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SULFONATION OF ALKYL BENZENES WITH SULFUR TRIOXIDE

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11 Claims. (Cl. 260—505)

My invention relates to the sulfonation of alkyl benzenes and is particularly concerned with improvements in the method of sulfonation in which the sulfonating agent comprises an air or other inert gas-sulfur trioxide gaseous mixture.

The sulfonation of alkyl benzenes by such gaseous sulfonation agents is known in the art. In accordance with such known procedures, a dry inert gas such as air or nitrogen is passed over a body of warmed liquid sulfur trioxide disposed in a suitable vaporizing vessel whereby to produce a gaseous mixture containing, for instance, from 10 to 20% sulfur trioxide, although the content of sulfur trioxide in the gaseous mixture can be varied greatly as, for instance, up to of the order of 80%. The gaseous sulfonation agent is then passed into a sulfonating flask or chamber containing the liquid alkyl benzene to be sulfonated, said gaseous sulfonation agent being passed into the alkyl benzene below the surface thereof while the latter is suitably being stirred or agitated. The reaction temperature is controlled by cooling of the reaction mixture so as to maintain the sulfonation temperature between about 40 and about 70, preferably about 50 to 60 degrees C., the sulfonation time being about one-half to about several hours or more, depending upon the size of the reaction batch, the exact alkyl benzene being sulfonated and the exact sulfonating temperature utilized. Thereafter, the reaction mass is neutralized with an alkali or amine such as sodium hydroxide, potassium hydroxide, calcium hydroxide, ammonium hydroxide, monoethanolamine, triethanolamine or the like. Inert solvent media such as dioxane and the like can be used but are not necessary. Such procedures and equipment arrangements are described, for instance, in Industrial and Engineering Chemistry, September, 1953, pp. 2065–2072. It has also been proposed, as shown in U. S. Patent No. 2,616,936, to effect the sulfonation utilizing an inert paraffinic hydrocarbon, such as liquid butane, to entrain the sulfur trioxide, and then introducing the liquid butane-sulfur trioxide mixture into the sulfonating zone.

The aforementioned types of procedures have a number of advantages over various other previously known sulfonation mehtods, of which those versed in the art are aware, including the advantage of producing sulfonated alkyl benzenes having a low content of inorganic salts, generally ranging from about 2% to about 4 or 5%, depending upon the exact conditions of the sulfonation reaction and the neutralizing agent employed.

For certain uses, one of which is for emulsifying agents for toxicant concentrates, such as insecticides, fungicides, herbicides, weed killers, disinfectants and the like, it is particularly important that the inorganic salt content of the neutralized alkyl benzene sulfonates be as low as possible. The above described procedure, while possessing certain advantages in this regard, is not fully satisfactory because the inorganic salt content is still too high for fully satisfactory results.

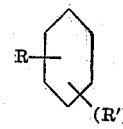
My present invention results in substantial and significant improvements in that it enables the production of

neutralized alkyl benzene sulfonates of extremely low contents of inorganic salts, for instance, of the order of 1% or less, without the necessity of resort to expensive and difficult purifying procedures. The method of my present invention also has a number of other important advantages over heretofore known procedures of the type described above among which may be mentioned the fact that higher yields of alkyl benzene sulfonates are obtained from a given quantity of sulfur trioxide.

I have discovered that if, after the sulfonation reaction is carried out in the manners described above, the reaction mixture is subjected to a certain after-treatment, the advantageous results of the invention are obtained. This after-treatment comprises raising the temperature of the sulfonated reacton mixture to a temperature in the range of about 105 to about 145 degrees C., preferably in the range of about 115 to about 130 or 135 degrees C., and particularly to about 125 degrees C., and especially while blowing a vigorous stream of a dry inert gas through the reaction mixture. Where color considerations are of no materiality, the higher temperatures can effectively be used but, in those cases where a product of light color is a desideratum, it is desirable to operate at the lower scale of said temperature range. The temperature of the sulfonated reaction mixture is maintained within said range of about 105 to about 145 degrees C. for from about 15 minutes to about 1½ hours, particularly while continuing to blow dry inert gas through said reaction mixture. The length of time of this terminal heating step, generally speaking, varies inversely with the temperature. Thus, for instance, at a temperature of about 105 degrees C., the time period will range from about 1 to 1½ hours; whereas, at a temperature of about 145 degrees C., the time period may be as low as about 15 minutes or even somewhat less. At the preferred temperature range of 115 to 130 or 135 degrees C., the time period is advantageously from about 40 to about 50 minutes.

After such terminal heating step, the reaction mixture is preferably cooled, and, particularly advantageously, while continuing to maintain a vigorous flow of dry inert gas through the reaction mixture. A variant desirable procedure comprises blowing dry inert gas through the mixture after the completion of the terminal heating step, no dry inert gas being used during the terminal heating step. The final reaction product is then neutralized in accordance with conventional techniques and procedures.

