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STEAM CYLINDER OIL

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This invention relates to lubricating oils, and more particularly to compounded lubricants which are effective in the presence of steam, i. e. are suitable for use in the lubrication of steam engines and the like.

Lubricants to be used in steam engines must possess certain properties not required of most lubricants. In such engines the temperatures may be of the order of 550° F. and higher if superheated steam is employed, and accordingly the lubricant must have high heat-resisting qualities to prevent gumming and carbon formation. The presence of moisture in a steam engine is inherent in its operation, even though such engines may be operated with superheated or dry steam; at certain stages in the operation moisture or wet steam will usually be present. Moisture tends to scour the metal parts free of oil and prevent the spread of oil over the surface to be lubricated. As a result the relative movements of various metal parts may become jerky due to increased friction.

The lubrication of the moving parts of such engines is usually accomplished by atomizing the lubricant through a quill into the steam line and utilizing the steam to carry the lubricant to the moving parts. Inasmuch as superheated steam is not a good carrying medium for lubricating oil, the latter must be readily atomizable to be effective in the presence of dry steam. Further, such oils must be thermally stable to prevent carbon deposits from forming and clogging the quill.

It is an object of this invention to provide a lubricant having greater utility in the presence of steam than had lubricants heretofore provided for such a purpose. It is another object of this invention to provide a lubricant for use in the presence of dry or wet steam. Another object of this invention is to provide an oil that will readily spread to provide an oil film on a surface to be lubricated in the presence of steam. Still another object is to provide an oil of greater adherence to metal surfaces in the presence of steam than oils heretofore employed. A further object is to provide an oil that is thermally stable in the presence of superheated steam.

I have found that one or more of the foregoing objects can be achieved with the aid of my new steam cylinder oil which comprises a heavy, asphalt-free lubricating oil to which have been

added a dispersing agent and petroleum resins, the various components being selected as will be described in the following.

Oils for use as base stocks in the compounding of steam cylinder oils should be heavier than lubricating oils used in internal combustion engines. Suitable ranges of viscosities for such oils normally range from about 100–300 seconds S. U. at 210° F., and preferably about 150–250 seconds at 210° F. Further, the base stocks should be composed mainly of saturated hydrocarbons in order to possess great stability under high heat conditions, and they should be free from asphaltenes which readily carbonize and thereby interfere with proper lubrication. Pennsylvania steam-reduced or, preferably, clay-filtered stocks or Midcontinent or California deasphalted or, if desired, solvent-extracted bright stocks, are suitable. In general, refined oils are preferred for reasons of preventing formation of coke-like material on heated metal parts to be lubricated. On the other hand, over-treated oils which readily oxidize, thereby forming excessive amounts of acidic oxidation products and sludge, should be avoided because they may cause severe corrosion and other difficulties.

Deasphalting may comprise asphalt precipitation with liquid propane, butane, pentane, etc., to which may have been added methane or ethane under high pressure; or, by vacuum distillation, to distill the lubricating oil, leaving the asphalts in the residue.

Solvent extraction may involve the use of a single selective solvent having preferential solvent power for aromatic hydrocarbons, such as furfural, nitrobenzene, phenol, cresols, dichloro-diethylether, antimony trichloride, etc.; or of a pair of mutually immiscible solvents, one being selective for aromatics and the other for paraffins, such as phenol and propane, etc.

Other refining methods may comprise treating with sulfuric acid, clay, aluminum chloride, etc.

Petroleum resins as herein defined are high-boiling organic compounds normally contained in unextracted bright stocks, which compounds are completely soluble in 86 Bé. naphtha, possess molecular weights in excess of about 500, have specific dispersions above 200, and contain substantial proportions frequently of the order of 30% or more of components adsorbable on silica

gel or other acidic adsorbents and the recovery of the adsorbed compounds, etc. Methods for producing such resins are described in Merrill U. S. 2,081,496 and in Anderson U. S. 2,201,466.

As indicated before, the petroleum resins for use in the instant invention must be substantially free of asphalts, particularly those obtained from cracked hydrocarbons, and should always be produced from deasphalted straight-run crudes. Unlike asphalts, the petroleum resins form true solutions in petroleum hydrocarbons.

The amounts of resins to be added to the base stock may vary somewhat, depending on the nature of the stock itself. Some stocks already contain appreciable amounts of resins naturally associated therewith, and such oils obviously require smaller quantities of additional resins than stocks which are substantially devoid of them. However, as a rule, the natural content of resins is insufficient for best results, and oils which naturally contain resins invariably are benefited by the further addition of resins, although perhaps not to so large an extent as oils originally free of resins.

As a rule, useful amounts of resins to be added range from about 1%–15% by weight of the base stock, and more often from 2%–10%.

