IMPACT, THERMAL, AND SHOCK SENSITIVITY OF MOLTEN TNT AND OF ASPHALT-CONTAMINATED MOLTEN TNT

by

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ABSTRACT

The research reported here was part of the effort to evaluate the safety of a process to recover TNT from MK-9 depth bombs by the autoclave meltout process. In this process the depth bombs are heated to 121ºC so that the TNT will melt and run into a vat. Unfortunately, asphalt lining the inside surface of the bomb also melts and flows out with the TNT. It is not known what effect the asphalt contamination and the higher than normal process temperatures (121ºC) would have on the sensitivity of the TNT.

Testing was conducted on molten TNT and molten TNT contaminated with 2 pct asphalt at 90, 100, 110, 120, 125, and 130ºC. In the liquid drop test apparatus with a 2 kg weight, the molten TNT yielded a 50 pct probability of initiation at a drop height of 6.5 cm at 110ºC, decreasing to 4.5 cm at 130ºC. Asphalt-contaminated TNT was somewhat less impact sensitive than pure TNT at temperatures of -110 to 125ºC, but became more sensitive at 130ºC; 50 pct probability of initiation at a drop height of 7.8 cm at 110ºC, decreasing to 3.3 cm at 130ºC. In the card gap test, the molten TNT detonated at high velocity for a gap of 0.25 inches at 90 to 125ºC and detonated at high velocity for a gap of 0.5 inches at 130ºC. For gaps of 0.5 to 3 inches at 90 to 125ºC and 0.75 inches to 3 inches at 130ºC, the TNT did not detonate at high velocity but produced a violent explosion that caused significant damage to the test fixture. For gaps of 4 inches the TNT did not react. In the gap test there was no significant difference between the pure and asphalt-contaminated TNT. The thermal analysis test results showed that when asphalt is present in TNT, it greatly accelerates the exothermic decomposition of TNT, starting at temperatures near 200ºC.

The research demonstrated that asphalt-contamination of recovered TNT does not appear to have a significant effect on TNT shock sensitivity, but does adversely affect impact and thermal sensitivity. The results also showed that molten TNT seems to be more shock sensitive than previously suspected. It appears that at relatively low shock stimulus levels, the molten TNT may be undergoing a low velocity detonation, wherein the shock wave traveling through the gap test pipe cavitates the molten TNT, greatly increasing its sensitivity.

INTRODUCTION

The Army is continually faced with the problem of what to do with unneeded or outdated munitions. Traditionally, these munitions were open-burned or detonated but these options are being discouraged, and there is a move to recover explosives and make them available for commercial use. The research reported here was part of the effort to evaluate the safety of a process to recover TNT from MK-9 depth bombs by the autoclave meltout process. In this process the depth bombs are heated to 121ºC so that the TNT will melt and run into a vat. Unfortunately, asphalt lining the inside surface of the bomb also melts and flows out with the TNT. It is not known what effect the asphalt contamination and the higher than normal process temperatures (121ºC) would have on the sensitivity of the TNT.

Three of the primary considerations in evaluating the safety of an explosive are its impact, shock, and thermal sensitivities. We decided to evaluate the impact sensitivity of pure and asphalt-contaminated TNT through the application of the drop weight impact test and their shock sensitivity (or explosion-by-influence) through the application of the card gap test, while differential scanning calorimetry was used for the evaluation of the thermal sensitivity. Comparison of the behavior of the contaminated and pure TNT will elucidate any additional hazards that must be considered when asphalt is present.

SAMPLES AND SAMPLE PREPARATION

Three types of TNT were utilized in this research program, crystalline TNT from the Bureau of Mines' inventory (designated Key Number M-7601), flaked TNT supplied by the Army, (Key Number X-4530A), and a mixture of flaked TNT with 2 pct asphalt (Key Number X-4530C), also supplied by the Army. The mixture of flaked TNT with asphalt was prepared by an Army ammunition plant to simulate the asphalt-contaminated TNT recovered from the depth bombs. The mixture was prepared by mixing flaked TNT with asphalt in a large steam kettle and heating it to above 120ºC with continuous stirring. The asphalt did not mix with the TNT and floated on top. When the mixture was processed to produce flaked TNT, the product was nonhomogeneous, and varied in color from yellow-brown to light gray. Utilizing the asphalt-contaminated TNT in testing was not straightforward since the composition of the sample was not uniform. Preparing a 45 mg sample of the TNT contaminated with 2 pct asphalt for the liquid drop tester was especially difficult; for these tests we assumed that the discolored flakes of TNT in the sample were essentially pure TNT and what appeared to be chunks of asphalt were essentially pure asphalt. We prepared test samples by weighing out 44 mg of the discolored, flaked TNT and adding a 1-mg piece of asphalt shaved off one of the asphalt chunks. For the gap test, we scooped a sample out of the box and assumed that since the sample size was relatively large (-700g), its overall composition was 2 pct asphalt. Preparation of samples for the thermal testing is discussed in the section of this paper on that work. The Army also supplied a quantity of asphalt, designated Key Number X-4530B.

