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CYLINDER OILS

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The present invention relates to the lubrication of steam cylinders and, more particularly, to improved steam cylinder oils containing a minor proportion of a material increasing the spreading characteristics of steam cylinder mineral oils.

The operation of steam engines involves lubrication of the cylinder walls in such a manner as to reduce the friction and wear of the piston and the walls. When conditions within the cylinder are such that substantially no condensation occurs within the cylinder, little difficulty is experienced in lubricating the cylinder with pure mineral oil. However, the ideal conditions under which no condensation occurs within the cylinder are rarely achieved in industrial operations. Condensation is eliminated only when the steam is superheated to such a degree that the expansion occurring in the cylinder is insufficient to lower the temperature of steam to that at which condensation occurs or when the steam is substantially dry throughout the piston cycle. Consequently, the steam in the cylinder is generally wet. The art has recognized that condensation practically always occurs in the cylinders of steam engines and has for many years striven to provide compounded oils which will lubricate the cylinder satisfactorily in the presence of condensate.

The art has recognized that when straight mineral oil is used under wet steam conditions, i. e., when condensate forms in the cylinder, the adhesion of the oil to the cylinder walls is poor and the quantity of oil required for satisfactory lubrication becomes excessive. This, in turn, causes the formation of carbon deposits which interfere with the smooth operation of the engine.

In order to improve the adhesion and spreading of pure mineral oils to cylinder walls under the usually prevailing wet steam conditions, various additives have been blended with cylinder stocks. In the past the conventional additives have been fatty acid esters of glycerol or other alcohols such as lard, tallow, neatsfoot oil and degreas. These additives under the conditions existing in the steam cylinder, i. e., in the presence of water and at high temperature and pressures, are hydrolyzed to the free fatty acids and the alcohol.

At the present time it is general practice to mix with the base mineral oil cylinder stock up to 12 per cent by weight of the afore-mentioned additives depending upon the quality of the steam in the cylinder. When the steam is superheated or dry throughout the piston cycle, compounding, i. e. mixing mineral oil and additive, is neither necessary nor desirable. However, as the quality of the steam decreases, i. e., as the amount of the liquid phase in the steam increases, it is necessary to increase the amount of additive. In other words, the wetter the steam, the greater the

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amount of additive. Accordingly, it would appear that the problem of lubricating steam cylinders involves spreading oil over a surface which is covered with a layer of water. In other words, the problem of lubricating steam cylinders involves at least one factor that is not encountered in the usual problems of lubricating surfaces which move relative to each other. For example, in lubricating the cylinder walls of internal combustion engines, the presence of a relatively large amount of water and high temperatures is not encountered. Consequently, many of the additives now incorporated in lubricants for internal combustion engines are not suitable for use in the lubrication of steam cylinders.

The role of the additive appears to be that of assisting in the spreading of the oil over the internal surface of the steam cylinder at the temperatures and pressures existing in the cylinder of a steam engine. Less mineral oil is required to provide satisfactory lubrication when the oil is spread uniformly over the internal surface of the cylinder. On the other hand, when the oil collects in globules larger amounts of oil are required to provide satisfactory lubrication of a steam cylinder. The use of a small amount of oil to properly lubricate a steam cylinder is accompanied by two advantages, (1) lower lubrication cost, and (2) less carbon deposited on the cylinder walls.

It has now been found that the disadvantages of prior art steam cylinder oils can be overcome by adding a minor proportion of the condensation product of a dicarboxylic hydroxy acid with a monohydric alcohol and preferably the reaction product of an unsaturated monohydric alcohol having about 16 to about 20 carbon atoms in the molecule and a dicarboxylic aliphatic hydroxy acid to a mineral oil fraction meeting the specifications for steam cylinders oils.

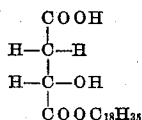
It is an object of the present invention to provide a compound cylinder oil containing a minor proportion of the condensation product of an aliphatic dicarboxylic hydroxy acid and a monohydric alcohol. It is another object of the present invention to provide a compound cylinder oil having an interfacial tension at 77 degrees Fahrenheit with distilled water of not more than about 25 dynes per centimeter and comprising a major proportion of steam cylinder oil fraction of a mineral oil and a minor proportion of the condensation product of an aliphatic dicarboxylic hydroxy acid and a monohydric alcohol.