To the mixture of base stock and petroleum resins, a minor proportion of the order of .05% to 1%, and preferably from .1% to .5%, of a dispersing or emulsify agent capable of spreading hydrocarbon oil on metal surfaces wetted by water is added. Such an additive preferably comprises a salt of an alkali metal with an organic detergent-forming acid. However, alkaline earth metals or amino base salts with such acids may be used.

The organic detergent-forming acids may comprise, for example, carboxylic acids of the type $R-COOH$, such as lauric, palmitic, stearic, oleic, linoleic, ricinoleic acids, oxidized paraffin acids, tall oil acid, rosin acids, abietic acid, wool fat acids, naphthenic acids, alkylated benzoic and naphthoic acids, aromatic fatty acids such as phenyl stearic acid, terpenic acids, etc.; acids of the sulfonic acid type $R-SO_3H$, for example petroleum sulfonic acids such as the mahogany acids or "green acids" produced in the manufacture of medicinal oils by treatment with fuming sulfuric acid of paraffinic mineral oils such as lube oil, etc.; or of various aliphatic or alicyclic sulfonic acids such as fatty sulfonic acids, fatty aromatic sulfonic acids, naphthene sulfonic acids; or of sulfonic acids of various aromatic hydrocarbons, particularly those which contain one or more alkyl radicals and which may contain non-functional substituents, such as various alkylated benzenes, diphenyls, xylenes, diphenyl methanes, naphthalenes, anthracenes, phenanthrenes, tetralines; alkyl phenols such as those contained in cracked petroleum distillates; alkylated chlornaphthalenes, naphthylamines, diphenyl oxides, chlorinated diphenyl oxides, diphenyl sulfides, diphenyl amines, phenyl naphthylamines, dinaphthyl oxides, sulfides, or amines; alkylated pyridines, quinolines, isoquinolines, pyrrol, pyrrolidines, piperidine, thiophenes, thiophanes, etc.; or of various sulfonic acids of carboxylic acid esters or amides; acids of the sulfuric acid ester type, $ROSO_3H$, for example turkey red oil, sulfated fish oils, sulfated fatty acids such as mono lauryl, cetyl, stearyl, etc., sulfate acids; or mono esters of sulfuric acid obtained by treating with strong to moderately strong sulfuric acid various olefines or alcohols

such as the long-chain olefines obtained in the vapor phase cracking of wax at about 550° C–560° C., polymers obtained in the polymerization of normally gaseous olefines with inorganic polyoxy acids or Friedel-Crafts catalysts, fatty or naphthenic alcohols obtained in the catalytic reduction of fatty or naphthenic acids, alcohols obtained by condensation of ketones or aldehydes followed by hydrogenation; or alkyl aromatic mono esters of sulfuric acid, etc. A convenient source for many of the active sulfate ester acids is the sludges obtained in the acid treatment of cracked distillates, or the spent acids obtained in the polymerization of olefines or in the alkylation of isoparaffins with olefines with sulfuric acid. Suitable organic detergent-forming acids such as have been described in the foregoing may, if desired, contain non-functional radicals such as halogen, hydroxyl, ether, amino, imino, hydrosulfide, sulfide, carboxyl ester, etc.

Fatty oils such as tallow, frequently used as steam cylinder oils, should be avoided as under superheat conditions they decompose and form deposits of carbon as well as corrosive acids.

It will be understood that the foregoing order of mixing of the various components of my compounded oil need not be observed.

In order to evaluate the lubricants prepared in accordance with the invention, the following experiments were performed.

A piston in a steam engine was lubricated with a fixed quantity of the oil under test, after which it was run as long as possible at a constant steam pressure without the addition of further amounts of oil. The number of strokes made and the smoothness of operation were noted and were taken as indicative of the quality of the oil. Thus, an oil that was well dispersed and adhered to the surface to be lubricated in the presence of steam would enable the operation to continue smoothly for a long period before the drag of metal-to-metal contact stopped operation.

The apparatus used consisted of a 3"x2"x3" reciprocating steam pump, equipped with a mechanical lubricator. An insulated surge tank and steam gauge were connected to the steam inlet line between the control valve and the pump, which maintained a more constant pressure and reduced fluctuation in the gauge reading. The pistons and rings were removed from the fluid end of the pump and the rods at that end were kept well oiled so that practically all load on the pump was due only to friction in the steam end. A stroke counter was attached to the pump.

The testing procedure was as follows: The lubricator and its connection to the pump were carefully cleaned with gasoline and ether. They were then flushed and filled with the oil to be tested. The pump was then operated at a constant speed for 60 minutes, with the lubricating feed set at a definite rate. Lubrication was then stopped, the stroke counter placed in position, and the operation of the pump continued at the constant speed. The strokes were counted until the pump would no longer operate at 2.50 pounds pressure. The type of operation of the pump was carefully observed throughout the test and judged as smooth, jerky, or very jerky.

In order to prevent test from being affected by carryover from a previous oil which might have remained in the pump, a blank run was made on unfiltered bright stock between each stock on a different oil. Consecutive tests on different oils would not be run until a correct result was ob-

tained for the intermediate blank bright stock test.