DROP WEIGHT IMPACT TESTING

Many types of drop weight impact apparatus are available and it was uncertain which one would prove useful in evaluating the impact sensitivity of molten pure and asphalt-

contaminated TNT. The initial drop weight impact testing was conducted with two impact testers, namely, the Bureau of Mines Drop Weight Impact Tester and the Bureau of Explosives Machine(1); each apparatus was modified to permit the testing of molten TNT at the temperature range of 90 to 130ºC. In this series of tests the TNT would not initiate at the maximum drop heights available, probably because in both instruments the sample is not confined in the sample cup. During impact the sample was free to escape from the cup. The next series of tests was conducted in a liquid drop tester according to the procedure described in ASTM Method D2540-93(2). In this method a 2 kg drop weight is used and the sample is confined in a sealed sample cell. Since this impact tester is intended for liquids at ambient temperature, the test procedure does not require heating of the sample. To test molten TNT, the sample and portions of the equipment had to be heated, and maintained, at the desired test temperature. Procedures were developed to allow this.

Testing was conducted at 90, 100, 110, 120, 125, and 130ºC on flaked TNT and flaked TNT contaminated with 2 pct asphalt (Key Numbers X-4530A and X-4530C, respectively) using the Bruceton Up-and-Down method(3). Test results were used to calculate H_{50} values, the height corresponding to a 50 pct probability of a positive result; H_{50} values were determined for each temperature.

The results of the impact sensitivity tests for pure TNT and TNT-asphalt mixtures are presented in Tables 1 and 2 and Figure 1. The results show that impact sensitivity increases with temperature for TNT and for TNT with asphalt. The H_{50} values obtained at 90ºC, and perhaps even at 100ºC, may be out of line. These temperatures are close to the melting point of TNT, of -81ºC. During preparation and transfer of the sample from the oven to the impact tester, the sample, or a portion of it, might have solidified. If this were the case, unreliable H_{50} values would be obtained. At the temperatures above 100ºC, a trend is observed whereby, initially the H_{50} values for the TNT-asphalt samples are higher than the respective values for the pure TNT, and then at 125 and 130ºC the H_{50} values for the TNT-asphalt mixtures decrease more dramatically. These results suggest that at first asphalt can act as a soft wax, and lower sensitivity of the TNT, but at the higher temperatures, some reaction occurs between the two ingredients, and as a result the sensitivity of contaminated TNT increases.

Thermal Analysis of TNT and TNT-Asphalt Mixtures

The literature indicates that impact sensitivities of organic high explosives are primarily a function of the rates of thermal decomposition processes occurring in the temperature

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(1)The Bureau of Mines Drop Weight Impact Tester employs a 5 kg drop weight with drop heights up to 320 cm and the Bureau of Explosives Machine employs a 3.63 kg drop weight with drop heights up to 84 cm.

(2)"Standard Test Method for Drop-Weight Sensitivity of Liquid Monopropellants", ASTM Designation D2540-93.

(3)Mason, C.M. and E.G. Aiken "Methods for Evaluating Explosives and Hazardous Materials", Bureau of Mines Information Circular 8541, 1972.

range generated under the impact hammer. Thus, the thermal decomposition of TNT and of TNT-asphalt mixtures, as determined by thermal analysis are of interest to this study.

The thermal decomposition of TNT was studied by various researchers, using different test methods. These methods included gas evolution techniques (such as the modified Taliani test or other off-gas tests), weight loss measurements, time to explosion (such as the Henkin or modified Henkin test), and isothermal tests at different temperatures, among others. Results, as measured by values of activation energies, by products of decomposition, or by other parameters vary, depending on test instrumentation used, on test procedures, on sample size, and on other factors. Dacons, Adolph, and Kamlet(4) discuss the reasons for some of the differences in the results.

