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SULFONATION PROCESS

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This invention relates to improved sulfonation processes. More particularly, it relates to improved processes for the sulfonation of mixtures comprising alkyl aromatic hydrocarbons which form preferentially water soluble sulfonic acids upon sulfonation and alkyl aromatic hydrocarbons which form preferentially oil soluble sulfonic acids upon sulfonation.

Sulfonated alkyl aromatic hydrocarbons have found extensive application in industry, especially as wetting, washing and emulsifying agents. The length of the alkyl chain has been found to exert a remarkable influence on the properties of the sulfonates produced from alkyl aromatic hydrocarbons. Thus it has been found that sodium alkylbenzene sulfonates are preferentially water soluble and have a maximum detergency when the alkyl group contains about 10 to about 14 carbon atoms. Higher alkyl benzene sulfonates containing more than 16 carbon atoms in the alkyl group are preferentially oil-soluble and, in many respects, resemble the preferentially oil-soluble sulfonates obtainable from petroleum oils by treatment with fuming sulfuric acid. The latter are known in the petroleum refining art as mahogany soaps.

The mahogany-type higher alkyl aromatic sulfonic acids and salts are useful in a wide variety of applications to which mahogany acids and salts have been adapted, such as fat-hydrolysis, emulsification of mineral oils with water or aqueous solutions, in insecticidal spray oils, as textile assistants, and as rust inhibitors in slushing oils or greases.

It is highly desirable to be able to produce alkyl aromatic sulfonic acids which are preferentially water soluble and substantially free of preferentially oil soluble alkyl aromatic sulfonic acids, as well as preferentially oil soluble alkyl aromatic sulfonic acids substantially free of preferentially water soluble alkyl aromatic sulfonic acids from a crude mixture of alkyl aromatic hydrocarbons which yields both preferentially oil soluble and preferentially water soluble alkyl

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aromatic sulfonic acids upon non-selective sulfonation.

The desirability of segregating preferentially water soluble alkyl aromatic sulfonic acids on the one hand, and preferentially oil soluble alkyl aromatic sulfonic acids on the other, is dictated in large measure by the uses which each group of sulfonic acids or their salts is adapted best to fulfill. Formerly, alkyl aromatic hydrocarbons whose monosulfonic acids are preferentially water soluble were carefully fractionated, usually under vacuum, in advance of sulfonation to segregate them from alkyl aromatic hydrocarbons whose monosulfonic acids are preferentially oil soluble. Alternatively, methods of synthesis were employed which would yield substantially only alkyl aromatic hydrocarbons whose monosulfonic acids are either preferentially water soluble or preferentially oil soluble, and not mixtures of both types of alkyl aromatic hydrocarbons. Both of these procedures are laborious, time-consuming and expensive. By the process of our invention these procedures of preliminary purification of feed stock or the preparation of a feed stock of narrow molecular weight range are avoided.

It is an object of our invention to provide an improved process for the manufacture of alkyl aromatic sulfonic acids and salts containing alkyl groups of a narrow, selected molecular weight range from crude, wide boiling-range mixtures of alkyl aromatic hydrocarbons. Another object of our invention is to provide a process which obviates the necessity of purifying crude alkyl aromatic hydrocarbons prior to sulfonation to obtain alkyl aromatic hydrocarbons wherein the alkyl groups are restricted to a relatively narrow molecular weight range.

A further object of our invention is to provide a selective sulfonation process which will sulfonate only a selected group of alkyl aromatic hydrocarbons containing alkyl groups limited to a relatively narrow molecular weight range in admixture with other alkyl aromatic hydrocar-

bons. Yet another object of our invention is to provide a selective sulfonation process which avoids the necessity of segregating a selected feed stock by distillation from a crude mixture of alkyl aromatic hydrocarbons.

An additional object of our invention is to provide a selective sulfonation process wherein a mixture of alykl aromatic hydrocarbons capable of yielding both preferentially water soluble and preferentially oil soluble alkyl aromatic sulfonic acids upon non-selective sulfonation is sulfonated to yield preferentially water soluble alkyl aromatic sulfonic acids, to the substantial exclusion of preferentially oil soluble alkyl aromatic sulfonic acids.

