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Separation of Trinitrotoluene Isomers by Crystallization and Extraction with Nitric Acid as a Solvent

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Mixtures of 2,4,6-TNT, 2,4,5-TNT, and 2,3,4-TNT with a 1:1 ratio of 2,4,5-TNT to 2,3,4-TNT were crystallized or extracted when using nitric acid. Dinitrotoluene isomers were sometimes present in the mixtures investigated. The objectives were to determine crystal yields, product compositions, and the associated-phase equilibria. On the basis of data obtained, essentially complete separation and recovery of 2,4,6-TNT from crude TNT are possible, and a flow sheet is proposed.

2,4,6-Trinitrotoluene (2,4,6-TNT) is widely used as an explosive for both industrial and military purposes (Fordham, 1980). It is the predominant isomer produced when toluene is nitrated with mixtures of nitric and sulfuric acids (Prime, 1964). The crude TNT produced normally contains 4–5% total of 2,4,5-TNT and 2,3,4-TNT. In many cases, some dinitrotoluenes (DNT's) are also present in the crude TNT product (Kohlbeck et al., 1973). The product from the Radford Army Ammunition Plant contains, for example, about 0.4% and 0.1%, respectively, of 2,4-DNT and 2,6-DNT. Other DNT and TNT isomers and oxidation products are also present in small amounts (Gehring, 1970).

Separation of the various TNT and DNT isomers and of other byproducts from 2,4,6-TNT is necessary since relatively pure 2,4,6-TNT is required for processing and storage. For example, impurities tend to exude because of the formation of low-melting eutectics when loaded into shells or storage containers. Pure or essentially pure 2,4,6-TNT crystallizes at about 80 °C, and it stores well for long periods of time. Pure 2,4,5-TNT or 2,3,4-TNT would probably store well and would certainly serve well as explosives. These latter two TNT isomers are produced in conventional processes in small quantities, and there has been to date only small incentive to develop recovery schemes.

The most important method for recovery of relatively pure 2,4,6-TNT from crude TNT is currently the Sellite process (Kohlbeck et al., 1973). In this process, the molten crude TNT is washed with hot water to remove any entrained nitrating acids and is then contacted with an alkaline water solution of sodium sulfite or Sellite solution. The solution reacts with the unsymmetrical TNT isomers to form sodium dinitrotoluenesulfonate salts which are water soluble and can be easily separated. A 92% molar yield (or recovery) of Military Specification TNT is obtained based on the starting toluene as reported by Clift and Jablonsky (1955). The major disadvantages of the Sellite process are as follows: (1) Both 2,4,5-TNT and 2,3,4-TNT are destroyed when potentially they could be recovered and used as explosives. (2) Wastewaters containing sodium dinitrotoluenesulfonates and some base-complexed 2,4,6-TNT are not easily disposed. (3) About 3% of the 2,4,6-TNT is lost to the wastewater (Kohlbeck et al., 1973). (4) The Sellite process does not remove or separate DNT isomers, oxidation products, and products introduced during purification.

Crystallization of crude TNT from various solvents including methanol, ethanol, and other organics has been

investigated (Leonard Process Co., 1970). Nitric acid, however, is a preferred solvent since it is readily available in a TNT plant, is quite effective as a solvent, is non-flammable, and is easily recovered and recycled. Two modifications of the basic technique have been developed by utilizing nitric acid as the solvent: one by AB Bofors of Sweden (Gilbert, 1977) the other by the Leonard Process Co., Inc. (1970). Both processes rely on a single crystallization to produce crystals with a minimum composition of 99.2% 2,4,6-TNT (Military Specification TNT) and crystal yields of 85% and 92% based on the crude TNT, respectively. The TNT's remaining in the mother liquid are often called isotriol and have a composition of about 45–55% 2,4,6-TNT, 30–35% unsymmetrical TNT isomers, 15–20% DNT isomers, and small amounts of oxidation products (Gilbert, 1977). Isotriol has been used in the manufacture of dynamite in Sweden, but no commercial use for it has yet been developed in the USA. Burning is one possible method of disposal unless improved separation techniques can be developed.

