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J. T. GRAGSON ETAL
OVERBASING LUBE OIL ADDITIVES

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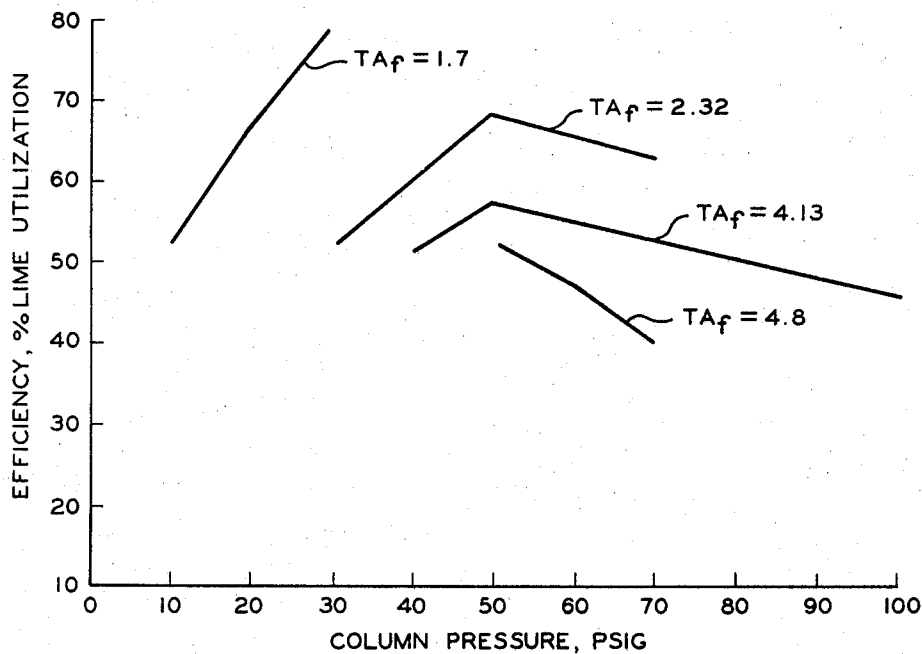


FIG. 1

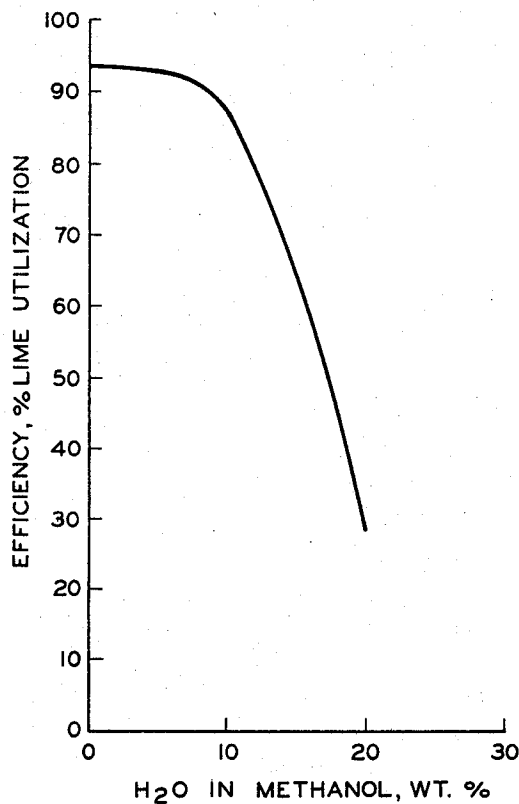


FIG. 2

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OVERBASING LUBE OIL ADDITIVES

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ABSTRACT OF THE DISCLOSURE

A method of overbasing metal petroleum sulfonates wherein methanol is added to a mixture of metal petroleum sulfonate, a hydroxide or oxide of a base metal and diluent just prior to treatment with carbon dioxide; the treatment being effected by contacting the mixture in a discontinuous liquid phase with the carbon dioxide in a continuous gaseous phase under a pressure of 10 to 100 p.s.i.g.

This invention relates to lubricating oil additives. In one aspect this invention relates to increasing the base number of a metal petroleum sulfonate.

Metal petroleum sulfonates and overbase metal petroleum sulfonates are widely used as additives for lubricating oils in combustion engines. These materials impart detergency lubricating oil and thus assist in keeping internal engine parts clean and reducing sludge formation in the oil. By increasing the alkaline reserve of the additive, equivalent detergency is obtained with a lower concentration of additive in the lubricating oil. A higher alkaline reserve neutralizes larger quantities of acidic combustion products which accumulate in the oil. Alkaline reserve can be increased by a process which comprises contacting the metal petroleum sulfonates with a metal-containing compound, a process being designated in the art as overbasing.

