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Optimization of TATB Processing

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DEVELOPMENT DIVISION

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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 and then aminated to form TATB. The effects of several critical variables, the process procedures, and the equipment are discussed.

INTRODUCTION

TATB is probably the safest of all explosives to handle. It is essentially insensitive to mechanical shocks, inert to most chemical attack, and thermally stable, decomposing about 330 C. Other properties are

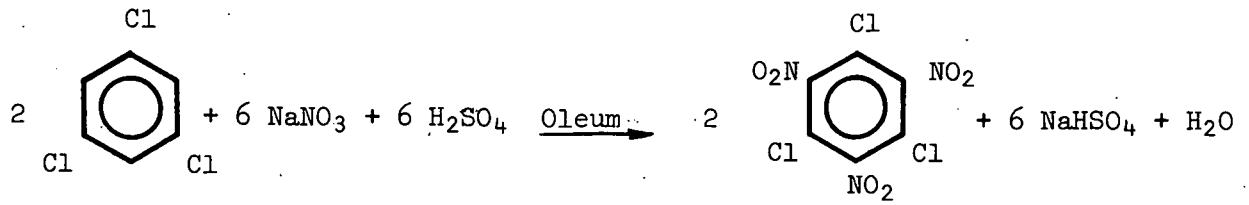
Crystal density	1.938 g/cm^3
Solubility in Organic Solvents	Nil
Shipping Classification	Class A Explosive
Drop-Weight Impact Test (12/12B)	320 cm
Gap Sensitivity (1-5/8 in Dia)	0.863 inches of Dural

It is usually detonated by another explosive charge. TATB comes out of the pilot plant as a yellow, free flowing powder. Particle size and chloride content have been used to characterize and compare batches of TATB. Due to its insolubility in essentially all solvents, a quantitative assay is not practical at this time.

The two step synthesis route was scaled-up by Benziger and Rohwer at Los Alamos Scientific Laboratories. Pilot scale work began at Pantex in June of 1972. The scale-up of the nitration has been very predictable. The particle size distribution from the amination reaction was difficult to control. The pilot scale production ceased in mid-1976 after 9100 kg of TATB was produced. The maximum production rate (starting with TCB) was 545 kg per month of TATB, operating two shifts, five days a week.

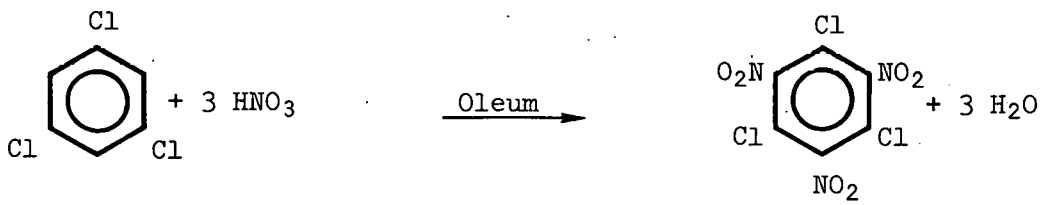
SYNTHESIS OF TCTNB

The intermediate product, TCTNB, is made by nitrating symmetrical trichlorobenzene (TCB). Two nitrating agents have been used. Both employ oleum (or concentrated sulfuric acid) as the reaction medium. Sodium nitrate or nitric acid is used as the nitrating agents. The reactions are:



[1] [6.68] [33.67]

Mole Ratio Charged



[1] [5.16] [16.58]

Mole Ratio Charged

Both nitrating agents work well and produce essentially identical products. The pilot scale sodium nitrate process is shown in Fig. 1.

Two nitration by-products are generated in significant amounts. 1,3-dinitro-2,4,6-trichlorobenzene (TCDNB or Di) and 1,3-dinitro-2,4,5,6-tetrachlorobenzene (T_4CDNB or T_4) are found in all batches of TCTNB. A 3 1/2 - 4 hour, 150 C reaction minimized the amount of impurities. Shorter or colder reactions resulted in high percentages of the incompletely nitrated TCDNB. Longer or higher temperature runs show an increase in the amount of T_4CDNB. This may be due to some oxidation of the TCB which could liberate chlorine. An average yield of 75.8% of pure TCTNB was obtained. A total of 219 batches (yielding 8,580 kg) of crude TCTNB had an average analysis of:

3.2% TCDNB
9.4% T_4CDNB
87.4% TCTNB

Precautions must be taken to prevent the nitration mixture from overheating. Near 165 C, a violent exotherm (probably due to an oxidation reaction) is initiated. Once started, this exotherm is essentially uncontrollable, and the entire nitration mixture may be lost in a matter of seconds.

