

HAZARDS OF INADVERTENT MIXING OF CHEMICALS USED IN THE BACHMANN PROCESSES FOR MANUFACTURING THE MILITARY EXPLOSIVES RDX AND HMX

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Summary

Reactivity tests were conducted and a CHETAH diagram constructed to evaluate the hazards of inadvertent mixing of chemicals used at Holston Army Ammunition Plant in modified Bachmann processes for manufacturing the military explosives RDX and HMX. When mixed in an unconfined, insulated vessel, certain combinations of Bachmann chemicals, initially at ambient temperatures, were found to generate fires spontaneously. Other combinations spontaneously generate explosions when mixed in a closed vessel.

Introduction

The military explosives, RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane) are manufactured at Holston Army Ammunition Plant (HAAP) in Kingsport, Tennessee. HAAP is operated by Holston Defense Corporation (HDC), a subsidiary of Eastman Kodak Company. Both RDX and HMX are manufactured according to modified Bachmann processes using the same chemicals [1,2]. The chemicals are:

- (1) a solution of ammonium nitrate in nitric acid (56.4 ± 0.5 weight percent HNO_3 and $43.5 \pm 0.5\%$ NH_4NO_3);
- (2) a solution of hexamethylenetetramine, known locally as hexamine, in glacial acetic acid (38.0 ± 0.3 weight percent hexamine and $62.0 \pm 0.3\%$ acetic acid);
- (3) acetic anhydride (97.0 weight percent minimum purity, 99.3% average purity).

The three chemicals are combined in HAAP's nitrolysis buildings to produce anhydrous acetic acid slurries of crude explosives. Although munitions manufacturers have been aware for many years that uncontrolled mixing of Bachmann chemicals could result in fires and/or explosions, specific reactivity hazards data on the Bachmann system, heretofore, had not been developed.

Experimental

1. CHETAH diagram

The first step taken in obtaining information on the hazards of mixtures of Bachmann chemicals was to request that Design Data Laboratory personnel, Tennessee Eastman Research Laboratories, generate the theoretical graph shown in Fig. 1. The graph, generated using the ASTM CHETAH computer program [3], predicts the maximum energies of decomposition obtainable from the various possible mixtures. Those mixtures with decomposition energies of -0.7 kcal/gram, or more, are regarded as potentially sensitive to the heavy confinement liquid impact test [4].

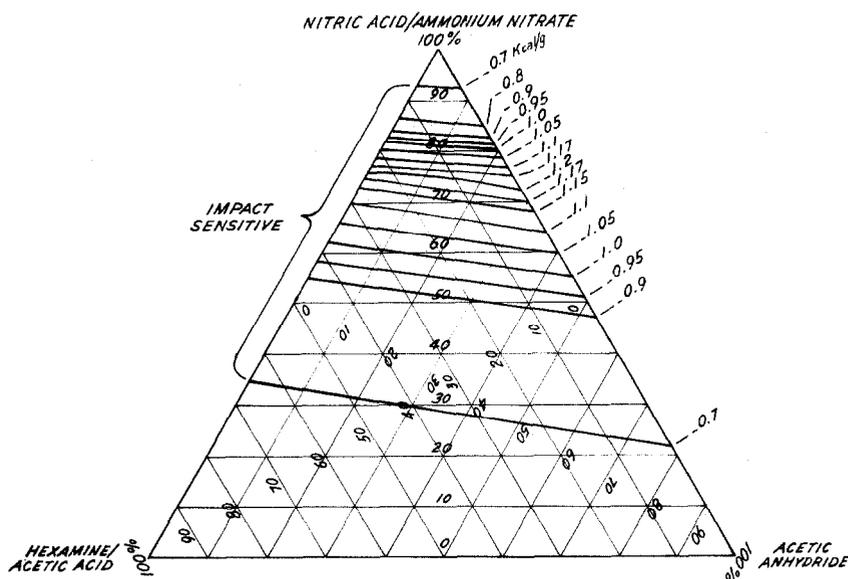


Fig. 1. CHETAH diagram for Bachmann chemical system.

2. Preliminary reactivity tests

The chemicals used in preliminary reactivity tests were nitric acid/ammonium nitrate solution (55.9% HNO_3 , 44.1% NH_4NO_3), hexamine/acetic acid solution (60.5% acetic acid, 0.49% H_2O , 39.0% hexamine) and acetic anhydride (99.5% acetic anhydride, 0.5% acetic acid) obtained from normal production supplies.

