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Pilot Plant Production of Triaminotrinitrobenzene (TATB)

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Pilot Plant Production of Triaminotrinitrobenzene (TATB)

by

Theodore M. Benziger
Robert K. Rohwer

ABSTRACT

A process development study was made on an existing method for preparing 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Modifications developed in the laboratory and pilot plant gave improved process yields and reaction times. Using a high temperature amination process, TATB of good purity was produced in a large particle size quite suitable for explosive compounding. A cost analysis indicated that the in-plant cost for TATB production by these methods would be approximately $4.06 per pound.

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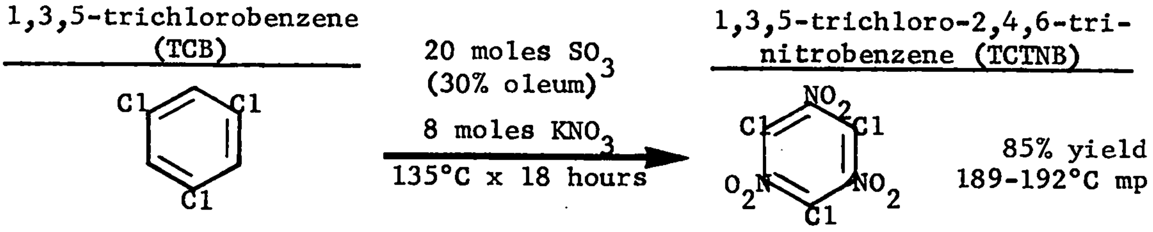
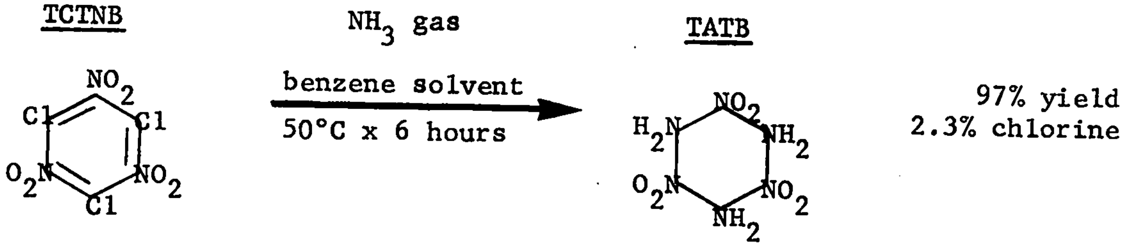
I. INTRODUCTION

While TATB is a less powerful explosive than HMX and similar materials, its excellent thermal stability and sensitivity characteristics make it a most interesting candidate for special applications. The material currently being offered is quite costly ($100/lb in 50-lb lots) and is in the form of extremely fine particles (74% below 20 μ) which are difficult to handle in normal explosive compounding methods. The surface area and wetting characteristics of this fine powder also limit the amount of explosive which may be incorporated in a plastic bonded form that has adequate strength.

With cost and particle size in mind as major impediments to the practical utilization of TATB, this modification study was conducted on the procedures developed by the Naval Ordnance Laboratory[1]. Their process consists of the following steps.





II. NITRATION

While a laboratory evaluation of the NOL nitration procedure showed it to be an effective method, significant gains resulted from the use of a higher reaction temperature (150°C) and substitution of sodium nitrate for potassium nitrate as the nitrating agent.

Data on a typical pilot plant run are as follows.

Reactants (mole ratio) - 1/6.6/15.6 - TCB/$NaNO_3$/SO_3(30% oleum)

Conditions - 150°C for 4 hours

Product yield - 92%

Product melting point - 188-191°C (195°C pure)

Analysis -

	Found	Calculated
C	22.58	22.75
N	12.49	13.27
Cl	34.05	33.65

A. Reaction Temperature

A higher reaction temperature is desirable from the standpoint of both yield and process time. At temperatures below 140°C, various nitrated products precipitate early in the reaction as a somewhat unreactive, gummy mass. At 150°C the solution stays clear throughout most of the reaction, giving a one-phase, more reactive system and a more completely nitrated product. The effect of temperature on the degree of nitration is shown by the following data.

