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Technical Report ARMET-TR-12014

1,3,6,8-TETRANITROCARBAZOLE (TNC) SYNTHESIS AND OPTIMIZATION

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14. ABSTRACT

The purpose of this program was to optimize the synthesis of 1,3,6,8-tetranitrocarbazole (TNC). This material is used in pyrotechnic formulations. The process begins with the addition of carbazole to 90% nitric acid while maintaining the reactor temperature at 45°C. After all the carbazole is added, more nitric acid is introduced to raise its final concentration to 94%. The mixture is then heated to 80°C and held for 2 hrs. A 55% nitric acid quench (55%) is added to the mixture and allowed to cool to ambient temperature. The product is filtered and washed with 70% nitric acid and water. The yield of crude TNC is 40 to 65%. The TNC purification process involves digesting the TNC in acetone at reflux for 30 to 60 min, followed by quenching the slurry with water. Finally, the TNC solids are filtered, further washed with water, and recovered as a crystal product.

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Synthesis of 1,3,6,8-tetranitrocarbazole (TNC)   TNC purification process

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INTRODUCTION AND BACKGROUND

The objective of this program was to optimize the synthesis of 1,3,6,8-tetranitrocarbazole (TNC). This material is used in pyrotechnic formulations. The scope of the program is to develop a simple and efficient method for the nitration of carbazole that produces, exclusively, the 1,3,6,8 isomer in good yields. The product obtained is also tested for compliance to TNC military specification MIL-T-13723A.

SYNTHESIS OF 1,3,6,8-TETRANITROCABAZOLE

The TNC has traditionally been synthesized with a mixed acid system of sulphuric acid and nitric acid. The carbazole is added to the sulphuric acid and heated until the carbazole becomes fully sulfonated (fig. 1). Then nitric acid is added to the mixture and heated until the sulfonate groups are replaced by nitro groups to afford TNC.

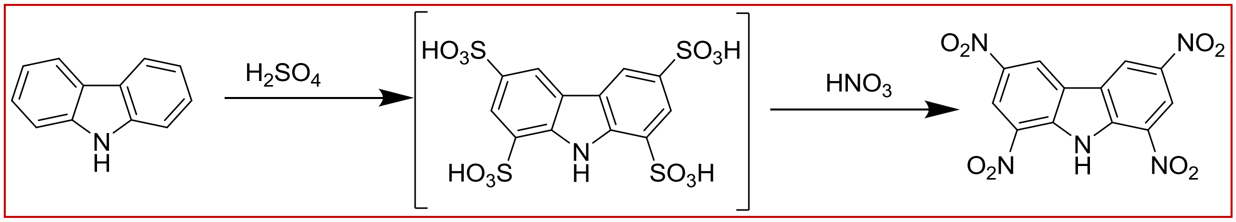

Figure 1
Carbazole added to sulphuric acid, heated until carbazole becomes sulfonated

Within this program, one objective was to avoid the use of sulfuric acid and be able to only use nitric acid. This desired process will be a better fit with the infrastructure at Holston Army Ammunition Plant (HSAAP). Initially, a three-stage, three-pot process was developed at HSAAP (fig. 2). The carbazole was added to a weak nitric acid solution; the same as in the aforementioned process. In this design, the reaction mixture was then added to 99% nitric acid to increase the overall nitric concentration in the reaction mixture. That mixture was then heated for a short time before adding that mixture to nitric acid again to bring the nitric concentration up further. That mixture was then heated for a few hours, cooled, quenched, and the product washed with water. However, the final TNC product did not meet purity requirements, not to mention that such a complex process is not the most desirable from a large scale manufacturing standpoint.

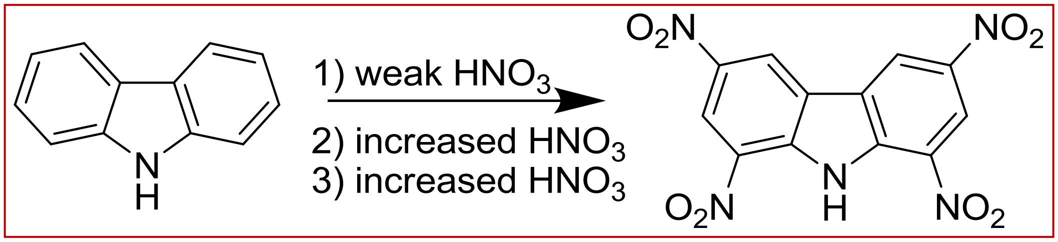

Figure 2
Three-stage, three-pot process

Taking this process as a starting point, OSI scientists sought to make improvements by attempting to move to a one-pot, two-stage process (fig. 3). The carbazole was added to a weak nitric acid solution; the same as in the aforementioned process. In this new design, however, 99% nitric acid was then added to increase the overall nitric concentration in the reaction mixture. That mixture was then heated for a few hours, cooled, quenched, and the product washed with water. However, reaction exotherm issues (see next section) and reactor volume logistics did not make this the ideal process either, albeit improved from prior processes.

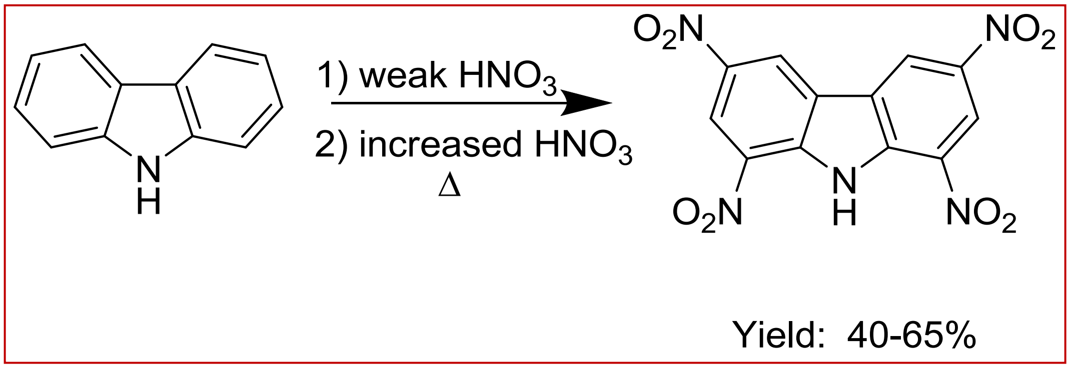

Figure 3
One-pot, two-stage process

Reaction Calorimeter Results

Work on this phase of the program also focused on using reaction calorimetry to study the heat flow of the nitration of carbazole to give TNC. These results will be used to better understand applicable risks during the scale-up procedure. There were two reaction calorimeter reactions performed. In the first, 99% nitric acid was added to the reaction mixture at 40°C. In the second, the nitric acid was added at 50°C. These results were compared to the previous reaction calorimetry results where nitric acid was added at 25°C.

The results of each step of the reaction calorimeter runs are shown in the tables 1 and 2. Table 1 shows the total quantity of heat evolved (Q_r) in each step of the reaction. Table 2 shows ΔT_{ad}, which is the temperature rise (or decrease) that would occur in the absence of any heat removal or dissipation. Both tables summarize the reaction calorimetry results from the 99% nitric acid addition at 25 (reported previously), 40, and 50°C.

Table 1
Total quantity heat evolved, Q_r

	25°C	40°C	50°C
Carbazole addition	9.38 kJ	37.94 kJ	111.02 kJ
99% HNO_3 addition	326.73 kJ	413.01 kJ	785.76 kJ
Heat up and hold	-667.33 kJ	-332.49 kJ	-63.64 kJ

Table 2
Temperature rise (or decrease), ΔT_{ad}

	25°C	40°C	50°C
Carbazole addition	4.40°C	19.75°C	23.04°C
99% HNO_3 addition	145.87°C	86.51°C	163.05°C
Heat up and hold	-146.18°C	-69.63°C	-13.21°C

In the first step of the reaction, carbazole was added to weak HNO_3 in the 2-L Mettler-Toledo RC1 reaction calorimeter at 25°C. For the first RC1 reaction (fig. 4), the reactor was then heated to 40°C in preparation for the next step. In the second RC1 reaction (fig. 5), the reactor was heated to 50°C. As can be seen in both reactions, there was a slight exotherm after the carbazole was added to the 50% nitric acid. This matches what was seen during the previous RC1 experiment. There are additional small exotherms in both reactions as the reactor was heated. Although small, these exotherms could be further mitigated by adding carbazole slower and introducing a wait period before the reactor is heated.