Samples of TNT, of asphalt, and of TNT-asphalt mixtures were tested in the differential scanning calorimeter (DSC), and the results are reported. The effect of rust on the thermal behavior of TNT was also evaluated.

A Dupont 990 DSC(5) was used in all the tests. The tests were conducted in an atmosphere of static air, or more specifically, in a self-generated atmosphere of gaseous vaporization and decomposition products mixed with the original air atmosphere. Various heating rates were used, and they are cited for each test. Aluminum pans with lids were used to contain the samples during the tests. Inert glass microspheres, likewise contained in an aluminum pan with lid, were used as reference material. The lids were not crimped onto the pans; they were just pressed together.

Two samples of TNT were tested, Key Numbers M-7601 and X-4530A. The first sample, Key Number M-7601, was crystalline and a darker yellow in hue than the second sample, Key Number X-4530A, which consisted of flakes. Each of the two TNT materials was lightly ground in a glass mortar and pestle prior to being sampled.

The crystalline TNT was heated at 10 and 20ºC/min and resultant thermograms were essentially the same. The thermogram for the test at 20ºC/min is shown in Figure 2. The thermogram contains the melting endotherm of TNT, followed by an endotherm due to the evaporation of the TNT. The onset temperature for evaporation is a function of the heating rate, and increases with higher heating rates. The flake TNT sample, Key No. X-4530A, was heated at 20 and 50ºC/min. The resultant thermogram for the test at 50ºC/min is presented in Figure 3. The two endotherms in the figure, as in Figure 2, signify the melting and evaporation of the TNT. Small exothermic peaks, at 325, 378, 420, and 447ºC, suggest decomposition of left-over, trace amounts of TNT that did not evaporate. To determine the ignition/explosion temperature of TNT in the DSC, or in other analytical instrumentation, the TNT must be hermetically sealed, or be present in large amounts. If it

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(4)J.C. Dacons, H.G. Adolph, and M.J. Kamlet, "Some Novel Observations Concerning the Thermal Decomposition of 2,4,6-Trinitrotoluene", Journal of Physical Chemistry, v. 74, 1970, pp. 3035-3040.

(5)Reference to specific products does not imply endorsement by the Bureau of Mines or USADACS.

is not confined, it evaporates. Results for the tests are presented in Table 3.

Asphalt, Key No. X-4530B, supplied by the Army, was tested in the DSC, at heating rates of 10 and 20ºC/min. Thermograms are shown in Figures 4 and 5, and both display the exothermic decomposition behavior of the asphalt, including the ignition of the flammable, volatile decomposition products, when present in sufficient quantities, as indicated by the sharp peak at 391ºC, in Figure 4. Onset of exothermic behavior is at 260 and 230ºC, for the heating rates of 10 and 20ºC/min, respectively. A small endotherm, at 67ºC, is indicative of the softening of the asphalt. The cause for the second endotherm, at about 125ºC, is not known. Results for the two tests with asphalt are given in Table 4.

The flake TNT, which was a fresher and more pure sample, was used for the preparation of mixtures with asphalt, for tests in the DSC. The amount of asphalt in the mixtures varied from test to test, and was as high as 31 pct. Larger amounts of asphalt were used on purpose, in order to show clearly any reactions between the two materials. The asphalt is sticky, and it was not easy to obtain samples of a desired weight. The asphalt was placed first in the sample pan, and the TNT powder was sprinkled on top of it. Weights, when available, and heating rates for the tests are cited in Table 4, and thermograms are presented in Figures 6 to 9. It is evident from these thermograms that TNT reacts with asphalt in an exothermic fashion, and the extent of reaction appears to depend on the amount of asphalt. Onset temperature for exothermic behavior for the test in Figure 6 is 200ºC, while for Figures 7 to 9, onset temperatures are between 225 and 235ºC. Some evaporation of TNT is indicated in Figures 7 and 9 by the presence of endotherms, but the amount of evaporation is relatively small. As the asphalt softens, it may engulf and/or hold on to the TNT, and slow down TNT evaporation. Even with smaller amounts of asphalt, as in Figure 6, exothermic reaction starts prior to the decomposition of the asphalt by itself.