The objective of this work is to obtain crystallization data for a wide range of TNT mixtures and to obtain information for the recovery and separation of the TNT isomers. Finally, a separation technique will be proposed, resulting in higher yields of Military Specification TNT.

Experimental Details

Crystallization experiments were conducted in an Ace-jacketed fritted funnel. Crystallization is defined here as the formation of TNT crystals when a solution of nitric acid and dissolved TNT is cooled. The funnel used had a 30 mm diameter disk with 25–50 μ m diameter pores. TNT–nitric acid mixtures were retained above the frit during crystallization by providing a pressure slightly greater than atmospheric on the receiving flask located beneath the funnel. A magnetic stirrer was positioned in the funnel to provide agitation. The temperature of the mixture was maintained at the desired value within ± 0.5 °C by pumping thermostatically controlled water through the jacket of the funnel and through a glass cap located above the funnel.

Dry nitroaromatic materials and standardized nitric acid solutions were weighed and charged to the funnel. This arrangement was employed to measure the transition temperatures discussed later and the various crystallizations. The funnel permitted the separation of the crystals from the mother liquid. These crystals were washed with cold, dilute nitric acid; this wash was combined with the mother liquid so that no loss of TNT occurred. Other

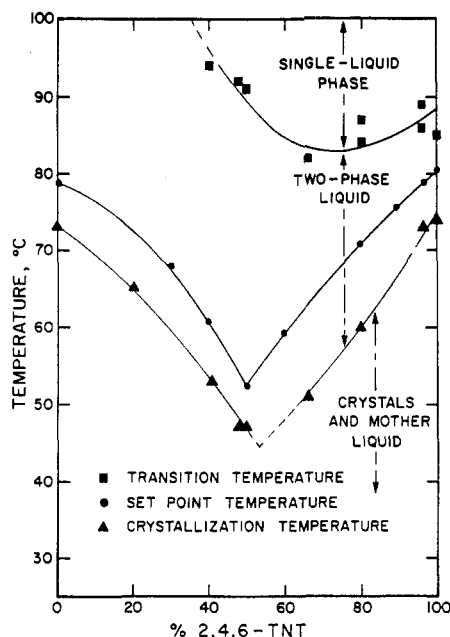


Figure 1. Phase transformation temperatures for feedstocks containing 2,4,6-TNT and a 1:1 ratio of 2,4,5-TNT to 2,3,4-TNT (0.5:1 ratio of TNT to 63 wt % nitric acid).

experimental details are described by Spalding (1982).

TNT mixtures were combined with nitric acid usually at temperatures of 60 °C in a well-agitated 13 × 100 mm test tube; often two liquid phases resulted. After 30 min, the liquid phases were allowed to separate, and were removed by using a pipet.

TNT mixtures containing 90% or greater 2,4,6-TNT were analyzed by using a set-point technique developed in this investigation. The set point is defined here as the freezing temperature of TNT mixtures (or the temperature at which the first solid TNT crystals existed in contact with molten TNT mixtures). For this technique, 15 mg of dried TNT sample was heated in a capillary tube until complete melting occurred. The melt was then slowly cooled and seeded with a wire to which were attached minute amounts of TNT crystals; these crystals were obtained from the sample by inserting the wire into the melt, retracting the wire which cooled, resulting in the formation of crystals, and finally reinserting the wire into the melt. The temperature when the first crystal coexisted with the melt (less than 5 % crystallized) is defined as the set-point temperature. It was measured to within ± 0.1 °C; the temperature when the crystals first appeared upon cooling agreed within 0.1 °C of the temperature at which the crystals melted upon reheating. Cooling and reheating were repeated several times to obtain duplicate data and to test for reproducibility. The set point of pure 2,4,6-TNT was measured at 80.3 °C, and the set point of TNT samples decreased about 0.48 °C for every additional 1.0% of combined 2,4,5-TNT and 2,3,4-TNT in this range as shown in Figure 1.

All other samples were analyzed by gas chromatography, using a Tracor Model 550 programmable gas chromatograph equipped with a thermal conductivity detector and recorder. The column was 3.2 mm diameter stainless steel tubing, 275 cm long, and was packed with 4% UC-W-98 on 80/100-mesh Anakrom support.