It is a further object of the present invention to provide a steam cylinder oil having an interfacial tension at 77 degrees Fahrenheit with distilled water of not more than about 25 dynes per centimeter and comprising a major proportion of a mineral oil fraction having a Saybolt viscosity at 210 degrees Fahrenheit of about 100 seconds

to about 300 seconds and a minimum flash point of about 425 degrees Fahrenheit and a minor proportion of a condensation product of an aliphatic dicarboxylic hydroxy acid and an unsaturated monohydric alcohol. Other objects and advantages will become apparent from the following description.

The present invention, generally stated, comprises mixing about 0.1 per cent to about 1 per cent by weight of the product produced by condensing an aliphatic hydroxy dicarboxylic acid with a monohydric alcohol having at least five carbon atoms with a mineral oil fraction, known to the art as steam cylinder stock, and having a Saybolt viscosity at 210 degrees Fahrenheit of about 100 seconds to about 300 seconds and a minimum flash point of about 425 degrees Fahrenheit. Preferably, the additive is the reaction product of an aliphatic dicarboxylic hydroxy acid and an unsaturated aliphatic monohydric alcohol. Of these latter compounds, the reaction product of oleyl alcohol and malic acid is especially preferred.

Products produced by the reaction of a given amount of hydroxy aliphatic dicarboxylic acid and the stoichiometric amount of monohydric aliphatic alcohol necessary to produce either the neutral ester or the acid ester have given satisfactory results. These products have a neutralization number within the range of 5 milligrams to 100 milligrams KOH per gram which, e. g., when calculated in terms of the acid ester of oleyl malate



Acid ester of oleyl malate (molecular weight=384)

is equal to about 3.5 per cent to about 69 per cent mono-oleyl malate. However, products having acid ester concentration up to 100 per cent may be used. It is preferred to use products of the condensation of oleyl alcohol and malic acid which have a neutralization number of about 9 to about 100 milligrams of KOH per gram equivalent to an acid ester concentration calculated as mono-oleyl malate of about 6 to about 69 per cent.

As has been pointed out hereinbefore, the measure of the efficacy of an additive in a steam cylinder oil is the effect of the additive on the rate and degree of spreading of a drop or globule of oil on the surface of water. The data presented in the following table shows very well that typical products produced by the condensation of an aliphatic monohydric alcohol and an aliphatic dicarboxylic hydroxy acid increase the tendency of a steam cylinder oil to spread on the surface of water. The reaction products of oleyl alcohol, lauryl alcohol and stearyl alcohol with malic acid, tartaric acid, succinic acid and maleic acid were selected as illustrative of the effect of various condensation products upon the lubricating effect of a steam cylinder stock selected as the base steam cylinder stock and having the properties set forth hereinafter:

Steam cylinder stock
A. P. I. gravity, 24.8
Flash point, 610° F.
S. U. V. at 210° F., 235 seconds
Carbon residue, 2.8% (maximum)

To provide a means of comparison with prior art additives, lard oil was selected as representa-

tive. The lard oil had the properties set forth hereinafter:

Specific gravity, 0.916
Flash point, 500° F. (minimum)
S. U. V. at 100° F., 211 seconds
Saponification number, 190 (minimum)
Iodine number, 75 (maximum)
Free fatty acids, 3% (maximum)

Comparison of the effect of the addition agents disclosed herein upon the lubrication of steam cylinders has been correlated with the rate of spreading and completeness of spreading of cylinder oil and compounded cylinder oil, with surface tension and with interfacial tension. Those oils which provide satisfactory cylinder lubrication are characterized by almost instantaneous and complete spreading in the test described hereinafter and by an interfacial tension with distilled water of not more than about 25 dynes per centimeter (d. cm.) at 77 degrees Fahrenheit.

