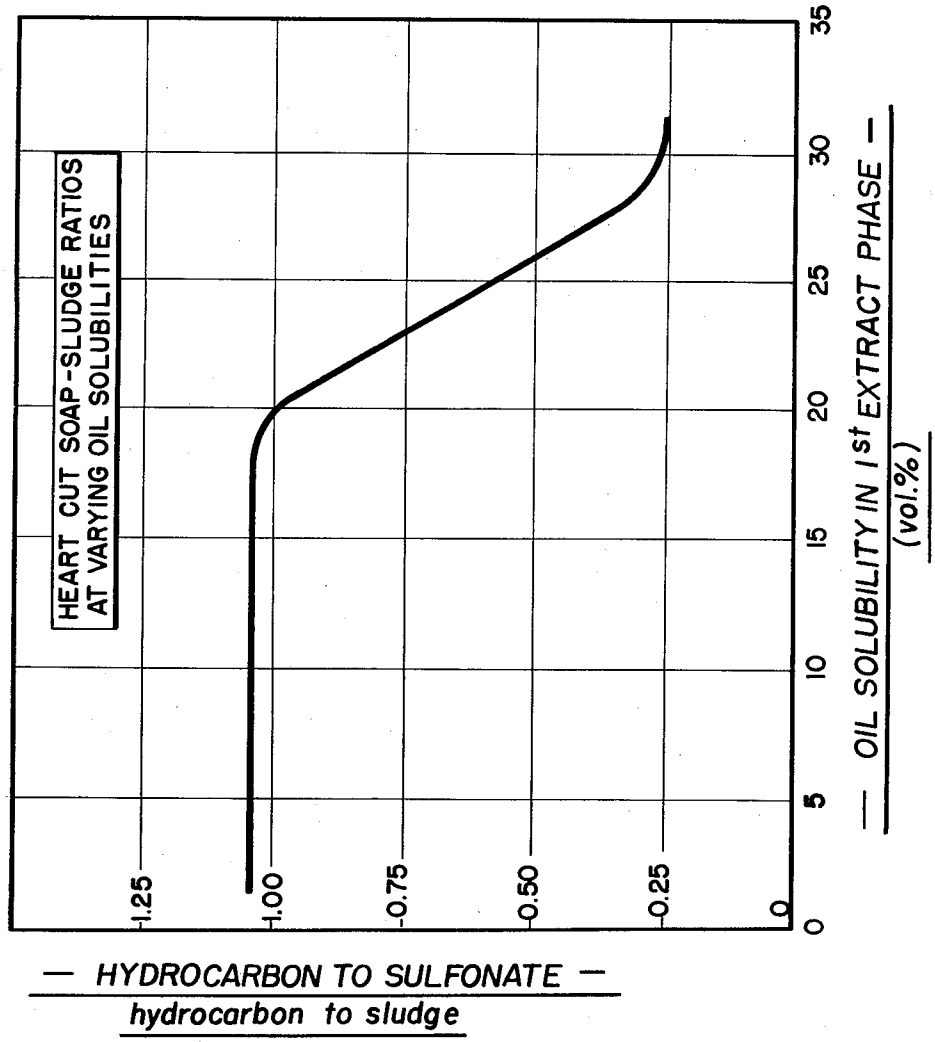
Nov. 8, 1955 J. STEWART ET AL 2,723,219

PREPARATION OF SULFONATION FEED STOCK

Filed Dec. 18, 1952



Joseph Stewart
Albert J. Ward Jr. Inventors
Carter E. Porter
By Henry Berk Attorney

United States Patent Office

2,723,219

Patented Nov. 8, 1955

2,723,219

PREPARATION OF SULFONATION FEED STOCK

Joseph Stewart, Cranford, Albert J. Ward, Jr., Metuchen, and Carter E. Porter, Cranford, N. J., assignors to Esso Research and Engineering Company, a corporation of Delaware

Application December 18, 1952, Serial No. 326,742

3 Claims. (Cl. 196—14.42)

This invention relates to an improved process for obtaining superior feed stocks for the preparation of oil-soluble sulfonates particularly adapted for use as lubricating oil additives.

