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MANUFACTURE OF TRIAMINOTRINITROBENZENE*

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Process studies were made on the preparation of triaminotrinitrobenzene (TATB), an explosive of unusual insensitivity and high thermal stability. Reaction conditions and procedures were determined that allowed its practical manufacture in batch reactors on a 200-kg scale.

1. INTRODUCTION

In many modern applications of high explosives, new requirements appear for improved safety and also stability at high temperatures. With regard to these demands, triaminotrinitrobenzene (TATB) is an explosive of special interest because of its unusual insensitivity, heat resistance and respectable performance, which closely approaches that of Composition B.

Since 1964, when its distinctive insensitivity was recognized at the Los Alamos National Laboratory, Los Alamos and other facilities of the U.S. Department of Energy have made an extensive examination of its properties. This examination has shown that TATB offers a degree of safety that is unique. It has been subjected to severe mechanical and thermal stimuli in a variety of tests(1) simulating stimuli expected in realistic accident situations. In none of these tests could TATB or its plastic-bonded compositions(2) be brought to detonation. These tests are described in Table I and Fig. 1.

The work described here originated in filling the material needs of the test program. The present process for the manufacture of TATB was based on synthesis studies(3-5) that began as early as 1887. In making improvements on these methods, emphasis

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TABLE I. Safety Tests on TATB Composition(1)

Test	Conditions
Susan	900 m/s
Skid	45 m, 10.4 kg charge
Bullet	0.30 and 0.50 cal., confined
Heating	285°C, slow, confined
Hot ignition	191°C charge temperature
Fuel fire	confined, jet fuel
Vacuum stability(2)	2 ml/g, 12 days at 200°C
DTA(2)	stable to 340°C

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(1) PBX9502, 95/5 wt% - TATB/Kel-F 800