Alkaline reserve can be measured by a "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 1-gram sample. A product having a base number higher than can be obtained from the sulfonate compound itself is said to be overbased. The excess of base present in an overbased sulfonate apparently is in the form of very finely divided solid metal compound particles sufficiently fine that they pass through a 1-micron filter and are not visible to the naked eye. The suspension is stable and does not change on standing. Overbased lube oil additives are especially useful when conditions are such that large quantities of acids are formed, as in diesel engine burning high sulfur fuels.

The present invention provides a method of increasing alkaline reserve by incorporating a very high metal content in a filterable dispersion of metal petroleum sulfonate.

It is an object of this invention to increase the base number of metal petroleum sulfonates.

Another object of this invention is to control the amount of alkaline reserve in an overbased metal petroleum sulfonate.

Another object is to effect economies in overbasing metal petroleum sulfonates by increasing efficiency and by reducing equipment costs.

Other and further objects of this invention will be apparent to one skilled in the art upon study of the disclosure and claims of the present application.

When a sulfonic acid is neutralized with a hydroxide or oxide of a base metal to form a sulfonate, the resulting product has an alkaline reserve. Addition of a large excess of neutralizing material normally does not materially increase the alkaline reserve since the excess material is removed, for example, by filtration prior to the use of

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the sulfonate in a lubricant. The alkaline reserve of a metal petroleum sulfonate can be increased by contacting the metal petroleum sulfonate with a metal-containing material in the presence of an acid anhydride gas.

In one process, metal petroleum sulfonate, the hydroxide or oxide of a base metal and an alcohol are mixed with a diluent, such as naphtha, to form a slurry and alkaline reserve is increased by contacting a suitable acid anhydride with the slurry. The efficiency of an overbasing process can be measured by comparing the amount of base metal compound utilized during gas treatment to the amount added.

This invention comprises an improved method of contacting an acidic gas with a slurry of metal petroleum sulfonate, metal hydroxide or metal oxide, alcohol, and diluent. Alkaline reserve is increased by contacting the slurry while in a discontinuous liquid phase with an acidic gas which is in continuous gas phase. The conditions of this gas phase contact method are controlled in order to obtain a desired amount of increase in alkaline reserve.

In preparing the metal petroleum sulfonate of this invention a suitable lubricating oil fraction is contacted with a sulfonating agent. A suitable lubricating oil fraction to be so treated is one having a viscosity of at least 90 SUS at 210° F. One suitable lubricating oil fraction is a propane fractionated, solvent-extracted, and dewaxed Mid-Continent oil of about 200 to 215 SUS at 210° F. and having a viscosity index of about 85 to 100 or higher. These oils are contacted with a sulfonating agent such as fuming sulfuric acid, chlorosulfonic acid, sulfur trioxide, or other suitable sulfonating agents known to the art. Sulfonation conditions are selected to produce the desired reaction.

The effluent from the sulfonation step comprises a petroleum sulfonic acid and this material is converted to a metal petroleum sulfonate. In one method petroleum sulfonic acid is contacted with an aqueous slurry of the oxide or hydroxide of a basic metal compound. Specific examples of suitable basic metals are calcium, barium, sodium, lithium, chromium, zinc, nickel, and lead. Good results are obtained with the alkaline earth hydroxides, for example calcium hydroxide and barium hydroxide. These materials are introduced in an amount sufficient to neutralize the sulfonated material being treated and usually the quantity of neutralizing agent is substantially in excess of that required for neutralization, for example, 150 percent of the quantity theoretically required. Preferably the petroleum sulfonic acid mixture has been heated under vacuum to remove SO₂ and diluted with a hydrocarbon such as naphtha prior to neutralization. The resulting solution of metal petroleum sulfonate is then stabilized by heating under pressure, for example, 350 to 400° F. at 150 to 200 p.s.i.g. The water can be removed from the stabilized solution by such methods as evaporation.

According to the invention, the alkaline reserve of a metal petroleum sulfonate is increased by forming a feed mixture of metal petroleum sulfonate, an oxide or hydroxide of a base metal, an alcohol and a diluent, introducing the mixture into a treatment chamber, simultaneously introducing an acid anhydride gas into the treatment chamber and controlling conditions within the chamber to obtain a desired increase in alkaline reserve.

Further in accordance with the invention, contact of the mixture with an acid anhydride gas is achieved under conditions of discontinuous liquid phase in a continuous gas phase.

In forming a feed mixture, metal petroleum sulfonate is mixed with a hydroxide or oxide of a base metal, for example calcium hydroxide or barium hydroxide. The amount of hydroxide or oxide of the base metal added is dependent upon the base number desired in the product.

