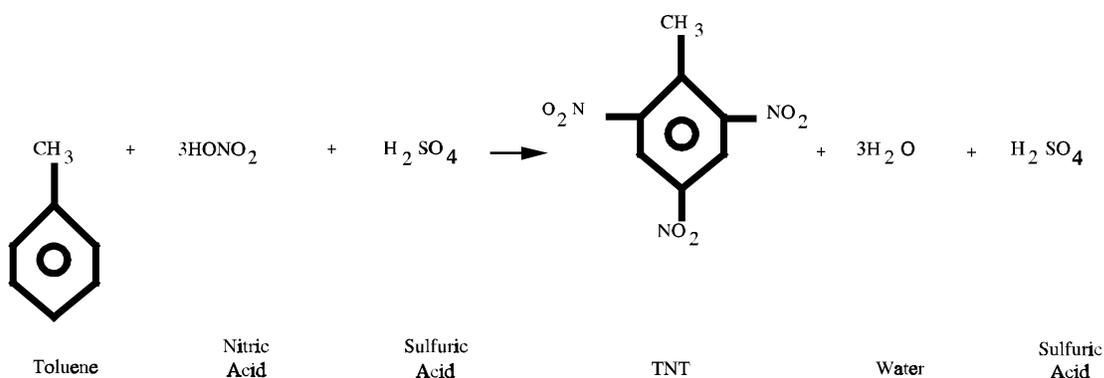## 6.3 Explosives

6.3.1 General[1]

An explosive is a material that, under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of large amounts of heat and gas. There are two major categories, high explosives and low explosives. High explosives are further divided into initiating, or primary, high explosives and secondary high explosives. Initiating high explosives are very sensitive and are generally used in small quantities in detonators and percussion caps to set off larger quantities of secondary high explosives. Secondary high explosives, chiefly nitrates, nitro compounds, and nitramines, are much less sensitive to mechanical or thermal shock, but they explode with great violence when set off by an initiating explosive. The chief secondary high explosives manufactured for commercial and military use are ammonium nitrate blasting agents and 2,4,6,-trinitrotoluene (TNT). Low explosives, such as black powder and nitrocellulose, undergo relatively slow autocombustion when set off and evolve large volumes of gas in a definite and controllable manner. Many different types of explosives are manufactured. As examples of high and low explosives, the production of TNT and nitrocellulose (NC) are discussed below.

6.3.2 TNT Production[1-3,6]

TNT may be prepared by either a continuous or a batch process, using toluene, nitric acid (HNO_3) and sulfuric acid as raw materials. The production of TNT follows the same chemical process, regardless of whether batch or continuous method is used. The flow chart for TNT production is shown in Figure 6.3-1. The overall chemical reaction may be expressed as:

| Toluene | | Nitric Acid | | Sulfuric Acid | | TNT | | Water | | Sulfuric Acid |

