

# UNITED STATES PATENT OFFICE

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## MANUFACTURE OF ALKYLATED SULPHONIC ACIDS AND ESTERS

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This invention relates to a method for the preparation of alkyl esters of alkylated and sulphonated aromatic bodies.

It is an object of the invention to provide a novel method for the production of esterified, alkylated and sulphonated aromatic bodies by the direct union of olefins therewith.

Another object is to provide a novel method for the sulphonation, alkylation and esterification of aromatic hydrocarbons by a single reaction.

A further object is to provide a novel method for the alkylation and esterification of sulphonated aromatic bodies by the direct union of olefins therewith.

A further object is to provide a method whereby a sulphonated aromatic body may be first alkylated by direct union with an olefin and thereafter esterified if desired by direct union with the same or a different olefin.

The invention may be employed for the production of derivatives of a variety of aromatic hydrocarbons including for example polycyclic bodies such as naphthalene and anthracene and monocyclic bodies such as benzene and toluene. The alkyl groups which it is desired to introduce into the aromatic nucleus and to combine with the sulphonic group are provided by using the proper olefin or mixture of olefins such as propylene, amylene, etc., or mixtures thereof. These olefins may be employed in the pure state, either separately or as mixtures of pure olefins as may be desirable, or olefin-bearing gases from any suitable source may be employed provided no large amount of aromatic bodies is present. For example, pressure still gas from oil refineries and cracked gasoline contain large amounts of olefins and can be employed in the process as starting materials.

Where the starting material is naphthalene or other aromatic body the process may be carried out in such a manner as to include sulphonation together with alkylation of the aromatic nucleus and if desired by esterification, and in most cases it will be preferred to carry out these reactions in a single step, although a plurality of separate steps may be employed if desired. Where the sulfonic acid is readily available as a starting material, however, the sulphonation is unnecessary. If desired, the process may stop with the alkylation of the aromatic nucleus so as to provide an alkylated sulphonic acid, or it may be carried further to include esterification of the acid, or in some instances the reaction may be so carried out that the acid is only partly esteri-

fied, the procedure depending on whether the uses to which the product is to be put are such that the acid or the ester or both are suitable.

Generally it will be suitable that the alkyl group or groups which are introduced in the aromatic nucleus be the same as the group or groups which combine with the sulphonic acid group, and in such cases it will be desirable in the interest of simplicity and economy to carry out the entire process in a single reaction, using only one olefin or mixture of olefins or olefin-bearing material. When mixtures of olefins are employed the reaction product may vary both as to the alkyl groups which are introduced in the nucleus and as to those combined with the sulphonic acid group. However, if desired, the process may be carried out in steps in such a way that the alkylation of the aromatic nucleus is separate from the esterification, so that particular olefins or different olefins can be employed in the separate steps.

In general, the procedure consists in preparing a mixture of the desired aromatic hydrocarbon, sulphuric acid at least sufficient to sulphonate the hydrocarbon and produce the desired sulphonic acid, preferably a quantity of an inert solvent for the hydrocarbon and olefin such as a light fraction of gasoline or some previously prepared ester, and the olefin or mixture of olefins which it is desired to react. When these reagents are brought together, a vigorous reaction takes place with evolution of heat, and when the absorption of the olefin ceases it is found that sulphonation, alkylation of the nucleus and esterification have all taken place. The resulting product comprises principally alkyl esters of alkylated aromatic sulphonic acids, but may also contain a certain quantity of alkylated hydrocarbon which was not sulphonated. For some purposes, however, the presence of some alkylated but non-sulphonated hydrocarbon is not objectionable.

In case quantities of a suitable aromatic sulphonic acid are readily available as a starting material, the reaction may be carried out in substantially the same way except that sulphuric acid is unnecessary in order to carry out the sulphonation described above. In this case the sulphonic acid is preferably mixed with a quantity of the solvent and reacted with the desired olefin or mixture of olefins as hereinafter described, with formation of alkyl esters of the alkylated and sulphonated aromatic hydrocarbons.

The conditions under which the reaction takes

place are subject to considerable variation. In general, the mixture should be agitated during the reaction in order to insure thorough mixing of the reagents. The olefin may be added in any suitable manner, either as a gas or liquid depending on the specific olefin or olefins employed and the temperatures used for the reaction. It has been found that excess sulphuric acid acts as a carrier or catalyst and accelerates the reaction so that it may be carried out at room temperatures. Hence it is desirable in many cases to employ an excess of sulphuric acid over that required for sulphonation, or when sulphonic acid is available as a starting material, to add a small quantity of sulphuric acid for this purpose. The use of sulphuric acid as a catalyst is unnecessary, however, if a temperature of 80° C. to 120° C. is maintained during the reaction, as under these conditions the alkylation proceeds substantially to completion and then is followed by esterification. The reaction in the case of mono-cyclic aromatic bodies is somewhat slower than with polycyclic bodies and hence it is desirable when treating mono-cyclic bodies to take advantage of the accelerating action of sulphuric acid as well as to raise the temperature somewhat, say to 50° C.