A sample of TNT already mixed with asphalt (Key No. X-4530C), sent by the Army, was also tested. This material is the asphalt-contaminated TNT recovered from munitions. Despite heating to above 120ºC in a steam kettle with continuous mixing, the TNT and asphalt did not mix significantly. The sample consisted of large chunks of either yellow-brown or gray material. The concentration of asphalt in the sample varied from chunk to chunk, and probably within each chunk. For a test, a sample was lightly ground in a glass mortar and pestle. Two tests, both at 10ºC/min, were done. In one test only the yellow-brown portion was utilized, and the resultant thermogram is shown in Figure 10. In the second test, the sample contained mostly the yellow-brown portion, plus a small amount of the gray portion. The thermogram for the latter test is presented in Figure 11. A small amount of evaporation is evident in both figures, but more so in Figure 11, and it is followed by an exothermic behavior. Onset of exothermic behavior is at 240 to 250ºC. Both thermograms contain a sharp endotherm, with peak temperature at 286 and 273ºC, respectively. This endotherm may be indicative of some boiling; a reaction of the sample with the DSC surface is also possible, however, evidence of leakage onto the surface was not observed. Melting of a compound or an adduct, formed between TNT and the asphalt during the preparation stage, is more probable. Results are summarized in Table 4.

In addition to asphalt, TNT may come in contact with rust, during the recovery phases. Therefore, it was desired to find out if these two ingredients interact thermally. The effect of rust on the thermal behavior of both TNT samples was thus determined. In the case of

the crystalline TNT (Key No. M-7601), the TNT was weighed first, and rust was then sprinkled on it, with the idea of slowing down the evaporation of the TNT somewhat. In the case of the flake TNT (Key No. X-4530A), the rust was placed first in the pan, and the TNT was then placed on top of the rust. Both tests were conducted at a heating rate of 50ºC/min in the temperature range of interest, in an attempt to minimize vaporization, and have a sufficient amount of TNT for reaction. Figures 12 and 13 display the thermograms for the crystalline and flake samples, respectively. As can be seen in the thermograms, the presence of the rust contributed to the exothermic behavior of the mixture, either catalytically or due to a chemical reaction between TNT and the rust. Additionally, the rust may have slowed down the evaporation of the TNT so that enough TNT was available for reaction. Onset temperature of exothermic reaction in Figure 12 is not easy to determine exactly; the endotherm due to evaporation masks the exothermic initiation. However, at 300ºC exothermic behavior is clearly visible. In Figure 13, onset of exothermic behavior is seen at 280ºC. The addition of small amounts of many diverse materials has been found to accelerate the thermal decomposition of TNT. Strong promoters of decomposition include iron compounds(6). According to Robertson, ferric oxide, present to the extent of 10 pct in TNT caused ignition at 300ºC with no perceptible prior decomposition, probably as a result of a reaction between the TNT and the ferric oxide. The temperatures of the first exothermic peak in the thermograms in Figures 12 and 13 are both at 310ºC. Within experimental variation these temperatures agree with the temperature quoted by Robertson. At the termination of the tests with the rust, the sample pans contained a black residue. Charring of the TNT is probable. The rust, (Fe_2O_3•XH_2O), originally brown in color, may have converted to FeO or Fe_3O_4 (both black), or to ferrous and/or ferric nitrate. The latter two salts are not black, but would be masked by the char. All test results are summarized in Table 4.

Onset temperatures for exothermic decomposition of flake TNT-asphalt mixtures, prepared individually for each test in the DSC varied from 200 to 235ºC. The onset temperatures for the mixtures prepared by the army were slightly higher at 240 to 245ºC. In all of these tests, the samples were not confined or hermetically sealed. In comparison, corresponding onset temperatures, obtained in DTA tests for confined TNT samples heated at 10 and 20ºC/min, were about 296 and 308ºC, respectively(7). These results present clear evidence that asphalt affects the thermal decomposition of TNT, and lowers its initiation temperature, and its presence will, likewise, affect the sensitivity of TNT in impact tests at elevated temperatures.

The effect of asphalt on the decomposition of TNT was evaluated by T.B. Joyner(8). In his tests, isothermal runs were made at 10-degree intervals over the range of 160 to 270ºC. The

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(6)A.J.B. Robertson, "The Decomposition, Boiling, and Explosion of Trinitrotoluene at High Temperatures", Trans. Faraday Soc., v. 44, 1948, pp. 977-983.

(7)J. Harris, "Autoignition temperatures of Military High Explosives by Differential Thermal Analysis", Thermocheimica Acta, v. 14, 1976, pp. 183-199.

