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PILOT SCALE SYNTHESIS OF TATB

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DEVELOPMENT DIVISION

JULY 1976
(SUMMARY)

Normal Process Development
Endeavor No. 106

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ABSTRACT

The processes developed by Mason & Hanger for the pilot scale production of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) are described. 1,3,5-trichlorobenzene (TCB) was nitrated to form 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) and then aminated to TATB. The effects of several variables, the process procedures and the equipment are discussed.

INTRODUCTION

TATB was successfully produced in 16 to 22 kilogram batches at the Pantex Plant Development Pilot Plant using sym-trichlorobenzene (TCB) as a starting material. The reaction route involved two steps, the nitration of TCB to yield sym-trichlorotrinitrobenzene (TCTNB) and its subsequent amination to TATB. Pilot scale work began in June of 1972 and since that time has produced 9100 kg of TATB.

This synthesis route was reported by Kaplan(*1*), then scaled-up by Benziger(*2*). The work at Pantex has been based on these two reports. The scale-up of the nitration has been very predictable. A successful scaled-up process for the amination has been attained but some difficulties were encountered with the particle size of the TATB powder.

The maximum production rate attained was 545 kg per month of TATB, starting from TCB, and operating two shifts, five days a week.

SYNTHESIS OF TCTNB

TCTNB can be made in 30% oleum with sodium nitrate or concentrated nitric acid. Concentrated sulfuric acid can also be used in the place of oleum in the nitric acid process.

All of the Pantex TCTNB was made by nitrating TCB from American Hoechst. The Hoechst TCB was very pure (99+%) and no problems have been associated with its purity. The purity of TCB has generally been determined by gas chromatography (GC). Two GC procedures were successfully used, the methods of Yasudia(*3*) and of Hrivak(*4*).

TCTNB is a white-to-buff colored, crystalline solid. Since it is aminated in solution, the particle size is not critical. The melting point is approximately 190 C, and is affected by the amount of TCDNB and T_4CDNB present. Fig. 1 shows a DTA scan for TCTNB. TCTNB can be analyzed by liquid chromatography(*5*). Fig. 2 shows a liquid chromatogram for a batch of TCTNB(*6*). Pantex purchased 1800 kg of TCTNB from United Technology Corporation, for amination(*7*). This material met the following criteria:

0.1% acid maximum, as H_2SO_4
0.1% maximum, toluene insolubles
85% minimum TCTNB
188 C minimum melting point.