The spreading characteristics of mineral oil and mineral oil compounded with various prior art and novel additives have been compared by allowing a drop of test oil weighing approximately 35 milligrams to fall from the orifice of 5 millimeter glass tubing onto the surface of a pool of distilled water at a temperature of about 190 degrees Fahrenheit held in a Petri dish cover having a diameter of 10 centimeters. The container was cleaned before each test by washing with water, drying with a soft towel, washing again in a bath of petroleum ether and a bath of acetone and drying. The surface and interfacial tensions of the various oils were determined with a du Nouy Tensiometer. Data thus obtained are tabulated in the table for the test steam cylinder oil and the oil compounded with prior art additives, the novel additives and analogous esters.

Reaction product A was obtained by reacting 0.25 mole of malic acid and an amount of commercial lauryl alcohol slightly in excess of 0.5 mole without a catalyst. The reaction mixture was digested at about 240 to about 250 degrees Fahrenheit for about 3 hours. Thereafter about 40 parts by volume of toluene were added and the mixture refluxed for about 6 hours at a pot temperature of about 285 to about 290 degrees Fahrenheit. The reaction mixture was then topped under vacuum. The residue comprising the reaction product immediately after preparation had a neutralization number (N. N.) of 16 which is equivalent to a concentration of about 10 per cent of the acid ester.

Reaction product B was obtained by reacting about 0.2 mole of malic acid and an amount of commercial stearyl alcohol sold under the trade name of "Stenol" slightly in excess of about 0.4 mole in the absence of a catalyst. (As those skilled in the art know, "Stenol" is a mixture of C₁₈ alcohols containing substantially no unsaturated alcohols.) The reaction mixture was digested at 240±10 degrees Fahrenheit (bath temperature about 250 to about 260 degrees Fahrenheit) for about 4 hours under atmospheric pressure. Thereafter the mixture was digested under a vacuum for about 11 hours at a temperature of about 250 to about 260 degrees Fahrenheit. The reaction product immediately after preparation had a neutralization number (N. N.) of 26.

Reaction products C and G were obtained by reacting 1 mole of malic acid and an amount of commercial oleyl alcohol (sold under the trade

name of "Ocenol") slightly in excess of 2 moles in the absence of catalyst. The reaction mixture was digested for several hours and the reaction product treated to separate acid esters from neutral esters. The reaction mixture immediately after preparation had a neutralization number (N. N.) of 17. The reaction mixture was extracted to remove water soluble acids. A petroleum ether solution of the residue was extracted with 2 per cent solution of potassium hydroxide in 50 per cent alcohol to remove the acid esters. The residue from the alcoholic potassium hydroxide solution is neutral ester (product C). The alcoholic potassium hydroxide solution of acid ester was acidified and the acid ester recovered (product G). The neutralization number (N. N.) of product G immediately after preparation was 106, equivalent to about 70 per cent acid ester.

Product F was prepared by digesting about 0.33 mole of maleic acid and an amount of "Ocenol" slightly in excess of 0.66 mole for about 0.75 hour. Thereafter about 50 to about 60 parts by volume of toluene were added and the mixture refluxed at a pot temperature of about 285 degrees Fahrenheit for about 10 hours. The reaction mixture was filtered and topped.

Product D was prepared by mixing about 1 mole of "Ocenol," about 0.5 mole of succinic anhydride and about 350 cubic centimeters of xylene. The mixture was heated to reflux and maintained at about reflux temperature for about 12 hours. Water produced in the reaction was removed while refluxing. The reaction mixture was filtered and the filtrate topped to remove the xylene. The topped filtrate had a neutralization value of 19.0.

Product E was produced from tartaric acid and oleyl alcohol in a manner similar to the foregoing procedures. The product had a neutralization value of about 7 immediately after preparation and an OH value of 179 average.

