a viscosity ranging from 30 SSU at 210°F (2.0 cst at 98.9°C) to about 600 SSU at 210°F (130 cst at 98.9°C) and a molecular weight ranging from about 250 to 950.

The mineral oil component hereof is selected from any commercial lubricating mineral oil having a preferred viscosity in the range of about 50 to 1,000 SSU at 100°F.

The additives useful herein are mineral oil sulfonic acid superbased with an alkali-forming metal oxide or hydroxide such as of an alkali or alkaline earth metal, typically potassium or sodium oxide or hydroxide, or calcium, magnesium, barium or strontium oxide or hydroxide. It is preferred to use the calcium petroleum sulfonic acid herein referred to as calcium sulfonate. Such sulfonate is prepared by sulfonation of crude or fine petroleum fractions at a temperature of 50° – 200°F, by reacting with a sulfonating agent, typically fuming sulfuric acid, for a period of about 30 – 60 minutes. Usually the mineral oil is a refined petroleum fraction solvent, refined with a solvent such as propane to remove usual impurities such as asphalt and waxes. The base oil to be sulfonated may be any common oil, typically mid-continent oil, having a viscosity range of 50 – 230 SSU at 210°F. The sulfonated product soluble in the oil base is neutralized with calcium or barium oxide or hydroxide. Such calcium petroleum sulfonic acid is available as a commercial product, for instance, Lubrizol 239, formed as described above. The additive may further include a viscosity index improver such as polymethacrylate having a molecular weight range between about 10,000 – 20,000, typically about 15,000; and zinc dialkyldithiophosphate, typically zinc diethyldithiophosphate and diisobutyl catechol.

Other typically useful additives may be a mixture of a superbased phosphonate and sulfonate of barium, both formed from mineral oil, such mixture typically having a sulfur content of 0.9 percent by weight, a phosphorous content of 1.44 percent by weight and a barium content of 7.05 percent by weight.

A third useful additive is one of the so-called ashless types, and consists of an alkenyl succinimide formed by reacting an alkylene polyamine consisting typically of triethylene tetramine or tetraethylene pentamine with alkenyl succinic anhydride to form the imide, the alkenyl substituent being an olefine of from about two to about sixteen carbon atoms, usually isobutylene or polyisobutylene. The preparation of that compound is as described in U.S. Pat. No. 3,310,492.

In a second aspect of this invention, where the lubricant is sprayed into the cylinder for two-cycle low speed marine diesel lubrication, the polybutene imparts greater adhesion and rapid spread as well as increased anti-rust properties. The formulation includes a quantity of polybutene in the range of 10 to 75 percent, preferably 12 to 24 percent. An increased quantity of a specific additive is preferred; namely, a sulfonated mineral oil superbased with an alkaline earth metal oxide or hydroxide, preferably of calcium, magnesium or barium formed as stated above, which is used in the preferred range of 5 to 30 percent. The quantity of the mineral oil component is the remainder and is in the range of 5 to 80 percent, all proportions being by weight. The viscosity and molecular weight characteristics of the preferred polybutene and mineral oil for both types of lubricant are the same as those given above.

A preferred method of forming the polybutene is shown in United States patent to Jackson, U.S. Pat. No. 2,957,930, issued Oct. 23, 1960. Such method forms a superior product in that the polybutene is formed more homogeneously in a narrow molecular weight range.

Because of the polymeric structure of the polybutene, it decomposes at a relatively low temperature leaving only minor amounts of deposits which are more friable and easily blown out into the exhaust system. Also, because of the presence of liquid polybutene, the composition hereof adheres to the metal surfaces over long storage periods so that the anti-rust additive the composition contains is able to exert its full anti-rust effect.

In the high efficiency and supercharged two-cycle marine diesel engines, running temperature and pressure are very high. Under these conditions the conventional oils decompose with formation of oxidation and decomposition products which polymerize and lead to the formation of deposits on and between the different parts of the engine, and particularly on the skirt and in the grooves of the piston as well as in the combustion chamber. Those deposits promote piston ring sticking and decrease the heat exchange between the piston skirt and the cylinder. In the very high efficiency and supercharged engines lubricated with conventional oils cokefied deposits may also occur on the piston undercrown, act as a thermal insulator on the heat transfer on the head of the piston, and thereby increase the temperature of the piston and induce seizure. The polybutene in this lubricant contributes a marked reduction of the amounts of objectionable deposits. Moreover, the use of polybutene in a marine two-cycle engine gives the composition a remarkable spreading property in contrast to the spreading of conventional oils.

Finally, this combination of mineral oil with polybutene and additives selected is overall superior as a lubricant for these engines as shown in the following examples.