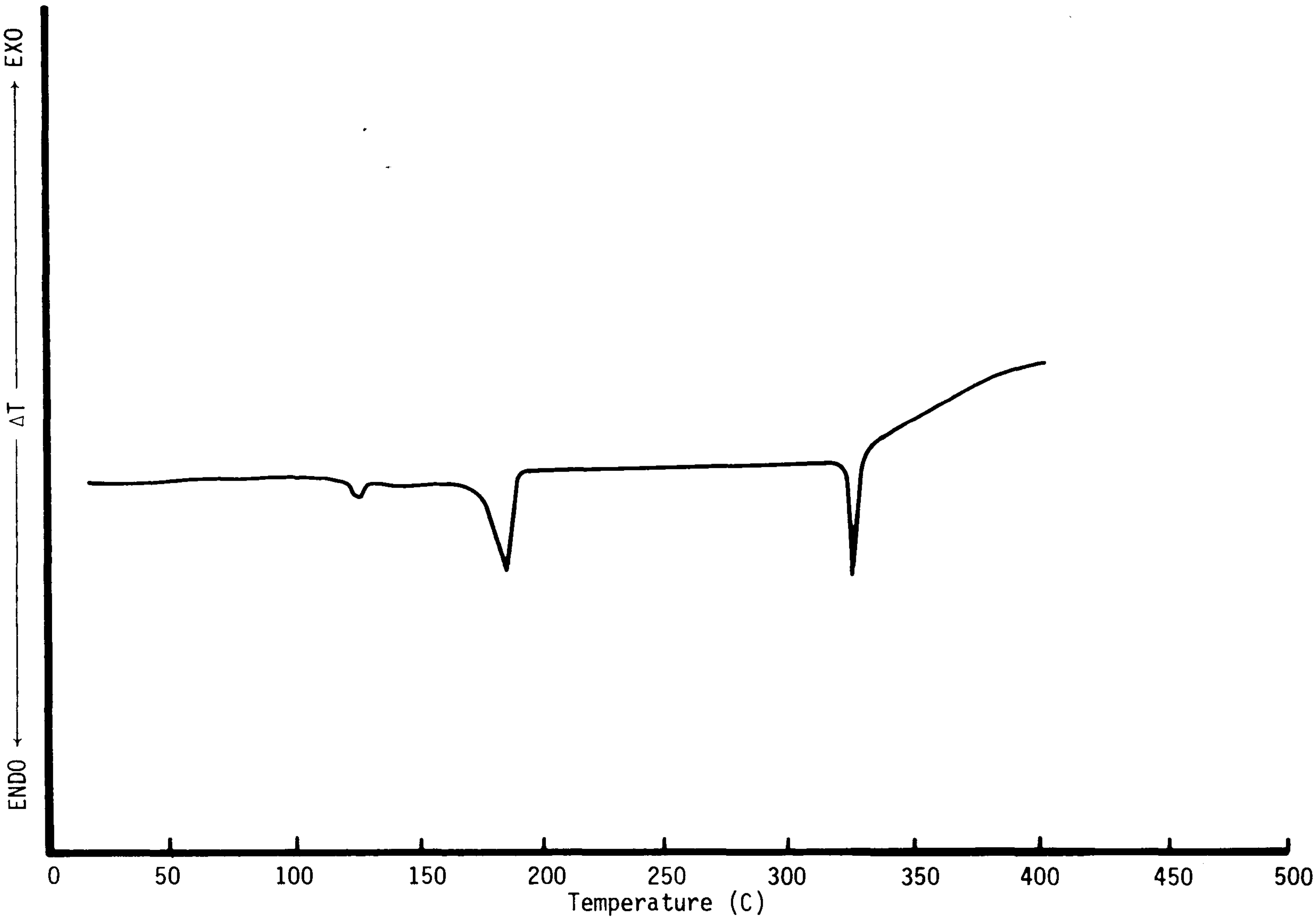


Fig. 1. Pantex TCTNB Batch No. 5212-14-02 (87.6% TCTNB, 9.7% T_4CDNB, 2.7% TCDNB)

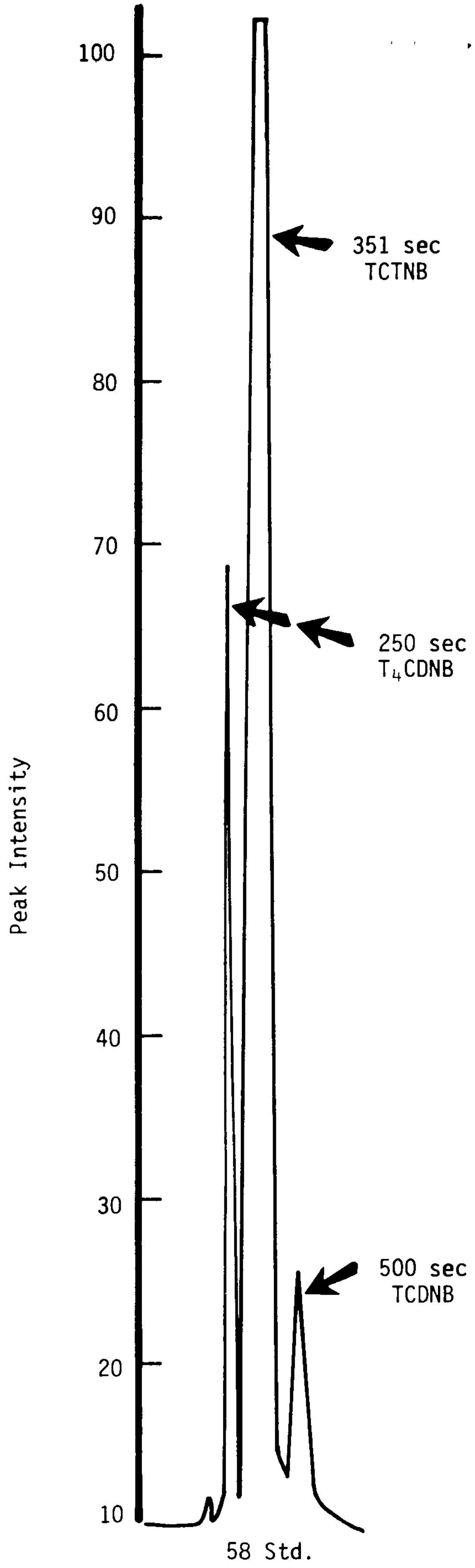
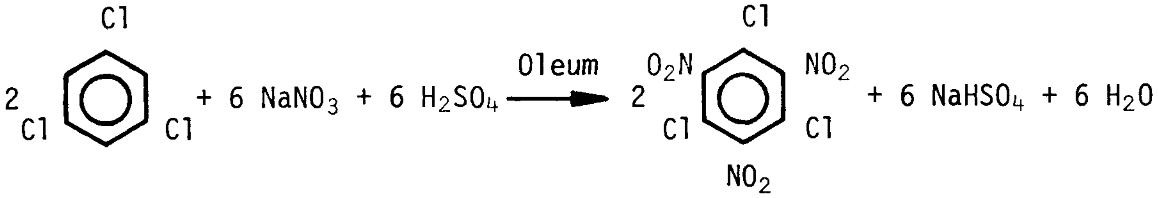


Fig. 2. Liquid Chromatogram of Production TCTNB

Also, the moisture content must be known for shipping information and for pre-amination drying.