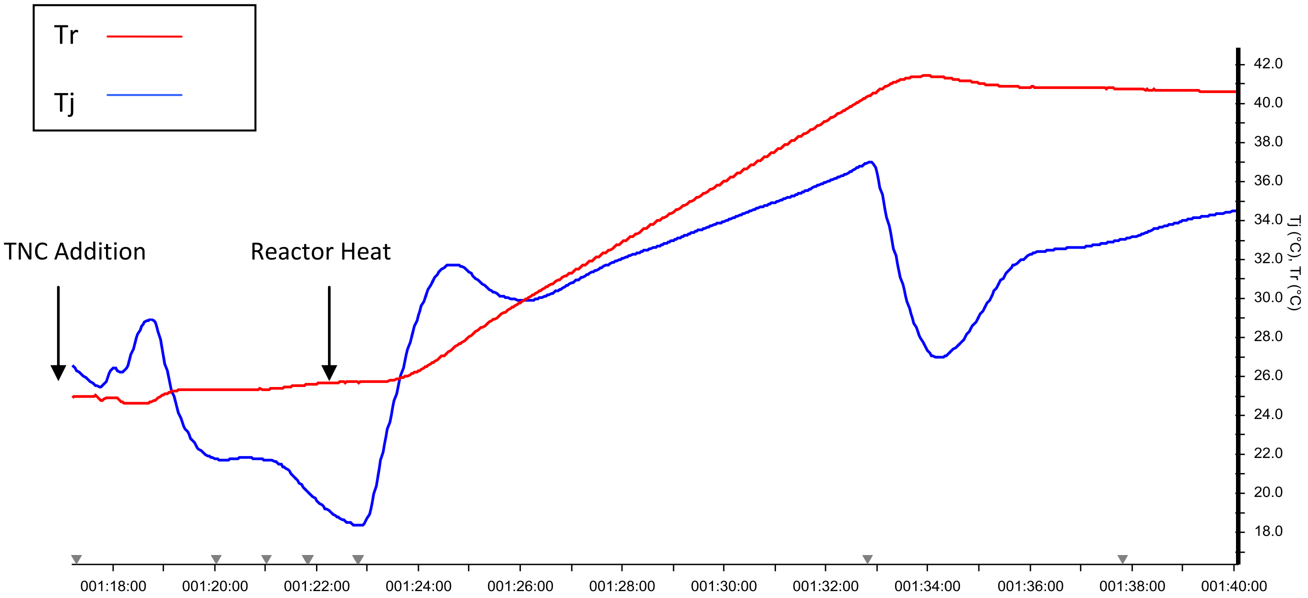

Figure 4
Carbazole addition and heated to 40°C

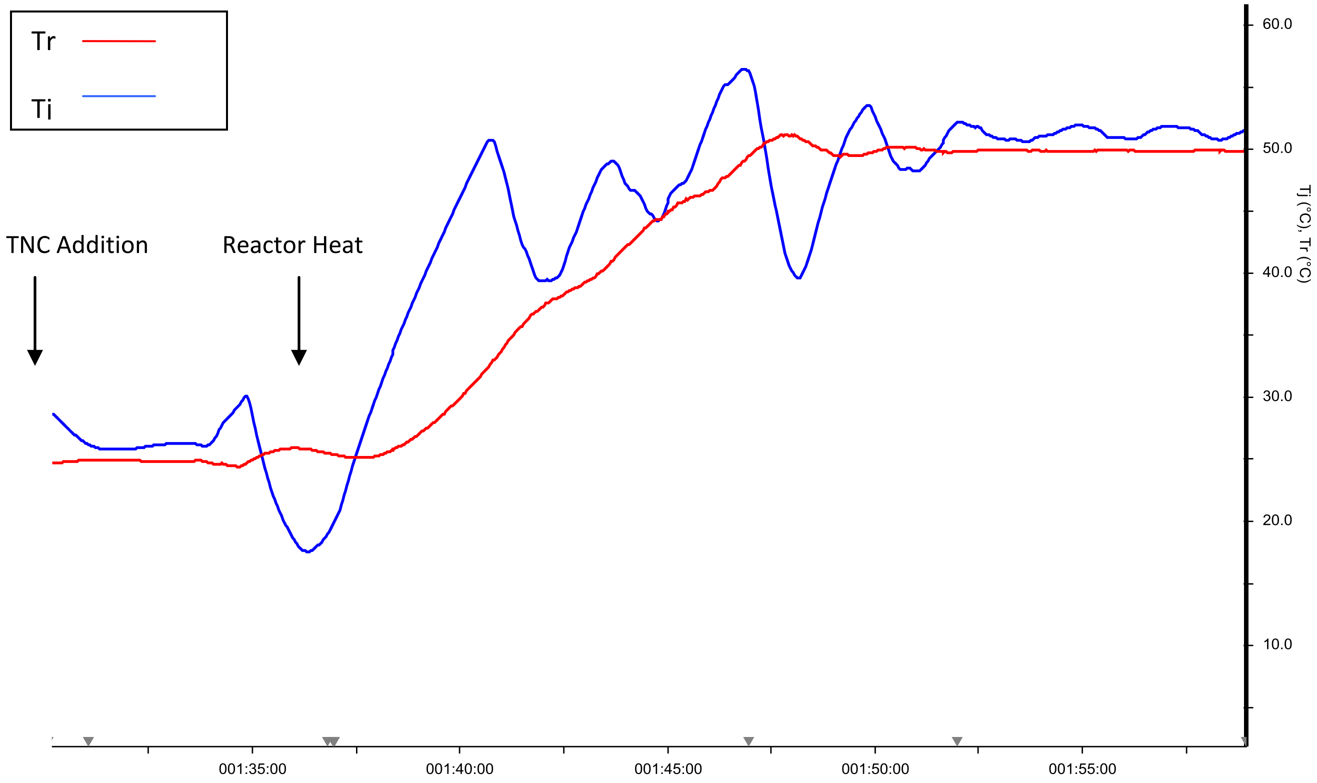

Figure 5
Carbazole addition and heated to 50°C

In the second step of the reactions, 99% HNO_3 was slowly added to the weak nitric acid carbazole slurry in order to increase the HNO_3 concentration and nitrate the material. At all three initial temperatures, the addition of nitric acid was very exothermic. Based upon the data from the 25°C addition, the rate of addition for the 40 and 50°C reactions was doubled to 90 min. For the 40°C addition, the temperature of the reactor (Tr) initially spiked 5 to 45°C upon nitric acid addition (fig. 6). The reactor jacket (Tj) cooled to 11°C to compensate for the exotherm. For the rest of the addition, the reactor temperature never went above 42°C. However, the jacket fluctuated between 10 and 35°C in order to compensate for multiple exotherms and maintain a 40°C reactor temperature.