Yet another object of our invention is to provide a two-stage sulfonation process in the first stage of which sulfonation of alkyl benzene hydrocarbons containing less than 17 carbon atoms in the alkyl group is selectively effected and in the second stage of which sulfonation of alkyl benzene hydrocarbons containing at least 17 carbon atoms in the alkyl group is effected.

A further object of our invention is to provide a process for the preparation of pure, preferentially oil-soluble alkyl aromatic sulfonic acids and soaps from a mixture predominating in alkyl aromatic hydrocarbons adapted to yield preferentially oil-soluble alkyl aromatic sulfonic acids upon monosulfonation and containing a minor proportion of alkyl aromatic hydrocarbons adapted to yield preferentially water-soluble alkyl aromatic sulfonic acids upon monosulfonation.

We have found that mixtures of alkyl aromatic hydrocarbons which yield both preferentially water-soluble and preferentially oil-soluble alkyl aromatic sulfonic acids upon non-selective sulfonation can be selectively sulfonated to yield substantially only preferentially water-soluble alkyl aromatic sulfonic acids by proper choice of the initial and final sulfuric acid concentrations and other reaction variables such as temperature, rate of agitation of the reaction mixture and acid: feed stock ratio used in sulfonation.

We have also found that the unreacted alkyl aromatic hydrocarbons whose monosulfonic acids are preferentially oil soluble can be separated from the selective sulfonation reaction mixture and sulfonated with sulfuric acid having a higher initial concentration than that used in selective sulfonation to produce sulfonic acids having many characteristics in common with mahogany acids.

An especially desirable application of our process may be made to feed stocks predominating in higher alkyl aromatic hydrocarbons, whose monosulfonic acids are preferentially oil soluble, particularly alkyl benzene hydrocarbons containing 17 or more carbon atoms in the alkyl group, and containing a minor proportion, e. g. about 5 to about 15 percent by volume, of lower alkyl aromatic hydrocarbons whose monosulfonic acids are preferentially water soluble, particularly alkyl benzene hydrocarbons containing less than 17 carbon atoms in the alkyl group. Feed stocks of this nature are sulfonated to produce preferentially oil soluble sulfonic acids and soaps substantially free of preferentially water soluble alkyl aromatic sulfonic acids. For certain purposes it is highly desirable that oil soluble alkyl aromatic sulfonic acids be substantially free of the lower, preferentially water soluble alkyl aromatic sulfonic acids containing less than 17 carbon atoms in the alkyl group.

Our invention can be applied to a wide variety of alkyl aromatic compounds. The aromatic nucleus can be, for example, benzene, toluene, xylenes, cumene, naphthalene, methyl naphthalenes, ethyl naphthalenes, isopropyl or other alkyl naphthalenes, diphenyl, alkyl diphenyls, anthracene and alkyl anthracenes or their naturally occurring or artifically prepared mixtures. Halogen, nitro, hydroxy, or other derivatives of the above aromatic hydrocarbons may also be sulfonated by our process.

The aromatic nucleus may be alkylated with a mixture of alkylating agents wherein the length of the alkyl group can vary from about 3 to about 30, 40, 50 carbon atoms or more to produce mixtures of alkyl aromatic compounds yielding both preferentially water-soluble and preferentially oil soluble sulfonic acids upon non-selective sulfonation. The alkylating agents may be haloparaffins, olefins, olefin polymers, alkyl sulfates, aliphatic alcohols, or aliphatic esters of wide molecular weight range. Any method of securing a mixture of alkyl aromatic hydrocarbons wherein the alkyl chain length varies over a wide range is satisfactory for the purposes of our invention.

Alkylation may be effected with 90–100 percent sulfuric acid, aluminum chloride activated with a trace of hydrogen chloride, hydrogen fluoride, boron fluoride and other known alkylation catalysts.

