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[54] **LUBRICATING COMPOSITIONS FOR MARINE DIESEL ENGINES**

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[58] **Field of Search** 252/59, 18, 33, 42.7; 44/58

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[57] **ABSTRACT**

A lubricating composition for marine diesel engines comprising (1) 50 to 90 parts by weight of mineral base oil, (2) 50 to 10% parts by weight of a mixture of polymers selected from the group consisting of hydrogenated and non-hydrogenated polybutenes and polyisobutylenes, said mixture comprising a polymer having a Saybolt viscosity at 210°F of between 150 and 3,000 SSU and a polymer having a Saybolt viscosity at 210°F of between 40 and 100 SSU, and (3) a superbasic additive, said lubricating composition having an alkalinity index of between 60 and 70.

5 Claims, No Drawings

LUBRICATING COMPOSITIONS FOR MARINE DIESEL ENGINES

The present invention relates to lubricating compositions. More particularly, the present invention relates to lubricating compositions which are most useful for the lubrication of marine diesel engines.

The present marine diesel engines most often are low-speed engines (120 r.p.m. maximum) having a high power which may reach 4,000 H.P. per cylinder. These engines have two separated lubricating systems, one system for the lower part of the engine (bearings, cross head, crank heads) and the other system for the cylinders. This separated lubrication of the cylinders operates by having the lubricant directly injected into each cylinder during each cycle. The lubricating composition is radially injected by nozzles around the cylinder. The number of lubrication inlets is limited for practical design reasons. For example, the distance between two inlets is about 35 cm in big engines having cylinders with a bore up to 100 cm. In this type of engine, increasing high pressures existing between the cylinder walls and the piston rings and also larger spacing of the lubrication inlets, cause the injected lubricant to spread thereover with great difficulty. This hinders uniformity and complete lubrication and, therefore, leads to an abnormal wear of the engine.

In addition, it is common to run marine diesel engines with low-priced fuels, more particularly heavy fuels, which contain significant quantities of sulfur and ash-forming impurities. Such fuels directly or indirectly cause rapid wear of the cylinders by corrosion and by abrasion. It is well known that these 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 acids. These acids shorten the life of the engine not only because of their corrosive action, but also because these acids promote the formation of deposits (namely sulfates) which increase the wear of the piston rings and of the cylinder walls.

It is an object of the present invention to provide new and improved lubricating compositions for marine diesel engines.

It is a further object of the present invention to provide lubricating compositions which fulfill specific requirements and possess special qualities for marine diesel engines.

Another object of the present invention is to provide lubricating compositions for diesel engines, these compositions forming a continuous and homogeneous film, even between the lubricating inlets, and protecting the metallic surfaces against corrosion and erosion and decreasing the wear.

According to the present invention, lubricating compositions for marine diesel engines are presented, such lubricating compositions comprising (a) 50 to 90% by weight of a mineral base oil, (b) 50 to 10% by weight of a mixture of a polymer selected from the group consisting in hydrogenated and non-hydrogenated polybutene and polyisobutene, said mixture consisting in a polymer having a Saybolt viscosity at 210°F comprised between 150 and 3,000 SSU and a polymer having a Saybolt viscosity at 210°F comprised between 40 and 100 SSU, and (c) a superbasic additive, said lubricating compositions having an alkalinity index of between 60 and 70.

The mineral base oil which is used in the lubricating compositions of the present invention is one having a Saybolt viscosity of between 50 and 1,000 SSU at 100°F. Mineral oils giving decomposition products which do not act as linking agents for the solid particles resulting from the fuel combustion preferably are used. Mineral base oils of the naphthenic type preferably are used. The importance of the chemical nature of the additives is greater, however, than the importance of the chemical nature of the base oil and, therefore, paraffinic base oils also may be employed.

In order to decrease the corrosion wear on the cylinders, basic additives generally are incorporated into the lubricating compositions of the present invention. These additives act as neutralizing agents for the corrosive acids which are formed by the combustion of the fuel. The efficiency of the lubricant, with regard to the anti-corrosive properties, depends upon the alkalinity index of this lubricant. The alkalinity index (which is also called Total Base Number or TBN) is the equivalent in mg. of KOH per gram of lubricant. As a result, the lubricating composition should have a TBN as high as possible in order to neutralize the important amounts of acidic combustion products. Comparative experiments, however, have shown that a level should exist for this TBN and that a TBN higher than this level does not result in an improvement of the anti-corrosive efficiency of the lubricant. An excessive amount of basic additive is even detrimental, the amount of deposits being increased. Lubricating compositions with an alkalinity which does not exceed 70 and which generally is within the range of 60 and 70 are preferred.