The alkyl benzenes which are utilized in the practice of the present invention contain at least 5 carbon atoms and, more advantageously, contain from 8 to 22 carbon atoms, particularly predominately 12 carbon atoms. Such alkyl benzenes are well known in the art and they and their preparation are disclosed in a large number of U. S. patents, illustrative of which are 1,992,160; 2,161,173; 2,210,962; 2,218,472; 2,223,364; 2,220,099; 2,232,117; 2,232,118; 2,233,408; 2,267,725; 2,283,199; 2,390,835; 2,437,356; and 2,597,834. Typical examples of such alkyl benzenes are amyl benzene, diamyl benzene, octyl benzene, nonyl benzene, decyl benzene, dodecyl benzene, tridecyl benzene, tetradecyl benzene, hexadecyl benzene, octadecyl benzene, nonyl toluene, decyl toluene, dodecyl toluene, dodecyl xylene, dodecyl ethyl benzene, dodecyl isopropyl benzene, and the like. Such alkyl benzenes can conveniently be represented by the formula.



wherein R is an alkyl radical, straight chain or branch

chain, containing at least 5 and preferably from 8 to 22 carbon atoms, R' is an alkyl radical containing from 1 to 3 carbon atoms, and *n* is from zero to 3.

Where the gaseous process is used, in connection with which my present invention is especially applicable, the dry inert gas is advantageously air although other inert gases such as nitrogen, argon, carbon dioxide, neon, helium and the like can be used but, for economic reasons, are unnecessary. Other gaseous materials such as butane or the like can be utilized, the term "inert" as used herein meaning that said gas is unreactive or substantially so in the environment in which it is used herein.

The following examples are illustrative of the practice of the invention. It will be understood, of course, that numerous other examples will readily occur to those versed in the art in the light of the guiding principles and teachings set forth herein. The examples, therefore, are not to be construed as in any manner restricting the proper scope of the invention.

Example 1

(*a*) 245 grams of dodecyl benzene (approximately 1 mol) are placed in a sulfonation flask equipped with a stirrer or agitator. Approximately 80 grams of liquid sulfur trioxide are placed in a vaporizer and dry air is passed over the surface thereof while gently warming said liquid sulfur trioxide. The air-sulfur trioxide gaseous mixture (containing about 20% sulfur trioxide) is passed into the dodecyl benzene below the surface thereof with continuous stirring of the reaction mixture. The reaction tempreature is controlled, by means of external cooling, to between 50 and 60 degrees C. The sulfonation is completed or substantially completed in about ¾ hour. The above procedure represents essentially standard practice.

(*b*) The sulfonation reaction product of part (*a*) is heated to about 125 degrees C. while a vigorous stream of dry air is continuously passed therethrough. The said reaction mixture is maintained at approximately said temperataure for about 45 minutes and then cooled or allowed to cool to approximately 90 degrees C., a vigorous flow or stream of dry air being continuously maintained through said reaction mixture during the heating and cooling steps. The said reaction mixture is then neutralized.

Example 2

(*a*) 260 grams of dodecyl toluene (approximately 1 mol) are placed in a sulfonation flask equipped with a stirrer or agitator. Approximately 80 grams of liquid sulfur trioxide are placed in a vaporizer and dry nitrogen gas is passed over the surface thereof while gently warming said liquid sulfur trioxide. The nitrogen-sulfur trioxide gaseous mixture (containing about 25% sulfur trioxide) is passed into the dodecyl toluene below the surface thereof with continuous stirring of the reaction mixture. The reaction temperature is controlled, by means of external cooling, to between 50 and 65 degrees C. The sulfonation is completed or substantially completed in about ¾ hour. The above procedure represents essentially standard practice.

(*b*) The sulfonation reaction product of part (*a*) is heated to about 120 degrees C. while a vigorous stream of dry nitrogen gas is continuously passed therethrough. The said reaction mixture is maintained at approximately said temperature for about 50 minutes and then cooled or allowed to cool to approximately 85 degrees C.

Example 3

(*a*) 330 grams of octadecyl benzene (approximately 1 mol) are placed in a sulfonation flask equipped with a stirrer or agitator. Approximately 80 grams of liquid sulfur trioxide are placed in a vaporizer and dry air is passed over the surface thereof while gently warming said liquid sulfur trioxide. The air-sulfur trioxide gaseous mixture (containing about 30% sulfur trioxide) is passed into the octadecyl benzene below the surface thereof with continuous stirring of the reaction mixture. The reaction temperature is controlled, by means of external cooling, to between 60 and 70 degrees C. The sulfonation is completed or substantially completed in about an hour. The above procedure represents essentially standard practice.

