United States Patent Office

3,591,498

Patented July 6, 1971

3,591,498

SULFONATION OF NEUTRAL OIL-BENZENE ALKYLATE BLEND

Lemuel S. Benbury, Whittier, and Ulric B. Bray, Pasadena, Calif., assignors to Bray Oil Company

No Drawing. Filed May 6, 1968, Ser. No. 727,022

Int. Cl. C10m 1/40

U.S. Cl. 252—33 5 Claims

ABSTRACT OF THE DISCLOSURE

A blend of petroleum lubricating oil of 400–600 molecular weight and linear alkyl benzene of about 25–35 carbon atoms is sulfonated with oleum. The reaction mixture is immediately diluted with about two volumes of non-aromatic naphtha without hydrolyzing the sludge which is separated and discarded. The naphtha solution is extracted with 8–15% by volume of water, then neutralized with 50 to 100% excess fine hydrated lime and filtered. Calcium sulfate is adsorbed in the excess lime. Naphtha is recovered by distillation.

The residue oil-sulfonate solution containing about 40% sulfonate, is a clear, bright oil soluble sulfonate substantially free of sulfates and chlorides. It is useful as a detergent additive in motor oils and anti-rust compounds.

This invention relates to the manufacture of preferentially oil soluble sulfonates of alkali and alkaline earth metals, such as sodium, lithium, calcium, and barium, metals, such as sodium, lithium, calcium, and barium, useful in compounding lubricating oils for internal combustion engines, jet engine oils, hydraulic oils and rust protection oils and greases. More particularly, the invention relates to manufacture of mahogany sulfonates of acceptable concentration of 30 to 65% from lubricating oil distillates without the necessity of concentrating. Heretofore, it has generally been the practice in manufacturing sulfonates from lubricating oils, first, after discarding sludge, to neutralize the sulfonated oil with caustic soda, forming the sodium salt, from which unreacted oil could be eliminated by treating with water and solvents, usually alcohols such as methanol or butyl alcohol. By this method, the sulfonate concentration can be increased form about 12% to the desired 40%–60%. At the same time, sulfuric acid, which is associated intimately with the sulfonic acids, can be eliminated as water soluble sulfate. When sulfonates of the alkaline earth metals were desired, the sodium salt was converted to the calcium or barium salt by treatment with the corresponding chloride in a metathesis reaction. Extensive washing with water was then required to reduce the chloride content to acceptable limits. This process is described in U.S. Patents of Bray, 2,396,673 and 2,689,221. No practical method has heretofore been available for directly neutralizing the acid oil fram sulfonation with alkaline earth bases because of the difficulty or near impossibility of concentrating the resulting highly oil soluble alkaline earth metal sulfonate and separating insoluble sulfates which form when the sulfuric acid associated with the sulfonic acid is neutralized with lime or baryta, often in collodial form impossible to remove by filtration. The sludge layer has generally been considered a nuisance although it was recognized by some that the sludge phase carried away a portion of the desired sulfonates and attempts were made to recover these as by extraction with solvents such as carbon

tetrachloride (U.S. 2,530,757) and xylene (U.S. 2,732,344). The use of paraffinic type hydrocarbon solvents such as the petroleum naphthas has been generally found less effective for the purpose.

One object of our invention is to improve the yield of valuable oil soluble sulfonates without resorting to complicated extraction techniques. Another object is to sulfonate a blend of neutral oil and alkylate such that the product sulfonate will have the concentration desired, usually 40 to 50%, but, in some cases, as low as 30% and as high as 65%. Still another object is to make the sulfonates of the desired metals directly without intermediate conversion and purification operations. A further object is to avoid the formation of alkali metal sulfates in colloidal form and to condition the alkali metal sulfates for easy filtration. A still further object is to avoid entirely the use of chlorides, thus producing a product sulfonate free of chlorides or other halogen.

We now have discovered that the foregoing objects can be achieved by initially blending with the lubricating oil distillate, an alkylate of benzene having about 25 to 35 carbon atoms corresponding to a molecular weight of about 345 to 485, resulting from the alkylation of benzene with linear olefines or chlorparaffins having about 11 to 13 carbon atoms, using a Friedel-Crafts catalyst, perferably aluminum chloride. During the alkylation, numerous side reactions take place giving some dialkyl benzenes along with some alkyl indane and polynuclear aromatics. Where the latter appear in quantity corresponding to more than 20% of the dialkyl benzene content, we generally prefer to eliminate these impurities in the dialkyl benzenes by a refining treatment with a selective solvent such as furfural or with sulfuric acid of 95 to 100% concentration, inasmuch as these polynuclear aromatics increase the sludge loss in the sulfonation reaction and interfere with the sulfonation of the dialkyl benzene. For our purpose, the benzene alkylate is fractionally distilled to remove low boiling alkylates suitable for manufacture of water soluble sulfonates and secondary plasticizers, thus recovering a higher boiling fraction, with a boiling range between about 400° and 600° F. at 10 mm. mercury pressure. Typically, an alkylate suitable for our process will have a viscosity of 45 SSU at 210° F. and 187 at 100° F., with an aniline point of 130° F., an API gravity of 28° at 60° F., and a flash point of 430° F.

