

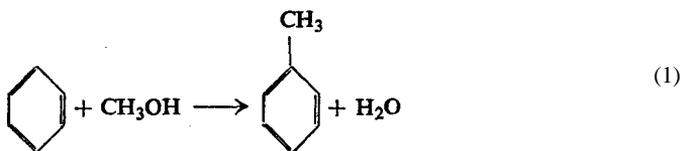
CHAPTER IX
TNT MANUFACTURE

TOLUENE

TOLUENE is the principal raw material for the manufacture of TNT. It is produced from light oil and from the gases obtained by the dry distillation of coal.

In some oil producing countries (e.g. U.S.S.R.), toluene is obtained from aromatic fractions of petroleum or by aromatization of heavy petroleum hydrocarbons by cracking processes (in Poland studies on aromatization of petroleum were carried out by K. Smolenski [1] between 1922 and 1939). In war-time the demand for toluene for nitration was so large, that these two sources were inadequate. During World War II new methods of toluene manufacture on an industrial scale were developed starting from benzene and methyl alcohol and from n-heptane.

The reaction of toluene formation from benzene and methyl alcohol can be represented by the following scheme:

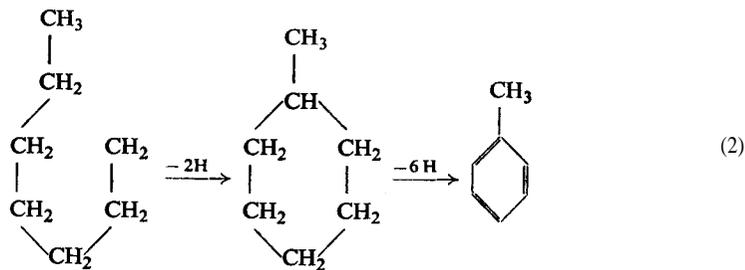


The reaction proceeds at a temperature of 340-380°C and at pressure of 30-35 atm in the presence of zinc diphosphate on silica catalyst.

Since under these conditions higher homologues of toluene (xylenes, etc.) can readily be formed, a large excess of benzene is used for the process. The yield of toluene obtainable by this method (calculated on methyl alcohol) is close to the theoretical one.

In Germany, during World War II nearly 4000 tons of toluene were produced monthly by this method.

The method of preparation of toluene from n-heptane was mainly developed in the U.S.A. It is based on the following reaction:



It is carried out at 480-530°C at a pressure of 15 atm in the presence of a $\text{Cr}_2\text{O}_3 + \text{MoO}_3$ catalyst, on a Al_2O_3 or MgO carrier. The yield obtained amounts to 72% of the theoretical.

Crude toluene obtained by this method contains 3-5% olefins, so it must be purified by refining with sulphuric acid, followed by washing with water and distillation.

Toluene for nitration must be of high purity, in fact almost chemically pure. The boiling range of the product should be 109-111°C, with at least 95% distilling within a range of 1°C. The specific gravity should be 0.870 ± 0.002 at 15°C.

Only an insignificant amount of unsaturated aliphatic hydrocarbons is admissible in toluene for nitration. They may be detected by shaking a sample with concentrated sulphuric acid. If the toluene is pure, the sulphuric acid separates very quickly as a colourless or slightly yellow ("straw yellow") lower layer. If unsaturated hydrocarbons are present in significant quantities a stable emulsion is often formed, and the sulphuric acid turns brown or even black. Such a product cannot be used for nitration.

Nowadays an infra-red spectrophotometric technique is usually applied in testing toluene for purity (Gore and Patberg [2]).

It should be noted that toluene purity cannot be assessed by the ultra-violet technique, since strong bands produced by toluene (as about 262 $\text{m}\mu$) mask those that may be produced by olefins.

Toluene obtained from petroleum should contain no more than 4% of paraffinic hydrocarbons. The content of the latter is determined by sulphonation of the toluene with concentrated sulphuric acid or with 20% oleum. Sulphonated aromatic compounds are washed out with water to leave the paraffin hydrocarbon which is not affected by oleum.

If the toluene contains a higher proportion of paraffinic hydrocarbons it can still be nitrated, provided the mononitration product is subjected to distillation (preferably with steam) to remove saturated hydrocarbons. According to Desseigne, Gladel, Guillemin and Sousselier [3], toluene containing 30-40% of saturated hydrocarbons can be treated in this way to obtain nitrotoluene suitable for further nitration.

The U.S.S.R. specification (OST 464) for nitration grade toluene requires the following properties (Table 81):

TABLE 81

	Toluene from coal	Toluene from petroleum
Specific gravity at 15°C	0.870±0.002	0.863-0.870
Boiling range	109-111°C	108.5-111°C
	(95% distils within a range of 1°C)	
Colouration with sulphuric acid (comparison with standard potassium dichromate solutions of concentrations x grammes per 1 l. of 50% sulphuric acid)	x 0.5	x 0.5
Bromine number (y grammes of bromine decolourized by 100 ml. of toluene)	y 0.8	y 0.8
Sulphonation test with 5% oleum	-	not less than 96 vol. % should be sulphonated

According to a German standard, toluene for nitration shall distil within a range not wider than 0.8°C.

NITRATION OF TOLUENE TO TNT

GENERAL REMARKS

The nitration of toluene to TNT is carried out by successive introduction of nitro groups. Such a method is justified from the points of view both of safety and economy as it permits the most efficient use of acids and produces a final product of high purity due to the purification of the intermediate products obtained in the separate stages of the process.

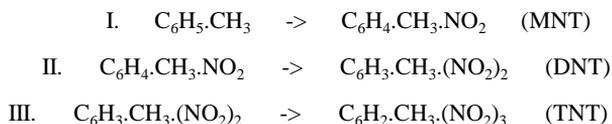
Nitration is commonly carried out in three stages, and less often in two stages.

The principle of economical acid usage is simply achieved by using the spent acid from a higher nitration stage for the lower stage, after it has been fortified to the required concentration.

The diagram presented below illustrates the reactions occurring, and shows the average composition of the products and heat effects of the reactions. Another diagram (Gorst [4]) gives the yields of nitration of intermediate compounds.

THREE-STAGE PROCESS FOR MANUFACTURE OF TNT

The three-stage nitration of toluene to TNT comprises the following processes:



OLD FRENCH PROCESS

This process, as described by Pascal [5], was used in France both during World War I and in the early period of time between the two wars. Separate operations in the three-stage nitration process are carried out in the following way:

Nitration of toluene to MNT (“mononitration”). To introduce one nitro group into toluene a mixture of acids is used (sp. gr. 1.672) of composition:

HNO ₃	28%
H ₂ SO ₄	56%
H ₂ O	16%

Toluene (650 kg) is run into a nitrator, and 1580 kg of the nitrating mixture is added with vigorous stirring. The temperature in the nitrator should be maintained at 40°C by using a cooling jacket and a coil situated inside the nitrator. After the reagents have been mixed thoroughly the temperature of the mixture should be raised to 60°C and maintained then for 45 min to 1 hr. When the reaction has been completed the nitrator contents are cooled to room temperature and the stirrer is stopped. The liquid is allowed to stand still until quiet, and then the lower layer, i.e. the spent acid, is drained off.

The composition of the spent acid (sp. gr. 1.66) is:

HNO ₃	trace
H ₂ SO ₄	69%
H ₂ O	29%
NO ₂	2%

From 650 kg of toluene 910-950 kg of MNT is obtained, i.e. 140-146 kg for 100 kg of toluene. Since the theoretical yield is 149 kg of MNT for 100 kg of toluene, the actual yield amounts of 94-98% of theory. Losses are due mainly to dissolution of the nitration product in the spent acid (up to 4.5% of the total amount of nitro-toluene).

Nitration of MNT to DNT (“dinitration”). The acid from the first stage of nitration, composed of:

HNO ₃	32%
H ₂ SO ₄	61%
H ₂ O	7%

is run into MNT over a period of 2 hr, with constant stirring. The amount of the acid should correspond to a 45% excess of HNO₃. During stirring the temperature should be maintained at 40°C for the first hour and at 50°C for the next hour.

When all the acid has been run into the nitrator the mixture is heated to 90°C and maintained at this temperature for half an hour. Then the nitrator contents are cooled to 60-65°C, i.e. to a temperature at which crude DNT remains liquid (m. p. 56-58°C).

Spent acid from dinitration has the composition:

HNO ₃	2.5%
H ₂ SO ₄	76.0%
H ₂ O	20.0%
NO ₂	1.5%

DNT, being lighter than the spent acid (sp. gr. at 60°C - 1.337, at 80°C - 1.318) rises to the surface. The spent acid is drained off and DNT, while still hot, is run into a vessel with concentrated sulphuric acid.

From 100 kg MNT 130 kg of DNT are obtained (the theoretical amount is equal 133 kg), hence the yield amounts to 98% of the theoretical. When calculated on toluene, 188 kg of DNT are obtained from 100 kg of toluene (theoretically 198 kg), which corresponds to 95% of the theoretical yield.

Nitration of DNT to TNT ("trinitration"). An anhydrous mixture of acids is used for the third stage of nitration. Mixture of the composition

HNO ₃	49%
H ₂ SO ₄	49%
NO ₂	2%

is run into the nitrator where it is heated to 80-90°C. Then the DNT from the preceding stage of nitration dissolved in concentrated sulphuric acid in 1: 1 weight ratio is added with stirring. Prior to mixing, the solution is heated to 60°C.

The resultant composition of the nitrating mixture is:

HNO ₃	19%
H ₂ SO ₄	80%
NO ₂	1%

1500 kg of it are used for 1000 kg of DNT, this being one charge.

The two solutions are stirred for about 2 hr during which time the temperature of the liquid should rise to 105°C. The nitrator contents are then heated up to 120°C, and this temperature is maintained for one hour and a half.

In consequence of such drastic conditions of nitration several side reactions of oxidation and break-down processes take place, giving rise to the products mentioned above (trinitrobenzoic acid, trinitrobenzene, tetranitromethane). A decomposition reaction (p. 76) also gives off a large volume of carbon monoxide, which may form an explosive mixture with air. Several explosions of such mixtures have been described.

When nitration is completed, stirring is stopped. TNT separates from the spent acid, forming the upper layer (sp. gr. of TNT at 80°C is 1.467, and at 100° it is 1.443).

Spent acid from trinitration has the composition:

HNO ₃	1.5%
H ₂ SO ₄	92.0%
H ₂ O	4.0%
NO ₂	2.5%

Separation of the molten product by decantation at this moment would result in heavy losses, as the solubility of TNT in hot acid is rather high (3.5% at 50%). For this reason the separation of TNT may be carried out in one of the following ways:

1. The reaction mixture is run into a cooling crystallizer. TNT solidifies on the surface of the liquid, forming a crust which is stripped off and washed with water. To the remaining acid 7% water is added, thus changing the solubility of TNT in the acid and causing a second batch of TNT to rise to the surface.

2. Another method of TNT separation from spent acid consists in bringing the TNT to crystallization point by stirring and adding water to the nitrator contents until cool. The reaction mixture is then transferred to filters to separate the crystals from the acid.

From 100 kg of DNT 102 kg of TNT are obtained (theoretical yield 124 kg), which makes about 82% of the theoretical yield.

When calculated on toluene, 190 kg of TNT are obtained from 100 kg (instead of 246 kg calculated theoretically) which makes the actual yield nearly 77% of theory.

Acid usage control. The French method is based on the use of the spent acid from trinitration for dinitration after it has been fortified, and on further utilization of the spent acid from dinitration in the mononitration stage. The composition of the mixtures is calculated as described above.

The spent acid obtained from mononitration by the method described should contain traces of nitric acid (0.2-0.4% of HNO_3). Its absence may be an indication that the amount of nitric acid used for the nitration was insufficient and consequently that part of the toluene has remained unnitrate. In such cases the portion of acid used for the next batches should be richer in HNO_3 , since in the old French method the unreacted toluene is not distilled off from the mononitrotoluenes.

The H_2SO_4 content in the spent acid should not be less than 70%. A lower content is not advisable, for a less concentrated sulphuric acid may attack the iron equipment.

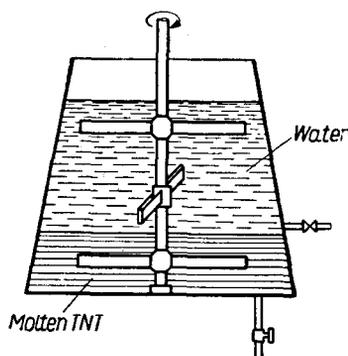


FIG. 78. Wooden tank for washing TNT (Pascal [51]).

Washing the TNT and preparing it for final purification. Crude, separated TNT, as described above, is transferred to a separator - a heated iron vessel, in which a temperature of 80°C or somewhat higher is maintained for about 3 hr in order to keep the product therein in a molten state. The remaining spent acid flows down to be then drawn off and added to the main portion of the spent acid. The molten TNT is transferred to a tank in which a preliminary washing (deacidification) is effected. For this purpose wooden tanks, shaped like truncated cones, are used. They are of about 20 m^3 capacity and are equipped with stirrers (Fig. 78).

15 m^3 of water heated to 85°C are run into the tank where this temperature

is maintained by introducing live steam. 4000 kg of molten TNT (the amount obtained from 4 nitrators) are run into the tank and stirred for half an hour. Then the stirrer is stopped and water decanted off. This operation is repeated 3-4 times, then the molten TNT is drained off at the bottom of the tank into pans (2 m x 0.6 x x 0.12 m), six of which are placed on top of each other on carts (Fig. 79).



FIG. 79. Pans for crystallization of TNT (Pascal [5]).

The construction of these pans is such as to allow TNT to flow down to the lowest pan after the upper ones have been filled. The TNT solidifies slowly in the and forming large crystals, separated from lower melting impurities, which accumulate in the lowest pan in the form of oil. This product is a grade III TNT (“liquid TNT”) used for the manufacture of mining explosives. The main product is removed from the pans, crushed with wooden hammers, and ground finally in a cylindrical mill. During the grinding TNT is sprayed with water to prevent it from emitting dust. The ground TNT is ready for further purification.