(2) TATB

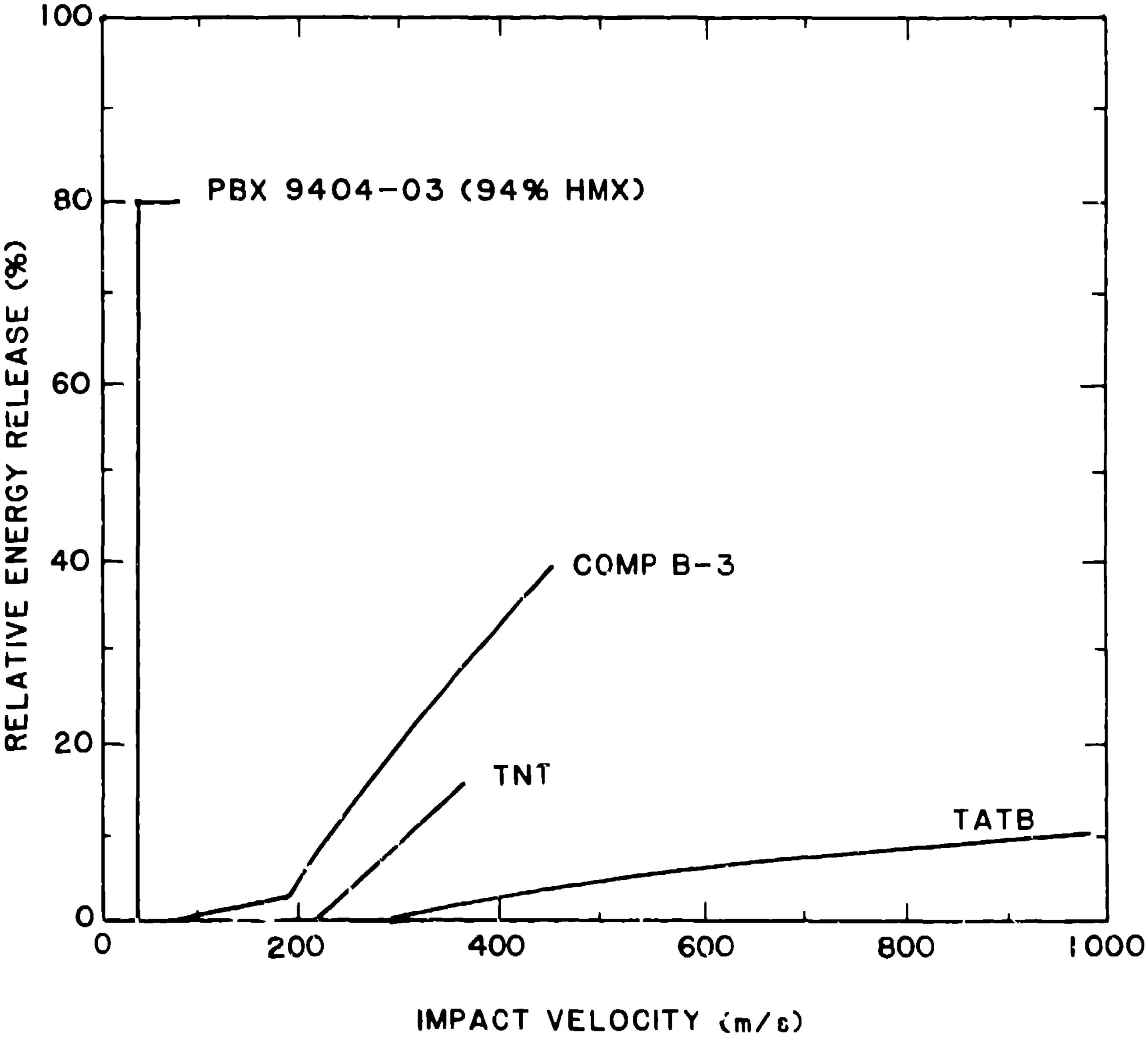


Figure 1. Sensitivity of explosives in the Susan test.

was on producing material of a reasonably large particle size and high purity, properties not available in the product from prior methods. The current manufacture of TATB on a 200-kg scale is described here followed by a discussion of the more important process conditions and procedures.

2. MANUFACTURE

The process steps in the preparation of TATB are shown in Fig. 2. In nitration, 1,3,5-trichlorobenzene (TCB) is converted to 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) in a nitric acid-oleum medium. In the subsequent amination, TCTNB as a toluene solution is reacted with gaseous ammonia to yield TATB and by-product ammonium chloride. The present procedure is based on experimental work in the laboratory and 40-, 120-, and 400-liter reactors.(6-9) Current production is done in 4000-liter reactors. The quantity of TATB that has been produced using the described procedure exceeds 70 metric tons.

2.1 NITRATION

The nitration of TCB is relatively simple with the exception that it requires a very high reaction temperature. Its flowsheet is given in Fig. 3. The reactor is a 4000-liter, glass-lined vessel equipped with two baffles and a 3-blade turbine impeller. Accessory equipment is constructed of stainless steel.

In the first process step, the addition of molten TCB to hot mixed acids is not hazardous; it serves to shorten the heating time to the 150°C reaction temperature. As the mixture is heterogeneous throughout the 2.5-h reaction period, vigorous agitation is required. The water quenching step, employed after cooling the reaction mixture, is used to fully precipitate the product. In recovery, the slurry is filtered, washed with water

