RUST PREVENTIVE COMPOSITIONS OF PARAFLIN MINERAL OIL THICKENED WITH POLYETHYLENE AND MICROCRYSTALLINE WAX

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This invention relates to hot-dip rust preventive compositions comprising oil thickened with a synergistic mixture of polyethylene and microcrystalline wax to a solid or semi-solid gel and containing various rust preventive additives.

Hot-dip rust preventive compositions are used to protect metal surfaces, particularly ferrous metals, from corrosion, due to humidity, rain, sea water and the like. To apply, the metal is dipped into the melted rust preventive and a soft grease-like coating results upon cooling. One advantage of this rust preventive is that after the rust is coated, it can be packaged immediately with essentially no delay for drying and there is no fire hazard from volatile solvents. In addition, the protective films of hot-dip rust preventive compositions are relatively soft and thus do not readily chip or flake if the film is accidentally struck. Since the film is soft, it can be readily removed by simple wiping and any film not removed from metal parts, such as from bearings and the like, does not interfere with subsequent lubrication. Because of its gel-like structure at room temperature, a relatively heavy coating of the rust preventive is obtained (as compared to a slushing oil) and better rust protection results.

Fluid type preventive compositions have been prepared using a blend of a mineral oil and microcrystalline wax, the microcrystalline wax improving the effectiveness of the composition. It has now been found that by the simultaneous use in oil of a small amount of polyethylene along with small quantities of microcrystalline wax, that gelting occurs and a solid composition results. This finding was surprising, since much larger amounts of either microcrystalline wax or polyethylene when used alone are required to thicken oil to a gel.

The mineral oils useful in the composition of the invention will have a viscosity at 210°F. of about 25 seconds to 500, preferably 30 to 150 SUS and a pour point below about 30°F. Such mineral oils may be fractions from low cold test crude oils which contain only small amounts of naturally occurring wax. Such mineral oils may also be obtained from wax crude oils by removing essentially all of the wax therefrom by a dewaxing step such as solvent (methyl ethyl ketone, propane, etc.) dewaxing, plate and frame pressing and the like. Either naphthenic or paraffinic oils may be used, although the paraffinic oils appear to have a greater solvating effect on the polyethylene thereby requiring a larger relative amount of polyethylene for thickening.

Microcrystalline waxes useful in this invention have melting points (E.M.P.) of about 130° to 210°F., preferably 140° to 200°F., and are obtained as a by-product from the dewaxing of heavy mineral oils such as cylinder oils and bright stocks. It will be understood, however, that it is within the scope of this invention to use naturally occurring waxy oils which have an SUE viscosity at 210°F. of about 30 to 200 seconds which contain the proper amount (about 8 to 30% by weight) of these microcrystalline waxes and which are essentially free of lower melting point waxes, i.e., those melting below about 150°F. Also, if desired, the microcrystalline wax may be added in the form of a petroleum, that is, a wax containing a relatively high proportion of oil, such as 10% to 60% by weight of oil, and 90% to 40% by weight of microcrystalline wax. The preferred microcrystalline waxes are commercial waxes containing less than about 35%, and preferably less than about 25%, by weight of oil.

The polyethylene which are used in the invention are those oil-dispersible polyethylenes having molecular weights of 9,000 to 200,000, preferably 10,000 to 100,000. These polyethylenes may be prepared either by the older high pressure system wherein pressures of 1,000 atmospheres are used to produce branched chain polyethylene or the polyethylene may be a substantially linear polyethylene produced by the newer low pressure method utilizing catalyst mixtures such as aluminum trialkyls in combination with titanium tetrachloride. Processes for production of high pressure polyethylene are well known in the art while the low pressure method is described in Ziegler's Belgian Patent 333,362.

Rust preventive agents which may be used in the composition include the C_{12} to C_{22} fatty acid partial esters of aliphatic polyhydric alcohols containing from 2 to 12, preferably 3 to 8, carbon atoms and about 2 to 8, e.g., a minimum of 2 hydroxy groups per mole. Preferred materials are the mono- and diesters of C_{3} to C_{6} fatty acids containing from 3 to 6 hydroxy groups and prepared from C_{12} to C_{18} fatty acids. The above type of partial esters includes the partial esters of the mono-dehydrated aliphatic polyhydric alcohols as well as partial esters of non-dehydrated aliphatic polyhydric alcohols. Examples of these partial esters are: sorbitan monooleate, glyceroy monooleate, pentanoyl monooleate, the di-esters of sorbitan, mal- nitan, pentaerythritol and related polyhydric alcohols, the corresponding partial stearic and palmitic acid esters of these alcohols, and partial esters of these alcohols made from mixtures of these fatty acids. Agents of this type are well known in the art, e.g., U.S. 2,434,490 and 2,716,611.