OLD BRITISH METHOD [6]

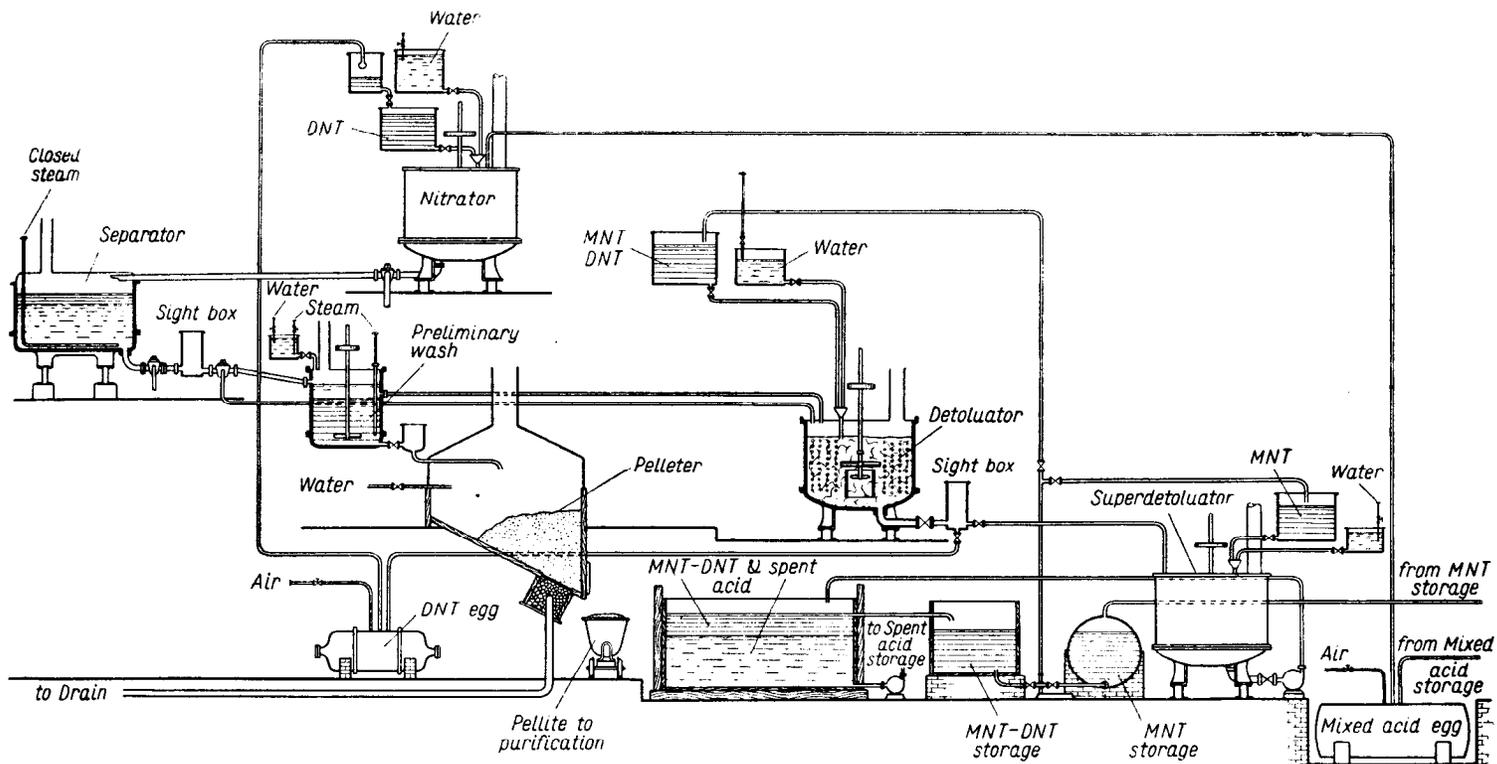
Some features of the British method which was developed during the 1914-1918 period are worth mentioning. One of them was the use of toluene derived from petroleum (Borneo petroleum), as well as toluene from coal.

Petroleum fractions distilling from 95°C to 115°C containing 55-60% of toluene, were used. The remainder constituted aliphatic hydrocarbons which would not nitrate under the conditions of the process. The MNT thus obtained, containing some petroleum components, was purified by distilling off the petroleum fraction.

Detoluation. Another characteristic feature of this method was the extraction of higher nitrated toluene derivatives, dissolved in the spent acids. The latter were conveyed to denitration and distillation (concentration) only after the nitro compounds present in them had been extracted with nitrotoluene, an operation which was called “detoluation”. Primarily it consisted in stirring the spent acids, heated to 75-80°C with a quantity of crude MNT, amounting to one quarter of the acid volume. A slight amount of nitrotoluene became nitrated due to the presence of the unreacted HNO₃ in the spent acid.

Later the detoluation operation was combined with partial nitration of MNT to DNT, by adding to the spent acid a certain quantity of nitric acid from the recovery operation (denitration).

Detoluation consisted of two stages, carried out in a detoluator and in a super-detoluator (Fig. 80).



Fro. 80. Diagram of the lay-out of manufacture of TNT with detoluation [6].

The product of trinitration was drained off to a separator, where a temperature of about 80°C was maintained by means of a steam heating coil. When the product had set in two layers the lower one, i.e. the spent acid in a quantity of about 5000 kg, was transferred to the detoluator, into which a mixture of MNT and DNT from a superdetoluator was run with simultaneous cooling and stirring. While maintaining a temperature of 75-80°C by cooling, some 240 kg of 50% nitric acid were introduced into the detoluator and after the mixture had been stirred for half an hour it was cooled to 50°C. About 160 l. of acid water from the preliminary washing of TNT were then added.

Stirring was continued for another 15 min after which the contents were allowed to remain at rest for 30 min in order to set in two separate layers. The batch was then drained off through a sight-glass, the "twice used" acid being directed into the superdetoluator, and the nitro compounds to a pressure-egg, which in turn conveyed them into a tank. From this the nitro compounds were transferred for further trinitration.

Mononitrotoluene along with the acid from which nitro compounds had been partly removed (the "twice used" acid) were run into a superdetoluator, a temperature of 50°C being maintained. Then about 200 l. of water were added to reduce the concentration of H₂SO₄ below 73%. When the mixture had been cooled to 20-25°C stirring was stopped and the nitro compounds were separated and transferred to the detoluator (as described above).

Spent acid of an average composition

H ₂ SO ₄	71.2%
HNO ₃	trace
HNO ₂	3.0%
organic matter (nitro compounds)	0.4%
H ₂ O	25.4%

was conveyed to denitration and concentration.

The spent acid from trinitration contained nearly 3.5% of nitro compounds before detoluation.

The composition of the detoluation product was:

30-40%	of MNT
40-50%	of DNT
20-30%	of TNT

It was an oily liquid with a specific gravity of 1.29-1.30.

The extraction of acids with nitrotoluene not only made possible the utilization of the dissolved nitro compounds, but it also enabled direct use to be made of the diluted nitric acid (50% of HNO₃) from the distillation of the spent acid, so that concentration of this acid was not necessary. Apart from the extraction, a partial dinitration took place, the whole process consisting of the following stages:

Toluene -> Mononitration -> Detoluation and preparation of the mixture of MNT, DNT and TNT -> TNT.

Nitration of MNT and DNT to TNT. The mixture of nitrotoluenes was converted into TNT in the following way:

The nitrator was charged with 4800-5000 kg of acids in the following proportion :

H ₂ SO ₄	79.5%
HNO ₃	17.8%
H ₂ O	2.7%

Then crude DNT from the superdetoluator was added at a temperature of 66°C (maintained by heating). The temperature was then raised to 100°C at a rate not higher than 50°C per 10 min. Nitration ended at this temperature and the melting point of a sample of TNT in the nitrator, after it had been acid washed, was 72.5°C (this corresponded to the melting point 76°C of the dry product).

After nitration was completed, 550 l. of water were run into the nitrator to reduce the solubility of the TNT in the acid, and the mixture was then transferred to a separator, where TNT was separated from the spent acid.

After 30-45 mm the acid was drained off through the sight-glass to a detoluator, and the molten TNT to a preliminary washing tank fitted with a mechanical stirrer made of acid resistant material. 160 l. of boiling water were fed into the washing tank prior to the TNT. The mixture was kept boiling by direct steam heating.

Stirring was discontinued after 5 min and after another few minutes the acidic water (containing about 14% of acid) was drained off and transported to the detoluator as described above.

The washed, molten TNT was poured in streams into a granulator, to which a stream of water was also directed, so as to make two streams collide. TNT solidified at once in the form of granules at the bottom of the granulator. Water was run away through a filter, and the TNT, still wet, was unloaded for final purification. The impurities it contained were:

water	about 19.0%
H ₂ SO ₄	0.3%
HNO ₃	1.0%
tetranitromethane	0.15%

OLD U.S.S.R. METHOD (ACCORDING TO GORST [7])

The main feature of the old method used in the U.S.S.R. is the presence of separation columns which are combined with each of the three nitrators. Also the spent acid from the third nitration stage is kept for some time in a column in which the nitro compounds swim to the top. The columns are ca. 4 m high and of ca. 2 m diameter. They are made of sheet iron, clad inside with lead.

The flow-sheet is given in Fig. 81. Toluene flows from the tank (1) through the measuring tank (2) to the mononitrator (4). The acid flows through the measuring tank (3). After nitration the products pass through the pressure-egg (5) to the separating column (6). The mono-spent acid flows through (7) to denitration, and the MNT through (8) to the "bubbler" (10) fed through (9) with the spent acid from dinitration.

TNT and then sent to denitration. Excess of spent acid from dinitration (14) is diluted to separate dissolved nitro compounds and also sent to denitration.

The main features of the nitration conditions are given below.

TABLE 82
MONONITRATION OF TOLUENE

	Nitration acid	Spent acid
HNO ₃	27-28%	0.5%
H ₂ SO ₄	54-55%	68.5%
H ₂ O	17-19%	18.7-18.8%
N ₂ O ₃	-	1.5%
Nitro compounds		0.7-0.8%
Quantity of the nitrating mixture	103% of theoretical	
Temperature of nitration :		
on mixing reagents	15-40°C	
after „ „	40-50°C	
Time :		
in winter (better cooling)	1 2 - 1 3 h r	
in summer	3 0 - 3 6 h r	
Yield of MNT	95% of theoretical	

TABLE 83
DINITRATION OF MNT

	Nitration acid	Spent acid	
		before “bubbling”	after “bubbling”
HNO ₃	23%	2.5%	0.8%
H ₂ SO ₄	67%		
H ₂ O	10%		
Nitro compounds	-	4%	0.7-0.8%
Quantity of the nitrating mixture	111% of theoretical		
Temperature of nitration :			
on mixing reagents	20-80°C		
after „ „	80-105°C		
Time	8 hr		
Yield	95% of theoretical		

Mononitration of toluene. The nitrator is filled with toluene and nitration acid is added (Table 82).

Dinitration. The nitrator is filled with MNT and nitrating mixture is added (Table 83).

Trinitration. The nitrator is filled with DNT and nitrating mixture is added (Table 84).

TABLE 84
TRINITRATION OF DNT

	Nitration acid
HNO ₃	17.5-18.5%
H ₂ SO ₄	81.5-82.5%
H ₂ O	-
Quantity of nitrating mixture	164% of theoretical
Temperature of nitration :	
on mixing reagents	72-77°C
after " "	115°C
Time	6-6½ hr

GERMAN METHOD

This method known from the description of the process at the Krümmel factory was used by the German explosives industry during World War II. Figure 82 represents a flow diagram of the manufacture of TNT by this method.

The characteristic features of the method were:

- (1) two-stage mononitration, i.e. a preliminary and a final one;
- (2) use of a nitrating mixture prepared from fresh acids for mononitration;
- (3) purification of MNT prior to further nitration to DNT;
- (4) low temperature during the trinitration process (max. 96°C);
- (5) exclusive use of iron in the plant; such units as the washing vessels for TNT being constructed from materials other than wood.

Mononitration. For the nitration of toluene a mixture T₁ of the composition:

HNO ₃	28%
H ₂ SO ₄	56%
H ₂ O	16%

was used.

The nitrating mixture is prepared from fresh concentrated nitric acid, 55% regenerated nitric acid (from the denitration of spent acid), and 96% sulphuric acid recovered by distillation. The mixture of acids is fed into the nitrator from a metering tank through a vacuum started siphon. Toluene is conveyed to the nitrator from another metering tank by means of compressed nitrogen. Air is considered as too dangerous to use, because the explosibility of mixtures of toluene vapour with air.

Plant for mononitration consists of two cast iron pre-nitrators, each having a capacity of 0.5 m³ and a main cast iron nitrator of 15 m³ capacity. Toluene and acid are run into the pre-nitrators, a toluene to acid ratio of 1 : 2.5 being maintained. The mixture is transferred to the main nitrator through an overflow in the quantity necessary to fill the nitrator (10-12 m³). A temperature of 34-40°C is maintained in both nitrators by means of a cooling coil.

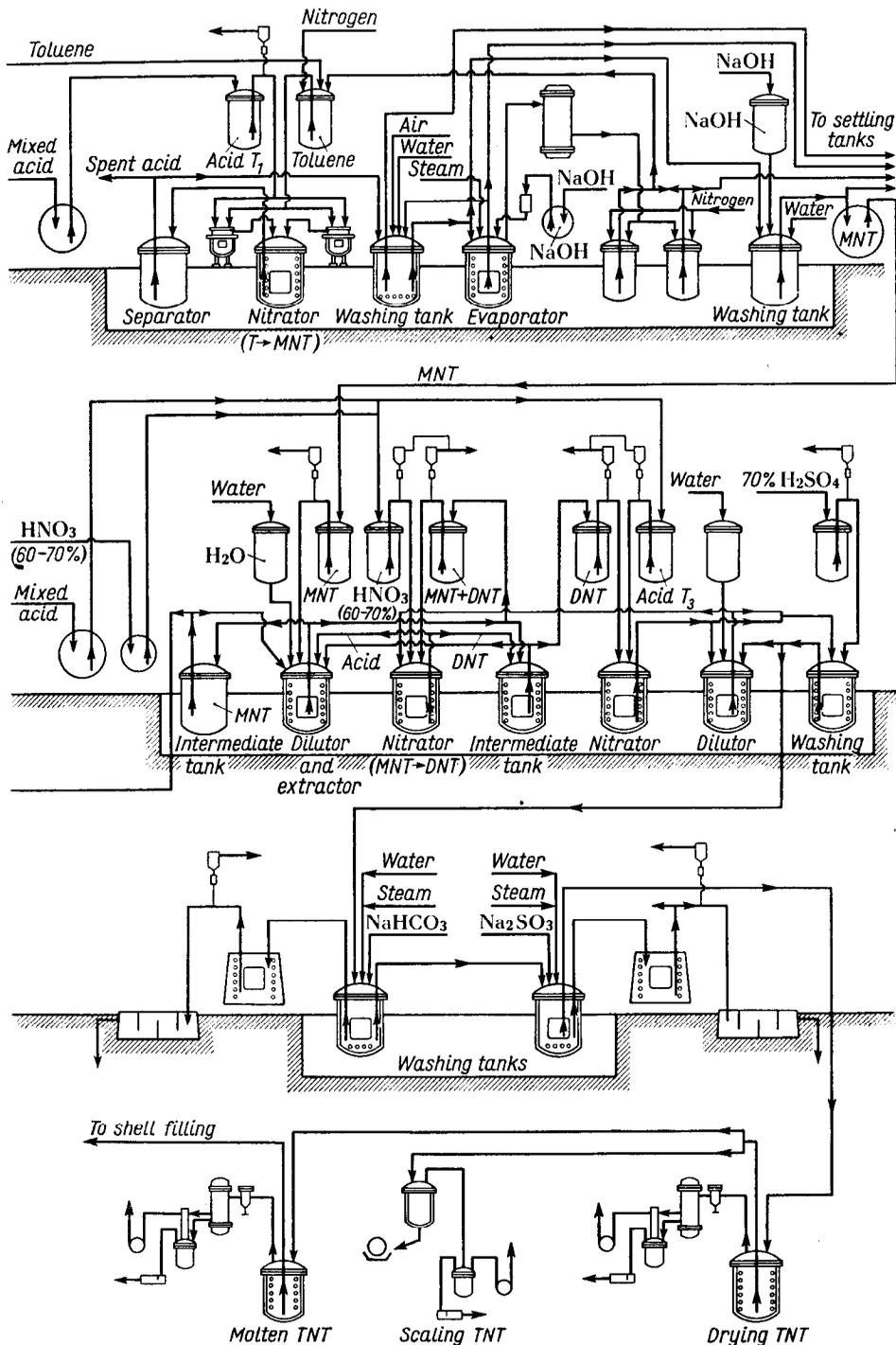


FIG. 82. Flow sheet of TNT manufacture in Krümmel.

The aim of dividing the operation into two stages is to achieve the most effective thermal control, since the conversion of toluene to mononitrotoluene is the most exothermic of all the stages of the reaction, as already mentioned in the section dealing with the theory of nitration. The operation is effected in 5-6 hr. 5000 kg of MNT is obtained from each charge of the nitrator.

