INCREASING THE BASE NUMBER OF CALCIUM PETROLEUM SULFONATE

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INCREASENIG THE BASE NUMBER OF CALCIUM PETROLEUM SULFONATE

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This invention relates to increasing the base number of a calcium petroleum sulfonate. In one aspect, the invention relates to a process for increasing the base number of a calcium sulfonate of a high viscosity paraffinic petroleum lubricating stock by contacting with methanol, either calcium oxide or calcium hydroxide, and one or more of ammonium carbonate, ammonium acid carbonate or ammonium carbamate. In another aspect, this invention relates to an improved lubricant additive comprising an overbased calcium petroleum sulfonate produced by the process of this invention. In another aspect this invention relates to an improved lubricant containing the novel lubricant additive of this invention.

Calcium petroleum sulfonates are widely used in the manufacture of additives for lubricating oil used in combustion engines. These materials impart detergency to the lubricating oils and thus assist in keeping the internal engine parts clean and reducing sludge formation in the oils. By increasing the alkaline reserve of the additive (overbasin the additive), equivalent detergent is obtained with a lower concentration of additive in the lubricating oil. Also, higher alkaline reserve neutralizes larger quantities of acidic combustion products which accumulate in the oil.

A recently developed detergent additive is produced by the novel process described in copending application Ser. No. 222,357, Whitney et al., filed Sept. 10, 1962, now U.S. Patent No. 3,135,693. This additive, which comprises a calcium petroleum sulfonate, not only gives excellent results in increasing the detergency of lubricating oils and reducing sludge formation, but also has quite adequate alkaline reserve for many applications. However, for some uses, for example, under conditions such that large quantities of acid are formed, as in diesel engines burning high sulfur fuels, it is desirable to increase the alkaline reserve of this detergent additive. Many previously known processes for overbasin the lubricant oil additives, specifically those processes for overbasin metal sulfonates of mahogany acids, have not proved to be applicable to the Whitney et al. developed additive.

It is an object of this invention to increase the base number of a calcium petroleum sulfonate.

Another object of this invention is to provide novel overbasin calcium petroleum sulfonates.

Another object of this invention is to provide improved lubricants containing novel overbasin calcium petroleum sulfonates.

Other aspects, objects, and advantages of our invention are apparent in the written description, the drawing and the 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 a one-gram sample. A compound having a base number higher than can be obtained from the calcium petroleum sulfonate alone is said to be “overbasin,” sometimes “superbasin.” In this application the reported base numbers are obtained by the method described in Analytical Chemistry, volume 23, page 337 (1951), and volume 24, page 519 (1952).

Petroleum sulfonic acid which is neutralized to form petroleum sulfonates normally includes 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 the sulfonic acid is neutralized with an excess of calcium oxide or calcium hydroxide to form the sulfonate, the resulting product has a relatively small alkaline reserve. Addition of a large excess of neutralizing material normally does not materially increase the alkaline reserve beyond this point, since the excess material is removed, for example, by filtration, prior to the use of the sulfonate in a lubricant.

According to our invention, the alkaline reserve of the additives of U.S. Patent No. 3,135,693 is increased by contacting with methanol, a compound selected from the group consisting of calcium oxide and calcium hydroxide, and a compound selected from the group consisting of ammonium carbonate, ammonium acid carbonate (ammonium bicarbonate) and ammonium carbamate, followed by heating the resulting mixture to a suitable temperature for sufficient time to overbasin the composition. The amount of the methanol usually is in the range of 5 to 100 volume percent of the lubricant additive composition which is overbasin. By lubricant additive compositions is meant either an unadulterated calcium petroleum sulfonate or a mixture of calcium petroleum sulfonate with unsulfonated oils, either oils present when the sulfonate is produced or an oil added later.

The amount of uncombined water in the mixture must be severely limited for successful operation of our invention. Preferably the amount of water is not more than about 5 volume percent of the amount of methanol present and in any event should not exceed about 7 volume percent of the methanol.

The amount of calcium oxide or hydroxide to be used depends upon the amount of overbasin which is to be effected. The calcium compound used is added in an amount equal to 2 to 6 times the amount chemically equivalent to the desired overbasin.

A complex equilibrium exists among ammonium carbonate, ammonium bicarbonate and ammonium carbamate. All of these compounds tend to break down to ammonia and carbon dioxide, although ammonium carbamate needs water to accomplish this. When using ammonium carbamate, the needed water can be added as an external gas or in the stripping gas or chemically combined water by use of calcium hydroxide. At least a sufficient amount of the ammonium compound is used to furnish sufficient carbon dioxide by decomposition to react with all of the calcium compound.