A highly satisfactory method of preparing a crude mixture of alkyl aromatic hydrocarbons for the purposes of our invention comprises alkylating an aromatic hydrocarbon with an olefin polymer. Suitable olefin polymers are those of ethylene, propylene, the butylenes, pentenes and the like, or mixtures thereof, preferably of wide boiling range and varying in chain length in the range of about C_3 to about C_{30} or more, preferably about C_{10} to about C_{20}. We may also use olefin co-polymers produced by co-polymerizing two or more of the above or similar olefins.

We have found that propylene polymers having a wide boiling range and correspondingly wide molecular weight range are particularly suitable alkylating agents for aromatic hydrocarbons and produce a highly satisfactory feed stock for our sulfonation processes. Propylene can be polymerized by passing it in the liquid phase through a pool of dispersed aluminum chloride catalyst to yield a polymer of relatively wide boiling and molecular weight ranges. We may, but preferably do not, use the total polymer. We prefer to use the light ends of the polymer which would normally be considered a waste product, since they boil too high for use in gasoline and are too volatile and non-viscous for inclusion in lubricating oil. The boiling range of these light ends will vary depending upon the conditions used in polymerization and upon the degree that the total polymer is reduced by distillation. Table I contains the A. S. T. M. distillations and other inspections of steam distillates from total propylene polymers. Such waste products are suitable starting materials for the alkylation of aromatic compounds, preferably hydrocarbons, to produce alkyl aromatic mixtures for our sulfonation processes. Refinery propylene was polymerized by the use of an aluminum chloride catalyst at the temperatures shown in Table I and the total polymerizate was distilled with fire and steam. In Table I, under tests A and C the first 10% of the polymer to be distilled was segregated and subjected to the following inspections: A. S. T. M.

distillation, bromine number (Francis) refractive index (n_D^{20}) and A. P. I. gravity. In test B the first 5% of the polymer to distill was analyzed in the same fashion.

TABLE I

	A		B		C	
Temp. of Polymerization, °F.	85		85		115	
Wt. Per cent Distilled Overhead	10		5		10	
A. S. T. M. Distillation	Per cent Off	Temp., °F.	Per cent Off	Temp., °F.	Per cent Off	Temp., °F.
	Initial	310	Initial	174	Initial	358
	10	384	10	354	10	402
	20	416	20	416	20	432
	30	442	30	454	30	452
	40	466	40	494	40	474
	50	488	50	518	50	492
	60	506	60	538	60	520
	70	526	70	550	70	540
	80	552	80	570	80	564
	90	584	90	600	90	606
	Max.	628	Max.	620	Max.	656
Bromine No.	79		69		67	
N_D^{20}	1.4512		1.4410		1.4499	
Gravity, A. P. I.	44.8		48.9		43.8	

In our process the total steam distillate or relatively wide boiling fraction of propylene polymer is alkylated. A close fractionation of the polymer is not necessary. However, in the alkylation of benzenes, we prefer to employ a polymer of which a substantial proportion boils within the range of about 300 to about 500° F.

By way of example, descriptions are given of the alkylation of benzene with propylene polymers. The alkylation conditions, yields and other pertinent data are shown in Table II:

TABLE II

Run No.	Alkylation of Benzene with Propylene Polymers					
	1	2	3	4	5	6
Charge:						
Mols Polymer	.68	.68	.68	.72	1.36	1.36.
Mol Wt. (Ave.)	235	235	235	220	238	238.
Mols C_6H_6	.68	2.72	1.36	1.36	2.72	2.72.
Catalyst	96% H_2SO_4	H_2SO_4	$AlCl_3$	$AlCl_3$	$AlCl_3$	$AlCl_3$.
Cat. Wt. (g.)	450	450	25	25	25	25.
HCl	0	0	Trace	Trace	Trace	Trace.
Conditions:						
Temp., °F	50	50	70	65	65	65.
Time, Hrs.	15	15	.33	.45	1.0	0.5.
Products:					Combined	
Mols Alkylate	.485	.51	.59	.59	2.32	
Mols C_6H_6	.03	1.8	.62	.67	3.22	
Mols polymer	.01	.07	0.0	0.0	0.0	
Properties of Crude Alkylate:						
N_D^{20}	1.4795	1.4825	1.4802	1.4792	1.4771	
Specific Dispersion			122	116	122	
Gravity, A. P. I.			24.8	34.9	34.4	
Yields:						
Per cent Theory	71	75	87	82	85	
Vol. per cent Crude Alkylate Based on Polymer	91	108	110	103	107	