The production of TNT by nitration of toluene is a 3-stage process performed in a series of reactors, as shown in Figure 6.3-2. The mixed acid stream is shown to flow countercurrent to the flow of the organic stream. Toluene and spent acid fortified with a 60 percent HNO_3 solution are fed into the first reactor. The organic layer formed in the first reactor is pumped into the second reactor, where it is subjected to further nitration with acid from the third reactor fortified with additional HNO_3. The product from the second nitration step, a mixture of all possible isomers of dinitrotoluene (DNT), is pumped to the third reactor. In the final reaction, the DNT is treated with a fresh feed of nitric acid and oleum (a solution of sulfur trioxide [SO_3] in anhydrous sulfuric acid). The crude TNT from this third nitration consists primarily of 2,4,6-trinitrotoluene. The crude TNT is washed to remove free acid, and the wash water (yellow water) is recycled to the early nitration stages. The washed TNT is
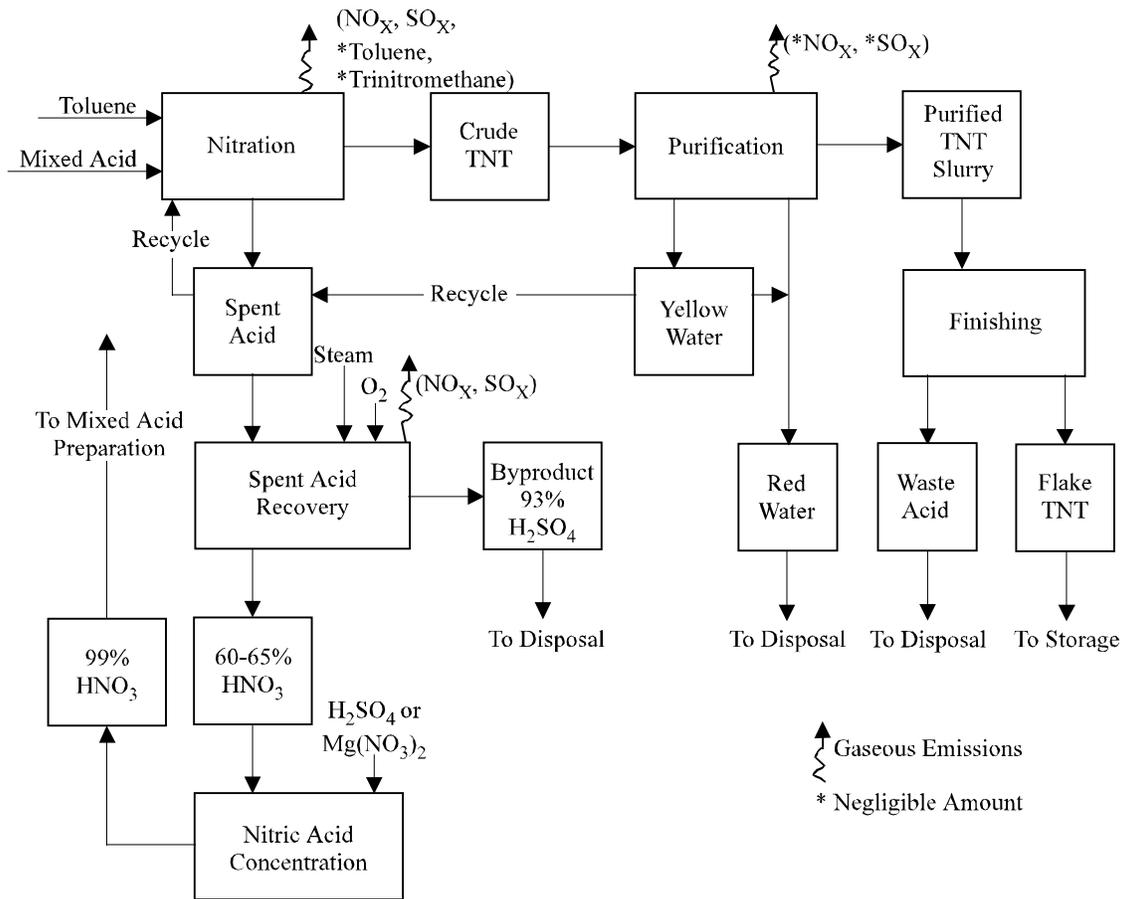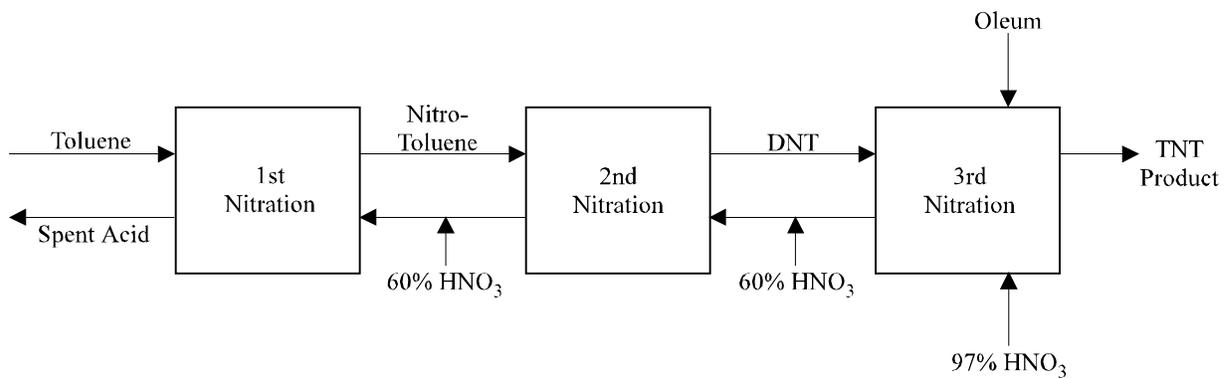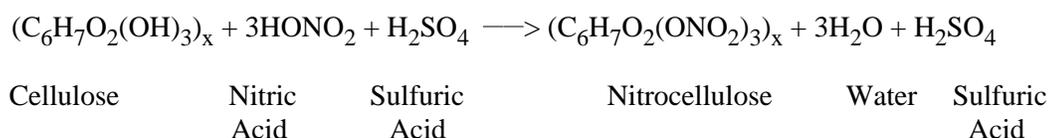
Figure 6.3-1. TNT production.