The sodium nitrate process was outlined in Los Alamos Scientific Laboratory (LASL) report LA-3632 by T. M. Benziger and R. K. Rohwer. Most of the TCTNB was made with this process. Much of the early TCTNB was recrystallized in trichloroethylene to reduce the impurities. Optimization of the nitration and improved amination techniques eliminated the recrystallization step in April, 1973. The final sodium nitrate process used the reaction:



Pure TCTNB could not be obtained. Two byproducts were generated in significant amounts. 1,3-dinitro-2,4,6-trichlorobenzene (TCDNB) and 1,3-dinitro-2,4,5,6-tetrachlorobenzene (T_4CDNB) were found in all batches of TCTNB. A 3-1/2 hour, 150 C reaction minimized the amount of impurities(*8*). Shorter or colder reactions resulted in higher percentages of the incompletely nitrated TCDNB. Longer or higher temperature runs showed an increase in the amount of T_4CDNB. This may be due to partial oxidation of TCB which produces additional chlorine. A total of 219 batches (yielding 8,580 kg) of TCTNB were made using a charge of 25 kg of TCB and 78.2 kg of sodium nitrate slurried in 455 kg of 30% oleum. The large excesses of sodium nitrate and oleum are required for effective nitration. A few minor variations were made in these quantities but no improvements were evident. The mean batch, with the above quantities gave:

37.8 ± 2.6	kg dry product
3.2 ± 2.8%	TCDNB
9.4 ± 2.3%	T_4CDNB
87.4 ± 3.2%	TCTNB

This represents a 75.8% theoretical yield of pure TCTNB.

The nitrations were conducted by charging 455 kg of oleum to a 100-gallon glass lined reactor. With cooling water circulating in the reactor jacket and vigorous agitation the sodium nitrate was slowly added to the oleum with the temperature maintained below 130 C. After reducing the temperature to below 115 C, the TCB was added in three portions. A five minute interval between each portion allowed the operator to watch for any rapid temperature changes. No TCB was added to the nitrating mixture above 130 C. With full cooling, the TCB additions had a minimal effect on the slurry temperature. Laboratory work indicated that a rapid exotherm developed if the slurry reached 165 to 170 C. Once started, this exotherm is essentially uncontrollable and the entire slurry could be lost in a matter of seconds. After the

TCB additions, the reaction mixture was heated to 150 C. A stirring rate of 180 rpm was used. Even at elevated temperatures, the liquid TCB formed a layer above the acid. Therefore, vigorous agitation was required to mix the reactants.

During all nitration steps, acid and nitrogen oxide vapors were removed by ventilation ducts. A five centimetre open port vented the reactor during the chemical additions and during the reaction. Also, during the reaction, a sublimate of TCTNB and byproducts collected on the top inside surfaces of the reactor. The vent port was regularly freed of sublimate.

At the end of the reaction period, the mixture was cooled to below 50 C and with vigorous agitation, 75 litres of water was slowly added. During all quench steps, the temperature was maintained below 115 C. Failure to do so would result in the formation of large agglomerates of TCTNB (often, exceeding two centimeters in diameter). After the 75-litre quench, the reacted slurry was added to 230 litres of cold water in a cooled, agitated 800-litre quench vessel and the temperature was reduced to below 50 C. After two hours, the solid product settled and most of the acid was decanted (siphoned) into a vacuum receiver for disposal. An additional 230 litres of water was introduced to wash the TCTNB. This additional dilution of the acid made the filtration easier and less hazardous. Originally, the quench step used ice to aid in cooling. The two-step quench described above is much more desirable. The quench could be completed in the nitration vessel but was normally accomplished in a 200-gallon reactor(*9*). If the nitration slurry fills the vessel to a high level, it may be necessary to decant and add water several times. This would lower the acid concentration for filtration if only one vessel was available. The granular TCTNB, 25 to 300 microns in diameter, was isolated and washed again on a large porcelain filter until the wash water was neutral. After pulling air through the filter for at least six hours, the product was sampled and packaged.

A nitric acid/oleum process was also used to nitrate TCB. The process was identical to the sodium nitrate procedure except for the amount of material used. Five batches of TCTNB were made using 70 kg 98% nitric acid, 370 kg 30% oleum and 39.1 kg TCB. Due to the volatility of nitric acid, a higher ratio of nitric to sulfuric acid would have required a pressure nitration(*10*) or a reflux condenser. The batch average for these runs were:

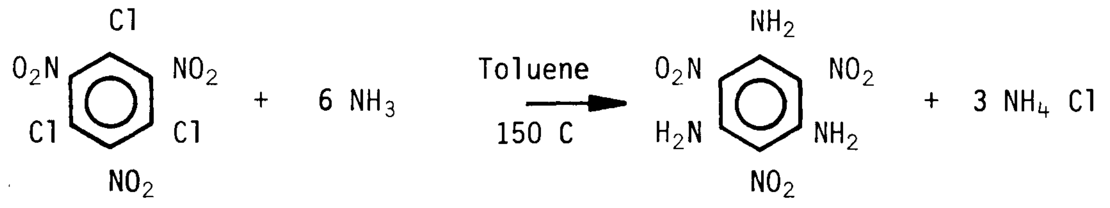
60.8 ± 2.3 kg dry product
2.4 ± 0.2% TCDNB
8.1 ± 1.0% T_4CDNB
89.5 ± 1.1% TCTNB

Two larger nitric acid batches using 47.3 kg of TCB, 84.5 kg 98% HNO_3, and 440 kg oleum were made with satisfactory results. For larger scale processing, the nitric acid process has several advantages over the sodium nitrate reaction. The solid sodium nitrate is replaced by the liquid acid which is much easier to transfer and control. The mixed acids can allow some reuse and/or reconstitution. The mixed acid system has a lower viscosity aiding filtration and agitation. Also, an increased throughput and cost savings are gained with the use of nitric acid.