In preparing the stock for sulfonation, we prefer to blend about equal volumes of lubricating distillate and alkylate. In general, about 40–60% by volume of alkylate in the oil is satisfactory. A blend of 45% alkylate and 55% oil will result in a product having about 40% by weight of calcium sulfonate in oil—an acceptable concentration for the market. It is desirable that sufficient alkylate be present to provide sufficient sulfonate which, when combined with the sulfonate yielded by the neutral oil in the blend, will give a total sulfonate content of about 30% to 70%, depending on the specification for the finished product. It is desirable to employ sufficient oleum in the sulfonation reaction to completely sulfonate the aromatic hydrocarbons present, usually about 55 to 82% by volume based on the alkylate present.

The sulfonation reaction is carried out as shown in the following example: To 1,000 volumes of the alkylate-neutral oil blend is added gradually 330 volumes of oleum having 25% SO_3 content, with good agitation, and sufficient cooling to hold the temperature below about 110° F. To the reaction mixture is then added 2,000 volumes of petroleum naphtha, which is free of aromatic hydrocar-

bons. Varnish makers' and painters' naphtha or Stoddard solvent is satisfactory after they have been treated with sulfuric acid of 101.13% strength (5% SO_3) to remove aromatics. Straight run naphtha from paraffinic crude, boiling within the range of 250 to 400° F., is suitable. Sludge is settled from the naphtha solution by standing for 1 to 6 hours, then separated and discarded. The naphtha solution of acid oil, having an acid value of about 25 to 35, is then treated with water to remove as much of the contaminating sulfuric acid as possible before neutralization. This is a critical step in the process, inasmuch as serious emulsification difficulties are encountered when too great dilution of the acid in the aqueous phase is attempted. At the same time, we have found that too little dilution of the acid results in a product oil which is hazy and opalescent, unsuitable for market.

The water treatment can be conducted in one, two, or more contacting and settling stages, but it is essential that the concentration of acid in the final stage be not less than 25 A.V. or more than 200 A.V. for good results.

When these conditions are satisfied, the aqueous phase containing most of the H_2SO_4 and undesired, water soluble organic acids, usually settles clear in from one to five hours and is withdrawn. The separation can be speeded by centrifuging, utilizing the considerable difference in density between the phases.

After the water treat, the acid oil having an acid value of about 20–25 is neutralized by thorough agitation with dry powdered lime ($Ca(OH)_2$), baryta, or other base as desired. Finely powdered Na_2CO_3 or Li_2CO_3 can be used, preferably in the range of about 100–300 mesh. Likewise, powdered $CaCO_3$ or $BaCO_3$ can be used. Neutralization is facilitated by heating, for example to 150° F., and an excess of the base must be used—usually 50% to 100% of theory—preferably 75% excess over theory when

$Ca(OH)_2$

is used. The reason for the excess rquirement is obscure, but it appears to be required to absorb in a basic complex the sulfate produced in the neutralization. Addition of a small amout, e.g. 1%, of a contact agent such as methanol will hasten the neutralization, but is not necessary in commercial practice. We find that the sulfonic acid-naphtha solution retains in solution the correct amount of water to promote neutralization without emulsification and provide the water needed to form the complex between sulfate and excess base just described.

When neutralization is complete, as shown by an acidity test, the solution is filtered free of precipitated sulfate-hydrate complex. The clear filtrate is then distilled to recover the naphtha for re-use in the process. It is advisable to add a small amount of the base, e.g. lime, to the still to insure a neutral or basic condition during the distillation and thus prevent decomposition of the product sulfonate. Steam distillation is preferred, the steam assisting in removing all the naphtha from the oil, generally at 350°–400° F. A final "polish" filtration with a small amount, e.g. 1–3%, of a filter aid such as diatomaceous earth—"Filter Sel," "Dicalite," etc., can be performed on the product while hot. The product is bright and clear with a color ranging from yellow to mahogany. The sulfate content is low, usually about 0.1% or less, expressed as Na_2SO_4.