Because of the potential hazards of TNT mixtures, the maximum amounts investigated were about 1.0 g per run. A polycarbonate safety shield was also employed.

Materials. Crude TNT, Military Specification TNT, 2,4,5-TNT, 2,3,4-TNT, 2,4-DNT, and 2,6-DNT were sup-

plied by the U.S. Army Armament Research and Development Command. No impurities were detected by gas chromatography when the 2,4,5-TNT, 2,3,4-TNT, and DNT isomers were analyzed. Crude TNT contained 96.5% 2,4,6-TNT, as determined by set-point analysis (78.6 °C); the remaining nitroaromatics were determined by gas chromatography to contain essentially equal amounts of 2,4,5-TNT and 2,3,4-TNT. Military Specification TNT contained 99.6% 2,4,6-TNT and a total of 0.4% 2,4,5-TNT and 2,3,4-TNT; it had a set point of 80.1 °C. Concentrated nitric acid, obtained from Mallinckrodt Inc., was diluted with water to the desired concentration and used for the extraction and crystallization investigations.

Results

In addition to set-point determinations, the following were obtained for various TNT mixtures.

(a) Transition Temperature. As a single-phase solution of nitric acid containing dissolved TNT was slowly cooled, two liquid phases formed. One phase was TNT-rich and was the denser phase. The second phase was nitric acid-rich. The temperature of this transformation is designated by the transition temperature. In general, for a given run, the appearance of this second phase upon cooling and its disappearance upon heating agreed within 2 °C and often within 1 °C. For replicate runs, however, there were some scatter in the temperatures, up to perhaps 5–8 °C. The reason for this scatter is not known, but it may have been caused by small differences in the concentrations of the nitric acid solutions due to preferential evaporation of water; a 1% increase in the concentration of the nitric acid would result in an 8 °C decrease in the transition temperature (Pickel, 1953). The transition temperatures reported are the arithmetical average of these two temperatures.

(b) Crystallization from Solutions. As the TNT-rich and nitric acid-rich liquid phases were slowly cooled with seeding, a temperature was reached when crystals were first detected. Upon slowly reheating the mixtures, a temperature was reached at which the crystals melted and the two liquid phases re-formed. The latter temperature was easier to measure because supercooling of the two liquid phases was a significant problem especially in the 40–65° 2,4,6-TNT range. The crystal melting temperature during heating was generally 2–7 °C higher than the temperature at which the first crystals formed during cooling. The melting temperature is reported here as the crystallization temperature. Without seeding of the solutions, the solutions had to be cooled 10–15 °C below the crystallization temperature before any crystals were noted.

The temperatures for the set point, transition transformation, and the start of crystallization were determined for several TNT mixtures. Figure 1 shows the temperatures for the transition transformation and for crystallization when a 0.5:1 weight ratio of TNT to 63% nitric acid was employed. In these cases, the TNT mixtures contained 0–100% 2,4,6-TNT; the remainder was an equal molar mixture of 2,3,4-TNT and 2,4,5-TNT. For these runs, the set-point temperatures were always 5–10 °C higher than the crystallization temperatures. The temperatures for all three phase changes passed through minima. Interestingly, the temperature minima for the set points and for crystallizations were at about 50% 2,4,6-TNT. Much greater difficulty was experienced in initiating crystallization in the 40–65% range of 2,4,6-TNT mixtures. Because of safety considerations, no attempt was made to measure the transition temperature for mixtures containing low amounts of 2,4,6-TNT since such temperatures were above 95 °C.

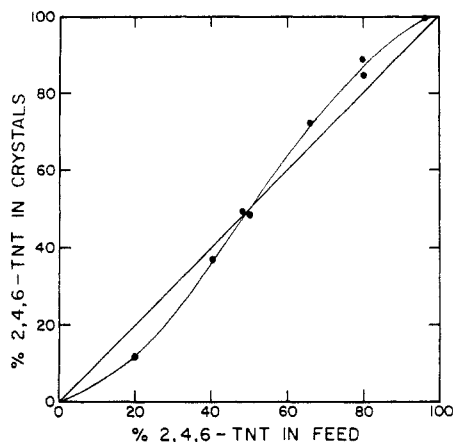


Figure 2. 2,4,6-TNT composition of crystals (0.5:1 ratio of TNT to 63 wt % nitric acid).

