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CORROSION-PREVENTIVE HYDROCARBON OIL

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This invention deals with normally liquid hydrocarbon oils, especially lubricants having improved anti-corrosive properties and wetting properties for metals. More particularly, it deals with lubricants comprising mineral lubricating oils in which have been dissolved certain high-molecular weight amines or combinations of these amines with relatively high-molecular weight carboxylic acids having 12 or more carbon atoms and being preferably predominantly aliphatic.

It is known that at elevated temperatures mineral lubricating oils in general wet metals rather poorly. Inasmuch as parts of engines to be lubricated are frequently heated during use, the wetting power of the oil for the metal at these temperatures may be highly important. Tests have been developed for measuring the critical adhesion temperatures of oils for metals, which tests show that a wide variety exists between the critical adhesion temperatures of different types of oils.

It is a purpose of this invention to produce a lubricating oil which has a high critical adhesion temperature. It is another purpose to produce an oil which not only does not withdraw from metals at high temperatures, but on the contrary, tends to spread over them in spite of the high temperature. Another purpose is to produce oils which have powerful anti-corrosive properties and which can be used for coating freshly machined metal parts to prevent their being attacked by moisture.

I have discovered that the addition of a substance which I call "wax amine" and which will be described hereinafter in more detail, has the peculiar property of greatly increasing the wetting power of mineral lubricating oils or other refined liquid or solid hydrocarbons to which it is added. This wetting power is greatly enhanced by the further addition of a carboxylic acid having at least 12 carbon atoms. Hydrocarbon oils to which the invention is particularly applicable comprise oils substantially free from asphalts, such as refined mineral lubricating oils or lubricants containing them, such as various greases, e. g., soda soap greases, calcium soap greases, aluminum soap greases, etc. Oils used for dipping metals to prevent their being attacked by moisture or acids in the atmosphere may, if desired, be lighter than lubricating oils and may comprise gas oil, kerosene or naphtha. Other compositions for rust protection may comprise petrolatum, paraffin wax, etc.

The amount of paraffin wax to be added to mineral lubricating oils to be effective for my

purpose may range from about .25% to 5%, and preferably from around .5% to 2%. Amounts of the carboxylic acids, if added, may range from about .1% to 2%, it being preferred that at least a slight excess of the wax amine over the stoichiometric equivalent of the monocarboxylic acid be present.

Wax amines of this invention are reaction products of chlorinated hydrocarbon wax treated with ammonia under conditions to cause ammonolysis. Following is a description of the process by which they are manufactured:

A paraffin wax or petrolatum is chlorinated by bubbling chlorine through it, preferably at a temperature between 105° and 125° C. until a chlorine content above at least 20% and preferably 25%–38% by weight is reached. The chlorinated wax is dissolved in a suitable solvent, such as absolute ethyl alcohol, and ammonia is added thereto in sufficient quantity, e. g., 8%–10% by weight. The mixture is heated in an autoclave to a temperature of the order of 150°–175° C. which produces a pressure of about 300–500 lbs. until ammonolysis is substantially completed, which may require, for example, 6 hours. The ammonium chloride, solvent and excess ammonia are then separated by filtration and distillation.

Wax amines prepared under the above preferred conditions have more pronounced metal-wetting properties than wax amines prepared under different conditions.

The composition and properties of wax amines vary in general within the following normal range:

They are translucent viscous liquids of amber to brown color having an average molecular weight of 450–600; bromine number below 100, usually 25–100 (gms. Br/100 gm.); a nitrogen content of 3%–6%, of which about 10%–50% is tertiary and the remainder primary or secondary amines. A typical sample of wax amine had an average molecular weight of 505, bromine number of 60, contained 5.50% nitrogen, of which 69% was in the form of primary or secondary amines and 31% of tertiary amines.

Thus it can be seen that wax amine is a mixture of aliphatic amines, containing no appreciable proportion of quaternary ammonium compounds. Most paraffin chains carry more than one nitrogen and are slightly unsaturated. However, the molecules contain no aromatic groups.

Carboxylic acids to be added in addition to the wax amine should have at least 12 carbon atoms and should preferably be saturated, i. e., be free or substantially free from olefinic double bonds.

Saturated acids in general are less apt to break down through oxidation, and also in general are far more effective in the matter of enhancing the effect of the wax amines. They should preferably be predominantly aliphatic, i. e., should contain more than half of their carbon atoms in aliphatic formation, inasmuch as the predominantly cyclic acids, and particularly the aromatics, are normally less effective. The acids may be mono- or polycarboxylic.

Suitable acids are, for example, lauric, palmitic, stearic, behenic, arachic, phenyl stearic, etc., acids. Other suitable acids may be produced by oxidation of paraffin wax, for example, by blowing air through it at an elevated temperature, if desired, in the presence of an oxidation catalyst. Of the polycarboxylic acids, the alkylated succinic acids and agaric acids are very suitable. Still other acids are the alkylated glutaric, adipic, pimelic, suberic, azelaic, sebacic, tricarballic, wax phthalic, polymerized oleic, etc., acids. Amino, hydroxy, halogen, sulfur, etc., derivatives of the above may be used, as, for example, hydroxy or amino palmitic or stearic acids, chlorinated or sulfurized fatty or alkyl maleic acids, N-amino bis fatty acids, etc.

