

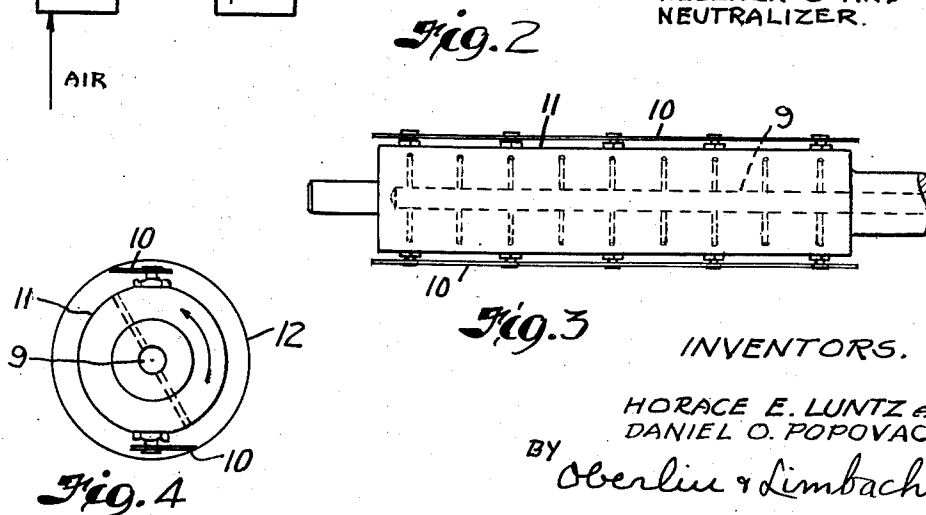
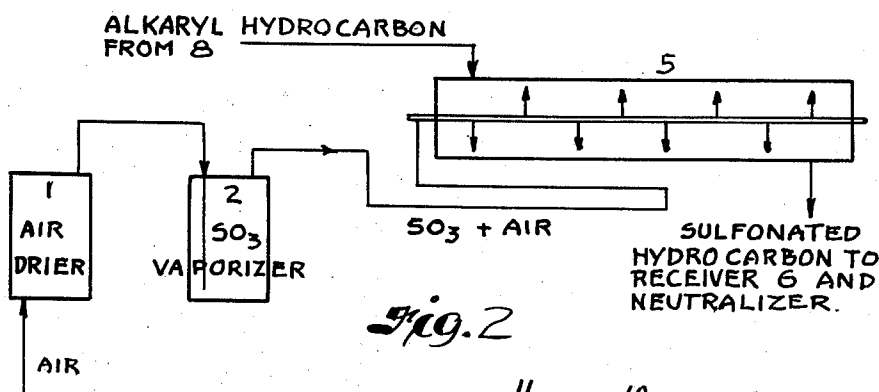
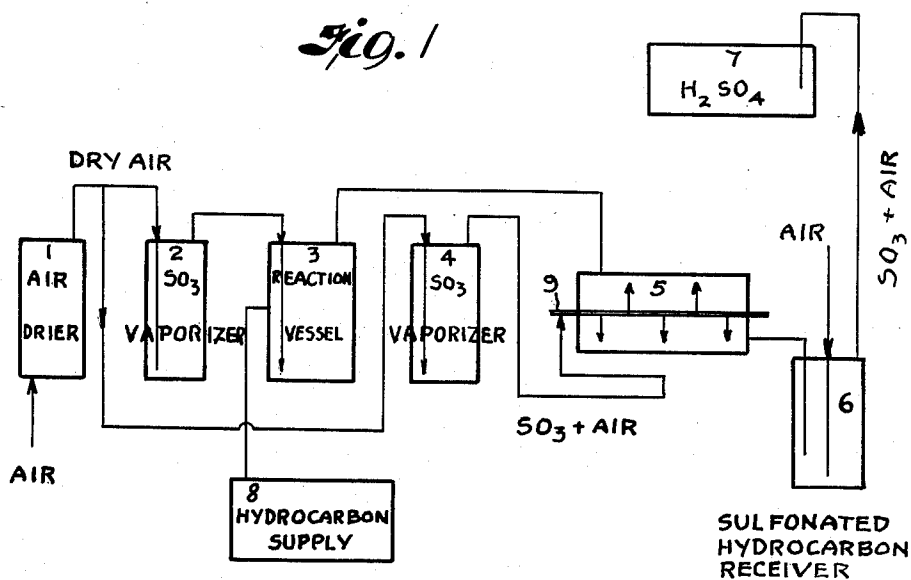
Oct. 23, 1956