Preferably a stripping gas is passed through the mixture during the heating step, the gas being one which is non-reactive under the conditions of the heating step. Suitable gases include natural gas, nitrogen, etc. The heating step normally is accomplished at a temperature in the range of 150 to 550° F., preferably 200 to 300° F., until basic vapors no longer are evolved, usually 35 to 48 hours. However, higher temperatures can be used if desired, the upper limit usually being determined by cracking of the petroleum sulfonate material. A temperature of 500° F. normally will avoid substantially all cracking, but temperatures up to about 600° F. can be used without appreciable cracking. The striping gas effects mixing and removes the basic vapors from the liquid phase more quickly. The gas stripping is not essential to accomplish overbasin, but shortens the reaction time at a given temperature.

After the reaction is complete, solids are removed from the reaction mixture, for example, by filtering or centrifuging, and the additive then is ready for use in blending of the lubricating oils.

In producing the sulfonated petroleum material of this invention, the base stock is selected from highly paraffinic, deasphalted and solvent refined petroleum fractions hav-
ing a viscosity of about 180 to 230 SUS at 210° F. and having a viscosity index of at least about 85. A pre-
ferred material is a propane-fractionated, solvent-ex-
tacted Mid-Continent oil of about 200 to 215 SUS at 210° F. and having a viscosity index of
about 85 to 100 or higher. The residual material from
the propane fractionation step, the overhead oil fraction is solvent extracted to re-
move additional aromatic hydrocarbons.
A Mid-Continent oil is more precisely defined as a
mixed base or intermediate base oil. The base of a
crude petroleum is descriptive of the chemical nature
of its main constituents. A petroleum can be described as
paraffin base, asphalt base or mixed base (intermediate base), accordingly, as paraffin wax, asphalt, or both par-
affin wax and asphalt are present in the residue after
distillation of the lighter components. In this applica-
tion, Mid-Continent oil and intermediate base oil are
used interchangeably.
These oils are contacted with sulfonating agents such as
fuming sulfuric acid, chlorosulfonic acid, and sulfur
trioxide, a particularly preferred sulfonating agent be-
ing a solution of sulfur trioxide in liquid sulfur dioxide.
The petroleum stocks are contacted with the sulfonating agents
at temperatures of from 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 gen-
erally is within the range of from about 0.1:1 to 1:1 on
a weight basis, the sulfonating agent being calculated
as 20 percent fuming sulfuric acid.
The effluent from the sulfonation step is a petroleum
sulfonic acid and this material is converted to an over-
base calcium petroleum sulfonate by the method of this
invention.
In the embodiment illustrated in the drawing, a selected
petroleum stock is introduced to sulfonation zone 10
through conduit 11. A sulfonating agent such as sulfur
trioxide dissolved in sulfur dioxide is introduced to sul-
fonation zone 10 through conduit 12. The reaction
products are transported through conduit 13 to flash
zone 14, where sulfur dioxide is removed through conduit
15. The remaining reaction product passes through con-
duit 16 to neutralization zone 17 where 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 neutral-
ized slurry of calcium sulfate and calcium hydroxide in
water and of diluted sulfonation reaction effluent is passed
through conduit 20 to stabilization zone 21, where 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. The stabilized
material then proceeds through conduit 22 into drying
zone 23 in which step substantially all of the water
is removed through conduit 24. The stabilized and dehy-
drated reaction product is passed through conduit 26.
In a preferred process, filtration zone 27 is eliminated
and this is illustrated in the drawing by the inclusion of
conduit 44 having a valve 44A therein. Conduit 44 con-
nects conduit 22 with conduit 29, thus by-passing the
filtration zone 27. In this manner, excess lime present
in the effluent from drying zone 23 is retained whereby
the amount of lime introduced through conduit 31 can
be reduced or, in some cases, eliminated entirely.
When it is desired to include a filtration step at this
point, the product is passed through conduit 26 to fil-
traion zone 27, valve 44A being closed and valve 45 being
open. It is desirable in most instances to add a solvent
such as naphtha to conduit 26 to facilitate the filtration
step. A solids containing stream is removed through con-
duit 28 while the filtrate comprising a metal petroleum
sulfonate continues through conduit 29 into mixing zone
30 wherein any needed lime is added through conduit 31,
along with methanol in conduit 32 and the ammonium
compound in conduit 33. The mixture then passes through
heating zone 36 from which vapor is removed through conduit 38. Preferably, a non-re-
active gas is passed through the heating zone as through
conduit 37. The overbased material then is passed through
conduit 39 to filtration zone 41 from which a
solids containing stream is removed through conduit 42
while the product continues for further treatment through
conduit 43.