In addition to the above compounds, other agents may be added, such as oxidation inhibitors, blooming agents, detergents, etc. The presence of anti-oxidants, such as oxidation inhibitors or retarders is particularly desirable, inasmuch as they will not only protect the mineral lubricating oil from deterioration, but the wax amine as well. Suitable oxidation inhibitors may be of the aromatic hydroxy or amino type.

Example I

The critical adhesion temperature of an oil with and without the wax amine additive was measured as follows: The critical adhesion temperature apparatus comprises a 1" x 2" bar of cold rolled steel having a trough on one side. The bar is placed in a position of 1° inclination to horizontal with the trough on the upper surface. The bar is then heated at the lower end so as to maintain there a temperature of 400° F. Two or three drops of oil to be tested are placed in the trough at a point where the temperature is exactly 400° F., and the movement of the oil is then noted. The oil then begins to move up against the gravitational force away from the source of heat. If the oil has good adhesion qualities, it will stop at a relatively short distance from the source of heat. If it has poor adhesion qualities, it will travel farther. The temperature of the spot at which the oil stops is then noted and recorded as the critical adhesion temperature.

A western mineral lubricating oil S. A. E. 30 was tested by the above test. Its critical adhesion temperature was 150° F. To a sample of this oil was added 1% of the wax amine and 2.5% of a calcium petroleum sulfonate, the latter being a detergent having no influence on the adhesive properties of the oil. The critical adhesion temperature rose to 164° F. To another sample was added 1% wax amine, 5% stearic acid and 2.5% of the calcium petroleum sulfonate. The critical adhesion temperature now rose to 269° F., and the oil spread up the sides of the trough, leaving a continuous film, thus showing excellent wetting power.

Example II

Stainless steel balls were coated with doped and undoped S. A. E. 30 lubricating oil. The coated balls were placed in a water bath maintained at 40° C. After 64 hours, the balls were examined with the following results:

Addition agent	Condition of stainless steel balls
None	Rusted.
1/4% free wax amines	2 or 3 small dark spots.
1% free wax amines	Few dark spots.
1% wax amine + 1/4% stearic acid	1 dark spot, very small.

Example III

Mild steel plates were coated with doped and undoped S. A. E. 30 lubricating oil. The coated plates were then left undisturbed, exposed to the atmosphere for three days. At end of that period, they were examined with the following results:

Addition agent	Condition of plates after 3 days
None	Edges rusted.
5% free wax amines	Edges somewhat rusted.
5% free wax amines + 5% stearic acid	No rust.

I claim as my invention:

1. A corrosion-protective composition for metals comprising a normally non-gaseous hydrocarbon oil substantially free from asphalt and containing dissolved a small amount of a hydrocarbon wax amine substantially free from chlorine which amine is a reaction product of chlorinated paraffin wax and ammonia.

2. The composition of claim 1 wherein said non-gaseous hydrocarbon comprises a refined lubricating oil.

3. The composition of claim 1 wherein said non-gaseous hydrocarbon is a petrolatum.

4. A corrosion-protective composition for metals comprising a normally non-gaseous hydrocarbon oil substantially free from asphalt and containing dissolved a small amount of a hydrocarbon wax amine substantially free from chlorine having a molecular weight of about 450-600, a nitrogen content of 3%-6% and a bromine number below 100 which amine is a reaction product of chlorinated paraffin wax and ammonia.

5. A corrosion-protective composition for metals comprising a normally non-gaseous hydrocarbon oil substantially free from asphalt and containing dissolved 25%-5% of a hydrocarbon wax amine substantially free from chlorine which amine is a reaction product of chlorinated paraffin wax and ammonia.

6. A corrosion-protective composition for metals comprising a normally non-gaseous hydrocarbon oil substantially free from asphalt and containing dissolved 5%-2% of a hydrocarbon wax amine substantially free from chlorine which amine is a reaction product of chlorinated paraffin wax and ammonia.

7. A corrosion-protective composition for metals comprising a normally non-gaseous hydrocarbon oil substantially free from asphalt and containing dissolved small amounts each of hydrocarbon wax amine substantially free from chlorine and a predominantly aliphatic carboxylic acid having at least 12 carbon atoms.

8. The composition of claim 7 wherein said acid is saturated.

9. The composition of claim 7 wherein said acid is a saturated fatty acid.

10. The composition of claim 7 wherein said acid is a saturated dicarboxylic acid.

11. The composition of claim 7 wherein said acid is a saturated alkyl succinic acid.

12. A corrosion-protective composition for metals comprising a normally non-gaseous hydrocarbon oil substantially free from asphalt and containing dissolved from .25%-5% of a hydrocarbon wax amine substantially free from chlorine and from .1%-2% of a predominantly aliphatic saturated carboxylic acid having at least 12 carbon atoms.

13. A corrosion-protective composition for metals comprising a normally non-gaseous hydrocarbon oil substantially free from asphalt and containing dissolved from .25%-5% of a hydrocarbon wax amine substantially free from chlorine

and from .1%-2% of a saturated predominantly aliphatic carboxylic acid having at least 12 carbon atoms, the amount of the wax amine being in excess of the stoichiometric equivalent of said acid.

14. A blended mineral lubricating oil having anti-corrosive properties for metals and a critical adhesion temperature substantially higher than that of said mineral lubricating oil alone, containing dissolved .25%-5% of a hydrocarbon wax amine substantially free from chlorine which amine is a reaction product of chlorinated paraffin wax and ammonia.

15. The composition of claim 7 wherein said acid is a saturated monocarboxylic acid.

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