The polymer used in runs 1, 2, and 3 of Table II was polymer A of Table I. The polymer used in run 4 of Table II was the first 36 weight per-cent distilled overhead of a propylene polymer prepared in the same fashion as polymer A of Table I. The polymer used in runs 5 and 6 was C of Table I. The average molecular weights of the polymers used was determined by a standard method, viz., the A. W. Francis bromine number method, Ind. Eng. Chem. 18, 821 (1926). In all the runs except number 1, a considerable molar

excess of benzene was used with respect to the polymer. Accordingly, the polymer was entirely consumed and the sole remaining problem was to separate benzene from the alkylated benzene.

Benzene was stripped from the alkylate merely by heating the mixture and passing steam or air as a stripping gas through the alkylate to remove the benzene which was thereafter condensed from the vapor stream.

We have found that crude alkylates obtained from benzene and propylene polymers, even when prepared from narrow boiling polymer fractions, have a wide boiling range and contain high boiling paraffins and other impurities in appreciable proportions.

Illustrative of results obtainable by sulfonation of wide boiling range mixed alkylates of benzene are the data shown in Table III. Runs A, B and C in Table III were made using alkylates produced by runs 1, 3 and 4, respectively, of Table II. The alkylate in run D of Table III was similar to that produced in run 5 of Table II. By the Draves and Clarkson Wetting Speed Test, the soaps from our selective sulfonation process are effective wetting agents, wetting times varying from 5 to 15 seconds for 0.5% solutions in water.

TABLE III

Sulfonation of mixed alkylates

Run No.	A	B	C	D
Charge:				
Crude Alkylate, cc.	182	200	196	400
H_2SO_4, cc. of 96%	150	150	150	300
Conditions:				
Type of Agitation	(1)	(2)	(2)	(2)
Time, Hrs.	20	16	16	16
Temp., °F.	80	80	80	80
Products:				
Acid Layer (spent) cc.	145	118	95	240
Crude sulfonic acid, cc.	32	103	130	183
Oil residue, cc.	140	122	90	255
Crude Soap, g.	30	86	104	[3] 106
Properties of Oil Residue:				
Vol. Per cent of Charge	78	61	53	64
N_D^{20}	1.4760	-----	-----	-----
Gravity (A. P. I.)	34.6	-----	-----	-----
S. D.	117	-----	-----	-----

[1] Mechanical.
[2] Air.
[3] Purified soap.

In general we have found that alkyl aromatic compounds whose monosulfonic acids are preferentially water soluble, and particularly alkyl benzenes containing less than 17 carbon atoms in the alkyl group, may be selectively sulfonated in admixture with higher alkyl aromatic compounds whose monosulfonic acids are preferentially oil soluble by the use of about 88 to about 98 weight percent sulfuric acid at temperatures in the approximate range of about 50 to about 150° F. The initial sulfuric acid strength and other reaction conditions are so adjusted in our process that selective sulfonation is effected only of those alkyl aromatics whose monosulfonic acids are preferentially water soluble. In particular instances it may be necessary to use somewhat stronger or more dilute sulfuric acid than indicated by the range of about 88 to about 98 weight percent sulfuric acid. We prefer to use about 0.2 to about 2.0 volumes of acid per volume of feed stock. The reaction period may vary from about 1 to about 20 hours or more, depending upon the nature of the specific feed stock, acid strength and other reaction conditions. It is desirable to maintain the sulfonation mixture in a state of agitation during the reaction period; agitation may be effected by the use of any of a large variety of known methods, but we prefer to use a mechanical agitator or to bubble an inert gas, such as air, through the reaction mixture.