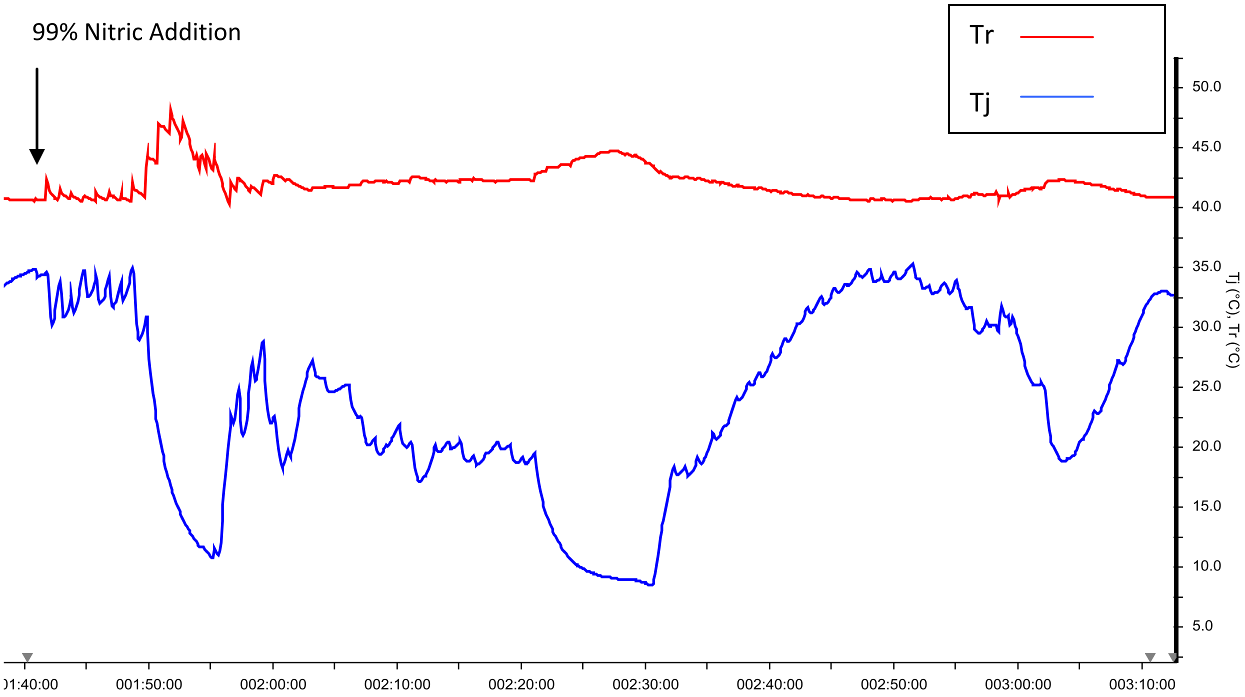

Figure 6
99% nitric acid addition at 40°C

For the 50°C addition, the temperature of the reactor (Tr) initially raised 3 to 53°C upon nitric acid addition (fig. 7). The reactor jacket (Tj) cooled to 20°C to compensate for the exotherm. The large exotherm persisted through approximately the first half of the addition. For the rest of the addition, the reactor temperature never went above 50°C, with the jacket temperature slowly rising to 48°C. As was shown in table 1, there was significantly more heat evolved during the 50°C nitric acid addition than the 25 or 40°C addition. However, in both the 40 and 50°C additions, the cooling water was able to maintain the exotherm with a ΔT between Tr and Tj of no more than 30°C. Finally, the doubling of the addition rate to have a 90-min addition appears to noticeably help maintain the desired reactor temperature.

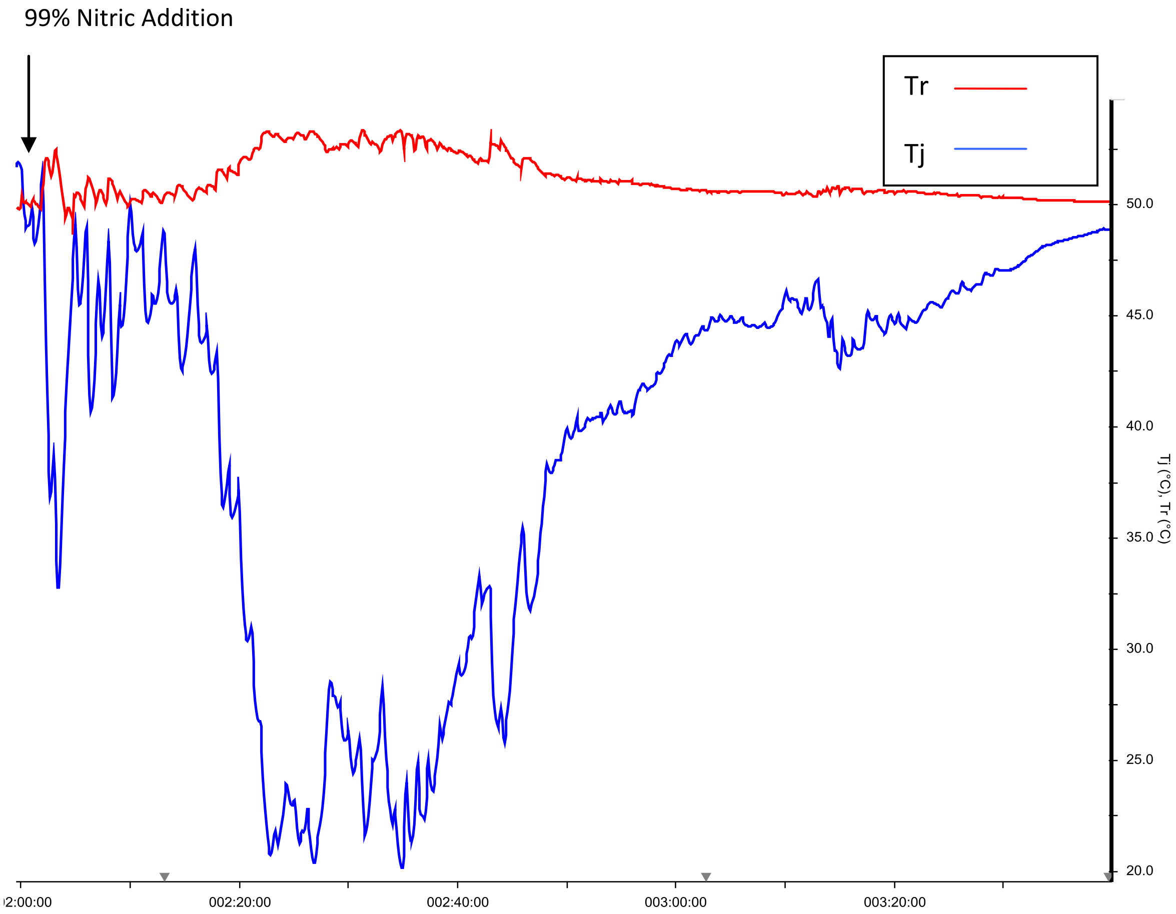

Figure 7
99% nitric acid addition at 50°C

CURRENT 1,3,6,8-TETRANITROCARBAZOLE PROCESS

Figure 8 shows the latest process developed by OSI scientists. This is a true one-pot, one-stage process. The carbazole was added to a concentrated nitric acid solution, heated for a few hours, cooled, quenched, and washed with water to obtain TNC with acceptable particle size and purity. Currently, yields are approximately 50%, which, although not ideal, is acceptable due to the low cost of the starting materials and the process.

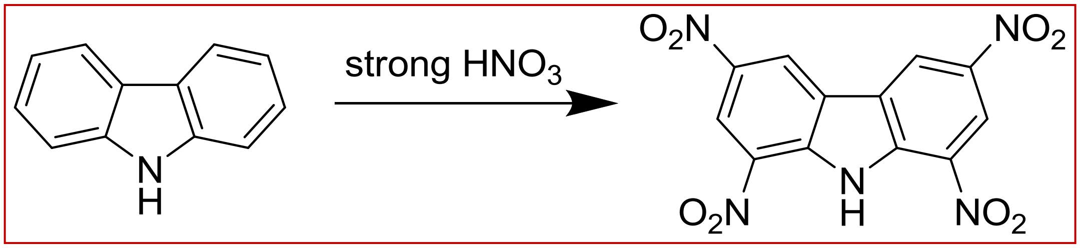

Figure 8
True one-pot, one-stage process

The quench process, using a weak nitric acid solution, helps to provide a higher yield of TNC, more than what precipitates out of the reaction mixture. Figure 9 shows the effect of the amount of quench used on the yield and purity as estimated by differential scanning calorimetry (DSC). It was evident that a significant increase in yield (from approximately 40 to 55%) can be achieved before the melting point of the TNC becomes suppressed to below 295°C in order to maintain a purity of 89% minimum.

