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LUBRICATING COMPOSITION CONTAINING AN INORGANIC MANGANESE COMPOUND AND METHOD OF REDUCING ENGINE WEAR THEREWITH

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This invention relates to the lubrication of internal combustion engines, and more particularly to lubricating compositions having wear and corrosion reducing characteristics which suit them for use in the lubrication of internal combustion engines.

While the problem of combatting engine wear is important in the lubrication of all types of internal combustion engines the problem is particularly serious in the lubrication of low-speed marine diesel engines which operate on residual type fuel oils. It is known that residual fuel oils can be used to power low-speed marine diesel engines in lieu of the more costly lighter diesel fuels. Residual fuel oils of this type frequently contain sulfur and substantial amounts of vanadium and it has been recently observed that a large part of the wear occurring within the engine is attributable to the vanadium content of the fuel. The ash resulting from the combustion of the vanadium containing fuel is highly corrosive to engine parts such as cylinder walls, pistons, etc., which it contacts. The corrosive nature of the ash appears to be due to its vanadium oxide and sulfur content.

It has now been found that wear occurring in internal combustion engines which operate on fuels containing vanadium in amounts sufficient to cause corrosion can be effectively minimized by the use of a lubricating oil having incorporated therein certain inorganic compounds of manganese. The inorganic manganese compounds are employed in the lubricating oil in small amounts sufficient to reduce corrosion by reaction of the manganese with vanadium to form a non-corrosive ash. The inorganic manganese compounds disclosed herein are effective to reduce wear when employed in the lubricating oil in relatively small amounts thus making the resulting compositions particularly advantageous for use in the lubrication of diesel engines and the like wherein the introduction of large amounts of metallic additives is to be avoided in order to prevent the metallic constituents of the additives themselves forming abrasive deposits. By having an inorganic compound of manganese present in the lubricating oil, it is available as a protective coating on metallic surfaces of the engine to react with the vanadium to render it non-corrosive.

Lubricating compositions of the invention comprising a major amount of a lubricating oil and a minor amount of an inorganic manganese compound are employed as lubricants in internal combustion engines which operate on fuels containing vanadium in amounts sufficient to cause corrosion. The new lubricants are particularly suited for the lubrication of low-speed marine diesel engines which operate on high vanadium content fuels. The lubricating compositions of the invention can advantageously be employed as crankcase lubricants or upper cylinder lubricants in engines which employ separate cylinder lubrication.

The lubricating oil which constitutes the major ingredient of the new composition is selected from a wide variety of lubricating oils such as naphthenic base, paraffinic base and mixed base lubricating oils. In general, any

mineral oil of lubricating viscosity or any synthetic lubricating oil such as polymerized olefins, polyalkylene oxides such as polypropylene oxide, polymerized glycols such as polyethylene glycol, organic esters or mixtures of esters such as di-2-ethylhexyl sebacate, di-2-ethylhexyl azelate and the like, can be used as the base oil to form a lubricating composition in accordance with the invention. The lubricating oil employed possesses certain characteristics which suit it for use as a lubricant and in general, is an oil having a viscosity above about 300 SUS at 100° F., and a flash point of above about 350° F. For the lubrication of low-speed marine diesel engines a lubricating oil having a viscosity in the range of about 500 to 3000 Saybolt Universal seconds at 100° F. is generally employed.

The manganese compounds which are employed in lubricating compositions of the invention are inorganic compounds of manganese which are sufficiently soft in nature so as not to scratch glass. The degree of hardness of the inorganic manganese additives is important inasmuch as we have found that those inorganic manganese compounds which are sufficiently hard to scratch glass promote rather than decrease engine wear when employed as a lubricant component. Thus, in general, the inorganic manganese compounds which are suitable for use in the lubricating compositions of the invention are those possessing a degree of hardness of less than about 5 on the Mohs hardness scale. Determination of the scratch hardness of the inorganic manganese compounds can be readily made by the use of available sclerometers in accordance with the standard procedures. Representative inorganic manganese compounds possessing suitable hardness characteristics and which are therefore suitable for use in the lubricating compositions of the invention include manganese carbonate, manganese phosphate, manganese chloride, manganese bromide, manganese fluoride, manganese iodide, manganese hydroxide and the like.

Inasmuch as it is desired to form a fairly stable dispersion or suspension of the inorganic manganese additives when blended with the lubricating oil, the manganese additives are employed in finely divided form. Moreover, the more finely divided materials are more efficient in forming uniform blends and rendering non-corrosive the vanadium content of the fuel employed. However, the degree of subdivision is not critical. The inorganic manganese additives are therefore employed in particle size range of less than 250 microns and preferably less than 50 microns. However, where the inorganic additives are water soluble, for example, in the case of manganese nitrate or manganese chloride and the like, it is unnecessary to employ finely divided material since, if desired, the additives can be dissolved in water to form a more or less concentrated solution and the water solution emulsified in the lubricating oil.