Three glassed-steel vessels were used in the nitration of TCB. The nitration vessel was a Pfaudler 100-gallon, "P" Series reactor. The quench vessel was a Pfaudler 200-gallon, "EM" Series reactor. The standard three blade, retreat "S" agitator and "H" baffel were used in both of these reactors. A Pfaudler 200-gallon, glassed-steel vacuum receiver retained the decanted acid and acid filtrates. A 25-gallon, chemical stoneware filter (M. A. Knight Co., No. 285-A) was used to filter, wash, and dry the TCTNB. Polypropylene cloth served as the filter media.

SYNTHESIS OF TATB

Amination of TCTNB involved solution in toluene, filtering the solution and aminating with ammonia. TATB synthesis followed the reaction:



The reaction is slightly exothermic; however, no rapid heat rise was encountered. Aminations at 150 C were the most successful. Two characteristics of TATB have been used to compare batches. These are chloride content and particle size. The resulting TATB powder varied with changes in process parameters. Agitation rate and the TCTNB concentration had the most significant effect on the product.

TATB is a yellow, free flowing powder. It melts about 330 C. Fig. 3 shows a DTA scan for a batch of Pantex TATB. The chloride content and particle size specifications have varied since this pilot plant work began. Originally, the maximum accepted levels were:

0.60% chloride
8.0% of the particles less than 20 μm
40.0% of the particles less than 44 μm

In June of 1975 the levels were increased to

0.75% chloride
15.0% of the particles less than 20 μm
40.0% of the particles less than 44 μm

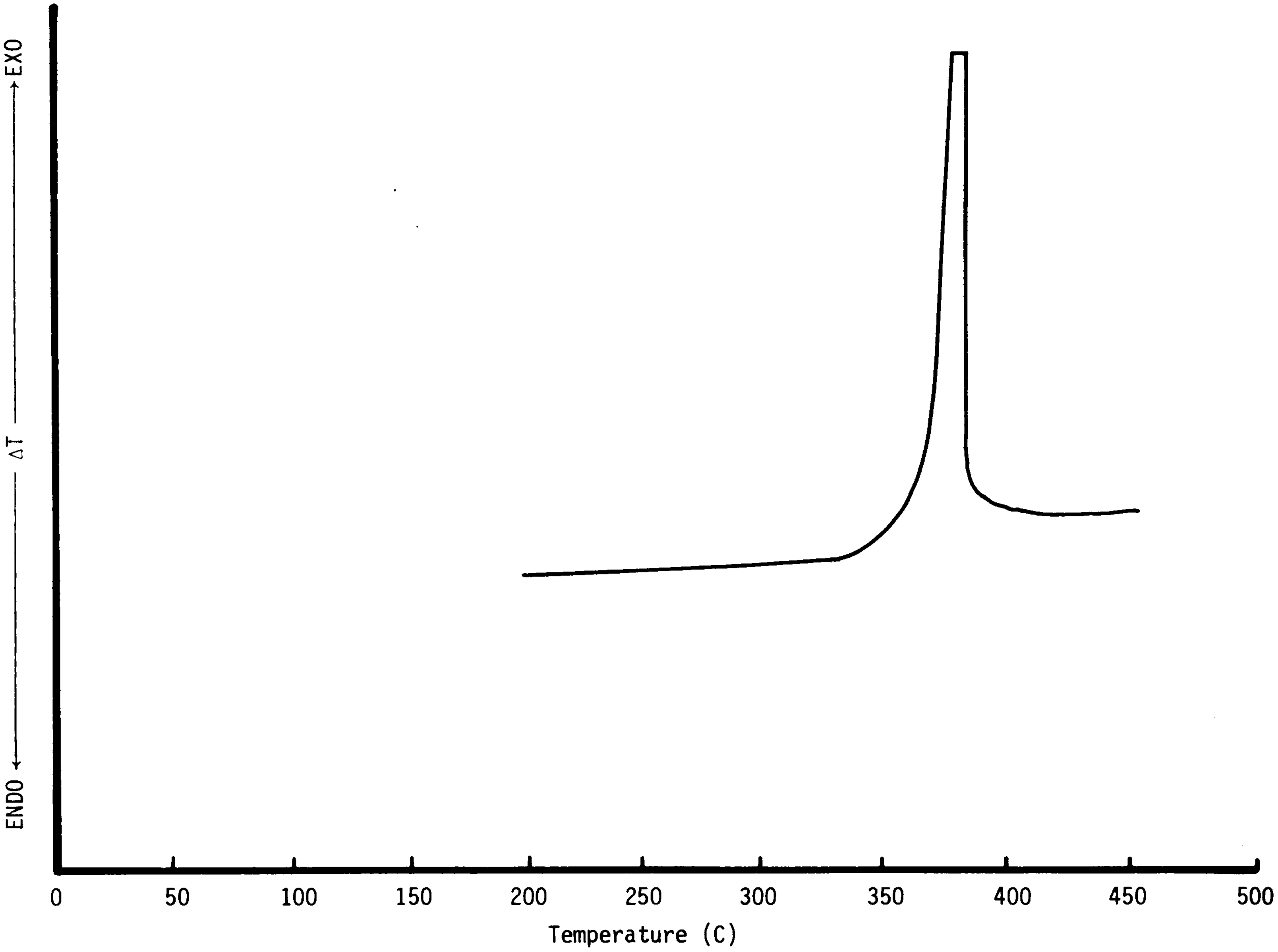


Fig. 3. Pantex TATB Batch 5231-16-02 (0.74% Cl, 12.2% < 20 μm, 35.3% < 44 μm)

In June of 1976 they were changed again to

0.75% Chloride
25.0% of the particles less than 20 μm
50.0% of the particles less than 44 μm

Other characteristics of TATB quality include foreign inclusions, moisture content, percent dimethylsulfoxide (DMSO) extractables, and inorganic chlorides.