In our co-pending application, Ser. No. 651,695, we described a method of making oil soluble sulfonate free of haze by avoiding the use of solvent naphtha in separating sludge from the sulfonation reaction mixture. However, in that process, somewhat lower yields were obtained. Also, we there employed lower molecular weight neutral oils in the sulfonation feed and obtained our sulfonate product from the alkylate exclusively.

EXAMPLES

The following examples will illustrate the improved results obtained with new process. The feed stock employed in these experiments was a blend of "500" neutral oil and linear alkylate with characteristics shown in the following table:

	Neutral oil	Linear alkylate	Blend[1]
Gravity, ° API	28.0	28.5	28.2
Pour point, ° F	+10	−70	−10
Flash, C.O.C.	380	420	450
Viscosity, c.s.:			
@100° F	119.01	35.24	64.40
@210° F	11.38		7.87
Aromatics (Watson), percent	23.47	66.95	46.86
Molecular weight	513	397	460
Distillation at 10 mm. Hg:			
Initial ° F	506	412	416
5%	536	444	472
10%	542	464	484
20%	552	478	502
30%	560	486	512
40%	567	450	24
50%	575	494	38
60%	584	498	552
70%	595	502	572
80%	608	512	590
90%	620 (86%)	534	610

[1] Alkylate; 55% neutral oil.

EXPERIMENT 1

One thousand cc. of the above blend was sulfonated with 338 cc. oleum (25%) equal to 75% by volume of the alkylate content of the blend, keeping the temperature below 115° F. The reaction mixture was diluted with 2,000 cc. naphtha—VM&P. After settling one hour, 520 cc. (756 grams) sludge was separated, leaving 2,790 cc. acid oil having an acid value (mg. KOH per gram of sample) of 32.6. The acid oil was then treated by thoroughly mixing with 5% by colume of water and separating an aqueous phase of 54 cc. greenish yellow acid which settled rapidly, having an acid value of 330.

The naphtha solution, now having an acid value of 23.2, was divided into two equal parts of 1,425 cc. each. One part was given a second treatment with 5% by volume of water, making a total of 10% in two stages. The second water wash phase analyzed 66 acid value. Both naphtha solutions were then neutralized with hydrated lime using an excess of 80% of the theory in each case. Results are as follows:

Water treatment	5%	2 × 5%
Volume of solution, cc	1,425	1,430
Acid value, oil phase	23.2	17.9
Lime used, grams	45.0	31.0
pH after neutralizing	8–9	9
Filtered—precoat—no aid	Slow	Rapid
Alkali value of filtrate	0.9	0.8
Steam stripping to 340° F. with 2 gm. lime, yield of sulfonate, gm	370	377
Refiltered with 2% Hy Flo, hot	Rapid	Rapid
Product:		
Appearance	(1)	(2)
Alkali value	8.6	8.9
Ash, sulfated, percent	7.738	7.62
QAS calcium, percent	1.85	1.77
Sulfate as Na_2SO_4, percent	0.162	0.11

[1] Opalescent, hazy.
[2] Clear, bright.

The above results show that repeating the water treatment and separating the solution from an aqueous phase of 66 acid value instead of 330 acid value, gave a final product of superior appearance and lower sulfate while greatly improving the rate of filtration.

EXPERIMENT 2

The sulfonation in Experiment 1 was duplicated, producing 2,780 cc. of acid oil-naphtha solution with acid value—30.8. The solution was divided, one-third being treated with 10% (volume) of water and two-thirds with 5% water. The latter portion was then again divided, one-

half being given a second 5% water treat. Results are as follows:

Water treatment	10%	5%	2 × 5%
Volume of solution, cc	900	1,860	
Water phase separated, cc	42	26	
Acid value of water phase	129	310	
Volume in second 5% treat, cc			900
Water phase in second, cc			29
Acid value of water phase			74
Acid value of oil phase	23.2	24.2	21.2
Lime used, grams	28	30.2	23.0
Filter rate, Hy Flo precoat	Rapid	(1)	Rapid
Alkali value of filtrate	1.0	1.2	1.1
Steam stripped to 340° F., yield, gm	246	261	234
Refiltered, 2 gm. Hy Flo	Rapid	Rapid	Rapid
Appearance	(2)	(3)	(2)
Alkali value	2.6	3.5	2.4
Ash, sulfated, percent	6.93	7.26	6.96
QAS calcium, percent	1.82	1.82	1.80
Sulfate as Na_2SO_4, percent	0.115	0.133	0.115
Halogen	Nil	Nil	Nil

[1] Slow and very slow.
[2] Bright, clear.
[3] Opalescent, hazy.

