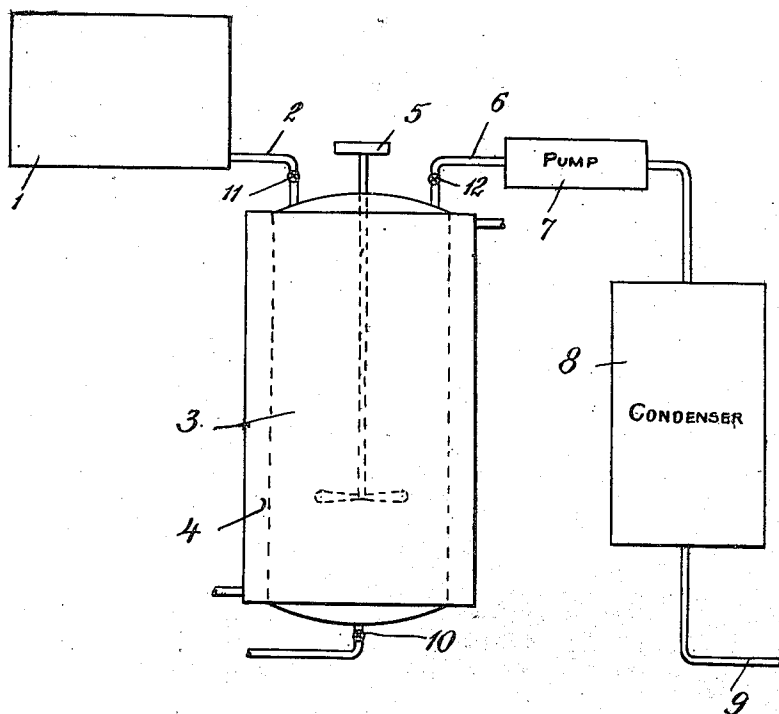


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SULFONATION OF HYDROCARBONS AND HYDROCARBON DERIVATIVES.
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To all whom it may concern:

Be it known that I, CHARLES R. DOWNS, a citizen of the United States, residing at Cliffside, in the county of Bergen and State of New Jersey, have invented certain new and useful Improvements in the Sulfonation of Hydrocarbons and Hydrocarbon Derivatives, of which the following is a specification.

10 This invention relates to the sulfonation of hydrocarbons and hydrocarbon derivatives, and more particularly to the sulfonation of benzene and the production of higher sulfonated derivatives; such as the di-sulfonic acid, therefrom.

15 The sulfonation of hydrocarbons and hydrocarbon derivatives, for example, benzene, involves the substitution of one or more hydrogen atoms of the aromatic nucleus by sulfonic acid groups, with accompanying formation of water. As the sulfonation reaction progresses, the formation of water likewise progresses, and the water formed, unless removed, dilutes the reaction mixture and the acid present, and correspondingly retards the sulfonating process.

20 According to the present invention, the water formed as the result of the sulfonation process is removed by subjecting the reaction mixture to a sufficient degree of vacuum to maintain the acid of the proper strength for the continuation of the reaction.

25 The invention will be described more in detail in connection with the sulfonation of benzene and the production of higher sulfonation derivatives, such as the di-sulfonic acid, therefrom.

30 The benzene is "dissolved" in a mass of sulfuric acid sufficient for the production of the di-sulfonic acid, and of a strength which may be that commonly employed in the production of the di-sulfonic acid. By mixing the benzene with such an amount of sulfuric acid, the benzene can be readily sulfonated and converted at least to the mono-sulfonic acid stage. This sulfonation may be effected under the usual conditions, but the excess of sulfuric acid over and above that required for forming the mono-sulfonic acid, and the increased strength of the acid where a stronger acid than that commonly employed for producing the mono-sulfonic acid is used, will correspondingly facilitate the initial sulfonation of the benzene.

35 When the benzene has been thus "dis-

solved" and converted into the mono-sulfonic acid derivative, or into a mixture of the mono-sulfonic acid with some di-sulfonic acid, the benzene will have been thereby rendered non-volatile. The formation of the non-volatile sulfonic acid derivative will be accompanied by the formation of a corresponding amount of water, so that the remaining mixture will be diluted by the water thus formed.

40 According to the present invention, the non-volatile sulfonic acid derivative is then subjected to a vacuum sufficient to remove the water and maintain the acid at the strength required for the production of the di-sulfonic acid; and the temperature of the re-action mixture is likewise maintained at the proper temperature for the formation of the di-sulfonic acid. Since sufficient sulfuric acid was added at the outset, the reaction will proceed to substantial completion when the vacuum is applied and the water of reaction removed, provided the reaction mixture is maintained at the proper temperature.

