

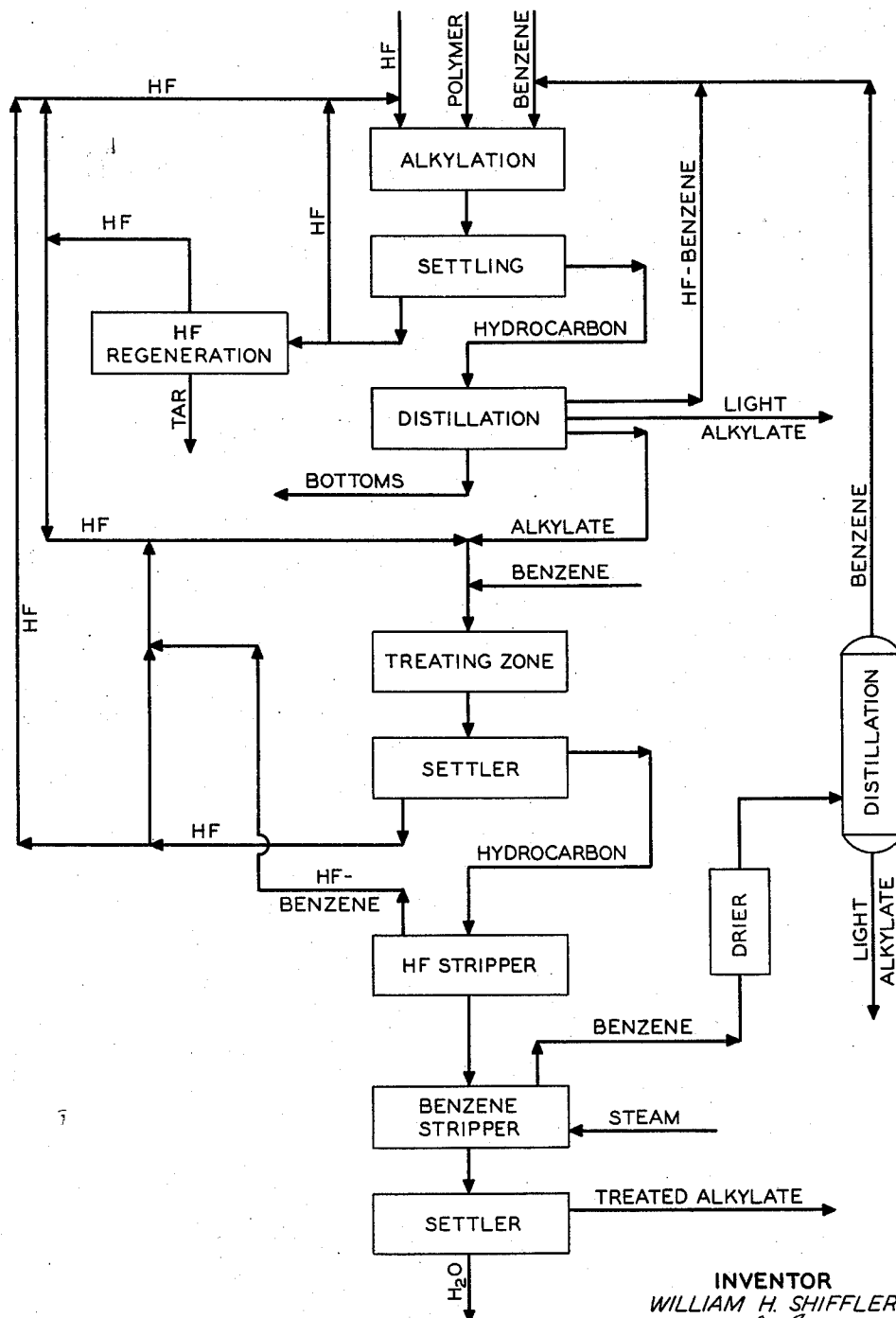
Sept. 9, 1958

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2,851,503

ALKYLATE HAVING IMPROVED SULFONATING CHARACTERISTICS

Filed Oct. 20, 1954



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ALKYLATE HAVING IMPROVED SULFONATING CHARACTERISTICS

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Application October 20, 1954, Serial No. 463,390

4 Claims. (Cl. 260—671)

This invention relates to a process for producing alkyl benzenes having improved sulfonating characteristics. More particularly, it relates to a method for treating alkyl benzenes prepared by alkylating benzene with lower olefin polymers to improve the sulfonating properties of the alkyl benzenes.