The apparatus consisted of 50-ml burettes to dispense nitric acid/ammonium nitrate solution and acetic anhydride; an adjustable, repeating pipette to dispense hexamine/acetic acid solution; a thermometer graduated in 0.1°C increments; a glass stirring rod; a burette stand; a cylindrical Dewar flask, 27 mm inside diameter and 105 mm deep; and a transparent safety shield.

The procedure used to determine reactivity was as follows:

The chemicals were given ample time to reach ambient room temperature. Increments of hexamine/acetic acid solution and nitric acid/ammonium nitrate solution were dispensed into the Dewar flask, and the contents stirred briskly with a glass stirring rod. An increment of acetic anhydride was added to the flask, the contents (30 grams, or less, total quantity) were again stirred briskly, and the times required for the mixtures to reach either a maximum value or 90°C were noted. Those mixtures which would reach at least 90°C with the temperature continuing to increase were designated "Highly Exothermic" and were quenched, for safety reasons, by dumping the flask contents into a large beaker of cold water.

The results of 75 tests were used to plot the triangular graph shown in Fig. 2. Results of preliminary tests, which necessarily involved small quantities of materials, were considered in planning the larger scale experiments described below.

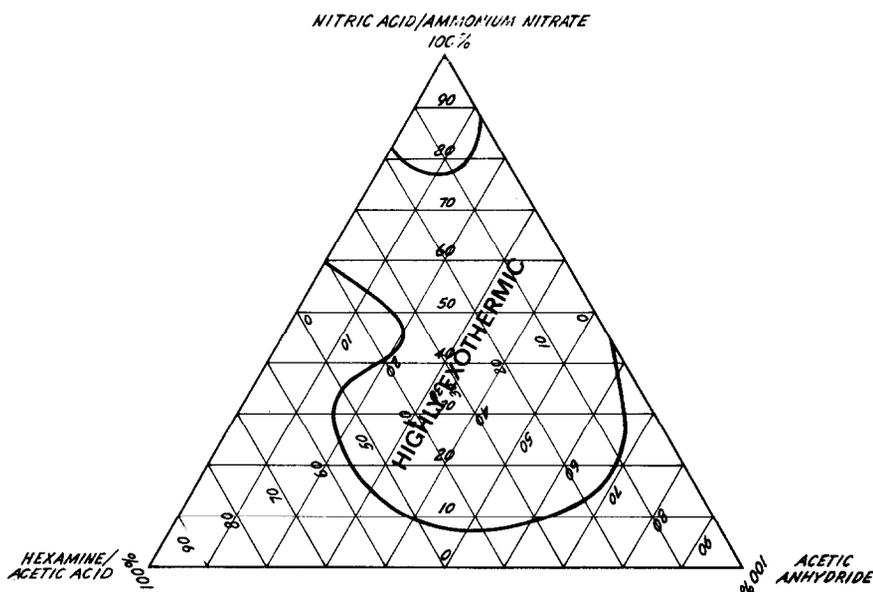


Fig. 2. Results of preliminary tests on Bachmann chemical systems.

3. Remotely controlled mixing experiments

The chemicals used in all remotely controlled mixing experiments were hexamine/acetic acid solution (61.3% acetic acid, 38.4% hexamine, 0.33% H_2O), nitric acid/ammonium nitrate solution (55.5% HNO_3 , 44.5% NH_4NO_3) and acetic anhydride (99.3% acetic anhydride, 0.7% acetic acid) obtained from production supplies.

The apparatus for unconfined mixing experiments consisted of an unsilvered Dewar flask, 50 mm inside diameter and 150 mm deep; an air-driven

agitator; a ring-stand; a water hose, for quenching reactions when desired; 3/8 in. o.d. 304 stainless steel feed lines for delivery of nitric acid/ammonium nitrate solution and anhydride; and a stainless steel pan, approximately 3 ft. wide, 3 ft. long and 6 in. deep used to catch chemicals overflowing from the Dewar flask. Temperature was measured and recorded using the system described in the following paragraph.

