My invention relates to an improved heat transfer oil composition comprising a base stock which is preferably a hydrocarbon, and an effective amount of a basic calcium sulfonate, having a base number of at least 15, wherein the basicity is due to calcium hydroxide.

BACKGROUND

The present invention relates to an improved heat transfer oil composition comprising a base stock, preferably a hydrocarbon base stock, and an effective amount of a basic calcium sulfonate, having a base number of at least 15, wherein the basicity is due to calcium hydroxide.

The use of hydrocarbon oils as a heat transfer agent is well known. For example, the Kirk-Othmer "Encyclopedia of Chemical Technology" describes use as a heat transfer oil as one of many uses for hydrocarbon lubricating oils derived from petroleum.

A major problem resulting from the use of hydrocarbon oils as a heat transfer agent is heat exchanger fouling. At relatively high temperatures, for example above 350°F, and particularly above 600°F, hydrocarbon oils decompose and form gums and coke-like materials which deposit on heat exchanger surfaces. These deposits greatly reduce heat transfer efficiency and are the cause of frequent maintenance.

In the past one means of overcoming, or minimizing, the problem has been to prevent formation of the degradation products. The use of oxidation inhibitors, of virgin aromatic-type oils, and of highly cracked stocks have been the chief means of imparting stability to a base oil. But even with the use of these materials, fouling still occurs.

Miller and Patzelt in U.S. Pat. No. 3,105,810, teach a process for preventing fouling of metal conductors in a refinery process wherein various refinery stocks are passed through the metal conductor at temperatures in the range of 200 to 1100°F. The process of Miller and Patzelt comprises incorporating in the refinery stock from 1 to 500 parts per million of an alkaline earth metal (e.g., calcium) salt of a petroleum sulfonic acid.

I have found that a basic calcium sulfonate, having a basicity of at least 15 and wherein the basicity is due to calcium hydroxide, is particularly effective in reducing fouling in heat transfer oils. Furthermore, I have found that the use of a basic calcium sulfonate as described in the foregoing gives a substantial improvement over the use of a neutral calcium sulfonate as taught by Miller and Patzelt. Moreover, I have found that a basic calcium sulfonate wherein the basicity is due to calcium hydroxide gives a substantial improvement over a basic calcium sulfonate wherein the basicity is due to calcium carbonate.

In addition to the Miller-Patzelt patent discussed above, a search of the prior art related to the present invention produced the following U.S. patents as references: 2,442,820, 2,626,207, and 2,639,227. Inasmuch as these references are much less pertinent than U.S. 3,105,810, it is not believed necessary to discuss them.

BRIEF SUMMARY OF MY INVENTION

My invention relates to an improved heat transfer oil composition comprising a base stock which is preferably

DETAILED DESCRIPTION

Materials used

The basic calcium sulfonate of my invention can be used with a variety of heat transfer oils, both hydrocarbon and nonhydrocarbon. Since the hydrocarbon heat transfer oils are inexpensive and have many applications, they are considered more suitable for use in my heat transfer oil composition.

The term hydrocarbon heat transfer oil is well understood in the art. Usually, it refers to a lubricating oil fraction having viscosity, volatility, and vapor pressure properties which render it suitable. Generally, it is desirable that the hydrocarbon oil have an initial boiling point of at least 450°F. Preferably, it has an initial boiling point of at least 550°F. Examples of suitable hydrocarbon heat transfer oils include the following:

Refined mineral cylinder oils having a viscosity of 20–300 S.S.U. at 210°F. (these are also known as "pale oils")

Bright stocks having a viscosity of 90–150 S.S.U. at 210°F.

Refined aromatic oils having a viscosity of 230–300 S.S.U. at 210°F.

Another group of suitable hydrocarbon heat transfer oils are the bottoms fractions derived from the preparation of detergent alkylate (both "soft" and "hard" detergent alkylate—these terms being well understood in the art).

Examples of suitable bottoms fractions derived from the preparation of detergent alkylate include the following:

Postdecylenbenzene which is a bottoms product resulting from the manufacture of dodecylbenzene. Postdecylenbenzene is described in detail in U.S. Pat. No. 3,150,088, which patent is made a part of this disclosure.

"Dimer alkylate bottoms" which is the bottoms fraction resulting from the preparation of "dimer alkylate" prepared by the following steps:

(1) dimerization of a suitable feedstock such as cat poly gasoline,

(2) alkylation of an aromatic hydrocarbon (preferably benzene) with the dimer from step (1).

Preferably, the dimerization step uses a Friedel-Crafts alkylation sludge as the catalyst. This process and the resulting product are described in application Ser. No. 367,417, now U.S. Pat. No. 3,410,925 filed May 14, 1964, and having the same assignee as the present application.