The great bulk of the synthetic sulfonate detergents currently produced is prepared by sulfonating alkyl benzenes of the character described in U. S. Patent No. 2,477,382. Alkyl benzenes of this character are prepared by polymerizing lower olefins, in particular propylene and butenes, or mixtures of propylene and butenes, to produce polymer fractions containing 8 to 18 carbon atoms per polymer molecule. Benzene is then alkylated with the polymers and the alkylation reaction mixture is fractionally distilled to separate a heart cut alkylate material characterized by having a number of carbon atoms in the alkyl side chains corresponding to the number of carbon atoms in the polymer molecules employed in the alkylation reaction. In the distillation, lower alkyl benzenes containing 4 to 7 carbon atoms in the alkyl side chains, and higher alkyl benzenes and dialkyl benzenes containing a larger aggregate number of carbon atoms in the alkyl side chains than were contained in the polymer employed in the alkylation, both of which are produced by side reactions such as disproportionation, polymerization and alkylation which occur during the main alkylation reaction, are rejected from the whole alkylation reaction product mixture.

The alkylates produced in the above-described manner have proven highly satisfactory materials for use in the production of synthetic detergents by sulfonation, neutralization and compounding with builders, foam adjuvants, and the like. These materials are used in the production of millions of pounds of synthetic sulfonate detergents each year.

As the synthetic sulfonate detergent market has developed, rigorous property requirements have been imposed on the alkyl benzenes which are produced and sold for use in the production of sulfonates. The alkyl benzenes must yield a sulfonate which is essentially pure white in color, which is free of cracked or kerosene-like odor, and which is extremely low in residual sulfonated oil. The sulfonates produced by sulfonating alkyl benzenes obtained by alkylating benzene with lower olefin polymers commonly exhibit undesirable color and odor characteristics.

It is an object of this invention to provide a method for treating alkyl benzenes produced by alkylating benzene with lower olefin polymers to effect a substantial improvement in the sulfonating characteristics of these alkyl benzenes and, in particular, to produce a treated alkyl benzene which yields a sulfonate product of superior color.

It has now been found that the sulfonating charac-

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teristics of alkyl benzenes prepared by alkylating benzene with lower olefin polymer fractions containing from 8 to 18 carbon atoms per molecule can be very markedly improved by intimately mixing the alkylate with substantially anhydrous hydrofluoric acid and benzene, settling the resultant mixture to separate a predominantly hydrocarbon layer and an acid layer, and fractionally distilling the hydrocarbon layer to separate hydrofluoric acid and benzene from it.

Color measurements of synthetic sulfonates are commonly made by the Tristimulus Method of Color Determination, described in Handbook of Colorimetry, A. T. Hardy, 1936, Technology Press, M. I. T., Cambridge, Massachusetts. The color data reported hereinafter were determined by this method.

EXAMPLE 1

An alkyl benzene prepared by alkylating benzene, pursuant to U. S. Patent No. 2,477,382, with a propylene polymer prepared by polymerizing a predominantly propylene feed and having an A. P. I. gravity of 49.7 and ASTM-D-86 distillation inspections as follows:

	° F.
Start	359
5%	369
50%	379
95%	412
End point	434

was treated with hydrofluoric acid and benzene pursuant to the invention. The properties of the alkyl benzene subjected to the treatment are shown in Table I below. The treatment was carried out by vigorously mixing the alkyl benzene with substantially anhydrous hydrofluoric acid and benzene at 70° F. for 10 minutes. The resultant mixture was then stirred for 15 minutes to separate an upper hydrocarbon layer and a lower acid layer. The hydrocarbon layer was washed to remove residual acid, distilled under a vacuum to remove the major part of the benzene, and steam stripped to remove the final traces of benzene. The data in Table I sets out the properties of the treated and untreated alkylates. The mol ratio of alkylate to benzene to HF employed in the production of the treated alkane described in Table I was 1:1:10.