As has been stated, a sufficient amount of an inorganic compound of manganese is employed in a lubricating oil to confer improved wear reducing properties to the composition. Thus, the specific amounts to employ vary with the severity of the lubricating services required. In general, the amount of the inorganic manganese additives to be employed depends upon the vanadium content of the fuel and the rate of consumption of the fuel and lubricant. Thus, where the rate of consumption of the lubricant is relatively high with respect to fuel consumption as when the lubricating composition is employed as an upper cylinder lubricant and injected directly into the cylinders of the engine, relatively small amounts of the manganese compounds are employed. When the lubricating composition is employed as a crankcase lubricant the rate of consumption of the lubricant

is lower and accordingly larger amounts of the inorganic manganese compounds are employed. In each instance, the inorganic manganese compounds are employed in the lubricating oil in amounts sufficient to provide within the engine from about 0.01 atom weight to about 4 atom weights or more of manganese per atom weight of vanadium in the fuel consumed. The exact amount of the inorganic manganese compound to employ in the lubricating oil can be readily determined from the vanadium content of the fuel and the respective rates of consumption of the fuel and lubricant.

The following examples further illustrate the invention which is not to be construed as limited thereby. The manganese content of the lubricating compositions shown in the examples is about 0.17 to about 1 percent by weight.

Example I

Formulate a lubricating composition containing about 1 percent by weight of manganese by uniformly blending 2 percent by weight of manganese carbonate with a lubricating oil. The lubricating oil employed has the following inspection.

Gravity, ° API	21.0
Viscosity, SUV, sec.:	
100° F	1,550
210° F	84.0
Flash, OC, ° F	435
Fire, OC, ° F	495
Pour, ° F	0
Color, ASTM union	5.0
Carbon residue, Conradson, percent	0.25
Copper strip test, 212° F., 3 hrs	1
Neutralization value, ASTM D974:	
Total acid No	0.03

Example II

Formulate a lubricating composition containing about 0.18 percent by weight of manganese by uniformly blending 0.38 percent manganese carbonate with 99.62 percent of the above lubricating oil.

Example III

Utilizing a lubricating oil comprising di-2-ethylhexyl sebacate blend 1 percent by weight of manganese chloride with 99 percent by weight of the lubricating oil to obtain a lubricating composition containing about 0.44 percent by weight of manganese.

Example IV

Utilizing a mineral lubricating oil uniformly blend 0.5 percent by weight of manganese phosphate with 99.5 percent by weight of the lubricating oil to obtain a lubricating composition containing about 0.17 percent by weight of manganese.

Example V

Utilizing the same lubricating oil as in Example I uniformly blend 0.63 percent manganese carbonate with 99.37 percent of the lubricating oil to obtain a lubricating composition containing about .03 percent by weight of manganese.

Example VI

Formulate a lubricating composition by uniformly blending 1.1 percent manganese phosphate with 98.9 percent of the lubricating oil employed in Example I to obtain a lubricating composition containing about 0.38 percent by weight of manganese.

Example VII

Dissolve 0.87 percent of manganese chloride in 300 milliliters of water and combine the water solution with approximately one gallon of the lubricating oil of Example I. The emulsion concentrate is then blended with the remaining lubricating oil and stirred for approximately ten minutes at about 150° F.

In order to test the effectiveness of the lubricating compositions of this invention in reducing wear, the lubricating compositions were employed as lubricants in an L-1 single cylinder Caterpillar diesel engine having a bore of 5¾ inches and a stroke of 8 inches. The top ring of the diesel was activated to render it radioactive. The engine was flushed twice with portions of the test oil after which six quarts of the test oil were placed in the crankcase and the engine started. A summary of the test conditions is as follows:

Water out	140° F.
Oil temperature	140° F.
R.P.M	825.
Horsepower	15.
Oil pressure	30 lbs./sq. in.
Oil charge	6 quarts.
Length of test	20 hours.

During the test the oil was continuously circulated through a well wherein a scintillation counter continuously recorded the radioactivity of the oil on a chart. The increase in radioactivity of the oil is utilized to indicate the degree of wear occurring within the engine by substituting into the following formula:

$$\text{Iron (milligrams)} = \frac{\text{pounds of oil} \times 454 \times \text{counts per gram of oil}}{\text{counts per milligram of iron in the standard}}$$

In the above formula, the counts per milligram of iron in the standard is obtained by measuring the activity of a solution containing a weighed amount of a second iron ring which had been irradiated in the same manner as the test ring employed in the engine. The fuel employed in these tests was a residual type fuel having the following inspection.