When nitration has been completed the reaction mixture is transferred by compressed air to a cast iron separator with a capacity of 15 m³, where it is allowed to remain at rest for 6 hr to separate into two liquid phases. Then the spent acid is conveyed to a special cast iron tank, where it stays for a few days to recover the remainder of the MNT, which is collected from the surface and added to the toluene to be mononitrated. The spent acid, having a composition:

H ₂ SO ₄	70.0%
NO ₂	0.5%
H ₂ O	29.5%

is conveyed to denitration, which yields 67-68% sulphuric acid. Subsequently this is concentrated by distillation to obtain a 96% product.

MNT thus prepared is washed with water in a wrought iron tank, lined with sheet lead. Washing is effected by vigorous stirring until the product is free from acid (test with Congo red paper). The neutralized MNT is transferred to a so-called distillation unit (of cast iron), where it is mixed with a dilute solution of NaOH, (ca. 1%), the latter being used in a quantity equal to 1 wt. % of MNT (i.e. about 50 kg of NaOH). Washing with alkali not only aims at a complete removal of acids, but also it converts nitroresols impurities into water soluble nitroresolates.

Live steam is passed through the mixture of MNT and alkali. The unnitrated toluene and benzene (the latter is a common impurity of toluene) are thus expelled. The steam is introduced until MNT begins to distil, after all the hydrocarbons or other volatile impurities have been expelled. The condensate, containing toluene and MNT, is either recycled for nitration to liquid nitro compounds, e.g. for mining explosives, or is used as a solvent for varnishes.

The alkali layer is separated by decantation and distilled. The MNT recovered is added to the main product. The latter is conveyed from the distiller to a washing tank where it is washed with water, then again with alkali and finally with a sodium carbonate solution. The moist MNT is conveyed by means of compressed air to a cast iron tank for temporary storage.

From 100 parts of toluene 140-144 parts of MNT are obtained by this method, containing about 4% of *m*- nitrotoluene.

Dinitration. Dinitration is carried out in two stages. The first consists of the following operations. The spent acid from trinitration, of the composition:

HNO ₃	4-5%
NO ₂	34%
H ₂ SO ₄	80%
H ₂ O	11-13%

having a temperature of about 85°C is fed into a cast iron nitrator of 15 m³ capacity and cooled to 30°C.

The MNT which has already been used for the extraction of the spent acid from dinitration and which contains some DNT, is introduced at first slowly and then as HNO₃ is used up in the nitration to DNT, the flow rate is gradually increased. The temperature in the nitrator rises to 60-65°C and then falls as the nitric acid is consumed. When all the MNT has been run in, the temperature falls to 55°C. Then the second stage begins. Nitric acid of a concentration of 60-70% of HNO₃ is added. The rest of the MNT is nitrated to DNT, the temperature rising to 70-72°C. The nitration is considered complete when MNT no longer steam-distils from a sample taken from the nitrator.

The reaction mixture is allowed to remain at rest for one hour, then the acid and DNT are separated. The composition of the spent acid is:

HNO ₃	0.6%
NO ₂	5-6%
H ₂ SO ₄	78-80%
H ₂ O	13.4-16.4%

The spent acid is transferred to a cast iron dilutor-extractor, and the acid containing DNT goes to a cast iron tank for temporary storage.

The spent acid in the dilutor-extractor is diluted with water to reclaim the greater part of the dissolved DNT. The following composition of the spent acid is obtained on dilution :

HNO ₃	0.5%
NO ₂	4-5%
H ₂ SO ₄	73%
H ₂ O	21.5-22.5%

The reclaimed DNT is added to the main yield of DNT, and the spent acid in the extractor is stirred with MNT. Thus the rest of HNO₃ is used for nitration to DNT, and at the same time the dissolved DNT is extracted. The MNT obtained, containing dinitrotoluene, is used later for dinitration.

Spent acid from the extraction process has the following composition:

NO ₂	44.5%
H ₂ SO ₄	73-74%
nitro compounds	0.2-0.3%

It is transferred to an intermediate storage tank, where it remains for 4-5 days. During this time the rest of the MNT rises to the surface. It is collected and added to the main portion, while the spent acid is conveyed to distillation.

Trinitration. This can be effected either by adding acid to dinitrotoluene or by the reverse operation.

The acid liquid DNT is metered and fed into a cast iron nitrator of 12 m³ capacity by means of compressed air. Then acid T₃ of the composition:

HNO ₃	24%
H ₂ SO ₄	70%
SO ₃	6%

is added. This T₃ mixture is prepared from concentrated nitric acid and 27% oleum. Alternatively, the nitrator may be fed first with acid and then with DNT.

The DNT to acid ratio is 1:2.5-2.6 4000 kg of TNT are obtained per batch, The reaction is completed in 35 hr, and the post-reaction period is 24 hr.

If acid is added to the DNT in the nitrator, the temperature within is kept at 83-85°C, and then raised to 96°C while if DNT is added to the acid, a temperature of 74-78°C should be maintained. When the two substances have been mixed, the temperature is gradually raised to reach 96°C in one hour.

The whole process lasts for 6 hr. Then the reaction mixture is allowed to remain at rest for half an hour, to separate the product from the acid. After separation, the molten TNT is conveyed by means of compressed air to a cast iron washing tank of 8 m³ capacity and the spent acid to a wrought iron diluter of 15 m³ capacity.

The TNT in the washing tank is stirred, while hot, with nearly 70% sulphuric acid, to wash out nitrogen oxides and the rest of the HNO₃ or nitrosyl-sulphuric acid. Then it is separated from the acid and transferred to a separate, building for final washing. TNT, after it has been washed with sulphuric acid, contains 1-2% of HNO₃ and 1-2% of H₂SO₄.

The spent acid, to which the acid from TNT washing has been added, is diluted with sufficient water to obtain the composition given above. The dilution results in further separation of TNT, which is added to the main portion. The diluted spent acid is conveyed to dinitration.

Nitration plant. The nitrators for mononitration (both the pre-nitrators of 0.5 m³ capacity and the main nitrators of 15 m³ capacity) are made of cast iron. The same material is used for all other parts of the plant in which not too concentrated acids are processed, e.g. diluters, washing tank, tanks for nitro compounds, etc.

Those parts of the plant which are used for operations with concentrated acids (e.g. nitrators of 15 m³ capacity for di- and tri-nitration) are made of wrought iron.

Washing tanks for the final washing of nitro compounds with water (the water from the operation is slightly acid) are made either from stainless steel or from wrought iron lead lined or they may be constructed of bricks bonded by an acid resistant cement and lined with sheet lead and with acid resistant tiles (Fig. 83).

All pipes for conveying molten TNT from one part of the plant to another are heated either by hot water or steam jackets.

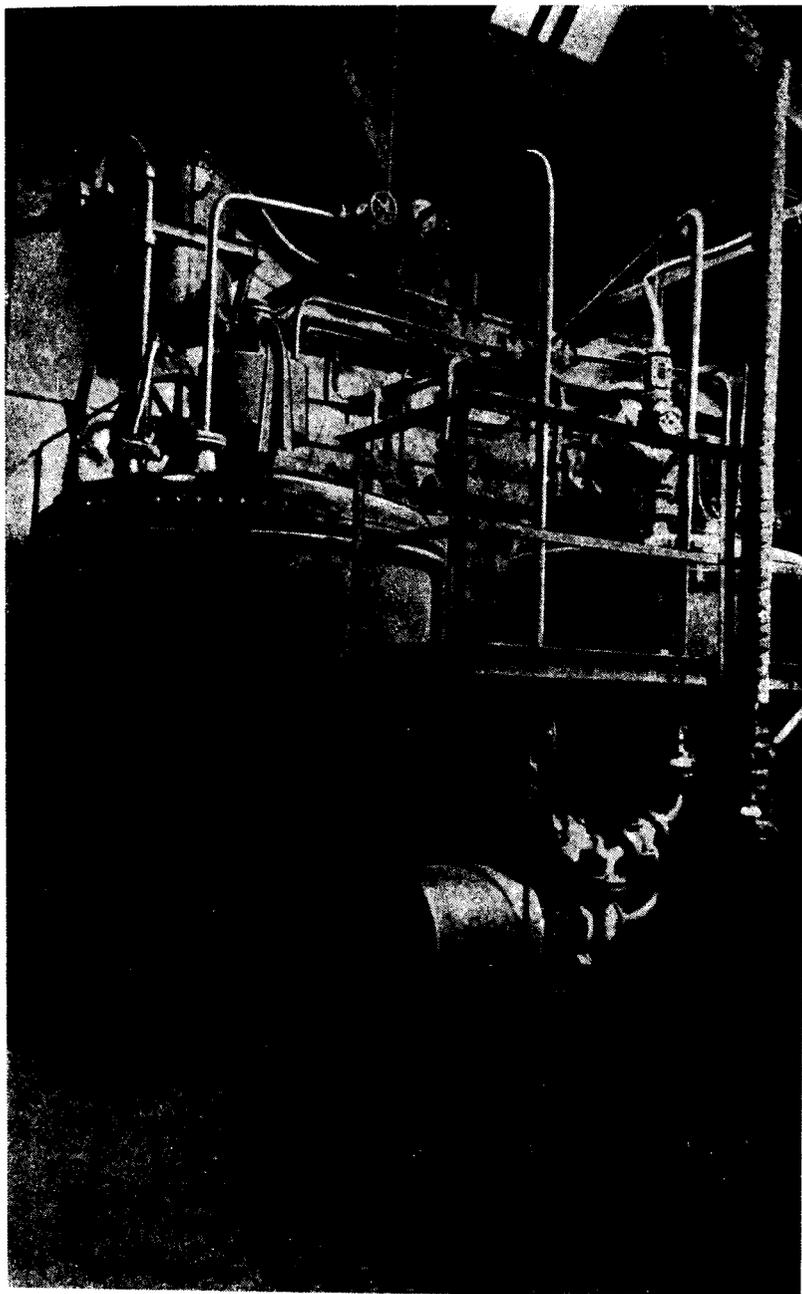


FIG. 83. Washing tank for TNT (Bofors Nobelkrut).

TWO-STAGE MANUFACTURE OF TNT (OLD ITALIAN METHOD)

In Italy a two-stage process of nitration has been used:



For the nitration of toluene to dinitrotoluene a nitrating mixture of the composition :

HNO_3	28%
H_2SO_4	60%
H_2O	12%

is used.

Crude DNT, after it had been separated from acid and washed with water, was sometimes purified by sulphitation. This material partly freed from isomers and derivatives of m-nitrotoluene, was further nitrated.

The trinitration did not differ much from that described above. The mode of separating crystalline TNT from acid is worth mentioning. In this method the nitrator played the role of a crystallizer after nitration had been completed. The reaction mixture was cooled with continuous stirring until crystallization of the TNT began. To initiate the crystallization some water was added to the nitrator. Some of the crystalline TNT obtained in a previous batch might also be added if necessary.

TNT formed crystals which, while still in a hot state, were separated from the spent acid in a vacuum filter or in a centrifuge. The degree of TNT purity could be regulated by temperature during crystallization. A very pure product could be obtained, by using a relatively high temperature (e. g. 75°C).

From the spent acid TNT of lower quality was obtained on cooling. By using a lower temperature of crystallization in the nitrator, crystals of grade II TNT were obtained which in turn could be purified by sulphitation.

Belenkii [8] describes the U.S.S.R. process of crystallization of TNT in the nitrator as follows. TNT crystallization begins at 76°C. This temperature rises by 0.5°C owing to heat of crystallization. By this time the quantity of TNT dissolved in the spent acid amounts to about three quarters of the total. At the initial stage of crystallization, at a temperature of 76°C to 75°C cooling should be very slight. Usually the flow of cooling water to the coil is stopped.

As soon as the temperature falls to 75°C the nitrator contents should be cooled vigorously and simultaneously the speed of rotation of the stirrer should be reduced to avoid pulverizing the crystals. When the temperature has fallen to 30-35°C cooling is discontinued, and almost pure α - trinitrotoluene is filtered off. If the Process of crystallization is properly carried out most of the impurities will remain in the acid.

The TNT is filtered off in a vacuum tank and washed, first with 70% and then with 45% sulphuric acid, each used in the proportion of 800 kg for 1000 kg of TNT, and finally several times with water. By using acid of a gradually reduced concentration for washing a very effective removal of oily impurities of DNT and of isomers of trinitrotoluene can be achieved.

The water-washed TNT contains 0.3-0.5% of acid. This value falls to 0.005% after repeated washing with boiling water.

Pure TNT may be granulated. For this a stream of molten TNT is introduced into a vat, at a place where two jets of cold water impinge on each other (Fig. 84). In this way a product melting at 79.5-80.2°C can be obtained.

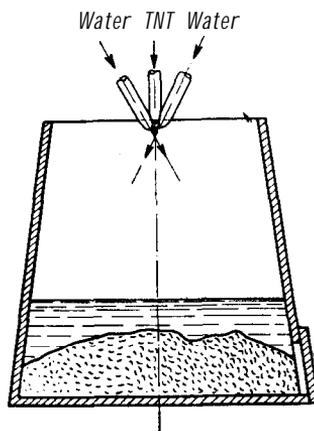


FIG. 84. Granulation of TNT.

The purity of the TNT obtained depends to a great extent on the size of the crystals formed. The best results are achieved when the crystals are of equal size and 1-2 mm in diameter.

If grade I crystalline TNT is required the acid free TNT is sulphitated. In this way the melting point may be raised to 80.5°C.

MATERIAL BALANCE

Belenkii [8] reported data on the weight of acids used for 1000 kg of crude TNT (Table 85).

TABLE 8.5
QUANTITY OF ACIDS USED FOR 1000 KG OF CRUDE TNT

Process	Mixed acid (87.3% of HNO ₃ and 8.4% of H ₂ SO ₄)		Oleum (104% H ₂ SO ₄) kg	93% sulphuric acid (as H ₂ SO ₄) kg	Spent acid from trinitration kg
	H ₂ SO ₄ kg	HNO ₃ kg			
Mononitration	34.4	342.0	~		664.5
Dinitration	35.0	349.0	197.6		841.0
Trinitration	52.2	518.3	1990.0	178.0	
Total	121.6	1209.3	2187.6	178.0	1505.5

The following nitric acid balance for the nitration of over 800 tons of toluene is given below (according to British data of 1914-1918). The balance takes into account both the quantity of nitric acid introduced into TNT in the form of nitro groups and that lost in various ways:

nitric acid used for the formation of NO ₂ groups	79.64%
oxidation losses in the form of "fumes" and in wash waters from trinitration	11.22%
losses in mononitration ("fumes", washing out with water)	1.08%
losses at denitration	1.75%
losses in the nitric acid plants	6.31%
Total	100.00%

CONTINUOUS METHODS OF NITRATION

EARLIER METHODS

Although various descriptions of the continuous nitration of aromatic hydrocarbons have been known for a long time (e.g. patents granted to the companies: Meister, Lucius and Brüning in Höchst [9]; Weiler-ter-Meer in Uerdingen [10]; Westphalisch-Anhaltische Sprengstoffe A. G. [11] and a well-known patent granted to Kubierschky [12]), until recently these methods were not widely used. Particularly in the explosives industry, conservatism and fear of the adoption of any new untraditional methods not known to be safe, have been strong enough to prevent their realization. Hence most of the proposed methods have not been put into practice.

Methods of continuous nitration of aromatic hydrocarbons may be based on one of the following principles:

1. *Nitration in the vapour phase.* In methods of this kind (e.g. the Wilhelm method [13]) a continuous stream of vapours of the aromatic hydrocarbon and nitric acid or nitrogen dioxide is introduced into the reactor. Sulphuric acid is not used in this reaction.