The metal sulfonates which can be used as rust preventive agents are the oil-soluble alkali metal and alkaline earth metal salts of high molecular weight sulfonic acids, generally produced by the treatment of petroleum oils of the lubricating oil range with fuming sulfuric acid. The sulfonic acids useful in preparing sulfonate additives generally have molecular weights of about 300 to 700, e.g., 350 to 500. Petroleum sulfonates have been described in numerous patents, e.g., U.S. 2,467,176 and are well known in the art. The sulfonates can also be derived from naturally pure alkyl aryl sulfonic acids having from about 10 to 33 carbon atoms per molecule. For example, sulfonated products of alkylated aromatics such as benzene, toluene, xylene, naphtalene, etc., alkylated with olein or olefin polymers of the type of polypropylene, polysobutylenes, etc. can be used. Specific examples of sulfonates which can be used as additives include petroleum sulfonates such as calcium petroleum sulfonate, barium petroleum sulfonate, sodium petroleum sulfonate and synthetic sulfonates such as calcium di-C_{6} alkyl benzene sulfonate, barium di-C_{6} alkyl naphthalene sulfonate and sodium C_{17} alkyl benzene sulfonate, wherein the C_{17} alkyl group is derived from laurylbutane; the C_{6} from tripropylene and the C_{16} from tetraisobutylenes.

The metallic sulfonates may be either neutral sulfonates, i.e., where the sulfonic acid is neutralized with an equal molar equivalent amount of metal base, or the sulfonates may be of the so-called "high alkalinity" type. In the latter case, additional metal base, in excess of that required for simple neutralization, is reacted with the sulfonate to form an alkaline product which can then be blown with carbon dioxide to reduce its alkalinity and form a substantially neutral final product. Recent work has indicated that such so-called high alkalinity sulfonates are nothing more than dispersions of neutral sulfonates and a carbonate of the metal used which are believed to exist in the form of colloidal sols.

Other additives which may be added to the composition
are oxidized wax esters, metal xanthates, metal phenolates, metal naphthenates, metal organo phosphates and thiophosphates, vegetable and animal fatty oils, degras, lecithin, etc., and in general, any other oil-soluble additive commonly used in rust preventive compositions.

The compositions of the invention will comprise an oil base and about 1 to 10, preferably 2 to 5 weight percent of the gelling agent, based on the weight of the total composition. The gelling agent in turn will comprise about 0.5 to 5.0, preferably 1 to 4 parts by weight of the polyethylene per part by weight of microcrystalline wax. In addition to the oil and gelling agent, the composition will also contain about 1 to 10, preferably 2 to 8 weight percent active ingredient, of a rust preventive agent of the type outlined above. The composition may also contain minor amounts of materials such as water displacing agents, paraffin waxes, metal soaps, etc.

The invention will be further understood by the following examples:

**EXAMPLE 1**

A series of compositions was made by adding to a base oil, polyethylene of 20,000 molecular weight available under the trade name “Alathon,” which was prepared by the high pressure method and a microcrystalline wax having a melting point (English) of 180° F. This microcrystalline wax was a solvent recrystallized, low oil content, micro wax known commercially as Crown 180 wax, marketed by the Petroleum Corp., of Kilgore, Texas. The base oil used in preparing the above compositions was a paraffinic mineral lubricating oil having a viscosity of 30 SUS at 210° F. obtained by acid treatment of a Mid-Continent crude. The compositions were prepared by adding the polyethylene and the microcrystalline wax to the oil and heating while stirring to about 300° F. in order to melt the polyethylene and the microcrystalline wax and disperse them into the oil. The compositions were then allowed to cool and their physical form noted. For comparison purposes, oil compositions were also prepared containing the polyethylene alone and the microcrystalline wax alone. The compositions prepared and their physical form when cooled to room temperature, are summarized in Table 1 which follows:

**Table I**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (20,000 mol. wt.)</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Microwax (300 F. E.M.P.)</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Mineral Oil (30 SUS 210° F)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Physical form</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
</tr>
</tbody>
</table>

Compositions 8 to 12 of Table I, containing the polyelethylene and micro wax were prepared using a naphthenic their physical form when cooled to room temperature, are summarized in Table 1 which follows:

**Table I**

**GELLING EFFECTS OF POLYETHYLENE AND MICROCRYSTALLINE WAX**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (20,000 mol. wt.)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Mineral Oil (30 SUS 210° F)</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Physical form</td>
<td>Semt.</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
<td>Semt.</td>
<td>Gel</td>
</tr>
</tbody>
</table>

Compositions 8 to 12 of Table II, containing the polyethylene alone in the oil resulted in a fluid product. Also, 10 weight percent of the microcrystalline wax alone in the oil resulted in a fluid product. However, by using minor amounts of these two materials in combination, it was possible to prepare semi-gels and gels as illustrated by samples 1 through 5. As seen by the above table, it is desirable to have in excess of 1% of polyethylene, preferably at least 2 weight percent of the polyethylene in order to form a solid gel.

The above data was obtained using a paraffinic, low viscosity oil which has a higher solvating power for the polyethylene than would have a higher viscosity naphthenic oil. Thus, 10 weight percent of polyethylene added to certain high viscosity naphthenic oils will result in a solid composition. However, the above test does show that for a given base oil, whether paraffinic or naphthenic, that the combination of polyethylene and micro wax will have a much greater thickening effect than a like amount of either component alone.

