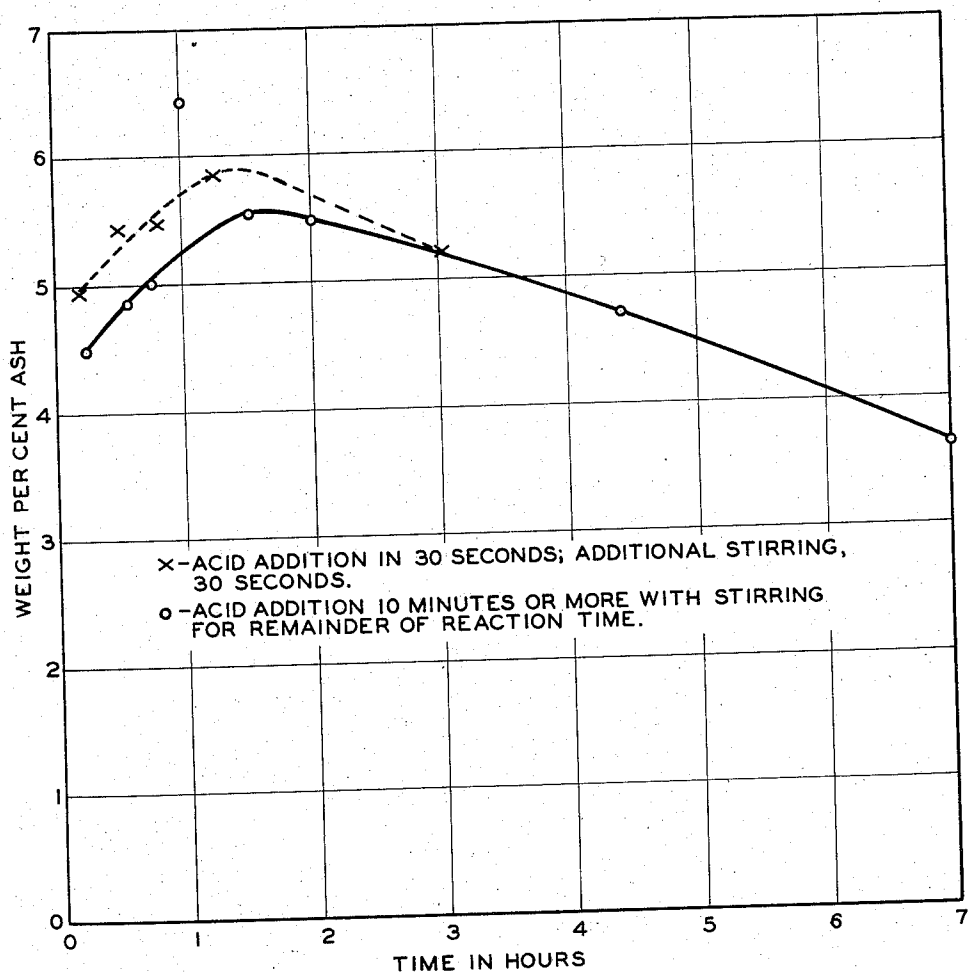


April 28, 1959

W. N. AXE ET AL
METAL PETROLEUM SULFONATES

2,884,445

Filed Dec. 17, 1956



INVENTORS
W. N. AXE
J. T. GRAGSON
BY *Hudson and Young*
ATTORNEYS

1

2,884,445

METAL PETROLEUM SULFONATES

William N. Axe and James T. Gragson, Bartlesville, Okla.,
assignors to Phillips Petroleum Company, a corporation
of Delaware

Application December 17, 1956, Serial No. 628,780

9 Claims. (Cl. 260—504)

This invention relates to a method for making an improved metal petroleum sulfonate and to a lubricant embodying such metal petroleum sulfonate as an additive.