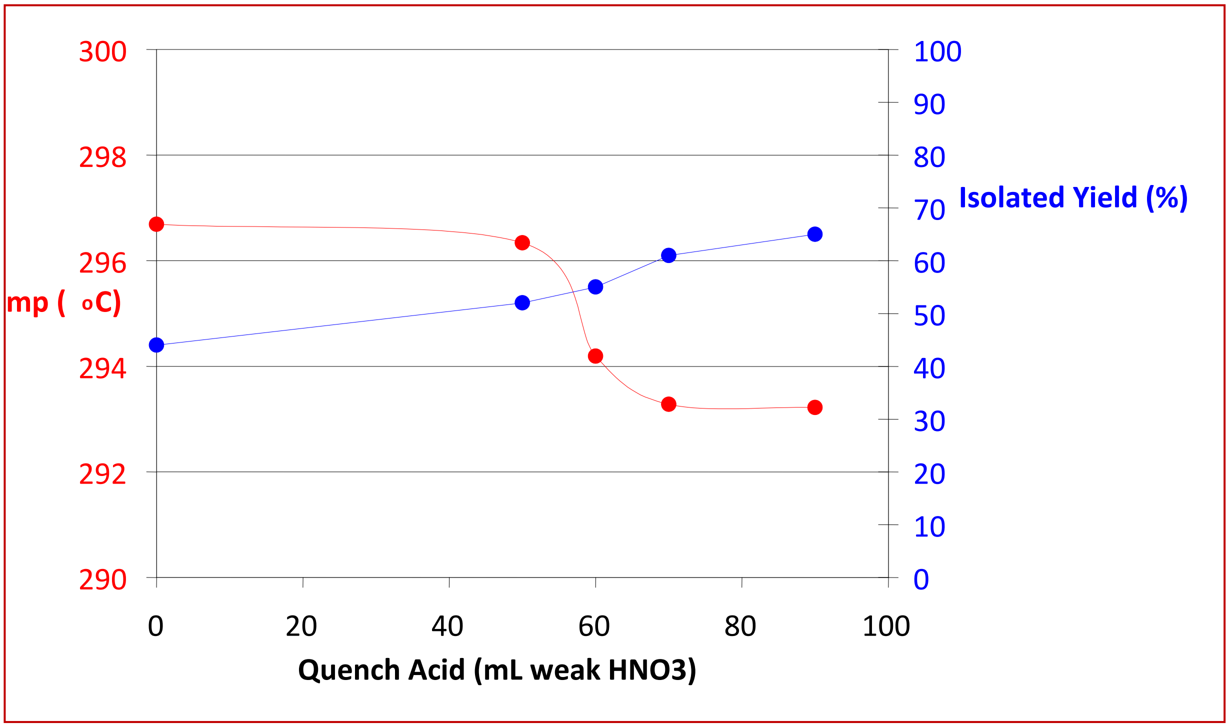

Figure 9
Effect of quench on yield and purity through DSC

Figure 10 shows the visual differences in TNC obtained from small scale studies. In the left picture is TNC that precipitates from the reaction medium. The center image is TNC afforded by the weak nitric acid quench, which shows a slightly different texture and color. The image on the right is TNC obtained from a full quench of the mixture with water. Clearly, by visual examination, this TNC product is not acceptable.

Figure 10
Visual differences in TNC from small scale studies

Microscopic evaluations of the same materials were performed (fig. 11). On the left, again, is TNC that crystallizes from the mixture. The center image is TNC from the weak nitric acid quench and on the right is TNC from the full quench. It is apparent that large crystals of TNC crystallize from the reaction, while a quench provides smaller crystals, as well as the larger crystals. Laser diffraction particle size data provides more insight into this phenomenon (fig. 12). The TNC that crystallizes from the reaction averages around 80 to 100 µm. Quenched TNC has this same 80 to 100 µm material, but also now contains smaller crystals with average particle size of approximately 20 µm. However, both types of TNC meet particle size requirements.

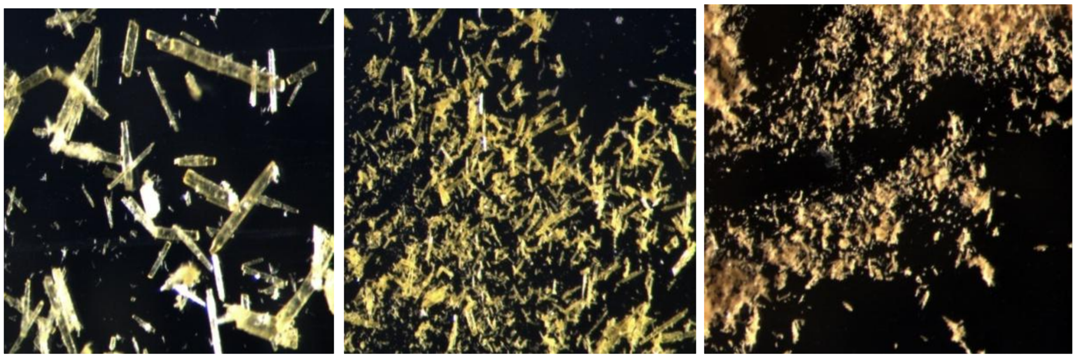

Figure 11
Microscopic evaluation

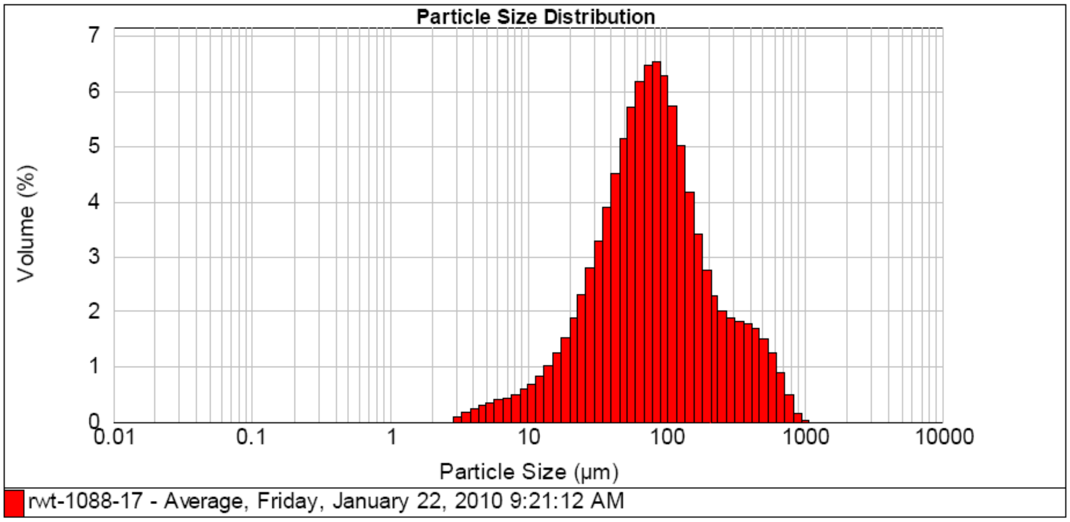

Figure 12
Laser diffraction particle size, rwt-1088-17-average

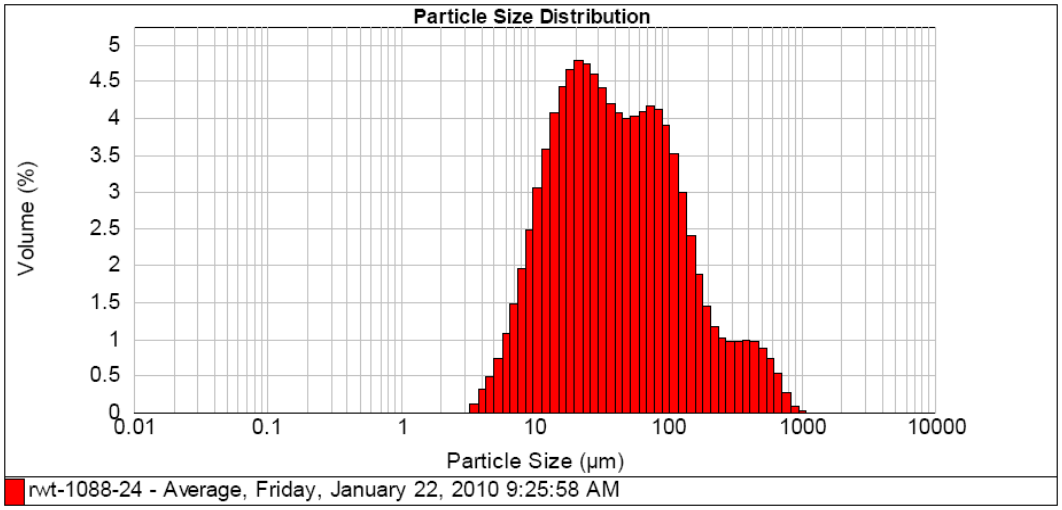

Figure 12
Laser diffraction particle size, rwt-1088-24-average
(continued)

CONCLUSIONS AND FUTURE WORK

The current process for 1,3,6,8-tetranitrocarbazole (TNC) developed by OSI scientists at Holston Army Ammunition Plant (HSAPP) produces a high purity TNC, meeting all MIL-T-13723A specification requirements. The nitration process is simple and scalable at HSAAP. The process is a one-pot, one-stage process that affords TNC that requires limited purification, making this an affordable process. Future work will include further scaling of the TNC reaction and ultimately to full-scale production batches at HSAAP.

APENDIX
MIL-T-13723A

MIL-T-13723A
14 OCTOBER 1959

SUPERSEDING
MIL-T-13723 (ORD)
22 OCTOBER 1954

MILITARY SPECIFICATION

TETRANITROCARBAZOLE (TNC) (FOR ORDNANCE USE)

This specification has been approved by the Department of Defense and is mandatory for use of the Departments of the Army, the Navy, and the Air Force.

1. SCOPE

1.1 This specification covers one grade of tetranitrocarbazole for Ordnance applications.

2. APPLICABLE DOCUMENTS

2.1 The following documents, of the issue in effect on date of invitation for bids, form a part of this specification:

SPECIFICATIONS

FEDERAL

RR-S-366 — Sieves; Standard for Testing Purposes.

UU-P-236 — Paper, filtering.

MILITARY

MIL-C-13618 — Carbazole.

DRAWINGS

ORDNANCE CORPS

F7548644 — Box, Packing for High Explosive. Assembly, Details Packing and Marking.

F7548645 — Carton, Packing, Reuseable-Collapsible, for High Explosives. Assembly, Details, Packing and Marking.

F7548646 — Carton, Packing, Reuseable-Collapsible Alternative for High Explosives. Assembly, Details, Packing and Marking.

(Copies of specifications, standards, drawings, and publications required by contractors in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

3. REQUIREMENTS

3.1 **Material.** The carbazole used in the manufacture of tetranitrocarbazole shall comply with Specification MIL-C-13618.

3.2 **Moisture.** The moisture content shall be 0.20 percent, maximum (max.) when determined as specified herein.

3.3 **Nitro-nitrogen.** The nitro-nitrogen content shall be 15.50 percent, minimum (min.) when determined as specified herein.

3.4 **Surface alkalinity.** The surface alkalinity (as NH_3) shall be 0.05 percent max. when determined as specified herein.

3.5 **Surface acidity.** The surface acidity (as H_2SO_4) shall be 0.01 percent, max., when determined as specified herein.

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3.6 Total acidity. The total acidity (as H_2SO_4) shall be 0.20 percent max., when determined as specified herein.

3.7 Total alkalinity. The total alkalinity (as NH_3) shall be 0.05 percent, max., when determined as specified herein.

3.8 Melting point. The melting point shall be 285° C, min., to 300° C, max., when determined as specified herein.

3.9 Acetone insoluble material. The acetone insoluble material shall be 0.15 percent, max., when determined as specified herein.

3.10 Granulation. The TNC shall pass through a No. 50 sieve, 100 percent, and through a No. 100 sieve, 75 percent, min., when determined as specified herein.

4. QUALITY ASSURANCE PROVISIONS

4.1 General quality assurance provisions.

4.1.1 *Contractor inspection.* Unless otherwise specified herein, the supplier is responsible for the performance of all inspection requirements prior to submission for Government inspection and acceptance. Except as otherwise specified, the supplier may utilize his own facilities or any commercial laboratory acceptable to the Government. Inspection records of the examinations and tests shall be kept complete and available to the Government as specified in the contract or order.

4.1.2 *Contractor quality assurance system.* The contractor shall provide and maintain an effective quality assurance system, acceptable to the Government, covering the supplies under the contract. A current written description of the system shall be submitted to the contracting officer prior to initiation of production. The written description will be considered acceptable when, as a minimum, it provides the quality assurance required by this specification and other applicable documents referenced herein. The contractor will not be restricted to the inspection station or to the method of inspection listed provided that an equivalent control is included in the approved quality assurance procedure. In cases of dispute as to whether or not certain procedures of the system provide equal assurance, the comparable procedure of this specification shall be used. The contractor shall notify the Government of and obtain approval for any change to the written procedure that might affect the degree of assurance required by this specification or other applicable documents referenced herein.

4.1.3 *Government verification.* All quality assurance operations performed by the contractor will be subject to Government verification at unscheduled intervals. Verification will consist of (a) surveillance of the operations to determine that practices, methods, and procedures of the written inspection plan are being properly applied, and (b) Government product inspection to measure quality of product offered for acceptance. Deviation from the prescribed or agreed-upon procedures, or instances of poor practices which might have an effect upon the quality of the product, will be immediately called to the attention of the contractor. Failure of the contractor to promptly correct deficiencies discovered shall be cause of suspension of acceptance until correction has been made or until conformance of product to prescribed criteria has been demonstrated. To avoid interference with operations, the contractor shall designate a responsible official or officials to whom the Government inspector will report such instances.

4.1.4 *Submission of data.* At the time the product is submitted to the Government for acceptance, the contractor shall supply the following information accompanied by a certificate which attests that the information provided is correct and applicable to the product being submitted:

(a) A statement that the lot complies with all Quality Assurance Provisions and requirements as required by the contractual documents.

(b) Quantity of product inspected.

(c) Results obtained for all inspections performed.

(d) Drawing and specification numbers and dates, together with an identification and date of changes.

(e) Quantity of product in lot.

(f) Certificates of analysis including results of tests on materials used in the lot.

(g) Date submitted.

4.1.4 The certificate shall be signed by a responsible agent of the contractor's organization and shall be accompanied by evidence of the agent's authority to bind his principal.

4.2 Lot. A lot shall consist of batches of the TNC from the same blending operation, subjected to the same processing operations and conditions. Each batch shall consist of that quantity of material which has been subjected to a unit chemical process or physical mixing process intended to make the final product substantially uniform.

4.3 Sampling. One sample, of approximately eight ounces in weight, consisting of eight representative one ounce portions shall be taken from each batch. Each sample shall be placed in a chemically clean and dry air-tight container. Each sample container will be labeled to show the name of the material, manufacturer, plant, contract or purchase order number, lot number, batch number, batch size (pounds), and date and time sample was taken. The tests specified in 4.5.1, 4.5.3, 4.5.4, 4.5.5 and 4.5.6 shall be made on each sample. The test specified in 4.5.2, 4.5.7, 4.5.8 and 4.5.9 shall be made on three samples, including the samples from at least one of the first five batches, and at least one of the last five batches produced for this lot. However, if it becomes apparent during sampling that the lot is not uniform, the inspector may require that more samples be tested as specified in 4.5.2, 4.5.7, 4.5.8 and 4.5.9.

4.4 Packing and marking. The contractor shall ascertain that the packing and marking of the product conform to this specification.

4.5 Tests. The supplier is not restricted in his methods of quality control, other than their being acceptable to the procurement agency. Test methods prescribed in this specification shall be used by Government inspectors in acceptance testing when required as specified in 4.1.3 and as reference methods in event of disagreement or dispute on acceptability of the product.

4.5.1 *Moisture.* Approximately five grams (g) of the sample shall be transferred to a tared, glass stoppered weighing dish and accurately weighed. The dish and contents shall be heated in an oven for approximately 1½ hours to a constant weight at 105° ± 5° C., cooled in a desiccator, and weighed. The loss in weight of the sample shall be calculated to percent moisture, to determine compliance with 3.2, as follows:

$$\text{Percent moisture} = \frac{100\,(A - B)}{W}$$

where:

A = Weight of dish and contents before heating.
B = Weight of dish and contents after heating.
W = Weight of sample.

4.5.2 *Nitro-Nitrogen.* The volumetric solutions that are necessary for this determination shall be prepared with freshly distilled water which is free from atmospheric oxygen. The siphon tubes and burets shall be connected in such a way that only carbon dioxide (CO_2) gas, supplied from a Kipp generator, will be drawn into the stock bottles as the solutions are used. The rubber tubing used for connections, shall be replaced whenever cracks appear. When no titrations are being made, the stopcock, in the tube connecting the generator with the stock bottle of titanous chloride solution and the buret, shall be turned off (fig. 1).

4.5.2.2 *Titanous chloride solution.* A 0.2 normal solution of titanous chloride shall be prepared by mixing 150 milliliter (ml) of 20 percent titanium chloride with 100 ml of 38 percent hydrochloric acid for each liter of solution. The mixing operation shall take place before diluting. In these operations, the solution shall be mixed thoroughly with a current of carbon dioxide and stored in a bottle covered with black paint or black paper to exclude light. The titanous chloride solution shall be standardized by preparing a standard potassium dichromate solution. This solution shall be prepared by transferring an *accurately weighed portion of approximately* 9.8 gm of Bureau of Standard potassium dichromate, No. 136, to a calibrated 1 liter volumetric flask. Sufficient distilled water shall be added to dissolve the potassium dichromate, and the solution diluted to the mark. The normality of the potassium dichromate solution shall be calculated from the following formula:

$$\text{Normality of potassium dichromate solution} = \frac{W}{49.035}$$

where:

W = Weight of potassium dichromate taken.

A current of carbon dioxide (CO_2) shall be passed through a special type titration flask (fig. 2) for five minutes, to displace the air in the flask. A 25 ml portion of the standard potassium dichromate solution shall be added to the flask with the aid of a buret and followed with approximately 50 ml of 10 percent sulfuric acid solution. This process of passing the carbon dioxide through the flask shall be continued and the mixture titrated with the titanous chloride solution. Three drops of 0.01 molar sodium diphenylbenzidine sulfonate indicator solution, or three drops of 0.01 molar barium diphenylamine solfonate indicator solution, shall be added as the end point is approached. Titration shall be made drop-wise to the end point. The color change of the indicator shall be from a brownish purple to purple to a distinct blue. The necessary temperature and buret corrections shall be applied to the observed reading.

$$\text{Normality of titanous chloride solution} = \frac{A \times B}{C}$$

where:

A = Volume of standard potassium dichromate solution.

B = Normality of standard potassium dichromate solution.

C = Corrected volume of titanous chloride solution required.

4.5.2.3. *Titanous chloride solution from titanium hydride (alternate method)*. Using a well ventilated hood the 0.2 normal solution of titanous chloride shall be prepared by adding, in small portions, 12g of titanium hydride to 100 ml of concentrated hydrochloric acid (warmed to 70° — 80° C.) for each liter of solution desired. The solution shall be kept warm until practically all evolution of hydrogen ceases. The reaction vessel shall be covered with a water glass except during the addition of titanium hydride. After the reaction has been completed, the reagent shall be cooled and about 250 ml of oxygen-free distilled water added. The solution shall be thoroughly mixed by bubbling oxygen free CO_2 or N_2 through the solution for 5 to 10 minutes, then filtered using a filter paper conforming to type II, Class 5, Specification UU-P-236. If the first portions of the filtrate are cloudy, the portions shall be refiltered until a completely clear filtrate is obtained. An additional 100 ml of concentrated hydrochloric acid and enough oxygen free distilled water shall be added to make a total of 1000 ml of solution. The reagent shall be agitated with oxygen-free CO_2 or nitrogen (N_2) for a few minutes before storing. Standardize as described in paragraph 4.5.1.1.

4.5.2.4 *Ferric ammonium sulfate solution (0.15N)*. A 0.15 normal ferric ammonium sulfate solution shall be prepared by mixing 75 g of hydrated sulfuric ammonium sulfate ($Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24\,H_2O$) with 25 ml of 95 percent sulfuric acid for each liter of solution, and thoroughly mixed by means of a current of carbon dioxide. The air in the titration flask shall be displaced with carbon dioxide. A 40 to 45 ml portion of the ferric ammonium sulfate solution shall be accurately measured into the flask, then 25 ml of 15 percent hydrochloric acid solution of 50 ml of water shall be added. This solution shall be titrated with 0.2 normal titanous chloride solution until near the end point, then five ml of 20 percent ammonium thiocyanate solution added. This titration shall be continued until the red color disappears. The temperature and buret correction shall be applied to the observed readings and the normality of the ferric ammonium sulfate solution calculated. It may be assumed that the strength of the solution will remain constant for an indefinite period.

4.5.2.5 *Procedure.* Approximately 0.5 g of the dried sample shall be accurately weighed and transferred to a 250 ml volumetric flask. A 100 ml portion glacial acetic acid shall be added, and then the flask and contents heated on a steam bath to dissolve the sample. The sample shall be allowed to cool to room temperature and a sufficient amount of glacial acetic acid added to bring the level of the solution in the flask to the mark. The air in the titration flask shall be displaced by passing in a current of carbon dioxide for five minutes. A 25 ml portion of the acetic acid solution of the sample shall be transferred to the titration flask. Approximately 25 ml of 15 percent hydrochloric acid solution and exactly 50.00 ml of 0.2 normal titanous chloride solution shall be added to the titration flask. A few glass beads shall be added to prevent bumping when boiled. The flask shall be connected to a reflux condenser and boiled on a hot plate until all the yellow particles disappear. This should take place after boiling for approximately 30 minutes and will be accompanied by a color change in the solution from reddish brown to purple. The current of carbon dioxide shall be increased, and the flask cautiously immersed in a cold water bath, keeping the index finger over the top of the condenser until the hot vapors are condensed. After the flask and contents have cooled to room temperature, the condenser shall be disconnected and one-hole rubber stopper, which contains a short piece of glass tubing, shall be inserted. The top of the burette shall be inserted into the glass tubing, and the cooled solution titrated with 0.15 normal ferric ammonium sulfate solution to the first permanent red color; 5 ml of 20 percent ammonium thiocyanate solution shall be added near the end point. A blank shall be run on the reagents following the above procedure, to correct for reducible impurities in the reagents. The percentage of nitro-nitrogen in the sample shall be calculated as follows, to determine compliance with 3.3:

$$\text{Percentage of nitro-nitrogen} = \frac{0.233\,(V - AF)\,(N)}{W}$$

where:

V = Volume of titanous chloride added.
N = Normality of titanous chloride solution.
A = Volume of ferric ammonium sulfate solution.
F = Factor for converting the volume of ferric ammonium sulfate solution to an equivalent volume of titanous chloride solution.
W = Weight of sample represented by aliquot taken.

4.5.3 *Surface alkalinity.* Approximately 10 g of the sample accurately weighed, shall be transferred to a 400 ml beaker. A 200 ml portion of hot (90° to 100° C.) distilled water which has been boiled for five minutes and made neutral to methyl red indicator solution shall be added to the beaker. The sample shall be stirred for a few minutes and then the beaker and contents cooled to approximately room temperature in an ice bath with occasional stirring. The supernatant liquid shall be filtered through a filter paper, type II, class 6, Specification UU-P-236. Transferring more of the precipitate than is necessary to the filter paper shall be avoided, to facilitate filtration. The residue in the beaker and on the filter paper shall be washed with three 20 ml portions of cold distilled water which has been boiled for five minutes and made neutral to methyl red indicator solution. The washings and filtrate shall be collected in a clean 600 ml beaker. Five drops of methyl red indicator solution shall be added to the filtrate and stirred. If the resulting solution is yellow, the solution shall be titrated immediately, with approximately 0.05N hydrochloric acid solution of known normality, to the first permanent tinge of pink. The percentage of surface alkalinity of the sample shall be calculated according to the following formula to determine compliance with 3.4:

$$\text{Percentage of surface alkalinity, as } NH_3 = \frac{1.7BN}{W}$$

where:

B = ml of hydrochloric solution required.
N = Normality of hydrochloric acid.
W = Weight of sample.

4.5.4 *Surface acidity.* Approximately 10 g of the sample, accurately weighed, shall be transferred to a 400-ml beaker. A 200-ml portion of hot (90° to 100° C.) distilled water, which has been boiled for five minutes and made neutral to methyl red indicator solution, shall be added. The sample shall be stirred for a few minutes and then the beaker and contents cooled to approximately room temperature in an ice bath with occasional stirring. The supernatant liquid shall be filtered through a filter paper, type II, class 6, Specification UU-P-236. Transferring more of the precipitate than is necessary to the filter paper shall be avoided to facilitate filtration. The residue in the beaker and on the filter paper shall be washed with three 20-ml portions of cold distilled water which has been boiled for five minutes and made neutral to methyl red indicator solution. The filtrate and washings shall be collected in a clean 600-ml beaker. Five drops of methyl red indicator solution shall be added to the filtrate and stirred. If the resulting solution is red, the solution shall immediately be titrated, with approximately 0.05N sodium hydroxide solution of known normality, to the first permanent yellow color. The percentage of surface acidity of the sample shall be calculated according to the following formula to determine compliance with 3.5.

$$\text{Percentage of surface acidity, as sulfuric acid} = \frac{4.9AN}{W}$$

where:

A = Volume of sodium hydroxide solution required for titration.
N = Normality of sodium hydroxide solution.
W = Weight of sample.

4.5.5 *Total acidity.* Approximately 5 g of the sample, accurately weighed, shall be transferred to a 1500-ml beaker, and 400-ml of acetone added. The beaker and contents shall be heated on a steam bath with occasional stirring until the sample has dissolved. Sufficient acetone shall be added to bring the total volume of solution up to 400-ml and then the beaker and contents shall be removed from the steam bath and 400-ml of distilled water added. Two blanks shall be made up, each consisting of 50-ml of acetone and 50-ml of distilled water and the average of their pH values shall be used as standard. It should be noted here that the beaker containing the solutions should be adequately covered to prevent any interference from the atmosphere. If the pH of the solution is lower than the standard (average pH value obtained from the two blanks) the solution shall be titrated with 0.01 normal sodium hydroxide to the same pH as the blank. (If the pH is higher than that of the blank, the solution shall be rechecked and if the pH has changed more than ± 0.1, the entire determination must be repeated. The volume of sodium hydroxide solution required for titration to percent acidity as sulfuric acid, shall be calculated using the following formula to determine compliance with 3.6:

$$\text{Percent total acidity, as sulfuric acid} = \frac{4.9AN}{W}$$

where:

A = Volume of sodium hydroxide solution required for titration.
N = Normality of the sodium hydroxide solution.
W = Weight of sample.

4.5.6 *Total alkalinity.* If the pH obtained in 4.8 was higher than the standard, then the sample specification in 4.8 shall be titrated with 0.01N hydrochloric acid of known normality to the same pH as is obtained with the average of two blanks each consisting of 50 ml of acetone and 50 ml of distilled water. The total alkalinity shall be calculated as follows to determine compliance with 3.7:

$$\text{Percent total alkalinity, as } NH_3 = \frac{1.7AN}{W}$$

where:

A = Volume of hydrochloric acid solution required for titration.
N = Normality of sodium hydroxide.
W = Weight of sample.

4.5.7 *Melting point.* A portion of the dried sample shall be placed on a glass slide. The material on the slide shall be covered with a No. 1 Watch glass, and pressed down firmly to reduce the distance between the slide and cover glass. This assembly shall be placed on the stage of a Micro Hot Stage (see 6.4). The glass slide shall be covered with a baffle, and the stage covered with a glass cover. The microscope (see 6.3) shall be focused on a portion of the sample. The marker of the sliding tube rheostat shall be adjusted to a position on the arbitrary wooden scale so as to maintain a rate of heating which shall not exceed 1° C. per minute at the melting point of the sample. At a magnification of approximately 150 x by strong transmitted light the sample will consist of conglomerates of minute crystals which appear to be black. If the light is reduced sufficiently the masses of crystals are yellow. Over the range of 230° C. to 280° C. the sample apparently passes through a series of transition points resulting in the formation of larger yellow needle-like and plate-like crystals. Record as the observed melting point the temperature at which the crystals of average size become a yellow or brown liquid using a high range thermometer. Calibrate the thermometer with the air of the test reagents, the melting points of which are known. Apply any correction which is indicated to be necessary to the observed melting point of the material.

4.5.8 *Acetone insoluble material.* Approximately 5 g of the sample, accurately weighed, shall be transferred to a clean dry 400 ml beaker and 200 ml of acetone added. The sample shall be heated gently on a steam bath with occasional stirring for approximately ½ hour. The supernatant liquid shall be decanted through a tared filtering crucible of medium porosity, and any insoluble material retained in the beaker. A 200-ml portion of acetone shall again be added to the beaker and heated gently on the steam bath for ½ hour. This solution shall be filtered through the tared filtering crucible and any insoluble material remaining in the beaker transferred to the filtering crucible with five, 20 ml portions of hot acetone. The crucible shall be dried in an oven at 105° ± 5° C. for one hour, cooled in a desiccator and weighed. The above extraction, drying and weighing procedure shall be repeated, with individual 10 ml portions of acetone, until the loss in weight on subsequent extractions totals less than 0.001g. The acetone insoluble materials shall be calculated as follows, to determine compliance with 3.9:

$$\text{Acetone insoluble impurities, percent} = \frac{100\,(A - B)}{W}$$

where:

A = Weight of crucible and residue.
B = Weight of crucible.
W = Weight of crucible sample.

4.5.9 *Granulation.* An accurately weighed portion of approximately 50 g of the sample shall be transferred to a one-liter beaker containing approximately 400 ml of water and a few drops (sufficient to thoroughly wet the sample) of a suitable wetting agent, such as a 25 percent solution of sodium dioctylsulfosuccinate (see 6.5). With the aid of a rubber policeman attached to a glass stirring rod, the mixture shall be stirred for a few minutes, breaking up as many lumps as possible and thoroughly wetting every part of the sample. With a spray from a spray nozzle (see 6.6), under tap water pressure, this mixture shall be transferred quantitatively to a No. 50 U. S. Standard Sieve which has been fitted to the top of a No. 100 U. S. Standard Sieve; the sieves shall comply with Specification RR-S-366. This assembly should be set up near a water tap and drain. Provisions shall be made to prevent transfer of the explosive to the drain. The pressure of the spray shall be adjusted so that when the spray strikes the sample from a height of two to three inches, it is possible to wash the sample back and forth across the sieve without splashing any of the material over the sides of the sieve. The wet lumps shall be gently crushed on the upper sieve with the rubber policeman, and washing of the sample continued back and forth across the screen with the water until all the agglomerates have been broken and only individual crystals larger than the mesh of the sieve remain on the sieve. The rubber policeman shall be used in breaking up the agglomerates on the upper sieve only. The No. 50 sieve shall be removed, and a few drops of the wetting agent (see 6.5) added to the material on the No. 100 sieve, washing as described above for approximately 10 minutes or until only individual crystals larger than the mesh of the sieve remain on the sieve. After the washing has been completed the portions remaining on each of the screens shall be quantitatively transferred to separate 400 ml beakers as follows: the screen shall be held in an almost vertical position, and the material gently washed to the lower part of the screen, with a moderate spray of water from the spray nozzle, by drawing the spray back and forth across the screen, beginning at the top and moving slowly down the screen as the crystals move down. After the material has been collected at the lower part of the sieve, it shall be washed into the beaker with a stream of water from a wash bottle. The explosive in each of the beakers shall be quantitatively transferred to separate, previously tared 50 ml fritted glass filtering crucible of medium porosity. The crucible shall be aspirated during the transfer process and the aspiration continued on the contents and crucible for approximately five minutes after transfer has been completed. The suction shall be turned off and 15 ml of anhydrous methanol added to the crucible and contents; the methanol shall be allowed to remain in contact with the explosive for approximately five seconds and then removed with the aid of suction. The contents of the crucible shall be washed once more with anhydrous methanol as described above, and then the crucible and contents aspirated until the odor of the methanol is no longer discernible. The crucible and contents shall be dried in an oven maintained at 105° ± 2° C. for 45 minutes, cooled in a desiccator and weighed. The percentage of explosive passing through each of the sieves shall be calculated as follows to determine compliance with 3.10:

$$\text{Percent through No. 50 U. S. Standard Sieve} = \frac{(W-A) \times 100}{W}$$

where:

A = Weight of sample retained by No. 50 sieve.

W = *Weight of the original sample.*

$$\text{Percent through No. 100 U. S. Standard Sieve} = \frac{W-(A + B \times 100}{W}$$

where:

A = Weight of sample retained by No. 50 sieve.

B = Weight of sample retained by No. 100 sieve.

W = Weight of the original sample.

4.5.10 *Acceptance criteria.* A submitted lot *shall be acceptable if the samples selected* according to paragraph 4.3 meet the respective requirements of section 3 based on the determinations performed as specified herein. Otherwise, the lot shall be rejected. The procurement agency shall have the option of accepting individual batches from a rejected lot if the samples representing these batches comply with the respective requirements of section 3.

4.5.11 *Rejection and resubmission.* When a lot is rejected, the lot or all of the rejected batches, when the procurement agency exercises the option of accepting individual batches, shall be returned to the contractor. The contractor shall have the option of having a partial or complete analysis made on samples taken from all or any of the batches in the lot at no expense to the Government. The contractor may then remove the defective portion of the lot, and resubmit the lot, which shall be designated as a resubmitted lot. The resubmitted lot shall be accepted, provided all the samples comply in 3.2, 3.4, 3.5, 3.6 and 3.7 and six samples selected at random for tests specified in 4.5.2, 4.5.7, 4.5.8 and 4.5.9 comply with all of the requirements. The failure of a submitted lot to meet the requirements specified permanently rejects the lot unless specified by the procurement agency.

5. PREPARATION FOR DELIVERY

5.1 Packing.

5.1.1 *Level A*. The TNC shall be packed 40 lb net weight in a wooden box conforming to Drawing F7548644.

5.1.2 *Level C*. The TNC shall be packed 40 lb net weight in fiberboard cartons conforming to Drawing F7548645 or F7548646.

5.2 **Marking.** Containers shall be marked as specified on Drawing F7548644, F7548645 or F7548646 and MIL-STD-129. Each container shall be clearly marked to indicate the batch number.