Table I

	Alkylate	
	HF Treated	Untreated
Saybolt Color	>+30	+22
Color, Percent Saturation	1.5	8.7
SO ₂ Sulfonate Slurry Color, Percent Saturation	4.3, 4.7	28
Viscosity at 100° F., SSU	46.6	48.5
Aniline Point, ° F.	49.6	50.4
Odor	Light aromatic	Typical, kerosene
Gravity, ° API	30.6	30.6
Dialkylbenzenes, Percent	0.4	0.3
Distillation, D-447:		
St.	508	518
5	531	533
10	535	537
50	544	545
90	558	559
95	565	567
E.P.	589	575
Rec., Percent	98.2	98

EXAMPLE 2

The untreated alkylate described in Table I was subjected to further treatments in which the proportions of

hydrofluoric acid and benzene were varied. The results of these treatments are shown in Table II.

Table II

Run No.	Mol Ratio of Reactants			Temperature	Sulfonate Slurry Color, Percent Saturation
	Alkylate	Benzene	HF		
1	1	0	0	no treatment	28
2	1	0	10	70° F.	11.5
3	1	1	10	70° F.	4.3
4	1	1	0.5	70° F.	10.6
5	1	0.5	0.5	70° F.	14.3
6	1	20	20	70-75° F.	3.1
7	1	1	100	70-75° F.	7.0

¹ The treated alkylate showed an increase in dialkyl benzene content of 4.3 volume percent.

EXAMPLE 3

A higher boiling alkylate prepared by alkylating benzene with propylene pentamer and separating a heart cut pentamer alkylate fraction was treated with benzene and hydrofluoric acid as in Example 1. The untreated alkylate on an ASTM-D-447 distillation had:

Initial boiling point	559
5% point	578
50% point	594
95% point	614

The untreated alkylate itself had a Saybolt color of +12, while the treated alkylate had a Saybolt color of +25. The sulfonates produced by identical sulfonation treatments from the treated and untreated alkylates had tristimulus colors of 17% saturation and 22% saturation, respectively. The sulfonates in Examples 1 and 2 were prepared by sulfonating the alkylate by passing a stream of air and SO₃ containing 5 to 10% SO₃ through the alkylate at 50° C. until sulfonation was complete. In each color comparison made in Examples 1 and 2, the conditions of sulfonation were rigorously controlled and were identical for the sulfonation of both the treated and untreated samples. The SO₃-air sulfonation technique is growing in commercial importance in that it produces a neutral sulfonate having a low sodium sulfate content. This method of sulfonation causes substantially greater formation of color bodies during the sulfonation of any given alkylate than does the older method of sulfonation in which fuming sulfuric acid is employed as the sulfonating agent. The sulfonation of the two samples compared in Example 3 was carried out with 20% fuming sulfuric acid and the sulfonation conditions were identical.

From the data tabulated in the above examples, it is clear that very marked improvements in color of the sulfonate product are obtained when the alkylate is treated with hydrofluoric acid and benzene prior to sulfonation. The presence of benzene during the treatment is required to suppress the formation of dialkyl benzenes during the treatment. This is clear from the data in Table II. Dialkyl benzenes are highly undesirable in the alkylate subjected to sulfonation, since their presence increases the amount of residual unsulfonated oil in the sulfonate product and imparts a marked odor characteristic of cracked petroleum products to the freshly prepared sulfonate. The production of dialkyl benzenes during the treatment of the alkylate must, therefore, be suppressed.

A number of treatments of alkyl benzenes prepared by alkylating benzene with propylene polymers, butene polymers and mixed propylene-butene polymers was carried out using varying proportions of benzene and hydrofluoric acid. It was found that in order to effect a significant improvement in the sulfonating characteristics of the alkyl benzene, the ratio of hydrofluoric acid to alkylate in the treatment must exceed 0.5 mol of HF per mol of alkylate and that the ratio of benzene to alkylate in the treatment must exceed 0.25 mol per mol of alkylate. The employ-

ment of extremely high mol ratios of HF to alkylate and benzene to alkylate was found to produce treated alkylates having excellent sulfonating characteristics. It was observed, however, that little incremental improvement is obtained by employing hydrofluoric acid to alkylate mol ratios above 20:1, or by employing benzene to alkylate ratios above about 10:1.