One drawback of this method common to all processes taking place in the gaseous phase, is the necessity of using very large units, much larger than the capacity of the reactors for liquid processes. These methods have not found any practical uses.

2. *Partial pressures method.* Othmer and his co-workers [14-16] have suggested a method in which a mixture of hydrocarbon and nitric acid of about 61% concentration is boiled. The water liberated in the reaction is distilled off with part of hydrocarbon, as an azeotrope. The two components are separated in a receiver into two layers, the water being drained off and the hydrocarbon recycled. As a result of the reaction mono- and di-nitro derivatives can be obtained. The method has been developed on the laboratory scale only.

3. *Counter-current method.* The method was suggested by Kubierschky [12]. The nitrator for nitrating benzene to nitrobenzene takes the form of a column. A mixture of nitric and sulphuric acids is introduced at the top while a mist of hydrocarbon is fed in at the bottom. The middle part of the column plays the role

of nitrator. The nitration product collects at the top, where it flows off continuously, while the spent acid, which concentrates at the bottom, always flows downwards.

There is no need for a stirrer as the reacting liquids are mixed by the natural flow resulting from the difference in specific gravities of the components. Because of certain drawbacks inherent in the difficulty of removing the heat of reaction, and as an emulsion may be formed, the method has not found any permanent practical uses.

4. *Co-current method.* Such methods are described in patents, granted to Meister, Lucius and Brüning [9] and to Weiler-ter-Meer [10]. The nitrating mixture is fed to the nitrator simultaneously with the hydrocarbon to be nitrated. A set of nitrators arranged in series may be applied to make the nitration more complete.

In industrial practice the co-current and co-current-counter-current methods are used. Thus, for example, the process in single nitrators may be based on a co-current principle while a number of nitrators may be connected in such a way as to work as a battery of counter-current system.

MODERN METHODS

The continuous methods are in many respects superior to the batch methods. One of the advantages of the continuous methods is that a much lower quantity of explosive accumulates at any moment in the plant. According to A. B. Bofors [17], in a plant with a daily production of 7.5 tons of TNT by the batch process, 10 tons of explosive were accumulating at any moment in a volume of plant of ca. 50 m³. The corresponding figures for a plant with twice the capacity run continuously are 4 tons and 12 m³ respectively.

With regard to the hazards involved, the modern continuous methods offer a much higher degree of safety, thanks to automatic regulators which keep control over the rate of feed into the nitrators and separators, the temperature of the reaction etc. In the event of a breakdown in the power supply (which usually involves danger due to the stoppage of stirring) all proportioning apparatus automatically stops and the reacting quantities in the nitrators are too small to produce any alarming rise of temperature.

All the reactors are provided with regulators controlling the supply of cooling water so as to keep the temperature constant. The regulators are so connected that in the case of a power interruption, they will fully open the feed of cooling water. Accordingly since no special action is required of the operator, he may simply leave the building when a power failure occurs.

One of the advantages of the modern methods is the small size of the apparatus. According to A. B. Bofors [17], a continuous plant with a daily production of 15 to 40 tons requires a floor surface of only ca. 150 m² in a one-storey building.

British method

The detoluation method was developed as a continuous method of manufacturing TNT in the Oldbury plant which came into operation in 1917.

In this plant each of the nitrators is connected with a separator, into which the liquid from the nitrator overflows and where the nitro compound is separated from the acid. The upper, nitro compound layer then flows to the next nitrator, containing a more concentrated acid, while the lower acid layer passes through a siphon to another nitrator, where less vigorous nitration takes place. Both liquid phases—that of the acid and that of the material being nitrated—flow in counter-current to each other. Figure 85 represents a schematic diagram of a unit for continuous nitration (after MacNab [18]).

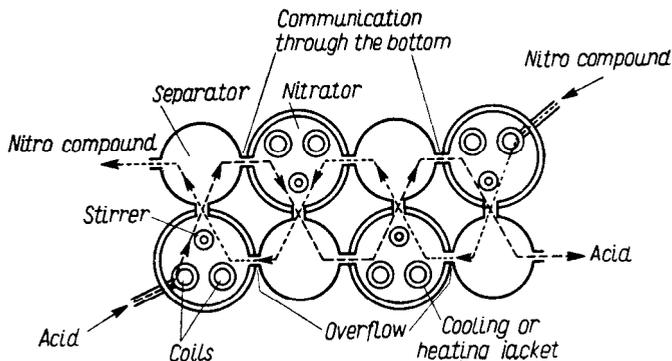


FIG. 85. Diagram of the British continuous nitration of toluene to TNT (according to McNab ([18])).

The unit comprises 14 nitrators and 14 separators. The first nitrator is fed with nitrotoluene, prepared in another unit by the batch process. Nitrators from (2) to (14) are fed with acids of an increasing concentration. The acid in the “middle” nitrators, from (5) to (22), is of the following composition:

HNO ₃	8-10%
NO ₂	1%
H ₂ SO ₄	80-82%
H ₂ O	11%

Into nitrator (24) a nitrating mixture prepared from 96% sulphuric acid and anhydrous nitric acid is introduced. The spent acid flowing from nitrator (2) to nitrator (I) is detoluated here by agitating with nitrotoluene whence it flows away as waste acid of the composition:

HNO ₃	1%
NO ₂	4%
H ₂ SO ₄	78-80%
H ₂ O	14-16%
organic matter	1-1.5%

In the nitrators the following temperatures are maintained:

Nitrators	1-2	40°C
	3	70°C
	4-13	100°C
	14	90°C

The composition of the nitration products obtained in the separate nitrators is reflected by the melting points of the products:

Nitrator	3	15°C	Nitrator	9	55°C
	4	35°C		10	63°C
	5	50°C		11	69°C
	6	45°C		12	72°C
	7	41°C		13	76°C
	8	35°C		14	77°C

The formation of trinitrotoluene begins in nitrator 5. For 1000 kg of TNT

470-480 kg of toluene

1090-1160 kg of HNO₃

410-440 kg of H₂SO₄

are used in the process.

German method

During World War II a continuous process for nitrating toluene to TNT developed by J. Meissner [19] and patented in 1941 was introduced at the Schlebusch factory in Germany. The nitration unit consisted of 5 nitrators and 4 separators, as shown in the schematic diagram in Fig. 86. Both the nitrators and the separators

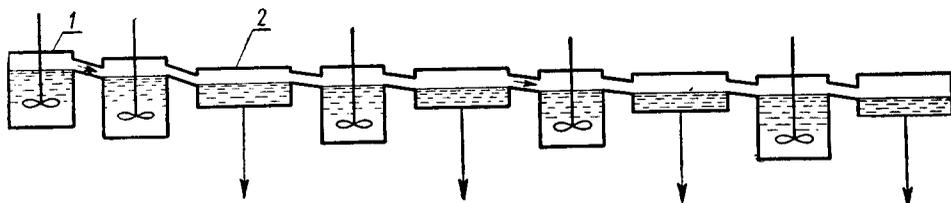


FIG. 86. Diagram of the German continuous nitration of toluene to TNT (CIOS XXIV 4).

are arranged in a cascade so as to enable the liquid to flow down from higher vessels to lower ones. In this way the nitration mixture can be transferred from the nitrator to the separator, where the nitro compound rises to the surface and flows off through a drain between the separator to the next nitrator. The waste acid flows down from the bottom of the separators to storage tanks.

The nitrators are 1.5 m high and 1 m in diameter. The separators are 0.75 m high and 1.5 m in diameter. Both are fabricated from cast iron.

Recently F. Meissner, Wannschaff and Othmer [20] have published some data on J. Meissner's continuous method of preparation of TNT, which is an improvement of an earlier patent of Meissner's.

The design of the plant is based on the combination of the co-current process with the counter-current-battery system. The plant consists of three aggregates, each of them comprising the following stainless steel parts:

- (1) tanks for reactants and metering tanks for the continuous supply of nitrating mixture and hydrocarbon;

- (2) the main nitrator ;
- (3) one or more supplementary nitrators;
- (4) a vessel for extraction of the waste acid (detoluator);
- (5) two separators.

A schematic diagram of such a nitration unit with a washing column and a separator is shown in Fig. 87.

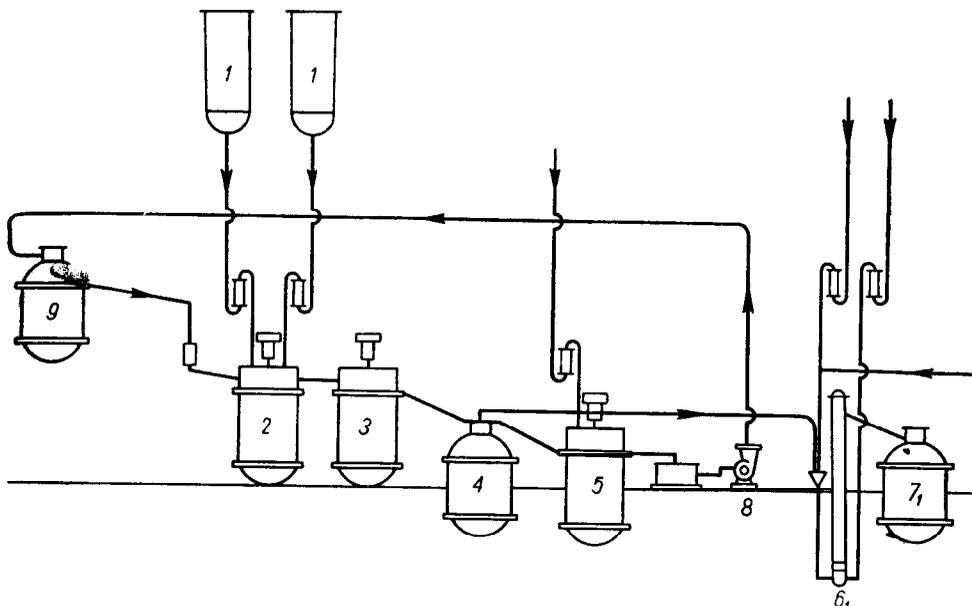


FIG. 87. Flow-sheet of continuous nitration of toluene according to J. Meissner ([20]).

The acid and toluene are introduced from tanks (1) to the nitrator (2), in which the main part of the nitration proceeds. From here the contents pass to another nitrator (3), and if necessary to still another where the reaction is completed. The nitrators are arranged in series, each of them being operated co-currently. The reaction mixture passes from nitrator (3) to separator (d), where the separation of the nitro compound from the waste acid takes place. The nitrotoluene then flows to a system of washing tanks ((6) is the first of these). The waste acid passes to vessel (5), also continuously fed with toluene. By stirring the spent acid with a very small quantity of toluene, the former is freed from any nitro compounds present and at the same time the nitric acid still remaining in the spent acid (1-3%) reacts with toluene to yield nitrotoluene. The purified acid along with toluene is transferred by pump (8) to separator (9), where they are separated. The toluene, still containing some nitrotoluene, is introduced to the main nitrator (2), in a continuous way, thus realizing the counter-current principle and the spent acid, now containing only about 0.3% of HNO_3 and not more than 0.5% of aromatic compounds, goes direct to concentration, previous denitration being unnecessary here.

Nitrators for continuous nitration are of about one twentieth the size of reactors for the batch process. They are equipped with very efficient stirrers and fitted with an external jacket and a coil for conducting away the reaction heat. Rotameters, measuring with an accuracy of about 1%, are used for proportioning the reagents.

The nitrotoluene produced in the first aggregate is sent to the second one, where further nitration to dinitrotoluene takes place in a similar way as that described above. Finally, in the third aggregate, nitration to trinitrotoluene occurs.

For the first nitration stage (toluene to mononitrotoluene) a mixture of 96-98% sulphuric acid and 60% nitric acid is used. Sulphuric acid is taken in such a quantity as to obtain the concentration of about 70% of H_2SO_4 in the acid after the first stage of nitration.

The loss of sulphuric acid is about 1% of the quantity used. A 1.5% excess of acid is used over the required amount theoretically. The yield of nitrotoluene is 98% of theory.

The quantity of alkali required for the neutralization of the wash water does not exceed 0.5% of the weight of nitrotoluene.

The unit is easy to operate. It is claimed that at an output of 20-60 tons of TNT a day (larger units are not advisable) not more than one skilled worker is needed.

The separation of the production unit of mononitrotoluene from the next stages of nitration is desirable so as to provide the mononitration unit with a unit for removing *m*-nitrotoluene by distillation. A mixture of *o*- and *p*- nitrotoluene or *o*- nitrotoluene alone is then used for further nitration. In the latter case *p*- nitrotoluene is utilized for the preparation of dyes (from *p*- toluidine, derivatives of stilbene, etc.) and pharmaceuticals (*p*- aminobenzoic acid.)

Swedish Bofors-Norell method

The Bofors-Norell process [21] was tried out in 1940-41 and has now been in full-scale operation for nearly two decades. The process includes both continuous nitration of toluene or mononitrotoluene to trinitrotoluene and continuous crystallization of the product from dilute nitric acid.

The nitration is carried out continuously in a series of nitrators through which the nitrating acids and toluene or nitrotoluenes pass in counter-current. Each nitrator is joined with a separator.

According to A. B. Bofors both nitrator and separator have been designed in such a way that no pumps or conveyors are needed to transport the nitrating acid and the nitrated product between the different nitrators. Reactants are supplied continuously in quantities adjusted by means of proportioners. The continuous flow of waste acid from the mononitration stage and also of trinitrotoluene keeps the plant running constantly.

One of the features of the method is its lower temperature as compared with the former Bofors discontinuous method which required a temperature up to 140°C at the last stage of nitration.

All nitrators are provided with regulators controlling the supply of cooling water. According to A. B. Bofors, the raw material consumption per 1000 kg TNT is as follows:

toluene	450 kg
nitric acid (99%)	1000 kg
sulphuric acid (100%) supplied in the form of 95% sulphuric acid and oleum	1850 kg

A flow sheet and general view of the Bofors plant is given in Fig. 88 and 89 respectively. A general lay-out is given below (Fig. 101).

Swedish-Norwegian Chematur and Norsk Spraengstoffindustri method

This method [22] patented in Sweden in 1953 employs stepwise nitration of mono- and/or di-nitrotoluene to trinitrotoluene in a series of counter-current units, each unit consisting of a nitrator and a separator.

The principle of the design of the unit is given in Fig. 90. Nitrator N consists of a U-vessel with two legs or shanks (1) and (2) joined by pipe (6). The components of the reaction are introduced through inlets (4) and (5). Liquid can be kept in circulation from leg (1) to leg (2) and back by the turbine-wheel (8) on the driving-shaft (7). By regulating the speed of the turbine (8) and adopting suitable proportions for pipes (3) and (6) it is possible to keep the liquid at a higher level in leg (2) than in leg (1). Separator S communicates with the nitrator through pipe (9). The separator is shaped as a rectangular box (10) with distributor (II) for the mixture coming from the reactor, an outlet (12) for the separated light component and an outlet (13) for the heavy component. At some distance from the inlet and between the levels of the outlets for the separated components there is also another outlet (14) for partly separated emulsion. This outlet has adjustable plates (15) and (16) to make it possible to adjust the opening of the outlet with reference to its level in the separator. The partly separated emulsion is led back to the reactor through pipe (18) and regulating valve (17). To control the temperature of the reaction mixture the unit is equipped with heat exchangers (19) and (20). The separator may also have a heat exchanger jacket not shown in the diagram.