Copending application, Serial No. 478,839, filed December 30, 1954, by W. B. Whitney, describes a method for preparing oil soluble metal petroleum sulfonates from highly refined, solvent extracted, high molecular weight petroleum stocks by treatment with a sulfonating agent, neutralization of the resulting oil-acid mixture with anhydrous ammonia, extraction of an ammonium petroleum sulfonate with an organic solvent, and conversion of the ammonium petroleum sulfonate to the metal petroleum sulfonate by reaction with an excess of a metal salt or hydroxide. It had heretofore been considered impossible to produce oil-soluble sulfonates from high molecular weight hydrocarbon fractions such as a Bright Stock having a viscosity of about 200 SUS at 210° F. because treatment of such highly refined lubricating oil stocks with fuming sulfuric acid produced no precipitate of acid sludge. Neutralization of the resulting acid-oil mixture with sodium hydroxide resulted in a very stable emulsion. Extraction of the petroleum sulfonate from such emulsion produced a low yield of product which was, in each case, contaminated with inorganic salts.

In accordance with the present invention, an improved process is provided for making metal petroleum sulfonates from heavy oil stocks. We have discovered that the ash content of oil-soluble metal petroleum sulfonates prepared from highly refined, solvent-extracted high molecular weight petroleum stocks is dependent upon the contact time of the sulfonating agent with the oil and also the manner in which the contact is attained. By the process of our invention, an additive is obtained having a high metal and ash content with resulting high activity and detergency. It is an object of this invention to provide a process for increasing the yield of metal petroleum sulfonates prepared from high molecular weight petroleum stocks. It is also an object of this invention to provide an improved metal petroleum sulfonate useful as a lubricating oil additive. It is a further object of this invention to provide a means for preparing a metal petroleum sulfonate having a high ash content. It is still another object of this invention to provide a simplified process for the preparation of metal petroleum sulfonates of high quality and in high yield. Other and further objects of this invention will be apparent to one upon study of the disclosure of the present invention.

Broadly, the invention contemplates admixing the oil to be sulfonated with the sulfonation agent in a short period of time, preferably not exceeding 10 minutes, vigorously agitating the mixture to attain intimate contact of the oil with the sulfonation agent and then allowing the mixture to rest in a quiescent state for a period of one to one and one-half hours and then neutralizing the reaction mixture with the oxide or hydroxide of the desired metal. An excess of the base is used so as to assure complete neutralization. The neutralized reaction product is then diluted with an inert organic solvent, heat-

2

ed to expel moisture present, after which the metal petroleum sulfonate together with unreacted oil is separated from the inorganic salts by centrifugation, filtration, decanting, or other known means of separation. The product can be used in the form in which it is obtained or can be concentrated by removal of a portion or all of the unreacted oil by a separation step such as propane fractionation. Thus, a high quality lubricant additive is obtained which can be mixed with lubricating oil of, say SAE-5W to SAE-50 grade in an amount of 0.1 to 20 percent by weight based on the oil whereby a high detergency oil with improved characteristics is obtained. The additive of this invention is also useful in the formation of greases upon addition of suitable thickening agents.

The drawing is a graphical illustration of the advantages which are gained by practice of the invention.

According to more specific aspects of the invention, the starting material is a refined lubricating oil stock such as a de-asphalted and solvent-refined petroleum fraction having a viscosity range between about 120 and 700 SUS at 210° F. An especially preferred sulfonation stock is a propane-fractionated, solvent-extracted and de-waxed Mid-Continent oil of about 200 to 235 SUS at 210° F. having a viscosity index of about 85 to 95 or higher.

In the sulfonation step, the oil starting material is intimately contacted with a sulfonation agent of which fuming sulfuric acid and chlorosulfonic acid are especially suitable. A temperature within the range of 50 to 200° F., and preferably 130 to 150° F. is maintained during the sulfonation together with an acid-to-oil weight ratio of 0.175:1 to 1:1 using 20 percent oleum. An acid-oil weight ratio of about 0.3:1 to about 0.6:1 is preferred from a standpoint of yield, reaction rate and color of product. When a high ratio of acid to oil is employed the product is dark, almost black, and tarry in contrast to the red, resinous product obtained employing the preferred acid to oil ratio. It is believed that oxidation occurs at high acid to oil ratios. The sulfonation agent is preferably added to the oil as rapidly as possible and with vigorous agitation. The agitation is continued only so long as is required to assure satisfactory dispersion of the sulfonation agent in the oil. The mixture is then allowed to rest in a quiescent state for the required reaction time after which it is immediately neutralized with an excess of the desired metal oxide or hydroxide. The reaction temperature is maintained during the time the mixture is quiescent.