The basic additives employed in accordance with the present invention are selected from the group consisting of the superbasic sulfonates or phenates of magnesium or other alkaline-earth metals, more particularly superbasic petroleum sulfonates of calcium or barium. A superbasic sulfonate of barium is prepared, for example, by reacting a petroleum sulfonic acid with barium methylate and then bubbling CO_2 therethrough. Thus, these superbasic sulfonates are different from the petroleum sulfonates of calcium, which generally are used as dispersing agents in lubricating compositions for 2-stroke and 4-stroke engines. The superbasic sulfonates or phenates have a viscosity index of about 250 to 400. The lubricating compositions of the present invention generally contain 15 to 30% by weight (based on the weight of the total composition) of superbasic additive.

Wear by corrosion is reduced with lubricating compositions consisting in a mineral base oil and a superbasic additive. In order to reduce the wear caused by deposits and by lubricant films which are not homogeneous, it has been suggested to use lubricants containing polymers of butene or isobutene, having a viscosity of between 30 and 600 SSU at 210°F and having a molecular weight which does not exceed 1,000. Wear on marine diesel engines and the formation of deposits which are detrimental to the life and the efficiency of these engines, are reduced with such lubricating compositions.

With the use of higher power and large size engines, it has been found that mechanical wear is now more important than wear caused by combustion products. At the present time, lubricating compositions have to fulfill stringent requirements, with regard to homogeneity and stability of the lubricating film at the high pressures and temperatures at which the engines work. It has been unexpectedly found that this engine wear is noticeably lowered when a mixture of polybutenes and/or polyisobutenes is incorporated into the mineral base oil. Comparative experiments have shown that such results are obtained when one of the polymers has a Saybolt viscosity at 210°F not higher than 100 SSU and generally, between 40 and 95 SSU, and the other polymer has a Saybolt viscosity at 210°F of between 150 and 3000 SSU. Such polymers have a relatively low molecular weight which does not exceed 1,500. These polymers are polybutenes or polyisobutenes which are produced by polymerizing hydrocarbon fractions containing mainly olefines having 4 carbon atoms in the presence of Friedel-Crafts type catalysts. Since isobutene is the most reactive monomer, the first polymerization first gives a product consisting mainly in polyisobutene. The residual fraction is then polymerized with production of a polymer consisting primarily of polybutene with a low percentage of polyisobutene. According to this invention, the lubricating compositions contain as well polyisobutenes as polybutenes, these polymers being previously hydrogenated or not. The most important factor is the viscosity of the polymers. For a sake of brevity, poly-C_4 will be used for these polymers.

The lubricating compositions of the present invention generally comprise 50 to 90% by weight of mineral base oil, such as above defined, and 50 to 10% by weight of a mixture of poly-C_4. According to a preferred embodiment of this invention, the compositions contain 80 to 65% by weight of mineral base oil and 20 to 35% of a mixture of poly-C_4.

Comparative experiments have shown that by adding the mixture of poly-C_4 to a mineral base oil, the resulting compositions are particularly suitable lubricants for marine diesel engines, although these poly-C_4 are polymers with a relatively low molecular weight. Indeed, the prior art teaches that lubricating oils contain generally mineral base oils and poly-C_4 having a high molecular weight higher than about 5,000, or mixtures of poly-C_4 and olefines copolymers. Moreover, for lubricating at high temperature with continuous introduction of the lubricant, as for instance in diesel engines, it has been suggested to use compositions containing a base oil and a mixture containing a major part of poly-C_4 having a mean molecular weight of about 5,000 and a minor part of poly-C_4 having a mean molecular weight of about 150,000. The main object of these compositions containing polymers with a high molecular weight is to avoid important variations of viscosity as a function of the temperature and to lower the formation of carbon deposits at high temperatures. In the modern diesel engines, however, the effectiveness at high temperatures is only one of the requirements and the above lubricating oils are not satisfactory. The lubricant must form a continuous and homogeneous film and spreading, oiliness, mechanical stability and evaporation rate are further important criteria. By using mixtures of poly-C_4 as hereinabove defined, and having relatively low molecular weight, these requirements are fulfilled.

The following examples are given to illustrate the present invention. In these examples, the performance of the lubricating compositions of the present invention have been evaluated by using such compositions for the lubrication of a BOLNES 3DNL marine diesel engine. This engine is a two-stroke engine with 3 cylinders. The cylinder diameter is 190 mm and the piston stroke is 350 mm. Such engine with supercharging has a power of 350 HP at 500 r.p.m. Lubrication of the pistons and of the bearings was performed by a separated feed for each cylinder by individual pumps and oil vessels, so that the oils for the 3 cylinders might be compared during the tests. Each cylinder had two opposite inlets for lubrication. The bushings and other auxiliary devices were lubricated by the oil in the crankcase, this oil being used also to cool the interior of the pistons.