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2,768,199

METHOD OF SULFONATING ALKYL AROMATIC HYDROCARBONS

Filed Dec. 8, 1953



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2,768,199

METHOD OF SULFONATING ALKYL AROMATIC HYDROCARBONS**Horace E. Luntz and Daniel O. Popovac,
Ponca City, Okla.****Application December 8, 1953, Serial No. 396,822****10 Claims. (Cl. 260—505)**

This invention relates to a method and means by which sulfonation of sulfonatable materials particularly alkyl aromatic hydrocarbons may be carried out continuously and economically.

Heretofore the sulfonation of alkyl aromatic hydrocarbons has been most generally carried out in batch operations. In these processes it has been customary to sulfonate the hydrocarbon by treating the hydrocarbon with a large excess of 20 percent oleum to drive the reaction to completion, after which the mixture is diluted with water and then stratified to separate the sulfonic acid from the excess diluted sulfuric acid after which the sulfonic acid is converted to the sulfonate by neutralization. In these processes the highest active ingredient content obtainable is in the range of 85 to 87 percent.

Efforts have been made to develop continuous sulfonation processes, such as one in which the acid is flowed counter-currently to an excess of the hydrocarbon in liquid phase, and another in which an excess of preheated acid is flowed counter-currently to a stream of the hydrocarbon vapors. Up until the present time, however, a continuous process for the sulfonation of such hydrocarbons has not been considered commercially practical. Since the residual sulfuric acid must be removed from the product when oleum is used as the sulfonating agent, attempts have been made to employ an agent which does not form sulfuric acid in the process. Although such attempts have eliminated the presence of sulfuric acid in the product, the results have not been successful for a number of reasons. For example, when sulfur trioxide was used as the sulfonating agent, the resulting product exhibited a pH drift to the acid side after apparent neutralization. Furthermore the sulfonate prepared by the prior art processes either possesses an off odor or will develop such an odor on standing.

It is therefore a principal object of our invention to provide a process for the sulfonation of alkyl aromatic hydrocarbons which obviates the disadvantages of the prior art processes.

It is another object of this invention to provide a practical sulfonation process and apparatus in which the reactants may be continuously fed and products may be continuously withdrawn at controlled rates correlated to the rate of reaction, with reaction of the sulfonating agent progressing to completion in the direction of flow of the reactants.

Another object of our invention is to provide a method and means for obtaining improved control of reaction conditions in a continuous sulfonation of hydrocarbons through efficient mixing and heat transfer with consequent avoidance of localized hot spots and localized high concentrations of sulfonating agent.

Further objects and advantages will become apparent from the following description.

Broadly stated, the invention provides an improved process for the production of an alkaryl sulfonate of good odor, color, purity, and other desirable properties economically by the sulfonation of an alkaryl hydrocarbon

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which comprises passing such a hydrocarbon through a reaction vessel together with SO_3 as the sulfonating agent wherein the reaction vessel is provided with means by which the SO_3 may be introduced into the hydrocarbon at a multiplicity of points and with means for dissipating the heat of reaction. The resulting sulfonic acid is withdrawn from the reaction vessel and converted to the sulfonate by neutralizing it with an alkali hydroxide or carbonate. In view of the fact that the particular sulfonatable material or alkaryl hydrocarbon may be selected from a large list, it is not possible to state any one best operating temperature. Furthermore, the exact means for dissipating the heat of the reaction introduces another variable. Generally, the temperatures employed may vary from about 50 to about 200° F.; preferably within the range of about 120 to 150° F. At temperatures much below 50° F. the product is quite viscous and if the temperature exceeds 200° F. the resultant product is dark. Depending upon the specific organic compound used and the temperature, the reaction time may vary from a fraction of a second to 2 minutes or longer. As a general rule, however, a contact time of 2 minutes or less is preferred. Following the procedure outlined above, we are able to obtain consistently a product consisting of 95 percent active ingredients. Obviously the process may be carried out either as a batch process or as a continuous process. For economical reasons the latter procedure is preferred.