The several figures of drawing graphically illustrate the test results:

FIG. 1 illustrates graphically the comparative results upon the relative merits of three oils —mineral oil, mineral oil and polyisobutylene, and mineral oil and hydrogenated isobutylene— upon a piston skirt;

FIG. 2 has the same graphical illustrations as to the effect of these oils upon the piston lands;

FIG. 3 graphically illustrates the effect of these same oils upon the piston grooves;

FIG. 4 illustrates graphically the spreading effect of mineral oil containing additive A as identified before Table VI below, and

FIG. 5 comparatively graphically identifies a mixture of polyisobutylene and mineral oil.

## EXAMPLE 1

### Thermal Behaviour Test on the Antar Cokefaction Bench

The purpose of this test is to determine the tendency of a lubricating oil to form varnish and carbon deposits in contact with a hot surface, such deposits being insoluble in petroleum ether.

This laboratory method of deteriorating an oil as a function of the temperature gives a closer approach to the practical conditions under which a thermal engine runs, than a simple static heating. It is derived from the cokefaction test described in the French norme Air 16, 51–59.

### Test Method and Material Used

An oil volume of 450 $cm^3$, kept at a moderate temperature (as in the case of an engine crankcase), is projected continuously in the form of droplets on a hot metallic surface (as in the case of a cylinder, a piston and so on) from where it is allowed to fall down.

The projection system is composed of a broom made of fine steel rods which dip into the oil, the broom being rotated at exactly 1,000 rpm by an electric motor.

The apparatus is practically closed and the cooling of the walls, obtained through water circulation, brings about a condensation of the vapors, thereby ensuring an almost thorough recycling of the tested oil.

The hot metallic surface is represented by the external part of the bottom of an aluminum alloy Becker (of a composition similar to that of the pistons of a thermal engine) within which heating resistance are installed.

A control and regulation system connected to calibrated thermocouples keeps the hot surface within very narrow temperature limits; indeed, the amount of deposits formed increases almost exponentially with the temperature above 220/240°C.

The test conditions for an oil containing additives are as follows:

| | |
|---|---|
| - Plate temperature: | 290°C |
| - Duration of the test: | 12 hours |

The rating is based on the aspect and the location of the varnish rather than on its amount.

Experience has shown that the bottom of the Becher is representative of the state of the lands of a Petter diesel AVI piston.

The skirt of the Becher is representative of the Petter diesel AVI piston ring grooves.

The results of tests run on the cokefaction bench with a multigrade 10w/30 type oil of the S1 level are presented on Table 1 hereunder.

The additive X used below is composed predominantly of mixed barium superbased phosphonate and sulfonate having a sulfur content of 0.9 percent by weight, a barium content of 7.05 percent by weight, and a phosphorous content of 1.44 percent by weight, the balance being mineral oil residues with both phosphonates and sulfonates. The total additive further contains about 2 percent of polymethacrylate having a molecular weight of about 15,000 and 1 percent of zinc diethyldithiophosphate.

The method allows the following rating:

ring sticking

formation of carbon and lacquers deposits

At the end of the test, the engine is dismantled and carefully examined according to an IP merit rating in which the following points are considered:

degree of piston ring sticking

scraper ring sludge

deposit formation on the piston skirt after washing according to a certain procedure

TABLE I

| Tests on the cokefaction bench | | | |
|---|---|---|---|
| Oils | 15% additive X* 85% mineral oil | 15% additive X* 65% mineral oil 20% hydrogenated polybutene | 15% additive X* 65% mineral oil 20% polybutene |
| Rating: | | | |
| Bottom | Fair | Excellent | Excellent |
| Skirt | Fair | Excellent | Excellent |

* % by weight

The results obtained on the cokefaction bench are considerably improved by the use of polybutene. The following engine tests confirm the laboratory results.

## EXAMPLE 2

Comparison trials were conducted on Petter Diesel AVI with various formulations with varying oil/polybutene ratios.

A four-stroke single-cylinder diesel engine of 553 $cm^3$ was used in accordance with the modified IP.175/60T procedure of the War Office. This procedure is more severe than the standard CEC/AT4 method.

The running conditions of the modified IP.175/60T War Office method are presented hereunder.

| | | CEC/AT[4] IP Modified |
|---|---|---|
| Speed | r.p.m. | 1500 ± 10 |
| Load | HP | set by adjusting the consumption |
| Oil temperature | °C | 63 ± 2 |
| Temperature of the coolant | °C | |
| inlet | | 88 ± 2 |
| outlet | | 95 ± 2 |
| Coolant liquid | | kerosene |
| Kerosene flow rate | L/H | 1090 ± 45 |
| Oil pressure | kg/cm² | 2.5 ± 0.4 |
| Gas oil consumption | kg/h | 1088 ± 0.023 |
| Injection APMH | | 20° ± 1° |
| Duration | H | 100 |
| Oil capacity | | 2.270 kg |

deposit formation on the lands of the piston

deposit formation in the piston grooves

deposit formation inside the piston

The tests were run with the following lubricating compositions belonging to the multigrade low/30 type of S1 level with respect to the additives (the percents being expressed by weight and X is the same additive as in Example 1).