The unit is operated in the following way. The reactants are introduced through inlets (4) and (5), mixed with the help of turbine (8) and circulated through pipe system (1), (3) and (6) chemical reaction and physical exchange being simultaneously effected. They are continuously transported to the separator in the form of an emulsion. In the separator the components are separated, the light component (nitro compounds) rising to the surface and flowing off continuously through outlet (12). The heavier component (spent acid) sinks to the bottom and is removed continuously through outlet (13). In the area between the separated components the partly separated emulsion is withdrawn and led to mixing part of the reactor. This transport is possible because the level of the liquid in the separator through leg (2) is higher

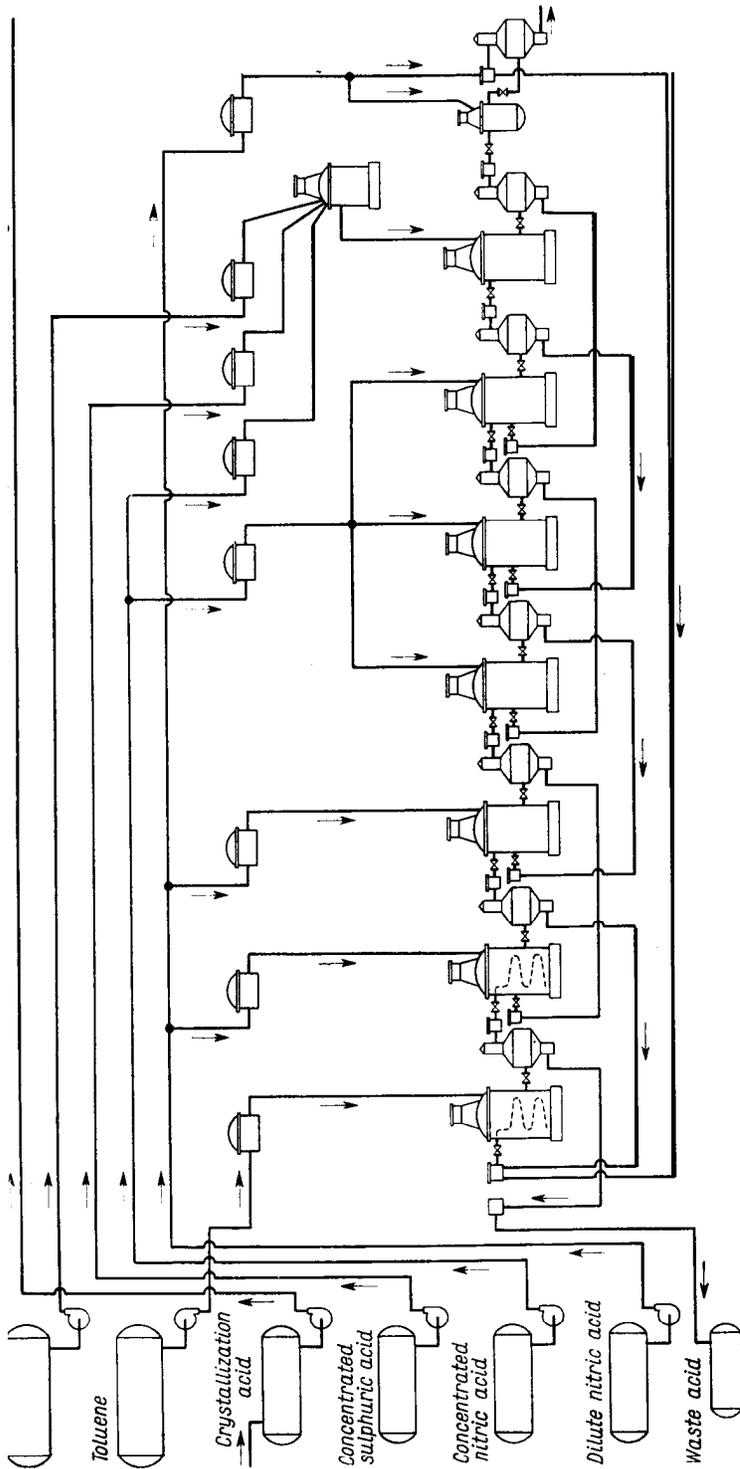


Fig. 88. Flow-sheet of Bofors-Norell method of continuous manufacture of TNT (I17).

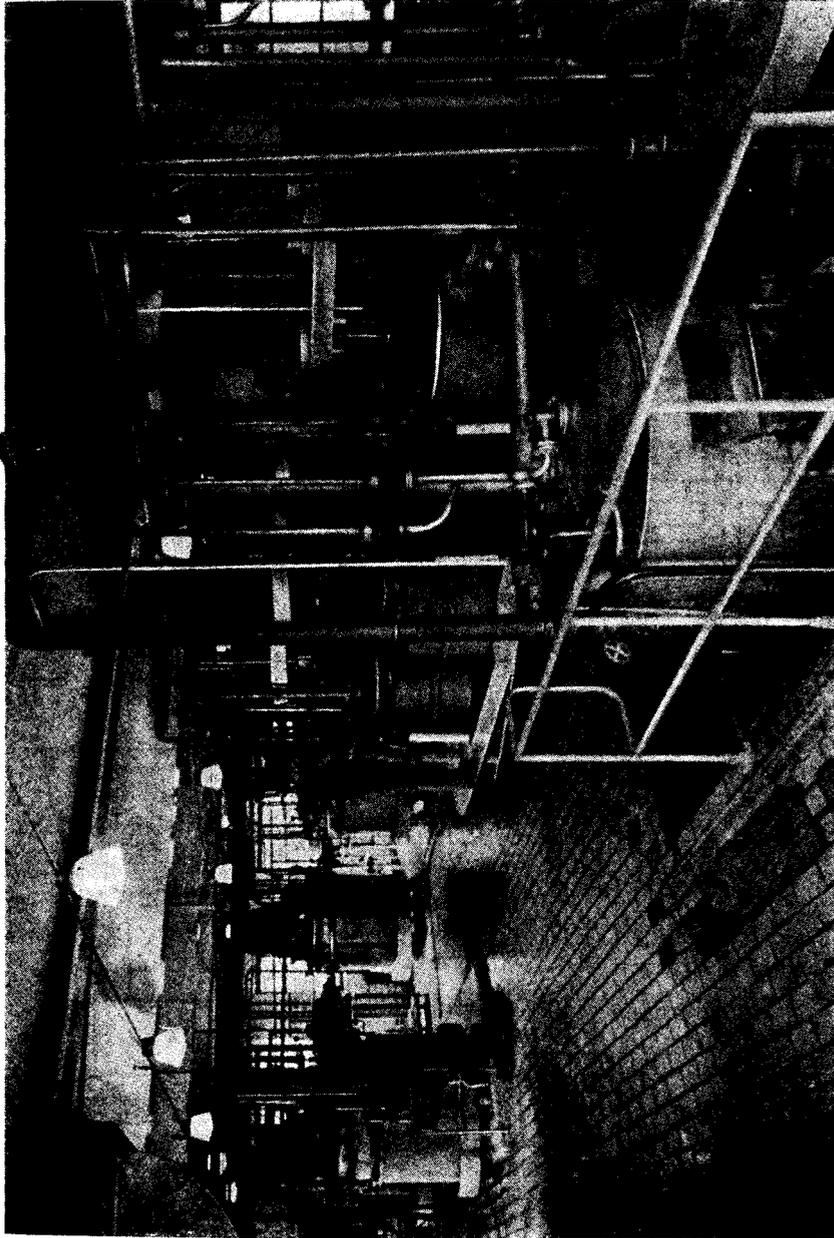


FIG. 89. General view of Bofors plant for continuous manufacture of TNT (Bofors-Norell method). Nitration and crystallization of TNT.

than in leg (1). The rate of feed of partly separated emulsion can be regulated by means of valve (17).

With plates (15) and (16) adjusted to lower levels of the feedback currents through

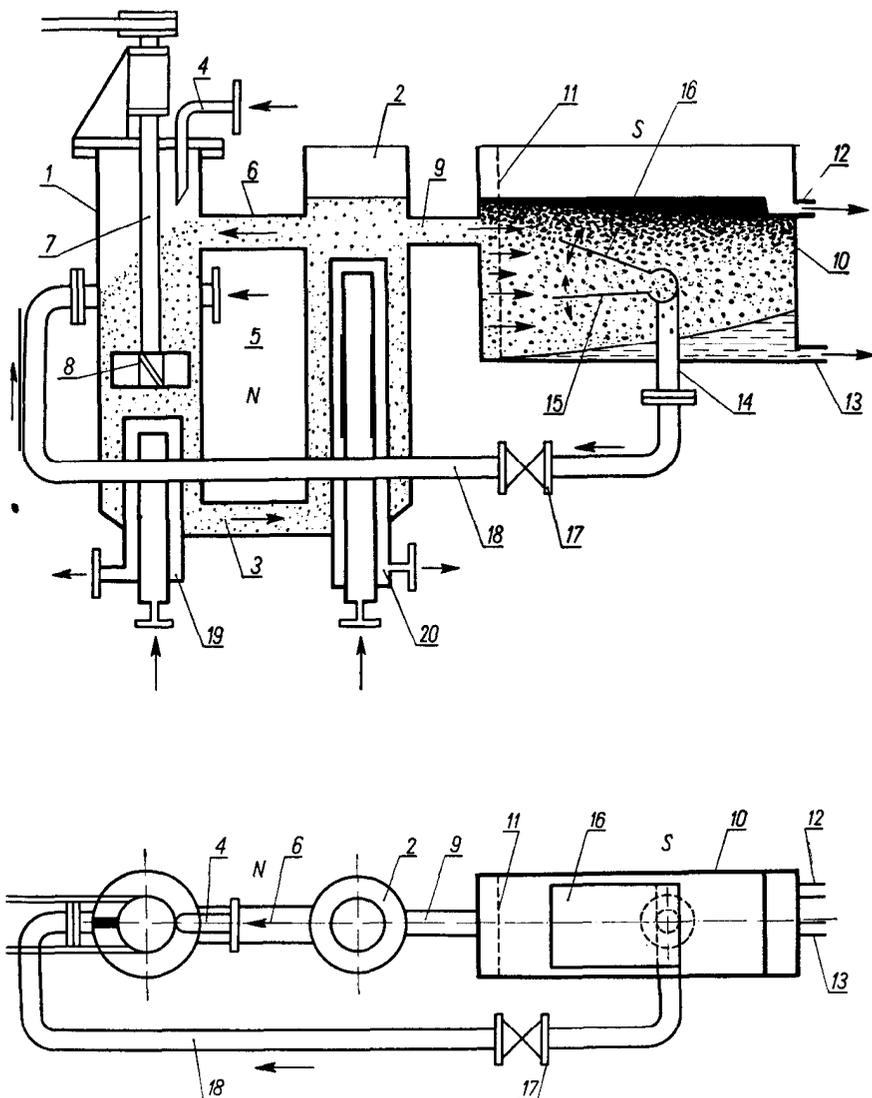


FIG. 90. Nitratator for continuous manufacture of TNT (Chematur method ([22])).

pipe (18) they will be more enriched with the heavy component and this component will therefore be concentrated in the system.

If eighteen nitrating units are applied, the composition of the nitrating mixtures and the temperature during the process will be as follows (Table 86).

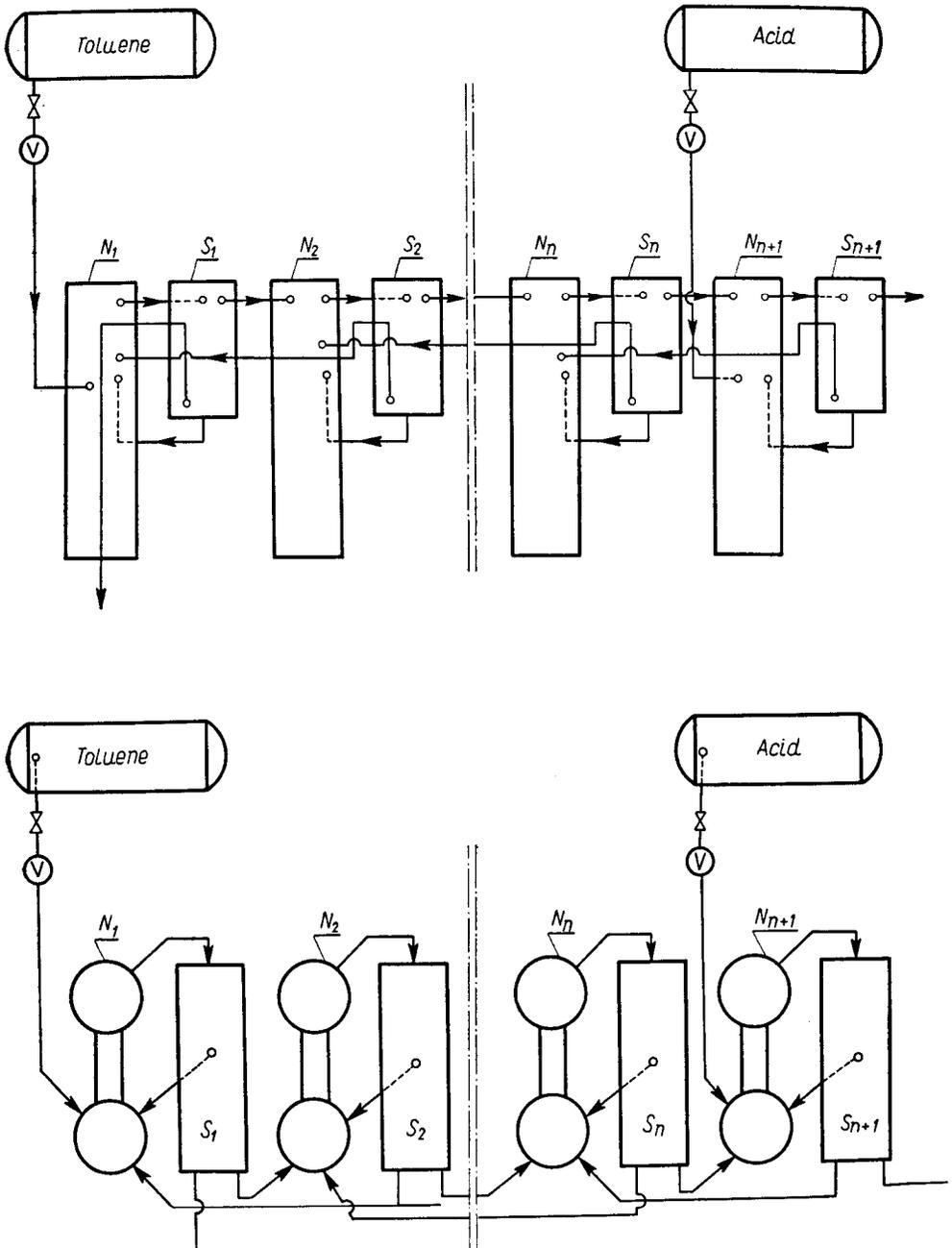


FIG. 91. Diagram of a system of nitrators (N) and separators (S) in the Chematur method of continuous manufacture of TNT [22].

The yield of TNT is as high as 97-99% of theory.

If an unfractionated mixture of the mononitrotoluene isomers is used (i.e. the product of straight nitration of toluene), TNT with a melting point of 78.7°C results. If the starting material is free from *m*- nitrotoluene, e.g. if pure *o*- nitrotoluene is used, TNT with a melting point of 80.6°C is produced.

TABLE 86

Nitrators Nos.	Composition of nitrating mixtures, %			Temperature °C
	HNO ₃	H ₂ SO ₄	H ₂ O	
1-3	0.9	89.2	9.9	65
4-6	3.0	90.1	6.9	75
7-9	7.9	87.8	4.3	80
10-12	7.5	89.8	2.7	85
13-15	7.5	91.4	1.1	90
16-18	7.7	91.8	0.5	90

PURIFICATION OF TNT

In the purification of TNT the following impurities have to be removed:

- (1) traces of nitric and sulphuric acids;
- (2) unsymmetrical isomers;
- (3) products of incomplete nitration;
- (4) by-products (tetranitromethane, trinitrobenzene, nitrobenzoic acids, nitro-cresols, etc.).

