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TOLUENE NITRATION PROCESS

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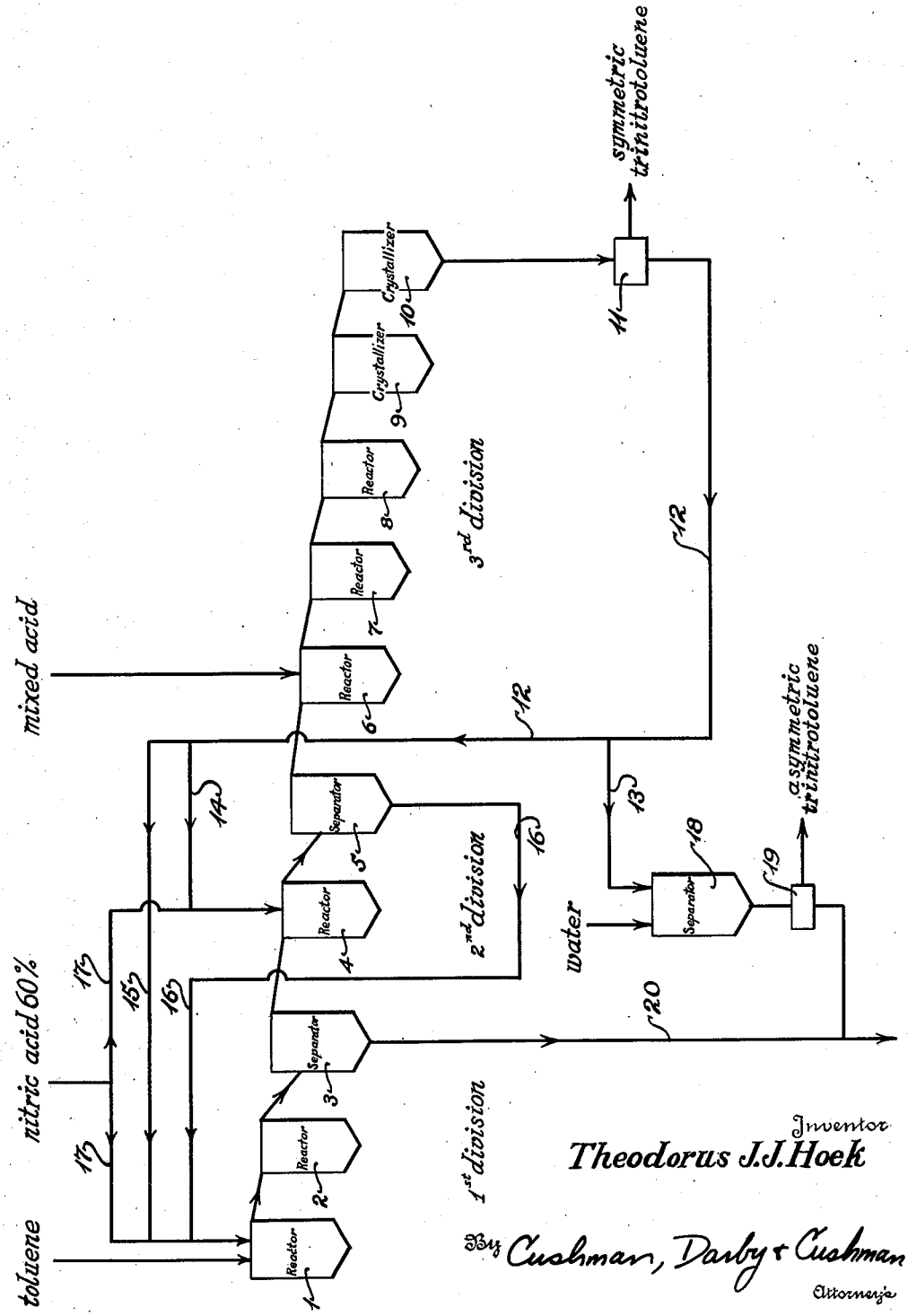

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TOLUENE NITRATION PROCESS

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This invention relates to toluene nitration processes and, more particularly, it is concerned with a method for the manufacture of trinitrotoluene by continuous operation as contrasted to batch nitration methods.

The manufacture of trinitrotoluene by a continuous method has long been desired in the explosives field. However, it is understood that a satisfactory commercial method for continuous nitration of toluene to trinitrotoluene has never been developed. Thus, either the methods proposed heretofore have been associated with inherently dangerous steps, or have involved the use of an extremely large and impractical number of nitration steps, or have produced yields which are very low in comparison with the highly concentrated spent acids which are obtained.