For example, when it is desired to produce an overbased calcium petroleum sulfonate with a total base number of approximately 100 about 2.5 weight percent calcium hydroxide is added. The hydroxide used for overbasing can be added after stabilization and removal of water but it is preferred to add the amount required in the neutralization step. Diluent is added in an amount which is not detrimental to hydroxide or oxide utilization yet forms a slurry which can be handled practically. For example, 100 parts of calcium petroleum sulfonate per 250 parts naphtha diluent form a workable slurry and allows effective utilization of lime.

When alcohol is added, aging begins; the mixture deteriorates upon standing prior to contact with the acidic gas. An aged mixture results in a lower base number than comparable fresh mixtures. For example, overbasing of a calcium petroleum sulfonate-lime-methanol mixture which has been aged for two hours results in approximately 25 percent less alkaline reserve than results from overbasing the fresh mixture. Because of this deterioration it is preferred to add the alcohol just prior to and not more than one hour before gas treatment. Water in small amounts can be tolerated in the process thus permitting usage of aqueous alcohol, but when the alcohol contains more than 10 weight percent water there is a sharp drop in efficiency as measured by base metal compound utilization. It is preferred to add no more than 5 weight percent alcohol to the feed mixture and to limit the water content of the alcohol to less than 10 weight percent.

Feed mixture of metal petroleum sulfonate, base metal compound, alcohol, and diluent is introduced into the gas treatment chamber in disperse droplet form. Disperse freely falling droplets can be formed by spraying the mixture into the treatment chamber or by allowing the mixture to flow over a series of baffles within the treatment chamber. It is preferred to avoid formation of a slowly settling mist. Formation of disperse droplets provides for maximum contact between the liquid and the gas. Droplet contact with the walls of the chamber should be avoided as far as practical. Acid anhydride gas is introduced into the treatment chamber under pressures from 10 to 100 p.s.i.g. Pressures above 100 p.s.i.g. in the gas phase result in low process efficiency while in order to efficiently utilize the base metal compound gas pressures of at least 10 p.s.i.g. must be maintained. It is preferred to operate with gas pressures of from 20 to 50 p.s.i.g. In one advantageous practice of the invention, feed mixture is pressured through spray nozzles in the top and free-falls the length of a column while gas is supplied to the column on a demand basis to maintain a constant pressure.

After intimate contact between the discontinuous liquid phase of the mixture and the continuous gas phase of the acidic gas, the mixture forms a continuous liquid phase which is retained in the treatment chamber for a time sufficient to allow completion of the reaction.

The effluent from the gas treatment chamber contains overbased metal petroleum sulfonate, solids, methanol, water added or liberated during the gas treatment, and diluent. Methanol and water are removed from the mixture by stripping. The mixture is then filtered and stripped of solvent. The solvent-free filtrate comprises overbased metal petroleum sulfonate.

This invention's method of gas treatment is advantageous in that no gas repressure and recycle system is necessary. The method permits control within a wide range of the amount of alkaline reserve added to a metal petroleum sulfonate and results in effective utilization of reactants. The following specific examples will further illustrate the invention.

Example I

A calcium petroleum sulfonate was prepared from a solvent-refined, dewaxed lubricating oil fraction derived from Mid-Continent petroleum and having the following

properties: viscosity 4278 SUS at 100° F., 203 SUS at 210° F., and a viscosity index of 93. A charge stock identified as finished 250 stock was sulfonated with liquid SO₃ in SO₂ in a continuous operation. The SO₃-to-oil weight ratio was about 0.078 and the temperature of the reaction was controlled to 115°. The total reaction time was 10 minutes including mixing and soaking. The SO₂ was removed under vacuum and effluent diluted with naphtha was run into a vessel containing calcium hydroxide-water slurry for neutralization. The mixture was agitated during the neutralization period. For each 2400 gallons of SO₂ flash effluent, 720 gallons of naphtha was used along with a slurry of 1400 pounds of calcium hydroxide and 1100 gallons of water. The neutralized mixture was pumped through a 370° F. zone at 225 p.s.i.g. where its residence time was maintained for about 8 minutes, thus stabilizing the mixture. The stabilized calcium petroleum sulfonate was then dried at a temperature of 240°. The dried product contained calcium petroleum sulfonate, oil, naphtha, excess lime, and inorganic salts formed during the neutralization step. This mixture was designated dryer tower bottoms.

Slurries containing different amounts of dryer tower bottoms and calcium hydroxide were made. The total alkalinity of each carbonation feed slurry was determined as weight percent lime (TA_f). The theoretical base number of each feed slurry was calculated according to the formula:

Theoretical base number (mg. KOH/g.) =

$$\left(\frac{TA_f}{TA_f + \text{wt. percent calcium petroleum sulfonate in feed}} \times 1515 \right) + K$$

A K value of 8 was used as this was the base number of the calcium petroleum sulfonate and it was assumed that this value carries through the carbonation process.