The apparatus shown in Fig. 3 was used in confined mixing experiments. This was a sealable reactor having an outer vessel fabricated from a 10 in. length of 3 in. i.d., 0.216 in. wall thickness, 304 stainless steel (S.S.) pipe, flared at each end and fitted with S.S. flange rings. A blind S.S. flange (about 1 in. thick) was fitted to the bottom side of the vessel after an initial test distorted the 1/4 in. S.S. plate bottom shown in Fig. 3. The vessel was drilled and fitted with five 1/4 in. S.S. pipe couplings, as indicated, to accommodate chemical feed lines; a thermowell; a Bourdon tube pressure sensor line; and a solenoid operated vent/water purge system. The top of the vessel was arranged to accommodate 3 in. diameter rupture disks, designed to fail at 260–275 psig when used in the manufacturer's recommended configuration. Stainless steel feed lines (3/8 in. o.d. tubing) were equipped with S.S. check valves which had Teflon seats and were designed to withstand 3,000 psig back-pressure. Temperature was recorded by means of stripchart recorder/iron-constantan thermocouple system, the measuring thermocouple, mounted in a 1/4 in. o.d. stainless steel thermowell, being connected so that the EMF opposed that of a reference thermocouple which was immersed (in a glass thermowell) in an ice-water bath. The net EMF was recorded on the 10 millivolt full scale, or 100 millivolt full scale, range of the recorder. The system was calibrated against a mercury-filled laboratory thermometer using an oil bath heated by an electric hot plate.

The pressure of the reactor vessel was measured by means of a Leeds and Northrup pressure sensor (Model 1970) which employs the Bourdon tube

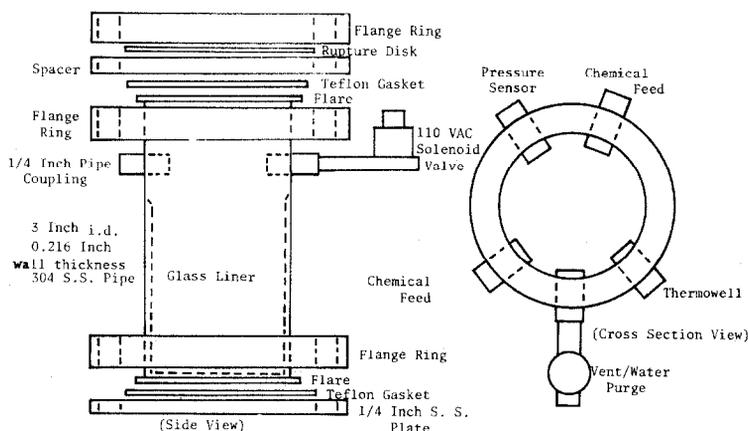


Fig. 3. Schematic drawing of sealable reactor vessel used in confined mixing experiments.

type pressure measuring system. The electrical output of the measuring system was modified to be compatible with the 100 millivolt full scale range of the stripchart recorder. The system was calibrated against a Matheson Model No. 26260-35 pressure regulator/gauge system which was attached to a helium cylinder and connected to the reactor system to provide a means for checking the entire system for leaks. Two types of borosilicate glass vessels were used as liners for the sealable reactor vessel. The first, used for those reactions which resulted in explosions, was fabricated from glass tubing sections, 75 mm o.d. and 125 mm long with 3 mm wall thickness. The second type consisted of cylindrical Dewar flasks with 50 mm inside width and 100 mm depth.

For personnel safety, the test apparatus was arranged so that reactor vessels were located on the side of a 1 ft. thick concrete barricade opposite to the operators when tests were being performed. Chemical reservoirs and associated control valves, the pressure transducer, and recorder were located on the operator side of the barricade.

Procedure

Unconfined tests. The chemicals (190 grams total quantity in final mixture) were weighed, using a triple beam balance, to the nearest 0.1 gram. Hexamine/acetic acid solution was placed directly in the Dewar flask and the air-driven agitator started. Nitric acid/ammonium nitrate solution and acetic anhydride were added simultaneously to the Dewar flask (Reactor) from reservoirs placed on the opposite side of the barricade. Temperature versus time was recorded on the first channel of the stripchart recorder. The reactor vessel was observed visually through a set of mirrors.