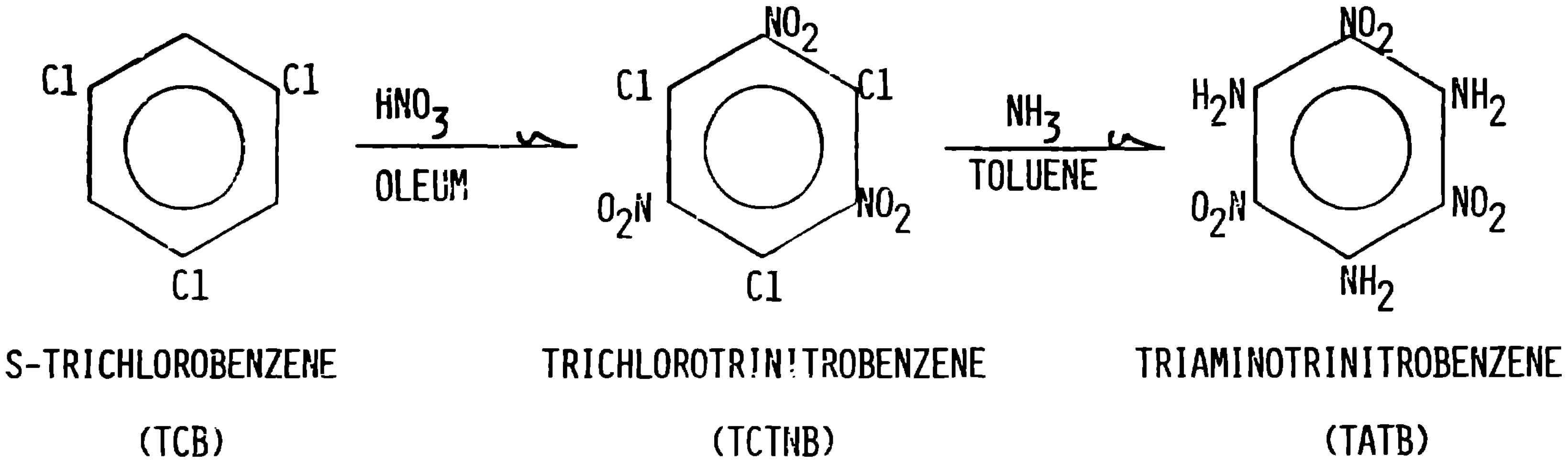
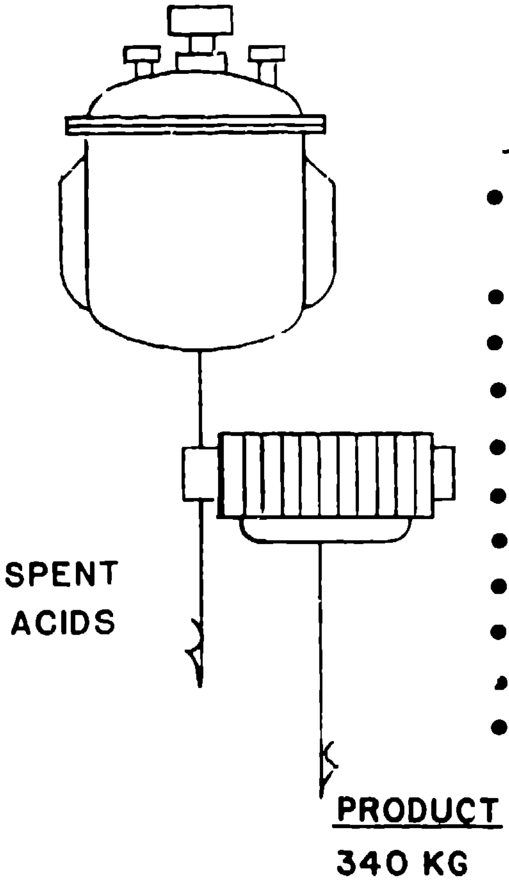


Figure 2. Synthesis of TATB.

TATB MANUFACTURE – NITRATION



MATERIALS

TCB	213 KG
HNO (95%),	395 KG
OLEUM (25%),	2220 KG

PROCEDURE

- ADD TCB AT 75°C TO ACIDS AT 90°C
- REACT 2.5H AT 150 °C
- COOL TO 45°C
- ADD 400 KG WATER
- COOL TO 30°C
- FILTER
- SPENT ACIDS TO WASTE
- AIR BLOW CAKE
- WASH CAKE WITH WATER
- AIR BLOW CAKE
- CAKE TO STORAGE

PRODUCT

89% SYM TRICHLOROTRINITROBENZENE (TCTNB)
8% 1,2,3,5-TETRACHLORO-4,6-DINITROBENZENE (T4)
3% 1,3,5-TRICHLORO-2,4-DINITROBENZENE (T3)

YIELD

CRUDE, 1.6 KG/KG TCB
CONVERSION, 0.80 MOL TCTNB/MOL TCB

Figure 3. Preparation of TCTNB.

until the filtrate is free of acids and then blown dry in the press with air. Being quite resistant to hydrolysis, the TCTNB product can be stored in a damp state for use in the subsequent amination.