1° — 85 percent mineral oil + 15 percent additive X

2° — 45 percent mineral oil + 40 percent polybutene + 15 percent additive X

3° — 45 percent mineral oil + 40 percent hydrogenated polybutene + 15 percent additive X

The ratings obtained after 100, 200 and 300 hours of running are presented in FIGS. 1, 2 and 3 respectively.

In order to control the detergent properties of the oils over a long period of time, the duration of the test was extended to cover 3 + 100 hours without oil change. The evolution of the detergency of the oils with time for the three main rating points of the engine; namely, the skirt, the lands, and the piston grooves, is also shown in Table II.

It will be noted that the compositions 2 and 3 containing polybutene gave good results. Composition 3, containing hydrogenated polybutene, is the best. The skirt and lands ratings brings it to the S3 oil level. The ratings of an S3-type oil, based on mineral oil after 100 and 200 hours, is presented in Table II for comparison purposes.

TABLE II - Petter Diesel AVI Motor Tests of Multigrade Oils

| | 15% additive X 85% mineral oil | | | 15% additive X 24% polybutene 61% mineral oil | | | 15% additive X 24% polybutene hydrogen 61% mineral oil | | | Multigrade mineral oil | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 100h. | 200h. | 300h. | 100h. | 200h. | 300h. | 100h. | 200h. | 300h. | 100h. | 200h. |
| Piston ring sticking max. 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Scraper ring sludge max. 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Piston skirt after washing max. 10 | 9.69 | 9.63 | 9.63 | 9.59 | 9.51 | 9.47 | 9.76 | 9.75 | 9.85 | 10 | 10 |
| Piston lands (average of 3) max. 10 | 4.42 | 4.17 | 4.25 | 5 | 4.63 | 4.08 | 7.12 | 6.5 | 6.46 | 6.5 | 3.83 |
| Carbon in piston grooves (average of 3) max. 10 | 7.5 | 6.83 | 5.92 | 8.75 | 7.33 | 6.42 | 8.42 | 7.33 | 7.08 | 8.42 | 6.42 |
| Lacquer in piston grooves (average of 3) max. 10 | 8.75 | 9.25 | 8.75 | 8 | 8.67 | 9.58 | 9 | 9.42 | 9.58 | 7.75 | 6.92 |
| Inside of piston max. 10 | | | 3 | | | 4 | | | 6.75 | | 3.5 |

## EXAMPLE 3

Various lubricating compositions have been tried according to the SNCF-SNCB procedure. This cyclic test with the Petter Diesel AVI lasts about 150 hours and includes three 45 hour cycles with a high temperature refrigeration and oil, alternating with three 5 hour cycles running on no load and at a low temperature, with 10 cm$^3$ of a glycol and water mixture being introduced in the crankcase at the beginning of each cycle.

After about 150 hours, the engine is completely dismantled and examined according to a rating system close to that of the CEC/AT4 method with regard to:

ring sticking
the sludge and lacquer deposits on the piston skirts before and after cleaning
piston ring scraper sludge blocking
carbon and lacquer deposits on the cylinder walls
deposits on the piston lands
deposits on the piston grooves
deposits on the main parts by a direct measure of the sludge thickness with a graduated guage

The total merit is then established by adding the above elements, each of which is modified by a factor according to its importance.

3.5 for ring sticking
3 for the piston skirt before and after washing
2 for the main parts
0.5 for the crown cutting
1.5 for the lands average
2 for the lacquer and carbon of the second and third groove

The following compositions were tested:

1. 92 percent mineral oil + 8 percent additive Y
2. 76 percent mineral oil + 16 percent polybutene + 8 percent additive Y
3. 76 percent mineral oil + 16 percent hydrogenated polybutene + 8 percent additive Y, all percentages being expressed by weight.

The additive Y is a commercial additive of the Ba and Ca superbased sulfonated mineral oil having a Ba content of 3.45 percent by wt., a Ca content of 3.55 percent by wt. and a S content of 2.3 percent by wt.

The results of the various test runs are presented in Table III.

The results obtained with compositions **2** and **3** clearly show that the addition of a certain amount of polybutene greatly improves the ratings of the SNCB test.

Again, the results of the third test confirm the beneficial effect of hydrogenated polybutene. Only the composition based on hydrogenated polybutene fully satisfies the requirements of the SNCB test. SNCB tests have been run with other compositions which pass the various physico-chemical and corrosion requirements of the SNCB.

The engine tests run with the following compositions are presented in Table IV:

1. 90.5 percent mineral oil + 9.5 percent additive Z
2. 75.5 percent mineral oil + 15 percent hydrogenated polybutene + 9.5 percent additive Z, all percentages being by weight.

