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June 13, 1939

UNITED STATES PATENT OFFICE

2,162,269

SULPHURIC ACID DERIVATIVES OF ALKYL-PHENOLS

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No Drawing. Application November 7, 1936, Serial No. 109,676

18 Claims. (Cl. 260—512)

This invention relates to improved detergent aids and methods of preparing same and it relates more particularly to the preparation of detergent aids by reacting together olefines, phenols, and a strong polybasic mineral acid.

By the term "detergent aids" it is intended to include wetting, dispersing and emulsifying agents and detergents. Frequently, a single material or chemical compound functions satisfactorily in several of these capacities and generally if the molecular weight of the compound in question can be varied to any substantial extent, it is usually possible to make products having predominantly any one of these characteristics, depending upon the molecular weight of the compound. It is realized, of course, that not all wetting agents will serve as detergents or emulsifying agents. However, although the invention is intended to be applicable to all of these four classes of detergent aids by making modifications in the process of preparation, it will be described more particularly as applied to the preparation of wetting agents, inasmuch as the determination of the wetting out number of a product is a very simple procedure and is a quick means of estimating the quality of the product.

Many different types of wetting agents are already known but, as is the case in many other industries, the highest quality products are very expensive and the cheaper products are relatively inefficient. Besides, few, if any, of the products now marketed for use as wetting agents have the desired stability with respect to hard water, generally forming an appreciable precipitation of insoluble calcium or magnesium compounds which result in a very undesirable scum which either becomes deposited on clothing or other material being laundered or on the sides of the container in which the cleaning is taking place.

Without going into detail too much as to the properties of the individual products, a number of those now on the market are listed in Table 1 with their approximate chemical structure (where known) and their wetting number.

Table 1

	Chemical nature	Wetting No. (seconds)*
	Plain water	About 1 day
A	Water-soluble petroleum sodium sulphonates	700
B	Stearyl sodium sulphate	175
C	Turkey red oil	140
D	Isopropyl napthalene sodium sulphonate	115
E	Oleyl ethyl amide sodium sulphonate	95
F	Oil-suluble petroleum sodium sulphonates	90
G	Lauryl sodium sulphate (*a*)	45
H	Sodium salt of alkylated aryl compound (*a*)	40
I	Sodium salt of alkylated aryl compound (*b*)	25
J	Lauryl sodium sulphate (*b*) containing 20% salt	25
K	Lauryl sodium sulphate (*b*) salt-free	19
L	Sodium salt of alkylated aryl compound (*c*)	7
M	Sodium stearate	300

* Wetting No. is measured by the disc method and represents the number of seconds it takes for a small circular disc (2 cm. diam.) of cotton cloth to become completely wetted when gently laid on the surface of an 0.2% solution of the product in distilled water.

The present invention provides for the preparation of wetting agents having valuable properties as measured by the wetting number, clarity of hard water solution, cost, etc., and by reason of the flexibility of the process, due to variations of the temperature, concentration of the reactants and the time of reaction, detergent aids may be obtained having various characteristics such as wetting power, detergency value, etc., in substantially any desired degree.

It has previously been proposed to prepare wetting agents and detergents by reacting cracked paraffin wax, or cracked petrolatum or other cracked hydrocarbon distillates, with phenols and sulphuric acid, neutralizing the product and separating soaps therefrom. By that process, wetting agents having a wetting number of about 25 to 100 have been prepared.

The present invention constitutes an improvement over that process in that wetting agents having an even lower wetting number, e. g. from about 5 to 50, are produced. A preferred source of olefines constitutes the essence of the invention over the above mentioned process. It has been found that instead of using cracked distillates as the source of olefines, better results may

be obtained by using polymers of low molecular weight olefines.