Mole ratio - 1/6.6/15.6 - TCB/$NaNO_3$/SO_3 (30% oleum)

Time - 4 hours

Reaction temperature, °C	Product mp, °C (195°C pure)
130	115-160
140	170-185
150	188-191

With a 150°C reaction temperature, lengthy nitration periods are not required, and optimum purity and yield are attained in three to four hours. The course of a typical laboratory nitration is as follows.

Time at 150°C	Product mp, °C (max)
15 min	115
45 min	118
1 hr 45 min	183
2 hr 30 min	191 (89% yield)
3 hr	191
4 hr	191
5 hr	191 (89% yield)

B. Nitrating Agent

Sodium nitrate, used in these studies, proved to be as effective as potassium nitrate. It also has a substantial cost advantage over the potassium salt on a lb-mole basis.

C. Mole Ratio

Only a limited study was made on this parameter. In general, our work confirms the NOL value as being near optimum.

D. Product Recovery

In pilot plant work the reacted mixture was quenched in a large volume of ice, and the TCTNB product was recovered by filtration in a plate and frame press. If suitable equipment were available, a preferable method would be the filtration of the undiluted mixture. Laboratory studies on this operation showed that when the mixture was cooled to 25°C about 99.5% of the product would precipitate and could be recovered using a fritted glass filter. The soluble fraction, recovered by dilution with ice water, was a low-melting impurity (115-120°C).

This method of recovery might be attractive in production since the undiluted used filtrate still demonstrates efficacy in nitration and might lend itself to recycle operations. Such a spent mixture was recycled with the same amount of starting TCB reactant and gave a good yield of partially nitrated material with a melting point range of 115-175°C.

III. AMINATION

A major hindrance to the use of TATB has been the extremely fine particle size of the available product (74% below 20 µ). Our studies have shown that the use of a high amination temperature (150°C) and toluene as the solvent results in the production of relatively large TATB crystals of good purity.

Data on a typical pilot plant product are as follows.

Yield (based on crude TCTNB) - 89.0%
Impurity content (chlorine) - 0.6%
Particle size (see Fig. 1) - 4% below 20 µ
Crystal density (sink-float) - 1.93 gm/cc
Analysis -

	Found	Calculated
C	27.14	27.91
N	32.53	32.56
H	2.79	2.34
Cl	0.59	-----

A. Operating Parameters

The reaction temperature, as it affects the solubility and nucleation of the product, is most important. TATB is an extremely insoluble material in almost all solvents and is formed very quickly from the reaction of ammonia with a TCTNB solution. As a result, when it is generated in situ in a solvent, a very high level of supersaturation is reached almost immediately upon adding the ammonia. Spontaneous nucleation occurs continuously, and the product precipitates in the form of extremely small crystals. By increasing the temperature of the system, the solubility of TATB is increased and the amount of supersaturation is reduced to a level at which the crystal growth process can compete with the rate of nucleation. Under this condition of higher temperature, the ammonia addition rate is not so critical and can be controlled to maintain only a moderate amount of supersaturation, so that the crystals are able to grow to a reasonable size.

This temperature effect is best demonstrated by the sieve analysis data presented in Figure 1 and the photomicrographs of typical products shown in Figure 2. As these figures demonstrate, the dependence of particle size on temperature is quite marked, especially in the region of 130 to 150°C.

A high initial concentration of the TCTNB in the solvent imposes a problem with excessive local TATB supersaturation by rapid reaction at the vapor/liquid interface. The data presented are based on a concentration of 10 lb of TCTNB per 100 lb of toluene. This was chosen as a practical minimum working concentration. At high levels it was found that the particle size was smaller. Another step taken to reduce any TATB concentration gradient was to add the ammonia above the solution rather than to inject it through a sparger. It was added to the reactor at a rate sufficient to maintain its partial pressure at 5 psi through most of the reaction, with good agitation of the TCTNB solution.

B. Impurity

In the production of TATB the only detected impurity is 1,3,4,5-tetrachloro-2,6-dinitrobenzene. It is removed in the toluene mother liquor separated in the final filtration of the TATB crystals. Initially it was thought that this material was the result of nitrating a precursor impurity, 1,3,4,5-tetrachlorobenzene, carried in the TCB. This precursor, however, cannot be detected in the TCB, which is shown by several analytical methods to be quite pure. The final impurity, however, has been found by thin-layer chromatography in the crude TCTNB. While its method of formation has not been determined, early TATB investigators did report the presence of its bromo analog in the product of nitration of 1,3,5-tribromobenzene; they attributed its formation to a transbromination reaction[2].