The aim of final purification is to remove all those products which are present

TNT and which are more reactive than TNT itself (isomers, nitrocresols, nitrobenzoic acids etc.) or which can easily give oily exudation products (isomers, lower nitrated substances).

The oily exudation product (TNT-oil) is very undesirable for the following reasons :

(a) Exudation produces porosity of the TNT charge and reduces its density. This reduces its explosive effect. In artillery shells it can produce a dislocation of the charge on firing, compression of the air included in the cavities, and pre-matured explosion.

(b) The oily products can penetrate into the threaded parts of the shell and form "fire channels" through which the ignition of propellant can ignite the charge.

(c) The oily products can penetrate into the detonating gaine if the charge of the gaine is unprotected by a metal envelope (e.g. former English gaine made up of TNT in a silk bag). The oily products reduce the detonating powers of the gaine.

The first purification step is thorough washing of the TNT with hot water, in washing tanks or by emulsification.

PURIFICATION BY CRYSTALLIZATION

In the past the TNT, washed free from acids, was further purified by crystallization. For this purpose 95% alcohol was mostly used. Since alcohol is not a very good solvent for TNT, in several countries it was customary to add a certain quantity of benzene (e.g. 5%) as in Germany before World War II. In other countries toluene was added. Since benzene and toluene vapours are more toxic than that of alcohol, in some U.S.S.R. factories alcohol alone was used for the crystallization.

Various other solvents for the crystallization of TNT have been suggested: carbon tetrachloride (U.S.A., World War I), benzene, *o*-nitrotoluene (Stettbacher [23]). More modern method consists in crystallizing TNT from nitric acid (see below under continuous method of crystallization).

With the outbreak of World War I the shortage of alcohol compelled German factories to give up the crystallization method and to confine purification either to thorough washing with hot water or to crystallization by dissolving the TNT in concentrated sulphuric acid followed by precipitation with water (Vender's method [24]). The precipitation could be controlled by adding sufficient water to allow lower nitrated and unsymmetrical derivatives of TNT to remain in solution.

After the war the method of purification by crystallization was not resumed, as purification by means of sodium sulphite was introduced.

The reason why the use of alcohol for crystallization was abandoned can be ascribed to the constant risk of fire when handling a large quantity of this volatile and inflammable solvent. Attention had been drawn to this by the explosion which took place in the TNT drying building at the Allendorff factory in Schbnebeck in 1909. The cause of that dangerous explosion which destroyed both the crystallization building and the drying building was fire started by ignition of the mixture of alcohol vapour and air. It is very likely that the fire started in a centrifuge where TNT had been separated from the solvent after crystallization. The crystallization of TNT from alcohol solution had been the cause of many other fires, so when sulphitation was developed it was readily adopted.

Although the purification of TNT by sodium sulphite was widely used after World War I a number of factories continued with the crystallization method using among other solvents toluene, which directly after crystallization was used for nitration.

In the United States a method of purifying TNT by washing with xylene is used (after Clift and Fedoroff [25]). The method is based on the view that the isomers of α -trinitrotoluene are located mainly on the surface of the grains of solid TNT. For purification, TNT is mixed with xylene in the cold, then the latter is filtered off on a vacuum filter. The operation is repeated with a smaller quantity of xylene the mixture is passed again through a filter and the rest of the xylene is removed by pressing to a content of 3-4%. Finally the product is dried under vacuum, at 60°C. The xylene from the washing operation is sent to distillation.

The residue left after the solvent - alcohol (in the earlier crystallization method) or xylene (from the washing technique) - has been distilled off, is a semi-solid substance consisting of α - trinitrotoluene, its isomers, dinitrotoluenes and other nitro compounds, all of them found as impurities in TNT.

The mixture, known as "TNT oil", generally melts within a wide temperature range, for example from room temperature up to 60°C. It may be used as a component of ammonium nitrate explosives for the mining industry.

The "exudation process" is a modified purification by crystallization. At present it is applied to purify grade III TNT and to recover impurities present in TNT for use as "TNT oil" in the preparation of explosive compositions. The process may be carried out in two ways.

In one of them TNT, scattered over sloped flat pans (Fig. 79, p. 351), is put into a chamber heated to 60°C. After several hours the low-melting impurities segregate as oil which collects in a special vessel placed below the pans.

Another method consists in melting TNT in tilting kettles (converters) heated by steam or hot water which are then left at rest at room temperature or slightly higher (e.g. 30°C) for slow crystallization. Under such conditions large crystals of TNT are formed immersed in an oily mixture of other nitro compounds. The latter is removed by breaking the solidified substance and inclining the kettle so as to enable the oil to run out.

The oily product has been used as an ingredient of coal mining explosives as so-called "liquid TNT". This material also comprised the liquid mixture of nitro compounds forming the residue after distillation of alcohol (or any other solvent) used for crystallization of TNT.

In an earlier Russian method (Belenkii [8]) crude, granulated TNT was washed with hot water in wooden tanks lined with sheet lead, and equipped with an air bubbler.

For a batch of 1000 kg of TNT 1000 l. of water were used at a time. The water was brought to boiling by direct heating with steam (1-2 hr). After boiling for 5 min heating and air mixing were stopped, and the TNT allowed to settle at the bottom. After 10-15 min the water was separated by decantation. This operation was repeated 6-8 times with new portions of fresh water, until the acidity of the TNT fell to 0.02% (calculated on H_2SO_4). The whole washing process took about 7 hr. The use of lead-lined tanks for the first two washings, and a wooden tank for the next ones proved advantageous,

Norell [26] invented a continuous method of crystallization of TNT from nitric acid. A diagram is given in Fig. 92, according to the A. B. Bofors patent.

The crystallizing vats (1).-(5) are provided with heating jackets (3) and stirrer (4). The vats communicate through the overflow (7) and pipes (6). The last crystallizer has an outlet (8) provided with a screw type conveyer to remove a semi-solid mixture of crystals of TNT plus mother liquor.

The first vat is provided with pre-crystallizer (9) and a stirrer (10). The molten TNT (II) and solvent (12) (i.e. nitric acid) is introduced to the pie-crystallizer in which TNT

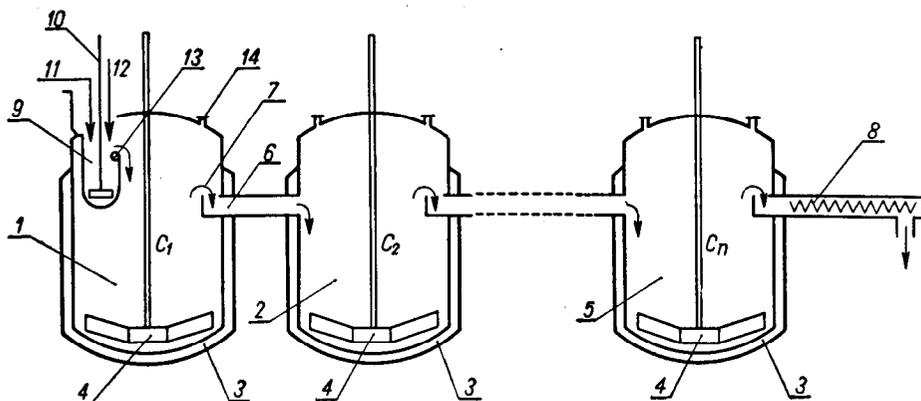


FIG. 92. Continuous crystallization of TNT (Bofors-Norell method [26]).

is dissolved. The solution flows to the crystallizer (1) through an overflow weir (23). Mechanical impurities are held back by the weir. The crystallizer decks are provided with apertures (24). Vat (1) is heated, vat (2) is cooled. Here crystallization begins, and is ended in vat (5).

SULPHITATION AND DRYING OF TNT

There are various methods of purification of the TNT with sodium sulphite.

French method

In the French method the ground TNT is mixed with a 7.5% solution of Na_2SO_3 at room temperature for 2 hr. The operation is carried out in wooden vats, 1.3 m high and 1.3 m in diameter (Fig. 78), using 750 kg of TNT and 750 l. of the solution at a time. Then the mixture in the vat is drained off to a vacuum filter, where the TNT is filtered off, washed with water four times, and sent to a drier.

For drying, an iron vessel of construction similar to that of the nitrator, is charged with TNT (2250 kg). The TNT is melted by passing steam through the jacket of the drying vessel, after which dry air is passed from the bottom through the molten product.

The vessel is covered by a hood with a ventilation pipe through which the moisture escapes (Fig. 93). Initially a temperature of 90°C is maintained, and toward the end of the operation it is raised to 105°C to let the rest of moisture escape.

The dry, molten TNT is subsequently flaked. The equipment for this, operation consists of a rotating steel drum (I), cooled by water from inside. The lower part of the drum is dipped in molten TNT, the temperature of which is about 80°C (Fig. 94). The cooled surface of the drum causes the TNT to solidify on it, and a bronze knife (2) scrapes off the TNT coating in fine flakes, which fall into hopper (3). Flaked TNT is the most convenient form for transport, storage and further use, and is therefore the most widely used form of this substance. Alternatively pure TNT is sometimes used in the form of granules, obtained by granulating in cold

water. For this purpose the installation described on p. 364 may be used, in which a stream of molten TNT ejected under pressure impinges on two streams of cold water at their point of contact (Fig. 84). Grains of TNT together with water fall into a tank, and are conveyed to a centrifuge or to a vacuum filter. To remove water the product is dried in a tunnel or tray drier at 50-60°C, i.e. at a temperature below its melting point.

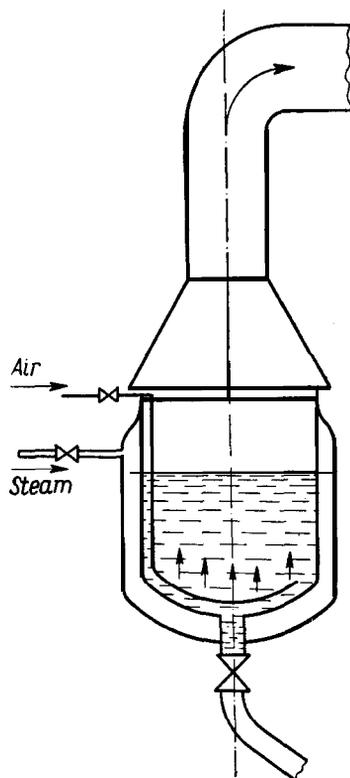


FIG. 93. Vessel for drying TNT.

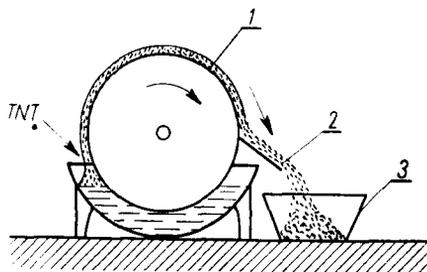


FIG. 94. Flaking of TNT.

The water and liquors from washing and sulphitation of TNT contain some TNT both dissolved and suspended. For recovering the latter the water and wash liquor are conveyed to "labyrinth" tanks equipped with baffles barring the passage of suspended TNT, which settles at the bottom. In this way a certain amount of lower grade TNT may be recovered.

British method

In the British method, crude, granulated TNT prior to sulphitation is washed either batchwise - an operation not differing from the one described above - or continuously.

The plant for continuous washing (Fig. 96) consists of a rectangular trough, 8 m long, 1.4 m wide and 1.3 m high. The trough is made of cast iron sections screwed



FIG. 95. General view of drying and flaking TNT (Bofors Nobelkrut).

together to form a unit. It is divided into sections by vertical walls, each section consisting of two parts: a larger one for mixing the TNT with water (mixers), and a smaller one for separating both phases (separators).

The vertical walls are provided with holes to allow both molten TNT and water to flow through. Each segment is also provided with horizontal perforated iron plates. The mixers are equipped with stirrers, rotating at high speed, which can direct the contents of the unit upwards or downwards.

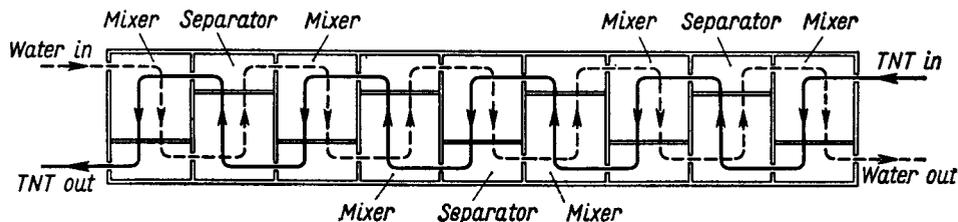


FIG. 96. Continuous washing of TNT (British method [6]).

It can be seen from the diagram that the molten TNT to be washed flows in counter-current against a stream of hot water. In the mixers, emulsification of the TNT in water takes place. The emulsion then passes through an overflow at the top or at the bottom of the mixer (depending on the direction given by the stirrer) to the separator, where the TNT collects at the bottom and flows to the adjacent mixer by an outlet near the bottom. Water rises to the top of the separator and passes in counter-current through an overflow to another mixer. By direct steam heating a temperature 80-100°C is maintained in the trough. The cover of the latter is provided with vent ducts for escaping vapours.

For 1000 kg of TNT about 2500 l. of water is used. The output amounts to 1.5 tons of TNT per hour. After washing the acidity of TNT falls to 0.1-0.2% of H_2SO_4 .

The sulphitation of TNT is carried out in a unit illustrated in Fig. 97.

The granulated, crude TNT is washed with hot water in a wooden vat A, equipped with a stirrer rotating at a speed of 75 r.p.m., and with a sheet metal lid connected to a ventilating pipe. The mixture in the vat is heated by steam introduced through a silicon-iron pipe. The acidity of the TNT falls after washing to below 0.1% of H_2SO_4 . The number of washing operations depends on the initial acidity.

The molten, deacidified TNT is drained off to a crystallizer, placed below. The crystallizer consists of a wooden cylindrical vessel, 0.9 m high and 2.8 m in diameter, equipped with a wooden stirrer.