All metals are suitable for preparing the metal petroleum sulfonates of this invention. Metals which have been found to be particularly suitable for preparing the metal petroleum sulfonates include barium, calcium, lithium, potassium, nickel, cobalt, cadmium, silver, iron, aluminum, copper, magnesium, lead, beryllium, mercury, sodium, tin, and zinc. The alkaline earth metals are preferred and barium and calcium are especially preferred in preparing metal petroleum sulfonates for use as additives in lubricants.

The following examples will illustrate the invention but are not to be construed as limiting the invention.

EXAMPLE I

A solvent refined and de-waxed lubricating oil fraction containing an average of about 52 carbon atoms per molecule derived from a Mid-Continent petroleum and having a viscosity of 208 SUS at 210° F. and a viscosity index of 96 was sulfonated with 20 percent fuming sulfuric acid at an acid-to-oil ratio of 0.4. The sulfonation was carried out in a reaction vessel equipped with a stirrer and 5 runs were made in the following manner: the fuming sulfuric acid was added to the oil at a starting temperature of about 65° F. Fuming sulfuric acid was added with rapid stirring in a period of 30 seconds

and after an additional 30 seconds stirring the stirrer was removed and the mixture allowed to remain motionless at a temperature maintained at 130° F. for the remainder of the reaction time. The reaction mixture was then neutralized with an excess of calcium hydroxide slurried in water. The neutralized material was then stripped of water by heating to about 400° F. and was then diluted with about 3 volumes of pentane and centrifuged to remove inorganic salts. The pentane was then evaporated and a sample analyzed for ash. The data are presented in Table I and are plotted in the drawing.

Table I

Total reaction time:	Ash content, weight percent
10 minutes	4.9
30 minutes	5.39
50 minutes	5.42
1 1/4 hours	5.8
3 hours	5.17

EXAMPLE II

Samples of the oil described in Example I were sulfonated with 20 percent fuming sulfuric acid with an acid-to-oil ratio of 0.4 in the following manner: the reaction vessel equipped with a stirrer was charged with the oil and the fuming sulfuric acid was added in the time shown in Table II and stirring was maintained at 130° F. for the total reaction time shown in Table II after which the material was neutralized and treated in the same manner as described in Example I. The results of eight runs are presented in Table II and are graphically illustrated in the drawing.

Table II

Total Reaction Time	Time of Acid Addition ¹	Ash Content, Weight Percent
15 minutes	10 minutes	4.42
35 minutes	15 minutes	4.83
45 minutes	10 minutes	4.97
1 hour	15 minutes	6.37
1 1/4 hours	30 minutes	5.5
2 hours	30 minutes	5.46
4 hours, 25 minutes	25 minutes	4.72
7 hours	5 hours	3.66

¹ Time of acid addition included in total reaction time.

² Stood 72 hours at room temperature without stirring before neutralization.

EXAMPLE III

The data shown in Table III were obtained in pilot plant operation under two sets of conditions. These conditions were: (1) the acid and oil were mixed in a centrifugal pump and then passed into a jacketed steel pipe and allowed to stand for the required residence time; (2) the acid and oil were mixed in a centrifugal pump and the product was allowed to stand in glass beakers at the required temperature for the desired residence time. In all cases the samples after standing for the desired residence time were neutralized with an excess of calcium hydroxide slurried in water. The water was evaporated by heating to about 400° F., the residue was cooled, diluted with pentane and centrifuged to remove inorganic salts. The pentane solvent was evaporated and the ash content determined on the residue.