IV. PILOT PLANT PROCEDURE

A. Equipment

1. A 10-gallon, glass-lined Pfaudler reactor capable of operation over a range of 20-150°C and pressures of 70 mm Hg absolute to 100 psig; agitation provided by an anchor type blade at speeds of 20 to 200 rpm.

2. A glass-lined, concentric tube reflux condenser, integral with the reactor.

3. A 50-gallon, stainless steel reactor with agitator used in ice quenching of the nitration mixture.

4. Two 60-gallon, stainless receivers used in filtrate storage and recovery.

5. A stainless steel, 11" x 11" x 2" plate and frame filter press, closed delivery washing type.

B. Nitration

Sixteen plant nitrations were made with a total production of 137 lb of TCTNB. Product yield in this series ranged from 87-96% with the average value at 92%. The minimum melting point measured on any run was 184°C with the normal melting point range being 187-191°C.

1. Materials

Mole ratio: 1/6.6/15.6 - TCB/$NaNO_3$/SO_3 (30% oleum)
5.5 lb TCB, mp 63-64°C, Eastern Chemical Corporation
17.0 lb $NaNO_3$, AR, granular
126.0 lb oleum (30%)

2. Procedure

a) The oleum is charged to the glass-lined reactor, and the sodium nitrate is then added at a slow rate with full agitation. The reaction is quite exothermic, and jacket cooling is used to keep the temperature at 60-70°C. When the entire amount of $NaNO_3$ has been added and the exotherm peak has passed, the kettle contents are brought to a temperature of 100°C.

b) The TCB is then charged to the reactor, and steam is applied to the jacket to bring the temperature quickly to 145-155°C. Only a small amount of exothermicity was noted in this step. The reactor contents are maintained at this temperature for a period of four hours. The small amounts of gases generated during the nitration are vented through the reflux condenser.

c) At the end of the four-hour reaction period, the contents are cooled to 40°C and discharged into the 50-gal stainless steel reactor which contains approximately 250 lb of crushed ice. Full agitation is used during this quench step, and the nitrous fumes are removed using a water-sealed vacuum pump. The TCTNB product precipitates in the form of heavy white crystals. With the stated quantity of ice, the temperature during dilution does not exceed 40°C, and hydrolysis of the product does not occur.

d) The quenched reaction mixture is then pumped through the plate and frame press which discharges into a 60-gal holding tank. Dynel cloth is used as the filtering medium. Only two frames (0.24 cu ft) are needed for the amount of cake produced. The cake is washed with several 20-gal quantities of water, each followed with an air blow. This is continued until the wash water pH is 6-7. The cake is dried in open trays in a forced-draft oven at 60°C for 16 hours.

C. Amination

Fifteen plant aminations were made with a total production of 70 lb of TATB. Product yield in this series ranged from 85-94% with an average of 89%. In the last five runs, made under optimum conditions, product yield varied from 85.7-89.8%, chlorine content 0.59-0.61%, and particle size (as % > 20 μ) from 95.1-99.7%.

1. Materials

Mole ratio: 1/7.1 - TCTNB/NH_3
6 lb TCTNB
60 lb toluene, tech grade
2.3 lb NH_3, anhydrous, refrigeration grade (includes leakage and blowdown)
Product yield: 4.4 lb

2. Procedure

a) The TCTNB is dissolved in the toluene, and the solution is clarified by filtration using Celite filter aid before transfer to the 10-gal reactor.

b) Since water will interfere with the amination of TCTNB, the reactor system is purged of any water by an atmospheric pressure distillation of the water-toluene azeotrope. Dryness of the system is indicated when the distillate changes from a cloudy, two-phase material to a clear liquid. When this occurs the reactor system is sealed and heating is continued until the contents are at 145°C.

