Metal petroleum sulfonates are recovered from commercial oil-containing concentrates by diluting the concentrate with a volatilizable hydrocarbon diluent, and extracting the mixture with a lower alcohol such as methanol or ethanol. The metal petroleum sulfonate, which is useful as a detergent additive for lubricating oils, is recovered from the alcohol phase as a substantially dry powder.

7 Claims, No Drawings
This invention relates to metal organic sulfonates. In accordance with another aspect, this invention relates to an improved process for the recovery of metal petroleum sulfonates from oil concentrates containing same by a process comprising dilution followed by extraction. In accordance with a further aspect, this invention relates to a recovery process for recovery of substantially oil-free metal petroleum sulfonates from oil-containing concentrates by diluting the concentrate with a volatilizable diluent, and then extracting the mixture with a lower alcohol whereby the metal petroleum sulfonate is recovered from the alcohol.

Oil soluble alkaline earth metal salts of petroleum sulphonates are widely known and widely used materials. They have particular application as additives in lubricating oils. An example of such a material is the calcium petroleum sulfonate whose preparation is described in U.S. Pat. No. 3,135,693.

William B. Whitney et al. in general, the sulfonate salts are prepared by sulfonating a suitable petroleum stock such as a high viscosity solvent refined Mid-Continent oil. The resulting sulfonic acid mixture is neutralized with a base, such as lime, and the metal sulfonate salt is generally utilized in the form of a concentrate in its residual unsulfonated oil from which it is ordinarily difficult to separate. For example, there are occasions when it would be highly desirable to obtain and to use a metal sulfonate which has been isolated from its carrier oil. Such a product, for example, would provide significant savings in shipping because of its reduced total weight and volume.

Accordingly, an object of this invention is to provide a process for recovering oil-soluble metal petroleum sulfonates from oil solutions containing same.

Another object of this invention is to provide a process for recovering a substantially oil-free metal petroleum sulfonate from commercial oil-containing concentrates containing same.

A further object of this invention is to provide a process for recovering metal petroleum sulfonate from its concentrate in residual unsulfonated oil in a practical and efficient manner.

Other objects, aspects, and the several advantages of and features of this invention will become apparent to those skilled in the art from the specification and appended claims.

SUMMARY OF INVENTION

In accordance with this invention, it has now been found that the principal active ingredient, namely, the metal sulfonate salt, can be isolated or recovered from its concentrate in residual unsulfonated oil by a process comprising dilution of a concentrate with a volatilizable hydrocarbon solvent and extraction with a lower alcohol.

The extraction of the invention differs from other previously used extraction techniques in that it utilizes the lower alcohols as the extracting agents and in that it extracts the sulfonate salt from a concentrate rather than extracting the oil from the concentrate.

In accordance with one embodiment, the invention comprises a process of diluting the sulfonate-containing concentrate with a suitable volatile solvent, preferably a volatilizable hydrocarbon diluent, and then extracting, preferably repeatedly, the diluted concentrate with an alcohol such as methanol or ethanol.

Extraction of the diluted concentrate with the alcohol results in an alcohol-containing extract phase containing the sulfonate salt and a raffinate oil phase comprising the hydrocarbon diluent, the residual unsulfonated oil and a depleted quantity of the sulfonate salt. These phases are subsequently separated from each other.

The extract phase comprising alcohol and sulfonate salt can be subjected to evaporation or other treatment to remove the alcohol and leave the sulfonate salt substantially as a dry powder. Similarly, the raffinate phase of hydrocarbon diluent, oil, and some sulfonate salt can be subjected to further recovery for removal of the hydrocarbon diluent for reuse in the process as desired.

DESCRIPTION OF PREFERRED EMBODIMENT

The metal sulfonate salts to which the present invention applies include any conventional alkaline earth metal petroleum sulfonate prepared from any useful petroleum-derived stock by any conventional process which produces a concentrate in an oil carrier. The process of Whitney et al. is particularly applicable. Overbased concentrates are also applicable, but the sulfonate becomes separated from the overbased agent.

The sulfonate salts are made from concentrated solutions of metal and are usually pre-neutralized with calcium, barium, or magnesium oxide to produce a concentrated solution in either water or a mineral oil. The aqueous concentrate is preferably further concentrated by evaporation. This concentrate is then neutralized with an organic base such as a fatty amine or a mineral base such as calcium hydroxide or calcium carbonate. The resulting concentrate is then contacted or reacted with an alcohol to form the sulfonate salt. The sulfonate salt is then extracted with a suitable hydrocarbon diluent to obtain a concentrate of sulfonate salt.

The settling period can range from about 1 minute to several hours, but is preferably about 15 minutes. The settled concentrate is then contacted with the alcohol in order to remove any remaining sulfonate salt. The concentrate and the raffinate oil phase are then separated and the alcohol is recovered for reuse. The remaining concentrate is then contacted with water in order to remove any remaining sulfonate salt. The concentrate and the water are then separated and the remaining concentrate is then contacted with a second alcohol in order to recover any remaining sulfonate salt. The concentrate and the alcohol are then separated and the alcohol is recovered for reuse.
phase containing the sulfonate salt will generally be the upper phase, except when relatively large amounts of relatively low density paraffinic diluent are used in the process.