Our selective sulfonation depends upon the use of the proper strength and amount of sulfuric acid. Thus, in the sulfonation of alkyl benzenes it is important that the acid strength be such that only alkyl benzenes containing fewer than 17 carbon atoms in the alkyl groups are sulfonated. It is likewise important that the amount of acid be sufficient so that the spent acid is of sufficient strength to retain in solution the alkylbenzene sulfonic acids containing fewer than about 9 carbon atoms. We have found that spent acids having specific gravities within the range of from about 1.70 (78% acid) to about 1.80 (88% acid) perform this function satisfactorily. The specific gravity of the acid in our selective sulfonation process, as applicable to alkyl benzenes, decreases from an initial of about 1.83 to a gravity within the above range.

Following selective sulfonation, the reaction products may be separated by a variety of methods, e. g. by solvent extraction, dilution with water and stratification, etc. We prefer to allow the reaction mixture to stratify without adding water

or other diluting medium thereto. Three strata are thus obtained.

The lower stratum consists of spent acid and alkyl aromatic sulfonic acids in which the alkyl group is too small (less than 9 carbon atoms in the case of alkyl benzene sulfonic acids) for good detergents.

It should be noted that the sulfonic acids which are preferentially acid soluble and which are recoverable by dilution of the acid layer yield soaps which are inferior detergents. This emphasizes the necessity of controlling the final as well as the initial acid strength in our selective sulfonation process.

The upper stratum consists of unsulfonated alkyl aromatics which form preferentially oil soluble sulfonic acids upon monosulfonation, as well as paraffins and dialkyl aromatic hydrocarbons.

The middle stratum consists predominantly of alkyl aromatic sulfonic acids which are preferentially water soluble. The middle stratum obtained by stratification of the reaction mixture when alkyl benzenes are selectively sulfonated consists of alkyl benzene sulfonic acids in which the alkyl group contains from 9 to 16 carbon atoms, while the upper stratum contains alkyl benzenes in which the alkyl group contains 17 or more carbon atoms. There is also in the middle stratum considerable dissolved sulfuric acid. If sufficient time is allowed, for example about 5 hours, for complete stratification, no oil remains in the middle stratum. Traces of preferentially oil soluble sulfonic acids are likewise absent since these are selectively extracted by the upper stratum.

Since detergents of this type are most effective when compounded with sodium sulfate in the proportion of about 40% soap to 60 % salt by weight, it is not necessary to separate the sulfonic acid from the sulfuric acid. The middle stratum can be neutralized with strong caustic solution, the soap-salt mixture dried at about 260° F. and additional sodium sulfate added.

When pure soap is desired we prefer to add to the middle stratum about an equal volume of water. This results in the separation of a relatively pure sulfonic acid solution upper stratum and a strong sulfuric acid lower stratum. The upper stratum is neutralized and alcohol added to precipitate the salt. Thereafter the alcohol is evaporated and the residue dried.

The residual oils produced in our selective sulfonation process consist in major part of higher alkyl aromatic hydrocarbons which form preferentially oil soluble sulfonic acids upon monosulfonation. In addition they contain relatively small proportions of high boiling paraffin hydrocarbons and complex aromatic products. We have found that residual oils from our selective sulfonation process may be readily sulfonated by the use of sulfuric acid containing at least about 80 weight percent of sulfur trioxide to produce preferentially oil-soluble sulfonic acids and soaps having valuable emulsifying properties.

By way of example, a composite sample of residual oils which resisted sulfonation with 96 weight percent sulfuric acid in the selective sulfonation of a mixture of alkyl benzenes containing less than 17 carbon atoms in the alkyl group and at least 17 carbon atoms in the alkyl group was prepared and sulfonated as follows: All parts are by weight. Seventy-five parts of the composite sample were cooled to about 40° F., 15 parts of 96 weight percent sulfuric acid were added and the mixture was agitated vigorously.