The crude yield in nitration is 91% with a purity of 89%. The conversion, as moles of TCTNB per mole of TCB, is 0.80. Fortunately, the two impurities that are shown, T3 and T4, are quite unreactive in amination and go through relatively unchanged.

The product is a white, crystalline material, with a melting point of 190°C and is stable in a DTA test to 300°C. As an explosive, it is similar to ammonium picrate in sensitivity.

2.1.1 DISCUSSION

The nitration of TCB takes place with rates that are controlled by the heterogeneous nature of the system. Its sequence is shown in Fig. 4. As seen, the dinitro intermediate (T3) is quickly formed in quantitative yield. At the 150°C reaction temperature, it is above its melting point of 130°C and is present as a separate phase. In the reaction of T3 to form TCTNB, the rate is first controlled by its solubility at saturation in the mixed acids. As the reaction reaches a conversion of about 0.6 mol TCTNB/mol TCB, a crystalline TCTNB product begins to precipitate that contains the remaining, separate, liquid-phase T3. From this point, the rate slows significantly as it is now controlled by T3 diffusion in the solids.

For an efficient nitration, the reaction temperature should be controlled within a narrow range. This is shown in Fig. 5, which shows the effect of both temperature and time on conversion. The optimum conditions are a temperature of 150-155°C and a reaction period of 2.5 h. The effective conversion rate is substantially less at lower temperatures. Here solids form early