In practicing our invention, we prefer sulfur trioxide because of the following advantages:

1. More rapid sulfonation.
2. Lower net consumption of sulfonating agent.
3. Increased throughput.
4. Higher active ingredient product.
5. Elimination of spent acid disposal problems.
6. Lower capital investment.
7. Less corrosion.
8. Absence of a dealkylation catalyst.

It should be understood, however, that the invention is not to be limited to the use of sulfur trioxide only as any fluid stream which is capable of supplying sulfur trioxide may be used. An example of the latter is concentrated sulfuric acid containing sulfur trioxide dissolved or absorbed therein which is also known as fuming sulfuric acid or oleum. The proportions of the reactants, namely, the sulfonatable material and the sulfur trioxide, used in our process may be varied over a rather wide range. Theoretically, one mole of the sulfonatable material reacts with one mole of sulfur trioxide to produce the sulfonic acid. In practice, however, we prefer to employ an excess of about 10 percent sulfur trioxide over the sulfonatable material. Although generally we prefer to carry out the sulfonation process using the two reactants, sulfur trioxide and the sulfonatable material only, occasionally more satisfactory results, for a particular purpose, are obtained by a modification of that procedure. As for example, a lighter colored product can be produced by diluting the sulfonatable material with sulfuric acid or the sulfur acid "heel" from absorbing vessel prior to the treatment of the sulfonatable material with sulfur trioxide.

A stabilized liquid sulfur trioxide having more than 99 percent available SO_3 content is available commercially under the trade name "Sulfan" and is particularly desirable for use in our invention. For best results we prefer to dilute the sulfur trioxide with a gas which does not react with the other components such as dry air, nitrogen, carbon dioxide, sulfur dioxide, or a lower alkane. When dry air is used as the diluent the preferred weight ratio of air to sulfur trioxide may vary from about 9:1 to 1:1. It is to be understood, however, that

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higher or lower ratios may be used as, for example, 1 percent sulfur trioxide in the mixture will effect sulfonation and at the other extreme concentration of up to 100 percent sulfur trioxide in the mixture may be used. When low concentrations are used the reaction becomes slow and at high concentrations adequate heat dissipation becomes difficult. Apparently the preferred concentration of sulfur trioxide in the mixture is independent of the particular diluent used.

Salient features of the present invention comprise effective mixing, circulation of the reactants passed confluent through a liquid phase reaction zone, and efficient removal of the heat of reaction therefrom. The sulfonating mixture and the hydrocarbon feeds are preferably measured and continuously introduced as a gas and a liquid respectively into the reaction vessel.

The heats of sulfonation of an aromatic compound using oleum and sulfur trioxide as the sulfonating agents are about 200 and about 306 B. t. u., respectively, per pound of the aromatic compound sulfonated. In addition to the great heat of reaction when sulfur trioxide is used the reacting mixture is very viscous, consequently special means must be provided for heat removal. The continuous reaction vessel or sulfonator suitably designed to contain the liquid reactants and products meeting this requirement is of an elongated form and in addition it allows adequate space of travel for the reaction mixture to obtain the desired amount of reaction therein before the mixture reaches the end of the reaction zone. Such a reaction vessel as just described and which is well suited to the sulfonation process according to the present invention after certain modifications as will be hereinafter pointed out is commercially available and known to the trade as a Votator, and is generally described in United States Patents Nos. 2,063,065 and 2,063,066, issued December 8, 1936. For practical reasons the capacity of the reaction vessel is limited and accordingly the rates of flow of the reactants through the vessel must be adjusted to provide the necessary reaction time.

To obtain uniformity of reaction, the liquid reaction product is separated from the non-reacted sulfonating agent thus the desired end product may be continuously withdrawn containing substantially none of the unreacted sulfonating agent.

A more detailed description of the process and apparatus will be given with reference to the accompanying drawing in which Figure 1 is a drawing showing diagrammatically a view of the reaction vessel and a full plan of auxiliary equipment as used in one form of the invention. Figure 2 shows diagrammatically a view of another form of the invention. A cross-sectional view of the reaction vessel or sulfonator is shown in Figure 3.