The transition temperature depends on the concentration of the nitric acid and on the ratio of TNT to nitric acid, as predicted from solubility data (Pickel, 1953). Several experiments were performed on crude TNT and a mixture of 80% 2,4,6-TNT, 10% 2,4,5-TNT, and 10% 2,3,4-TNT with either a 1:1 ratio of TNT to 63% nitric acid or a 0.5:1 ratio of TNT to 55% nitric acid. In all cases, the transition temperatures were above 95 °C. For these experiments, the crystallization temperature agreed within ± 2 °C of the comparable values shown in Figure 1.

In all crystallization experiments of this work, crystallization was initiated from a two-phase liquid system, producing crystals and a single-phase mother liquid. Studies were made to determine the preferred phase for crystal initiation and growth as follows. A well-mixed two-phase liquid system (0.5:1 ratio of crude TNT to 63% nitric acid) was cooled in the extraction apparatus to 65 °C without seeding. This temperature was 7 °C below the crystallization temperature, but no crystallization had started. Agitation was stopped, and the phases were allowed to separate. Both phases were then seeded by using a stainless steel wire. The upper nitric acid-rich layer formed some crystals, but on the basis of visual observations, considerably more crystals were formed in the lower organic-rich layer.

Several crystallization runs were made to determine both the amount and composition of TNT crystals formed when TNT-nitric acid mixtures were cooled. Crystallization occurred as the mixtures were cooled with gentle agitation at a rate of about 1 °C/min from the crystallization temperature to 25 °C. During cooling to 25 °C, the TNT-rich liquid phase disappeared in all cases. The exact temperature at which it disappeared could not be determined because the TNT crystals masked the nature of the liquid phases present. Three runs were made at identical conditions except for the time the slurry was maintained at 25 °C. The crystal yields were found to be essentially identical for hold periods of 10, 30, and 600 min. It was concluded that crystallizations at 25 °C are completed within about 10 min.

Figures 2 and 3 indicate the composition of TNT crystals when TNT mixtures such as used for Figure 1 experiments were employed. Crystallization of feedstocks with 60% or greater 2,4,6-TNT resulted in crystals with enriched fractions of 2,4,6-TNT. Crystallization of feedstocks with 40% or less 2,4,6-TNT, however, resulted in crystals with lower concentrations of 2,4,6-TNT than those of the feedstocks. No significant enrichment of 2,4,6-TNT occurred with the crystallization of feedstocks containing about 50% 2,4,6-TNT. For crude TNT feedstocks, the

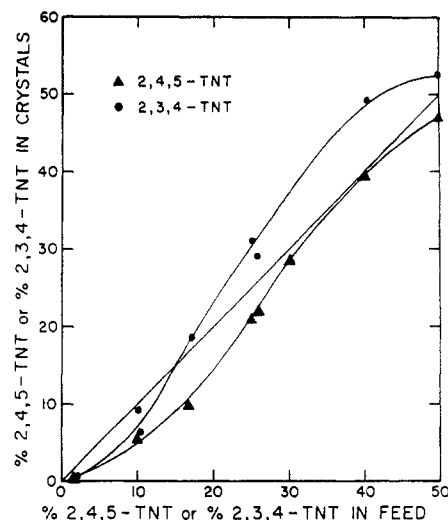


Figure 3. 2,4,5-TNT and 2,3,4-TNT compositions of crystals (0.5:1 ratio of TNT to 63 wt % nitric acid).

crystal compositions and yields were in good agreement with the rather limited data of Pickel (1953) and Clift and Jablonsky (1955).

For TNT mixtures containing about 16–50 % 2,3,4-TNT and having a 1:1 ratio of 2,3,4-TNT to 2,4,5-TNT, 2,3,4-TNT enrichment occurred in the crystals, as shown in Figure 3. For all crystallization experiments of the present investigation, there were reduced fractions of 2,4,5-TNT in the crystals as compared to the starting mixture. Figure 3 also shows this result. The mother liquor of course had an increased relative amount of 2,4,5-TNT.