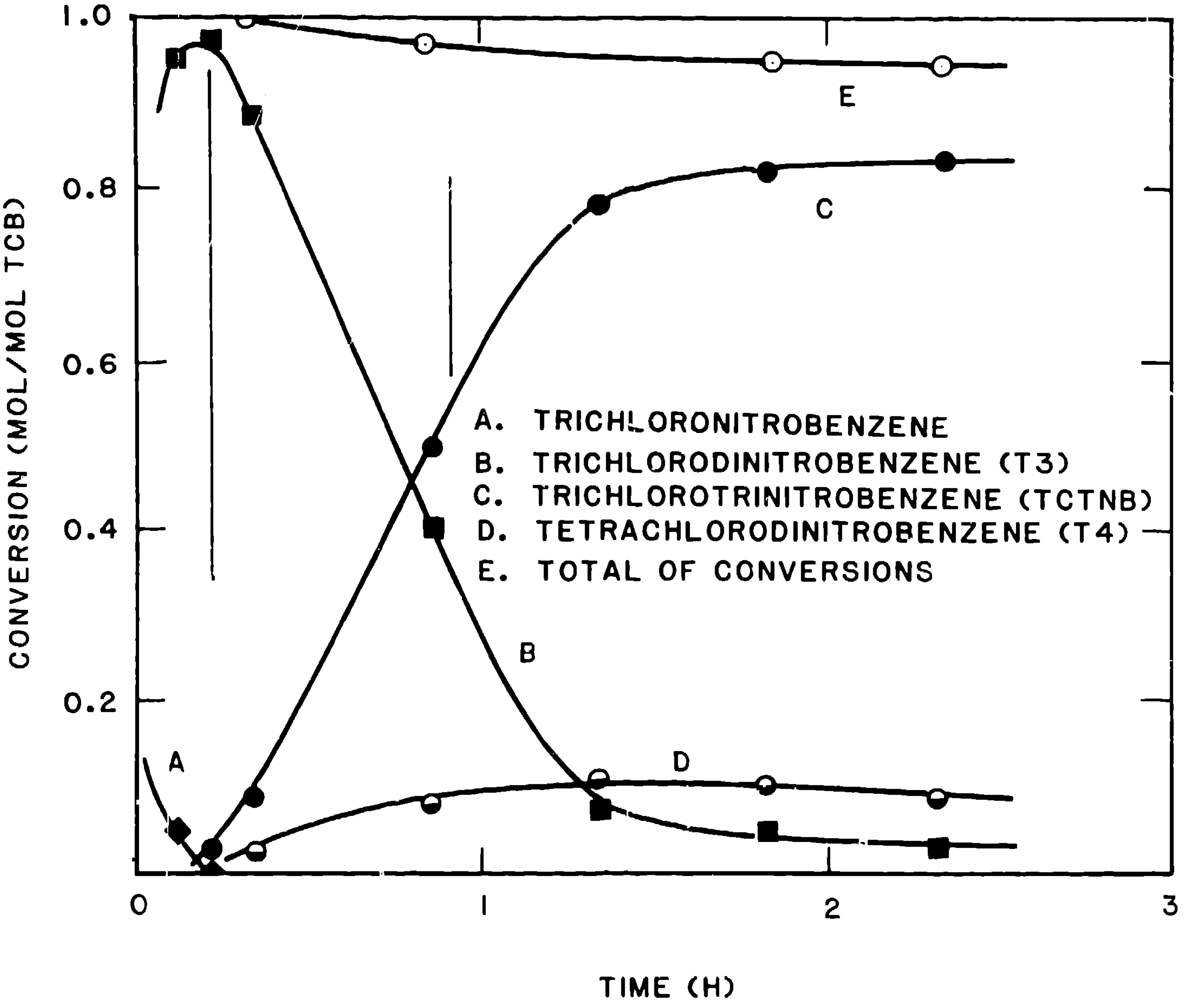


Figure 4. Nitration of sym-trichlorobenzene (TCB).