The mixture was maintained at a temperature between 35 and 40° F. while 90 parts of 30% fuming sulfuric acid were added dropwise over a period of three hours. The reaction mixture was then allowed to warm up and agitation was continued for one hour. It was again cooled, diluted with 40 parts of water and allowed to stratify. A lower acid stratum was withdrawn. The upper stratum was diluted with 90% alcohol and neutralized with caustic solution. The alcoholic stratum was extracted with an equal volume of hexane. Both the alcoholic and hexane strata were reduced in volume by distillation of the solvent therefrom. The alcoholic stratum yielded 31 parts of a solid soap. The hexane stratum yielded 56 parts of an oil-soap mixture which is preferentially soluble in oil and has good emulsifying properties.

It will be apparent from the foregoing description that we have discovered a novel and highly useful selective sulfonation process and products. We have also discovered and successfully applied a unitary process comprising a selective two-stage sulfonation technique to mixtures of alkyl aromatic hydrocarbons to secure the most rational utilization thereof, while obviating expensive and laborious fractionation of the feed stock prior to sulfonation.

We claim:

1. The process of sulfonating a mixture of alkyl aromatic hydrocarbons which yields both preferentially water-soluble and preferentially oil-soluble alkyl aromatic sulfonic acids upon non-selective sulfonation, which comprises contacting said mixture with at least 20 volume percent, based on said mixture, of sulfuric acid having an initial strength between about 88 and about 98 weight percent of sulfuric acid at a temperature between about 50° F. and about 150° F. for a period of at least one hour to effect substantial preferential sulfonation of alkyl aromatic hydrocarbons whose sulfonic acids are preferentially water-soluble, separating preferentially water-soluble alkyl aromatic sulfonic acids from the sulfonation reaction mixture, separating residual alkyl aromatic hydrocarbons from the sulfonation reaction mixture, and sulfonating said residual alkyl aromatic hydrocarbons with fuming sulfuric acid to produce preferentially oil-soluble alkyl aromatic sulfonic acids.

2. The process of sulfonating a mixture of alkyl benzene hydrocarbons which yields both preferentially water-soluble and preferentially oil-soluble alkyl benzene sulfonic acids upon non-selective sulfonation, which comprises contacting said mixture with at least 20 volume percent, based on said mixture, of sulfuric acid having an initial strength between about 88 and about 98 weight percent of sulfuric acid at a temperature between about 50° F. and about 150° F. for a period of at least one hour to effect substantial preferential sulfonation of alkyl benzene hydrocarbons whose sulfonic acids are preferentially water-soluble, separating preferentially water-soluble alkyl benzene sulfonic acids from the sulfonation reaction mixture, separating residual alkyl benzene hydrocarbons from the sulfonation reaction mixture, and sulfonating said residual alkyl benzene hydrocarbons with fuming sulfuric acid to produce preferentially oil-soluble alkly benzene sulfonic acids.

3. The process of sulfonating a mixture of alkyl benzene hydrocarbons having alkyl groups containing less than 17 carbon atoms and alkyl groups containing at least 17 carbon atoms, which comprises contacting said mixture with at least 20 volume percent, based on said mixture, of sulfuric acid having an initial strength between about 88 and about 98 weight percent sulfuric acid and a final strength between about 78 and about 88 weight percent sulfuric acid at a temperature between about 50° F. and about 150° F. for a period of at least one hour to effect substantial preferential sulfonation of alkyl benzene hydrocarbons containing less than 17 carbon atoms in the alkyl group, separating sulfonated hydrocarbons from the sulfonation reaction mixture, separating unsulfonated alkyl benzene hydrocarbons containing at least 17 carbon atoms in the alkyl group from the sulfonation reaction mixture and subjecting said unsulfonated alkyl benzene hydrocarbons to sulfonation with sulfuric acid containing at least 80 weight percent sulfur trioxide for a period of time sufficient to effect substantial sulfonation to produce preferentially oil-soluble alkyl benzene sulfonic acids, and separating said preferentially oil-soluble alkyl benzene sulfonic acids from the last named sulfonation operation.

4. The process of claim 1 wherein the final sulfuric acid strength in the first sulfonation stage is between about 78 and about 88 weight percent sulfuric acid.

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