The additive Z is a commercial additive of the Ba and Ca superbased sulfonated mineral oil having a Ba content of 4.3 percent by wt., a Ca content of 3.4 percent by weight and a S content of 2.4 percent by wt.

In order to satisfy the new SNCB specifications, the tests were run on the Petter AVI as well as on the Petter WI. Once again, a clear improvement is noted with regard to the performance of the composition based on hydrogenated polybutene. This composition easily passes the two engine tests.

Deposits in the grooves and at the bottom of the pistons are negligible.

TABLE III

| SNCB Tests on Solna HD S1 SAE 40 | | | | |
|---|---|---|---|---|
| Composition of the oil W/W | | Composition 1 92% mineral oil 8 % additive Y | Composition 2 76% mineral oil 8% additive Y 16% polyybutene | Composition 3 76% mineral oil 8% additive Y 16% hydrogenated polybutene |
| Piston ring sticking | /35 | 35 | 35 | 35 |
| Scraper-ring sludge | /10 | 10 | 10 | 10 |
| Carbon deposits in the third groove | /10 | 9 | 9.25 | 10 |
| Piston skirt before washing | /30 | 23.22 | 26.61 | 29.19 |
| Piston skirt after washing | /30 | 29.70 | 28.74 | 29.70 |
| Deposits on the main parts | /20 | 17.75 | 18.90 | 19.15 |
| Deposits inside the cylinder wall | /10 | 10 | 10 | 10 |
| Crown cutting | /5 | 4.75 | 4.88 | 4.75 |
| Piston lands (average of three) | /15 | 11.38 | 9.50 | 13.13 |
| Piston grooves (2nd and 3rd) | /20 | 12.75 | 15.50 | 16 |
| TOTAL MERIT | /100 | 82.01 | 87.10 | 93.39 |

TABLE IV

| SNCB Tests With An S1 Type Oil | | | | |
|---|---|---|---|---|
| | | 90.5% mineral oil 9.5% additive Z | 79.5% mineral oil 9.5% additive Z 15% hydrogen polybutene | Minimum required |
| | | Tests with Petter AV1 Diesel | | |
| Piston ring sticking | /35 | 35 | 35 | 35 |
| Scraper ring sludge | | 10 | 10 | 10 |
| Carbon deposits in the third groove | | 9.27 | 10 | |
| Piston skirt before washing | | 25.50 | 29.94 | |
| Piston skirt after washing | | 29.40 | 30 | |
| Deposits on the main parts | | 18.40 | 19.15 | |
| Deposits inside the cylinder wall | | 10 | 10 | |
| Crown cutting | | 4.35 | 4.88 | |
| Piston lands (average of 3) | | 11.70 | 14 | |
| Piston grooves (2nd and 3rd) | | 16.64 | 19.88 | |
| Total merit on 100 | | 87.89 | 98.87 | 92 |
| | | Test With Petter W1 Gasoline | | |
| Merit of the piston skirt | /10 | 9.4 | 10 | |
| Inside of piston | /10 | 7 | 10 | |
| Weight loss in mg. | | 21.9 | 4.1 | 25 |
| Piston grooves | | | | |
| 1 | | 5 | 9.9 | |
| 2 | | 6.2 | 9.6 | |
| 3 | | 8.5 | 10 | |

## EXAMPLE 4

Other tests have been run with the Petter WI gasoline engine normally used for the DEF-2101 C specification.

This technique is designed to provide a method for investigating and studying the copper-lead bearings corrosion and oxidation characteristics of engine oils as well as the detergency and the oxidation stability after a relatively short running period, namely **36** hours.

The running conditions are described in the following table:

| | |
|---|---|
| Duration | 36 hours |
| Speed | 1500 rpm ± 15 |
| Load | adjusted in order to reach the consumption mentioned below |
| Air/gasoline ratio | 11.7 : 1 to 12 : 1 |
| Consumption | 50 ml in 113 ± 0.5 sec. |
| Temperature of the coolant inlet: | 146° ± 4°C |
| outlet: | 150° ± 1°C |
| Oil pressure | 8 ± 3 lbs/in |
| Temperature of the heated plate | 200 ± 5°C |

The end results are assessed by inspecting the following engine parts:

ring sticking

scraper ring sludge

cleanliness of the piston skirt--the merit rating is based on a scale where 0 denotes a surface completely covered by a black lacquer and 10 denotes an absolutely clean surface.

inside of the piston--the merit rating is based on a scale where **0** denotes black lacquers and **10** absolute cleanliness.

weight loss of the two half shells of the big-end bearing.

The following compositions were tested in this Petter WI test. They belong to the Multigrade 10W/30 type of the SI level as far as the additives are concerned, which are similar to those of Example 1.