These polymers may be produced in various ways. For instance, low molecular weight gaseous olefines, e. g. ethylene, propylene, butylene, isobutylene, and even amylenes or mixtures thereof, such as those present in refinery gases resulting from the cracking of high molecular weight hydrocarbons, may be polymerized merely by heating under pressure, e. g. a temperature above 900° F. and a pressure of 800 lbs. or more, or in the presence of contact masses, e. g. clay, charcoal, bauxite, silica gel, etc., or activated contact masses, e. g. charcoal impregnated with phosphoric acid, at slightly lower temperatures, e. g. 600 to 900° F., at slightly elevated pressures, e. g. 50 to 500 lbs. Polymerization may be accomplished at even lower temperatures, e. g. 100 to 300° F. or so, by contacting the polymerizable olefines with a liquid catalytic agent such as sulphuric acid, phosphoric acid, or with sulphates or phosphates of various metals, e. g. zinc, silver, cadmium, aluminum, etc. The temperature and the concentration of the catalyst are regulated so as to induce polymerization to obtain a maximum yield of liquid products boiling between the approximate range of 100 to 400° F. but with a minimum production of high-boiling tarry materials. Polymerization may also be carried out by means of catalysts of the active halide type, e. g. $AlCl_3$, BF_3, zinc chloride, titanium fluoride, and the like, and, in such cases, the temperature may be even lower than indicated in the previous method. For example, it may be as low or even lower than room temperature.

This polymerization step may satisfactorily be carried out by using as a raw material an olefine-containing fraction known in the petroleum industry as C_4 cut which contains generally 30 to 50% of olefines including, among others, 10 to 15% of isobutylene. A sample of C_4 cut had approximately the following composition:

	Per cent
Isobutane	15
Beta-butylene	18
Isobutylene	14
Alpha-butylene	7
n-Butane	46

Other sources of olefines are the fractions called "stabilizer overhead" and "stabilizer bottoms" which have approximately the following composition:

	Percent in stabilizer	
	Overhead	Bottoms
Propane	42.3	0.57
Propylenes	22.7	0.34
Butanes	1.2	16.58
Butylenes	0.8	8.80
Pentanes		19.13
Pentylenes		12.03
Hexanes		16.83
Hexylenes		10.12
Residue		15.60

It is desired to use olefines of an average molecular weight of not more than 70, and preferably between 40 and 60. It is even more preferable to use isobutylene itself for the polymerization so as to obtain a relatively pure di-isobutylene or tri-isobutylene. This is preferably accomplished by extracting isobutylene from C_4 cut by concurrently dispersing the C_4 cut through 60% sulphuric acid in an absorption vessel by means of porous thimbles by using superatmospheric pressure of about 40 lbs. and a temperature of about 90° F., a C_4 cut feed rate of about 2,000 gallons per hour and an acid feed rate of 300 gallons per hour. The acid extract is then separated and polymerized at about 212° F. to 250° F. with a 10–15 sec. time of contact. The polymer is separated from the acid and the latter is recycled to the absorber and the polymer is washed with caustic soda. This polymer, which may amount to about 9% yield on the C_4 cut charged, contains about 70% dimer and 25% trimer, with about 5% of either gaseous or heavier hydrocarbons.

Variations may be made in the extraction process such as by absorbing the C_4 cut in 65% sulphuric acid at 32° F. and polymerizing the extract at 180° F. The dimers, trimers, and higher polymers may be separated by fractional distillation.

The phenol to be used according to the present invention may be phenol itself or derivatives, e. g. ortho-cresol or thio phenols, or, under some circumstances, a crude commercial product containing substantial quantities of phenol, for example, the crude phenol fraction obtained in the by-product distillation of coal. Also, polyhydroxy derivatives of phenols may be used, e. g. one or more of the dihydroxy benzenes or trihydroxy benzenes, or one may use mono- or poly-hydroxy derivatives of poly-nuclear aromatic hydrocarbons, e. g. alpha- or beta-naphthol, or one may use aryl-substituted phenols.

The sulphating agent is preferably either strong sulphuric acid (of 90 to 95% concentration) or fuming sulphuric acid, or liquid sulphur tri-oxide, e. g. 20% oleum. Although sulphuric acid is preferred, it is possible to use other strong polybasic mineral acids, such as chlor-sulphonic acid or phosphoric acid, under some circumstances.

The reaction is carried out at a temperature between the approximate limits of 0° and 160° F., preferably between the approximate limits of 120° and 160° F., and generally the temperature to be used varies indirectly with the concentration of the acid, i. e. the stronger the acid the lower the temperature, and likewise the temperature may vary to some extent, depending upon the type, molecular weight, etc. of the olefine polymer being treated, as well as the exact characteristics desired to be produced in the finished product.

Under some circumstances, it may be desirable to carry out the reaction in the presence of an inert diluent or solvent such as pentane, hexane or heptane or commercial petroleum ether.