(*b*) The sulfonation reaction product of part (*a*) is heated to about 135 degrees C. and maintained at approximately said temperature for about 1 hour and then cooled or allowed to cool to approximately 95 degrees C., a vigorous flow or stream of dry air being continuously maintained through said reaction mixture during the cooling step.

Example 4

(*a*) 220 grams of diamyl benzene (approximately 1 mol) are placed in a sulfonation flask equipped with a stirrer or agitator. Approximately 80 grams of liquid sulfur trioxide are placed in a vaporizer and dry air is passed over the surface thereof while gently warming said liquid sulfur trioxide. The air-sulfur trioxide gaseous mixture (containing about 20% sulfur trioxide) is passed into the diamyl benzene below the surface thereof with continuous stirring of the reaction mixture. The reaction temperature is controlled, by means of external cooling, to between 40 and 50 degrees C. The sulfonation is completed or substantially completed in about ½ hour. The above procedure represents essentially standard practice.

(*b*) The sulfonation reaction product of part (*a*) is heated to about 105 degrees C. while a vigorous stream of dry air is continuously passed therethrough. The said reaction mixture is maintained at approximately said temperature for about 1 hour and then coolel or allowed to cool to approximately room temperature, a vigorous flow or stream of dry air being continuously maintained through said reaction mixture during the heating and cooling steps.

Example 5

(*a*) 275 grams of dodecyl xylene (approximately 1 mol) are placed in a sulfonation flask equipped with a stirrer or agitator. Approximately 80 grams of liquid sulfur trioxide are placed in a vaporizer and dry carbon dioxide gas is passed over the surface thereof while gently warming said liquid sulfur trioxide. The carbon dioxide-sulfur trioxide gaseous mixture (containing about 22% sulfur trioxide) is passed into the dodecyl xylene below the surface thereof with continuous stirring of the reaction mixture. The reaction temperature is controlled, by means of external cooling, to between 50 and 60 degrees C. The sulfonation is completed or substantially completed in about ¾ hour. The above procedure represents essentially standard practice.

(*b*) The sulfonation reaction product of part (*a*) is heated to about 125 degrees C. while a vigorous stream of dry carbon dioxide gas is continuously passed therethrough. The said reaction mixture is maintained at approximately said temperature for about 45 minutes and then cooled or allowed to cool to approximately room temperature, a vigorous flow or stream of dry carbon dioxide gas being continuously maintained through said reaction mixture during the heating and cooling steps.

Example 6

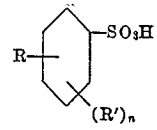
250 grams of sulfonated dodecyl toluene, produced generally as described in Example I of Patent No. 2,616,936, are heated to about 110 degrees C. while a vigorous stream of dry nitrogen gas is continuously passed therethrough. The said reaction mixture is maintained at approximately said temperature for about 50 minutes and then cooled or allowed to cool to approximately room temperature, a vigorous flow or stream of dry nitrogen gas being continuously maintained through said reaction mixture during the heating and cooling steps.

What I claim as new and desire to protect by Letters Patent of the United States is:

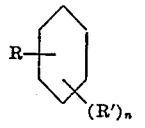
1. In that method of preparing alkyl benzene sulfonates

in which the alkyl radical contains at least 5 carbon atoms and wherein said alkyl benzene is sulfonated with sulphur trioxide carried in an inert medium, the improvement which comprises heating the reaction product, after substantial completion of the aforesaid sulfonation reaction, to between about 105 and about 145 degrees C.

2. In that method of preparing alkyl benzene sulfonates corresponding to the formula

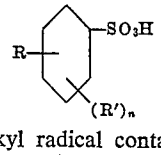


wherein R is an alkyl radical containing from 8 to 22 carbon atoms, R' is an alkyl radical containing from 1 to 3 carbon atoms, and *n* is from zero to 3, wherein an alkyl benzene, corresponding to the formula

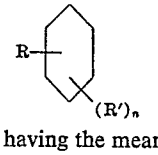


in which R, R' and *n* having the meanings set forth above, is sulfonated at a temperature in the range of about 40–70 degrees C. with an inert gas-sulfur trioxide gaseous mixture, the improvement which comprises heating the reaction product, after substantial completion of the aforesaid sulfonation reaction, to between about 105 and about 145 degrees C. while blowing a substantially dry inert gas therethrough.