For runs using a 0.5:1 weight ratio of TNT to 63% nitric acid, approximately 82% of the initially dissolved TNT isomers were recovered as crystals when the mixtures were cooled to 25 °C. These specific runs were made with TNT mixtures containing 20–100% 2,4,6-TNT. Such a recovery (or yield) is considered reproducible within $\pm 4\%$ (80% confidence limit). When, however, a 1:1 mixture of 2,3,4-TNT and 2,4,5-TNT that contained no 2,4,6-TNT was dissolved and then crystallized, 94% of the TNT isomers was recovered as crystals. This latter high yield is likely caused by the relative low solubility of 2,3,4-TNT in nitric acid (Pickel, 1953). In this experiment, the crystals were significantly enriched with 2,3,4-TNT, as shown in Figure 3 (see results of 50% 2,3,4-TNT and 50% 2,4,5-TNT).

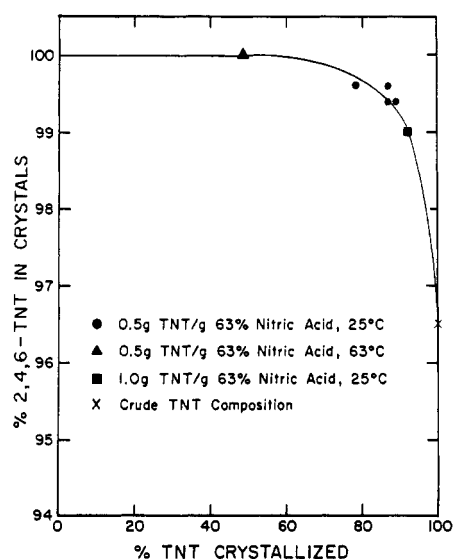
Two runs were performed to investigate the effect of adding 2,4-DNT and 2,6-DNT to TNT mixtures. The two mixtures tested were as follows: (a) 92% of 2,4,6-TNT; 2% each of the following were present, 2,3,4-TNT, 2,4,5-TNT, 2,4-DNT, and 2,6-DNT; and (b) 86% of 2,4,6-TNT and 7% each of 2,4-DNT and 2,6-DNT.

The crystals of the first experiment contained no detectable DNT isomers and the crystals in the second experiment contained 99.6% 2,4,6-TNT and about 0.4% 2,6-DNT. The presence of moderate amounts of DNT isomers in the TNT mixtures hence had only a very small effect on the recovery of high-purity TNT crystals.

The ratio of TNT feedstock to nitric acid, the concentration of nitric acid, and the filtration temperature all affected the crystal compositions and percent recovery of TNT in the crystals. Such a conclusion is expected since these factors influence the solubility of the TNT isomers in nitric acid. Experiments were performed on both crude TNT and a mixture with 80% 2,4,6-TNT, 10% 2,4,5-TNT, and 10% 2,3,4-TNT. With a 1:1 ratio of crude TNT to 63% nitric acid and a filtration temperature of 25 °C, there

Table I. Crystal Compositions and Percent Recoveries at 25 °C

run	TNT feed	% nitric acid	TNT/nitric acid	% recovery	TNT comp of cryst, %
1	crude	63	0.5	86.9	99.6
2	crude	63	1.0	92.2	99.0
3	crude	55	0.5	95.0	98.6
4	80% 2,4,6-TNT	63	0.5	80.2	88.8
5	80% 2,4,6-TNT	63	1.0	85.0	84.6
6	80% 2,4,6-TNT	55	0.5	92.0	82.9