Referring to Figure 1, 1 represents an air drier consisting of a tower packed with silica gel, 2 serves as a vaporizer for the sulfur trioxide, 3 is a reaction vessel or sulfonator where the hydrocarbon is partially converted to sulfonic acid, 4 is a second vaporizer for the sulfur trioxide, 5 is a second reaction vessel or sulfonator, 6 is a receiving drum for the sulfonic acid, and 7 is a vessel partly filled with sulfuric acid serving as an absorber of sulfur trioxide. In operation, air is passed through the drier 1 where any moisture contained in the air is removed and from the drier the air passes through the sulfur trioxide vaporizer 2. The sulfur trioxide laden air then enters the reaction vessel 3 where the hydrocarbon added thereto from drum 8 is partially sulfonated to an extent of not to exceed 80 percent completion. If an attempt is made to exceed this figure the material becomes very viscous, easily overheated and overheating produces a dark colored product. From vessel 3 the partially sulfonated hydrocarbon is mixed with an additional quantity of sulfur trioxide laden air. The mixing of these two materials may be carried out in any form of a reactor in which thorough contact of the two reactants may be effected and in which simultaneously the heat of reaction

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liberated may be removed quickly so as to maintain the desired temperature. We have found that these requirements may be fulfilled by contacting the hydrocarbon feed with the sulfur trioxide laden air in a modified Votator. As will be apparent from Figure 3, vessel 5 is a Votator especially designed for use in our invention comprising a rotatable shaft fitted with scrapers within a jacketed elongated cylinder. The scrapers 10 remove that portion of the reaction mixture present on the inner or heat exchange surface 12 of the Votator thus making way for an additional quantity of the mixture to come in contact with the heat exchange or refrigerated surface for cooling. The inlets for the sulfonating agent from passageway 9 preferably are so arranged on the Votator shaft 11 that the sulfonating agent is added to the reaction mixture at a multiplicity of points and just ahead of the scrapers. The addition of the sulfur trioxide at a multiplicity of points is important as such a procedure minimizes the presence of excess sulfur trioxide at any one point in the reaction vessel, thus eliminating localized hot spots. Overheating, as is well known, causes the development of color and odor in the product. As a further aid to minimize overheating, a portion of the reaction mixture may be withdrawn and recycled through the Votator. In brief, the reaction may be described as follows: The sulfonatable material is introduced into one end of the Votator and in passing therethrough the sulfonatable material forms a film on the refrigerated surface of the Votator. When first contacted with sulfur trioxide, this film is only partially sulfonated and is removed in that condition by the progressively moving scrapers. The partially sulfonated material is then re-applied to the refrigerated surface further along in the Votator as a film and contacted with an additional quantity of sulfur trioxide. The steps of removing the film, reapplying to the surface and contacting with additional sulfur trioxide are repeated until the completely sulfonated material is removed from the other end of the Votator. The total residence time of the sulfonatable material in the Votator may vary from a fraction of a second to 2 minutes when the temperatures employed vary from about 50 to about 200° F. We have found the Votator when used as described in our process to be highly efficient as a heat exchanger and as a result the temperature of the reaction mixture only exceeds the temperature of the refrigerated surface by a few degrees. From Votator 5 the sulfonic acid containing a minor quantity of unreacted sulfur trioxide enters the receiving drum 6 where the unreacted sulfur trioxide is removed and recovered by blowing with air and passing the air-sulfur trioxide mixture through the absorbing vessel 7 where the sulfur trioxide is absorbed, thus producing the so-called sulfuric acid "heel" which can be used to dilute the aromatic compound prior to its sulfonation if that procedure becomes desirable. Under certain conditions it may be desirable to recycle this sulfur trioxide laden air adding it to the system just ahead of the sulfur trioxide vaporizer 2. As an alternative method, which is generally preferred, the hydrocarbon may be sulfonated in a one step process as is diagrammatically shown in Figure 2 wherein the partial sulfonation of the hydrocarbon in reaction vessel 3 is eliminated. In this latter procedure the hydrocarbon is added directly to the Votator where it is contacted with the sulfur trioxide.

In order to disclose the nature of the present invention still more clearly, the following illustrative example will be given in which parts where used are parts by weight.