A principle object of this invention is the provision of a new method for the nitration of toluene to produce trinitrotoluene. A further object is a provision of such a procedure which is conducted in a continuous manner. Further objects include the provision of such a process (1) which will produce high yields of product in proportion to the amount and concentrations of the nitration acids employed, (2) which will permit the nitration to be completed at a maximum rate, thus, reducing the number of nitration steps to a minimum, and (3) which may be carried out without recourse to the use of intricate or involved apparatus.

These objects are accomplished according to the present invention by effecting the nitration of toluene to trinitrotoluene in a continuous operation by means of mixed acid containing free SO_3 with the operation separated into a plurality of divisions. The hydrocarbon and acid are reacted in continuous parallel flow in each separate division, and at the end of each division the nitro product obtained in that division is separated from the mixed nitration acid and is treated by stronger acid in the subsequent operation division. Fresh mixed acid is used in the highest division of the process and spent acid form one or more of the higher divisions, mixed with nitric acid, is used in each lower division of the process.

The success of the present invention is dependent to a large extent on the discovery that mixed acids containing a large quantity of SO_3 may be employed to nitrate toluene without undue oxidation of the organic material at a reaction velocity which makes possible successful continuous operation. The success of the invention is also dependent upon the discovery that a successful continuous toluene nitration procedure could be

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developed if the operation is divided into a plurality of divisions so that the reactants, namely the mixed acid and organic matter, are caused to undergo parallel or co-current flow in each of the separate operation divisions, but are made to undergo counter-current flow between each of the separate steps. The separation of the continuous procedure into separate divisions makes possible the application of the conditions of temperature, acid concentration and the like which have been found necessary for the successful operation of the process. Furthermore, the operation of the process in plurality of divisions makes possible the economical and efficient use of the nitration acids. Thus, the spent acid from one step may be used, preferably with the addition of a controlled amount of concentrated nitric acid, as the mixed acid for the next lower step so that the process can be conducted without addition of water to the acid during any of the operation.

It has been found that the separation of the nitration process into three separate divisions is desirable. In the first division toluene is nitrated to mononitrotoluene, in the second division the mononitrotoluene thus produced is formed into a mixture of mono- and dinitrotoluene and, finally, in the third division, this mixture of mono- and dinitrotoluene is formed into the final product trinitrotoluene.

The course of the process as a whole is diagrammatically illustrated in the attached drawing which constitutes a flow diagram of the operation. In the drawing, 1 and 2 are nitration vessels in which the formation of mononitrotoluene takes place. The reaction mixture, after having passed 1 and 2, enters into the separator 3, from which mononitrotoluene runs over to the nitration vessel 4 of the second division. The reaction mixture formed here is next separated in the separator 5. The upper layer, being a mixture of mono- and dinitrotoluene is led to the nitration vessels 6, 7 and 8 to be cooled afterwards in the crystallizers 9 and 10. The removal of the crystallized product takes place in the centrifuge 11; the remaining acid is returned to lower operation divisions through the conduit 12, save the part that is let off through conduit 13. The rest is led partly through 14 to 4, partly through 15 to 1. In 4 the nitrating acid mixture is formed by the spent acid supplied from the third division through 14 and nitric acid from the conduit 17. The spent acid from the second division flows from the separator 5 through conduit 16 to 1, being mixed at the same time with the part of the spent acid from the third step supplied

through 15 and with nitric acid from conduit 17. The spent acid from the third step let off at 13 is diluted with water in the agitator 18, so as to separate the dissolved nitro compounds. After these have been removed at centrifuge 19, the remaining diluted acid is added to the spent acid from the first step removed through conduit 20.

Stirrers in the nitration vessels and crystallizers, buffer tanks in the acid conduits, and bypasses by which part of the spent acid obtained in a certain step may be returned to the reaction mixture of the same step, have not been indicated.

It is not desirable that any toluene remain unconverted in the first division because this unconverted toluene first of all impedes the separation of mononitrotoluene and then enters into the second step where the temperature is higher so that a certain oxidation of toluene will take place. On the other hand, it is not desirable to bring about a partial conversion into dinitrotoluene in the first division.