c) As the amination step is moderately exothermic, the jacket steam is turned off at this time. Ammonia gas is then added to the reactor gas phase through an opening on the top of the kettle. It is metered through a rotameter at a rate of about 0.8 lb/hr. When the NH_3 overpressure reaches about 5 psi, the reactor system is purged of residual air by venting through the reflux condenser. The system is then resealed, and the reaction is continued for a total of approximately three hours. Moderate agitation is used during this period. In the course of the reaction, conducted at 150°C, the system pressure will remain at 35-40 psig for most of the three-hour reaction period. This represents an NH_3 partial pressure of about 5-10 psi. As the reaction progresses, a small amount of jacket heating may be necessary to maintain the 150°C temperature. The termination of the amination reaction is marked by a sharp rise in system pressure to about 60 psig. This occurs under the stated conditions with our equipment after about three hours of reaction time.

d) After the pressure rise is noted, the NH_3 flow is shut off and the system is cooled to about 60°C. The system is vented, and approximately ten gal of water is added to the reaction mixture with good agitation. The TATB product is recovered by filtration using the plate and frame press, equipped with cotton cloths backed with filter paper. One frame (0.12 cu ft) is sufficient for the amount of product produced. The cake is washed three times with 20-gal portions of water, interspersed with air blows. This is sufficient to remove by-product NH_4Cl. To dry the cake and remove volatile impurities, the cake is steamed for about ten minutes and air-blown before removal from the press.

The cake is then dried in open trays in a forced-draft oven at 100°C for 16 hours.

V. COST ANALYSIS

Assumptions:

200,000 lb/yr TATB production rate
5-day week - 2-shift operation
2 operators and 1 foreman/shift
1 supervisor

A. Capital Cost

The plant investment is estimated at $1,500/annual ton, or $150,000. This rough value is derived from published figures for various chemical processes[3]. It represents an average for industries comparable in terms of operations, processes, corrosion problems, and safety hazards (DDT and smokeless powder production).

B. Labor

Wages are set at $3.00/hr for operators, $4.00/hr for foremen, and a salary of $10,000/yr for the one supervisor. A 100% overhead factor is used for supporting facilities.

Basis:	250-day year	
	4 operators (8000 mh)	$ 24,000
	2 foremen (4000 mh)	16,000
	1 supervisor	10,000
		50,000
	100% overhead	50,000
	Total labor	$100,000

C. Utilities

The estimated consumption is based on smokeless powder production.

Steam:	
8 lb/lb product at \$0.70/1000 lb	\$1,120
Process water:	
15 gal/lb product at \$0.25/1000 gal	750
Electrical power:	
1 KWH/lb product at \$0.02/KWH	4,000
Total utilities	\$5,870

D. Raw Materials

The only unusual item is TCB. The cost used is that quoted by a custom chemical manufacturer for 10,000-lb lots.

TCB:	
172,000 lb at \$3.50/lb	\$602,000
$NaNO_3$:	
530,000 lb at \$50/ton	13,250
Oleum:	
3,930,000 lb at \$25/ton	49,125
NH_3:	
100,000 lb at \$100/ton	5,000
Toluene loss at 1 lb/lb product:	
200,000 lb at \$0.25/gal	6,850
Total materials	\$676,225

E. Cost Summary

Raw materials	\$676,225
Labor	100,000
Utilities	5,870
Depreciation (10% of plant)	15,000

Maintenance and repair (7.5%)	11,250
Taxes and insurance (2.5%)	3,750
Total manufacturing cost	$812,095

Plant cost/lb - $4.06

Assuming that TATB production would be considered economically as a high risk venture, a return of 45% before taxes on total investment (plant plus working capital) would be considered necessary. Including working capital at $67,675 (one month of total manufacturing cost), a return on investment of $97,954 would result. On this basis a selling price of approximately $4.50/lb would appear reasonable.

VI. SUMMARY

Simple modifications to an existing process have eliminated problems of purity and particle size which have impeded the utilization of TATB.

In a scale-up of this process, problems would undoubtedly exist with exothermicity, corrosion, product recovery methods, and disposal of spent acids. Economies might result from recycling of the nitrating mixture, adaption of nitration to a continuous process, and a possible reduction in the cost of TCB when purchased in quantity.

REFERENCES

1. L. Kaplan and F. Taylor, Jr., NAVORD Report 6017, "Process Development Study of 1,3,5-Triamino-2,4,6-trinitrobenzene", 10 March 1958, Confidential.