1. 85% mineral oil + 15 percent additive X
2. 45% mineral oil + 40 percent polybutene + 15 percent additive X
3. 45% mineral oil + 40 percent hydrogenated polybutene + 15 percent additive X

The various percentages are expressed by weight.

The results of this test are presented in Table V. It will be noted once more that the use of polybutene has a beneficial effect from a point of view of detergency and oxidation.

However, in order to rate the oil over a period of time, in respect of the oxidation and corrosion of the bearings, the duration of the standard Petter WI test has been extended from 36 to 60 hours.

The results with the three compositions tested for 60 hours are presented in Table V. A marked improvement of the results will be noted when polybutene is used. The beneficial effect of hydrogenated polybutene is particularly obvious in respect of the reduction of deposits in the grooves and at the inside of the piston.

The gasoline Petter tests are run with an oil having a paraffinic nature, and refined with a solvent.

## EXAMPLE 5

The increase of the available power output results in a temperature increase in the rings area and under the piston crown. At higher temperatures the oil is exposed to thermal shocks and to a heavier oxidation due to the blowby of the gases which themselves are hotter.

The Ford test with the Cortina engine is commonly used for the purpose of studying the behaviour of oils at these high temperatures. This test is run on a four cylinder 1,500 $cm^3$ engine under full load (48 HP at 35,000 r.p.m.) during 100 hours.

After the test the main parts are examined with respect to sludge and ring sticking. The merit rating is obtained by means of scale where 0 denotes a surface completely covered by black lacquers and 10 an absolutely clean surface.

TABLE V

Test With Petter Wi

| COMPOSITION | | 15% additive X 85% mineral oil | 15% additive X 61% mineral oil 24% hydrogenated polybutene | 15% additive X 61% mineral oil 24% polybutene |
|---|---|---|---|---|
| Ring sticking | /10 | 10 | 10 | 10 |
| Piston skirt merit rating | /10 | | | |
| 36 hours | | 9.9 | 9.9 | 9.9 |
| 60 hours | | 9.9 | 9.9 | 9.9 |
| Bottom of piston (end of test) | /10 | | | |
| 36 hours | | 6 | 9 | 8 |
| 60 hours | | 4.75 | 9.8 | 6 |
| Piston grooves merit rating (end of 60 hours test) | 1st | 0.5 | 6.5 | 5.25 |
| | 2nd | 1.75 | 8.75 | 6.25 |
| | 3rd | 8.75 | 9.50 | 8.50 |
| Weight loss in mg. | | | | |
| 36 hours | | 19.9 | 11.2 | 15.9 |
| 60 hours | | 41 | 19.1 | 31.3 |

On Table VI, the results of gasoline Petter tests are presented which were run with naphthenic oils. Additive A is a commercial additive comprising a Zn diethyldithiophosphate antioxidant having a Zn content of 8.6 by weight, and a P content of 7.7 percent by weight, and a detergent which is a Mg and Ca mineral oil sulfonate having an Mg content of 0.68 percent by weight and a Ca content of 0.23 percent by weight.

The superiority of the composition based on hydrogenated polybutene with respect to the deposits in the grooves and on the inside of the piston is again demonstrated when the test is run for 84 hours. The type of the base oil does not effect the beneficial effect of the polybutene addition.

TABLE VI

Petter WI gasoline tests

| Composition | | 95% mineral oil 5% additive A | 20% hydrogenated polybutene 75% mineral oil 5% additive A |
|---|---|---|---|
| Skirt merit | | | |
| 36 hours | /10 | 9.8 | 10 |
| 60 hours | | 9.7 | 10 |
| 84 hours | | 9.5 | 9.7 |
| Inside of piston | /10 | | |
| 84 hours | | 5.5 | 8.7 |
| Piston grooves | /1 | 1.2 | 6 |
| 84 hours | 2 | 3.5 | 6.2 |
| | 3 | 6 | 3.8 |
| Weight loss in mg | | | |
| 36 hours | | 17.4 | 13.8 |
| 60 hours | | 31.5 | 26.3 |
| 84 hours | | 49.3 | 32.4 |

The results obtained with 2 multigrade 10W/30 compositions of the SI level containing four-stroke engine additives identical to those used in the compositions of the Example 2, are given in Table VII.

The use of hydrogenated polybutene improves the properties of the oil when tested for oxidation at high temperatures, also the lacquers on the skirts, the lands and the grooves of the pistons being markedly reduced.