**Figure 4.** 2,4,6-TNT composition of crystals as a function of the percent crystallized from crude TNT feedstocks.

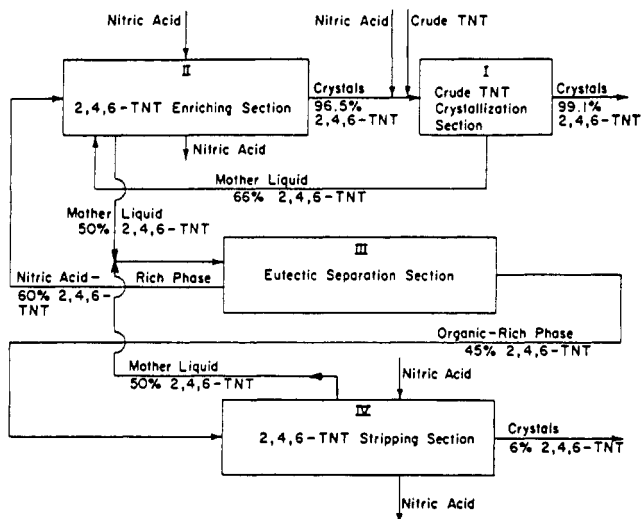
was a 5% increase in the recovery and a decrease in the 2,4,6-TNT concentration in the crystals as compared to a ratio of 0.5:1, as shown in Table I (run 1 vs. 2). A similar recovery increase occurred when a feedstock containing 80% 2,4,6-TNT feedstock was used (run 4 vs. 5). A comparison of the results of runs 1 and 3 and runs 4 and 6 indicates that the crystals formed when 63% nitric acid is used have a higher concentration of 2,4,6-TNT than when 55% nitric acid is used.

For runs using the crude TNT product stream from the Radford Arsenal as a starting mixture and crystallization cooling rates of 1 °C/min, a plot was obtained as shown in Figure 4 of the 2,4,6-TNT composition of the crystals vs. the percent TNT crystallized. Four runs were made by using a ratio of 0.5:1 of TNT to 63% HNO₃ at 25 °C; the recovery of TNT in the crystals was about 87%, and the crystals contained about 99.5% 2,4,6-TNT. If the mixture was cooled just to 63 °C, only 49% of the TNT crystallized but the crystals were almost pure 2,4,6-TNT. A higher percent of TNT was crystallized when a higher ratio (1:1) of TNT to nitric acid was used, but as shown in Figure 4, the crystals contained less 2,4,6-TNT. The curve can of course be extrapolated to the crude TNT composition at 100% recovery. This curve is thought to be a rather general curve irrespective of the method of changing the percent TNT crystallized.

The results of the present investigation indicate that complete separations of the three major TNT isomers would be difficult and probably impossible with just crystallization. Enrichment of any TNT isomer in the crystals formed would be at best very small for TNT feedstocks containing 40–60% 2,4,6-TNT. Furthermore,

Table II. Extraction of a Feedstock Mixture of 50% 2,4,6-TNT, 25% 2,4,5-TNT, and 25% 2,3,4-TNT at 60 °C

run	7	8	9
TNT/63% nitric acid	0.5:1	0.25:1	0.5:1
TNT-rich phase			
2,4,6-TNT	44.9	42.3	46.6
2,4,5-TNT	27.3	22.3	23.0
2,3,4-TNT	27.8	35.4	30.4
nitric acid-rich phase			
2,4,6-TNT	61.4	54.8	59.3
2,4,5-TNT	19.5	24.7	24.4
2,3,4-TNT	19.1	20.5	16.3
organic-phase yield, %	61.9	71.9	67.3

**Figure 5.** Block diagram of the proposed crude TNT separation plant. 2,4,6-TNT stream compositions are on a nitric acid–water-free basis, and the remainders are 2,4,5-TNT and 2,3,4-TNT.

there are problems in initiating crystallizations for such feedstocks. Hence, an effort was made to determine if extractions with nitric acid could be used to obtain effective separations in this range of TNT compositions.

Three extraction runs were made starting with a feed mixture containing 50% 2,4,6-TNT and 25% each of 2,3,4-TNT and 2,4,5-TNT. Ratios of 0.25:1 and 0.5:1 of TNT to 63% nitric acid were investigated. As indicated by Table II, the TNT isomers dissolved in the nitric acid phase were significantly richer in 2,4,6-TNT but were poorer in 2,3,4-TNT as compared to the TNT's in the TNT-rich phase. About 60–70% of the TNT's were present in the TNT-rich phase at 60 °C.

