PROCESS FOR PREPARING NEUTRALIZED ALKYL PHENOL SULFIDES

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The instant invention relates to an improvement in the process for the preparation of lubricating oil additive materials. Particularly, the invention relates to an improved process for the preparation of neutral metal salts of alkyl phenol sulfides. More particularly, the invention relates to an improved process for the preparation of alkaline earth metal salts of alkyl phenol sulfides, wherein the alkyl phenol sulfide is first pretreated with a minor amount of a basic alkaline earth metal reacting material at a relatively low temperature and is thereafter neutralized with an alkaline earth metal basic reacting material at a temperature that is substantially higher than the temperature used in the pretreatment stage.

It is well known in the prior art that alkaline earth metal salts of alkyl phenol sulfides, such as the magnesium, calcium, barium or strontium salts of tertiary aminyl phenol sulfide, tertiary octyl phenol sulfide, nonyl phenol sulfides, their disulfides, polysulfides, and the like, are extremely useful as additive materials for lubricating oils. They are also useful as additives in other liquid hydrocarbons, such as diesel and oil burner fuels, and the like.

They have been found to be particularly useful in mineral base lubricating oil compositions for use in internal combustion engines. The alkyl phenol sulfides and their preparation are well known in the art; see, for example, U. S. Patent No. 2,518,379 (col. 2, line 3, to col. 3, line 3, for their description; and col. 3, line 45, to col. 4, line 53, for their preparation).

It has been found however that neutralized alkaline earth metal salts of alkyl phenol sulfides, particularly when combined with other additive materials such as the alkaline earth metal or alkali metal sulfonates, have a tendency to form sludge or other residue upon continued storage. The reason for this sludge or sediment formation is not clearly known at this time. Such sulfonates include the oil-soluble petroleum sulfonates and synthetic sulfonates (e. g., alkyl benzenesulfonates) conventionally employed as lubricant additives which are derived from sulfonic acids having molecular weights of about 400 to 500. The sediment problem occurs in lubricating oil concentrates containing about 20 to 75 wt. percent of the alkaline earth metal alkyl phenol sulfides and blends of such concentrates with concentrates of sulfonates containing 20 to 75 wt. percent of sulfonates, as well as in finished lubricating oils.

It has now been found, and forms the object of this invention, that a completely neutralized alkyl phenol sulfide that is not subject to sediment formation upon standing, can be prepared by a new process which involves a pretreatment of the alkyl phenol sulfide with a small amount of an alkaline earth metal base at a relatively low temperature followed by a neutralization step with alkaline earth metal base at an elevated temperature, substantially above the pretreatment temperature. The alkyl phenol sulfides employed in the present invention generally have to 18, preferably 6 to 10, carbon atoms in the alkyl group attached to each benzene ring. In accordance with the present invention, the alkyl phenol sulfide is first treated with a small amount of a basic reacting alkaline earth metal material. Such materials include calcium and/or barium hydroxides and their corresponding hydrates and the like. Compounds of barium are particularly preferred. Compounds of calcium are second choice. The amount of alkaline earth metal base employed in the pretreatment step should be about 3 to 15%, preferably about 3 to 10% of the amount of alkaline earth metal base which would be necessary to completely neutralize the alkyl phenol sulfide. Such amounts are particularly effective when employing barium bases. When calcium bases are employed, it is preferred to employ at least about 5% of the amount of calcium base which would be required for neutralization because of the fact that calcium is less basic than barium. For effective pretreatment, it is also necessary to have a small amount of water present, namely about 0.8 to 10.0% by weight based on alkyl phenol sulfide. This water may be present as free water and/or as water of hydration in the basic reacting compound (e. g., barium hydroxide pentahydrate). It is essential that the pretreatment be carried out at a temperature of about 130° to 160° F., and it is particularly preferred to employ a temperature of about 140° to 150° F. Generally the pretreatment will be carried out with agitation for about 0.1 to 2 hours (e. g. 0.2 to 0.5 hour). It has been found that the aforementioned conditions are necessary to prepare an alkaline earth metal alkyl phenol sulfide which is essentially free from sediment formation.

After the pretreatment step described above is completed, the temperature of the mixture is raised to one within the range of about 230° to 260° F., preferably from about 240° to about 250° F., and a sufficient quantity of alkaline earth metal basic reacting material is added to completely neutralize the alkyl phenol sulfide. Following addition of the neutralizing agent, the mixture is dehydrated, the temperature being at least 285° F. (e. g. 285° to 300° F.). The time required for the final neutralization and for dehydration is generally in the range of about 0.3 to 2 hours.