TABLE VII

Cortina Tests

| Composition | 85% mineral oil 15% additive X | 15% hydrogen polybutene 70% mineral oil 15% additive X |
|---|---|---|
| Sludge merit | | |
| Rocker box cover | 9.77 | 9.89 |
| Front cover | 10 | 10 |
| Oil pan | 10 | 10 |
| Deposit merit | | |
| Inlet valve | CRC' 2–3 | 1–2 |
| Exhaust valve | CRC' 2 | 1–2 |
| Lacquer merit | | |
| Piston skirt exterior | 8 | 8.3 |
| Piston skirt interior | 8.9 | 9.38 |
| Piston lands | 0.84 | 2.15 |
| Piston grooves | 1.02 | 2.28 |
| Rocker box cover | 9.75 | 10 |
| Ring sticking | 10 | 10 |

## EXAMPLE 6

### Thermal Behavior of a Two-Cycle Marine Diesel Engine

The general test conditions for a mineral oil were described under Example 1 above, the present test being modified as follows:

Plate temperature: **290°C**
Duration of the test: **6** hours

The rating is based on the aspect and the location of the varnish. Experience has shown that the aspect of the bottom of the Becher is representative of the lands of a piston of a Diesel engine such as the Petter Diesel AVI after the test CEC/AT4.

The skirt of the Becher is representative of the piston grooves of the same engine. The deposits reflect the oil tendency of producing them. Washing of those deposits with a solvent gives a measure of the amount of soot formed.

The results presented in the table below were obtained from three base oils having the same final viscosity; namely, 7 E.50 or 53 cst at 50°C.

Two drops each of the oils to be tested are allowed to drop from a height of 1 cm on a degreased and polished cast-iron plate of 10 × 10 cm, by use of calibrated capillary tubes with which the weight of the drops of each oil have been previously determined.

At the same moment a chronometer is stated for each oil. The plate is then stored horizontally in a heated closed set at 80°C. This temperature was chosen because it approximates that of the cooling water of marine diesel engines. There is practically no spreading of the oil for the first 5 minutes. Afterwards the spots begin to spread, taking the shape of an ellipse. The two diameters of each ellipse is measured every 15 minutes by use of a vernier in order to determine the spreading area as a function of time.

Since the weight and the density of the oils are known it is easy to calculate the volumes used and thereby to

TABLE VIII

Test on the Cokefaction Bench

| | Mineral Oil | Mineral Oil 20% poly-butene | Mineral Oil 20% hydroge-nated poly-butene |
|---|---|---|---|
| Bottom, max. 10 | 3.6 | 5.3 | 5.9 |
| Skirt, max. 10 | 7.6 | 8.8 | 9.1 |
| Deposits, before washing mg | 343 | 82 | 76 |
| Deposits, after washing mg | 241 | 77 | 72 |

The use of polybutene improves all the results obtained on the cokefaction test. The hydrogenated polybutene is the most effective of the two polybutene's tested.

The following engine tests confirm these laboratory findings.

EXAMPLE 7

Spreading Capacity

Observations carried out on the cylinders of ships have shown that the spreading capacity of the oil film can play an important part. Indeed warm areas have been formed on the cast-iron cylinder liners lubricated with a standard marine oil, between the lubrication inlets, where the lubricating oil does not seem to reach. Since this phenomenon apparently varies with different marine oils, it is inferred that some oils have a better spreading capacity on cast-iron than others. In order to ascertain this behavioral difference, a simple test has been devised by which the spreading rate of oils of identical viscosities and the same viscosity index on cast-iron can be compared. This test is described below.

Test to Establish the Spreading Rate of Oils on Polished Cast-Iron

establish the spreading area expressed in $cm^2$ per $cm^3$ of oil.

By plotting the spreading area as a function of time on a graph, curves are obtained which can be graphically derived in order to establish the spreading rate. As a preliminary approximation and in order to simplify, straight lines may be drawn between representative points and the angular coefficients of these straight lines taken as an average of the spreading rate under the test conditions.

Results:

These tests were run on the one hand with a base mineral oil and with a polybutene of the same viscosity, at a temperature of 80°C, and on the other hand with marine oils, one being a mineral oil and the other containing 45 percent polybutene. The amount and the nature of the additive was identical, and the two compositions had the same viscosity at the temperature of the test; namely, 80°C.

The results are presented in Tables IX and X as well as in FIGS. **4** and **5**. They may be summarized as follows:

Polybutene spreads twice as fast as mineral oil, the same applying also to ready-made marien oils based on polybutene.

