

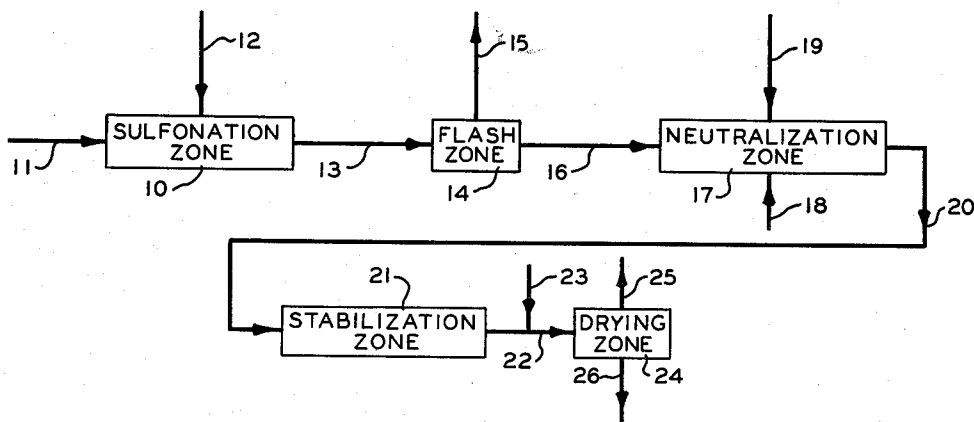
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INCREASING THE BASE NUMBER OF METAL PETROLEUM SULFONATE

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INCREASING THE BASE NUMBER OF METAL PETROLEUM SULFONATE

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This invention relates to increasing the base number of a metal petroleum sulfonate. In one aspect the invention relates to a process for increasing the base number of a metal petroleum sulfonate by contacting with calcium carbonate and an alkali metal hydroxide in the presence of water and alcohol. In another aspect this invention relates to an improved lubricant additive comprising a novel overbased metal petroleum sulfonate. In another aspect this invention relates to an improved lubricant containing such a novel additive.

Metal petroleum sulfonates are widely used in the manufacture of additives for lubricating oil used in internal combustion engines. These materials impart detergency to such lubricating oils and thus assist in keeping internal engine parts clean, and reduce sludge formation in the oil. The detergency is destroyed as acids formed from combustion products are neutralized by the basic petroleum sulfonates, and also the acids are then free to attack the metal of the engine parts. To prolong the life of such additives, the alkaline reserve of the oil composition is increased.

It is also desirable to maintain the ash content of the additive as low as possible. Thus, the value of increasing the base number of an additive may be lost if done at the expense of unduly increasing the ash content.

It is an object of this invention to increase the base number of a metal petroleum sulfonate without unduly increasing the ash content of the sulfonate. It is another object of this invention to provide novel overbased metal petroleum sulfonates. Another object of this invention is to provide an improved lubricant containing a novel overbased metal petroleum sulfonate.

Other aspects, objects and the several advantages of the invention are apparent from the disclosure, drawing and the appended claims.

Alkaline reserve can be measured by base number, which is the number of milligrams of potassium hydroxide equivalent to the amount of acid required to neutralize the alkaline constituents present in one gram of sample. A compound having a base number higher than can be obtained from the metal petroleum sulfonate alone is said to be "overbased" sometimes "superbasic."

Petroleum sulfonic acids which are neutralized to form petroleum sulfonates normally include appreciable amounts of various hydrocarbons not having the acid group so that, when the sulfonate is formed, the resulting product is a mixture of hydrocarbons and petroleum sulfonates. When substantially all of the sulfonic acid is neutralized to form the sulfonate, the resulting product has an alkaline reserve which depends upon the relative amount of sulfonate and hydrocarbon in the mixture. Addition of an excess of neutralizing material normally does not materially increase the alkaline reserve beyond this point, since the excess material is removed as for example by filtration prior to use of the sulfonate in a lubricant. It has been found that sulfonate mixtures can be treated to provide an increased alkaline reserve, as for example, by treatment with calcium chloride and calcium hydroxide. However, such a treatment increases the ash content along with the increase in alkaline reserve and this increase in ash content is undesirable.

I have found that the alkaline reserve can be increased without unduly increasing the ash content of the sulfonate

by treatment with calcium carbonate and an alkali metal hydroxide in the presence of water and an alcohol.

In this application the designation base number is used to indicate the alkaline reserve of the mixtures tested and is determined by titration with 0.1 normal hydrochloric acid to a pH of 4.0 and conversion of the value obtained to equivalent potassium hydroxide. Prior to overbasing, the sulfonates treated by my invention have a base number range of from about 5 to about 10.