Application of Results

The data obtained in this investigation have been used to make a preliminary design of a unit for essentially complete separation and recovery of 2,4,6-TNT from crude TNT feedstocks. The proposed process is for crude TNT feedstocks that have been hot water washed to remove any nitrating acids; the feedstocks contain about 96.5% 2,4,6-TNT and have approximately a 1:1 ratio of 2,4,5-TNT to 2,3,4-TNT. Only the separation of 2,4,6-TNT from 2,4,5-TNT and 2,3,4-TNT will be considered, and thus Figure 2 is applicable. Failure to consider DNT impurities is justified since their presence was shown to have no significant effect on the proposed TNT separation.

For essentially complete separation of 2,4,6-TNT, four sections are required as indicated in Figure 5. The feeds to section I include the crude TNT product from the nitration plant plus crystals from section II to be discussed later. The crystallizer in section I is the largest one, and in this crystallizer, Military Specification TNT is produced.

The crystallization can be accomplished by using a 1:1 ratio of TNT to 63% nitric acid and with a filtration temperature of 25 °C. The resulting crystals are washed, dried, and flaked. The mother liquid containing dissolved TNT is sent to section II. The dissolved TNT's contain about 66% 2,4,6-TNT.

Feeds to section II (the enriching section) are the mother liquid from section I and the nitric acid-rich extract from section III. The dissolved TNT's in this extract contain about 60% 2,4,6-TNT. This extract is first sent to an evaporator to remove some nitric acid and water; the concentrated extract is then sent to the first crystallizer in section II to produce TNT crystals containing about 66% 2,4,6-TNT. These crystals and the mother liquid of section I are combined. Further crystallizers plus evaporators are used to enrich the 2,4,6-TNT content of the crystal products up to about 96.5% 2,4,6-TNT; these crystals are then sent as feed to section I. Mother liquids that contain dissolved TNT's with about 45–55% 2,4,6-TNT are sent as liquid feeds to section III. Other mother liquids are combined with crystal streams of section II that have about the same TNT composition. It is estimated that up to six crystallizers will be needed in section II. The exact number will depend on the conditions used and on the amount of evaporation employed. The once-through recovery of 2,4,6-TNT entering section II is estimated to be about 80–85%.

Feeds to section III are the mother liquids from sections II and IV that contain dissolved TNT's with about 45–55% 2,4,6-TNT. Both water and nitric acid need to be removed by evaporation or stripping. Then, by adjusting the ratio of TNT to 63% nitric acid to about 0.5:1, two liquid phases result. The nitric acid-rich phase is sent to section II and the TNT-rich phase to section IV.

The feed stream to section IV (the stripping section) is the TNT-rich phase from section III. The TNT's in this phase contain about 45% 2,4,6-TNT, and the phase is combined with 63% nitric acid to produce a 0.5:1 ratio of TNT to nitric acid. A series of crystallizers, estimated to be about seven, could be used to produce crystals rich in 2,3,4-TNT and 2,4,5-TNT and containing perhaps only 6% 2,4,6-TNT. The mother liquids of section IV are sent to section III.

Crystallization could likely be employed to separate and recover both 2,3,4-TNT and 2,4,5-TNT as relatively pure crystals. No data were, however, obtained for such separations.

Clearly the expense of making a complete separation and recovery of the various TNT isomers would be high and probably prohibitive. An economic analysis and optimization of the process variables should be considered for each section. For example, if only the crude TNT section (I) is employed, a 92% yield of Military Specification TNT and a mother liquid TNT of 66% 2,4,6-TNT is obtainable. If, however, the enriching section (II) is added, then the mother liquid TNT will be rejected at about 50% 2,4,6-TNT, and the yield of Military Specification TNT will increase by about 2% to a total of 94%. With the subsequent addition of the eutectic separation section (III) and the stripping section (IV), the ultimate yields become 95% and 97%, respectively, based on crude TNT.

Once an economic analysis has been made and tentative conclusions have been reached on the level of 2,4,6-TNT recovery justifiable, some additional data should be obtained to permit an improved optimization of the process. Variables that need further investigation include the concentration and amounts of nitric acid to be used in extraction and crystallization and the preferred temperatures for each phase of the process.

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Registry No. 2,4,6-TNT, 118-96-7; 2,4,5-TNT, 610-25-3; 2,3,4-TNT, 602-29-9.

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