## TABLE IX

**BASE OILS**
Results of the Spreading Test at 80°C

| | Mineral Oil | | Polybutene | |
|---|---|---|---|---|
| Visc. Cst at 80°C | 24.1 | | 23.8 | |
| Diameters of the spots in cm | small $\phi$ (2r) | large $\phi$ (2R) | small $\phi$ (2r) | large $\phi$ (2R) |
| after 10 min. | 1.33 | 1.42 | 1.65 | 2 |
| 20 min. | 1.38 | 1.47 | 1.74 | 2.1 |
| 30 min. | 1.41 | 1.52 | 1.81 | 2.19 |
| 50 min. | 1.44 | 1.54 | 1.96 | 2.20 |
| 70 min. | 1.43 | 1.61 | 1.96 | 2.25 |
| 110 min. | 1.52 | 1.70 | 2.07 | 2.34 |
| Area of the spots in cm² ( . R . r ) | | | | |
| after 10 min. | 1.43 | | 2.61 | |
| 20 min. | 1.60 | | 3.00 | |
| 30 min. | 1.69 | | 3.14 | |
| 50 min. | 1.74 | | 3.38 | |
| 70 min. | 1.83 | | 3.49 | |
| 110 min. | 2.03 | | 3.82 | |
| Weight of the oil in mg | 56 | | 54 | |
| Volume of the oil in mm³ | 62 | | 64 | |
| Spreading area in cm² per cc of oil | | | | |
| after 10 min. | 23.1 | | 40.8 | |
| 20 min. | 25.8 | | 46.9 | |
| 30 min. | 27.3 | | 49.1 | |
| 50 min. | 28.1 | | 52.8 | |
| 70 min. | 29.5 | | 54.4 | |
| 110 min. | 32.7 | | 59.7 | |
| Average rate of spreading in cm²/cc/min. (angul. coeff. of the straight lines) | 0.106 | | 0.230 | |

## TABLE X

**MARINE OILS**
Results of the Spreading Test at 80°C

| | 80% mineral oil (base mineral oil) + 20% additive C* | | 35% marine oil +45% polybutene +20% additive C* | |
|---|---|---|---|---|
| Cisc. Cst at 80°C | 37.5 | | 36 | |
| Diameter of the spots in cm | small $\phi$ (2r) | large $\phi$ (2R) | small $\phi$ (2r) | large $\phi$ (2R) |
| after 10 min. | 1.82 | 2.33 | 2.07 | 2.6 |
| 20 min. | 1.94 | 2.52 | 2.19 | 2.93 |
| 30 min. | 1.98 | 2.66 | 2.24 | 3.18 |
| 50 min. | 2.14 | 2.93 | 2.34 | 3.57 |
| 70 min. | 2.19 | 3.04 | 2.35 | 3.91 |
| 110 min. | 2.34 | 3.10 | 2.66 | 4.27 |
| Area of the spots in cm² ( . R . r ) | | | | |
| after 10 min. | 3.31 | | 4.24 | |
| 20 min. | 3.84 | | 5.04 | |
| 30 min. | 4.13 | | 5.64 | |
| 50 min. | 4.90 | | 6.32 | |
| 70 min. | 5.20 | | 7.22 | |
| 110 min. | 5.69 | | 8.94 | |
| Weight of the oil in mg | 84 | | 81 | |
| Volume of the oil in mm³ | 91 | | 89 | |
| Spreading area in cm² per cc of oil | | | | |
| after 10 min. | 36.4 | | 47.6 | |
| 20 min. | 42.2 | | 56.6 | |
| 30 min. | 45.4 | | 63.4 | |
| 50 min. | 53.8 | | 71.0 | |
| 70 min. | 57.1 | | 81.1 | |
| 110 min. | 62.5 | | 100.4 | |
| Average rate of spreading in cm²/cc/min. (angul. coeff. of the straight lines) | 0.320 | | 0.500 | |

*Identification of additive C is given at the end of Example 8 below

### EXAMPLE 8

### Tests A B C

Field tests with the engines of ships are, of course, quite appropriate for the determination of oil properties. Unfortunately, obtaining such results is a time-consuming process. A test engine simplifies this operation by reproducing as closely as possible the running conditions of a low-speed marine engine using heavy fuel.

We chose the Anglo Belgian C° engine type 26 M 2 with two vertical cylinders and a dry sump. This type of engine is used on barges. With it very good indications can be obtained with respect to the performance of marine oils under service.

Test engine data

| | |
|---|---|
| Power: | 80 H.P. |
| Speed: | 400 r.p.m. |
| Cylinder bore: | 240 mm |
| Cylinder stroke: | 300 mm |

Test conditions

Before each test the engine is completely dismantled, the rings are cleaned, and the varnish deposits are removed.

The running conditions were the following:

| | |
|---|---|
| Duration: | 300 hours |
| Speed: | 320 r.p.m. |
| Power: | 50 H.P. |
| Temperature of the coolant at the outlet of the cylinder heat: | 75–80°C max. |

The fuel used was a 600 Redwood preheated to 60°C

Lubrication is of the waste lubrication type; each cylinder having a mechanical lubricating system with multiple pumps of the type ASEA n° BSP 4, which lubricates the cylinder (through four inlets), the piston trunnion and the big-end bearing.