In the second division, the nitration to dinitrotoluene is not carried to completion. A strong mixed acid is used in the third division, so as to convert the lower-nitrated product into trinitrotoluene. Moreover, the melting point of the product in the second division rises as the amount of dinitrotoluene increases. In any case, the product of the second division should remain in liquid state, so that it can more easily be separated and converted. Likewise, a high melting point of the product would also require a higher temperature and this would involve an increased rate of oxidation. The operation is preferably conducted in such a way that, at the end of the second division of the process on the average 1.4 to 1.6 nitro groups have been introduced into each molecule of toluene.

Under the conditions described, in the second step less nitro groups are introduced into the toluene than in the first division. Consequently, in the second division, less nitric acid will enter into reaction than in the first division. Therefore, it is recommendable to keep the total amount of mixed acid in the second division smaller than in the first division. This can be accomplished by leading the spent acid from the third division partly to the second and partly directly to the first. Thus, in the first division spent acid from the second as well as from the third is obtained.

The composition of the spent acid may be at the end of the first division; 71% H_2SO_4, 25% H_2O, 1% HNO_3 and 3% HNO_2; at the end of the second division: 78% H_2SO_4, 15% H_2O, 2% HNO_3, 2% HNO_2, and 3% nitro-products; and finally, at the end of the third division: 81% H_2SO_4, 3% H_2O, 6% HNO_3, 3% HNO_2 and 7% dissolved trinitrotoluene. It will be understood that these data are only given by way of example of desired values for operation.

In the system described, spent acid is let off in two places, namely part of it at the end of the highest division and the remainder at the end of the first. In the highest, comprising the removal of asymmetrical trinitrotoluene, the quantity of removed acid may amount to a third part of the total amount of spent acid of this division. This removed acid is diluted with water, so as to separate the dissolved nitro compounds. After these compounds have been removed, the diluted acid, together with the spent acid from the first division containing only traces of mononitrotoluene, may be led to the Glover tower of a sulfuric acid plant.

Mixed acids with at least 30 per cent of free SO_3 and at least 30 per cent of HNO_3 are preferably used as starting material. These acids can not be prepared from nitric and oleic acid, but must be made by use of sulfur trioxide (Netherlands Patent Spec. 49,773). As sulfur trioxide has a far stronger capacity to bind water than sulfuric acid has, the nitric acid content of these acids may be much higher than in the case of sulfuric acid acting as water-binding agent. Remarkably, the oxidizing action of these mixed acids is, in spite of their high nitric acid, content not great. An important advantage is furthermore the relatively slight heat evolution during the nitration with these acids which facilitates temperature regulation.

It is also possible, within the scope of this invention, to separate the operation of the process into 4 or 5 divisions, thereby subdividing the first and/or third division of the system just described, but these variations are not preferable.

While the exact temperatures used in each division of the process will depend to some extent upon the concentrations of the mixed acids used in the nitration process, we have found certain temperatures in each division are preferable for mixed acids of the proper concentrations as indicated above in order to obtain high product yields. Thus, it has been found that a temperature of about 20° to 30° C. should be used in the first division, a temperature from 40° to 50° C. should be used in the second division and a temperature of 55° to 85° C. should be used in the third division.

In the third division of the operation, it is advantageous to increase the temperature as the nitration proceeds, e. g., by leading the continuous flow of the reaction mixture through a number of spaces or heat exchangers with progressively increasing temperatures. The temperature in the third division is preferably increased progressively from 55° to 85° and can most readily be accomplished in three phases of 55° C., 75° C. and 85° C., respectively.

The present process results in the production of symmetrical trinitrotoluene. At the same time, however, a certain amount of asymmetrical trinitrotoluenes is formed which must be separated from the symmetrical product. This separation is effected by having care that the spent acid of the last division contains at most 8% of water or else at most a few percent of free SO_3. In an acid mixture of this composition, the symmetrical product crystallizes upon cooling, while the asymmetrical product remains dissolved. Since reintroduction of this spent acid into a lower division would result in an accumulation of asymmetrical products in the process, means are provided for letting off a certain part of the spent acid of the highest division. In this way an amount of asymmetrical product is removed, which is equal to the amount which is formed during the nitration. The crystal mass that is separated from such an acid by cooling, is centrifuged, then washed successively with concentrated sulfuric acid and water, and finally subjected to a simple treatment with sulfite, thus yielding a product with a melting point of 80.6° C.