According to my invention, the base number of a metal petroleum sulfonate is increased by contacting the sulfonate with calcium carbonate and an alkali metal hydroxide in the presence of water and alcohol. For each 100 parts by weight of petroleum sulfonate being treated 1 to 20 parts by weight of calcium carbonate, 0.5 to 5 parts by weight of an alkali metal hydroxide, 2 to 200 parts by weight of alcohol and 50 to 250 parts by weight of water are used. Suitable alkali metal hydroxides include potassium hydroxide and sodium hydroxide. The alcohols employed include those containing from 1 to 4 carbon atoms. Examples of such alcohols include methyl alcohol, ethyl alcohol n-propyl alcohol, isopropyl, and n-butyl alcohol. For economic reasons the preferred alcohols are methyl alcohol, ethyl alcohol and isopropyl alcohol. The treating temperature is preferably from about 150° to about 200° F. and treating time is about 15 minutes to 3 hours or more, good contacting being maintained.

Further according to my invention there is provided an improved overbased metal petroleum sulfonate formed by treating a normal metal petroleum sulfonate as outlined above. Improved lubricant compositions are formed by adding such an overbased petroleum sulfonate to lubricant base stocks.

Although my invention is applicable to many metal petroleum sulfonates, excellent results are obtained with the superior metal petroleum sulfonates formed by a recently developed process which comprises sulfonation of the more viscous bright stock fractions of petroleum. A petroleum fraction, having a viscosity of at least 90 SUS at 210° F. will produce a satisfactory petroleum sulfonate. The deasphalted and solvent refined petroleum fractions having a viscosity of about 140 to about 720 SUS at 210° F. are preferred. A specifically preferred sulfonation stock is a propane fractionated, solvent extracted and dewaxed Mid-Continent oil of about 200 to 230 SUS at 210° F. and having a viscosity index of about 85 to 100 or higher, particularly with the calcium petroleum sulfonates formed by this process. In the production of these high molecular weight calcium petroleum sulfonates, the oil is sulfonated with a sulfonation agent such as fuming sulfuric acid, chlorosulfonic acid, mixtures of chlorosulfonic acid and sulfur trioxide, sulfur trioxide dissolved in liquid sulfur dioxide and other similar sulfonating agents. The petroleum stocks are contacted with the sulfonating agents at a temperature of from about 50 to 200° F., preferably from 80 to 150° F. for about 1 to 90 minutes. The ratio of sulfonating agent to oil can vary considerably, but will generally be within the range of from about 0.1:1 to 0.7:1 on a weight basis, said acid level being calculated as 20 percent fuming sulfuric acid or equivalent. The resulting composition is neutralized with an aqueous slurry of a metal hydroxide such as calcium hydroxide (for example lime) so as to convert simultaneously the sulfonic acids to the corresponding metal petroleum sulfonates and to neutralize all of the inorganic acids in the reaction product. The resulting sulfonate has a base number in the range of about 5 to 10.

As illustrated in the drawing a feed stock such as a solvent refined, dewaxed lubricating oil fraction derived from a Mid-Continent petroleum, having a viscosity of about 200 to 230 SUS at 210° F. and a viscosity index

of 85 to 100 or higher, is introduced to sulfonation zone 10 through conduit 11. A sulfonating agent such as sulfur trioxide dissolved in sulfur dioxide is introduced to sulfonation zone 10 through conduit 12. The reaction products are transported through conduit 13 to flash zone 14 wherein excess sulfonation agent and solvent are removed through conduit 15. The remaining reaction product passes through conduit 16 to neutralization zone 17 wherein it is diluted with a hydrocarbon solvent such as naphtha introduced through conduit 18, and is neutralized by a slurry of metal hydroxide, such as an aqueous slurry of lime, introduced through conduit 19. The resulting substantially neutralized slurry of calcium sulfate and/or calcium sulfite, calcium hydroxide, water and diluted sulfonation reaction effluent is passed through conduit 20 to stabilization zone 21 wherein the reaction product is maintained in the presence of the metal hydroxide at elevated temperature and elevated pressure so that the base number of the sulfonate is raised as high as possible by this action.

To increase the base number still further, however, as the product is passed through conduit 22, calcium carbonate, alcohol and an alkali hydroxide are introduced through conduit 23 prior to entry of the mixture into drying zone 24. Sufficient contact time can be provided in conduit 22 or an additional contact zone can be provided upstream of drying zone 24. In drying zone 24 substantially all of the water is removed through conduit 25 and the stabilized and dehydrated reaction product is passed through conduit 26 to further treatment which ordinarily will include filtration.

In an example according to my invention, 40 grams of a calcium petroleum sulfonate having a base number of 7.7 mg. KOH/gm. and 4.65 percent ash was treated with 5 grams CaCO_3 and 1.0 gram NaOH in 40 grams of water and 10 grams of isopropyl alcohol for one hour at 160–180° F. The mixture was heated to expel water, diluted in benzene, centrifuged to remove solids, and stripped of solvent. The product had a base number of 17.4 mg. KOH/gm. and an ash content of 4.62 percent.

Using the same procedure and with a similar calcium petroleum sulfonate having a base number of 8.0 and 5.4 percent ash, but using CaCl_2 instead of CaCO_3 , the base number was increased to 22 mg. KOH/gm., but at the same time an undesirable increase of ash content was encountered, the final product having 6.8 percent ash.