Figure 6.3-2. Nitration of toluene to form trinitrotoluene.

then neutralized with soda ash and treated with a 16 percent aqueous sodium sulfite (Sellite) solution to remove contaminating isomers. The Sellite waste solution (red water) from the purification process is discharged directly as a liquid waste stream, is collected and sold, or is concentrated to a slurry and incinerated. Finally, the TNT crystals are melted and passed through hot air dryers, where most of the water is evaporated. The dehydrated product is solidified, and the TNT flakes packaged for transfer to a storage or loading area.

6.3.3 Nitrocellulose Production[1,6]

Nitrocellulose is commonly prepared by the batch-type mechanical dipper process. A newly developed continuous nitration processing method is also being used. In batch production, cellulose in the form of cotton linters, fibers, or specially prepared wood pulp is purified by boiling and bleaching. The dry and purified cotton linters or wood pulp are added to mixed nitric and sulfuric acid in metal reaction vessels known as dipping pots. The reaction is represented by:

$$(C_6H_7O_2(OH)_3)_x + 3HONO_2 + H_2SO_4 \longrightarrow (C_6H_7O_2(ONO_2)_3)_x + 3H_2O + H_2SO_4$$

| Cellulose | Nitric Acid | Sulfuric Acid | Nitrocellulose | Water | Sulfuric Acid |

Following nitration, the crude NC is centrifuged to remove most of the spent nitrating acids and is put through a series of water washing and boiling treatments to purify the final product.

6.3.4 Emissions And Controls[2-3,5-7]

Oxides of nitrogen (NO_x) and sulfur (SO_x) are the major emissions from the processes involving the manufacture, concentration, and recovery of acids in the nitration process of explosives manufacturing. Emissions from the manufacture of nitric and sulfuric acid are discussed in other sections. Trinitromethane (TNM) is a gaseous byproduct of the nitration process of TNT manufacture. Volatile organic compound (VOC) emissions result primarily from fugitive vapors from various solvent recovery operations. Explosive wastes and contaminated packaging material are regularly disposed of by open burning, and such results in uncontrolled emissions, mainly of NO_x and particulate matter. Experimental burns of several explosives to determine "typical" emission factors for the open burning of TNT are presented in Table 6.3-1.

Table 6.3-1 (English Units). EMISSION FACTORS FOR THE OPEN BURNING OF TNT[a,b]
(lb pollution/ton TNT burned)

Type Of Explosive	Particulates	Nitrogen Oxides	Carbon Monoxide	Volatile Organic Compounds
TNT	180.0	150.0	56.0	1.1

[a] Reference 7. Particulate emissions are soot. VOC is nonmethane.
[b] The burns were made on very small quantities of TNT, with test apparatus designed to simulate open burning conditions. Since such test simulations can never replicate actual open burning, it is advisable to use the factors in this Table with caution.

In the manufacture of TNT, emissions from the nitrators containing NO, NO_2, N_2O, TNM, and some toluene are passed through a fume recovery system to extract NO_x as nitric acid, and then are vented through scrubbers to the atmosphere. Final emissions contain quantities of unabsorbed NO_x and TNM. Emissions may also come from the production of Sellite solution and the incineration of red water. Red water incineration results in atmospheric emissions of NO_x, SO_2, and ash (primarily Na_2SO_4.)