In carrying out the present invention, the olefine polymers is first mixed with the phenol and then the sulphuric acid is added, cooling, if necessary, to keep the temperature from exceeding the predetermined maximum, e. g. from 50° to 70° C.

However, instead of reacting the olefine polymers, phenol and sulphuric acid simultaneously, the phenol may first be alklylated with the olefine polymer and the resulting product may be sulphated.

By way of illustration only, and not desiring to be limited thereby, the following detailed specific example is given:

A 3-liter, 3-way flask was fitted to a mechanical stirrer, dropping funnel and thermometer. The flask was first charged with tri-isobutylene and then to it was added phenol, and to this well stirred mixture was added dropwise 96% H_2SO_4.

The quantities of reactants were as follows:

	Grams
Tri-isobutylene, B. P. 170–175° C., Br. No. 0.73	663
Phenol	282
96% H_2SO_4	306

The maximum reaction temperature was kept at 140° F. during the addition of the acid. The total time required to add all of the acid was 1 hour and 10 minutes. After adding all of the acid the reaction mixture was well stirred for 35 minutes. Following this a 30 minute contact was allowed without stirring. The reaction mixture was kept between 120° and 130° F. during the contact after all of the acid was added. The reaction product was next neutralized while cooling, with an NaOH solution which was made up as follows:

NaOH	grams 260
H_2O	cubic centimeters 400

To this solution was then added 500 ccs. of 91% isopropyl alcohol and then this solution was refluxed for 1 hour. The solution was then cooled, transferred into a separatory funnel and the water layer which separated was drawn off and discarded. The alcoholic salt solution (I) was then treated with CO_2 to remove excess of NaOH. The salt solution was then filtered and the filtrate (II) was next extracted with equal portions of 54° naphtha and water. The naphtha extraction was followed by a benzol extraction. Extraction with benzol was continued until no further benzol soluble matter was obtained. In case the naphtha or benzol layers do not separate, this can be remedied by adding water. The naphtha and benzol extracted salt solution (III) was next dried on a drum drier. The dried product (IV) amounted to 1200 gms. (IV) was then taken up in 98% isopropyl alcohol and filtered. Filtered solution=(V). (V) was then re-dried.

An 0.2% solution of the product (V) gave a clear solution and a wetting No. of 3 secs. Upon adding calcium, 300 parts per million, in the form of $CaCl_2$ the solution became turbid with no precipitation taking place after the solution stood over night at room temperature. The wetting number of the solution containing calcium was 5 secs. An 0.2% solution of (V) in 0.3% H_2SO_4 solution gave a wetting No. of 6 secs.

Although substantially pure polymers such as tri-isobutylene are preferred, it is also possible to use more or less mixed polymers such as those obtained by commercial polymerization of normally gaseous olefines into liquid polymers of the gasoline boiling range, such as by heat and pressure alone or contacting with bauxite or other catalyst at elevated temperature and pressure, or by contacting with sulphuric acid or other liquid phase polymerization catalyst. The polymers to be used should ordinarily have a molecular weight range between the approximate limits of 56 to 224. These polymers should be of a substantially linear type in nature, although they may have short alkyl side chains but should not be cyclic.

By way of further illustration of the invention, a number of experimental results are set forth in Table 2 showing a comparison of the results of this process when applied to the olefine polymers in comparison with several cracked distillates.

Table 2

Test No.	Olefines	Gms./100 gms. olefine		Percent yield based on phenol	Wetting No. (disc method 0.2% conc.) neutral solution				Appearance of 0.2% solution	
		H_2SO_4 (95%)	Phenol		Mixed salts	Oil-soluble	Oil-insoluble	Hard water 300 p. p. m.	Neutral	300 p. p. m. hardness
1	A			150	95				Clear	
2	B			191	76				do	
3	C	52	*26	180	44					
4	C	38	17	105	28	27	49		Turbid	
5	D	85	37	435	11	10	102		do	Turbid.
6	E	73	35	160	7	6	68		Clear	Do.
7	F			330	17				do	Do.
8	F				7			14	do	Do.
9	G	175	84	75	8	6	63			
10	G				6			11	Clear	Do.
11	G			100	5				Almost clear.	Do.
12	F	116.5	**55.8	332	19			15		

*Cresylic acids.
**Materials mixed at 50° C. and held at 60–70° C. for 1½ hours.