Example 1

Dodecylbenzene sulfonic acid was prepared continuously in the modified Votator 5 having 0.7 sq. ft. of heat exchanger surface, two scraper blades, and 9 jets for sulfur trioxide before each scraper blade. The Votator shaft was operated at 400 R. P. M. Twenty-nine pounds per hour of dodecylbenzene was charged to the Votator

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and 12 pounds per hour of sulfur trioxide (122 percent theory) was vaporized in vaporizer 2 at 106° F. with a dry air stream of 0.7 cu. ft. per minute. The vapor from the vaporizer was diluted with 8.0 cu. ft. per minute of dry air and introduced into the Votator. (Calculates 1 part SO₃ to 4.7 parts air.) Contact time was approximately 1/4 second. Cooling water at a temperature of 60° F. was passed through the jacket of the Votator. Exit temperature was 171° F. There was obtained 38.6 pounds per hour of dodecylbenzene sulfonic acid which on neutralization with aqueous sodium hydroxide and subsequent drying analyzed: 3.15 percent sodium sulfate, 1.90 percent free oil (2.00 percent on actives), and 95.0 percent actives.

Example 2

Example 1 was repeated with the exception that 10 pounds per hour of sulfur trioxide (101.5 percent theory) was used instead of 12 pounds. The exit temperature was 167° F. The neutralized and dried product analyzed: 1.35 percent sodium sulfate, 1.93 percent free oil (2.00 percent on actives), and 96.6 percent actives.

Example 3

Example 1 was repeated with the exception that 33 pounds per hour of dodecylbenzene and 10 pounds per hour of sulfur trioxide (89 percent theory) was charged. The exit temperature was 154° F. The neutralized and dried product analyzed: 1.08 percent sodium sulfate, 6.64 percent free oil (7.20 percent on actives), and 92.3 percent actives.

Example 4

In a batch operation, 100 parts of dodecylbenzene was sulfonated by passing into the stirred mixture during one hour 26 parts of sulfur trioxide diluted with 10 parts of dry air per part of sulfur trioxide while maintaining the temperature at a maximum of 130° F. The reaction product then was charged continuously into a modified Votator as used in Example 1 at a rate of 33.3 pounds per hour. At the same time 3.50 pounds per hour of sulfur trioxide diluted with 10 parts of dry air per part of sulfur trioxide was introduced into the Votator. Exit temperature was maintained at 130° F. There was obtained 36.6 pounds per hour of dodecylbenzene sulfonic acid which, on neutralization, analyzed on a dry basis: 1.10 percent sodium sulfate, 1.75 percent free oil (1.81 percent on actives), and 96.6 percent actives.

Example 5

Example 1 was repeated with the exceptions that 10 pounds per hour of dodecylbenzene and 4 pounds per hour of sulfur trioxide diluted with 10 parts of air per part of sulfur trioxide. The exit temperature was 130° F. There was obtained 13.3 pounds per hour of product which, on neutralization, analyzed: 1.60 percent sodium sulfate, 1.70 percent free oil (1.77 percent of actives), and 96.0 percent actives.

Example 6

Two parts of 96 percent sulfuric acid was dissolved in 98 parts of dodecylbenzene. The resulting solution was charged into the modified Votator used in Example 1 at a rate of 20 pounds per hour along with 8.5 pounds per hour of sulfur trioxide diluted with 5.2 parts of dry air per part of sulfur trioxide. The exit temperature was maintained at 160° F. The product obtained was neutralized with 14.7 percent aqueous sodium hydroxide. The product analyzed on a dry basis: 1.90 percent sodium sulfate, 2.60 percent free oil (2.73 percent of actives), and 95.2 percent actives.

Example 7

In a batch operation, 100 parts of dodecylbenzene was sulfonated by passing into the stirred mixture during 1 hour and 50 minutes 36 parts sulfur trioxide diluted with 2.7 parts of dry air per part of sulfur

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trioxide while maintaining the temperature at a maximum of 130° F. There was obtained 133 parts of sulfonic acid which on neutralization by addition to aqueous sodium hydroxide and subsequent drying, gave sodium dodecylbenzene sulfonate analyzing: 1.99 percent sodium sulfate, 2.10 percent free oil, and 96.1 percent actives. The product of Example 7 was darker in color than the product obtained using the Votator.

Example 8

Example 1 was repeated with the exceptions that 10 pounds per hour of a fraction of dodecyl alkylated benzene having an average molecular weight of 370 and 2.2 pounds per hour of sulfur trioxide diluted with a total of 8.7 cu. ft. per minute of air. The exit temperature was maintained at 135° F. There was obtained 12.1 pounds per hour of product which on neutralization with aqueous sodium hydroxide and analyzed on a dry basis: 1.90 percent sodium sulfate, 10.90 percent free oil (12.45 percent on actives), and 87.3 percent actives.