For crystallization the molten TNT is run from vessel A into a crystallizer filled with water, heated to 90-100°C. The ratio of water to the TNT should be 1:1 by volume. The content of the crystallizer is allowed to cool. At about 75°C the TNT begins to crystallize. After the temperature has fallen to 50°C (in about 4 hr from the time the crystallizer was loaded) sodium sulphite solution is added and the mixture is allowed to react for half an hour at a temperature of 40-45°C. The concentration of Na_2SO_3 in the crystallizer is 34%. The weight of the Na_2SO_3

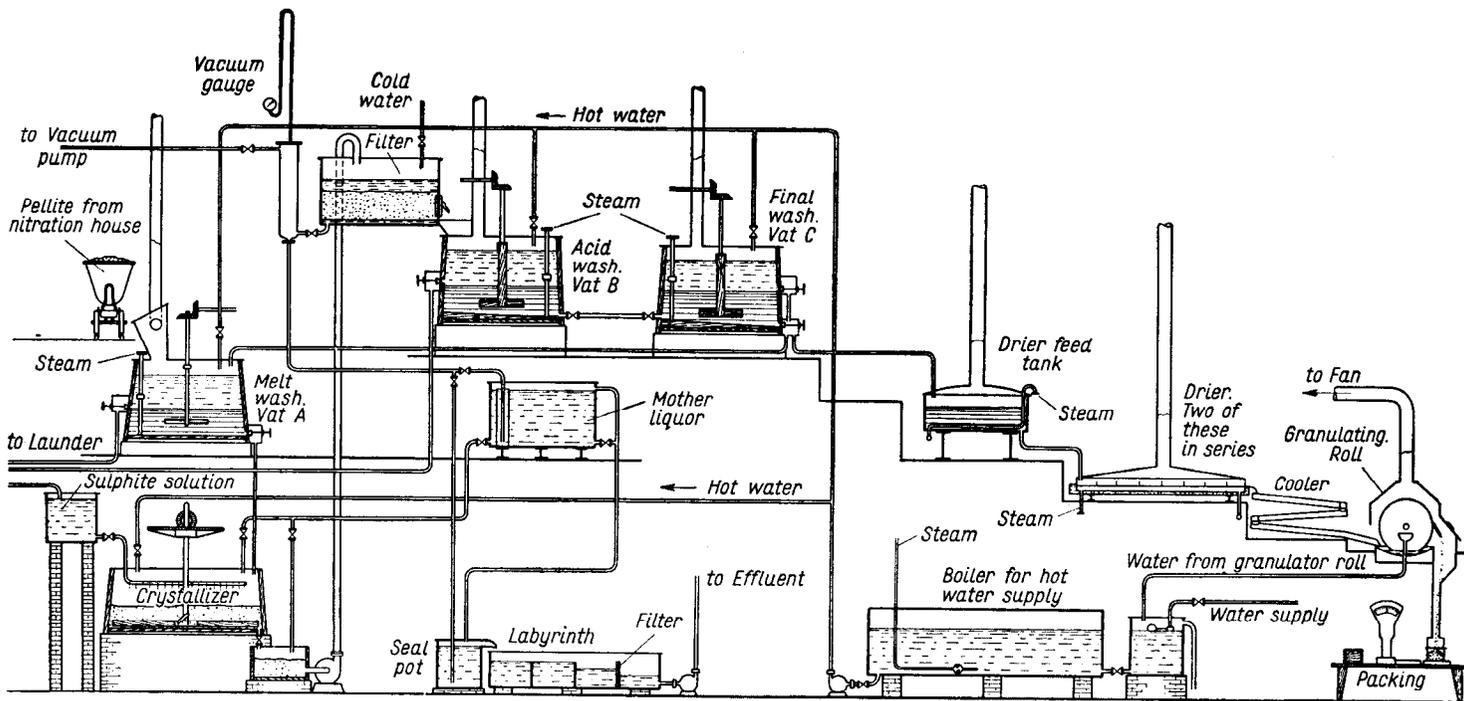


FIG. 97. Sulphitation of TNT (British method [6]).

used amounts to 3.54% of the weight of the TNT. The designers of this method believe that the uniform, fine crystals formed in the crystallizer are most suitable for the sulphitation process.

The suspension of crystals in sodium sulphite solution is pumped upwards by a rotary pump to a vacuum filter through a small tank in which the suspension is diluted with water. After the TNT has been separated from the liquor it is washed with cold water until its pink colour, produced during the sulphitation process, disappears. The aluminium filter plate in the filter bowl should be covered with linen cloth, which in turn is covered with a layer of pure, granulated TNT.

After sulphitation and washing, the TNT is transferred to tank *B*, containing water acidified with sulphuric acid (up to 0.1%). Here the TNT is freed from any traces of basic sodium sulphite. The acidified, molten TNT is then transferred to tank *C* for final washing with pure, hot water. The washing is repeated several times, until the wash water proves neutral.

The solution of sodium sulphite from filtration of the TNT is collected in an intermediate tank from which part may be directed back for the sulphitation and part to a settling tank (labyrinth). There a certain amount of TNT slurry sets and may be utilized as the grade III TNT.

The washed TNT is then transferred to a tank where it is kept in the molten state and thence through a bronze wire gauze (for retaining any impurities) it is poured in a thin layer on to a tray for drying. The tray is steam heated to keep the TNT at a temperature of 105-115°C. Due to this temperature and the thin layer of the product, drying takes only a short time. Free from moisture, hot TNT is allowed to flow via a spout (in which it is cooled to about 98°C) into a flaker. The drum and the knife of the flaker are made of bronze. The drum is 60 cm in diameter and is rotated at a speed of about 4.5 r. p. m. (Fig. 94).

All pipes for conveying the molten TNT are heated by steam located below the TNT pipes, both being heat insulated.

German method

In a German method, applied at the Krümmel factory, the crude acid TNT, after it has been washed free from nitrosylsulphuric acid, is washed several times with water at a temperature of 90°C in brick washing vats lined with sheet lead, or in stainless steel tanks. The deacidification is finally followed by neutralization with a NaHCO_3 solution of concentration about 1%. The product obtained in this stage has a freezing point of 78.8-78.3°C.

For further purification molten TNT and hot water in equal volumes are run into a cast iron tank of 15 m³ capacity, where the TNT is emulsified by vigorous stirring. The emulsion is cooled to 74-76°C and treated with a 25% solution of sodium sulphite, used in such a proportion as to obtain a final concentration of sodium sulphite in the mixture of 2.5%. During the sulphitation process 5-6% of trinitro compounds and 0.2-0.3% of tetranitromethane (calculated on the TNT) go into solution.

After half an hour the stirrer is stopped, the solution is separated by decantation and the TNT left behind is washed with water again at 85-90°C. If TNT of very high purity is required (m. p. 80.6%) it is sulphitated once more with a 0.5% solution of sodium sulphite.

The washed TNT is then air dried in a water heated tank of capacity 15 m³, at 85-90°C. At this stage of manufacture samples are taken for determining the freezing point of the product. Finally the dry TNT is flaked on a steel drum with a bronze knife.

Continuous methods

Continuous washing with sodium sulphite was also applied at Schlebusch (Fig. 98).

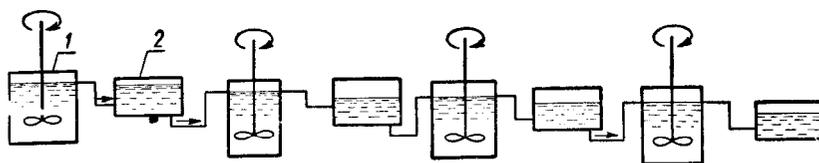


FIG. 98. Continuous washing with sodium sulphite of TNT in Schlebusch (CIOS XXIV - 4).

The purifying unit consisted of four washing tanks (I) and four separators (2). As in the nitration plant the vessels were arranged in cascade. The first washing tank was for washing the TNT with water, the next one for washing with sodium sulphite and the last two again for washing with water. Each was 0.5 m high and 0.8 m in diameter.

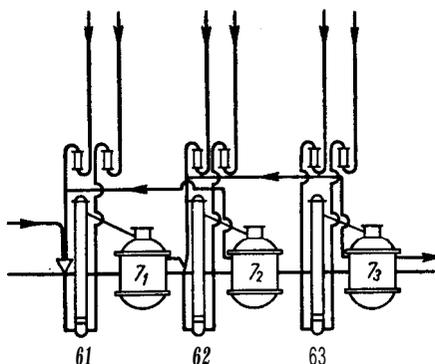


FIG. 99. Meissner's continuous process of washing nitrotoluenes including TNT (co-currentsounter-current method [20]).

Meissner's continuous process for washing nitrotoluenes, applied also for TNT (Fig. 99), belongs to the co-current-counter-current type. The quantity of water used should be as small as possible, thus reducing the losses of nitrotoluenes to

a minimum. The nitro compound, separated from acid in the separator (4) (see the diagram in Fig. 87) flows to the washing column (6₁), fed with fresh water. A mixture of the nitro compound and water flows off at the top of the column to the separator (7₁), where the nitro compound separates from acid washings. The washings (being the upper layer in the separator) are drained away, while the nitro compound flows to the next column (6₂), fed with the water from the third separator (7₃). A calculated weight of alkali is added to column (6₂) to neutralize any acid present. The neutralized mixture of the nitro compound and wash water flows off at the top of column (6₂) to separator (7₂). The water separated from the nitro compound is drained away while the nitro compound is transferred to column (6₃), whence it overflows to separator (7₃). The nitro compound from the third separator passes to further nitration or to a drier, while water is led to column (6₂).

The equipment is made of stainless steel, those parts that hold alkaline or neutral liquids may be made of carbon steel. The washing columns are equipped at the bottom with air injectors for emulsifying the nitro compounds in water. To avoid any hazards the plant is not equipped with mechanical stirrers.

To remove any acid present the TNT is water-washed, neutralized with a solution of sodium hydrogen carbonate, then with a solution of sodium sulphite and finally washed several times with water.

SCHEMATIC DIAGRAM OF A PLANT FOR CONTINUOUS TNT MANUFACTURE

A schematic diagram of such a plant is shown in Fig. 100. Separate buildings are denoted :

1. Packing department
2. Granulation
3. Sulphite washing and TNT drying
4. TNT washing
5. Nitration of nitrotoluene to di- and tri-nitrotoluene
6. Absorption
7. Concentration of sulphuric acid
8. Concentration of nitric acid
9. Preparation of washing solutions
10. Compressor house
11. Boiler house
12. Acid storage tanks for di- and tri-nitrotoluene
13. Acid storage tanks for mononitration
14. Distillation and mononitrotoluene separation plant
15. Toluene and mononitrotoluene separation tanks
16. Mononitration plant
17. Mononitrotoluene washing plant
18. Safety embankments
19. Safety walls for shielding passages.

A schematic diagram of a plant operated by the A. B. Bofors system is shown in Fig. 101.

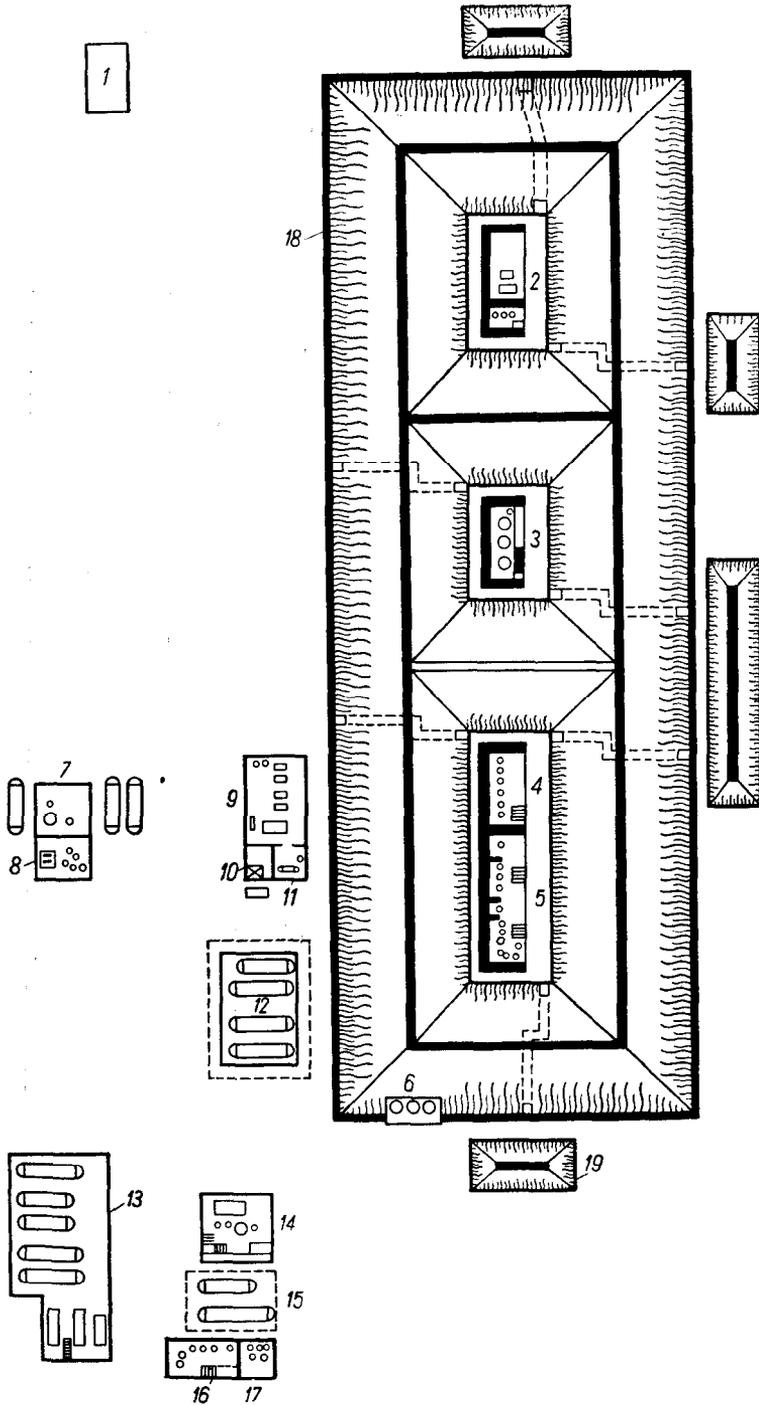


FIG. 100. Lay-out of a plant for continuous TNT manufacture according to Meissner [20].

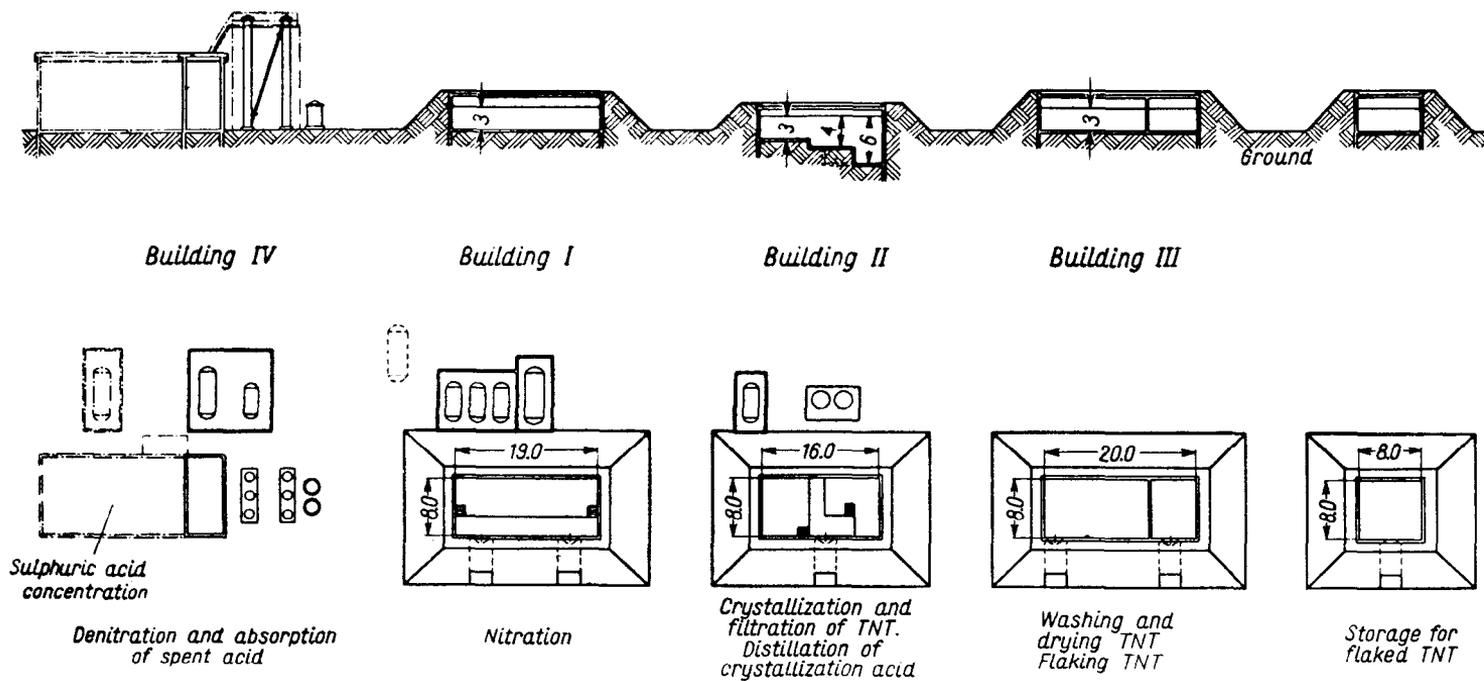
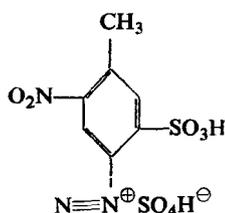


FIG. 101 Lay-out of a Bofors plant for continuous TNT manufacture [17]. (Dimensions in meters).