The alkyl phenol sulfides may be selected from the group which comprises Ca to C30 alkyl substituted phenol sulfides (including phenol polysulfides). Especially preferred, however, are the alkyl phenol sulfides wherein the alkyl group contains from 6 to 10 carbon atoms, particularly tertiary amyl, tertiary octyl and nonyl phenol sulfides. The alkaline earth metal basic reacting material used in the neutralization step is preferably barium hydroxide pentahydrate. However, calcium hydroxide, barium hydroxide and their corresponding hydrates may be used as well as mixtures of barium and calcium compounds. The pretreatment and neutralization of the alkyl phenol sulfide may be carried out in oil solution if desired containing about 20 to 75% by weight of the alkyl phenol sulfide. If desired, a plasticizing agent (e. g., C6—C10 alcohol) may be employed in the present process in the pretreatment and neutralization.

To more completely describe the inventive concept, the following examples, which are illustrative in nature, are presented.

EXAMPLES I—VII

Crude nonyl phenol was produced by alkylating phenol with tripropylene using BF3 catalyst under conventional process conditions. This crude nonyl phenol was then sulfurized in hexane solution with commercial sulfur dichloride to yield nonyl phenol sulfide resin containing about 10.0 wt. percent sulfur on a solvent-free basis. The hexane solvent and by-product HCI were stripped out and the resin diluted with a solvent extracted neutral oil to about 4.4 wt. percent sulfur. An amount of this
nonyl phenol sulfide in oil solution sufficient to contain about 75 grams of sulfur was used in these examples. To this alkylation sulfide there was added about 75 grams of Loral B alcohol and as a plasticizing agent. (Loral B alcohol is the alcohol obtained upon the hydrogenation of coconut oil and is a mixture of alcohols having an average carbon chain of about 13.5.)

A total of about 380 grams of Ba(OH)₂·5H₂O was used in each of Examples II to V to neutralize the alkylation sulfide. Amounts of this basic reacting material, varying from about 1.0% of the theoretical for neutralization to about 6% of the theoretical, were used in the pretreating steps of Examples II to V. This pretreatment was carried out at a temperature of about 140°F, by mixing the basic reacting material with the nonyl phenol sulfide oil solution. This required about 10 minutes. After this pretreatment, the temperature was elevated to about 248°F, and the alkaline earth metal basic reactant (i.e., barium hydroxide pentahydrate) was added for neutralization. A reaction period of 15 minutes at 248°F was allowed prior to dehydrating the mixture for 15 minutes at 285°F. The dehydrated product was then filtered. Examples VI and VII were carried out in a similar manner, except that 0.6% and 6.0%, respectively, of Ca(OH)₂ was used in place of the barium hydroxide.

The materials obtained in accordance with each of the Examples I to VII were then blended with a calcium salt of synthetic fatty acid (fatty acid salt). The resulting mixture, containing 65% by weight of the oil solution of the barium salt of nonyl phenol sulfide was mechanically mixed with 35 parts by weight of an oil solution of calcium sulfonate (about 30% soap, 70% oil) for about one hour at about 160°F. Each of the blends so prepared was subjected to a sediment test which is a modification of the ASTM B. S. and W. Test. This test is described in detail in ASTM Designation D96-50T. Generally, this test as used to evaluate the above blends may be described as follows: 50 ml of industrial 90 benzene is measured into a graduated 100 ml centrifuge tube; 50 ml of the additive concentrate is then added to the tube. The centrifuge tube is then stopped and shaken vigorously to thoroughly mix the contents. The tube is then centrifuged at about 2000 R.P.M. for 20 minutes and allowed to stand for 24 hours. The tube is then again centrifuged at about 2000 R.P.M. for 20 minutes, after which the sediment at the bottom of the tube is read. This reading is doubled and recorded as vol. per cent. B. S. and W. A value of about 0.02 or less in this test is necessary to prevent sediment formation. The results of the B. S. and W. test on the blends prepared in accordance with Examples I to VII are set out in Table I below:

<table>
<thead>
<tr>
<th>Example</th>
<th>Pretreatment</th>
<th>Percent Ba(OH)₂·5H₂O</th>
<th>Percent Ca(OH)₂</th>
<th>Percent Ba(OH)₂·5H₂O employed</th>
<th>Free Ca(OH)₂</th>
<th>B. S. and W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>None</td>
<td>None</td>
<td>0.0</td>
<td>0.9</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>II</td>
<td>1.0</td>
<td>None</td>
<td>0.0</td>
<td>0.9</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>III</td>
<td>3.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.7</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>IV</td>
<td>6.0</td>
<td>0.0</td>
<td>0.0</td>
<td>5.4</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>V</td>
<td>6.0</td>
<td>0.0</td>
<td>0.0</td>
<td>5.4</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>VI</td>
<td>6.0</td>
<td>0.0</td>
<td>0.0</td>
<td>5.4</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>VII</td>
<td>6.0</td>
<td>0.0</td>
<td>0.0</td>
<td>5.4</td>
<td>0.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