(8)T.B. Joyner, "Thermal Decomposition of Explosives, Part 2. Effect of Asphalt on the Decomposition of TNT", Report No. NWC-TP-4709, Part 2, April, 1969, 17 pp.

runs utilized 10- and 25-mg samples of TNT and asphalt, respectively, and were conducted under nitrogen pressure to minimize evaporation of the TNT. The progress of reaction was followed by pressure increase. Joyner found that asphalt greatly accelerated the decomposition of TNT. The percent of asphalt in his test samples was high, 71.4 pct. Asphalt by itself was also tested at 250ºC for 16 h, and decomposition was not observed. Although the reason for the proportions of TNT and asphalt chosen by Joyner is not given, it seems that there was a similar desire to easily observe the possibility of reaction between the two compounds.

The results of the tests with the rust mixtures, likewise show that the decomposition of TNT is sensitized by the rust, and onset temperature is lowered. DSC tests of TNT mixtures, with rust or with asphalt, at lower heating rates could possibly indicate still lower onset temperatures for decomposition.

Solid TNT is not very sensitive to impact (relatively speaking), unless confined by sand paper discs. Molten TNT, at temperatures near and above the melting point, is more sensitive to impact. The presence of asphalt desensitizes the TNT to a small extent. This is to be expected. Materials such as wax (C_xH_y) are used to desensitize explosives to impact and friction. Asphalt may contain wax, and it itself can act as a desensitizer, but if the mixture is heated to a higher temperature, such as 120ºC or 130ºC, and it reacts and forms a small amount of active intermediates, and then the impact hammer raises the temperature of the test sample to the range where TNT and asphalt interact much more rapidly, the temperature will rise and overall reaction in the impact test will be accelerated. Extent of reaction can be observed and assessed by the degree of damage to the test instrument. Indeed, the combined results from the impact and thermal tests support this hypothesis.

CARD GAP TESTING

Card gap testing was conducted to evaluate the sensitivity of TNT and TNT contaminated with asphalt to shock stimulus. The apparatus for the Bureau of Mines Gap Test is shown in Figure 14. The test sample was contained in a cylinder consisting of a 16-inch length of 1½-inch schedule 80 black seamless steel pipe. A mild steel witness plate 6 inches square and 0.125 inches thick was mounted at the upper end of the sample pipe and separated from it by Lucite spacers 0.062 inches thick. A 2-inch diameter, 2-inch long cast Pentolite booster placed against the bottom of the pipe provided the shock stimulus to the sample; a 2-inch diameter Lucite cylinder of different lengths, varying from 0.25 to 4 inches, was placed between the booster and the pipe to attenuate the shock to the desired stimulus level and acted as the gap. The Lucite cylinder was cemented to the pipe with high-temperature silicone rubber cement. A continuous probe of fine wire, which measured the velocity of detonation(9) was mounted on the inside wall of the sample pipe. The Pentolite booster was initiated by a No. 8 strength instantaneous detonator.

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(9)Ribovich, J., R.W. Watson, and F.C. Gibson, "Instrumented Card-Gap Test", AIAA Journal, vol. 6, no. 7, 1968, pp. 1260-1263.

The U.N. test protocol(10) calls for the use of a bubbler in testing liquids, but no bubbler was employed here since it was expected that due to its high viscosity, the molten TNT would not be agitated to the point where it would contain fine bubbles. In addition, since card-gap tests are generally not conducted at elevated temperatures, a procedure for doing this was developed by trial and error. Initially the gap test pipe was wrapped with nichrome heating ribbon with the intent of heating and melting the TNT directly in the pipe. Preliminary trials with wax showed, however, that a significant temperature gradient developed within the melt in the pipe and this technique was abandoned. The wraps of nichrome heating ribbon around the pipe did prove useful for preheating the pipe and were retained for this purpose. Pipe insulation was placed around the pipe-nichrome heating ribbon assembly to minimize heat loss. At the beginning of the test series, the TNT was heated in a large Pyrex beaker in a Fisher Isotemp Forced Draft Oven, Model 800. For this procedure the pipe was preheated to the test temperature using the nichrome heating ribbon and the TNT was heated to several degrees above the chosen test temperature. The TNT was poured into the pipe and the temperature was monitored using a thermocouple. It was surmised that by heating the TNT in the oven to several degrees above the test temperature, the TNT would be close to the test temperature after it was poured into the pipe and the shot could be fired immediately. This procedure worked quite well, however, due to evaporation TNT crystals precipitated on the outside of the oven. Due to the possibility of TNT crystals also being deposited within the oven, and the associated hazard, this procedure was also abandoned. Instead, a steam-heated kettle was used to heat the TNT. The steam heat heated the TNT to a temperature of 105-115ºC. The heated, molten TNT was poured into the pipe and then the nichrome heating ribbon wrapped around the pipe was used to heat the filled pipe up to the test temperature. This procedure proved satisfactory. Testing was conducted on pure TNT and TNT contaminated with 2 pct asphalt (Key Numbers X-4530A and X-4530C, respectively) at 90, 100, 110, 120, 125, and 130ºC.