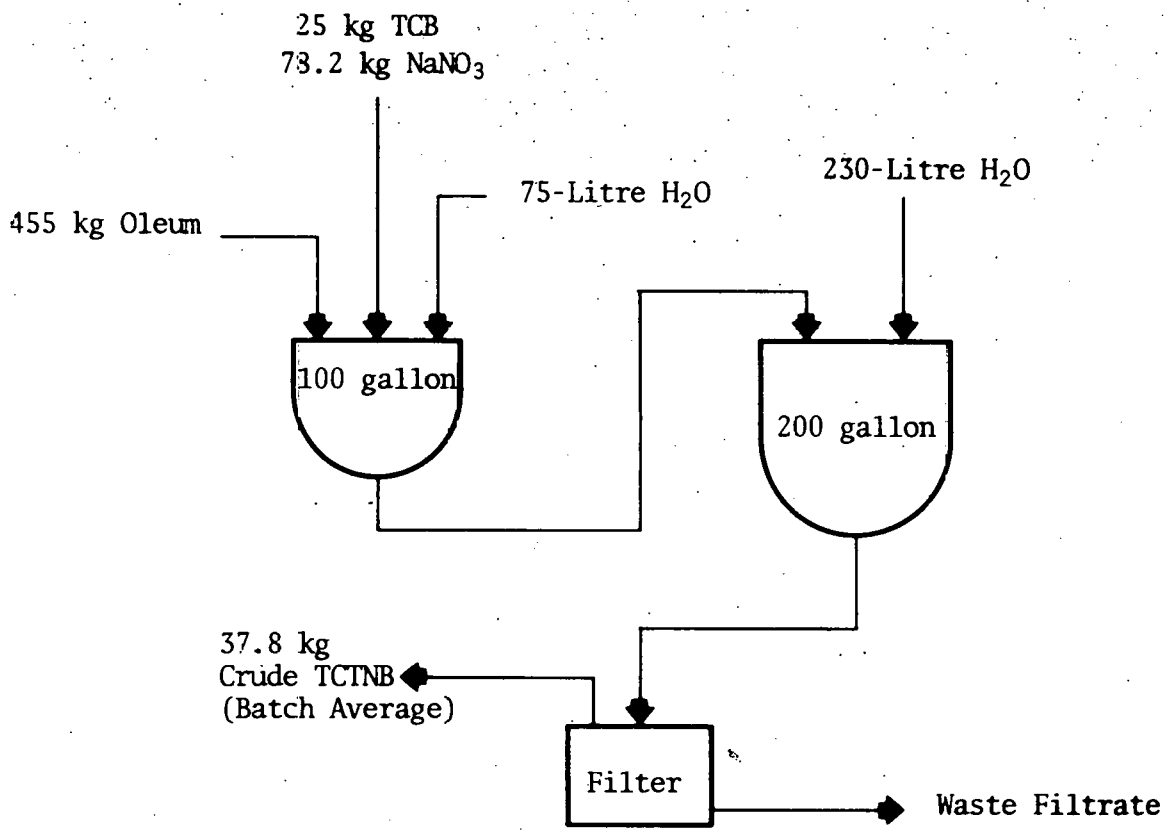
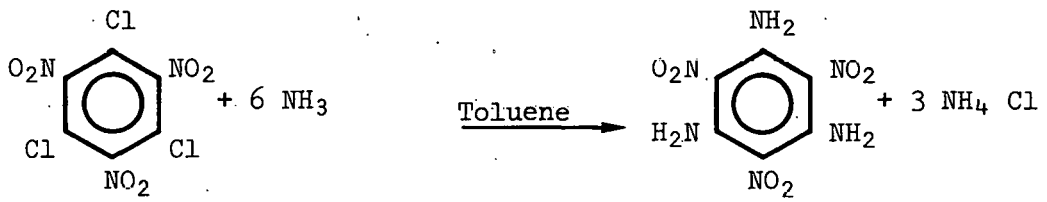