45 In the formation of the di-sulfonic acid from benzene, it is common to start with a strong sulfuric acid, usually oleum, and to carry out the sulfonation at a temperature around 260° C. At temperatures much above 260° C. carbonization tends to take place, so that this temperature may be considered as about the upper limit at which the sulfonation may be carried out. At temperatures below 260° C. if the process is carried out without the use of a vacuum and under the usual conditions, a mixture of mono and di-sulfonic acids is obtained and the content of the di-sulfonic acid does not materially increase even after a long continued heating. If the temperature is raised much above 260° C. in an attempt to remove the water of reaction, violent foaming results with evolution of very considerable amounts of sulfur dioxide, thus indicating decomposition, and with accompanying danger from carbonization.

50 Such limitations and objections are overcome by the present invention, according to which the maintenance of the reaction mixture under an appropriate vacuum makes it possible to carry out the reaction to substantial completion at temperatures at or below 260° C., and hence well below the temperatures of carbonization and of de-

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composition. The process can moreover be continued under such conditions to substantial completion.

A certain excess of sulfuric acid over the theoretical is required for the approximate completion of the reaction and the conversion of the benzene for the most part into the di-sulfonic acid. Any large excess, however, is unnecessary since the removal of the water of reaction maintains the strength of the remaining acid at that required for the further sulfonation. As the reaction nears completion, the small amounts of the remaining mono-sulfonated product, and of the remaining free acid, will be correspondingly diluted with the large amount of di-sulfonic acid produced, so that the reaction will tend to proceed more slowly; but the reaction will nevertheless be facilitated by the removal of the water of reaction and the maintenance of the remaining acid at the proper concentration, as well as at the appropriate temperature.

The invention will be further described in connection with the accompanying drawing, which shows, in diagram, an arrangement of apparatus appropriate to the practice of the invention, but it will be evident that various types of apparatus can be similarly used provided they enable the reaction mixture to be maintained at the proper temperature and under appropriate vacuum.

Referring more particularly to the sulfonation of benzene, the benzene and the sulfuric acid may be mixed in the receptacle 1, which may be provided with any suitable stirring or agitating means (not shown). The benzene may thus be mixed with sufficient sulfuric acid to form the di-sulfonic acid and the mixture effected under appropriate thermal conditions for the sulfonation of the benzene and the formation of the mono-sulfonic acid derivative. The benzene will be thereby converted into a non-volatile sulfonated derivative, which is nevertheless capable of undergoing further sulfonation to higher sulfonated derivatives. When the benzene has all reacted and been thereby rendered non-volatile the reaction mixture can be subjected to a vacuum without danger of removal of benzene by vaporation or volatilization.

The reaction mixture may then be transferred through the pipe 2 to the sulfonator 3, which may be provided with the heating jacket 4 for heating the same in any appropriate manner, as by steam or oil, or which may be heated by direct fire. This sulfonator is shown as provided with a conventional form of stirrer driven by a pulley or gear 5 so that the mixture may be maintained uniform throughout and maintained of uniform temperature. The sulfonator is connected through the vacuum pipe 6 with the pump 7 by means of which the vacuum

can be maintained. Beyond the pump is arranged a condenser 8 for condensing the water vapor and any other condensable vapors, which may be conducted by means of the pipe 9 to any suitable place of storage or further treatment. A draw-off pipe 10 is provided for the removal of the sulfonation product, and valves 11 and 12 are shown in the inlet to the sulfonator and in the vacuum pipe for regulation of flow therethrough.

In the practice of the invention the benzene is first converted into a non-volatile derivative, such as the mono-sulfonic acid, and this derivative is then subjected to the proper thermal conditions for the formation of the di-sulfonic acid and maintained under a sufficient vacuum for the removal of the water of reaction and the maintenance of the acid at the required strength toward the completion of the di-sulfonic acid reaction.

In case the acid used at the outset is more dilute than that required for the production of the di-sulfonic acid, this water may likewise be removed by the vacuum and a more concentrated acid thus produced.

The invention thus presents, from one aspect, a process of concentrating the sulfuric acid used for the sulfonation in order to maintain this acid at the proper concentration, and in order to bring this acid to the proper concentration in case it is initially too dilute.

The benzene and the sulfuric acid may be directly admitted to the sulfonator 3, and the initial sulfonation and formation of the mono-sulfonic acid carried out in this sulfonator without the application of a vacuum. The proper thermal conditions for this initial sulfonation may be obtained by means of the heating jacket 4, and the necessary intimacy of reaction can be maintained by the stirrer 5. It will be evident that all parts of the apparatus which come in contact with the concentrated acid should be of material resistant to corrosion thereby.