In order to demonstrate the effectiveness of the polyethylene and microcrystalline wax in the formation of actual rust preventive compositions, a second series of compositions was prepared incorporating a rust preventive.

**EXAMPLE 2**

This series of rust preventive compositions was prepared by dissolving in a mineral oil the polyethylene and microcrystalline wax, along with a rust preventive agent, by adding all the components to a mineral oil and heating to about 300° F. in order to dissolve the components into the oil. The compositions prepared were tested in a standard humidity cabinet (N.A. H-31 Humidity Cabinet Test) by dipping sandblasted steel panels into the melted rust preventive composition, and then suspending the coated dry panels in the humidity cabinet which was maintained at a temperature of 120° F. and 100% relative humidity. The compositions prepared and their humidity cabinet life are summarized in Table II which follows. Also, included for comparison purposes, are oil compositions containing the rust preventive but omitting the polyethylene and microcrystalline wax.

**Table II**

**EFFECTIVENESS OF RUST PREVENTIVE FORMULATIONS**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (20,000 mol. wt.)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Microwax</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Alathon 285</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Barium sulfonate</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
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<tr>
<td>Sodium sulfonate</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Oil (100 vis. 210° F)</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Physical form</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
</tr>
<tr>
<td>Humidity cabinet life in days</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

1. 20,000 mol. wt. polyethylene.
2. 300 F. E.M.P. microcrystalline wax.
3. Commercial turpentine naphthenate.
4. Commercial rust preventive additive material containing sodium-barium soap of oxidized wax acids, petroleum sulfonates and lecithin.
5. Commercial barium petroleum sulfonate (40% active ingredients in oil).
6. Sodium petroleum sulfonate (40% active ingredient in oil).
7. Acid treated Mid-Continent naphthenic oil.
8. Acid treated naphthenic oil.
oil having a viscosity of 30 SUS at 210° F. Compositions 13 to 16 which contained no polyethylene or micro wax were prepared from a naphthenic oil having a viscosity of 40 SUS at 210° F. These two different viscosity base oils were used in order to obtain compositions having comparable viscosities at the dipping temperature. In this manner, equal film thicknesses were obtained and the resulting test results made comparable.

As seen by Table II above, not only do the polyethylene and micro wax contribute toward forming a gel type rust preventive, but these gel type rust preventives have considerably longer humidity cabinet life than liquid type rust preventives consisting only of an oil and a rust preventive agent. The main reason for this is that the gel-type film provides an impregnable barrier to the penetration of water vapor.

While the preceding examples have shown the effectiveness of polyethylene with microcrystalline wax, comparable results are not obtained with other closely related polymers. For example, it had been previously proposed to incorporate relatively large amounts of micro wax and certain highly oil-soluble viscosity index improving polymers (such as polyisobutylene and low molecular weight polypropylene) into mineral oil. Here the purpose was to form a lubricating oil composition for aircraft engines which would also form a very soft rust preventive gel on the internal walls of the engine when the engine was not operating. This composition has been described in U.S. Patent 2,845,548. However, the compositions of said U.S. patent are not suitable for long term severe rust protective conditions since such compositions have rather low melting points (e.g. about 105° to 115° F.) and form an unstable structure easily disrupted by any slight shearing stress. On the other hand, the compositions of the present invention are directed towards higher dropping point materials (200° F., +) having high shear stability, and in addition require relatively small amounts of the polymer and micro wax.

What is claimed is:

1. A method of preventing rusting of metal surfaces which comprises coating said surfaces by dipping into a melted rust preventive composition consisting essentially of a major amount of paraffinic mineral oil, about 1 to about 2 wt. percent of polyethylene of 9,000 to 200,000 molecular weight, about 1 to about 3 wt. percent of microcrystalline wax having a melting point of about 150° to 210° F., and a rust inhibiting amount within the range of about 1 to 10 wt. percent of an oil-soluble rust preventive agent, and wherein the said polyethylene and microcrystalline wax exhibit a synergistic thickening effect.

2. A method according to claim 1, wherein said rust preventive agent is a fatty acid partial ester of an aliphatic polyhydric alcohol.

3. A method according to claim 1, wherein said rust preventive agent is a metal alkyl aryl sulfonate.

4. A method according to claim 1, wherein said oil has a viscosity of 25 to 500 SUS at 210° F.

5. A rust preventive gel composition consisting essentially of a major amount of paraffinic mineral oil of about 30 SSU viscosity at 210° F., about 1 to 2 wt. percent of polyethylene of 10,000 to 100,000 molecular weight, about 1 to 3 wt. percent of microcrystalline wax having a melting point of 140° to about 200° F., and about 1 to 10 wt. percent of an oil-soluble rust preventive agent, wherein said composition is a gel at room temperature, and wherein said polyethylene and said microcrystalline wax exhibit a synergistic thickening effect.

6. A composition according to claim 5, wherein said rust preventive agent is a metal sulfonate.

7. A composition according to claim 5, wherein said rust preventive agent is a C₁₂₅ to C₂₅₂ fatty acid partial ester of a C₄ to C₁₂ aliphatic polyhydric alcohol having 2 to 8 hydroxy groups.

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