Example 9

Example 1 was repeated with the exceptions that 10 pounds per hour of a nonyl naphthalene and 3.2 pounds per hour of sulfur trioxide diluted with a total of 8.7 cu. ft. per minute of air. The exit was maintained at 135° F. There was obtained 13.2 pounds per hour of product which on neutralization with aqueous sodium hydroxide and analyzed on a dry basis: 1.75 percent sodium sulfate, 3.9 percent free oil (4.14 percent on actives), and 94.5 percent actives.

All of the sulfonated products obtained using our modified Votator were light in color and did not exhibit a pH drift after apparent neutralization. In the examples by the phrase "exit temperature" is meant the temperature of the sulfonic acid mixture upon discharge from the Votator.

Obviously the apparatus should be constructed of materials which are not corrosive under sulfonating conditions. We have found stainless steel 316 suitable for piping and the reaction vessel. Nickel is also non-corrosive and may be profitably used for constructing the rotating shaft and heat exchange surface of the Votator. Since ordinary bearing metals are very corrosive under sulfonating conditions, the Votator should be provided with carbon bearings. A polytetrafluoroethylene resin obtainable under the trade name "teflon" is satisfactory as a gasket material.

While the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. As for example, in addition to dodecylbenzene, dodecyl alkylated benzene (polydodecylbenzene), and nonyl naphthalene used in the specific examples other alkaryl hydrocarbons of the benzene, naphthalene, and diphenyl series capable of combining with a sulfonating agent to form an organic sulfonate, aromatic hydrocarbons, and phenols may be used. Additional examples of sulfonatable materials include: dodecylbenzene intermediate, sulfonatable petroleum oils, and cyclic oils such as those obtained as extracts in the refining of petroleum oils with a selective solvent.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

We therefore particularly point out and distinctly claim as our invention:

1. A continuous sulfonation process which comprises: applying a film of an alkyl aryl hydrocarbon to a refrigerated surface, introducing a sulfonating agent into said film of alkyl aryl hydrocarbon in an amount that is

insufficient to effect complete sulfonation at a point closely in advance of a progressively moving scraper, re-applying to said surface the partially sulfonated alkyl aryl hydrocarbon scraped therefrom as a film, introducing an additional quantity of sulfonating agent into said film of partially sulfonated alkyl aryl hydrocarbon until sulfonation thereof is complete, and then collecting the completely sulfonated alkyl aryl hydrocarbon.

2. A continuous sulfonation process which comprises: applying a solution consisting of an alkyl aryl hydrocarbon and a sulfuric acid "heel" as a film to a refrigerated surface, introducing a gaseous mixture consisting of sulfur trioxide and an inert diluent into said film of alkyl aryl hydrocarbon and sulfuric acid "heel" in an amount that is insufficient to effect complete sulfonation at a point closely in advance of a progressively moving scraper, re-applying to said surface the partially sulfonated alkyl aryl hydrocarbon scraped therefrom as a film, introducing an additional quantity of said sulfur trioxide-inert diluent gaseous mixture into said film of partially sulfonated alkyl aryl hydrocarbon until sulfonation thereof is complete, and then collecting the completely sulfonated alkyl aryl hydrocarbon.

3. A continuous sulfonation process which comprises: applying a film of alkyl aryl hydrocarbon to a surface which is maintained within the range of about 50 to about 140° F., introducing a gaseous mixture consisting of sulfur trioxide in dry air into said film of alkyl aryl hydrocarbon in an amount that is insufficient to effect complete sulfonation at a point closely in advance of a progressively moving scraper, re-applying to said surface the partially sulfonated alkyl aryl hydrocarbon scraped therefrom as a film, introducing an additional quantity of sulfur trioxide-dry air mixture into said film of partially sulfonated alkyl aryl hydrocarbon until sulfonation thereof is complete, and then collecting the completely sulfonated alkyl aryl hydrocarbon.

4. A continuous sulfonation process which comprises: applying a film of dodecylbenzene to a refrigerated surface, introducing a gaseous mixture consisting of sulfur trioxide and an inert diluent into said film of dodecylbenzene in an amount that is insufficient to effect complete sulfonation at a point closely in advance of a progressively moving scraper, re-applying to said surface the partially sulfonated dodecylbenzene scraped therefrom as a film, introducing an additional quantity of said sulfur trioxide-inert diluent gaseous mixture into said film of partially sulfonated dodecylbenzene until sulfonation thereof is complete, and then collecting the completely sulfonated dodecylbenzene.