In case the initial "solution" of the benzene takes place in the sulfonator 3, the further sulfonation can be readily effected simply by increasing the temperature by means of the heating jacket or by the direct fire, where direct fire heat is used, and by the application of a vacuum sufficient to remove the water of reaction. The vacuum required will vary somewhat with the strength of the acid and the amount of water required to be removed as well as the rate of removal and the temperature to which the reaction mixture is heated.

It will be evident that the sulfonation of other volatile hydrocarbons or hydrocarbon derivatives can be effected in a manner similar to that above described by first converting the volatile substances into non-volatile

derivatives, for example, the mono-sulfonic acid derivatives; and by then subjecting the non-volatile derivatives thus produced, to further treatment, in admixture with sufficient sulfuric acid for the further sulfonation, to the temperature required for this further sulfonation and under a sufficient degree of vacuum to maintain the acid at the strength required for such further sulfonation.

In the case of hydrocarbons and hydrocarbon derivatives which are themselves non-volatile, no precautions are required for the prevention of their volatilization, and the reaction mixture may be subjected to a vacuum from the beginning of the reaction, and the water of reaction progressively removed as the reaction proceeds. Thus, if the mono-sulfonic acid of benzene has been otherwise produced, without the use of any considerable excess of sulfuric acid, the necessary acid for the further sulfonation may be added thereto and the resulting mixture then heated to the proper temperature and under the proper vacuum for the removal of the water of reaction and the formation of the higher sulfonated derivatives desired.

The present invention may, accordingly, from one aspect, be considered to involve the sulfonation or further sulfonation, of non-volatile hydrocarbons and hydrocarbon derivatives; while from another aspect it involves the preliminary conversion of volatile hydrocarbons such as benzene into non-volatile derivatives, such as the mono sulfonic acid, and the subsequent further sulfonation of the non-volatile derivatives thus produced.

The present invention has the important advantage over processes of sulfonation in which no vacuum is employed, for example, in the production of benzene di-sulfonic acid, that a great saving in the amount of acid necessary for the sulfonation may be effected. Thus, while it is possible to produce benzene di-sulfonic acid by the use of a sufficient excess of strong acid without the vacuum and removal of water thereby, a great saving is made in the amount of acid necessary when the removal of water by means of the vacuum takes place.

The present invention relates to certain specific aspects of the invention described and claimed in my copending application, Serial No. 210534 filed of even date herewith. Such co-pending application is of more generic and comprehensive scope, and certain of the claims of such co-pending application are likewise intended to be of a more comprehensive and generic character, and to include the specific improvements of the present invention as well as the other

specific improvements more particularly and specifically claimed in said co-pending application.

I claim:

1. The method of sulfonating volatile hydrocarbons and hydrocarbon derivatives, which comprises preliminarily sulfonating the same to form non-volatile derivatives, and effecting the further sulfonation of the non-volatile derivatives by subjecting them in admixture with the sulfonating acid, to the temperature required for the further sulfonation, and to a sufficient degree of vacuum to remove water from the reaction mixture.

2. The method of sulfonating benzene, which comprises preliminarily sulfonating the benzene and converting it into non-volatile sulfonic acid derivatives, and effecting the further sulfonation of the benzene by subjecting such derivatives, in admixture with the sulfonating acid, to the temperature required for the further sulfonation and to a sufficient vacuum to remove water from the reaction mixture.

3. The method of producing benzene di-sulfonic acid, which comprises preliminarily sulfonating the benzene with the amount of sulfuric acid required for the formation of the di-sulfonic acid, and thereby converting the benzene into a non-volatile sulfonic acid derivative, and subsequently subjecting the resulting reaction mixture to the temperature required for the formation of the di-sulfonic acid and to a degree of vacuum sufficient to remove the water of reaction and maintain the acid at the strength required for the completion of the sulfonation.

4. The method of sulfonating benzene mono-sulfonic acid and its derivatives, which comprises subjecting the same, in admixture with the sulfonating acid at the temperature required for sulfonation, to a sufficient degree of vacuum to remove water from the reaction mixture.

5. The method of producing di-sulfonic acid, which comprises the steps of forming mono-sulfonic acid by dissolving a hydrocarbon in sulfuric acid at atmospheric pressure, and subsequently subjecting the mono-sulfonic acid to an elevated temperature at such a degree of vacuum that the water of reaction is removed.

6. The method of producing benzene di-sulfonic acid, which comprises forming benzene mono-sulfonic acid by treating benzene with sulfuric acid at low temperature and normal pressure, and subsequently subjecting the mono-sulfonic acid to a temperature below 260° C. at such a vacuum that a substantial portion of the water is removed.

In testimony whereof I affix my signature.
CHARLES R. DOWNS.