At the end of the test the engine is dismantled and:

a. the wear of the cylinder liner and of the rings is measured

b. deposit, sludge and varnish on the piston and visiting ports are rated

The skirt rating is achieved by using the CRC/AT4 procedure, with a rating of 10 for an absolutely clean piston and a rating of 0 for a piston completely covered with carbon.

The following table gives the results of comparative ABC tests, run with conventional marine oils and with compositions containing polybutene.

The values quoted are the arithmetical mean of many tests run with those conditions.

It has been found that the polybutene has a beneficial effect with respect of the wear of the rings and the deposits. The deposits found in the exhaust system are negligible and easily removed.

There is little carbon in the piston grooves which explains why there is no ring sticking where polybutene is used.

on a two-stroke Burmeister & Wain supercharged engine, Model 984 VTKF 180, with a power output of 20.700 H.P. at 114 r.p.m. mounted on a motor ship.

This diesel engine uses a fuel with a viscosity of up to 3,000 sec. Redwood. It was found that the use of composition *n*° **1** on this engine reduces the wear expressed in millimeters per 100 hrs. running by 50 percent.

We claim:

**1.** A lubricant for internal combustion engines comprising from 10 to 75 percent of liquid polybutene having a viscosity in the range of about 30 up to 600 SSU at 210°F and a molecular weight of less than about 1,000, 5 to 80 percent mineral lubricating oil having a viscosity in the range of about 50 to 1,000 SSU at 100°F, and 3 to 30 percent of a sulfonic acid superbased with an alkaline earth metal selected from the group consisting of calcium, barium and magnesium, the proportions being by weight.

**2.** Crackcase lubricant as defined in claim **1** for four-stroke spark-ignition and compression ignition engines comprising from 10 to 24 percent of liquid polybutene, 5 to 80 percent mineral lubricating oil and 3 to 15 percent of said superbased sulfonate additive, the proportions being by weight.

**3.** Cylinder spray lubricant for low speed marine diesel engines as defined in claim **1** comprising from 10 to 24 percent of said liquid polybutene, 5 to 80 percent of said mineral lubricating oil and 5 to 30 percent of said superbased sulfonate additive, the proportions being by weight.

**4.** The lubricant as defined in claim **1,** wherein the polybutene is hydrogenated polybutene to stable, substantially colorless form.

**5.** The lubricant as defined in claim **2,** wherein the additive comprises a sulfonic acid superbased with two alkaline earth metal compounds selected from the group consisting of calcium, magnesium and barium.

**6.** The lubricant as defined in claim **3,** wherein the additive comprises a sulfonic acid superbased with magnesium.

**7.** A lubricant for internal combustion engines as defined in claim **1** further containing a small but effective quantity (comprising from **10** to **75%** of liquid polybutene having a viscosity in the range of about **30** up to **600** SSU at **210**°F and a molecular weight of less than about **1000, 5** to **80%** mineral lubricating oil having a viscosity in the range of about **50** to **1000** SSU at **100**°F, and **3** to **30%**) of an alkylene polyamine amide

TABLE XI

A. B. C. TESTS

| Oil Composition W/W | no 1<br>22.5% add. C*<br>10 % mineral oil<br>67.5% polybutene | no 2<br>22.5% add. C*<br>77.5% mineral oil | no 3<br>22.5% add. B**<br>77.5% mineral oil | no 4<br>22.5% add. B**<br>10 % mineral oil<br>67.5% polybutene |
|---|---|---|---|---|
| Engler at 50°C | 18.9 | 18.56 | 18.54 | 18.64 |
| Ring wear in gr | | | | |
| 1st | 1.6 | 2.7 | 2.6 | 1.50 |
| 2nd | 0.35 | 0.5 | 0.65 | 0.35 |
| 3rd | 0.2 | 1.15 | 0.50 | 0 .30 |

*Additive C: A superbased Mg petroleum sulfonate with a base number of 300 and an Mg content of 7.2% by weight.
**Additive B: A superbased Ca petroleum sulfonate having an alkalinity of 285 mg KOH/gr and a Ca content of 11.9% by weight.

EXAMPLE 9

The lubricating composition described under *n*° 1 of Example 8 has been used successfully for many months

of an alkenyl succinic acid in which the alkylene polyamine is triethylene tetramine or tetraethylene pentamine.

* * * * *

UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,852,204 Dated December 3, 1974

Inventor(s) Georges Jules Pierre Souillard et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 18, Claim 7 should appear as shown below:

7. A lubricant for internal combustion engines as defined in claim 1 further containing a small but effective quantity of an alkylene polyamine amide of an alkenyl succinic acid in which the alkylene polyamine is triethylene tetramine or tetraethylene pentamine.

Signed and Sealed this

*twenty-third* Day of *September 1975*

[SEAL]

*Attest:*

RUTH C. MASON
*Attesting Officer*

C. MARSHALL DANN
*Commissioner of Patents and Trademarks*