5. A continuous sulfonation process which comprises: applying a film of a dodecyl alkylated benzene fraction having an average molecular weight of 370 to a surface which is maintained within the range of about 50 to about 140° F., introducing a gaseous mixture consisting of sulfur trioxide and dry air into said film of dodecyl alkylated benzene fraction in an amount that is insufficient to effect complete sulfonation at a point closely in advance of a progressively moving scraper, re-applying to said surface the partially sulfonated dodecyl alkylated benzene fraction scraped therefrom as a film, introducing an additional quantity of said sulfur trioxide-dry air mixture into said film of partially sulfonated dodecylbenzene until sulfonation thereof is complete, and then collecting the completely sulfonated dodecyl alkylated benzene fraction.

6. A continuous sulfonation process which comprises: applying a film of dodecylbenzene to a surface which is maintained within the range of about 50 to about 140° F., introducing a gaseous mixture consisting of sulfur trioxide and dry air into said film of dodecylbenzene in an amount that is insufficient to effect complete sulfonation at a point closely in advance of a progressively

moving scraper, re-applying to said surface the partially sulfonated dodecylbenzene scraped therefrom as a film, introducing an additional quantity of said sulfur trioxide-dry air mixture into said film of partially sulfonated dodecylbenzene until sulfonation thereof is complete, and then collecting the completely sulfonated dodecylbenzene.

7. A continuous sulfonation process which comprises: applying a film of nonyl naphthalene to a surface which is maintained within the range of about 50 to about 140° F., introducing a gaseous mixture consisting of sulfur trioxide and dry air into said film of nonyl naphthalene in an amount that is insufficient to effect complete sulfonation at a point closely in advance of a progressively moving scraper, re-applying to said surface the partially sulfonated nonyl naphthalene scraped therefrom as a film, introducing an additional quantity of said sulfur trioxide-dry air mixture into said film of partially sulfonated nonyl naphthalene until sulfonation thereof is complete, and then collecting the completely sulfonated nonyl naphthalene.

8. A continuous sulfonation process which comprises: applying a film of dodecylbenzene to a surface which is maintained within the range of about 50 to about 140° F., introducing a gaseous mixture consisting of sulfur trioxide and an inert diluent into said film of dodecylbenzene in an amount that is insufficient to effect complete sulfonation at a point closely in advance of a progressively moving scraper, re-applying to said surface the partially sulfonated dodecylbenzene scraped therefrom as a film, introducing an additional quantity of said sulfur trioxide-inert diluent gaseous mixture into said film of partially sulfonated dodecylbenzene until sulfonation thereof is complete, and then collecting the completely sulfonated dodecylbenzene.

9. A continuous sulfonation process which comprises: applying a film of a dodecyl alkylated benzene fraction having an average molecular weight of 370 to a refrigerated surface, introducing a gaseous mixture consisting of sulfur trioxide and an inert diluent into said film of dodecyl alkylated benzene fraction in an amount that is insufficient to effect complete sulfonation at a point closely in advance of a progressively moving scraper, re-applying to said surface the partially sulfonated dodecyl alkylated benzene fraction scraped therefrom as a film, introducing an additional quantity of said sulfur trioxide-dry air mixture into said film of partially sulfonated dodecyl alkylated benzene fraction until sulfonation thereof is complete, and then collecting the completely sulfonated dodecyl alkylated benzene fraction.

10. A continuous sulfonation process which comprises: applying a film of nonyl naphthalene to a refrigerated surface, introducing a sulfonating agent into said film of nonyl naphthalene in an amount that is insufficient to effect complete sulfonation at a point closely in advance of a progressively moving scraper, re-applying to said surface the partially sulfonated nonyl naphthalene scraped therefrom as a film, introducing an additional quantity of sulfonating agent into said film of partially sulfonated nonyl naphthalene until sulfonation thereof is complete, and then collecting the completely sulfonated nonyl naphthalene.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 22,548	Brandt	Sept. 26, 1944
2,616,936	Mammen et al.	Nov. 4, 1952
2,630,302	Jones	Mar. 3, 1953

FOREIGN PATENTS

553,598	Great Britain	May 27, 1943
664,577	Great Britain	Jan. 9, 1952