Description of olefines

A—Cracked petrolatum (200–300° F. fraction).

B—Cracked wax (90–350° F. fraction).

C—Debutanizer bottoms (284–397° F.).

D—Polymer (average mol. wt. about 105) prepared by contacting at 450° F. and 100 lbs. pressure, refinery cracked gases with a catalyst consisting of charcoal impregnated with phosphoric acid.

E—Polymer (average mol. wt. about 102) prepared by subjecting refinery cracked gases to a temperature of about 980–1030° F. and 2,000 lbs. pressure, in 4–6% Cr and 0.5% Mo tubes for 100 seconds.

F—Tri-isobutylene separated by fractionation from a mixed polymer product made by treating isobutylene with 65% sulphuric acid at 248° F. with 15 secs. time of contact.

G—Di-isobutylene separated by fractionation from a mixed polymer product made by treating isobutylene with 65% sulphuric acid at 248° F. with 15 secs. time of contact.

From the above table it is apparent that the wetting agents prepared from the olefine polymers are distinctly superior, (i. e. have a lower wetting number), than wetting agents made from other types of olefines such as cracked petrolatum, cracked wax and debutanizer bottoms. It is also noted that if the mixed salts, resulting from the treatment with sulphuric acid and subsequent neutralization, are separated by solvent extraction into oil-soluble and oil-insoluble fractions, the wetting number may be still further slightly improved in most cases. Generally, the oil-soluble fraction has the lowest wetting number.

It is also noted that wetting agents may be prepared according to the present invention which, in concentrations of 0.2%, give clear solu-

tions in water and only turbid solutions in water containing 300 p. p. m. hardness (in the form of calcium chloride), whereas numerous prior art wetting agents and detergents actually cause voluminous precipitates or deposits which are difficult to remove either from clothing being laundered or from the washing vessels.

Although the exact limitations of the various factors involved in the preparation of detergent aids according to the present invention are not known with absolute certainty, the following ranges and preferred conditions are believed to be sufficiently definite to guide those skilled in the art in carrying out this invention. The strength of the sulphuric acid to be used should be between 85% H_2SO_4 and 20% oleum (fuming acid), and the stronger the acid the lower should be the temperature at which it is used, although generally, satisfactory results are obtained by using the ordinary concentrated sulphuric acid (95% H_2SO_4) at a temperature between 20° C. and 70° C. With stronger acid, the temperature may be lowered to 0° C. or even −10 or −20° C., using inert diluent, such as a straight run or hydrogenated naphtha, if necessary. In the above described process, the conditions of the reactions should be preferably maintained so as to produce primarily oil-soluble products and only a small proportion, if any, of oil-insoluble products (the oil-insoluble products are generally produced at higher temperature with relatively concentrated acid).

The wetting agents prepared according to this invention may be used for a large variety of purposes, including among others: scouring agents, in conjunction with alkali, soap or both, dispersion of pigments and paints in water, in dye baths, penetration of cosmetics, wetting of glue, with Portland cement to get better mixing, finishing pastes, removing grease from steel, in lacquer emulsions, in paper manufacture to give the paper better absorption qualities, in combination with derris and pyrethrum for use in sprays, to get best coverage and toxic action and may be used with lead arsenate in sprays.

Proportions of the three primary reactants, i. e. the olefine polymers, the phenolic bodies and the sulphuric acid, may be varied considerably, but ordinarily the proportion of olefines to phenol should be between the limits of 4 to 1 and 1 to 1, and the ratio of sulphuric acid to phenol should be between the approximate limits of 3 to 1 and 1 to 1 (by weight). The time of contact will, of course, vary inversely with the temperature and concentration of acid, but ordinarily will be between the approximate limits of 10 minutes and 1 or 2 hours. Extremely short times of contact, e. g. substantially less than 1 minute, may be used with relatively concentrated sulphuric acid and at relatively elevated temperature.

Although sulphuric acid has been described above as the treating agent for effecting the combination of the olefine polymers with the phenols and simultaneously attaching an inorganic radical which imparts good wetting properties to the compound, other strong poly-basic mineral acids, e. g. phosphoric acid, may be used instead of sulphuric acid.

This invention is not to be limited by any of the specific examples given, nor any theories advanced as to the mechanism of the operation of the invention, but only by the appended claims in which it is intended to claim all novelty inherent in the invention as broadly as the prior art permits.

