

[54] **PROCESS FOR THE MANUFACTURE OF TRINITROTOLUENE**

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[58] Field of Search **260/645**

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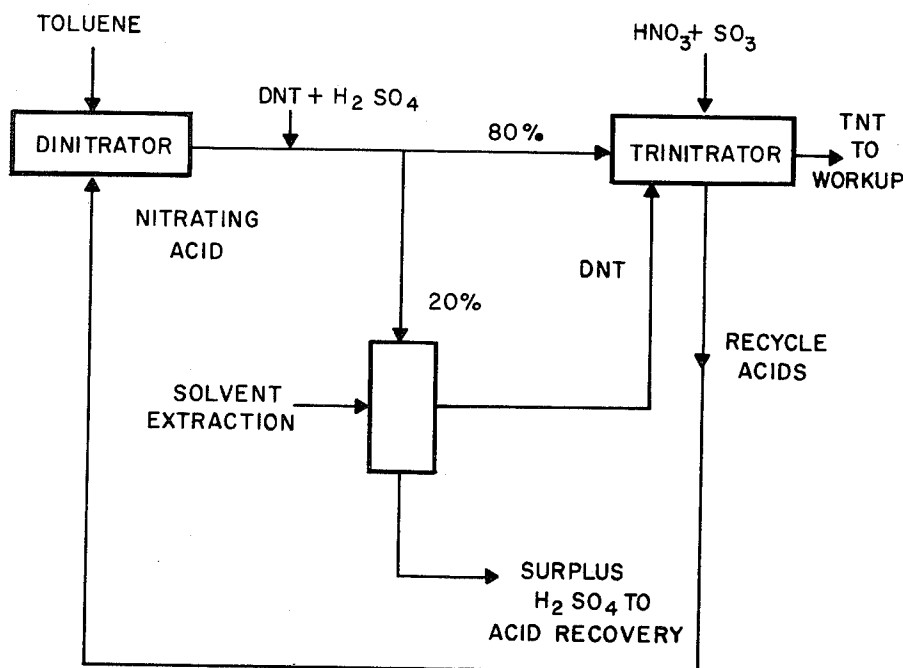
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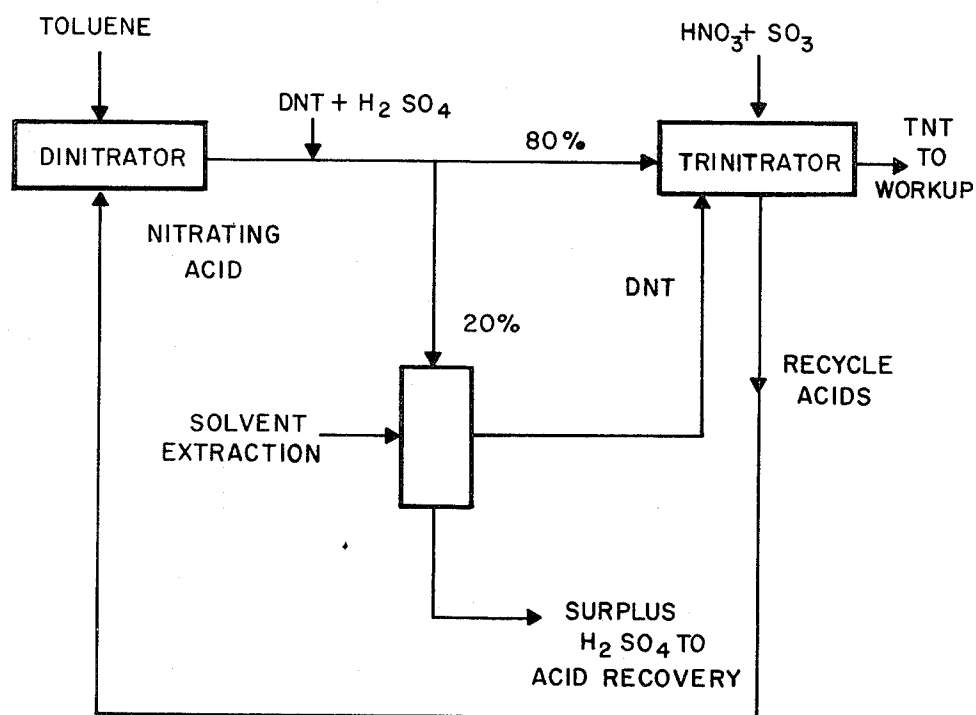
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[57] **ABSTRACT**

Process for preparing TNT comprises nitrating toluene with an anhydrous nitrating agent NO_2HSO_4 obtained by mixing HNO_3 and oleum. The process eliminates pollution problems associated with conventional manufacturing processes and produces TNT in high yields and rapid reaction rates.

14 Claims, 1 Drawing Figure





PROCESS FOR THE MANUFACTURE OF TRINITROTOLUENE

The invention described herein may be manufactured, used and licensed by or for the Government for governmental purposes without the payment to us of any royalties thereon.

BACKGROUND OF THE INVENTION

The invention relates to a process for producing TNT (2,4,6-trinitrotoluene). In particular the invention relates to a process for nitrating toluene to produce TNT.

TNT is conventionally manufactured by a multistep process, wherein toluene is first nitrated with a mixture of nitric acid and sulfuric acid to produce MNT (mononitrotoluene), the MNT is then nitrated to DNT (dinitrotoluene) and the DNT is finally nitrated to TNT, the acid strength and temperature being increased for each nitro group introduced. The TNT obtained contains small amounts of other TNT isomers in addition to the desired 2,4,6-isomer as well as DNT isomers, which must be removed in order to produce a TNT of sufficient purity for use as a military explosive. Such purification is usually accomplished by a selling process, which involves treating the crude TNT with aqueous sodium bisulfite solution, which selectively extracts the undesired TNT isomers from the desired 2,4,6-isomer. The waste liquors resulting from such selling operations, called "red water," cannot be economically purified without creating a serious pollution problem. In addition, large amounts of nitrogen oxide fumes are evolved from the nitration reactors and create a serious atmospheric pollution problem, which is costly to alleviate.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for nitrating toluene to TNT in high yields and rapid reaction rates.

Another object is to provide a novel process for nitrating DNT to TNT in high yields.

A further object is to provide a process for nitrating toluene to TNT, which produces TNT of military specification grade, eliminates the polluting nitrogen oxide fumes emanated from the conventional nitration reactions and eliminates the sellite process with its attendant red water disposal problem.

A still further object is to provide a process for nitrating toluene which minimizes the formation of metal isomers, maximizes the ratio of 2,4- to 2,6-DNT isomers produced and maximizes the yield of desired 2,4,6-TNT isomer.

Another object is to provide a continuous, closed loop process for nitrating toluene to TNT.

These and other objects and advantages are achieved by the process of this invention, which is based on the use of an extremely active anhydrous nitrating mixture prepared from HNO_3 and oleum. In accordance with the process of this invention, toluene is nitrated to DNT by reacting it at temperatures below about 40°C with an anhydrous mixture of HNO_3 and oleum, and the DNT thus produced is nitrated to TNT, without isolation from the dinitration reaction mixture, by treatment at a temperature of at least about 70°C with an anhydrous mixture of HNO_3 and oleum. When the trinitration reaction is complete, the reaction mixture is cooled to precipitate the TNT, which is separated, as

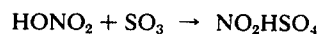
by filtration and washed with water to remove adhering acid. The concentrated nitric acid-sulfuric acid mother liquors have a high capacity for retaining impurities in solution so that a TNT product of excellent purity is thus obtained directly. If desired, a TNT product of greater purity can be obtained by washing the TNT crystals, prior to washing with water, with concentrated sulfuric acid and/or nitric acid.

BRIEF DESCRIPTION OF THE DRAWING

The drawing shows a schematic flow diagram of a continuous closed-loop process for manufacturing TNT from toluene according to this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

We consider that the high reactivity of the anhydrous nitrating mixture of HNO_3 and oleum is due in part to the formation of nitronium bisulfate (NO_2HSO_4) from HNO_3 and SO_3 :



The stoichiometric conversion of HNO_3 to this nitronium salt provides a high concentration of nitronium ion, which is recognized as the reactive species in most aromatic nitration reactions. The favorable solvation effect provided by anhydrous H_2SO_4 also contributes to the high reactivity of the system.

U.S. Pat. No. 2934571 discloses a process for producing DNT substantially instantaneously and in nearly quantitative yield by contacting toluene with a mixture of HNO_3 and oleum at a temperature between -50°C and 60°C . However, the process of this patent is limited to the production of DNT and other aromatic compounds containing not more than 2 nitro groups.

We have now found that TNT can be obtained in over 90% yield and rapid reaction rate by nitrating DNT with a mixture of HNO_3 and oleum at a temperature of about 70°C or higher. We have also unexpectedly found that the nitration of toluene in the aforesaid manner produces a DNT containing less than 2% of meta isomers, which is only half as much as in the current TNT process of manufacture; and that by nitrating the DNT further with a nitrating mixture of HNO_3 and oleum, a TNT product can be directly obtained having a purity sufficient for military use.

In carrying out the nitration of toluene to DNT with an anhydrous mixture of HNO_3 and oleum according to the present invention, two moles of HNO_3 are theoretically required to introduce two nitro groups into each mole of toluene; however, it is preferable to employ a small molar excess of HNO_3 , e.g. about 5%, over the theoretical amount required so as to maximize the yield of DNT produced. Considerably higher molar ratios of HNO_3 to toluene, e.g. 3 to 8 moles of HNO_3 per mole of toluene, can be employed to accomplish the dinitration reaction at the low temperatures employed in the present process, but provide no technical advantage. Further, it is preferable to employ a small, e.g. about a 10% molar excess of HNO_3 relative to free SO_3 , since an excess of SO_3 over HNO_3 is undesirable due to the competing sulfonation reaction with toluene. The ratio of free SO_3 to H_2SO_4 in the oleum employed is relatively less important and is conveniently about 1 part by weight per 4 parts H_2SO_4 . The nitration of toluene to DNT can be carried out at minus 40° – 50°C or lower; but it is preferably carried out at a temperature not ex-

ceeding about $+10^{\circ}\text{C}$ and especially at between about -10°C and -20°C . At these preferred temperatures the dinitration is rapid and the production of undesired meta isomers is minimized. Reaction temperatures above about 40°C are undesirable, since they promote the formation of undesired meta isomers.

After the dinitration reaction is complete, the reaction mixture containing the DNT and spent acid liquor can be charged with fresh HNO_3 and SO_3 , as required, and the resulting mixture is heated to a temperature of about 70°C or higher, preferably between 70° and 100°C , and especially about 90°C , to effect the nitration of DNT to TNT. The amount of HNO_3 is sufficient to provide at least one mole of HNO_3 per mole of DNT, as theoretically required. The amount of SO_3 is preferably about one mole, e.g. from 0.9 to 1.1 moles of SO_3 , per mole of HNO_3 . The ratio of SO_3 to H_2SO_4 employed in the trinitration reaction is not critical, since sulfonation is not a competing reaction in the nitration of DNT; it is conveniently about 0.43 to 1 by weight, which corresponds to oleum containing approximately 30% free SO_3 .

To ensure a rapid and complete nitration of DNT to TNT, an excess of HNO_3 and SO_3 is employed, preferably from about 3 to about 5 moles each of HNO_3 and SO_3 per mole of DNT. The use of excess reagents in the trinitration step does not impair the economy of the total process for TNT manufacture, since the excess HNO_3 and SO_3 can be employed in the dinitration step of a closed-loop process. Preferably, in a closed-loop process the amounts of HNO_3 and SO_3 added for the trinitration step are such that the acid liquor, recovered by filtration of the trinitration reaction mixture to remove TNT, has approximately the composition of the HNO_3 -oleum nitration mixture required for the dinitration step.

In the process of the invention additional amounts of sulfuric acid are SO by reaction of free SO_3 with the water formed in the nitration reactions. The production of such additional amounts of sulfuric acid results in an increase in both the volume and ratio of H_2SO_4 to SO_3 , which is undesirable in closed-loop operation. To prevent such build-up of sulfuric acid in a closed-loop process, a sufficient portion of the reaction mixture obtained in the dinitration step is withdrawn and the DNT content is separated therefrom, e.g. by extraction with a suitable inert organic solvent, e.g. methylene dichloride, which is then separated from the DNT by distillation. The DNT thus recovered is returned to said reaction mixture for the trinitration step and the acid liquor remaining after removal of its content of DNT is disposed or utilized in suitable manner.

We have found that the reaction mass obtained in the trinitration step possesses a high capacity for retaining the unsymmetrical TNT isomers and other by-products and DNT in solution, with the result that TNT of excellent purity can be obtained directly from the cooled reaction mass by filtration followed by washing with water to remove adherent acid. The TNT crystals recovered from the reaction mass can be further purified by washing with sulfuric acid or nitric acid of a concentration at least about 50%, or mixtures of such acids.

The following example specifically illustrates the process of this invention.

EXAMPLE

Part A. Preparation of Dinitrotoluene (DNT)

A nitrating mixture of 25.1 g (398 mmoles) of absolute nitric acid and 143.9 g of 20% oleum consisting of 29.6 g (370 mmoles) free SO_3 and 114.3 g H_2SO_4 was placed in a two-piece glass reactor provided with a thermometer and a glass agitator shaft with a Teflon blade. The bottom part of the reactor was a 100 ml flask, which was joined to the top by a ground glass flange and was fitted with an internal glass coil for heating the contents with steam or cooling with water; and the top part was fitted with a thermometer port and three other ground glass joints. 17.3 g (188 mmoles) of toluene (refined grade) were added dropwise during 100 minutes to the agitated nitrating mixture which was maintained at about -8 to -10°C , after which the reaction mixture was agitated for 15 minutes at -8 to -10°C and then allowed to warm to room temperature.

A sample (18.2g) of the solution thus obtained was removed, poured on ice and the DNT was separated. A yield of 99.4% (based on toluene) of DNT having the following composition (by glc analysis) was obtained:

2,6- DNT	15.6%
2,3- and 2,5- DNT	0.6%
2,4- DNT	82.6%
3,4- DNT	1.2%
	100.0%

The total meta isomers in the DNT thus obtained was 1.8%.

Part B. Preparation of TNT

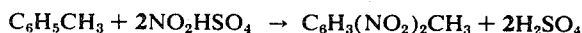
The solution remaining in the reactor after removal of the 18.2g sample in part A was fortified by adding 60.1 g. (751 mmoles) of SO_3 (a stabilized SO_3 marketed under the name Sulfan by Allied Chemical Corp.) and 46.1 g. (731 mmoles) of absolute HNO_3 in that order with ice bath cooling from dropping funnels equipped with Teflon stopcocks. The total amounts of SO_3 and HNO_3 in the resulting solution were 751 mmoles each, allowing for the HNO_3 remaining after the dinitration step and also the amount removed in the 18.2 g. aliquot; and the amount of DNT remaining in the reactor was 171 mmoles. Trinitration was effected by heating the resulting solution at 70°C for 30 minutes, then at 80°C for 15 minutes and finally at 90°C for 15 minutes. This was accomplished by placing an oil bath preheated to 70°C around the flask and introducing steam through the reactor coil to heat the solution to 70°C within 1 minute, and maintaining the temperature within $\pm 2^{\circ}\text{C}$ by intermittent flow of a small amount of cooling water. The temperature was raised to 80°C in 40 seconds and finally from 80° to 90°C in 45 seconds. The hot reaction mixture was poured into an Erlenmeyer flask and cooled to 0°C and the TNT crystals thus obtained were separated by filtration on a coarse, sintered glass funnel. The mother liquor was chilled to -10°C and filtered to obtain a second crop of TNT crystals on a separate filter. The crystal crops were combined, washed with water until acid free and dried. The dried crystals had a setting point of 80.2°C and weighed 36 grams, corresponding to a yield of 94% of theory based on the toluene starting material. (A product of somewhat higher setting point was obtained by washing the filter cake with 70% H_2SO_4 prior to washing with water as described below).

About 5% of the DNT was oxidized and the remaining 95% was converted to TNT. About 1% of the TNT was subsequently oxidized, resulting in a net yield of about 94%. The products of the DNT oxidation were

CO₂, CO, N₂O and H₂O while the TNT was converted, at least in part, to several by-products, mainly 2,4,6-trinitrobenzoic acid.

RECYCLE CLOSED-LOOP OPERATION

The acid filtrate, obtained by removing the TNT crystals from the reactor mass in Part B above had very nearly the desired composition for the dinitration reaction, as described in part A above, and its composition was adjusted, as required, by addition of a small amount of HNO₃ or SO₃ to provide the aforesaid ratio of 398 mmoles HNO₃, 370 mmoles SO₃ per 188 mmoles toluene as employed in part A above. The cycle was then repeated by adding 17.3 g. (188 mmoles) of toluene and conducting the dinitration and trinitration reactions as described in part A and part B above, respectively. For fortification of the reaction mass resulting from the dinitration reaction, the amount of DNT formed, the amount of HNO₃ remaining and the amount of H₂SO₄ produced were calculated on the assumption of a 100% yield of DNT according to the equation:



and adding the necessary amounts of SO₃ and HNO₃ to adjust the acids for trinitration as described in part B.

Nine cycles were carried out in the foregoing manner. The composition of the acid phases used for the dinitration and trinitration reactions in three of the cycles is shown in the following table:

ACID PHASE COMPOSITION

Cycle	Component	Dinitration		Trinitration	
		(%)	(%)	(%)	(%)
1	H ₂ SO ₄	67.6	67.6	49.7	56.0
	SO ₃	17.5	17.5	21.8	24.6
	HNO ₃	14.9	14.9	17.2	19.4
	NOHSO ₄	0	0	0	0
	Organics	0	0	11.3	0
		100.0	100.0	100.0	100.0
6	H ₂ SO ₄	58.2	61.4	45.9	53.1
	SO ₃	15.0	15.8	19.8	22.9
	HNO ₃	12.8	13.5	15.5	17.9
	NOHSO ₄	8.8	9.3	5.3	6.1
	Organics	5.2	0	13.5	0
		100.0	100.0	100.0	100.0
9	H ₂ SO ₄	58.0	61.1	45.7	52.6
	SO ₃	14.7	15.4	19.7	22.7
	HNO ₃	12.4	13.0	15.5	17.8
	NOHSO ₄	10.0	10.5	6.0	6.9
	Organics	4.9	0	13.1	0
		100.0	100.0	100.0	100.0

The dinitration reaction in the first cycle was carried out with fresh acids so that neither nitrosyl sulfuric acid (NOHSO₄) nor dissolved organics were present. NOHSO₄ was formed during each of the trinitration reactions due to the competing oxidation reaction. However, the buildup of NOHSO₄ was compensated by removing a portion of the filtrate after each trinitration reaction for analysis.

The NOHSO₄ concentration was lower in the trinitration step than in the dinitration step due to dilution by the SO₃ and HNO₃ added to fortify the acid phase. The dissolved organics present in the acid phase at the start of the dinitration reaction were the impurities and TNT that had not crystallized out following the previous trinitration reaction; these materials plus DNT constituted the organics dissolved in the acid phase at the start of the trinitration reaction. The columns headed

by %' give the relative weight percentage composition of the acids exclusive of the dissolved organics.

The average yield of TNT based on toluene was 93% of theory for the nine cycles. This figure included the TNT that crystallized out of the acid phase, together with the impure TNT that remained in solution, (2,4,6-TNT was the major component of the organic materials in the acid phase after crystallization of the TNT; the total amount of dissolved organics was regarded simply as impure TNT). The method of operation did not allow determination of a value for the yield of crystallized TNT due to loss of a portion of the dissolved TNT in the by-product acid. The quality of the TNT obtained in the nine cycles of operation was consistently good, indicating that the acid phase possessed a high capacity for retaining the unsymmetrical TNT isomers and other by-products.

PURIFYING TNT

The wet filter cake of TNT crystals obtained by separating the crystals from the nitration mixture in the last cycle, was slurried in about an equal weight of 70% H₂SO₄ (corresponding to about 1.5 g. of 70% H₂SO₄ per gram of TNT solids) at room temperature. The slurry was filtered and the filter cake was washed acid-free with water and dried. The purified TNT crystals thus obtained had a setting point of 80.3° C., which is satisfactory for type I military explosive-grade TNT. The foregoing demonstrates that the novel process is capable of producing TNT of acceptable military explosive grade without the use of the conventional sellite purification process.

The present process can be readily adapted for continuous manufacture of TNT. The drawing shows a schematic flow diagram of a continuous closed-loop process for production of TNT from toluene according to the process of the present invention. Metered streams of toluene and fresh or recycled nitrating acid, in the ratio of 2.1 moles of HNO₃, 2 moles of SO₃ and about 3-4 moles of H₂SO₄ per mole of toluene, are fed continuously to the dinitrator which is operated at about -10° C. Fresh nitrating acid is used for startup; thereafter recycled nitrating acid from the trinitrator is employed (see below). The dinitrator can be a stainless steel tank provided with an agitator, cooling coils, bottom feed ports and top outlet for effluent reaction mixture. The average residence time of the reactants in the dinitrator is about 30 minutes, which as noted above is substantially longer than the time required to complete the nitration of toluene to DNT under these conditions. The effluent from the nitrator containing the DNT in H₂SO₄ and little if any HNO₃ or NO₂HSO₄, is divided such that, for example, 80% thereof flows directly to the trinitrator and 20% flows to a solvent extraction unit, such as a Scheibel extractor, wherein the DNT is continuously extracted from the acid liquor with a suitable solvent, e.g. methylene chloride. The surplus acid from the extractor is pumped to storage for recovery or sale and the DNT extract flows to a still (not shown), where the solvent is separated by distillation, and the DNT thus obtained is fed to the trinitrator. Additional HNO₃ and SO₃ are continuously fed into the trinitrator along with the effluent from the dinitrator so as to provide approximately 3 moles of NO₂HSO₄ (3 moles each of HNO₃ and SO₃) per mole of DNT. The trinitrator, which can be a vessel similar to the dinitrator but provided with heating coils, is operated at about 90° C.

with an average residence time of reactants of about 1 hour, which is sufficient to complete the conversion of DNT to TNT under these conditions. Instead of a single trinitration vessel, the reaction mixture can be fed, for example, through a series of three trinitrators, wherein the first is maintained at 70° C., the second at 80° C. and the third at 90° C. and the residence time in each is suitably adjusted, as illustrated in the foregoing example. The reaction mixture from the trinitrator flows to a workup installation, where it is cooled to about -10° C. to crystallize the TNT, and the TNT crystals are filtered off and purified, if necessary, by suitable means, e.g. washing with 70% H₂SO₄, then washed with water and dried. The mother liquors separated from the crystallized TNT are of essentially the required concentration to convert the toluene feed to DNT and are recycled to the dinitrator, together with additional HNO₃ and SO₃, if required.

It is thus evident that the process of this invention provides an important advance in the manufacture of TNT, including the following specific advantages:

1. It provides rapid nitration reaction rates and high yields of TNT.

2. It produces TNT of military specification grade directly by crystallization from the trinitration reaction mixture followed by washing with water. If necessary, the TNT can be further purified by washing with conc. H₂SO₄.

3. It obviates the sellite process currently used to purify crude TNT and eliminates the "red water" disposal problem associated therewith, which is a major pollution problem that plagues the current method for TNT manufacture.

4. It does not produce NO₂ fumes as by-products because both NO₂HSO₄ and NOHSO₄ are thermally stable in the anhydrous HNO₃ - oleum system used in both the di- and trinitration reactions, thereby eliminating the atmospheric pollution due to NO₂ fumes evolved in the current process for TNT.

We wish it to be understood that we do not desire to be limited to the exact method and detail of construction described for obvious modification will occur to persons skilled in the art.

What is claimed is:

1. A process for producing TNT which comprises contacting toluene with an anhydrous nitrating mixture of HNO₃ and oleum at a temperature below 40° C to produce DNT, heating the DNT in situ at a temperature of at least about 70° C with an anhydrous nitrating mixture of HNO₃ and oleum to produce TNT, and recovering the TNT from the reaction mixture, wherein the amount of HNO₃ is at least 2 moles per mole of toluene and the amount of free SO₃ in the oleum does not exceed 1 mole per mole of HNO₃ in the nitration of toluene to DNT, and the amount of HNO₃ is between 1 and 5 moles per mole of DNT in the nitration of DNT to TNT.

2. The process according to claim 1, wherein the toluene is nitrated at a temperature between about -20° C. and +10° C. and the DNT is nitrated at a temperature between about 70° C. and 100° C.

3. The process according to claim 1, wherein the amount of HNO₃ is between about 3 and 5 moles per mole of DNT and the amount of free SO₃ in the oleum is about 1 mole per mole of HNO₃ in the nitration of DNT.

4. The process according to claim 3, wherein the amount of HNO₃ is between about 2.1 and 2.2 moles per mole of toluene.

5. The process according to claim 1, wherein the reaction mixture from which the TNT is recovered is recycled for use in the nitration of toluene.

6. The process according to claim 5, wherein a portion of the reaction mixture obtained by nitrating toluene to DNT, is contacted with an inert, immiscible liquid organic solvent for DNT, the resulting solvent solution of DNT is separated from the acid liquor, and the DNT is recovered from the solvent solution and submitted along with the remainder of the reaction mixture to the nitration of DNT to TNT.

7. The process according to claim 6, wherein the organic solvent is methylene chloride.

8. The process according to claim 1, wherein the TNT separated from the reaction mixture is washed with an acid of the group consisting of 50-100% H₂SO₄ and 50-100% HNO₃ and mixtures thereof.

9. A continuous process for producing TNT, which comprises feeding into a first reaction vessel toluene and an anhydrous nitrating mixture of HNO₃ and oleum wherein the amount of HNO₃ is at least 2 moles per mole of toluene and the amount of free SO₃ in the oleum does not exceed 1 mole per mole of HNO₃, maintaining the reactants in said vessel at a temperature below 40° C. to product DNT, passing the reaction mixture from said first reaction vessel into a second reaction vessel together with sufficient anhydrous nitrating mixture of HNO₃ and oleum to provide a ratio of between 1 and 5 moles of HNO₃ per mole of DNT, maintaining said mixture in the second vessel at a temperature of at least about 70° C. to product TNT, separating the TNT from the reaction mixture, and recycling the recovered reaction mixture to the first reaction vessel.

10. The process according to claim 9, wherein a portion of the reaction mixture from the first reaction vessel is contacted with an inert, immiscible liquid organic solvent for the DNT, the resulting solvent solution of DNT is separated from said reaction mixture, and the DNT is recovered from said solvent solution and introduced along with the remainder of the reaction mixture to the second reaction vessel.

11. The process according to claim 10, wherein the organic solvent is methylene chloride.

12. The process according to claim 10, wherein the amount of HNO₃ is between about 2.1 and 2.2 moles per mole of toluene and the amount of free SO₃ in the oleum is less than 1 mole per mole of HNO₃ in the first reaction vessel, and the amount of HNO₃ is between about 3 and 5 moles per mole of DNT and the amount of free SO₃ in the oleum is about 1 mole per mole of HNO₃ in the second reaction vessel.

13. The process according to claim 12, wherein the oleum in the first reaction vessel contains about 20% by weight of free SO₃ and the oleum in the second reaction vessel contains about 30% by weight of free SO₃.

14. The process according to claim 12, wherein the first reaction vessel is operated at a temperature between about -20° C. and +10° C. and the second reaction vessel is operated at a temperature between about 70° C. and 100° C.

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