EXPERIMENT 3

In another experiment, the sludge was separated from the sulfonation reaction product without naphtha dilution. The acid oil was then diluted with naphtha, a small amount of sludge was separated, and then 5% water was added. An acid of 195 A.V. separated. On neutralization with lime, filtration and stripping, the sulfonate obtained was clear and bright but the QAS calcium was only 1.49 instead of 1.80 showing loss of sulfonate in the sludge originally discarded.

EXPERIMENT 4

In this series of tests, the same acid oil was prepared as described in Experiment 1 with 28.3 acid value. The amount of water used in the water treatment was varied as shown in the following table:

Test No	1	2	3	4	5
Percent H_2O	5(2 & 3)	5	7.5	10	15
	2 & 3				
Acid value of aqueous phase	735	205	305	161	116	75
Acid value of oil phase	20.2	21.9	20.7	19.5	18.1

These data show that, when the water treatment is divided into two stages as in Test 1, the acidity of the aqueous phase in the second stage can be reduced to about two-thirds that when only a single stage treatment is used with the same amount of water (Test 2).

Determination of sulfonate by the QAS (quaternary ammonium sulfonate) method is described in Analytical Chemistry, volume 26, September 1954, pages 1942–97; also in Technical Bulletin, Rohm & Haas Company, February 1960, "Assay of Hyamine Products." Alkali value (or acid value) is determined by ASTM Method D664–58 and is expressed in milligrams KOH equivalent per gram of sample. The ash (sulfated) is determined by ASTM Method D874–59T.

Having thus described our invention, what we claim is:

1. The process of making oil soluble petroleum sulfonates of the alkali and alkaline earth metals, free of halogens and substantially free of sulfates having a sulfonate concentration in the range of 30 to 60 percent, which comprises blending a neutral oil of about 400–600 molecular weight with about 40–6 percent by volume of a benzene alkylate of about 25 to 35 carbon atoms prepared from alkylation of benzene with linear alkyl in presence of a Friedel-Crafts catalyst, sulfonating said blend with about 55 to 82% by volume of oleum sufficient to completely sulfonate the aromatic hydrocarbons present, forming desired oil soluble sulfonic acids and sludge, immediately, without separation or hydrolysis of said sludge, mixing the reaction product with 1.5 to 3 volumes of non-aromatic naphtha, separating and discarding sludge, treating the acid oil-naphtha solution with sufficient water to provide an aqueous phase with an acid value of about 25 to 200, separating the aqueous phase and neutralizing the acid oil with an excess of a basic powder selected from the class consisting of the oxides, hydroxides, and carbonates of the alkali and alkaline earth metals, filtering insoluble sulfate and excess basic compound from the naphtha solution, and stirpping naphtha from the oil-sulfonate product.

2. The process of claim 1 wherein the acid oil is neutralized with calcium hydroxide.

3. The process of claim 1 wherein the said basic metal compound is employed in an excess of 50 to 100% above the amount calculated on a stoichiometric basis.

4. The process of claim 1 wherein the said alkylate is a fraction boiling within the range of 400–600° F. at 10 mm. mercury pressure obtained from the alkylation of benzene with linear hydrocarbons of 11 to 13 carbon atoms.

5. The process of claim 4 wherein the neutral oil employed in said blend has a viscosity of about 119 centistokes at 10° F. and the ratio of alkylate to neutral in the blend is about 45/55 by volume.

References Cited

UNITED STATES PATENTS

3,476,800	11/1969	Cease	260—505S
2,573,675	11/1951	Bloch et al.	260—505S
3,007,868	11/1961	Eck et al.	260—505N
2,802,866	8/1957	Salzmann et al.	260—505S
2,843,626	7/1958	Gebelein et al.	260—505S

LEON ZITVER, Primary Examiner

L. DECRESCENTE, Assistant Examiner

U.S. Cl. X.R.

260—505S, 504R

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,591,498 Dated July 6, 1971

Inventor(s) Lemuel S. Benbury et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 31, cancel "metals, such as sodium, lithium, calcium, and barium,"; line 45, "form" should read -- from --. Column 3, line 58, "Filter Sel" should read -- Filter Cel --. Column 4, in the Table beginning line 5, temperature for Flash of Neutral Oil "80" should read -- 490 --; same table, last column, temperatures reading "24" and "38" should read -- 524 --, and -- 538 --; same table, footnote, "Alkylate; 55% neutral oil" should read -- 45% alkylate; 55% neutral oil --; same column 4, line 35, "colume" should read -- volume --. Column 6, line 9, "40-6 percent" should read -- 40-60 percent --.

Signed and sealed this 23rd day of May 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334