A material referred to as "NAB Bottoms" which are predominately di-n-alkyl aromatic hydrocarbons wherein the alkyl groups contain from 8 to 18 carbon atoms. The process of preparing these materials and the resulting product are described in application Ser. No. 529,284, filed Feb. 23, 1966, and having the same assignee as the present application. Another process of preparing a bottom product containing predominately di-n-alkyl aromatic hydrocarbons is described in application Ser. No. 521,794, filed Jan. 20, 1966, and having the same assignee as the present application.

For the purpose of making my disclosure even more complete, application Ser. Nos. 367,417, 529,284, and 521,794 are made a part of this disclosure.
3,554,914

Still another group of suitable hydrocarbon heat transfer oils are the substantially pure oil-soluble dialkylnaphthenes, i.e., those wherein the alkyl groups contain from 8 to 18, and preferably from 12 to 15, carbon atoms. One method of preparing these dialkylnaphthenes is disclosed and claimed in application Ser. No. 762,639, filed Sept. 25, 1968, said application having a common assignee with the present application.

Of the hydrocarbon heat transfer oils, those derived from refining of crude petroleum are considered more suitable, with the refined mineral cylinder oils (or "pale oils") being preferred.

Examples of the more suitable non-hydrocarbon heat transfer oils include the following: oil-miscible, high molecular weight polyglycol ethers, and alkyl phenol ethylene oxide ethers. Examples of other suitable non-hydrocarbon heat transfer oils include the diesters, silicate esters, chlorinated biphenyls, and the silicones.

It is to be understood that the term "heat transfer oil" or "heat transfer agent" as used herein refers to liquids having an initial boiling point of at least 450° F.

Suitable basic calcium sulfonates for use in my composition meet the following qualifications: base number (acet ic) of at least 15, preferably between 15 and 30; basicity is due to calcium hydroxide. In addition, preferably, the basic calcium sulfonate has an activity (i.e., sulfonate content) of 25 to 60 percent by weight, and more preferably 40 to 50 percent by weight.

Basic calcium sulfonates meeting my requirement can be prepared by double decomposition of a sodium sulfonate with calcium chloride followed by a "cook-in" with calcium hydroxide.

A particularly suitable basic calcium sulfonate is "Bryton" Calcium Sulfonate 45. This material has the following typical properties:

- Total calcium, wt. percent: 3
- Calcium sulfonate, wt. percent: 45
- Mineral oil, wt. percent: 53
- Water, wt. percent: 0.2
- Base number, acet ic: 22
- Color, ASTM Dill: 3/2

The basic calcium sulfonate, suitably, is used in my heat transfer oil composition in an amount of at least above 0.0050% by volume. More suitably, it is used in an amount of at least about 0.25% by volume. Preferably, it is used in an amount of at least about 1% by volume. Inasmuch as the effectiveness levels off and because of the cost, it is material that will be used in an amount in excess of 5% by volume. Knowing that the basic calcium sulfonate has a beneficial effect in heat transfer oils anyone skilled in this art can readily determine the effective amount to be used.

The term "base number" as used herein means acetic base number, which is determined by an acetic acid titration method which utilizes glacial acetic acid as the solvent and a solution of perchloric acid in glacial acetic acid as the titrant. The method is especially adapted for determinations of this type, since equilibria are obtained rapidly. The procedures for carrying out acetic acid titrations are generally outlined in Analytical Chemistry, vol. 23, No. 2, February 1951, page 337, and vol. 24, No. 3, March 1952, page 519. As used herein, base number refers to milligrams of potassium hydroxide per gram of sample.

ILLUSTRATIONS AND COMPARISONS

Heat transfer oil compositions for use in the claimed invention are illustrated hereinafter and are compared with certain other compositions. It is to be understood that this information is for purposes of illustration and not for any purpose of limitation.

The laboratory method 1 (ASTM-D-1600) employed for determining the fouling tendency of an oil consists of recycling the oil through a heating zone composed of two concentric hollow tubes. A rod heater is contained in the inner tube and the oil is pumped through a 0.035 inch annulus between the two tubes. The oil is pumped at the rate of 5 pounds per hour and leaves the heating zone at a temperature of 300° F. After leaving the heating zone the oil is cooled to around 70° F. and recycled to the feed tank. The oil is held in the feed tank at 200° F. throughout the test. The length of the test is five hours. In some cases the fouling tendencies is determined relatively by visual inspection of the amount of deposits on the inner tube of the heating zone. In other cases the fouling tendency is determined by the use of an Erdco tester.

(I) This illustrates the beneficial effect of a basic calcium sulfonate, as described in the foregoing, in hydrocarbon heat transfer oils.