Table III

CONDITION 1

Temperature, ° F.	Acid-Oil Ratio	Residence Time, minutes	Ash, Weight Percent
133	0.44	53	5.34
150	0.42	53	6.93

CONDITION 2

138	0.4	65	6.27
138	0.4	95	6.89
149	0.4	65	5.77
131	0.4	65	6.17
148	0.4	30	4.97

The data of the examples show the increase in the extent of sulfonation as reflected by the increase in ash, in the runs wherein rapid acid addition followed by a soaking period of one to one and a half hours was practiced. The ash is correspondingly more when a higher acid-to-oil ratio and/or a higher reaction temperature are utilized in the sulfonation step. The formation of sulfonate is dependent upon several variables including acid-to-oil ratio and temperature but in each case the sulfonate formation is increased by rapid acid addition followed by a soaking period of one to one and a half hours. The data in the examples also show that an acid-oil contact time of less than one hour or more than one and a half hours decreases the yield of sulfonate as reflected by the decrease in ash content. One explanation of this may be that a contact time of less than one hour is not sufficient for complete sulfonation while a contact time in excess of one and a half hours permits decomposition of those sulfonic acids unstable in the presence of concentrated sulfuric acid.

Variations and modifications are possible within the scope of the disclosure of the present invention the essence of which is the discovery that the extent of sulfonation of a highly refined, high viscosity lube oil fraction can be increased by rapid addition of the sulfonation agent followed by a soaking period of about an hour to an hour and a half.

That which is claimed is:

1. The process of making an alkaline earth metal petroleum sulfonate which comprises adding oleum to a propane-fractionated, solvent-extracted and de-waxed lubricating oil stock having a viscosity of about 200 to 230 SUS at 210° F. in a period of about one minute and with agitation; maintaining the resulting mixture quiescent for about one and one half hours at reaction temperature; neutralizing the mixture with an alkaline earth metal hydroxide; diluting the mixture with about three volumes of pentane; and recovering the resulting alkaline earth metal petroleum sulfonate.

2. The process of claim 1 wherein the alkaline earth metal is calcium.

3. The process of claim 1 wherein the alkaline earth metal is barium.

4. The process of claim 1 wherein the alkaline earth metal is magnesium.

5. The process of claim 1 wherein the alkaline earth metal is strontium.

6. The process for making a metal petroleum sulfonate which comprises adding oleum at an acid-to-oil weight ratio of 0.2 to 0.7 to a de-asphalted, solvent-refined lubricating oil stock having a viscosity of about 120 to 700 SUS at 210° F. within a period of about 10 minutes and with agitation; maintaining the resulting mixture quiescent for a time in the range of one to one and one-half hours at a temperature in the range 120 to 150° F.; neutralizing the reaction mixture with a basic metal compound; and recovering the metal petroleum sulfonate.

7. In the preparation of metal petroleum sulfonates wherein a de-asphalted, solvent-refined lubricating oil stock having a viscosity of about 120 to 700 SUS at 210° F. is sulfonated with a sulfonation agent at a temperature in the range of about 50 to 200° F., and the product of sulfonation is neutralized and converted to the metal petroleum sulfonate, the improvement comprising conducting the sulfonation step by adding the sulfonation agent to the oil within a period of time less than 10 minutes and with agitation; maintaining the reaction mixture

5

quiescent for a period of time in the range of one to one and one-half hours at the reaction temperature before neutralizing the reaction product; and recovering the metal petroleum sulfonate.

8. The process of claim 7 wherein the reaction mixture is neutralized with a basic metal compound; the reaction mixture is diluted with from 1 to 5 volumes of an inert organic diluent; and the metal petroleum sulfonate is recovered by centrifugation.

9. The process of claim 7 wherein the reaction mixture is neutralized with ammonia; the ammonium sulfonate is

6

extracted with an organic solvent and is converted to the metal petroleum sulfonate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,660,562 Axe et al. Nov. 24, 1953

OTHER REFERENCES

Kircher et al.: Industrial & Engineering Chemistry, vol. 46, No. 9, pp. 1925-1930 (6 pp.) 1954.