As is well known in the art, the sulfonation of petroleum fractions for the obtaining of oil-soluble sulfonates conventionally results also in the production of large quantities of sludge, e. g., 15 to 20 volume per cent or more based on the feed. This undesirable production of sludge, which is a nuisance to remove in itself, also results in the requirement of larger equipment sizes, utilization of more feed stocks for the same quantity of sulfonate product, and excessive requirements of sulfonating agent. The control of the amount of sludge produced is not a simple problem because of the complexity of the types of compounds found in petroleum oil stocks used for sulfonation. Typical of the compounds present are paraffins, olefins, substituted naphthenes or hydroaromatics, substituted benzenes, substituted naphthalenes, substituted anthracenes or phenanthrenes, substituted polycyclic aromatics containing more than three fused rings, and organic oxygen, nitrogen and sulfur compounds.

This invention provides an improved process for obtaining superior feed stocks for sulfonation. The utilization of the feed stock prepared by this process overcomes many of the beforementioned sulfonation difficulties. The method comprises extracting a specific type of petroleum lubricating oil with aqueous phenol of controlled concentration, at controlled temperatures, regulating both the feed cut point and the composition of feed oil segregated to the resultant extract phase, re-extracting the resultant raffinate from which the aqueous phenol has been removed with another batch of aqueous phenol of a controlled concentration utilizing again controlled temperatures, feed cut points, and the composition of feed oil segregated to the resultant extraction phase, and finally removing the aqueous phenol from the second extract phase or "heart cut" to obtain the superior feed stock of this invention.

The nature of the petroleum lubricating oil utilized has been found to be important. The oils are known in the art as coastal distillates. These can be further described by the following characteristics:

Specific gravity		0.90–0.94
Saybolt viscosity:		
100° F		950–2000
210° F		65–95
Aniline point	° F	185–210
Open cup flash	° F	425–500
I. B. P	° F	825–900
D. P	° F	1000–1200

Inspections on two samples of coastal distillates are detailed below under I and II.

	I	II
Specific Gravity	.9254	.9254
Saybolt Viscosity:		
100° F	989	1861
210° F	68.7	93.6
Aniline Point °F	193.5	206
Open Cup Flash °F	440	480
Vac. Engler Distn °F	848–1,055	863–1,070

In accordance with this invention the first and second extractions are conducted under carefully controlled conditions.

In the first extraction the aqueous phenol utilized is a 90 to 99 weight per cent solution, preferably 94 to 98 weight per cent phenol. The temperatures employed are in the range of 130° to 210° F., preferably about 160° to 170° F. The feed extracted is in the range of 40 to 50 volume per cent, and preferably 42 to 44 volume per cent. The amount of oil contained in the extract phase is not more than 20%, and preferably 15 to 20 volume per cent based on the total extract phase. As is further explained below, this 20% figure is extremely critical.

In the second extraction the phenol concentrations employed are the same as in the first extraction stage. The temperature is in the range of about 130° to 230° F., and preferably about 160° to 210° F., depending upon the mount of water in the phenol. The feed cut point based on the feed to the second extraction is in the range of about 25 to 45, and preferably about 31 to 34 volume per cent. The oil content of the extract phase is adjusted so that the latter contains 10 to 15 volume per cent oil.

It is extremely important that the oil content of the first extract phase does not exceed 20 volume per cent. The predominant proportion of the substituted polycyclic compounds in the lubricating oil are preferentially soluble in and extracted by the first aqueous phenol treatment under the conditions listed. Controlling the other variables without controlling this critical item is insufficient to obtain the results of this invention. This is apparent from the graph shown in the drawing. This graph presents data obtained by actual experiment. The graph illustrates that when the oil content of the first extract phase exceeds 20%, the hydrocarbon to sulfonate/hydrocarbon to sludge ratio drops precipitously. This may be due to the fact that the extract phase in any extraction acts itself as an extraction medium. The presence of excess oil in the aqueous phenol apparently reduces the selectivity so that less sludge-forming components are removed and consequently find their way into the final sulfonation feed. It is not intended, however, to be bound by any theory of operation presented.