A wide variety of solvents may be employed, provided they are inert with respect to the desired reaction. The action of the solvent is probably physical, the olefin being dissolved as well as the aromatic hydrocarbon or sulphonic acid and the contact between the reagents being thus improved. A quantity of alkylated ester from a preceding operation may be employed as these esters are good solvents for the sulphonic acids and for the aromatic hydrocarbons. Other solvents such as a light fraction of gasoline may also be used. The amount of solvent employed is not critical and may vary widely.

The reaction product, in addition to the esters referred to above, may contain some sulphonic acid which has not been esterified, as well as sulphuric acid and a quantity of water produced by the sulphonation reaction. The mixture is washed with water to remove any excess free acid, and the gasoline or other solvent may be separated from the mixture in any suitable way as by distillation.

The amount of olefin to be employed may vary considerably depending upon the extent to which the alkylation and esterification reactions are to be carried. As stated above, it has been found that the alkylation of the aromatic nucleus largely precedes the esterification of the sulphonic group. Hence by observing the acidity of the reaction mixture as the reaction proceeds, the progress of the reaction can be followed and the process may be controlled as to the results produced. For example, when it is observed that the acidity of the mixture has disappeared, the alkylation and esterification reactions have been substantially completed, unless excess sulphuric acid is used as a carrier or catalyst. In the latter case, the reaction will be substantially complete when the acidity of the mixture has been decreased to the point corresponding to that portion of the original acidity supplied by the excess sulphuric acid. If mixtures of acids and esters are desired, the reaction may be stopped before proceeding to this point.

Further, since as stated above, the alkylation reaction takes place before esterification, the completion of alkylation is substantially indicated by the point at which the acidity of the re-

action mixture begins to decrease. If the addition of olefin is stopped at this point, the resulting product will comprise substantially only alkylated sulphonic acid without esterification. These acids, as distinguished from their esters, may be desirable for certain purposes. A further step may then be carried out if it is desired to introduce one or more alkyl groups in the nucleus and a different group or groups in the sulphonic acid group. In this case the desired olefin is introduced until the alkylation is completed as indicated by the initial decrease in the acidity of the reaction mixture. The treatment with olefin is then discontinued and the alkylated sulphonic acid recovered from the mixture and thereafter converted to an ester by treatment with another olefin.

As an example of the process, 300 grams of naphthalene was added to 1000 cc. of a light gasoline fraction and 300 grams of sulphuric acid (specific gravity 1.84). This mixture was agitated with addition of propylene gas until 480 grams of propylene had been absorbed. The reaction was vigorous with much evolution of heat, and the reaction product consisted of a mixture of propylated naphthalene sulphonic acids and their esters and a certain amount of naphthalene which has been propylated but not sulphonated, together with excess sulphuric acid, gasoline and water produced by the sulphonation reaction. This mixture was washed with water for the removal of the excess sulphuric acid and then distilled off the gasoline.

In another example, 300 grams of naphthalene sulphonic acid was agitated at room temperature with 200 cc. of a light gasoline fraction and 40 grams of concentrated sulphuric acid (specific gravity 1.84) at room temperature and propylene gas was added until the total acidity of the mixture corresponded to that portion of the original acidity supplied by the sulphuric acid. The heavier acid layer was largely dissolved by the gasoline as the reaction proceeded. The mixture was washed with water for removal of free acid and the gasoline was distilled off, leaving a mixture of esters consisting largely of isopropyl di-isopropyl naphthalene sulphonate. The product was a light brown viscous oil somewhat heavier than water.

In a variation of the second example stated above, the treatment with propylene was discontinued as soon as the acidity of the mixture began to decrease, and the mixture was then treated with water and the propylated sulphonic acid recovered from the water layer. This propylated naphthalene sulphonic acid was then converted to an amyl ester by treatment with amylene in a similar manner. During the first step a small amount of isopropyl ester was formed, which was recovered from the gasoline layer.

It will be observed that the method described above can be used to produce either the alkylated acids or the esters of those acids. Thus with naphthalene sulphonic acid and propylene there may be obtained the isopropyl esters of mono, di, tri, etc., isopropyl naphthalene sulphonic acids, or if desired the unesterified acids. Similarly, with amylene and naphthalene sulphonic acid, there may be obtained the amyl esters of a series of amyl sulphonic acids, or the acids themselves, and with mixed olefins there may be obtained mixtures in which the alkyl groups vary, both those attached to the sulphonic group and those attached to the naphthalene or other aro-

matic nucleus. Also, by exercising proper control, the nucleus may be alkylated with one olefin, for instance amylen, and thereafter the alkylated acid may be esterified with another olefin, for instance propylene. The method as first described above provides a very simple way of forming the desired final products directly from the aromatic hydrocarbon and the olefin in a single step. However, if sulphonic acid is available, it may be employed as a starting material if desired according to the procedure indicated. The use of the solvent renders the sulphonic acid more mobile and also aids the reaction in the case of gaseous olefins by dissolving the olefin and thus improving its contact with the acid.