The present invention provides a simple, but effective method for the continuous nitration of toluene to trinitrotoluene. Because of the continuous manner of operation, it is possible to carry out the procedure automatically. Moreover, simple and uncomplicated apparatus may

be used, such as ordinary tank type separators, in which the outlet of the separators are regulated by means that are controlled by a float on the interface surface existing in the separator.

I claim:

1. A continuous process for the nitration of toluene to trinitrotoluene which comprises contacting toluene in continuous cocurrent flow with mixed acid comprising nitric acid and sulfur trioxide, said contact operation being separated into a plurality of divisions, the nitro product obtained in each division being separated from the flow of mixed acid, the resulting separated nitro product being then further continuously nitrated by cocurrent contact in a subsequent division with a flow of stronger acid, fresh mixed acid being used in the last division of the process, and the mixed acid for cocurrent flow in each lower division comprising spent acid from a higher division.

2. The process of claim 1, wherein fresh nitric acid is added to the spent acid from the last division to form the mixed acid for use in the lower divisions of the process.

3. The process of claim 1, wherein the mixed acid in each of said nitration divisions is stronger than the mixed acid in the preceding division.

4. A continuous process for the nitration of toluene to trinitrotoluene which comprises nitrating toluene by cocurrent contact with mixed acid comprising nitric acid and sulfur trioxide, said contact operation being separated into three divisions, toluene being nitrated to mononitrotoluene in the first division by continuous cocurrent flow of toluene with mixed acid, the resulting mononitrotoluene being nitrated to a mixture of mono- and dinitrotoluene in the second division by continuous cocurrent flow of mononitrotoluene and mixed acid, and the resulting mixture of division two being nitrated to trinitrotoluene in the third division by continuous cocurrent flow of said mixture with mixed acid, separating the nitro product obtained in each division from the mixed acid, and introducing the mixed acid from each division into the flow of reactants in the next lower division.

5. The process of claim 3, wherein the spent acid of the third operation division is separated into two portions, one of said portions being introduced into the flow of reactants in the second division and the other of said portions being introduced into the flow of reactants in the first division.

6. A continuous process for the nitration of toluene to trinitrotoluene which comprises nitrating toluene by cocurrent contact with mixed acid comprising nitric acid and sulfur trioxide, said contact operation being separated into three divisions, toluene being nitrated to mononitrotoluene in the first division by continuous cocurrent flow of toluene with mixed acid at a temperature between 20° to 30° C., the resulting mononitrotoluene being nitrated to a mixture of mono- and dinitrotoluene in the second division by continuous cocurrent flow of mononitrotoluene and mixed acid at a temperature of 40° to 50° C., and the resulting mixture of division two being nitrated to trinitrotoluene in the third division by continuous cocurrent flow of said mixture with mixed acid at a temperature of 55° to 85° C., separating the nitro product obtained in each division from the mixed acid, and introducing the mixed acid from each division into the flow of reactants in the next lower division.

7. The process of claim 4, wherein the temperature of the reactants, while travelling in continuous, cocurrent flow through the apparatus of said division 3, is progressively increased from 55° C. to 85° C.

8. The process of claim 4, wherein the conditions of reaction during the cocurrent flow in the second division is such that said resulting nitro-product mixture has an average of 1.4 to 1.6 nitro groups in each organic molecule.

9. A continuous process for the nitration of toluene to trinitrotoluene which comprises nitrating toluene by cocurrent contact with mixed acid comprising nitric acid and sulfur trioxide in three divisions of reaction mixture flow, toluene being nitrated to mononitrotoluene in the first division by continuous cocurrent flow of toluene with mixed acid at a temperature of between 20° to 30° C., the resulting mononitrotoluene being nitrated to a mixture of mono- and dinitrotoluene in the second division by continuous cocurrent flow of mononitrotoluene and mixed acid at a temperature of 40° to 50° C., and the resulting mixture of division two being nitrated to trinitrotoluene in the third division by continuous cocurrent flow of said mixture with mixed acid at a temperature of 55° to 85° C., separating the nitro product obtained in each operation division from the mixed acid, and introducing the mixed acid from each division into the flow of reactants in the next lower division, introducing fresh mixed acid having a composition of 30 to 60% SO_3, 30 to 60% HNO_3 and 10 to 40% H_2SO_4 into the flow of reactants in the third division, proportioning the mixed acid to organic material in said third division so that the reaction mixture produced by the step has a composition containing less than 2% SO_3 and less than 8% H_2O, cooling said resulting mixture to crystallize symmetrical TNT, and separating said crystallized TNT from the reaction mixture.

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