The amination process began by charging the toluene to a mixing vessel. Reagent grade toluene was normally used. A single reuse of the toluene filtrate, without distillation was found to be acceptable(*11*). After dissolving the TCTNB in toluene, the solution was passed through a ten micron filter in the transfer to the amination reactor. Due to the low flash point of toluene, nitrogen pressure was used to drive material from one vessel to another. Once loaded, the amination mixture was heated to about 110 C and the water/toluene azeotrope vented. These vapors were directed into the building exhaust system. When a sample of this condensed vapor was free of water (by visual inspection), the heating continued. At 140 C, anhydrous ammonia was allowed to enter the reactor ullage at a feed pressure of 0.41 MPa (60 psig). The ullage was purged three times with ammonia. The reactor pressure was raised slightly with ammonia and then vented for each purge. With the purge complete, and water and air eliminated, the amination reaction began. Ammonia was fed to the reactor at a rate of about two kilograms per hour from the 0.41 MPa source. This corresponded to an ammonia flux of 4.4 kg/m^2/hr of fluid surface (with no agitation). The reaction end point was noted when the vessel pressure approached the feed pressure and the ammonia flowrate decreased rapidly. Also, the temperature decreased as the reaction neared completion. A total of 6.3 to 6.8 moles of ammonia, were used for each mole of pure TCTNB. An average theoretical yield, based on TCTNB, of 97% was realized. After depressurizing and cooling the reaction mixture, 75 litres of water was used to dissolve the ammonium chloride in the finished slurry. The toluene/ water/TATB slurry was stirred at 100 C for a minimum of 30 minutes. After cooling to below 80 C, the TATB was recovered in a filter press. While still in the filter, the product was hot water washed and steamed. The finished material dried in a forced draft oven at 115 C for sixteen hours prior to sampling and packaging. Characterization of TATB by chloride content and particle size have been discussed in several reports. The sieve method used has been described by Duncan(*12*). Applications of this method to TATB were described in two reports(*13*). The chloride content of TATB has been determined by four methods. Total chloride is determined with an oxygen bomb calorimeter (Parr Model) and by X-ray flourescence. These two methods have been described by Faubion and Blair(*14*). A sulfuric acid method and a NMR method are used to determine the amount of inorganic chloride. The sulfuric acid method was described by Kohn(*15*) and NMR method by Clink(*16*).

The resultant TATB is dependent on processing conditions. The concentration of TCTNB in toluene and the agitation speed have pronounced effects on the product. TCTNB concentrations of 0.030 to 0.174 kg crude TCTNB/litre toluene were investigated. As shown in Fig. 4(*17*), higher concentrations gave finer particles. An agitation rate of 80 to 120 rpm (Fig. 5)(*17*) formed the largest particles. Also, the amount of chloride found in the TATB increased at the higher agitator speeds (Fig. 5). Many different combinations of TCTNB concentrations and agitation rates have been used to produce various sizes of TATB particles. Three processes developed and run extensively at Pantex were the 0.06 and the 0.108 kg/litre single additions and, the 0.072/0.060 kg/litre double addition batch.

Nineteen reactions with a 0.06 kg/litre concentration and an agitation rate of 80 rpm, for 312 litres of toluene, produced 226 kg of TATB with an analysis of:

6.7 ± 2.2% of particles less than 20 μm
37.0 ± 7.3% of particles less than 44 μm
0.56 ± 0.08% chloride
11.9 ± 0.9 kg yield.

This process served as a baseline to demonstrate the effects of experimental process changes. Also, when time was short, this batch provided a quick, four hour amination yielding very acceptable TATB.

Seventeen batches were made at 90 rpm, for 312 litres of toluene, at the 0.108 kg/litre. The analysis was:

9.5 ± 4.1% of particles less than 20 μm
27.4 ± 13.8% of particles less than 44 μm
0.68 ± 0.08% chloride
22.1 ± 0.9 kg yield.

This was the largest sized batch that was thoroughly investigated. Fig. 6 shows a typical particle size distribution for these runs.

A multiple addition technique was developed as a possible method for obtaining a larger batch size(*18*). In this process, one charge of TCTNB/toluene was aminated to its endpoint. No material was removed from the vessel and a second charge was added. Amination then continued again to the endpoint. Triple additions were also studied to a limited degree. One double addition procedure that worked well started with an initial charge at a 0.072 kg/litre concentration. After this TCTNB reacted, additional toluene and TCTNB filled the vessel to the second reaction level. The concentration of the slurry at the start of the second amination was 0.06 kilograms of unreacted, crude TCTNB per litre of toluene in the vessel (0.25 rpm per litre of toluene was used for each reaction). Twenty seven batches made with this technique gave an analysis of:

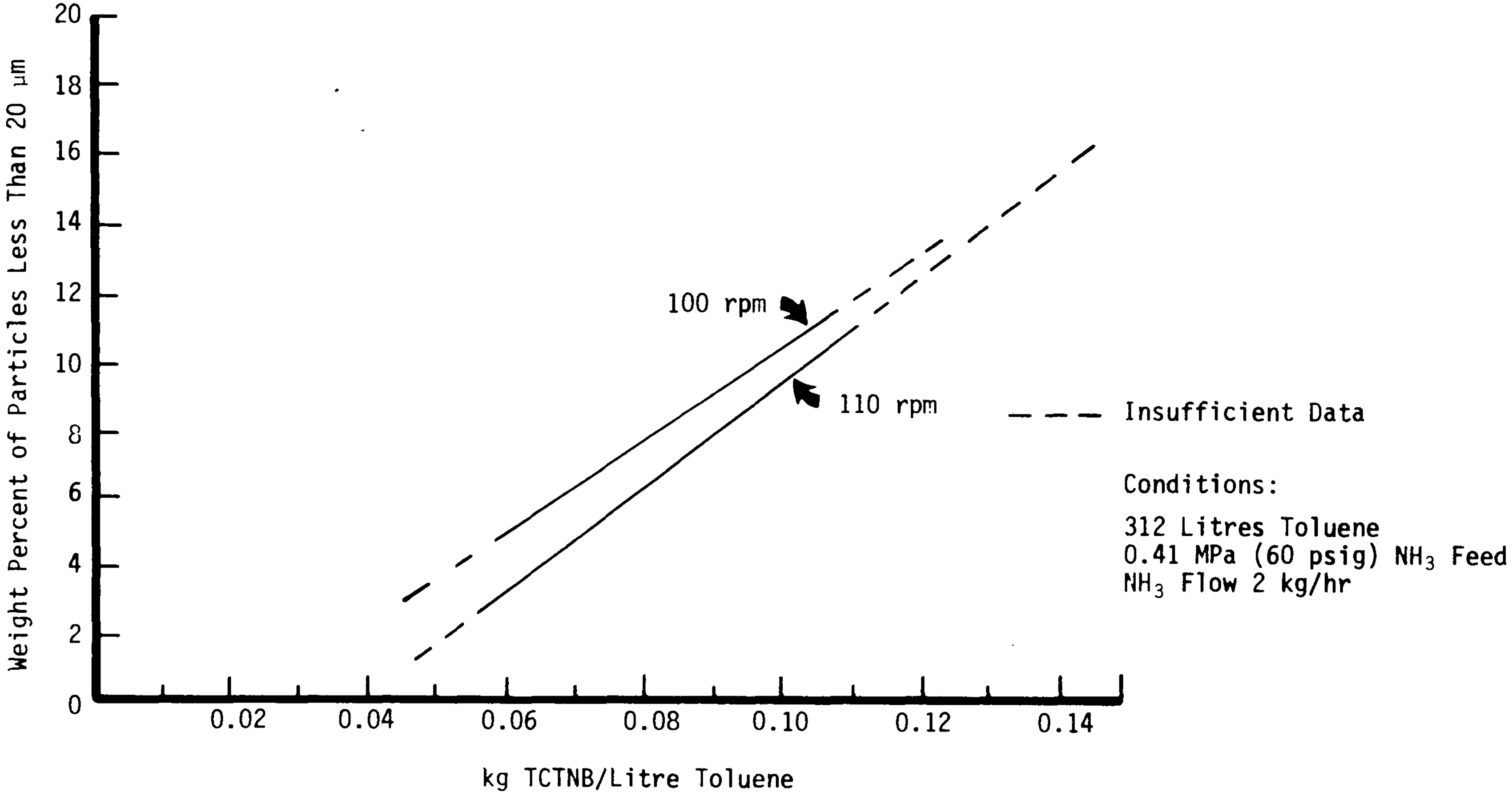
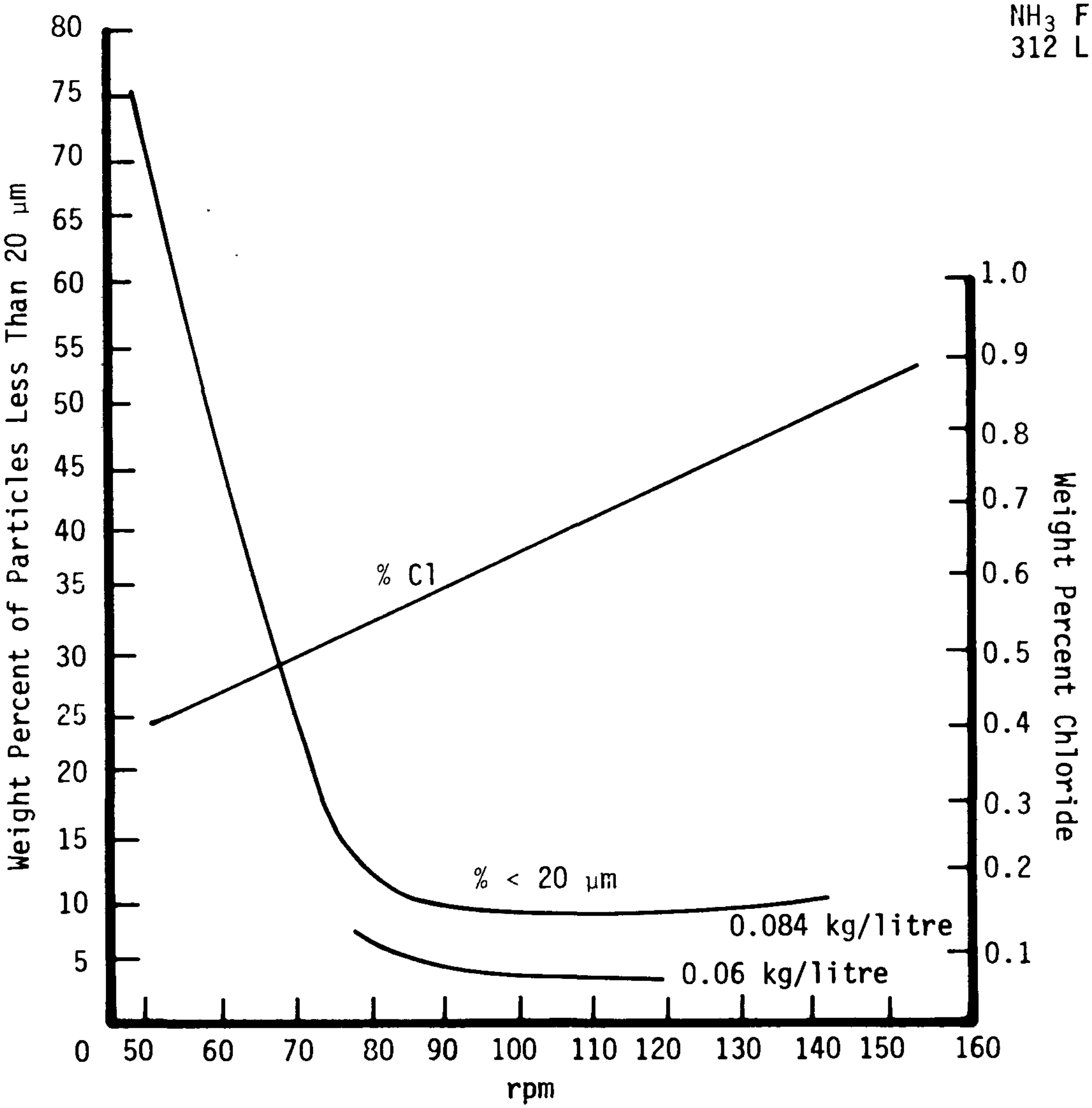