Fig. 1. Pilot Scale Sodium Nitrate Process (25 kg TCB)

At this time, the major problem with the nitration is the procurement of the symmetrical TCB. All of the Pantex TCTNB was made with TCB supplied from American Hoechst's plant in West Germany. This TCB is 99+% pure and no problems have been associated with it; however, the supply is very limited and susceptible to many transportation delays. Several domestic firms are now developing processes that should establish a reliable and economical United States source.

SYNTHESIS OF TATB

TCTNB is aminated in a toluene solution by the following reaction:



The reaction is slightly exothermic; however, no rapid temperature rises have been encountered. Aminations at 150 C have been the most successful. The pilot scale process is shown in Fig. 2.

The amination process begins 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. After dissolving the TCTNB in toluene, the solution is passed through a ten micron filter in the transfer to the amination reactor. Due to the low flash point of toluene, nitrogen pressure is used to drive material from one vessel to another. Once loaded, the amination mixture is heated to about 110 C and the water/toluene azeotrope vented. These vapors are directed into the building exhaust system. When a sample of this condensed vapor is free of water (by visual inspection), the heating is resumed. At 140 C, anhydrous ammonia enters the reactor ullage at a feed pressure of 0.41 MPa (60 psig). The ullage is purged three times with ammonia. The reactor pressure rises slightly with ammonia and then vented for each purge. With the purge complete, and water and air eliminated, the amination reaction begins. Ammonia feeds the reactor at a rate of about two kilograms per hour from the 0.41 MPa source. This corresponds 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 decreases as the reaction nears completion. A total of 6.3 to 6.8 moles of ammonia are used for each mole of pure TCTNB. An average