To evaluate the performance of the present lubricating compositions, the weight loss of each ring was controlled by weighing the rings before and after each test. Also, the cleanliness of the engine after each test was controlled in accordance with the CECM-02-T-70 procedure (European Coordination Council for the development of performance tests for engines lubricants and fuels). According to this procedure, the engine was examined with respect to mechanical and chemical degradations and deposits. The merit rating was obtained by means of a scale wherein 100 denotes an absolutely clean surface.

EXAMPLE 1

A lubricating composition was prepared by mixing 70 parts by weight of naphthenic base oil having a viscosity of 185 centistokes at 100°F, 24 parts by weight of polybutene having a mean molecular weight of 610 (Saybolt viscosity : 259 SSU at 210°F), and 6 parts by weight of polybutene having a mean molecular weight of 420 (Saybolt viscosity : 64 SSU at 210°F). To this mixture were added 25 parts by weight of superbasic calcium sulfonate (LUBRIZOL 56) having an alkalinity index of 285. The resulting lubricating composition had an alkalinity index or TBN of 62. This lubricating composition referred to as "Composition A" was tested in the hereinabove described diesel engine.

By way of comparison, a similar lubricating composition was prepared, but with the use of 30 parts of a polybutene having a molecular weight of 400, instead of the mixture of polybutenes. This composition was referred to as "Composition B".

The performances of Compositions A and B were compared with the performance of a commercial lubricating oil or reference oil. The weight loss with this oil is considered as being 100 and the weight losses with the Compositions A and B are given as relative losses by comparison with the index 100. The results are given in the following Table I.

TABLE I

	Merit rating	Weight loss
Reference oil	78.8	100
Composition A	91	77
Composition B	70	71

From Table I, it is seen that use of Composition A results in substantially reduced weight loss by wear. Also the merit rating is high. A high merit rating means a very low corrosion or deposit formation. The Composition B, containing only one poly-C_4 type, is shown to be good as to weight loss, but use of this composition results in a lower merit rating.

EXAMPLE 2

A lubricating composition similar to Composition A of Example 1 was prepared, but with the use of a mixture of 15 parts by weight of equal parts of polybutene and polyisobutene having a mean molecular weight of 1,290 (Saybolt viscosity : 3,000 at 210°F), and 15 parts by weight of polybutene having a mean molecular weight of 420 (Saybolt viscosity : 64 at 210°F), instead of the poly-C_4 mixture of Example 1. This lubricating composition was tested as described above. The merit rating was 81 and the weight loss was 95.

EXAMPLE 3

A lubricating composition was prepared by mixing 65 parts by weight of mineral base oil having a viscosity of 192 centistokes at 100°F, 20 parts by weight of hydrogenated polybutene having a mean molecular weight of 925 and a Saybolt viscosity of 1,008 SSU at 210°F, and 15 parts by weight of hydrogenated polybutene having a mean molecular weight of 635 and a Saybolt viscosity of 255 SSU at 210°F. This compositon was divided into three portions and an amount of superbasic magnesium sulfonate added to each portion, the amount varying in each portion such as to produce alkalinity indexes of 50, 65 and 85, respectively. These compositions were tested as above described. The results of these tests on the three compositions are set forth in Table II below.

TABLE II

	Merit rating	Weight loss
Composition with alkalinity index of 50	79	93
" 65	92	72
" 85	74	84

What is claimed is:

1. A lubricating composition for marine diesel engines comprising (1) 50 to 90 parts by weight of mineral base oil, (2) 50 to 10 parts by weight of a mixture of polymers all having a molecular weight below about 1500 and selected from the group consisting of hydrogenated and non-hydrogenated polybutenes and polyisobutylenes, said mixture comprising a polymer having a Saybolt viscosity at 210°F of between 150 and 3,000 SSU and a lower molecular weight polymer having a Saybolt viscosity at 210°F of between 40 and 100 SSU, the higher molecular weight and lower molecular weight polymers of said mixture being in the ratio of 4:1 to 1:1, and (3) super-basic additive, said lubricating composition having an alkalinity index of between 60 and 70.

2. The lubricating composition of claim 1 wherein the mineral base oil is a naphthenic oil having a Saybolt viscosity at 100°F of between 50 and 1,000 SSU.

3. The lubricating composition of claim 1 wherein the said composition contains from 15 to 30% based on the weight of said composition, of said superbasic additive.

4. The lubricating composition of claim 1 wherein said composition comprises 65 to 80% of said mineral base oil and 35 to 20% of said mixture of polymers.

5. The lubricating composition of claim 1 containing about 15 to 30% based on the weight of said composition of a super basic additive selected from a group consisting of super basic sulfonates and phenates of an alkaline earth metal.

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