When a calcium petroleum sulfonate having a base number of 7.7 KOH/gm. and 4.65 percent ash was treated with 5 gms. calcium carbonate and 40 gms. of water and 10 gms. of isopropyl alcohol for one hour at 160–180° F., the mixture heated to expel water, diluted in benzene, centrifuged to remove solids and stripped of solvent, neither the base number nor the ash content was affected.

Similarly, treating the same calcium petroleum sulfonate in the same manner but using 1 gm. NaOH alone, without CaCO_3 , resulted in no increase either in base number or ash.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, the drawing and the appended claims of the invention by which there is provided an improved process for increasing the alkaline reserve of a calcium petroleum sulfonate without increasing the ash content by treating with calcium carbonate and an alkali hydroxide in the presence of water and an alcohol.

I claim:

1. A process for increasing the alkaline reserve of a calcium petroleum sulfonate which comprises contacting said sulfonate with calcium carbonate and an alkali metal hydroxide in the presence of water and a lower alkanol having 1–4 carbon atoms per molecule.

2. A process for increasing the alkaline reserve of a calcium petroleum sulfonate which comprises contacting 100 parts by weight of such sulfonate with 1 to 20 parts

by weight of calcium carbonate, 0.5 to 5 parts by weight of an alkali metal hydroxide in the presence of 2 to 200 parts by weight of a lower alkanol having 1–4 carbon atoms per molecule and 50 to 250 parts of water.

3. The process of claim 2 wherein said alkali metal hydroxide is potassium hydroxide.

4. The process of claim 2 wherein said alkali metal hydroxide is sodium hydroxide.

5. A process for increasing the alkaline reserve of a calcium petroleum sulfonate which comprises contacting 100 parts of said sulfonate with 1 to 20 parts by weight of calcium carbonate, 0.5 to 5 parts by weight of an alkali metal hydroxide in the presence of 2 to 200 parts by weight of alcohol and 50 to 250 parts by weight of water at a temperature between about 150° F. to about 200° F. for from about 15 minutes to about 3 hours.

6. The process of claim 5 wherein said alkali metal hydroxide is potassium hydroxide.

7. The process of claim 5 wherein said alkali metal hydroxide is sodium hydroxide.

8. A process for increasing the alkaline reserve of a calcium petroleum sulfonate which comprises contacting 100 parts by weight of said sulfonate with 1 to 20 parts by weight of calcium carbonate, 0.5 to 5 parts by weight of an alkali metal hydroxide selected from the group consisting of potassium hydroxide and sodium hydroxide in the presence of 2 to 200 parts by weight of an alcohol selected from the group consisting of methyl alcohol, ethyl alcohol and isopropyl alcohol, and 50 to 250 parts by weight of water.

9. A process for increasing the alkaline reserve of a calcium petroleum sulfonate which comprises contacting 100 parts by weight of said sulfonate with 1 to 20 parts by weight of calcium carbonate, 0.5 to 5 parts by weight of sodium hydroxide in the presence of 2 to 200 parts by weight of an alcohol selected from the group consisting of methyl alcohol, ethyl alcohol and isopropyl alcohol, and 50 to 200 parts by weight of water at a temperature of from about 150° F. to about 200° F. for from about 15 minutes to about 3 hours.

10. An overbased calcium petroleum sulfonate formed by contacting 100 parts by weight of a metal petroleum sulfonate with 1 to 20 parts by weight of calcium carbonate, 0.5 to 5 parts by weight of an alkali metal hydroxide in the presence of 2 to 200 parts by weight of a lower alkanol having 1–4 carbon atoms per molecule and 50 to 200 parts by weight of water.

11. An overbased calcium petroleum sulfonate formed by contacting 100 parts by weight of a metal petroleum sulfonate with 1 to 20 parts by weight of calcium carbonate, 0.5 to 5 parts by weight of an alkali metal hydroxide in the presence of 2 to 200 parts by weight of a lower alkanol having 1–4 carbon atoms per molecule and 50 to 250 parts by weight of water, at a temperature of from about 150° F. to about 200° F. for from about 15 minutes to about 3 hours.

12. An overbased calcium petroleum sulfonate formed by contacting 100 parts by weight of a calcium petroleum sulfonate with 1 to 20 parts by weight of calcium carbonate, 0.5 to 5 parts by weight of an alkali metal hydroxide selected from the group consisting of potassium and sodium hydroxide in the presence of 2 to 200 parts by weight of alcohol selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol, and 50 to 250 parts by weight of water.

13. An overbased calcium petroleum sulfonate formed by contacting 100 parts by weight of a calcium petroleum sulfonate with 1 to 20 parts by weight of calcium carbonate, 0.5 to 5 parts by weight of sodium hydroxide in the presence of 2 to 200 parts by weight of an alcohol selected from the group consisting of methyl alcohol, ethyl alcohol, and isopropyl alcohol and 50 to 250 parts by weight of water at a temperature of from about 150°

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F. to about 200° F. for from about 15 minutes to about 3 hours.

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