2. Ibid, page 3.

3. F. Vilbrandt and C. Dryden, "Chemical Engineering Plant Design", pp 189-254. McGraw Hill, New York (1959).

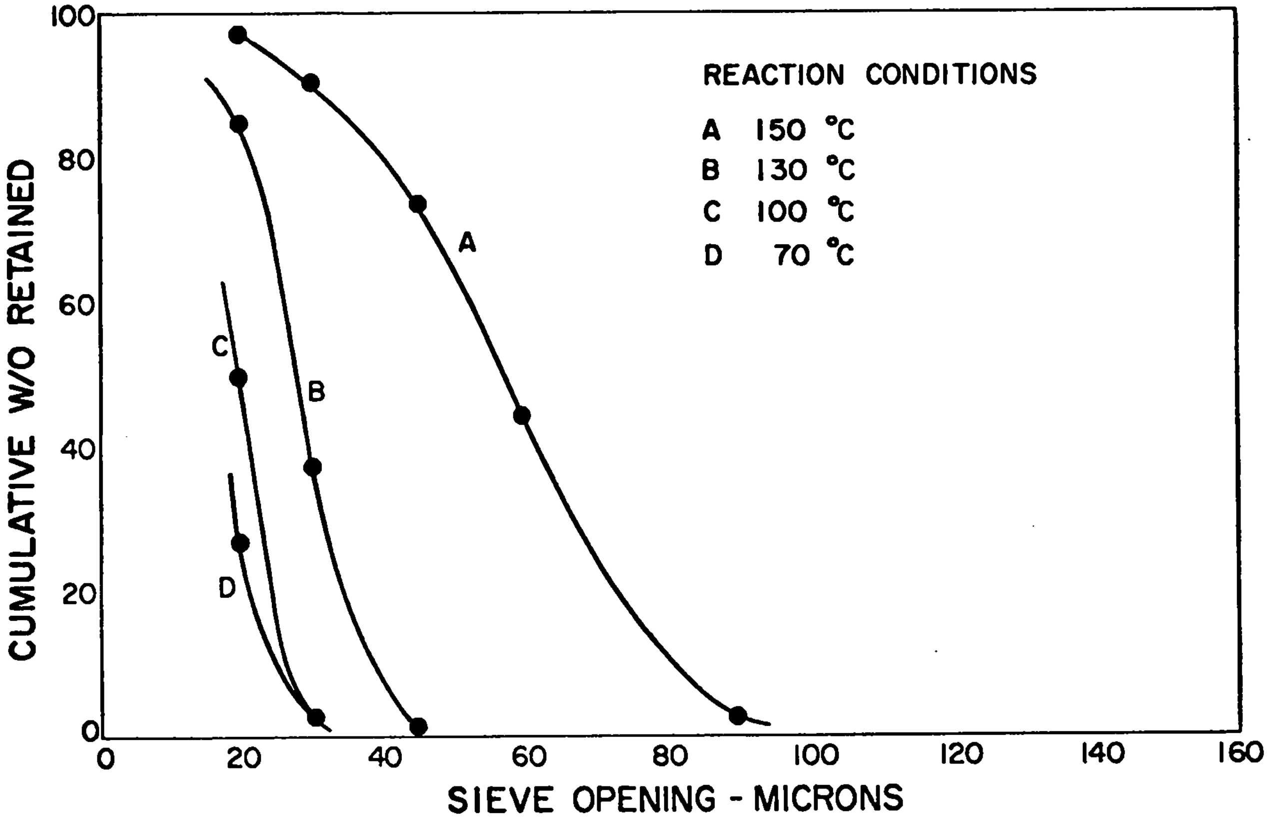