It will be understood that the invention is not limited to the specific examples given above and that changes may be made in the starting materials, their proportions, and details of the procedure without departing from the spirit of the invention. Thus the olefin and the aromatic body to be used may vary depending on the materials available and the uses to which the product is to be put, and the proportions of the materials may likewise be varied as will be apparent to those skilled in the art. Furthermore, the starting materials are not limited to the simple aromatic hydrocarbons mentioned above, but include also substituted derivatives such as phenols, chlorinated and nitrated compounds, etc. These derivatives may be alkylated, sulphonated and esterified in the manner described above to produce a variety of products, such as alkylated-alkoxylated-sulphonate esters from phenols, chlorinated alkylated sulphonate esters from chlorinated compounds, etc. Reference will therefore be had to the appended claims for a definition of the limits of the invention, and the term "aromatic bodies" as used in said claims will be understood as including substituted derivatives as well as simple aromatic hydrocarbons.

What is claimed is:

1. A process for producing alkylated sulphonated and esterified aromatic bodies which consists in reacting an aromatic body with a sulphonating agent and an olefin in the presence of an inert solvent for said aromatic body and olefin to sulphonate and alkylate said aromatic body and continuing the treatment with olefin to esterify the sulphonic acid group.
2. A process for producing alkylated sulphonated and esterified aromatic bodies which consists in reacting an aromatic body with sulphuric acid and an olefin to sulphonate and alkylate the aromatic nucleus and continuing the treatment with olefin to alkylate the sulphonic acid group.
3. A process for producing alkylated sulphonated and esterified aromatic bodies which consists in reacting an aromatic body with sulphuric acid and an olefin to sulphonate and alkylate the aromatic nucleus and continuing the treatment with olefin to alkylate the sulphonic acid group, the sulphuric acid being in excess of the amount required to produce the mono-sulphonic acid.
4. A process which consists in reacting an aromatic body with sulphuric acid and an olefin to sulphonate and alkylate the aromatic nucleus and continuing the treatment with olefin to alkylate the sulphonic acid group, in the presence of an inert solvent for the aromatic body and olefin,

whereby a mixture of alkylated sulphonated and esterified aromatic bodies and alkylated but non-sulphonated bodies is produced.

5. A process for producing alkylated sulphonated and esterified aromatic bodies which consists in reacting an aromatic body with sulphuric acid in excess of the amount required to produce the mono-sulphonic acid and with an olefin in the presence of an inert solvent for the olefin and aromatic body, and continuing the olefin treatment to alkylate the aromatic nucleus and to esterify the sulphonic acid group.

6. A process for sulphonating alkylating and esterifying an aromatic body in a single operation which consists in mixing an aromatic body with an inert solvent and sulphuric acid in excess of the amount required to produce mono-sulphonic acid and then adding an olefin to said mixture, whereby the aromatic nucleus is sulphonated and alkylated, and continuing the treatment with olefin until the sulphonic acid group is esterified.

7. A process for producing alkylated sulphonated and esterified aromatic bodies which consists in reacting an aromatic sulphonic acid with an olefin in the presence of an inert solvent and in the absence of other acids and at a temperature of the order of 80° C. to 120° C.

8. A process for producing alkylated sulphonated and esterified aromatic bodies which consists in reacting an aromatic sulphonic acid with an olefin in the presence of sulphuric acid to alkylate the aromatic nucleus and continuing the treatment with olefin to esterify the acid.

9. A process for producing alkylated sulphonated and esterified aromatic bodies which consists in reacting an aromatic sulphonic acid with an olefin in the presence of an inert solvent and sulphuric acid to alkylate the aromatic nucleus and continuing the olefin treatment to esterify the sulfonic acid group.

10. A process for producing alkylated sulphonated and esterified aromatic bodies which consists in sulphonating an aromatic body and reacting the sulphonated body with an olefin to alkylate the aromatic nucleus, then stopping the reaction and further reacting the sulphonated and alkylated body with a different olefin to esterify the sulphonic acid group.

11. The process which consists in reacting a sulphonated aromatic body with excess sulphuric acid and an olefinic material in the presence of an inert solvent for said aromatic body and olefinic material to alkylate the aromatic nucleus and continuing the olefin treatment to esterify the sulphonic acid group.

12. The process which consists in reacting an aromatic body with sulphuric acid in excess of the amount required to produce the mono-sulphonic acid and with an olefinic material in the presence of an inert solvent for said aromatic body and olefinic material to alkylate the aromatic nucleus and continuing the olefin treatment to esterify the sulphonic acid group.

13. The process which consists in reacting a sulphonated aromatic body with an olefinic material in the presence of an inert solvent for said body and material and in the absence of other free acid while maintaining a reaction temperature of the order of 80° C. to 120° C.

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