Confined tests. The chemicals (100 to 300 grams total quantity in final mixtures) were weighed to the nearest 0.1 gram. Hexamine/acetic acid solution was transferred directly to the reactor liner, and nitric acid/ammonium nitrate solution and acetic anhydride were transferred to the reactor feeds storage reservoirs. The reactor vessel was assembled with the liner and contents inside, and the reactor vessel tested for leaks by applying helium pressure (60 psig). Any leaks found were corrected prior to continuing the experiment. The reactor was vented by opening the electrically operated solenoid, and nitric acid/ammonium nitrate solution and acetic anhydride added simultaneously, by gravity flow, by opening the feed line valves. After 30 seconds had elapsed to provide drainage of the feed lines, the feed line valves and the reactor vent valve were closed, and the reactants were mixed by manually shaking the reactor vessel with the feed lines when necessary. The temperature of the reaction mixture was recorded on recorder channel No. 1 and pressure was recorded on channel No. 2.

Results of unconfined tests. Results of 117 unconfined tests are summarized graphically in Fig. 4. The boundary lines enclosing the "Highly Exothermic"

area of Fig. 4 were drawn through points at which reaction mixtures will just reach the boiling points. Those mixtures representing the "Fires" area of Fig. 4 produced actual flames. Flames were preceded by rapid heating to the boiling point and evaporation of liquid with the temperature gradually increasing up to about 180°C. At about 180°C, the increase in temperature became very rapid with evolution of white vapors (just prior to the appearance of flames). The residue in the reactor vessel changed from white to a deep brownish-orange just prior to the rapid temperature rise. In general, mixtures initially rich in hexamine/acetic acid solution and nitric acid/ammonium nitrate solution evolved colorless gas. Mixtures rich in nitric acid/ammonium nitrate solution and acetic anhydride evolved nitrogen dioxide fumes. The "Explosions" area of Fig. 4 indicates those mixtures which produced spontaneous explosions when they were mixed in a confined space.

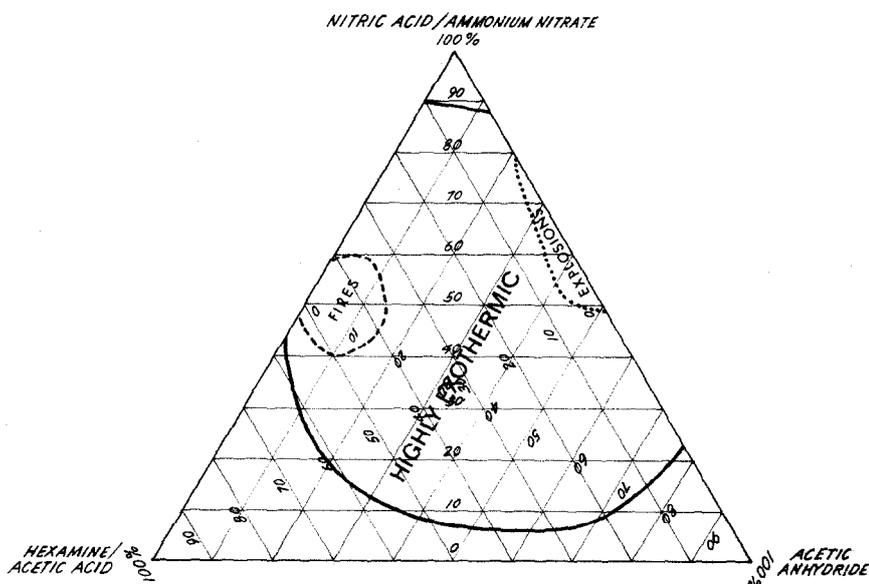


Fig. 4. Summary of hazards associated with inadvertant mixing of Bachmann chemicals.

Results of confined tests. A total of 60 tests were performed using the sealable reactor vessel. "Explosions" indicated in Fig. 4 are probably caused by accumulation and subsequent explosive decomposition of acetyl nitrate. Criteria used to designate an explosion as opposed to a simple failure of the rupture disk are (1) occurrence of the event at a low pressure reading (18–40 psig) and (2) a report louder than that produced by failure of the rupture disk. "Explosions", on two occasions, appeared to be bona fide detonations because, in both cases, extensive damage was done to the reactor vessels (Fig. 5 and 6). No residual chemicals remained in the portion of the vessel where the detonations occurred. In tests where only low order explosions



Fig. 5. Damage to reactor vessel (right) caused by spontaneous detonation of mixture of Bachmann chemicals.