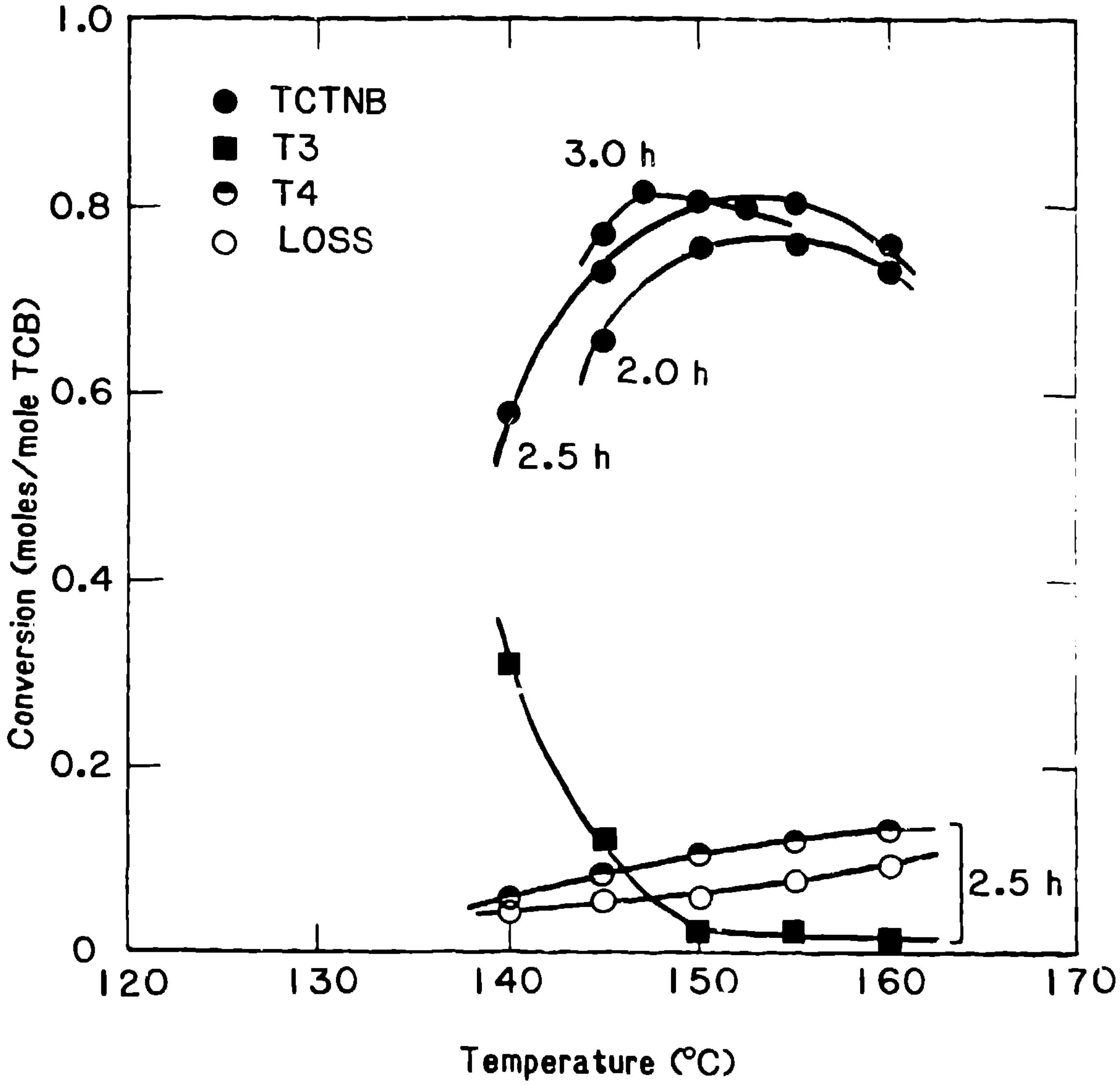


Figure 5. The effect of temperature and time in nitration.

in the reaction, and solid diffusion effects act to limit the rate. Prior investigators,$^{(4)}$ who used a low temperature of 135°C, reported that 18 h was required to complete the reaction. The increase in both decomposition losses and impurity formation above 155°C also act to limit the effective conversion rate.

With proper control, nitration does not present an exothermic hazard. The major portion of its heat is released in the fast dinitration stage. In establishing the hot-addition procedure, adiabatic nitrations were conducted in the laboratory. These showed that, with the stated addition temperatures, the reaction was self limiting at a temperature of 130°C, the melting point of the dinitro intermediate. It forms quickly in this procedure and is present as a solid until 130°C, where its heat of fusion effectively limits further temperature rise.

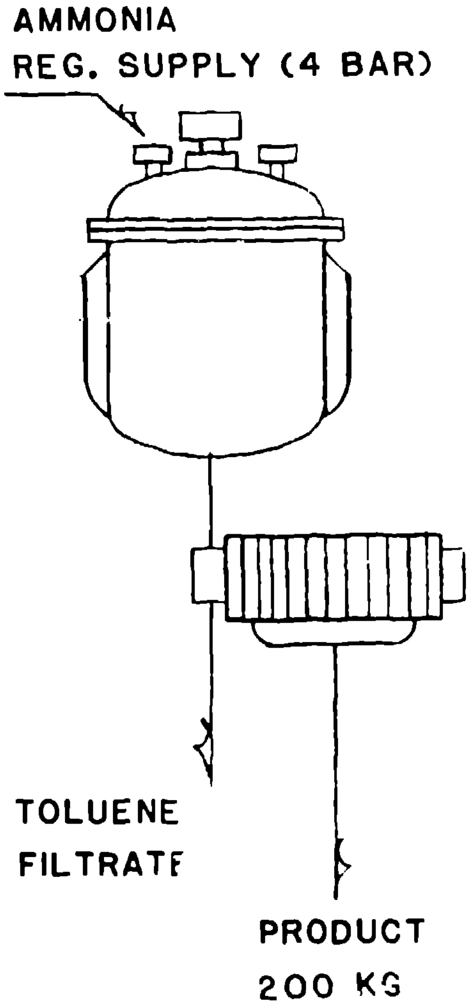
In determining the proper stoichiometry, the constraints were found to be a mixed acids composition that would not boil at high-reaction temperatures, a HNO_3/TCB molar ratio of at least 4.5 and a SO_3/HNO_3 ratio of about 1.0. The efficiency of both HNO_3 and SO_3 use is high in nitration, having a value of about 95% in a materials balance.