The improved feed stock prepared by this invention can then be sulfonated by agents known in the art, such as sulfuric acid, oleum, sulfur trioxide, etc. The neutralization of the sulfonic acids and the extraction of the soaps can be done by conventional means, and constitute no part of this invention and consequently need not be further described.

The following examples are given to illustrate this invention, and include both the preparation of the improved feed stock according to this invention and test results

obtained on the sulfonation of the feed stock as compared to the other feeds known to the art.

EXAMPLE I

A coastal distillate oil of the characteristics enumerated above was countercurrently contacted with 96 weight per cent aqueous phenol at a temperature of about 165° F. Forty-three volume per cent of feed was segregated to the extract phase, which in turn contained 19.4 volume per cent oil. This extract phase was discarded. The aqueous phenol was removed from the raffinate by distillation. The thus-treated raffinate was re-extracted with the same concentration of aqueous phenol at a temperature of 203° F. About 33% of the oil fed to the second extraction was segregated to the extract phase, which contained about 12.1 volume per cent oil. The raffinate from the second extraction was discarded. The removal of the aqueous phenol by distillation from the second extract phase gave the improved feed stock of this invention. The detailed operating conditions are presented in the following table:

Table I

OPERATING CONDITIONS FOR HEART CUT FEED

	First Extraction	Second Extraction
Oil Feed, Rate, cc./hr.	443	307
Solvent Phenol, Rate, cc./hr.	797	725
Extract, Rate, cc/hr.	192	100
Oil in Extract Phase, Vol. percent	19.4	12.1
Raffinate, Rate, cc./hr.	260	218
Column Temp., °F.	165	203
Make-up Phenol, Rate, cc./hr.	26.4	22.6
Make-up Water, Rate, cc./hr.	0.67	----------
Water in Phenol, Wt. percent	2.1	----------

EXAMPLE II

A test was run to demonstrate the critical nature of the upper limit on the oil content in the first extract phase. This test was performed as follows. Three types of feed stock were sulfonated with oleum utilizing controlled conditions detailed below. Run I was made on a 30–100% raffinate from a single phenol extraction of a coastal distillate. Runs II and III were made on a feed stock prepared by the double phenol extraction taught in this invention, except for one critical difference. In run II the oil content in the extract phase exceeded the critical limit, i. e., was 32.4 per cent. In run III the feed stock of this invention prepared in Example I was utilized, i. e., the oil content in the first extract phase was 19.4 volume per cent. The data are presented below.

Table II

Reaction time: Two minutes.
Technique: Treat (8 vol. per cent)—treat (8 vol. per cent)—wash.

	Run I	Run II		Run III	
		First Raff.	Heart Cut	First Raff.	Heart Cut
Cut Range, Wt. Percent [1]	0–70	0–60	42–60	0–59	41–59
Temperature, °C.	------	40–61.7	40–68	40–64	40–64.5
Oleum Conc., Percent	18	18	18	18	18
HC to Sludge, Vol. Percent	16.5	20.3	33.9	14.4	14.4
Total Sludge, Vol. Percent	30.0	31.9	44.9	28.1	26.2
HC to Sulfonate, Vol. Percent	8.1	7.4	8.5	8.22	16.1
HC to Sulfonate/HC to Sludge	0.49	0.36	0.25	0.57	1.12
Comb. Wt. of Sulfonate as Acid	500	479	473	357	--------
Oil in first Extract Phase, Vol. Percent	------	32.4	32.4	19.4	19.4

[1] Based on original feed.

Several figures should particularly be noted. The hydrocarbon converted to sulfonate in volume per cent in run III was almost twice as much as that in run II, where the oil content in the extract phase was permitted to exceed the critical limit. The ratio of hydrocarbon to sulfonate as compared to hydrocarbon to sludge was 4½ times better for run III than for run II. As a matter of fact, even run I using a single extraction gave a superior result on this criterion to that obtained from run II, substantiating that if the oil content in the extract phase is not controlled, the feed stock is no better than that obtained by a single unitary extraction.