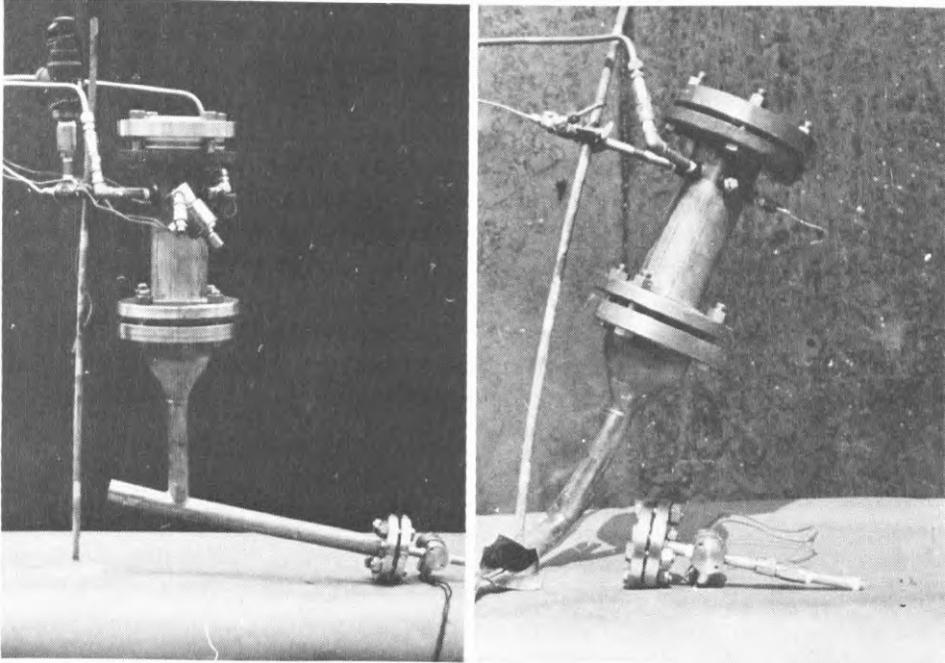


Fig. 6. Damage to simulated HMX slurry transfer line caused by spontaneous detonation of mixture of Bachmann chemicals.

occurred, residual acetic acid and ammonium nitrate were found in the reactor vessel. All "explosions" occurred at temperatures ranging from 90°C to 150°C. All mixtures inside other portions of the "Highly Exothermic" area of Fig. 4 were found to be capable of generating high temperatures and pressures in the sealed reactor vessel.

4. Nitric Acid/Ammonium Nitrate—Acetic Anhydride Layered Systems

The chemicals used in this work were nitric acid/ammonium nitrate solution, hexamine acetic acid solution and acetic anhydride, described previously under *Remotely Controlled Mixing*. Glacial acetic acid used to dilute acetic anhydride was obtained from normal production supplies (99.7% min. purity by freezing point measurement).

The apparatus used in this work was primarily an electric hot plate, 200-ml beakers and the chemical feedline/reservoir system, temperature measuring system, and barricade facility described previously. One test was performed using an electric heating mantle and a 500-ml round bottom flask rather than the hot plate and beaker.

Procedure

In the first test, 95 grams of nitric acid/ammonium nitrate solution were heated to 120°C in a 500-ml round bottom flask with an electric heating mantle. When 95 grams of neat acetic anhydride were fed into the flask onto the hot contents, the resulting mixture exploded in about 5 or 6 seconds, producing a fire and a loud report. No further tests of this type were performed since the equipment would be subjected to heavy damage.

A second series of tests was performed using the following procedure:

Approximately 75 ml of nitric acid/ammonium nitrate solution were placed in a 200-ml beaker, and an iron—constantan thermocouple in a 1/8 in. o.d. stainless steel thermowell arranged just below the surface of the liquid. About 75 ml of acetic anhydride were carefully layered on top of the nitric acid/ammonium nitrate solution layer, and the beaker and contents heated with an electric hot plate at a rate of 3–4°C/min. until the system either fumed-off (emitting reddish-brown fumes) or exploded. The acetic anhydride concentration of solution forming the upper layer was varied from 98.5% by weight (neat) to 30% by dilution with glacial acid.