2.2 AMINATION

The flowsheet for the conversion of TCTNB to TATB is presented in Fig. 6. The reactor and accessory equipment are similar to those used in nitration, with the exception that the reactor must be suitable for 4-bar operation at 150°C.

In this process, a solution of crude TCTNB in toluene is first heated to boiling to distill off any residual water as the toluene-water azeotrope. The reactor is then sealed and brought to a temperature of 150°C. Ammonia gas is then fed at a controlled rate of 8 kg/h to the reactor ullage from a regulated

TATB MANUFACTURE - AMINATION



MATERIALS

TCTNB (CRUDE), 275 KG
TOLUENE, 2500 KG

PROCEDURE

- DISSOLVE TCTNB
- PURGE ULLAGE WITH NITROGEN
- DRYING-AZEOTROPE DISTILLATION
- SEAL REACTOR - HEAT TO 150 C
- FEED AMMONIA TO ULLAGE AT RATE OF 8 KG/H
- REACTION PERIOD - 10 H
- COOL, ADD 350 KG WATER
- FILTER
- AIR BLOW - FILTRATE TO RECOVERY
- WASH CAKE - HOT WATER
- STEAM CAKE
- CAKE TO DRYING

PRODUCT

IMPURITIES (AS % CHLORINE), 0.6 %
PARTICLE SIZE, 50μm MEDIAN

CONVERSION

QUANTITATIVE ON TCTNB CONTENT
1.14 KG/KG STARTING TCB

Figure 6. Amination of TCTNB.

4-bar source. Reaction completion, which occurs in about 10 h, is marked by a relatively sudden increase in system pressure. In product recovery, the reactor is cooled, water is added to dissolve the ammonium chloride by-product, and the slurry is filtered in a plate-and-frame press. The TATB cake is then washed with hot water, followed by steaming in the press to remove volatile impurities.

The conversion in this process is essentially quantitative, based on the TCTNB content of the crude feed material. On an overall basis, including both nitration and amination, approximately 1.14 kg of TATB is produced for each kilogram of starting TCB.

The TATB product from amination is a yellow, crystalline material with a median particle size of 50 μm and a crystal density of 1.938 g/cm^3. It contains about 0.9% impurities, with the major one being occluded ammonium chloride. In DTA tests it has an exotherm onset at 340°C.

2.2.1 DISCUSSION

In amination, which includes both chemical reaction and crystallization processes, the formation of TATB occurs rapidly at the gas-liquid interface. As it has a very low solubility in the reaction solvent, a high supersaturation level can develop at the interface. Excessive nucleation will result with TATB precipitating as extremely small crystals of low purity.

To favor crystal growth, rather than nucleation, the supersaturation must be limited. It is controlled by two parameters, the production rate and the reaction temperature.

Of these, temperature has a significant effect. This is seen in Fig. 7, which presents particle size distributions obtained at several reaction temperatures. The favorable influence