Fig. 4. Effect of Concentration on Particle Size



Conditions:

0.06 & 0.084 kg TCTNB/Litre Toluene
0.41 MPa (60 psig) NH_3 Feed
NH_3 Flow 2 kg/hr
312 Litres Toluene

Fig. 5. Amination Effect of Stirring on Particle Size and Chloride Content

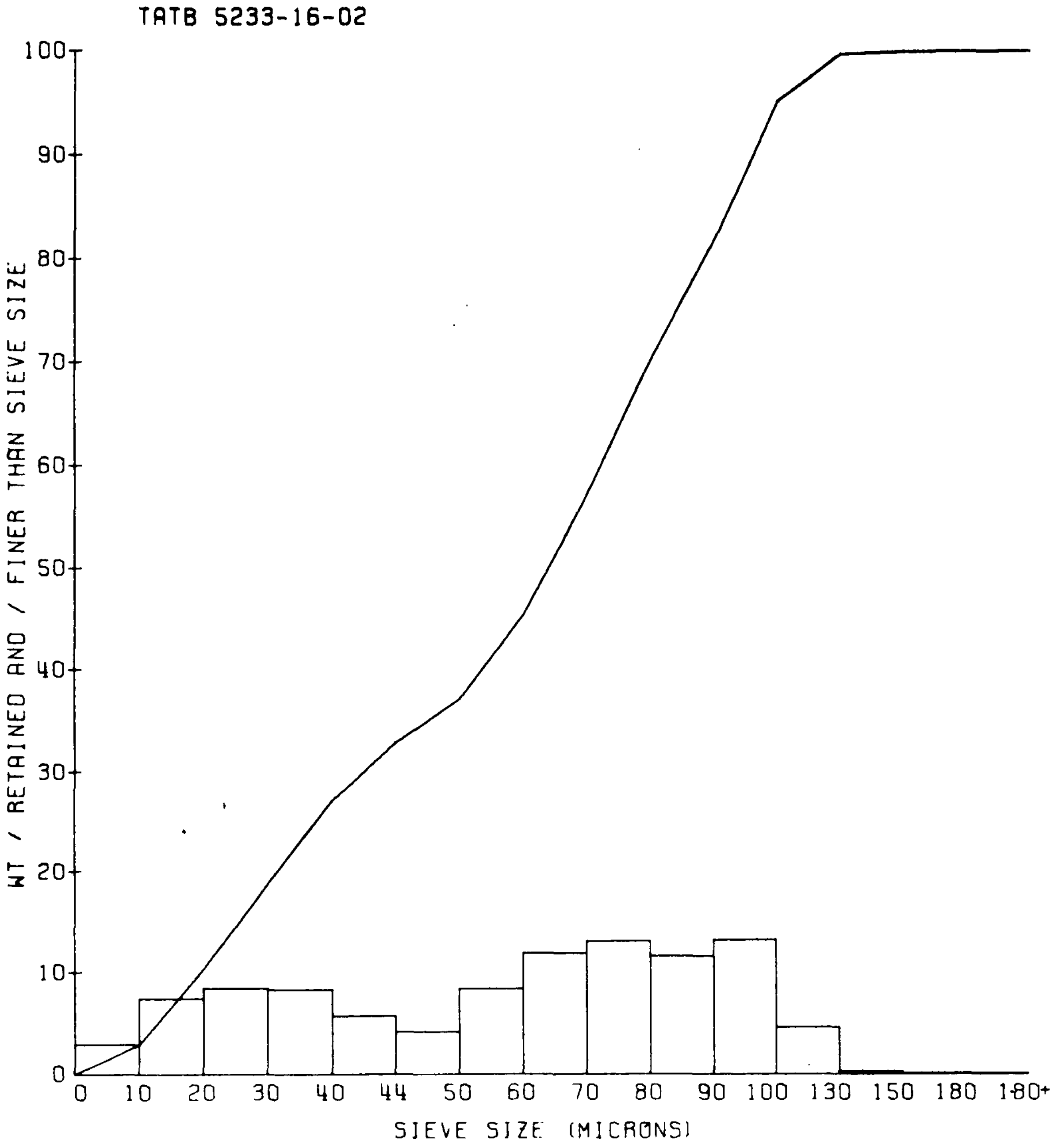


Fig. 6. Typical Particle Size Distribution

6.5 ± 2.6% of particles less than 20 μm
32.7 ± 7.1% of particles less than 44 μm
0.54 ± 0.09% chloride
16.0 ± 1.0 kg yield.

A Pfaudler, 100-gallon, 316 ℓ stainless steel reactor served as the aminator. Four standard sidewall baffles and a thermometer well were included. The impeller was a six-bladed turbine with pitched blades. This provided the axial flow required to raise the particles to the gas/liquid interface where reaction occurred. A Sperry, 12-inch type RC, 304 stainless steel filter press was used to filter the TATB slurry. Some corrosion was noted in the filter frames which was probably due to chloride attack. No. 1 cotton duck filter medium was used.

Both the nitration and amination have been scaled-up by others from this pilot scale work. TCTNB has been made in 550 kg batches using these nitration processes. No problems were seen. The amination reaction has been conducted on a scale that yields 130 kg of TATB(*19*). Some difficulty was encountered in obtaining the coarse particle size desired. Control of the ammonia flowrate and agitation rate improvements increased the particle size.

CONCLUSIONS AND FUTURE WORK

TATB can be made satisfactorily in pilot and large scale batch processes. TCTNB production is straightforward and easily scaled. The amination reaction to TATB requires careful scale-up analysis to duplicate the particle size when using the procedures in this report.