8, 12 and 13). It will also be observed that there is no apparent correlation between surface tension and the rate and degree of spreading of an oil. Thus, steam cylinder oil per se has a surface tension of 33 dynes per centimeter (d. cm.) at 77 degrees Fahrenheit but forms a globule on the surface of clean water at 190 degrees Fahrenheit. On the other hand, the same steam cylinder oil containing 0.67 per cent of mono-oleyl malate has a surface tension of 32 dynes per centimeter but spreads instantaneously and completely (compare items 2 and 13). Accordingly, it is manifest that reaction products of an aliphatic monohydric alcohol having at least 5 carbon atoms and aliphatic dicarboxylic hydroxy acid, which reaction products have a neutralization number of at least 5 are effective additives for lubricating oils to be used in the lubrication of steam cylinders. It will also be observed that an effective steam cylinder lubricant has an interfacial tension with distilled water at 77 degrees Fahrenheit not greater than about 25 dynes per centimeter and preferably has an interfacial tension of about 20 or less.

We claim:

1. A steam cylinder lubricant consisting essentially of a mineral oil fraction having a Saybolt viscosity from about 100 seconds to about 300 seconds, at 210° F., and a flash point of at least about 425° F., and about 0.2 per cent of the esterification reaction product of oleyl alcohol and maleic acid, said reaction product containing about 67 per cent of an acid ester of said alcohol and said acid.

2. A steam cylinder lubricant consisting essentially of a mineral oil fraction having a Saybolt viscosity from about 100 seconds to about 300 seconds at 210° F., and a flash point of at least about 425° F., and from about 0.2 per cent to about 1 per cent of the esterification reaction

Formula No.	Formulation	Neutralization No. of Additives	Per cent Acid Ester in Additive	Per cent Acid Ester in Formula	Surface Tension @ 77° F. ¹	Interfacial Tension @ 77° F. ¹	Spreading Characteristics @ 190° F.
1.	Distilled water				70		
2.	Steam cylinder oil				33	39	Globule; no spreading.
3.	99% S. C. O., 1% Lard oil	4.1			32	31	Globule; gradually widening to partial spreading.
4.	97% S. C. O., 3% Lard oil	4.1			32	22	Instantaneous and complete. ³
5.	93% S. C. O., 7% Lard oil	4.1			32	16	Instantaneous and complete.
6.	99% S. C. O., 1% Reaction Product A	11.3	6	0.06	32	13	Do.
7.	99% S. C. O., 1% Reaction Product B	12.8	9	0.09	32	25	Do.
8.	99% S. C. O., 1% Reaction Product C	12.5	8	0.08	32	11	Do.
9.	99% S. C. O., 1% Reaction Product D	8.7	6	0.06	32	29	Gradual; only partial.
10.	99% S. C. O., 1% Reaction Product E	9.2	6	0.06	32	10	Instantaneous and complete.
11.	99% S. C. O., 1% Reaction Product F	15.6	10	0.10	32	33	Gradual; only partial.
12.	99.8% S. C. O., 0.2% Reaction Product G	98.0	67	0.13	32	14	Instantaneous and complete.
13.	99% S. C. O., 1% Reaction Product G	98.0	67	0.67	32	6	Do.
14.	99.8% S. C. O., 0.2% oleyl alcohol	0.14			33	36	Gradual; only partial.
15.	99.8% S. C. O., 0.2% Maleic acid		Insoluble in	Steam cylinder oil			

¹ Values in dynes per centimeter.

² The term "partial" signifies that the oil film occupied over $\frac{1}{2}$ but less than the entire surface of the Petri dish.

³ The term "complete" signifies that the oil film occupied the entire surface of the Petri dish.

Inspection of the foregoing data establishes several criteria. The reaction products of monohydric aliphatic alcohols and aliphatic dicarboxylic hydroxy acids are more effective additives than the reaction products of monohydric aliphatic alcohols and non-hydroxylated aliphatic dicarboxylic acids although both additives have substantially the same acid ester concentration (compare items 9 and 10). It will also be noted that an increase in the concentration of acid ester in the steam cylinder oil beyond about 0.10 per cent while producing a decrease in interfacial tension appears to provide diminishing returns in so far as rate and completeness of spreading is concerned (compare items

product of oleyl alcohol and maleic acid, said reaction product containing about 67 per cent of an acid ester of said alcohol and said acid.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,370,299	Farrington	Feb. 27, 1945
2,096,390	Burwell	Oct. 19, 1937
2,025,984	Harris	Dec. 31, 1935