The treatment of the alkylate with benzene and hydrofluoric acid is ordinarily conducted at atmospheric temperature; temperatures of treatment may be higher or lower than atmospheric, for example, temperatures in the range 30 to 200° F. are fully operative.

A further significant characteristic of the treating method lies in the fact that the removal of hydrofluoric acid and benzene from the treated alkylate when the treatment is complete must be accomplished at temperatures below 400° F., and preferably below 350° F. if the full benefit of the treatment is to be realized in the final product. Accordingly, it is preferred to settle the mixture of benzene, hydrofluoric acid and alkylate at the end of the treatment to separate an upper hydrocarbon layer and a lower acid layer, and then to remove the hydrocarbon layer and distill residual hydrofluoric acid from it while maintaining the maximum temperature in the still pot below 350° F., and desirably at about 300° F., and then to remove residual benzene by steam distillation at temperatures below 300° F. If it is attempted to subject the mixture of treated alkylate, benzene and HF to conventional distillation at atmospheric pressure to remove hydrofluoric acid and benzene, still bottom temperatures of the order of 450° F. or higher must be employed in order to complete the removal of these two materials. Under such conditions it appears that a thermal degradation of the treated alkylate occurs, and it is found that upon sulfonation treated alkylate distilled in this manner shows much less color improvement than is obtained if the distillation temperatures are held below 350° F.

The appended drawing is a diagrammatic illustration of a process flow suitable for the practice of one embodiment of the invention in which hydrofluoric acid is employed as both the alkylation catalyst and the treating agent. Hydrofluoric acid, polymer and benzene are charged to an alkylation zone in which the alkylation is conducted pursuant to U. S. Patent No. 2,477,382. The alkylation reaction product is settled to separate a lower acid phase, a portion of which is recycled to the alkylation zone, and a portion of which is directed to a regeneration zone. In the regeneration zone the spent or partly spent hydrofluoric acid is fractionally distilled to remove essentially pure anhydrous hydrofluoric acid overhead and to separate a bottoms fraction comprising tarry materials contained in the spent acid and water in the form of the constant boiling HF water azeotrope. The hydrocarbon layer is fractionally distilled to separate a fraction comprising HF and benzene, which is returned to the alkylation zone, a light alkylate fraction characterized by a substantial content of alkyl benzenes containing from 4 to 7 carbon atoms in the alkyl group, a heart cut alkylate having a number of carbon atoms in the alkyl side chain corresponding to the number of carbon atoms contained in the polymer molecules charged to the alkylation zone, and a heavier bottoms fraction. The heart cut alkylate, benzene and HF are passed into a treating zone where these three materials are vigorously mixed for a period of from 1 second to 60 minutes. Very short contact times of the order of one second give satisfactory results when, for example, the alkylate, benzene and hydrofluoric acid are passed through an efficient line mixer and then directly into a settler. The mixture from the treating zone is passed into a settler to separate an upper hydrocarbon phase and a lower acid phase. A portion of the acid phase is recycled to the treating zone and a portion of it is recycled to the HF regeneration zone and to the alkylation zone, desirably via the settling vessel following the alkylation zone in the proc-

ess flow. The hydrocarbon layer is fractionally distilled at a maximum still bottom temperature usually in the range from 275° F. to 325° F. to remove substantially all of the HF overhead. This overhead HF is returned to the treating zone. After the stripping of the HF from the hydrocarbon layer is complete, the residual hydrocarbon material is passed into a benzene stripper where benzene is separated from the treated alkylate by steam distillation at a temperature usually in the range from 225° F. to 300° F. The benzene stripped from the treated alkylate is passed through a drier, distilled to remove lower alkyl benzenes and returned to the alkylation zone. This benzene stream may, if desired, be returned directly to the alkylation zone or a portion of it may be returned directly to the treating zone. This benzene is found to have an appreciable content of lower alkyl benzenes, however, and the bulk of it is, therefore, desirably distilled before return to the alkylation zone or to the treating zone. After the benzene stripping is complete, the treated alkylate is settled to separate water and withdrawn for sulfonation.