The compositions tested were the following:

<table>
<thead>
<tr>
<th>Material</th>
<th>Deposit covered by deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>170 pale oil</td>
<td>Dulling haze 25%</td>
</tr>
<tr>
<td>170 pale oil plus 1% Bryton Calcium Sulfonate</td>
<td>No deposit</td>
</tr>
</tbody>
</table>

(II) This illustrates the improvement of using the basic calcium sulfonate of my invention as compared to:

(a) neutral calcium sulfonate,
(b) basic calcium sulfonate wherein the basicity is due to calcium carbonate.

The compositions tested on the Erdco tests were as follows:

<table>
<thead>
<tr>
<th>Material</th>
<th>Approximate amount of Erdco tube covered by deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>170 pale oil</td>
<td>Dulling haze 25%</td>
</tr>
<tr>
<td>170 pale oil plus 1% Bryton Calcium Sulfonate</td>
<td>No deposit</td>
</tr>
</tbody>
</table>

(A) Base stock consisting of 25% commercial heat transfer oil A (see following table), 25% commercial heat transfer oil B (see following table), and 50% 170 pale oil (as used in I above).

(B) Base stock containing 1% (volume) neutral (base number less than 5) calcium sulfonate.

(C) Base stock containing 1% (volume) basic calcium sulfonate (base number of 25) wherein the basicity is due to calcium carbonate.

(D) Base stock containing 1% (volume) basic calcium sulfonate (base number of 22) wherein the basicity is due to calcium hydroxide ("Bryton" Calcium Sulfonate 45).

The commercial heat transfer oils had the following properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>API gravity, ° F.</td>
<td>32.8</td>
<td>30.6</td>
</tr>
<tr>
<td>Viscosity:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial, ° F.</td>
<td>650</td>
<td>375</td>
</tr>
<tr>
<td>End Point, ° F.</td>
<td>930</td>
<td>744</td>
</tr>
<tr>
<td>Color, ASTM Dill</td>
<td>31.63</td>
<td>67.66</td>
</tr>
<tr>
<td>C.O.C. flash point, ° F.</td>
<td>6.31</td>
<td>6.75</td>
</tr>
<tr>
<td>pour point, ° F.</td>
<td>-15</td>
<td>0</td>
</tr>
<tr>
<td>Color, ASTM</td>
<td>1.5</td>
<td>1</td>
</tr>
</tbody>
</table>
Using the tuberator method of rating the tubes, the following results were obtained:

<table>
<thead>
<tr>
<th>Tube deposits</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>8</td>
<td>7</td>
<td>7</td>
<td>6</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Composition:

III) Pilot plant tests were conducted on hydrocarbon heat transfer oils containing 1% (by volume) "Bryton" Calcium Sulfonate 45. The tests showed that basic calcium sulfonate gave improved results over previously available additives. The tests indicated that heat exchanger life can be doubled and that the furnace transfer temperature can be increased from 640° F. to 660–665° F. The tests further indicated that the heat transfer oil of my invention can be used continuously for at least 850 hours at 600° F. in a closed system.

While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto, since many modifications may be made; and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. A process for preventing fouling of a metal conductor through which is passing a heat transfer oil, said heat transfer oil being selected from the group consisting of hydrocarbon oils having an initial boiling point of at least 450° F., oil-miscible high molecular weight polyglycol ethers, alkyl phenol ethylene oxide ethers, silicate esters, chlorinated biphenyls and silicones, said heat transfer oil being normally susceptible to the formation of gums and coke-like materials on the metal conductor when the temperature of said heat transfer oil is above 350° F., said process comprising adding to said heat transfer oil an effective amount, in the range of from about 0.0050 percent to about 5 percent by volume, of a basic calcium sulfonate, having a base number of at least 15, the basicity of said basic calcium sulfonate being due to calcium hydroxide.

2. The process of claim 1 wherein the heat transfer oil is a hydrocarbon oil having an initial boiling point of at least 450° F.

3. The process of claim 1 wherein the basic calcium sulfonate has a base number of 15 to 30.

4. The process of claim 3 wherein the basic calcium sulfonate has a calcium sulfonate content of from 40 to 50 percent by weight.

5. The process of claim 2 wherein the heat transfer oil is a refined mineral cylinder oil having a viscosity of about 20 to about 300 S.S.U. at 210° F.

6. The process of claim 2 wherein the heat transfer oil is a bright stock having a viscosity of about 90 to about 150 S.S.U. at 210° F.

7. The process of claim 2 wherein the heat transfer oil is a refined aromatic oil having a viscosity of about 230 to about 300 S.S.U. at 210° F.

8. The process of claim 3 wherein the heat transfer oil is a refined mineral cylinder oil having a viscosity of about 20 to about 300 S.S.U. at 210° F.

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U.S. Cl. X.R.

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