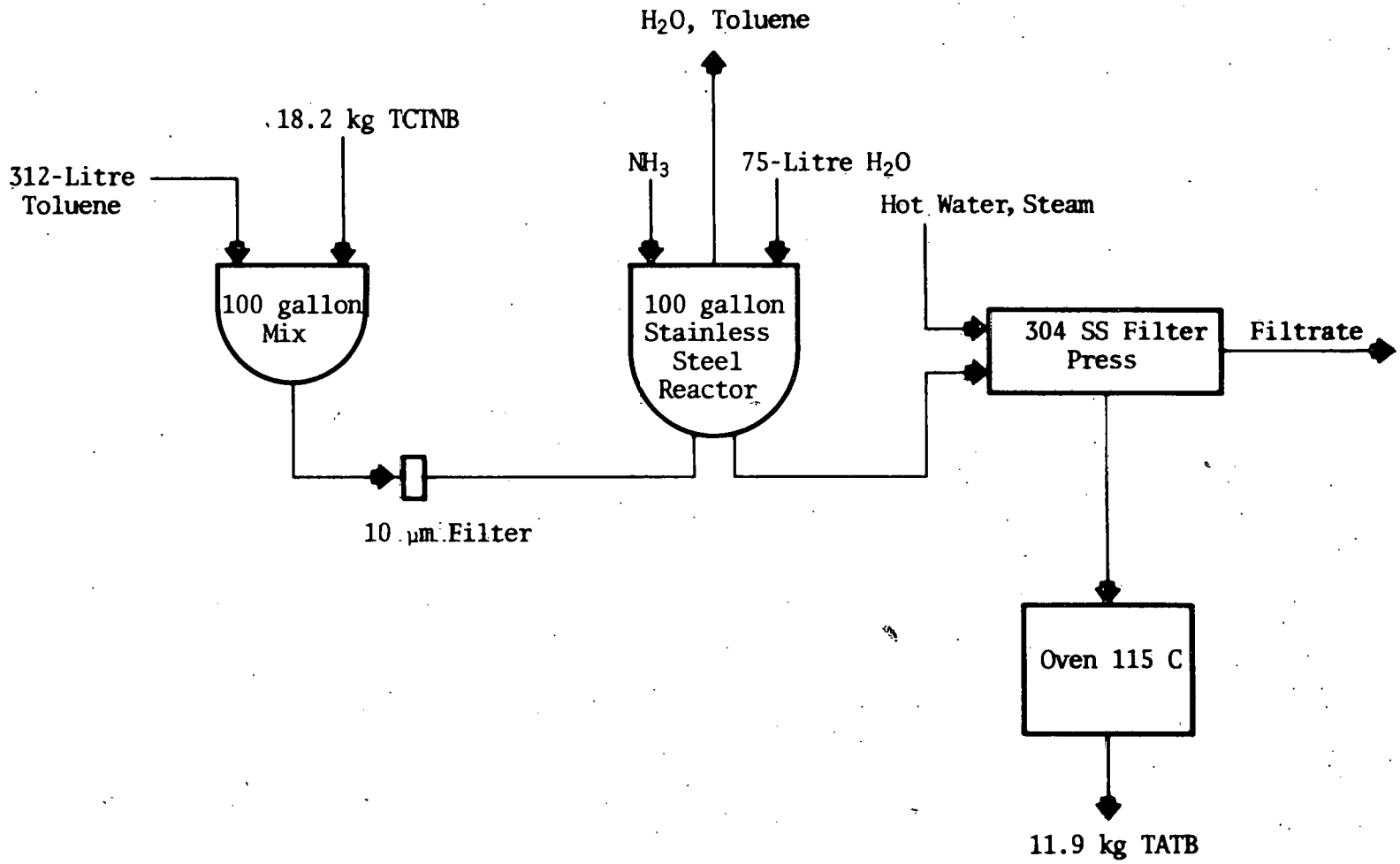


Fig. 2. Pilot Scale Amination Process

theoretical yield (based on TCTNB) of 97% was realized. After depressurizing and cooling the reaction mixture, 75 litres of water is 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 is recovered in a filter press. While still in the filter, the product is hot water washed and then steam washed. The finished material dries in a forced draft oven at 115 C for sixteen hours prior to sampling and packaging.

The charges shown in Fig. 2 are used for the baseline run. It produced high quality TATB and is used to demonstrate the effects of experimental process changes.

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. 3, higher concentrations gave finer particles. An agitation rate of 80 to 120 rpm (Fig. 4) formed the largest particles. Also, the amount of chloride found in the TATB increased at the higher agitator speeds (Fig. 4). 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.

With a 0.06 kg/litre concentration and an agitation rate of 80 rpm, and 312 litres of toluene, the average analysis was:

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.

At 90 rpm, for 312 litres of toluene, at the 0.108 kg/litre concentration the batches averaged,

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. 5 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. 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