3. In that method of preparing alkyl benzene sulfonates corresponding to the formula



wherein R is an alkyl radical containing from 8 to 22 carbon atoms, R' is an alkyl radical containing from 1 to 3 carbon atoms, and *n* is from zero to 3, wherein an alkyl benzene, corresponding to the formula



in which R, R' and *n* having the meanings set forth above, is sulfonated at a temperature in the range of about 50–60 degrees C. with an inert gas-sulfur trioxide gaseous mixture containing from about 10 to 20% sulfur trioxide and wherein the molal ratio of said alkyl benzene to the sulfur trioxide utilized in the sulfonation reaction is approximately unity, the improvement which comprises heating the reaction product, after substantial completion of the aforesaid sulfonation reaction, to between about 115 and about 130 degrees C. while blowing a substantially dry inert gas therethrough for of the order of about ½ hour to about 1 hour, and then cooling the reaction mixture while continuing to blow substantially dry inert gas therethrough.

4. In that method of preparing alkyl benzene sulfonates wherein the alkyl radical contains from 8 to 22 carbon atoms and wherein said alkyl benzene is sulfonated at a temperature in the range of about 50–60 degrees C. with an inert gas-sulfur trioxide gaseous mixture containing from about 10 to 20% sulfur trioxide and wherein the molal ratio of the alkyl benzene to the sulfur trioxide utilized in the sulfonation reaction is approximately unity, the improvement which comprises heating the reaction product, after substantial completion of the aforesaid sulfonation reaction, to about 125 degrees C. while blowing a substantially dry inert gas therethrough for of the order of about ½ hour to about 1 hour.

5. In that method of preparing dodecyl benzene sulfonate wherein dodecyl benzene is sulfonated at a temperature in the range of about 50–60 degrees C. with an inert gas-sulfur trioxide gaseous mixture, the improvement which comprises heating the reaction product, after substantial completion of the aforesaid sulfonation reaction, to between about 105 and about 145 degrees C. while blowing a substantially dry inert gas therethrough, and then cooling the reaction mixture while continuing to blow substantially dry inert gas therethrough.

6. In that method of preparing dodecyl benzene sulfonate wherein dodecyl benzene is sulfonated at a temperature in the range of about 50–60 degrees C. with a gaseous air-sulfur trioxide mixture containing from about 10 to 20% sulfur trioxide and wherein the molal ratio of the dodecyl benzene to the sulfur trioxide utilized in the sulfonation reaction is approximately unity, the improvement which comprises heating the reaction product, after substantial completion of the aforesaid sulfonation reaction, to about 125 degrees C. while blowing substantially dry air therethrough for of the order of about ½ hour to about 1 hour, and then cooling the reaction mixture while continuing to blow substantially dry air therethrough.

7. In that method of preparing alkyl benzene sulfonates wherein the alkyl radical contains from 8 to 22 carbon atoms and wherein dry air is passed into contact with liquid sulfur trioxide to produce a sulfonating gaseous mixture and said mixture is passed into said alkyl benzene below the surface thereof to effect sulfonation of said alkyl benzene, said sulfonation reaction being carried out at a temperature in the range of about 40–70 degrees C., and wherein the molal ratio of the alkyl benzene to the sulfur trioxide utilized in the sulfonation reaction is approximately unity, the improvement which comprises heating the reaction product, after substantial completion of the sulfonation reaction, to between about 115 and about 135 degrees C. while blowing substantially dry air therethrough, and then cooling the reaction mixture while continuing to blow substantially dry air therethrough.

8. In that method of preparing alkyl benzene sulfonates wherein the alkyl radical contains at least 5 carbon atoms and wherein said alkyl benzene is sulfonated with sulfur trioxide carried in an inert medium, the improvement which comprises heating the reaction product, after substantial completion of the aforesaid sulfonation reaction, to between about 105 and about 145 degrees C., while blowing a substantially dry inert gas therethrough for of the order of about ¼ hour to about 1 hour.

9. In that method of preparing alkyl benzene sulfonates wherein the alkyl radical contains at least 5 carbon atoms and wherein said alkyl benzene is sulfonated with sulfur trioxide carried in an inert medium, the improvement which comprises heating the reaction product, after substantial completion of the aforesaid sulfonation reaction, to between about 105 and about 145 degrees C. for of the order of about ¼ hour to about 1 hour, and then cooling the reaction mixture while blowing a substantially dry inert gas therethrough.

10. In that method of preparing dodecyl benzene sulfonate wherein dodecyl benzene is sulfonated at a temperature in the range of about 50–60 degrees C. with an inert gas-sulfur trioxide gaseous mixture, the improvement which comprises heating the reaction product, after substantial completion of the aforesaid sulfonation reaction, to between about 105 and about 145 degrees C. while blowing a substantially dry inert gas therethrough.

11. In that method of preparing dodecyl benzene sulfonate wherein dodecyl benzene is sulfonated at a temperature in the range of about 50–60 degrees C. with an inert gas-sulfur trioxide gaseous mixture, the improvement which comprises heating the reaction product, after substantial completion of the aforesaid sulfonation reac-

tion, to between about 105 and about 145 degrees C., and then cooling the reaction mixture while blowing a substantially dry inert gas therethrough.

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