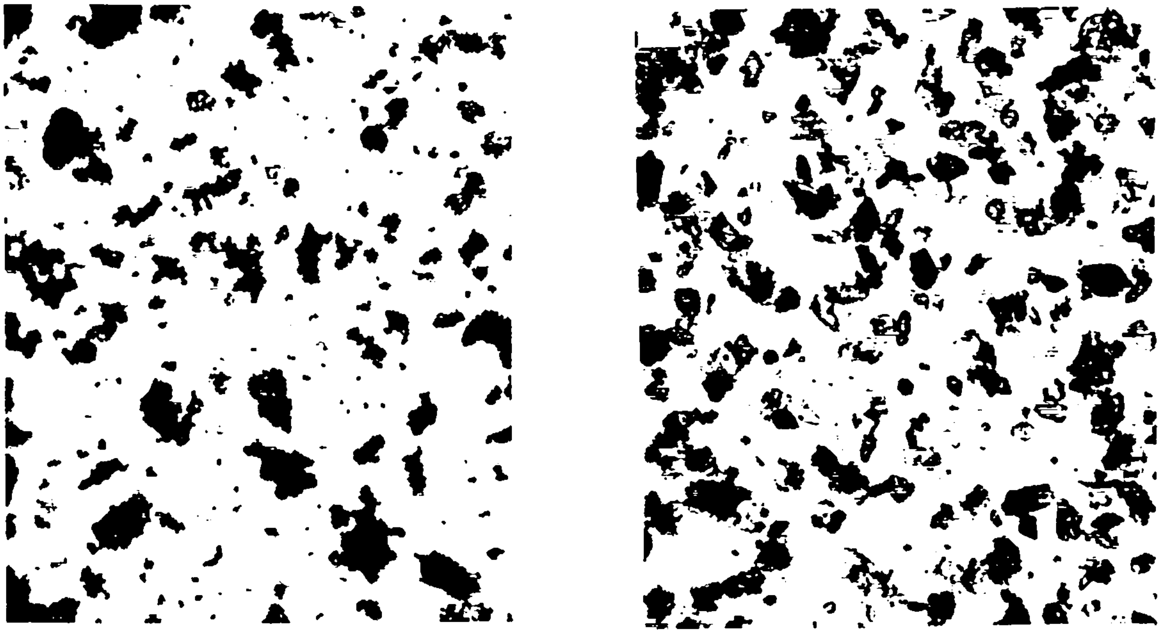
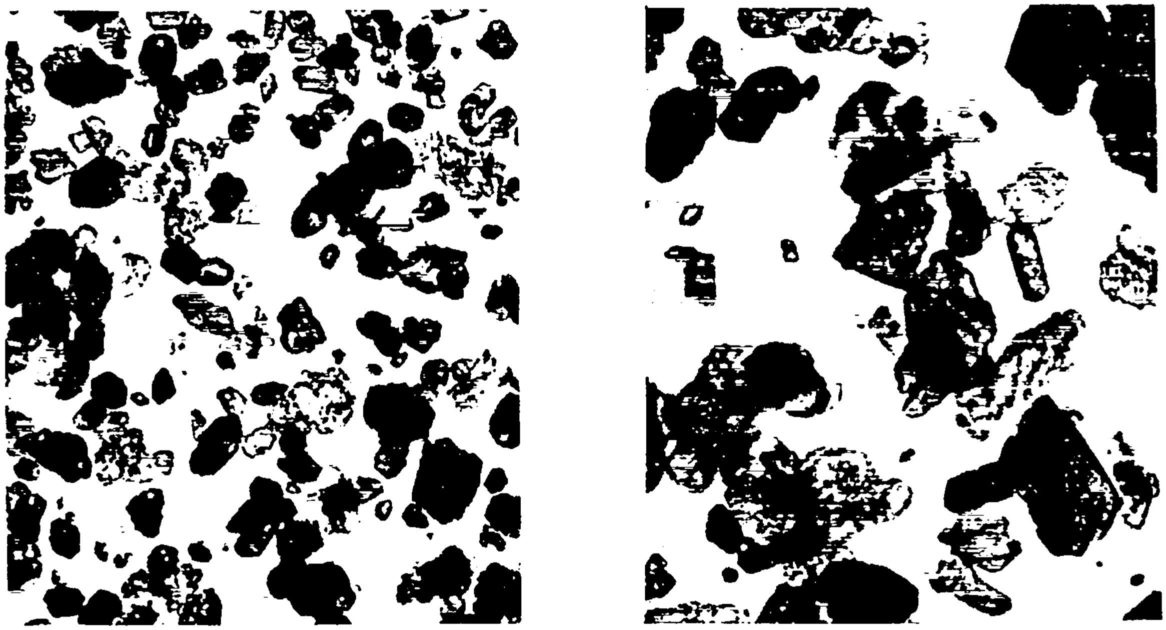


Figure 1. SIEVE ANALYSIS OF TATB POWDERS



70°C

100°C



130°C

150°C

Figure 2. TATB PRODUCED AT VARIOUS TEMPERATURES 100μ