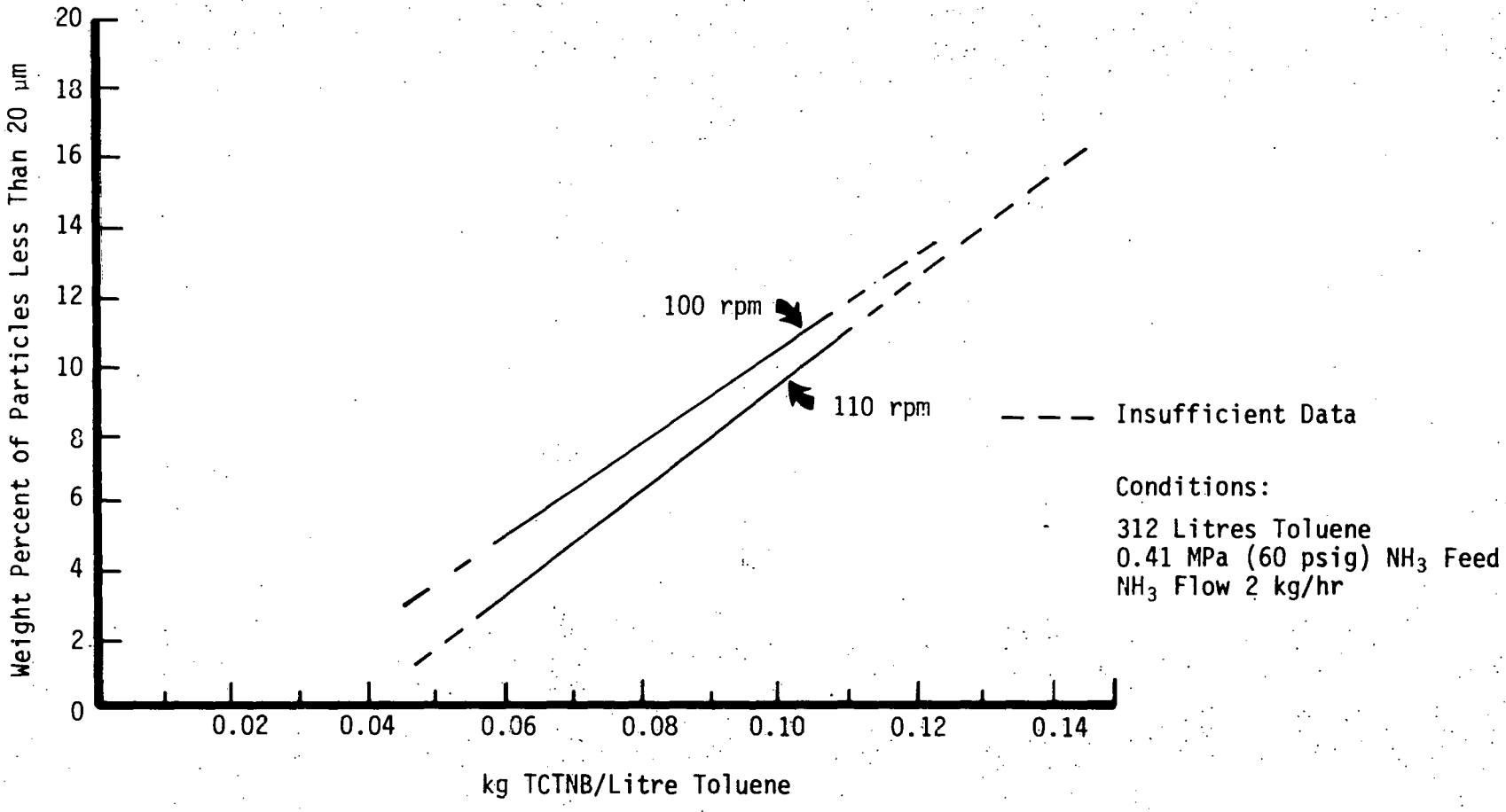


Fig. 3. Effect of Concentration on Particle Size

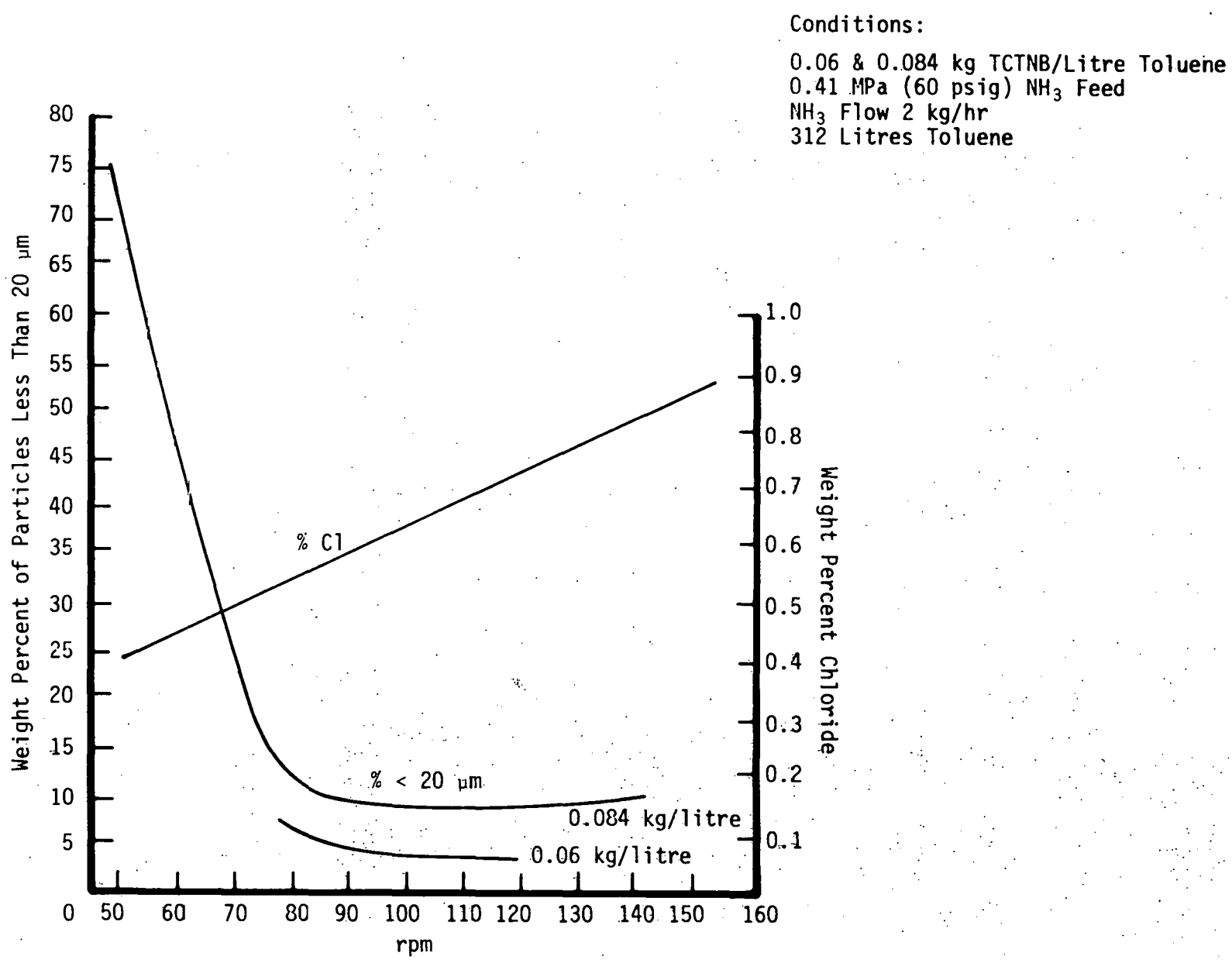


Fig. 4. Amination Effect of Stirring on Particle Size and Chloride Content

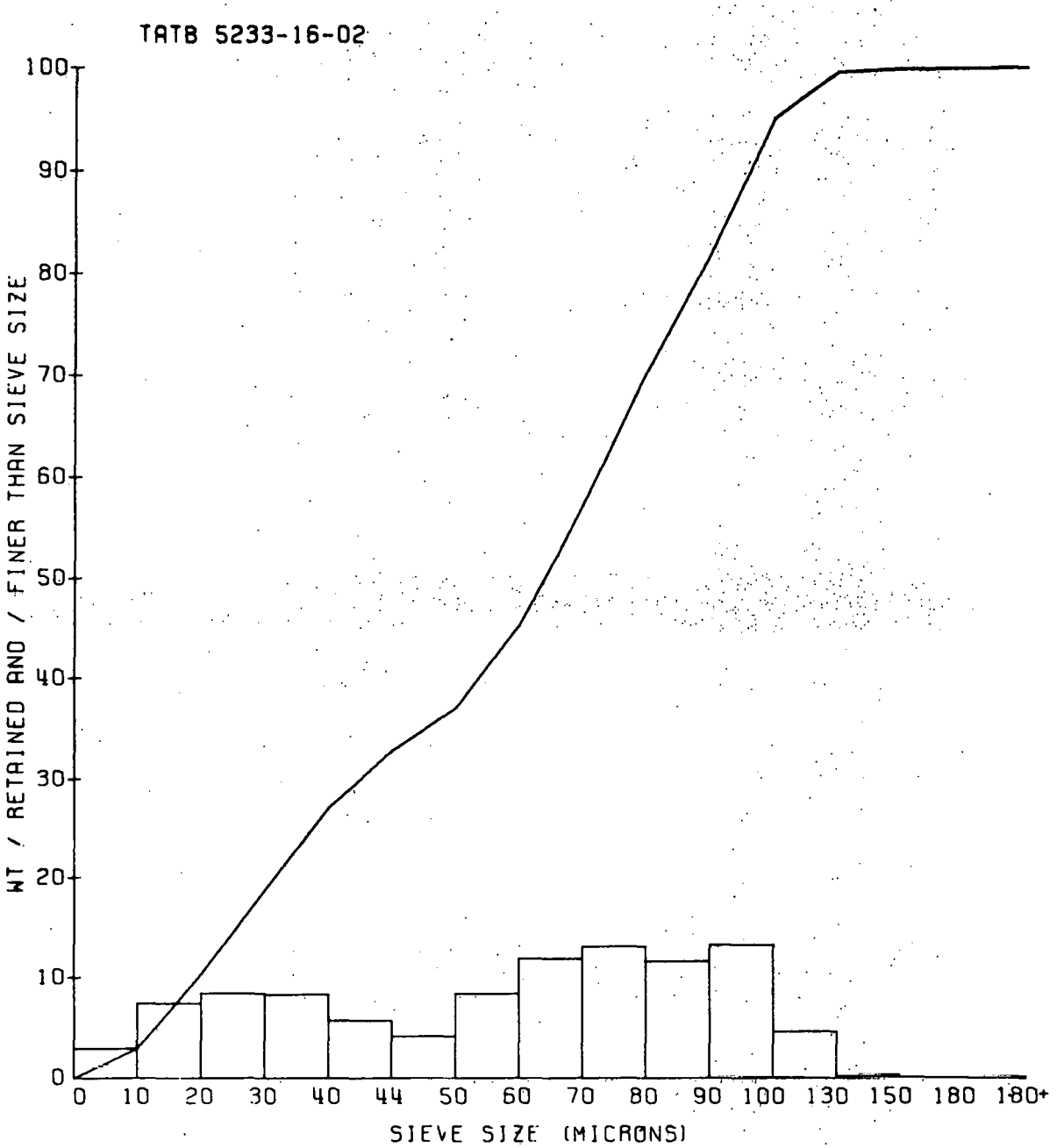


Fig. 5. Typical Particle Size Distribution

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). The batch average had an analysis of

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.

Several aminations have been made with small amounts of water present. In these runs, the venting of the azeotrope is omitted.

% H_2O	rpm	% Cl	% 20 μm	% 44 μm
10.0	65	0.16	29.82	63.62
10.0	110	0.07	32.17	75.38
2.5	80	0.10	31.56	66.81
2.5	110	0.17	19.95	75.21
1.25	90	0.29	11.69	66.74
1.25	110	0.25	30.10	72.90
0.35	80	0.31	36.07	61.14
0.35	110	0.27	41.10	64.5