6. NOTES

6.1 **Intended use.** This specification covers tetranitrocarbazole intended for use in pyrotechnic and igniting compositions.

6.2 **Ordering data.** Procurement documents should specify the following:

- (a) Title, number, and date of this specification.
- (b) Levels of protection (see 5.1).

6.3 An E. Leitz Wetzlar Microscope with 10X magnification eyepiece and No. 3 objective was found to be satisfactory.

6.4 A Kofler Micro Hot Stage, catalog No. 6886, Arthur H. Thomas Co., Philadelphia, Pa. (or equivalent) was found suitable for use.

6.5 This item is available commercially as Aerosol O. T.

6.6 A satisfactory spray nozzle can be made by fitting a Gooch crucible No. 4 Coors Porcelain, over a No. 8 one-hole rubber stopper filled with a short piece of glass tubing to which is attached a length of rubber hose of approximately 1.0 cm inside diameter. The free end of the hose is connected to the water tap and the Gooch crucible at the other end acts as a spray nozzle.

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APPARATUS FOR STORING AND USING TITANOUS CHLORIDE SOLUTION.

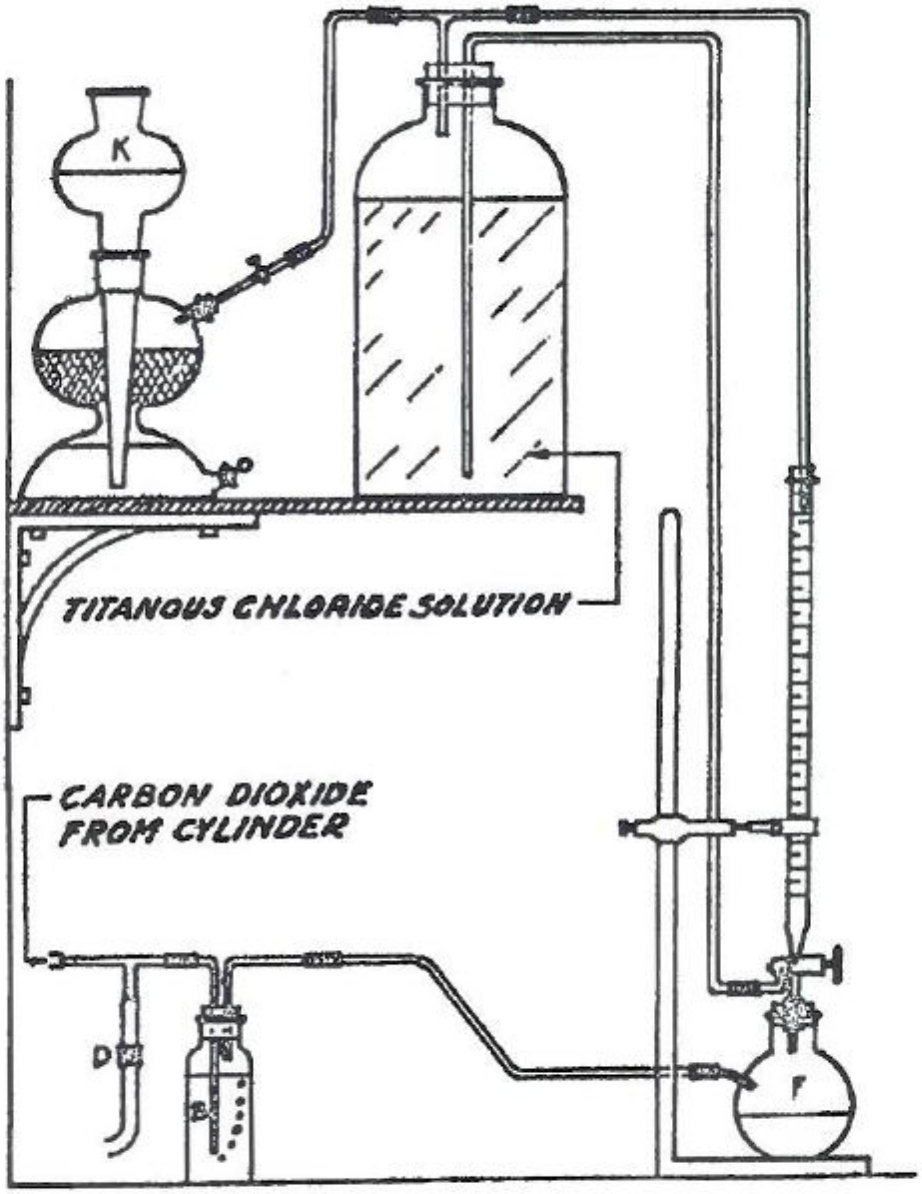
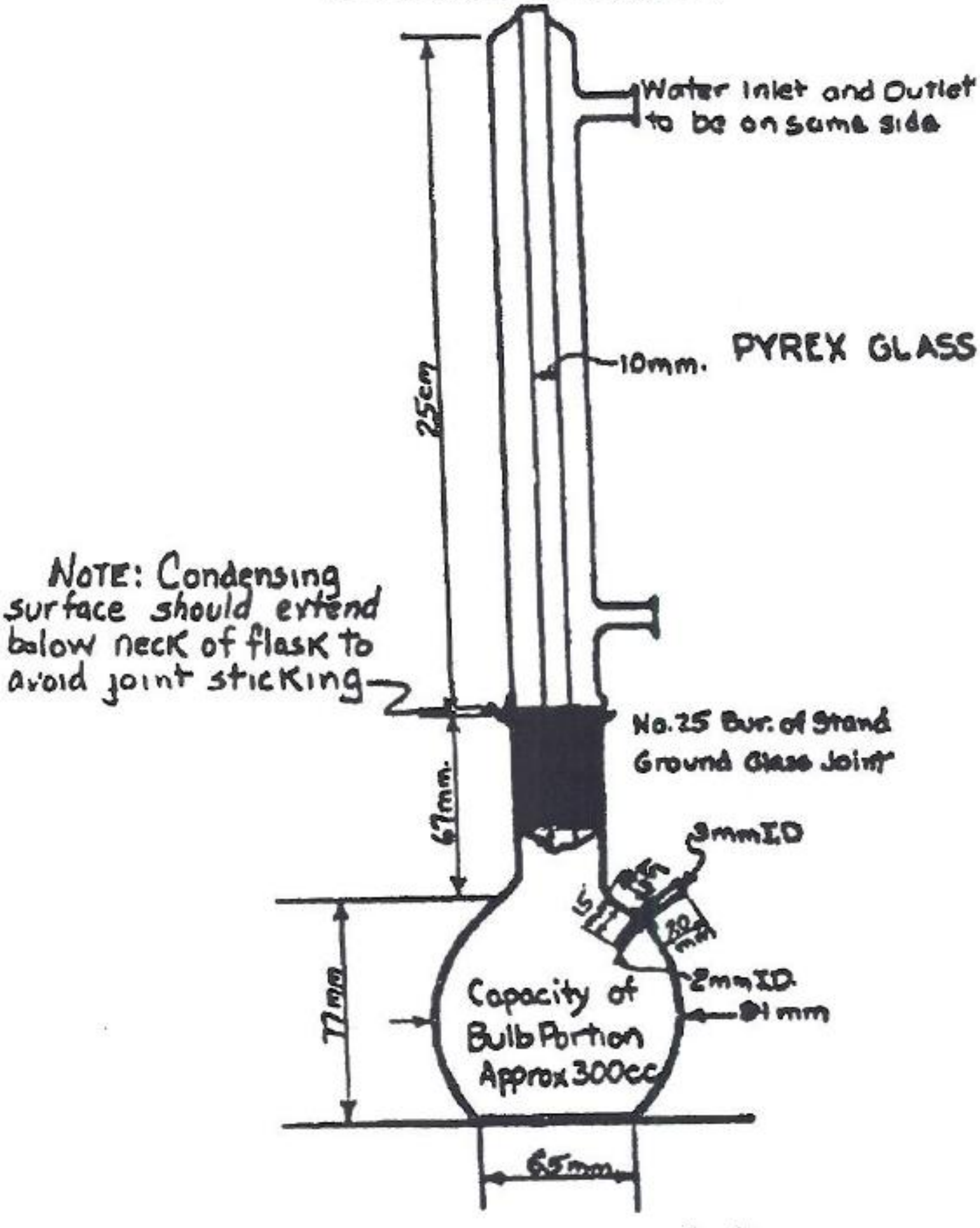


FIGURE 1.

TITRATION FLASK



All Dimensions Are Approximate

FIGURE 2.

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