In the manufacture of nitrocellulose, emissions from reactor pots and centrifuges are vented to a NO_x water absorber. The weak HNO_3 solution is transferred to the acid concentration system. Absorber emissions are mainly NO_x. Another possible source of emissions is the boiling tubs, where steam and acid vapors vent to the absorber.

The most important fact affecting emissions from explosives manufacture is the type and efficiency of the manufacturing process. The efficiency of the acid and fume recovery systems for TNT manufacture will directly affect the atmospheric emissions. In addition, the degree to which acids are exposed to the atmosphere during the manufacturing process affects the NO_x and SO_x emissions. For nitrocellulose production, emissions are influenced by the nitrogen content and the desired product quality. Operating conditions will also affect emissions. Both TNT and nitrocellulose can be produced in batch processes. Such processes may never reach steady state, emission concentrations may vary considerably with time, and fluctuations in emissions will influence the efficiency of control methods.

Several measures may be taken to reduce emissions from explosive manufacturing. The effects of various control devices and process changes, along with emission factors for explosives manufacturing, are shown in Tables 6.3-2 and 6.3-3. The emission factors are all related to the amount of product produced and are appropriate either for estimating long-term emissions or for evaluating plant operation at full production conditions. For short time periods, or for plants with intermittent operating schedules, the emission factors in Tables 6.3-2 and 6.3-3 should be used with caution because processes not associated with the nitration step are often not in operation at the same time as the nitration reactor.

Table 6.3-2 (Metric Units). EMISSION FACTORS FOR EXPLOSIVES MANUFACTURING[a,b]

EMISSION FACTOR RATING: C

Process	Particulates	Sulfur Oxides (SO_2)	Nitrogen Oxides (NO_2)	Nitric Acid Mist (100% HNO_3)	Sulfur Acid Mist (100% H_2SO_4)
TNT - Batch process[c]					
Nitration reactors					
Fume recovery	—	—	12.5 (3 - 19)	0.5 (0.15 - 0.95)	—
Acid recovery	—	—	27.5 (0.5 - 68)	46 (0.005 - 137)	—
Nitric acid concentrators	—	—	18.5 (8 - 36)	—	4.5 (0.15 - 13.5)
Sulfuric acid concentrators[d]					
Electrostatic precipitator (exit)	—	7 (2 - 20)	20 (1 - 40)	—	32.5 (0.5 - 94)
Electrostatic precipitator with scrubber[e]	—	Neg	20 (1 - 40)	—	2.5 (2 - 3)
Red water incinerator					
Uncontrolled[f]	12.5 (0.015 - 63)	1 (0.025 - 1.75)	13 (0.75 - 50)	—	—
Wet scrubber[g]	0.5	1 (0.025 - 1.75)	2.5	—	—
Sellite exhaust	—	29.5 (0.005 - 88)	—	—	3 (0.3 - 8)
TNT - Continuous process[h]					
Nitration reactors					
Fume recovery	—	—	4 (3.35 - 5)	0.5 (0.15 - 0.95)	—
Acid recovery	—	—	1.5 (0.5 - 2.25)	0.01 (0.005 - 0.015)	—

Table 6.3-2 (cont.).

Process	Particulates	Sulfur Oxides (SO$_2$)	Nitrogen Oxides (NO$_2$)	Nitric Acid Mist (100% HNO$_3$)	Sulfur Acid Mist (100% H$_2$SO$_4$)
Red water incinerator	0.13 (0.015 - 0.25)	0.12 (0.025 - 0.22)	3.5 (3 - 4.2)	—	—
Nitrocellulose[h]					
Nitration reactors[i]	—	0.7 (0.04 - 1)	7 (1.85 - 17)	9.5 (0.25 - 18)	—
Nitric acid concentrator	—	—	7 (5 - 9)	—	—
Sulfuric acid concentrator	—	34 (0.2 - 67)	—	—	0.3
Boiling tubs	—	—	1	—	—

[a] For some processes, considerable variations in emissions have been reported. Average of reported values is shown first; ranges in parentheses. Where only 1 number is given, only 1 source test was available. Emission factors are in units of kg of pollutant per Mg of TNT or nitrocellulose produced.