Gravity, ° API	23.4
Viscosity, SUS:	
100° F	76.7
130° F	55.3
210° F	37.8
Flash, ° F	205
Sulfur, percent	1.24
Ash as oxide, percent	0.03
Vanadium, p.p.m	172

The following table shows the significant reduction in ring wear provided by representative lubricating compositions of the invention as compared with the same lubricating oil containing no additives, and also with lubricating compositions containing inorganic manganese additives not possessing the hardness characteristics specified herein. The manganese metal and manganese dioxide employed in lubricating compositions A and B have a Mohs hardness above 5 and therefore are not satisfactory lubricating oil additives. The hardness of the various inorganic manganese compounds was determined by placing a small amount of the material to be tested between two microscope glass slides and rubbing the slides together under finger pressure.

Lubricant	Atom weight ratio [1] Mn: V	Percent change in wear over base oil
Lubricating composition of Example V	0.162:1	−42
Lubricating composition of Example VI	0.22:1	−28
Composition A comprising: 99.62% lubricating oil, 0.38% manganese metal	0.22:1	+45
Composition B comprising: 99.40% lubricating oil, 0.60% Manganese dioxide	0.22:1	+60

[1] Based on the vanadium content of the fuel and the amounts of the fuel and lubricant used.

As seen from the above data, the lubricating compositions of the invention comprising a major proportion of a lubricating oil and minor amounts of inorganic manganese compounds having the specified hardness charac-

teristics significantly reduce wear in internal combustion engines operating on fuel containing vanadium in amounts sufficient to cause corrosion. In contrast, the above data shows that lubricating compositions containing minor amounts of inorganic manganese compounds which will scratch glass, i.e., which have a hardness of above about 5 on the Mohs scale of hardness cause engine wear to be increased considerably.

It is apparent also that small amounts of the manganese compounds are effective to reduce corrosion due to vanadium, thus making unnecessary the introduction into the engine of excessive amounts of manganese such as to result in the manganese itself forming large amounts of abrasive deposits.

The lubricating oil compositions of the invention are particularly suited for the lubrication of diesel engines which operate on high vanadium content fuels. Furthermore, the new compositions may advantageously be utilized in the lubrication of all types of internal combustion engines which operate on fuels containing vanadium in amounts sufficient to cause corrosion.

In addition to the additives disclosed herein, there may be present in the lubricating compositions of this invention, other conventional additives such as antioxidants, pour point depressants, anti-rust agents, oiliness improvers, viscosity index improvers, detergents, anti-foam agents, dispersants, and the like.

Those modifications and equivalents which fall within the spirit of the invention and the scope of the appended claims are to be considered part of the invention.

We claim:

1. A lubricating composition adapted for reducing wear in an internal combustion engine operating on a fuel containing vanadium in an amount sufficient to produce a corrosive ash upon combustion thereof, said lubricating composition comprising a dispersion of an inorganic manganese compound in a major amount of a lubricating oil, said inorganic manganese compound having a degree of hardness on the Mohs hardness scale of not more than about 5 and being present in said lubricating composition in an amount sufficient to provide a manganese content of about 0.17 to about 1 percent by weight.

2. The lubricating composition of claim 1 wherein the inorganic manganese compound is manganese carbonate.

3. The lubricating composition of claim 1 wherein the inorganic manganese compound is manganese phosphate.

4. A method of reducing wear in a diesel engine operating on a fuel containing vanadium in an amount sufficient to produce a corrosive ash upon combustion thereof which method comprises introducing into said engine as a lubricant a composition comprising a dispersion of an inorganic manganese compound in a major amount of a lubricating oil, said inorganic manganese compound having a degree of hardness on the Mohs hardness scale of not more than about 5 and being present in said lubricating composition in an amount sufficient to reduce corrosion by reaction of the manganese compound with the vanadium to form a non-corrosive ash.

5. The method of claim 4 wherein said lubricating composition is introduced into the crankcase of said diesel engine.

6. The method of claim 4 wherein said lubricating composition is introduced directly into the cylinders of said diesel engine.

7. The method of claim 4 wherein the inorganic manganese compound is manganese carbonate.

8. The method of claim 4 wherein the inorganic manganese compound is manganese phosphate.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,009,875 November 21, 1961

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 60, for ".03" read -- 0.3 --; column 5, line 2, for "fuel" read -- fuels --.

Signed and sealed this 10th day of April 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents