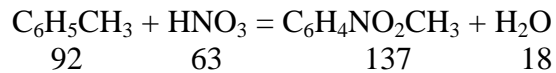


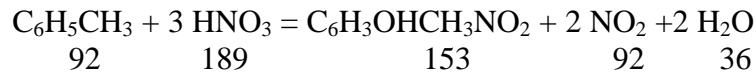
MATERIAL BALANCE

THE NITRATION PROCESS:

The reaction of toluene with nitric acid is normally out in the presence of sulphuric acid in order to avoid the slowing down of the reaction by dilution of nitric acid as it is used up and as water is liberated. The basic stoichiometric equation is: (*Ref. -1*)



The toluene used in the process is assumed to contain 1 percent of paraffins in accordance with a typical specification for nitration toluene. This will be unreacted and it is known that a small amount of the toluene remains unreacted. For a working basis this is assumed to amount to 1 percent and in addition a further 1 per cent is assumed to be converted by the side reaction to nitrocresol.



Then 1 ton of toluene will yield a product containing 0.01 ton of paraffins, 0.01 ton of unreacted toluene, $0.01 \times \frac{153}{92} = 0.016$ ton of nitrocresol and, $0.97 \times \frac{137}{92} = 1.443$ tons of mononitrotoluenes.

The amount of nitric and sulphuric acids to carry out this conversion must now be calculated. The stoichiometric equivalents of 100 per cent nitric acid, HNO₃, are:

$$\begin{array}{ll} \text{To mononitrotoluenes} & 0.97 \times \frac{63}{92} = 0.664 \\ \text{To nitrocresol} & 0.01 \times \frac{189}{92} = 0.020 \\ \text{Total} & = 0.684 \text{ ton} \end{array}$$

Allowing 1 per cent excess of nitric acid, 0.691 ton of 100 per cent HNO₃ are required.

For nitration, the choice can be made between the two strengths of nitric acid normally available. These are 60 per cent direct from the absorption tower of an ammonia oxidation process or 96 per cent from a nitric acid concentration plant. The sulphuric acid for making up the mixed acid for nitration can be obtained at 96 per cent strength from a plant carrying out the concentration of dilute sulphuric acid. The substitution of one nitro-group toluene can be carried out at reasonable rates, and with almost complete consumption of the nitric acid used, if the final acid strength is not allowed to fall below 70 percent. For calculating this process, it will be assumed that the final acid strength does not fall below 75 percent at which corrosion of cast iron and mild steel equipment in the cold is not serious.

This concentration allows 60 per cent nitric acid to be used without requiring an excessive quantity of sulphuric acid as will be calculated. The total water in the final acid is made up of that brought in with the nitric and sulphuric acids plus that formed in the reaction. If r is the quantity of 96 per cent sulphuric acid required, the total water from various sources is

$$\text{From 96 per cent sulphuric acid} \quad = 0.04 \gamma$$

$$\text{From 60 per cent nitric acid} \quad \frac{0.4}{0.6} \times 0.691 = 0.460$$

$$\text{From mononitrotoluene reaction} \quad 0.691 \times \frac{18}{92} = 0.190$$

$$\text{From nitrocresol reaction} \quad 0.01 \times \frac{36}{92} = 0.004$$

Since the final ratio of sulphuric acid to water is 75:25 we have:

$$\frac{0.96 \times \gamma}{0.04\gamma + 0.460 + 0.190 + 0.004} = \frac{75}{25}$$

from which γ equals 2.338 tons.

The quantities involved in the reactions can now be tabulated:

Table 4.1

Reactants			Products	
Toluene	0.97		Mononitrotoluenes	1.443
	0.01		Toluene	0.01
	0.01	0.990	Nitrocresol	0.016
Paraffins		0.010	Paraffines	0.010
60% Nitric Acid			HNO ₃	0.007
HNO ₃	0.691		NO ₂	0.010
H ₂ O	0.460	1.151		
96% Sulphuric Acid			H ₂ SO ₄	2.241
H ₂ SO ₄	2.241		H ² O	0.751
H ₂ O	0.097	2.338		
		4.488		4.488

Separation of Mononitrotoluenes:

The reaction products form a two-phase mixture, which can be separated *by* gravity owing to the difference in densities between the crude nitration product and the spent acid. These are respectively 1.167 and 1.670 at 18° C. The separation is not perfect and the Technical Records of Explosives Supply give a sulphuric acid concentration of 0.8 per cent in the nitration products and a mononitrotoluene content of 0.2 per cent in the acid.

The nitration balance can then be split up:

Table 4.2

<i>Component</i>	<i>Acid layer</i>	<i>Nitration product</i>
Mononitrotoluenes	0.003	1.440
Toluene	-	0.010
Nitrocresol	-	0.016
Paraffins	-	0.010
HNO ₃	0.007	-
H ₂ SO ₄	2.223	0.018
H ₂ O	0.747	0.004
	2.980	1.498

The NO₂ is assumed to pass from the system as fume.

Addition of Cycle Acid:

These are balance sheets for the nitration process and show the quantities theoretically necessary to meet the conditions so far laid down. These result in the nitrating acid having a composition:

HNO ₃	0.691	19.81%
H ₂ SO ₄	2.241	64.22%
H ₂ O	0.557	15.97%
	3.489	100.00%

It has been found by experience that a concentration of nitric acid as high as this causes a rapid nitration reaction and in batch nitrations could lead to a loss of control. To avoid this the concentration should be kept down to about 5 per cent as a precautionary measure. This is done by recirculating a large quantity of the spent acid separated after the nitration reaction.

Since the fresh mixed acid has 19.81 per cent of nitric acid in a total of 3.489 tons, about three times this quantity of cycle acid needs to be added to bring the final concentration of nitric acid down to 5 per cent.

This is an approximation and an exact balance needs to take in the nitric acid content of the cycle acid. If X is the weight of cycle acid added

$$\frac{0.691 + X \frac{0.007}{2.980}}{3.489 + X} = 0.05$$

and X equals 10.82 tons. The weight of cycle acid added and a balance for mixing fresh with cycle acid can be drawn up.

Table 4.3

<i>60 % Nitric Acid</i>			<i>Mixed Nitrating Acid</i>	
HNO ₃	0.691	1.151	HNO ₃	5.0%
H ₂ O	0.460		H ₂ SO ₄	72.1%
			H ₂ O	22.7%
			NO ₂ C ₁₀ H ₄ CH ₃	0.2%
<i>96% Sulphuric Acid</i>				100.0%
H ₂ SO ₄	2.241			
H ₂ O	0.097			
	2.338			
<i>Cycle Acid</i>				
HNO ₃	0.025			
H ₂ SO ₄	8.080			
H ₂ O	2.690			
NO ₂ C ₆ H ₄ CH ₃	0.025			
		10.820		
		14.309		

MATERIAL BALANCE FOR THE NITRATION REACTION:

To obtain the final materials balance for the process in which one of toluene is reacted with nitric acid, the quantity of cycle acid must be added to the balance already made. The actual quantities involved in tons day are given in the table below.

Table 4.4

Input			Output		
<i>Mixed Acid</i>			<i>Nitration product</i>		
<i>Item</i>	<i>Weight</i>	<i>Per cent</i>	<i>Item</i>	<i>Weight</i>	<i>Per cent</i>
HNO ₃	0.716	5.0	NO ₂ C ₆ H ₄ CH ₃	1.436	96.4
H ₂ SO ₄	10.321	72.1	NO ₂ CH ₃ C ₆ H ₃ OH	0.016	1.1
H ₂ O	3.247	22.7	C ₇ H ₈	0.010	0.7
NO ₂ C ₆ H ₄ CH ₃	0.025	0.2	Paraffins	0.010	0.7
	14.309	100.0	H ₂ SO ₄	0.012	0.8
			H ₂ O	0.004	0.3
				1.488	100.0

<i>Toluene</i>			<i>Acid layer</i>		
C ₇ H ₈	0.99	99.0	NO ₂ C ₆ H ₄ CH ₃	0.032	0.2
Paraffins	0.01	1.0	HNO ₃	0.032	0.2
	1.00	100.0	H ₂ SO ₄	10.318	74.8
			H ₂ O	3.429	24.8
				13.811	100.0

			<i>Fumes</i>		
			NO ₂	0.010	
Total	15.309		Total	15.309	

Washing the Nitration Products:

The process of purifying the crude nitration product after its separation from the used acid begins with a washing process. The treatment of the acid to recover the sulphuric acid in a concentration suitable for use again is not considered as part of the main material balance being drawn up on the toluene. The washing process is carried out in three stages: the first,

a water wash to take out the sulphuric acid, the second an alkali wash to neutralize the nitro cresol and any other acidic bodies, followed by a further water wash to remove excess alkali and dissolved salts.

First Wash:

The amount of water to be used in the first wash should be kept as small as possible, consistent with good washing, because of the loss of nitration product in solution. Experiments have shown that the water layer will contain about 0.7 percent by weight of mononitrotoluene and that the use of about one part by weight of water to three parts of nitration product gives satisfactory results in mixing with the removal of all the sulphuric acid. The material balance over this stage is then:

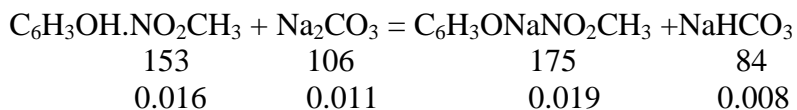
Table
4.5

Materials in		Materials out			
	<i>Crude nitration product</i>	<i>Washed nitration product</i>		<i>Water washings</i>	
Mnonitrotoluene	1.436	1.432	97%	0.004	0.7%
Nitrocresol	0.016	0.016	1.1%		
C ₇ H ₈	0.010	0.010	0.7%		
Paraffins	0.010	0.010	0.7%		
H ₂ SO ₄	0.012			0.012	2.3%
H ₂ O	0.004	0.007	0.5%	0.510	97.0%
	1.488	1.475	100.0%	0.526	100.0%
Wash water	0.513				
	2.001				
		Total: 2.001			

Alkali Wash:

In order to remove acidic bodies, particularly nitrocresol, the crude mononitrotoluenes are next washed with a dilute solution of sodium carbonate. As in the previous stage,

sufficient water is used to keep the proportion of the wash liquor up to about one-third that of the mononitrotoluenes. The nitrocresol reacts with sodium carbonate according to the equation:



Allowing for a slight excess of sodium carbonate 0.012 is added and total of 0.028 sodium salts is formed. Waste wash liquor will again contain 0.7 percent of mononitrotoluenes and the material balance for the stage is:

Table 4.6

	Materials in		Materials out	
	<i>Crude nitration product</i>	<i>Washed nitration product</i>		<i>Neutral washings</i>
Mnonitrotoluene	1.432	1.428	98.1%	0.004
Nitrocresol	0.016	Trace (Na salts)		
C ₇ H ₈	0.010	0.010	0.7%	
Paraffins	0.010	0.010	0.7%	
H ₂ O	0.007	0.007		
	1.475	1.455	100.0%	
<i>Wash liquor</i>				
H ₂ O	0.513			0.513
Na ₂ CO ₃	0.012			Na salts 0.028
	0.525			0.545
	2.00			Total: 2.00

Final Water Wash:

A final wash with water is given to remove traces of excess alkali and sodium salts in solution, which might be concentrated in subsequent processing to the point where they became explosive.

The materials balance is:

Table 4.6

Materials in		Materials out		
	<i>Crude nitration product</i>	<i>Washed nitration product</i>		<i>Waste water</i>
Mnonitrotoluene	1.428	1.424	98.1%	0.004
Nitrocresol	trace			
C ₇ H ₈	0.010	0.010	0.7%	
Paraffins	0.010	0.010	0.7%	
H ₂ O	0.007	0.007	0.5%	
	1.455	1.451	100.0%	
Wash water				
H ₂ O	0.513			0.513
				Na salts trace
				0.517
	1.968	Total: 1.968		

Purification of the Crude Mononitrotoluenes:

The washed nitration products shown in the material balance above is contaminated with paraffins, unreacted toluene and water. There may, in addition, be traces of polynitro compounds or other side reaction products. These must be separated before the mixed mononitrotoluenes can be obtained in a suitable state for the subsequent processing—separation of the isomers. The separation can be conveniently effected by batch distillation. The method of doing this is to charge one day's output to a batch still, take off water, paraffins and toluene as forerunnings, an intermediate fraction and about four-fifths of the

mononitrotoluenes as a heart-cut. The next day's output is charged on top of the residue) together with the intermediates) and the process repeated. This is repeated until the residue of about one-fifth of the still charge represents about 4 percent of the mononitrotoluenes distilled and it is then discarded. The material balance of each distillation is different, but it is not necessary to work through each in detail to obtain the overall result corresponding with one day's operation. From the composition of the nitration product in the balance for the last washing process, the overall balance is:

Table 4.7

Materials in		Materials out	
Washed nitration product	1.451	Forerunnings	0.027
		Pure mononitrotoluenes	1.367
		Residue	0.057
	1.451		1.451

It was calculated that feed of 18.105 tons of toluene per 24 h, with which are associated 0.183 tons of paraffins, 17.739 tons react with 12.143 tons of nitric acid to produce 26.20 tons of mixed mononitrotoluenes, leading in full scale production after allowing for losses to an output of 25 tons a day, while 0.183 tons react with 0.366 tons of nitric acid to form nitrocresol, and 0.183 tons remain unconverted. The nitric acid requirement is therefore 12.509 tons/24 h, and, allowing an excess of 1 per cent, 12.637 tons are used in the form of 22.906 tons of 60 per cent nitric acid. The reaction also requires 96 per cent sulphuric acid, and the two acids are mixed in a jet with cycle acid from the separator. *Table* below is a materials balance sheet over the nitrators. It shows the mixed nitric acid, sulphuric acid, and cycle

Table 4.8 Material Balance Sheet over Nitrators

Basis: 24 hrs.

Materials in	Tons		Tons	Materials out
H ₂ O	59.381	Mixed Acids	26.262	MNT
H ₂ SO ₄	188.75			0.293
HNO ₃	13.094	Toluene	0.183	C ₇ H ₈
MNT	0.457			0.183
	261.682		0.919	H ₂ SO ₄
C ₇ H ₈	18.105		0.073	H ₂ O
Paraffins	0.183		27.213	
	18.288		0.585	MNT
			0.585	HNO ₃
			188.696	H ₂ SO ₄
			62.710	H ₂ O
			252.576	
			0.183	NO ₂
TOTAL	279.970		279.972	TOTAL

acid containing some mononitrotoluene entering the nitrators, into which is also fed the toluene, which contains paraffins as impurity. A stream of liquid leaves the nitrators, consisting of nitrobody layer and acid layer, and some fumes are evolved. The composition of each stream is shown, with the totals for each, and the -inlet and outlet balance.

The acid layer is separated from the nitrobody in a gravity separator, and the nitrobody is then treated in three Holley-Mott washers in series, for which operation *Table* below is a materials balance sheet. This sheet sets out the composition of the feed to the first washer, and the washing agent for each washer, and shows the composition of the three washings and of the washed nitrobody, together with an overall materials balance.

The process then changes from continuous operation to batch distillation. The plant works continuously for 5 days, or 120 hr week, except for the distillation of the washed nitrobody in 4 batches a week. *Table 4.10* is a materials balance sheet for one of these batch distillations. The residue of 0.512 tons from each batch is collected for the 4 batches, and then the 26.05 tons are distilled to give a further 20.8 tons of mononitrotoluene and 5.2 tons of final residues; this second distillation is not shown on a material balance sheet.

Table 4.9. Materials Balance Sheet over Washer:

Basis: 24 hrs.

Materials in	Tons		Tons	Materials out
MNT	26.261			
Nitrocresol	0.293			
C ₇ H ₈	0.183			
Paraffin	0.183		9.327	H ₂ O
H ₂ SO ₄	0.219		0.219	H ₂ SO ₄
H ₂ O	0.073		0.073	MNT
	27.212	Nitrobody	9.619	
Water	9.382	Water		
H ₂ O	9.382		9.382	H ₂ O
Na ₂ CO ₃	0.219		0.510	N-creso salts
			0.073	MNT
	9.601		9.965	
			9.382	HO ₂
			0.004	Na ₂ CO ₃
			0.073	MNT
Water	9.382		9.459	
			26.042	MNT
			0.183	Paraffin
			0.128	H ₂ O
			0.183	C ₇ H ₈
			26.596	
TOTAL	279.970		279.972	TOTAL

The operation then becomes continuous again. The 20.05 tons of first distillate per batch, equivalent to 104.2 tons per 120 h, plus the 20.8 of second distillate, give a feed of 25 tons of mixed mononitrotoluenes per 24 h to the continuous still, for which *Table 4.11* is a materials balance sheet.

Table 4.10. Materials Balance Sheet For first Batch Distillation

Basis: One batch

4 batches in 120 hours.

Materials in	Tons			Tons	Materials out
MNT	32.562			0.229	C ₇ H ₈
C ₇ H ₈	0.229	0.229	Paraffins		
Paraffins	0.229	0.16	H ₂ O		
H ₂ O	0.160	0.160			
	33.180				
			20.05	MNT	
			6.512	MNT	
TOTAL	33.180		33.180	TOTAL	

Table 4.11. Materials Balance Sheet For Continuous Still

Basis: 24 hours

Materials in	Tons			Tons	Materials out
Ortho	15.000			14.700	Ortho
Meta	1.000	0.150	Meta		
Para	9.000	0.150	Para		
	25.000	15.000			
		0.300	Ortho		
		0.850	Meta		
		8.850	Para		
		10.000			
TOTAL	25.000	25.000	TOTAL		

This shows substantial removal of the ortho-compound in the fraction from the top of the still, while the para-compound with some meta-isomer and small amounts of the ortho-isomer is obtained from the bottom of the *Table 4.12* is a material balance sheet for the centrifuge.

Table 4.12. Materials Balance Sheet over Centrifuge

Basis: 24 hours

Materials in	Tons		Tons	Materials out
Ortho	0.300			
Meta	0.850			
Para	8.850			
	10.000			
			7.500	Para
			0.300	Ortho
			0.850	Meta
			1.350	Para
			2.500	
TOTAL	10.000		10.000	TOTAL