In pilot plant operation of the treating process above described, it has been observed that the desired improvement in the sulfonating characteristics of the alkylate can be obtained with very little accompanying stock loss. For example, in pilot scale treating employing ten mols of hydrofluoric acid and one mol of benzene per mol of alkylate, it was found that the volume of treated alkylate product was 99.3%.

I claim:

1. A process for improving the sulfonating characteristics of alkylates prepared by alkylating benzene with olefin polymer fractions containing 8 to 18 carbon atoms per polymer molecule, which comprises fractionally distilling the crude alkylate to separate a heart cut alkylate consisting essentially of monoalkyl benzenes having alkyl side chains containing a number of carbon atoms corresponding to the number of carbon atoms in the polymer charged to the alkylation zone, intimately mixing said heart cut alkylate with benzene and substantially anhydrous hydrofluoric acid, the quantities of hydrofluoric acid and benzene being such that in the resulting mixture the mol ratio of hydrofluoric acid to heart cut alkylate is in excess of 0.5:1 and the mol ratio of benzene to heart cut alkylate is in excess of 0.25:1, settling the resultant mixture to separate a predominantly hydrocarbon layer and an acid layer, and stripping hydrofluoric acid and benzene from the hydrocarbon layer below about 400° F.

2. A process for improving the sulfonating characteristics of alkylates prepared by alkylating benzene with olefin polymer fractions containing 8 to 18 carbon atoms per molecule, which comprises fractionally distilling the crude alkylate to separate a fraction having an initial boiling point above about 500° F., and consisting essentially of monoalkyl benzenes intimately mixing said fraction with substantially anhydrous hydrofluoric acid and benzene, the quantities of hydrofluoric acid and benzene being such that in the resulting mixture the mol ratio of hydrofluoric acid to said fraction is in excess of 0.5:1

and the mol ratio of benzene to said fraction is in excess of 0.25:1, settling the resultant mixture to separate a predominantly hydrocarbon layer and an acid layer and fractionally distilling the hydrocarbon layer to separate hydrofluoric acid and benzene while maintaining the maximum temperature during said distillation below 400° F.

3. A process for improving the sulfonating characteristics of alkylates prepared by alkylating benzene with olefin polymer fractions containing 8 to 18 carbon atoms per polymer molecule and distilling the resulting crude alkylate to separate a desired alkylate fraction consisting essentially of monoalkyl benzenes, which comprises intimately mixing the distilled alkylate with 0.5 to 20 mols of substantially anhydrous HF and with 0.25 to 10 mols of benzene per mol of alkylate, settling the resultant mixture to separate a predominantly hydrocarbon layer and an acid layer, subjecting the hydrocarbon layer to fractional distillation at a maximum distillation temperature below about 350° F. to separate hydrofluoric acid from the hydrocarbon layer, and then subjecting the resultant substantially acid-free hydrocarbon layer to steam distillation at a temperature below about 300° F. to separate benzene.

4. A process for producing alkyl benzenes having improved sulfonating characteristics, which comprises alkylating benzene with lower olefin polymer containing 8 to 18 carbon atoms in the polymer molecule in the presence of hydrofluoric acid as the alkylation catalyst, settling the alkylation reaction mixture to separate a hydrocarbon phase and an acid phase, returning a portion of the acid phase to the alkylation zone and introducing a portion of the acid phase into a regeneration zone and there regenerating the acid, fractionally distilling the hydrocarbon phase to separate a heart cut alkylate consisting essentially of monoalkyl benzenes having alkyl side chains containing a number of carbon atoms corresponding to the number of carbon atoms in the polymer charged to the alkylation zone, intimately mixing said heart cut with regenerated hydrofluoric acid and benzene in a treating zone, settling the mixture to separate a hydrocarbon phase and an acid phase, returning a portion of the acid phase to the treating zone and a portion to the alkylation zone, fractionally distilling the hydrocarbon phase to effect substantially complete separation of hydrofluoric acid and benzene from the heart cut alkylate while maintaining the maximum distillation temperature below 400° F., returning the separated hydrofluoric acid to the treating zone and returning the separated benzene to the alkylation zone and stripping residual benzene from the hydrofluoric acid-free hydrocarbon phase below a temperature of about 300° F.

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