These data plus the data summarized in the graph in the drawing clearly establish how important it is to maintain the oil content in the extract phase in the specified range.

The preparation of feed stocks as taught in this invention is productive of many advantages in the subsequent sulfonation process. These advantages include a reduction in sludge formation, reduced acid and feed requirements, reduced equipment sizes, and improved yields of product.

The techniques of this invention can be utilized with modifications in the processing of other similar petroleum oil fractions.

It is to be understood that this invention is not limited to the specific examples, which have been offered merely as illustrations, since modifications may be made without departing from the spirit of this invention.

What is claimed is:

1. A process for obtaining an improved sulfonation feed stock, which comprises the steps of extracting a petroleum lubricating oil having a specific gravity of 0.90–0.94, an aniline point of 185°–210° F., and boiling in the range of 825°–1200° F. with aqueous phenol of about 90 to 99 weight per cent concentration at a temperature in the range of about 130°–210° F. so as to extract about from 40 to 50 volume per cent of the lubricating oil, whereby not more than 20 volume per cent of a first extract phase consists of dissolved oil; discarding said first extract phase; distilling off the aqueous phenol from the resulting raffinate; extracting the thus-treated raffinate oil with aqueous phenol of 90 to 99 weight per cent concentration at a temperature of about 160°–210° F. so as to extract about from 25 to 45 volume per cent of the raffinate feed oil to the second extraction, whereby the second extract phase contains from 10 to 15 volume per cent dissolved oil; discarding the resulting raffinate from the second extraction; and distilling off the aqueous phenol from the second extract phase to obtain the improved sulfonation feed stock.

2. A process for obtaining an improved sulfonation feed stock which comprises the steps of treating a petroleum lubricating oil having a specific gravity of 0.90–0.94, an aniline point of 185–210° F., and boiling in the range of 825°–1200° F., with aqueous phenol of about 94 to 98 weight per cent concentration at a temperature in the range of about 160° to 170° F. so as to extract about from 42 to 44 volume per cent of the lubricating oil, whereby components preferentially soluble in the aqueous phenol are removed; treating the resulting raffinate oil with aqueous phenol of about 94 to 98 weight per cent concentration at a temperature of about 200° to 210° F. so as to extract about from 31 to 34 volume per cent of the raffinate oil whereby the improved sulfonation feed stock is preferentially concentrated in the aqueous phenol extract phase; and distilling off the aqueous phenol from this extract phase to obtain the improved sulfonation feed stock.

3. A process for obtaining an improved sulfonation feed stock, which comprises the steps of extracting a petroleum lubricating oil having a specific gravity of 0.90–0.94, an aniline point of 185°–210° F., and boiling in the range of 825°–1200° F., with aqueous phenol of about 94 to 98 weight per cent concentration at a temperature in the range of about 160° to 170° F. so as to extract about from 42 to 44 volume per cent of the lubricating oil, whereby from 15 to 20 volume per cent of a first extract phase consists of dissolved oil; discarding said first extract phase; distilling off the aqueous phenol from the resulting raffinate; extracting the thus-treated raffinate oil with aqueous phenol of about 94 to 98 weight per cent

concentration at a temperature of about 200° to 210° F. so as to extract about from 31 to 34 volume per cent of the raffinate feed oil to the second extraction, whereby the second extract phase contains from 10 to 15 volume per cent dissolved oil; discarding the raffinate from the second extraction; and distilling off the aqueous phenol from the second extract phase to obtain the improved sulfonation feed stock.

References Cited in the file of this patent

UNITED STATES PATENTS

2,265,567	Merrill	Dec. 9, 1941
2,330,054	Hibshman	Sept. 21, 1943
2,344,406	Hibshman	Mar. 14, 1944
2,392,497	O'Neill	Jan. 8, 1946