Example

Twenty parts of calcium petroleum sulfonate lubricating
oil additive comprising 50 percent calcium petroleum
sulfonate of a propane-fractionated, phenol-extracted and
dewaxed Mid-Continent lubricating oil fraction of about
203 SUS viscosity at 210° F. and a viscosity index of
about 93, made in accordance with the above description,
was diluted with an equal weight of SAE 10 refined lubri-
cating oil and mixed with 20 parts by weight of methanol,
11 parts by weight of calcium hydroxide and 15 parts by
weight of ammonium carbonate. The mixture was heated
to 250° F. and maintained at this temperature for 7 hours.
Natural gas was bubbled through the mixture during the
period of heating. At the end of the heating period, basic
vapors no longer were evolved. The reaction mass was
cooled, diluted with benzene, centrifuged for one
hour, the liquid decanted from the separated solid, and
the benzene diluent stripped from the liquid. The
product had a base number of 93 MgKOH/g., or a base
number of 186 based on the original amount of additive.
The base number of the additive before treatment (free of
SAE 10 diluent) was about 7.5 MgKOH/g.
Reasonable variation and modification are possible
within the scope of our invention which sets forth novel
lubricants and lubricant additives and a process for pro-
ducing the overbase calcium petroleum sulfonates from
high viscosity paraffinic petroleum lubricating stock.
We claim:
1. A process for producing a lubricant additive which comprises the steps of:
contacting a lubricant additive composition comprising a
compound selected from the group consisting of a
petroleum sulfonic acid and a calcium petroleum sul-
fonate, wherein the sulfonated stock is highly para-
affinic, desasphalted and solvent refined petroleum
fraction having a viscosity of about 180 to 230 SUS
at 210° F. and having a viscosity index of at least
about 85, with methanol, in an amount equal to 5
to 100 volume percent of said composition, an
amount of a calcium compound selected from the
group consisting of calcium oxide, calcium hydro-
oxide to provide 2 to 6 times the amount chemi-
cally equivalent to a desired overbasering, and a suf-
cient amount of an ammonium compound selected
from the group consisting of ammonium carbonate,
ammonium bicarbonate and ammonium carbamate
to furnish carbon dioxide by decomposition to react
with all of said calcium compound, while maintain-
ing the uncombined water content of the resulting
mixture below about 7 volume percent of the amount
of said methanol, and
heating to a temperature in the range of 150 to 500° F.
until basic vapors no longer are evolved.
2. A lubricant additive prepared by the steps of:
contacting a lubricant additive composition comprising
a compound selected from the group consisting of a
petroleum sulfonic acid and a calcium petroleum sul-
fonate, wherein the sulfonated stock is highly para-
affinic, desasphalted and solvent refined petroleum
fraction having a viscosity of about 180 to 230 SUS
at 210° F. and having a viscosity index of at least
about 85, with methanol, in an amount equal to 5
to 100 volume percent of said composition, an amount
of a calcium compound selected from the group consisting of calcium oxide and calcium hydroxide to provide 2 to 6 times the amount chemically equivalent to a desired overbasin, and a sufficient amount of an ammonium compound selected from the group consisting of ammonium carbonate, ammonium bicarbonate and ammonium carbamate to furnish carbon dioxide by decomposition to react with all of said calcium compound, while maintaining the uncombined water content of the resulting mixture below about 7 volume percent of the amount of said methanol; and heating to a temperature in the range of 150 to 500° F. until basic vapors no longer as evolved.

3. A process for producing a lubricant additive which comprises the steps of:

contacting a lubricant additive composition comprising a compound selected from the group consisting of a petroleum sulfonic acid and a calcium petroleum sulfonate, wherein the sulfonated stock is highly paraffinic, deasphalted and solvent refined petroleum fraction having a viscosity of about 180 to 230 SUS at 210° F. and having a viscosity index of at least about 85, with methanol, in an amount equal to 5 to 100 volume percent of said composition, an amount of a calcium compound selected from the group consisting of calcium oxide, and calcium hydroxide to provide 2 to 6 times the amount chemically equivalent to a desired overbasin, a sufficient amount of an ammonium compound selected from the group consisting of ammonium carbonate, ammonium bicarbonate and ammonium carbamate to furnish carbon dioxide by decomposition to react with all of said calcium compound, while maintaining the uncombined water content of the resulting mixture below about 7 volume percent of the amount of said methanol; and heating to a temperature in the range of 150 to 500° F. until basic vapors no longer as evolved while passing a non-reactive gas through the mixture to effect mixing and assist in removing said basic vapors.

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