1 Value expressed as percent of the base required to completely neutralize the alkyl phenol sulfide.
2 Carried out on blend of 85 wt. percent of nonyl phenol sulfide oil solution with 15 percent of calcium sulfonate solution.

What is claimed is:

1. A process for the preparation of alkaline earth metal salts of alkyl phenol sulfides, wherein an alkyl phenol sulfide is neutralized with basic alkaline earth metal compound, the improvement which comprises the steps of pretreating the alkyl phenol sulfide in the presence of a small amount of water with from 3.0% to 15.0% of the amount of alkaline earth metal basic reacting material (selected from the group of calcium and/or barium hydroxides and their hydrates) required to completely neutralize the alkyl phenol sulfide at a temperature within the range of from about 130° to 160°F, then completely neutralizing the pretreated alkyl phenol sulfide with basic alkaline earth metal compound and allowing the concentrated sulfonate to stand at a temperature of about 200° to 260°F, and then dehydrating the metal alkyl phenol sulfide product at a temperature of about 285° to 300°F.

2. A process for the preparation of neutral alkaline earth metal salts of Cs-C₁₅ alkyl substituted phenol sulfides, wherein a Cs-C₁₅ alkyl substituted phenol sulfide is neutralized with basic alkaline earth metal compound, and an improvement which comprises the steps of pretreating said alkyl phenol sulfide in the presence of about 0.8 to 10.0% by weight of water, on the basis of alkyl phenol sulfide, with from 3.0 to 10.0% of alkaline earth metal hydroxide which is required to completely neutralize said alkyl phenol sulfide at a temperature of about 140° to 150°F, for about 0.1 to 2 hours, then completely neutralizing the pretreated alkyl phenol sulfide with basic alkaline earth metal compound at a temperature of about 240° to 250°F, and then dehydrating the alkaline earth metal alkyl phenol sulfide product at a temperature of about 285° to 300°F.

3. An improved process for preparing neutral barium nonyl phenol sulfide which consists essentially of heating an oil solution of nonyl phenol sulfide to a temperature of about 140° to 150°F, pretreating this solution of nonyl phenol sulfide at a temperature of about 140° to 150°F with barium hydroxide pentahydrate for about 0.2 to 0.5 hour in the presence of about 0.8 to 10% by weight, based on nonyl phenol sulfide, of water including water of hydration and free water, the amount of said barium hydroxide pentahydrate employed in said pretreating step being about 3.0 to 10.0% of the amount of barium hy-
dioxide pentahydrate necessary to completely neutralize said nonyl phenol sulfide, heating the pretreated nonyl phenol sulfide to a temperature of about 240° to 250° F. and adding barium hydroxide pentahydrate in an amount sufficient to completely neutralize the pretreated nonyl phenol sulfide, and heating to about 285° to 300° F. to dehydrate the neutral barium nonyl phenol sulfide product, the time employed for neutralization and dehydration being about 0.3 to 2 hours.

4. An improved process for preparing neutral barium nonyl phenol sulfide which consists essentially of heating an oil solution of nonyl phenol sulfide to a temperature of about 140° to 150° F., pretreating the nonyl phenol sulfide at a temperature of 140° to 150° F. with calcium hydroxide for about 0.2 to 0.5 hour in the presence of about 0.8 to 10.0% by weight, based on nonyl phenol sulfide, of water including water of hydration and free water, the amount of said calcium hydroxide employed in said pretreating step being about 3.0 to 10.0% of the amount of calcium hydroxide necessary to completely neutralize said nonyl phenol sulfide, heating the pretreated nonyl phenol sulfide to a temperature of about 240° to 250° F. and adding barium hydroxide pentahydrate in an amount sufficient to completely neutralize the pretreated nonyl phenol sulfide, and heating to about 285° to 300° F. to dehydrate the neutral barium nonyl phenol sulfide product, the time employed for neutralization and dehydration being about 0.3 to 2 hours.

References Cited in the file of this patent

UNITED STATES PATENTS

2,399,877 McNab et al. 1946
2,761,845 Rogers et al. 1956