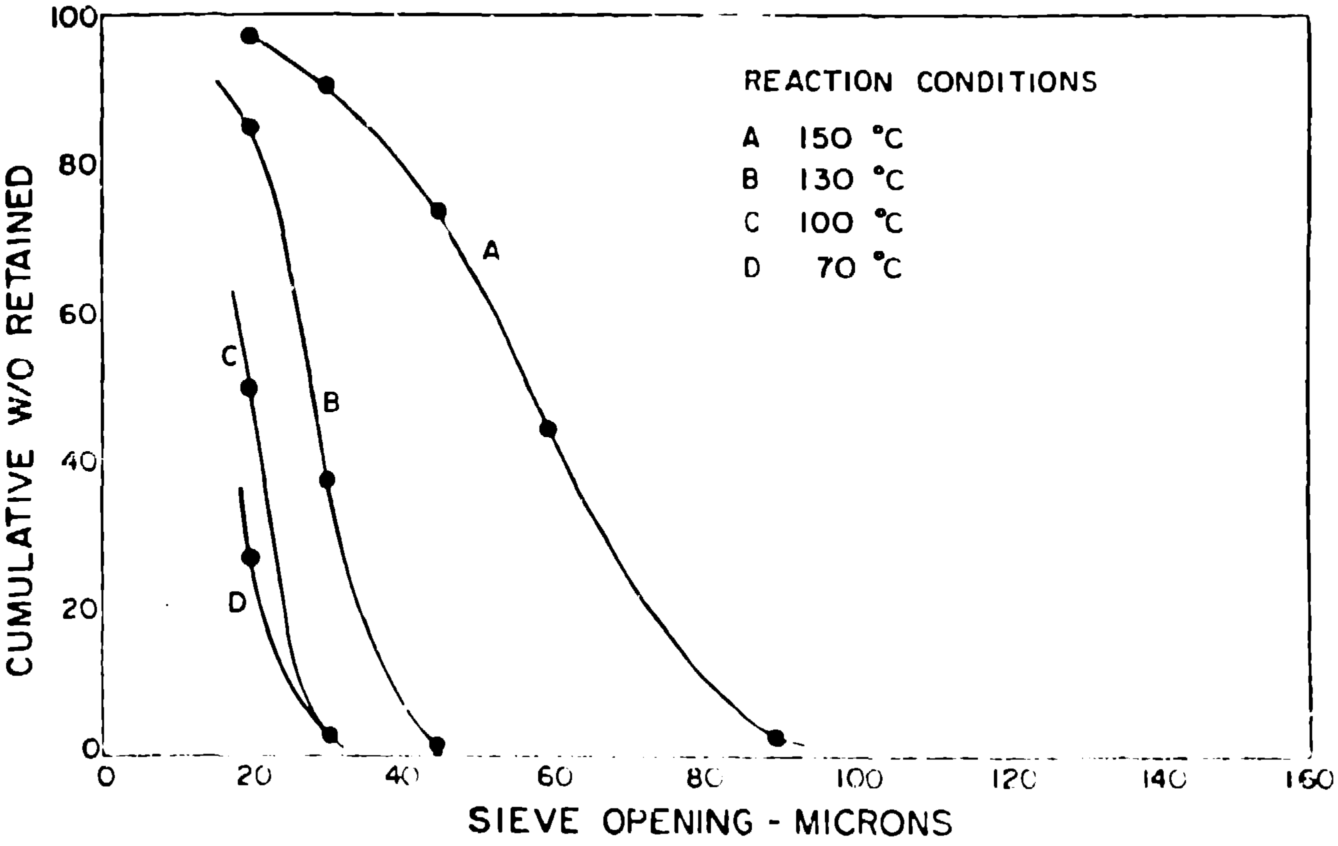


Figure 7. Sieve analysis of TATB powders.

of high temperatures in increasing crystal size is quite noticeable, especially above 130°C. At 150°C, as presently used, a suitably large product is formed. The extremely small material made in the prior study(4) is understandable, since a temperature of 70°C was used in amination.

Production rate, the other parameter that controls particle size, was examined on an area basis, because TATB formation is an interfacial process at high temperatures. In pilot-scale reactors of different cross-sectional area, its upper limit was determined to be about 12 kg TATB/h/m^2.

3. PROCESS IMPROVEMENTS

As improvements on the present method of manufacture, several changes are being investigated. These include a continuous amination process,(9), the recycle of unquenched spent acids, and the use of a method(10) for producing TATB of increased purity.

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