I claim:

1. The process of preparing detergent aids which comprises reacting together acyclic polymers having a molecular weight above 100 and produced from gaseous olefins with phenols and an amount of a strong poly-basic mineral acid sufficient to form acid derivatives of the resulting alkyl phenols, completely neutralizing the resultant product and separating therefrom the resulting salts of the sulphuric acid derivatives.

2. The process of preparing detergent aids which comprises polymerizing normally gaseous olefines into low molecular weight acyclic liquid products having a molecular weight between about 100 and about 224 and reacting said polymerization products with a phenol in the presence of an amount of sulphuric acid sufficient to form sulphuric acid derivatives of the resulting alkyl phenols, then completely neutralizing the resultant product and separating therefrom the resulting salts of the sulphuric acid derivatives.

3. The process of preparing detergent aids which comprises polymerizing normally gaseous olefines into low molecular weight acyclic liquid products having a molecular weight between about 100 and about 224, reacting said polymerization products with a phenol and an amount of sulphuric acid sufficient to form sulphuric acid derivatives of the resulting alkyl phenols at a temperature not substantially in excess of 80° C., then completely neutralizing the resultant product with an alkali metal base and separating therefrom salts having a wetting number below about 25 seconds.

4. Process according to claim 3 in which the olefine polymer is used in a proportion between the approximate limits of 1 part and 4 parts to every 1 part of the phenol and in which the amount of sulphuric acid used is between 1 and 4 parts by weight for every 1 part of the phenol.

5. The process according to claim 3 in which the polymer used is an iso-olefine polymer having a molecular weight between the approximate limits of 100 and 200.

6. Process according to claim 3 in which the polymer used is di-isobutylene.

7. The process of preparing detergent aids particularly useful as wetting agents which comprises reacting together about 1 to 4 parts of di-isobutylene and 1 to 4 parts of sulphuric acid with 1 part of phenol at a temperature between the approximate limits of 0° and 70° C. for a reaction time between the approximate limits of 10 minutes and 2 hours, whereby sulphuric acid derivatives of alkyl phenols are formed, then cooling the reaction product, completely neutralizing it with an alkali metal base and separating from the neutralized product a mixture of salts having a wetting number below about 25 seconds.

8. The product made by the process defined in claim 1.

9. The product of the process defined in claim 7.

10. A detergent aid particularly useful as a wetting agent comprising essentially a mono-alkali metal salt of the sulphuric acid derivative of a reaction product of acyclic hydrocarbon polymers having a molecular weight between about 100 and about 224 and a phenol.

11. Alkali metal salt of sulphuric acid derivative of an alkyl phenol, said alkyl group corresponding to an acyclic hydrocarbon polymer

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having a molecular weight between about 100 and about 224, of an olefin having a molecular weight below about 70.

12. Alkali metal salt of sulphuric acid derivative of an alkyl phenol, having pronounced wetting and detergent properties, soluble in isopropyl alcohol, soluble in oil, forming a clear solution in a concentration of 0.2% in water, the said alkyl group corresponding to an acyclic hydrocarbon polymer, having a molecular weight not higher than about 224, of isobutylene.

13. The product according to claim 10 having a wetting number below about 25.

14. Product according to claim 10 having been derived from a branched chain polymer.

15. Process according to claim 1 in which the said gaseous olefins comprise a fraction of cracked petroleum gases containing a major proportion of hydrocarbons of four carbon atoms per molecule.

16. The process of preparing detergent aids which comprises reacting together acyclic polymers having a molecular weight above 100 and produced from gaseous olefins with phenols and an amount of a strong polybasic mineral acid sufficient to form acid derivatives of the resulting alkyl phenols.

17. A detergent aid particularly useful as a wetting agent, comprising essentially sulphuric acid derivative of a reaction product of acyclic hydrocarbon polymers, having a molecular weight between about 100 and about 224 and a phenol.

18. Alkali metal salt of sulphuric acid derivative of an alkyl phenol, having pronounced wetting and detergent properties, soluble in isopropyl alcohol, soluble in oil, forming a clear solution in a concentration of 0.2 percent in water, the said alkyl group corresponding to an acyclic hydrocarbon polymer, having a molecular weight between about 100 and about 224, produced from an olefin-containing fraction of cracked petroleum gases containing a major proportion of hydrocarbons of four carbon atoms per molecule.

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