Results

Test results showed that layered systems with anhydride concentrations of 50% and greater in the upper layer will consistently explode and/or produce fires upon being heated to temperatures of 42–80°C when the temperatures of the starting materials are 25°C or less. Only fume-offs are observed when warm and/or dilute starting materials are used. Such behavior is probably due to rates of the competing reactions which lead to accumulation and decomposition of acetyl nitrate and the manner in which the rates vary with temperature.

5. Simulated HMX Reactor

A series of tests was performed to determine whether or not a nitric acid/ammonium nitrate-acetic anhydride mixture could be made to generate a spontaneous explosion with enough energy to demolish a simulated HMX slurry transfer line. Such an explosion was achieved (Fig. 6) when 200 grams of acetic anhydride were introduced on top of 200 grams of nitric acid/ammonium nitrate solution (both cooled to 10°C prior to contact) in a sealed vessel having a configuration similar to that of the HMX reactor/slurry transfer line equipment used at HAAP through 1976.

Discussion

The CHETAH diagram (Fig. 1) indicates that a large fraction of the possible combinations of Bachmann chemicals is potentially hazardous with respect to impact sensitivity. CHETAH predicted a maximum obtainable decomposition energy of -1.2 kcal/gram for the Bachmann system. The heat of explosion calculated for RDX is about -1.36 kcal/g [5]. Direct verification of CHETAH predictions for the Bachmann chemical system cannot be achieved readily because most of the possible mixtures are very reactive and can be tested in the heavy confinement apparatus only with considerable difficulty. However, two mixtures of hexamine/acetic acid-nitric acid/ammonium nitrate were tested using Tennessee Eastman's heavy confinement liquid impact test equipment. Chemicals were cooled in an ice-water bath during mixing and tested as soon as possible after mixing. The first mixture, 75% by weight hexamine/acetic acid solution and 25% nitric acid/ammonium nitrate solution, gave negative results as was predicted by CHETAH. The second mixture, 25% by weight hexamine/acetic solution and 75% nitric acid/ammonium nitrate solution, gave positive results as predicted by CHETAH. The safe course, in process equipment design considerations involving the Bachmann chemical system, probably would be to consider all CHETAH predictions to be accurate.

Ambient temperatures of 29°C, or higher, were required during reactivity tests to produce the fires indicated on the left side of Fig. 4. The fires are thought to result from (1) formation of hexamine dinitrate, which will bring the mixture to near boiling, (2) the ensuing oxidation and/or decomposition of hexamine dinitrate or its fragments by excess nitric acid, (3) and finally by the exothermic decomposition of ammonium nitrate. From 6 to 25 minutes reaction time was required to produce fires. The threat of such vigorous reactions was not apparent when small quantities of hexamine/acetic acid solution and nitric acid/ammonium nitrate solution were mixed in the laboratory with the ambient temperatures being about 21°C. The same ratios of components which eventually produced fires in remotely controlled tests appeared to be comparatively unreactive in preliminary tests.

The chemical literature contains reports of equilibrium studies of the acetic anhydride/nitric acid/acetyl nitrate/acetic acid system. The optimum molar

ratio of acetic anhydride to nitric acid for producing acetyl nitrate is slightly greater than one-to-one [6, 7]. This corresponds to a one-to-one (weight/weight) ratio of acetic anhydride to Bachmann nitric acid/ammonium nitrate solution. Confined mixing experiments confirmed that high energy explosive systems could be developed with such a component ratio. The literature further reports that acetyl nitrate explodes upon being heated above 60°C [8]

Results of the various tests indicate that the key to producing a high energy explosion (or detonation) in a system involving Bachmann nitric acid/ammonium nitrate solution and acetic anhydride lies in producing a high concentration of acetyl nitrate before sufficient heat is generated to cause initiation of decomposition of the explosive material. Such a situation exists when the chemicals (equal weights of each) are cooled prior to and during mixing.

No mention of the explosive nature of acetic anhydride layered on nitric acid/ammonium nitrate solution was found in the literature. Apparently this is new information, although it is not surprising in view of the lack of thermal stability of acetyl nitrate and the conditions required to synthesize the compound.

Conclusions

A CHETAH diagram and results of reactivity tests performed with both open and closed reactor vessels have contributed significantly to understanding the hazards of inadvertent mixing of Bachmann chemicals used in the manufacture of RDX and HMX. It is felt that the types of test apparatus and techniques used in this work can be of considerable value throughout the chemical processing industries, particularly when potentially hazardous new processes are being scaled up from bench levels to production levels.

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