The addition of water to the amination solvent decreases the chloride content significantly and higher water concentrations appear most effective. However, the particle size of the TATB is reduced in the water-toluene aminations and more work is needed to control both chloride concentration and particle size characteristics. Due to the higher vapor pressure of the water/toluene mixture, the reaction temperature is maintained at 125 - 130 C. The reactor is being set up to run at higher pressures so these aminations can be run at normal temperatures.

A Pfaudler, 100-gallon, 316-L stainless steel reactor served as the aminator. Four standard sidewall baffles and a thermometer well are 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 filters 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.

SUMMARY AND CONCLUSIONS

TATB and TCTNB can be made satisfactorily in pilot and in large scale batch processes. Both the nitration and the amination have been scaled up by others from this pilot scale work. TCTNB has been made in 550 kg batches. The amination reaction has been conducted on a scale that yields 130 kg of TATB. Some difficulty was encountered in obtaining the coarse particle size desired. Control of the ammonia flowrate and agitation improvements increased the particle size.

TCTNB production is straightforward and easily scaled-up. The amination reaction 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 will continue. A stable and economical supply of sym-TCB is a high priority concern at the present time. The nitration of TCB requires a tremendous excess of raw materials. Different batch reactor designs, continuous systems, and recycling 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. Different amination schemes have been suggested; however, none have been pursued in depth.