The following table shows the results of comparative tests as above outlined in the presence of wet steam on the newly compounded oils of the invention with conventional steam lubricating oil.

Oil sample	Strokes	Description of operation
1. 150 at 210° F. Unfiltered bright stock. ¹	Less than 500.	Very jerky.
2. 150 at 210° F. Unfiltered bright stock ² plus 8% acidless tallow.	do.....	Do.
3. 150 at 210° F. Unfiltered bright stock ² plus 5% petroleum resin plus .2% sodium oleate.	24,200.	Smooth.
4. 150 at 210° F. Dewaxed steam-refined stock. ¹	Less than 500.	Very jerky.
5. 150 at 210° F. Dewaxed steam-refined stock ¹ plus 8% tallow.	2,200	Jerky.
6. 150 at 210° F. Dewaxed steam-refined stock ¹ plus 5% petroleum resins.	Less than 500.	Very jerky.
7. 150 at 210° F. Dewaxed steam-refined stock ¹ plus .2% sodium oleate.	13,400.	Smooth.
8. 150 at 210° F. Dewaxed steam-refined stock ¹ plus 5% petroleum resins plus .2% sodium oleate.	24,866.	Do.
9. 150 at 210° F. Dewaxed steam-refined stock ¹ plus 4% petroleum resins plus .2% sodium oleate plus .3% sodium sulfonate of petroleum.	32,000.	Do.

¹ Midcontinent residual stock, propane-deasphalted and dewaxed.

² Duosol extracted stock, propane-deasphalted and dewaxed.

The above results show that the newly compounded oils (Examples 3, 8, 9) gave far better results than conventional unblended oils or oils blended with a soap or tallow. The effect of the combination of petroleum resins with soap in the oils of the invention is more than additive in that, as will be noted from the table, the combination improved operation far more than might be expected from the effect of soap or petroleum resins when added alone to a lubricating stock.

The oils were subjected to a second test to determine their chemical stability under high temperatures of the order of 550° F. attained by employing superheated or dry steam. They were injected into a highly superheated steam line through a quill, simulating actual engine lubrication practiced over a period of time.

It was found that compounded oils containing tallow decomposed on the quill, tarnished it, and formed carbonaceous deposits, while the steam-oleate-resin blends left the quill bright and free of any deposits.

I claim as my invention:

1. A steam cylinder lubricating oil consisting essentially of a mineral lubricating oil free from asphaltenes and of viscosity suitable for steam cylinder oil containing a minor proportion of a dispersing agent selected from the group consisting of salts of alkali metals, alkali earth metals and amines with organic detergent form-

ing acids, which agent is capable of spreading hydrocarbon oil on metal surfaces wetted by water, and from about 1% to about 15% by weight of added petroleum resins.

2. The composition of claim 1 in which the lubricating oil is a refined hydrocarbon oil of a viscosity of the order of 100-300 seconds S. U. at 210° F.

3. The composition of claim 1 in which the amount of the dispersing agent is between .05% and 1%.

4. The composition of claim 1 in which the amount of the dispersing agent is between about .1% and about .5%.

5. A steam cylinder lubricating oil consisting essentially of a mineral lubricating oil free from asphaltenes and of viscosity suitable for steam cylinder oil containing a minor proportion of an alkali metal salt of an organic detergent-forming acid and from about 1% to about 15% by weight of added petroleum resins.

6. A steam cylinder lubricating oil consisting essentially of a mineral lubricating oil free from asphaltenes and of viscosity suitable for steam cylinder oil containing a minor proportion of an amino base salt of an organic detergent-forming acid and from about 1% to about 15% by weight of added petroleum resins.

7. A steam cylinder lubricating oil consisting essentially of a mineral lubricating oil free from asphaltenes and of viscosity suitable for steam cylinder oil containing a minor proportion of an alkaline earth metal salt of an organic detergent-forming acid and from about 1% to about 15% by weight of added petroleum resins.

8. A steam cylinder lubricating oil consisting essentially of a mineral lubricating oil free from asphaltenes and of viscosity suitable for steam cylinder oil containing a minor proportion of sodium oleate and from about 1% to about 15% by weight of petroleum resins.

9. A steam cylinder lubricating oil consisting essentially of a mineral lubricating oil free from asphaltenes and of viscosity suitable for steam cylinder oil containing a minor proportion of an alkali metal salt of a rosin oil acid and from about 1% to about 15% by weight of added petroleum resins.

10. A process for preparing a steam cylinder oil comprising mixing a heavy lubricating oil which is substantially free from asphaltenes together with from about 1% to about 15% of petroleum resins and a sufficient quantity of a dispersing agent selected from the group consisting of salts of alkali metals, alkali earth metals and amines with organic detergent forming acids to cause the formation of a suitable water-in-oil emulsion when the resulting mixture is introduced into a steam cylinder.

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