UTILIZATION AND NEUTRALIZING OF SULPHITATION LIQUORS

The sulphitation liquors contain dinitrotoluenesulphonic acids in a quantity amounting to about 4% of the TNT produced. In a period of intensive manufacture of TNT this may be of considerable importance from an economic point of view. This is why the problem has arisen of how to utilize the organic compounds contained in sulphitation liquors.

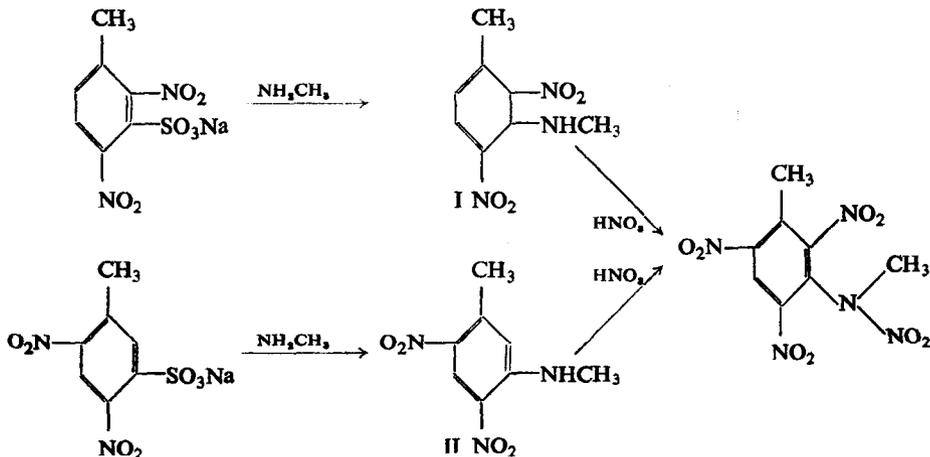
Batik [27] found that the acidification of sulphitation liquors with an inorganic acid resulted in the formation of NaHSO_3 , which reduced the nitro- to the amino group. Simultaneously, due to the presence of NaNO_2 , diazotization took place and a red diazonium salt



was precipitated.

The compound may be utilized for further reactions, for example in dyestuffs manufacture.

British Technical Records [6] mentioned another approach to the problem of utilization of sulphitation liquors. According to these data, attempts were made in Great Britain during World War I to make use of the reactivity of the sulpho group in the *ortho* or *para* position to the nitro ones. By acting with methylamine, N-methyl-dinitrotoluidine (I and II) was obtained, which, when further nitrated, yielded "methyltetryl". All the methods mentioned proved uneconomical.



Gornall and R. Robinson [28] suggested reducing sodium dinitrotoluene sulphate (e.g. the sodium salt of 2,4-dinitrotoluene-3-sulphonic acid) to yield *m*-toluenediamine-3-sulphonic acid which could serve as an intermediate for obtaining azo dyes. Oxidation of sodium 2,4-dinitrotoluene-3-sulphonic acid with potassium permanganate in alkaline medium gave 2,4-dinitro-3-sulphobenzoic acid, also an intermediate for azo dyes.

WASTE WATERS

The problem of the neutralization of waste water from the manufacture of TNT, and the possibility of utilizing the dinitrotoluenesulphonic acids present in them acquired a considerable importance during World War II, owing to the enormous output of TNT. In Germany alone the production of TNT was over 20,000 tons a month, whereas during the World War I it averaged merely 3000 tons a month.

Such a high output involved the use of tremendous quantities of water. According to Kratz [29], for an production of TNT of 4000 tons monthly, 40,000 m³ of water were used daily. Most of this was used for cooling, while the quantity of waste water containing nitro compounds and acids amounted to 5000-6000 m³. Kratz believed this consumption of water to be abnormally high, and caused by hasty production.

Kratz has classified the "acid" waters according to their origin as follows (Table 87):

TABLE 81

Origin of water	Output m ³ /hr	Colour and appearance	Acid content	Colour after purification with lime milk
Process water	50	brick-red turbid	4 g/l. H ₂ SO ₄ 2 g/l. HNO ₃	dark red
Condensed water from concentration of sulphuric acid	100	almost Colourless, clear	2 g/l. H ₂ SO ₄ 0.3 g/l. SO ₂	pale pink
Wash water	80	from light to dark brown from clear to turbid, with suspension	5 g/l. H ₂ SO ₄ 2g/l. HNO ₃ (changeable)	dark red

Channels for discharging waste water should be open gutters or loosely closed troughs. The channels should be built of acid resistant bricks, joined by asphalt (phenolic resin).

The removal of dinitrotoluenesulphonic acids from waste waters prevents a difficult problem since due to their high solubility they are difficult: to absorb on carbon or on anion exchangers, or to extract with dibutyl phthalate.

The water may be decolourized by chlorination, but this requires large quantities of chlorine. Biological processes can lead to destruction of TNT, but the sulphonic acids remain unaffected.

For this reason, according to Kratz, the most rational way of removing TNT and salts of nitrosulphonic acids from the water is by simply distilling off the water and then destroying the non-volatile residue.

Since this method is expensive as regards capital and operating costs, Kratz has suggested a method of treatment for acid waste water from the TNT manufacture consisting in agitating with 5-10% milk lime.

The reaction with calcium hydroxide is rather slow, so agitation should go on for some time (5-15 min). The mixture is then allowed to remain at rest for clarification. Treatment with milk of lime neutralized the acids and caused the precipitation of several coloured compounds, among others the products of the reaction of trinitrotoluene with calcium hydroxide. The amount of calcium oxide consumed in the process is 700 tons monthly, at an output of 4000 tons of TNT a month.

SAFETY IN TNT MANUFACTURE

The manufacture of TNT is one of the safest operations in the explosive industry. Nevertheless, any negligence about safety regulations may have disastrous consequences. Because the manufacturing process is regarded as safe, the fact must not be overlooked that less experienced personnel may disregard the regulations.

The most hazardous operation in TNT manufacture is nitration, primarily mono- and tri-nitration. In mononitration the hazard is due to the extremely violent reaction of the unreacted hydrocarbon with the nitrating mixture, and to the fact that nitro derivatives of cresols are formed in the process, along with nitrotoluenes. The last stage - trinitration - is dangerous due to the drastic conditions of the reaction which requires concentrated acids and a high temperature. The earlier method of trinitration at which temperatures up to 120°C were applied, was particularly hazardous. If the mononitrotoluene has not been freed from nitrocresols, trinitration is still more dangerous, due to the high reactivity of nitrocresols, and their liability to undergo oxidation. The formation of carbon monoxide may also be a cause of an explosion in the course of trinitration [33] (p. 339).

The spent acid from trinitration has also been the cause of several disasters, although it had been considered safe to handle. The most noteworthy example of this occurred in the Reinsdorf factory in Germany in 1935. The hot spent acid flowed down to open iron tanks, where, as the liquid cooled, a mixture of di- and Tri-nitrotoluenes rose to the surface. It was skimmed off from time to time and transferred to a washing tank, where it was washed with water. On skimming, a rubber glove and a shelf left on the brim of the tank with some cotton wool on it, fell into the tank. The reaction between the spent acid and the rubber and cotton wool initiated violent decomposition and fire. An attempt to extinguish the flames failed,

and soon the nitro compounds on the surface of the spent acid exploded. The explosion and fire spread over several nearby tanks, then to the nitro compounds in the washing tank. As a result the whole plant for the recovery of nitro compounds was destroyed. In addition to this the explosion tore away the roofs of some nearby buildings, among them drier buildings located at a distance of about 660 m. Parts of the tank thrown off by the explosion into one of the driers detonated the TNT present, and in another they caused the ignition of the load. Similar explosions or fires spread over further buildings of the TNT factory. Moreover, a neighbouring nitroglycerine plant also exploded. This disastrous explosion cost 82 human lives and in addition 104 people were seriously and 700 were lightly injured.

Accidents caused by spontaneous explosion of finished TNT are also known. Some of them could be ascribed to the presence of traces of trinitroresol salts. Others were presumably caused by products of decomposition of trinitrotoluene under the influence of sunlight or alkaline compounds used for deacidification of the TNT. Still others were due to the high sensitiveness of molten TNT to impact. This is why the drying of TNT should be regarded as a very dangerous operation.

Descriptions of several explosions that took place in French factories, may be very instructive. As an example, the explosion in the St. Chamas TNT factory in 1936 which caused the death of 53 people. Investigations showed that the explosion occurred after about 2000 kg of TNT in a drying tank had caught fire. The TNT in question was that recovered from the spent acid from trinitration ("plastic TNT"). It is known that such a product contains various impurities, among them the isomers of α -trinitrotoluene, nitroresols etc. It had first been washed with water at 90°C then with a 6% solution of sodium carbonate, and again with water. The drying was effected at 85°-90°C by passing air for 8 hr. In the case described, as the drying TNT still contained some acid, 7 kg of sodium carbonate (i.e. 0.35% in relation to TNT weight) were added to the tank with the drying TNT which at the time contained only a very small quantity of water. This must have led to the formation of typical decomposition products of TNT brought about by reaction with alkalis. It is highly probable that these compounds were the first to ignite. whereupon the flames spread over the whole drier.

A number of explosions in French TNT factories which occurred during 1917-18, in particular the one at Neuville-sur-Saone (1917) which caused the destruction of the whole plant, were presumably due to the decomposition of the products of reaction of metals, such as lead or iron, with TNT under the conditions described in a paper by Kovache and Thibon [31]. Products readily decomposed, and sensitive to friction and impact, were formed in various parts of the plant where contact between these metals and the TNT could occur in the presence of dilute nitric acid, for example in the TNT washing tank and granulators. Similar compounds were found in a nitrator where part of the TNT in close contact with metals was subjected to the action of nitric acid vapours, for example around the seals at the stirrer shaft bearings.

Similar compounds were also found in an iron sulphitation tank. TNT is in-

flammable, although this occurs under specific conditions of prolonged action of glowing material.

Steele [32] described the following accident in the amatol section of an ammunition factory. A worker smoking a cigarette (in spite of the regulations) threw it away when he saw a foreman coming up. The burning cigarette fell on a sack filled with TNT. After a while the jute sack caught fire causing the TNT to ignite, and then to explode. This involved the explosion of the amatol in a mixer located in the same premises. The explosion tore away the wooden roof, and its fragments scattered on to other buildings causing further explosions. Soon all buildings of the factory were on fire and destroyed and 11 lives were lost, mainly in fire fighting.

LITERATURE

1. K. SMOLENSKI, S. TUROWICZ and R. DOBROWOLSKI, *Przemysl Chem.* **5**, 201, 237 (1921); **6**, 250, 281 (1924).
2. R. C. GEORGE and J. B. PATBERG, *Ind. Eng. Chem. Anal. Ed.* **13**, 768 (1941).
3. G. DESSEIGNE, Y. GLALEL, A. GUILLEMIN and Y. SOUSSELIER, *Chimie et Industrie* **20**, No. spec. 290 (1954).
4. A. G. GORST, *Porokha i vzryvchatyye veshchestva*, Oborongiz, Moskva, 1957.
5. P. PASCAL, *Poudres, explosifs, gaz de combat*, Hermann, Paris, 1925.
6. *Technical Records of Explosives Supply 1914-1918*, No. **2**. Manufacture of TNT, HMSO, London, 1920.
7. A. G. GORST, *Khimiya i tekhnologiya nitrosoyedinanii*, Oborongiz, Moskva, 1940.
8. M. S. BIELENKII, *Spravochnik po proizvodstvu vzryvchatykh veshchestv* (Edited by USHAKOV-LEBEDEV), Goskhimtekhnizdat, Moskva-Leningrad, 1934.
9. Meister, Lucius, Brüning (Höchst), Ger. Pat. 201623 (1906).
10. Weiler-ter-Meer (Uerdingen), Ger. Pat. 228544 (1909).
11. Westphllisch-Anhaltische Sprengstoffe A. G., Ger. Pat. 274854 (1912); 281053 (1913).
12. K. KUBERSCHKY, Ger. Pat. 287799 (1914).
13. H. WILHELM, U.S. Pat. 2109873 (1938).
14. D. F. OTHMER, *Ind. Eng. Chem.* **33**, 1106 (1941).
15. D. F. OTHMER, J. J. JACOBS, JR. and I. F. LEVY, *Ind. Eng. Chem.* **34**, 286 (1942).
16. D. F. OTHMER and H. L. KLEINHAUS, JR., *Ind. Eng. Chem.* **36**, 447 (1944).
17. A. B. BOFORS, *TNT Manufacture by the Continuous Bofors-Norell Method*, 1956 (Specification).
18. W. MACNAB, *J. Soc. Chem. Ind.* **41**, 353 (1922).
19. J. MEISSNER, Ger. Pat. 710826 (1941); 732742 (1943).
20. F. MEISSNER, G. WANNSCHAFF and G. F. OTHMER, *Ind. Eng. Chem.* **46**, 718 (1954).
21. K. T. NORELL, U. S. Pat. 2594675 (1952).
22. A. B. Chematur, Norsk Sprengstoffindustri, Brit. Pat. 772895 (1957); 803370 (1958); Swed. Pat. 159862 (1953).
23. A. STETIBACHER, *Die Schiess- und Sprengstoffe*, J. A. Barth, Leipzig, 1919.
24. V. VENDER, Ger. Pat. 237738 (1909); Fr. Pat. 405812 (1909); Brit. Pat. 18281 (1909).
25. G. D. CLIFT and B. T. FEDOROFF, *A Manual for Explosives Laboratories, I-III* Lefax, Philadelphia, 1943-44.
26. K. T. NORELL, Swed. Pat. 152620 (1955); U.S. Pat. 2874196 (1959).
27. B. BATIK, *Chimie et Industrie* **29**, 960 (1933).
28. F. H. GORNALL and R. ROBINSON, *J. Chem. Soc.* **1926**, 1981.

29. B. KRATZ, *Vom Wusser* **17**, 83 (1949).
30. *Mém. poudres* **34**, 379 (1952).
31. A. KOVACHE and H. THIBON, *Mém. poudres* **34**, 369 (1952).
32. A. R. V. STEELE, *Industrial Hazards*, Reports on the Progress of Applied Chemistry, p. 810, Society of Chem. Industry, London, 1953.
33. A. EASTMAN, *Ind. Eng. Chem.* **11**, 1124 (1919).

Allied reports

- BIOS 1144, I. G. Farbenindustrie (Griesheim and Leverkusen).
Technical Report P. B. 925.
Explosive Plants D. A. G. Krümmel, Düneberg, Christianstadt, U. S. Dept. of Commerce, Washington, 1945.
CIOS XXIV-4, Dynamit A. G., Schlebusch.