After the settling period, the alcohol phase is decanted and the alcohol removed by evaporation to yield the dry metal sulfonate salt which appears to be hydroscopic. The evaporated methanol can be condensed and recycled to the extraction process. When the concentrate has been sufficiently depleted in the sulfonate salt, the diluent can also be removed by evaporation or distillation and recycled for use in the separation process.

Although the extract will contain most of the alcohol and the raffinate will contain most of the hydrocarbon solvent, it is readily understood that such a division is not complete and each phase will contain measurable but harmless amounts of the opposite solvent.

The evaporation of the alcohol phase to recover the sulfonate can be carried out in any conventional apparatus using any conventional technique. In some cases, during the alcohol evaporation stage, particularly when aromatic solvents such as benzene are used for the initial dilution, an oil phase will separate out. Removal of this intermediate oil phase will improve the dryness of the recovered sulfonate product.

The invention can be further demonstrated by the following example:

**EXAMPLE**

A 100 gram quantity of a commercial calcium petroleum sulfonate which contained about 50 weight percent of the solid sulfonate salt in a heavy residual oil was charged into a 600 ml. beaker and diluted with 150 g. of benzene. After the dilution, 100 g. of methanol was added and the mixture was agitated well with a stirring rod.

After about a 15 minute settling period, the upper alcoholic phase was drawn off and evaporated on a hot plate. The evaporation proceeded at a temperature of about 138° F. (a methanol-benzene azoetrop of about 40 – 50 ml. of the extract remained. At this time the temperature rose to about 140° F. and a lower liquid phase was visible in the evaporation vessel. The two extract phases were separated and the evaporation of each was continued, the temperature reaching about 147° F. before dryness. After evaporation on a hot plate the drying was completed in an oven at 200° F. for 1 hour. A total of 5 grams of hydroscopic product was obtained. The portion of the product obtained from the phase which settled out during the evaporation was a little tacky.

Several other additional tests were carried out using different diluents or different diluent to alcohol ratios. In addition, one test was made in which the extraction was attempted without the presence of a diluent. The results of these tests as well as the example shown above are found in the following table.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfonate test concentrate</th>
<th>Diluent g.</th>
<th>Alcohol g.</th>
<th>Isolated Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>200 Benzene</td>
<td>100 Methanol 3.0 dry powder</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>150 Benzene</td>
<td>100 Methanol 5.0 dry solid</td>
<td></td>
</tr>
</tbody>
</table>

*Very difficult to obtain initial phase separation.*

The data in the table above show that the invention process is capable of isolating a dry solid calcium petroleum salt which is essentially free of all visible oil. The data also show that both a hydrocarbon diluent and an alcohol must be present for a successful and convenient extraction. The use of benzene as a solvent results in greater recovery of product for extraction per extraction stage, but the product apparently contains traces of residual oil because it is a tacky solid.

**Claim:**

1. A process for the recovery of oil-soluble alkaline earth metal petroleum sulfonates from oil-containing concentrates said sulfonates obtained by neutralizing a sulfonated highly refined, high molecular weight petroleum fraction and said concentrates comprising oil-soluble alkaline earth metal petroleum sulfonates and unreacted or unsulfonated oil containing same which comprises (a) diluting said concentrate with a volatile hydrocarbon solvent containing up to about 12 carbon atoms selected from the group consisting of paraffins and aromatics, (b) extracting said sulfonate from said dilute concentrate with methanol or ethanol to form an extract phase comprising alcohol and alkaline earth metal petroleum sulfonate and a raffinate phase comprising oil and hydrocarbon solvent and separating said phases and (c) recovering the oil-soluble, alkaline earth metal petroleum sulfonates from said extract phase.

2. A process according to claim 1 wherein said concentrate is unsulfonated oil associated with said sulfonate and said extracting is repeated a number of times for greater sulfonate product recovery.

3. A process according to claim 1 wherein the concentrate of hydrocarbon solvent and alcohol mixture of step (b) is allowed to settle into phases and the alcohol phase containing the sulfonate is subjected to evaporation of the alcohol to yield a substantially dry alkaline earth metal methenol sulfonate powder as product.

4. A process according to claim 1 wherein said alkaline earth metal petroleum sulfonate is calcium petroleum sulfonate, said hydrocarbon solvent is benzene or n-pentane, and said alcohol is methanol.

5. A process according to claim 1 wherein the amount of hydrocarbon solvent used ranges from about 0.1 to about 3 parts by weight of hydrocarbon solvent for each weight of the concentrate.

6. A process according to claim 1 wherein the amount of alcohol employed will amount to one weight part of alcohol per 0.5 to about 10 parts of hydrocarbon diluent.

7. A process according to claim 3 wherein the alcohol recovered is recycled to step (b) and the hydrocarbon solvent is recovered from the raffinate phase and recycled to step (a).