Since large quantities of TATB will be required in the future, process development should continue. The nitration of TCB requires a tremendous excess of raw materials. Different batch reactor designs, continuous systems, and recycle of nitrating acids should be studied. The different nitration processes should be compared on a basis of product quality and cost. A process that can give larger particles, lower chloride contents, and more economical TATB should be developed. Any relaxation of the particle size specification would increase batch size and productivity and lower the price of TATB. Different amination schemes have been suggested; however, none have been pursued in depth. Some encouraging results were obtained when using a tubular reactor for aminations(*10*).

REFERENCES

1. Kaplan, L. and F. Taylor, Jr., "Process Development Study of 1,3,5-Triamino-2,4,6-trinitrobenzene (U)," NAVORD Report 6017 (Confidential) March 1958.

2. Benziger, Theodore M., and Robert K. Rohwer, "Pilot Plant Production of Triaminotrinitrobenzene," LA 3632.

3. Yasudia, S.K., "Determination of Impurities in 1,3,5-Trichlorobenzene," J. of Chromatography 75, 39 (1973).

4. Hrivak, H. and M. Michalex, "Gas Chromatographic Separation of Chlorine Substituted Benzene Derivaties," (Chromatography, 3) 1970.

5. W. T. Quinlin, MHSMP-74-8.

6. Analysis of s-trichlorotrinitrobenzene by Liquid Chromatograph, Mason & Hanger (Rough Draft).

7. C. L. Schaffer, M&H Technical Note PX-17-76.

8. W. T. Quinlin, MHSMP-72-43C, January-March 1972

9. W. T. Quinlin, Z. L. Estes, C. L. Schaffer, and V. H. Evans, MHSMP-75-20A.

10. W. T. Quinlin, V. H. Evans, Z. L. Estes, and C. L. Schaffer, MHSMP-75-24C.

11. V. H. Evans, W. T. Quinlin, C. L. Schaffer, and Z. L. Estes, MHSMP-76-5L.

12. A. A. Duncan, Particle Size Analysis of HMX, MHSMP-72-24.

13. A. A. Duncan, Particle Characterization of TATB, MHSMP-74-20 and 74-35P.

14. B. D. Faubion and C. C. Blair, MHSMP-75-20J.

15. E. Kohn, MHSMP-75-5K.

16. G. L. Clink, MHSMP-75-5L.

17. W. T. Quinlin, V. H. Evans, Z. L. Estes, and C. L. Schaffer, MHSMP-75-40E.

18. W. T. Quinlin, Z. L. Estes, V. H. Evans, and C. L. Schaffer, MHSMP-75-5H.

19. C. V. Ludington and D. H. Melin, Cordova Chemical Co., Report, April 25, 1975.