[b] Significant emissions of VOCs have not been reported for the explosives industry. However, negligible emissions of toluene and TNM from nitration reactors have been reported in TNT manufacture. Also, fugitive VOC emissions may result from various solvent recovery operations. See Reference 6.

[c] Reference 5.

[d] Acid mist emissions influenced by nitrobody levels and type of furnace fuel.

[e] No data available for NO$_x$ emissions after scrubber. NO$_x$ emissions are assumed to be unaffected by scrubber.

[f] Use low end of range for modern efficient units, high end for less efficient units.

[g] Apparent reductions in NO$_x$ and particulate after control may not be significant because these values are based on only 1 test result.

[h] Reference 4.

[i] For product with low nitrogen content (12%), use high end of range. For products with higher nitrogen content, use lower end of range.

Table 6.3-3 (English Units). EMISSION FACTORS FOR EXPLOSIVES MANUFACTURING[a,b]

EMISSION FACTOR RATING: C

Process	Particulates	Sulfur Oxides (SO_2)	Nitrogen Oxides (NO_2)	Nitric Acid Mist $(100\% HNO_3)$	Sulfur Acid Mist $(100\% H_2SO_4)$
TNT - Batch process[c]					
Nitration reactors					
Fume recovery	—	—	25 (6 - 38)	1 (0.3 - 1.9)	—
Acid recovery	—	—	55 (1 - 136)	92 (0.02 - 275)	—
Nitric acid concentrators	—	—	37 (16 - 72)	—	9 (0.3 - 27)
Sulfuric acid concentrators[d]					
Electrostatic precipitator (exit)	—	14 (4 - 40)	40 (2 - 80)	—	65 (1 - 188)
Electrostatic precipitator with scrubber[e]	—	Neg	40 (2 - 80)		5 (4 - 6)
Red water incinerator					
Uncontrolled[f]	25 (0.03 - 126)	2 (0.05 - 3.5)	26 (1.5 - 101)	—	—
Wet scrubber[g]	1	2 (0.05 - 3.5)	5	—	—
Sellite exhaust	—	59 (0.01 - 177)	—	—	6 (0.6 - 16)
TNT - Continuous process[h]					
Nitration reactors					
Fume recovery	—	—	8 (6.7 - 10)	1 (0.3 - 1.9)	—
Acid recovery	—	—	3 (1 - 4.5)	0.02 (0.01 - 0.03)	—

Table 6.3-3 (cont.).

Process	Particulates	Sulfur Oxides (SO$_2$)	Nitrogen Oxides (NO$_2$)	Nitric Acid Mist (100% HNO$_3$)	Sulfur Acid Mist (100% H$_2$SO$_4$)
Red water incinerator	0.25 (0.03 - 0.5)	0.24 (0.05 - 0.43)	7 (6.1 - 8.4)	—	—
Nitrocellulose[h]					
Nitration reactors[i]	—	1.4 (0.8 - 2)	14 (3.7 - 34)	19 (0.5 - 36)	—
Nitric acid concentrator	—	—	14 (10 - 18)	—	—
Sulfuric acid concentrator	—	68 (0.4 - 135)	—	—	0.6
Boiling tubs	—	—	2	—	—

[a] For some processes, considerable variations in emissions have been reported. Average of reported values is shown first, ranges in parentheses. Where only 1 number is given, only 1 source test was available. Emission factors are in units of pounds of pollutant per ton of TNT or nitrocellulose produced.

[b] Significant emissions of VOCs have not been reported for the explosives industry. However, negligible emissions of toluene and TNM from nitration reactors have been reported in TNT manufacture. Also, fugitive VOC emissions may result from various solvent recovery operations. See Reference 6.

[c] Reference 5.

[d] Acid mist emissions influenced by nitrobody levels and type of furnace fuel.

[e] No data available for NO$_x$ emissions after scrubber. NO$_x$ emissions are assumed to be unaffected by scrubber.

[f] Use low end of range for modern efficient units, high end for less efficient units.

[g] Apparent reductions in NO$_x$ and particulate after control may not be significant because these values are based on only 1 test result.

[h] Reference 4.

[i] For product with low nitrogen content (12%), use high end of range. For products with higher nitrogen content, use lower end of range.

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