Temperature of the slurries was controlled at 85° F. and water-free methanol was added just prior to carbonation. These slurries were contacted with CO₂ by spraying into a treatment chamber and forming dispersed droplets of the liquid. CO₂ was introduced at different pressures. After gas phase contact the carbonation effluents were stripped of methanol and water, filtered and stripped of naphtha. The base numbers of the different solvent-free products were determined by the following method.

A sample of about 0.2 to 0.3 gram was accurately weighed and dissolved in 100 ml. of titrating solvent. A mixture of toluene and isopropyl alcohol containing 0.5 percent water was used as a titrating solvent. The sample was then titrated potentiometrically with 0.1 N aqueous hydrochloric acid to a pH of 4. The base number of the sample was expressed mg. of KOH/g. of sample equivalent to the HCl used in the procedure.

The efficiency of the process utilization of lime at different CO₂ pressures was calculated according to the formula:

$$\text{Percent efficiency} = \frac{\text{actual base number of product}}{\text{theoretical base number}} \times 100$$

A plot of effect of CO₂ pressure on the efficiencies with respect to feeds of different alkalinities is shown in FIGURE 1.

This plot shows that CO₂ pressures above 50 p.s.i.g. reduce the efficiency of the process and that this limit is not dependent on the total alkalinity of the feed mixture.

Example II

Dryer tower bottoms as prepared in Example I were mixed with lime to obtain a slurry having a total alkalinity of 1.7. Portions of the slurry were treated with 3.3 weight percent methanol which contained different amounts of water just prior to gas contact. These slurries were contacted with CO₂ under 30 p.s.i.g. using the method set forth in Example I. The carbonation effluents were stripped and filtered. The efficiency as measured by per-

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cent lime utilization was determined by the method of Example I.

FIGURE 2 relates the efficiencies to the amount of water in the methanol and shows that addition of methanol containing more than 10 weight percent water greatly reduces the process efficiency.

Example III

One-hundred and sixty-four pounds of dryer tower bottoms as prepared in Example I were mixed with 3.6 pounds of calcium hydroxide and 10.8 pounds of methanol. The mixture was continuously stirred and samples were removed periodically. The samples were carbonated, dried, filtered, and stripped. The base numbers of the various samples are tabulated below:

Mixing time (hours):	Base No. of sample
0 -----	102
2 -----	73.8
4 -----	37.9
6 -----	30.0
8 -----	8.3

From the above data it can be seen that the base number decreased as the mixing time progressed.

Example IV

A dryer tower bottoms-calcium hydroxide mixture was continuously stirred. Samples containing 140 grams dryer tower bottoms and 3.15 grams of calcium hydroxide were withdrawn periodically. Ten ml. of methanol were added to each of these samples. The mixtures were carbonated, dried, filtered, and stripped and the base numbers were determined. The results are shown below:

Mixing time without methanol (hours):	Base No. of sample
0 -----	95.5
2 -----	86.5
4 -----	93.8

This data shows that mixing for long periods of time without introducing methanol has no detrimental effect on the base number of the product.

It is apparent from a comparison of the data of Example III and Example IV that prolonged contact with methanol causes deterioration of the mixture and lowers the base number of the product.

Reasonable variations and modifications are possible

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within the scope of this invention which sets forth a novel method of overbasing metal petroleum sulfonates.

That which is claimed is:

1. A process for producing overbased metal petroleum sulfonates which comprises:

forming a mixture comprising metal petroleum sulfonate, a hydroxide or oxide of a base metal, and diluent;

adding methanol to the mixture just prior to and not more than one hour before treatment with carbon dioxide;

contacting the mixture in a discontinuous liquid phase with carbon dioxide under a pressure of from 10 to 100 p.s.i.g. in a continuous gas phase;

stripping the methanol from the gas-treated mixture; filtering the mixture to obtain an overbased metal petroleum sulfonated.

2. The process of claim 1 wherein the mixture is contacted with the carbon dioxide by spraying the liquid phase into a treatment chamber and simultaneously injecting the carbon dioxide into the chamber.

3. The process of claim 1 wherein the mixture is contacted with the carbon dioxide by introducing the liquid over baffles contained in a treatment chamber into which the carbon dioxide is injected.

4. A process of claim 1 wherein the pressure of the carbon dioxide in the treatment chamber is in the range of from 20 to 50 p.s.i.g.

5. The process of claim 1 wherein said metal petroleum sulfonate is calcium petroleum sulfonate or barium petroleum sulfonate and said base metal is calcium or barium.

6. A process of claim 1 wherein the mixture comprises calcium petroleum sulfonate, calcium hydroxide or calcium oxide, and diluent.

7. The process of claim 1 wherein the mixture comprises barium petroleum sulfonate, barium hydroxide or barium oxide, and diluent.

8. The process of claim 1 wherein the methanol contains not more than 10 weight percent water.

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