Test results for the pure TNT and asphalt-TNT mixture were essentially the same, and will be discussed together. Three criteria were used in evaluating the results of the tests: a hole in the witness plate, fragmentation of the pipe, and the measured velocity of detonation. The results fell into one of three types. At small gaps, less than 1/2 inch, there was a clean hole in the witness plate, the pipe was fragmented into a hundred or more small pieces, and the detonation velocity was about 6,400 m/sec; all clear indications of a high velocity detonation. For gaps of 4 inches or more there was no damage to the pipe or witness plate, indicating that the TNT did not react. For the mid-range gaps, 1/2 to 3 inches, the witness plate suffered varying degrees of damage ranging from undamaged to being domed, bent, or torn, and the pipe was peeled open and sometimes fragmented into up to 43 pieces. It was clear that the TNT was not detonating at high velocity in the 1/2- to 3-inch gap range but a very energetic reaction was occurring. The violence of this reaction was further evidenced by the observation that the 8- by 8- by 24-inch logs set up around the card gap test assembly to stop shrapnel, were torn apart. Reaction velocities between 1,300 and

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(10)Recommendations on the Transport of Dangerous Goods: Tests and Criteria, Second Edition, Test 1 (a)(iii), "Gap Test for Solids and Liquids", published for the United Nations by Labelmaster, Chicago, IL, pp 19-23, 1990.

2,000 m/sec were recorded for these tests with mid-range gaps but it was not clear whether these values represented reaction of the TNT or the shock produced by the booster; this is discussed in more detail the next sections.

For comparison, a series of tests on an essentially inert aqueous solution of sodium nitrate at 80ºC, with a density similar to that of molten TNT (55 pct sodium nitrate in water with a density of 1.44 g/cc) were conducted at gaps of 1/2, 1, and 2 inches. In the tests of the aqueous sodium nitrate solution the witness plate was relatively undamaged; dome depths in the witness plate were 1/8 inch or less as compared to dome depths of up to 1/2 inch with broken or torn witness plates for TNT tests at a larger 3-inch gap. For tests with the sodium nitrate solution with a 1/2-inch gap, up to 6 inches of the pipe was split with no damage beyond minor flaring at gaps of 1 and 2 inches. Figure 15 presents a comparison of pipe and witness plate damage for TNT and the sodium nitrate solution at 100ºC; it is quite apparent from these photographs that in the 1/2- to 3-inch gap range, the damage wrought by TNT is well beyond that expected from the booster alone.

Test results for all of the gap tests are summarized in Tables 5 and 6. At 90 to 125ºC, the pure and asphalt-contaminated TNT detonate at high velocity for gaps of 1/4 inch or less, and undergo a low order reaction for gaps of 1/2 to 3 inches, inclusive. At 130ºC both the pure and contaminated TNT detonate at high velocity for a 1/2-inch gap but do not detonate at high velocity for gaps of 3/4 to 3 inches.

It is possible that the molten TNT is undergoing low velocity detonation for gaps of about 1/2 to 3 inches. In a low velocity detonation the shock wave travels through the walls of the pipe ahead of the shock wave in the molten TNT, causing the TNT to cavitate and hence sensitizing the molten TNT. It is of interest to note that the pure and asphalt-contaminated TNT change from low order reactions to no reactions in the 3- to 4-inch gap range, which is similar to the gap range Hay and Watson(11) found for molten TNT at 85ºC with added bubbles in an identical test configuration going from detonation to no detonation; at 3.5 inches the molten TNT with added bubbles detonated but at 4 inches it did not detonate. The molten TNT in the steel pipe seems to behave as if it were sensitized with added bubbles.

The origin of the recorded velocities for the tests of TNT at mid-range gaps (1/2 to 3 inches) is not clear; is this an indication of a reaction in the TNT or merely the booster-generated shock wave traveling through the molten TNT? Figure 16 presents velocity probe oscilloscope traces for tests of molten TNT at 100ºC for gaps of 0.25 to 4 inches, as well as analogous traces for tests of the aqueous sodium nitrate solution. Comparison of results for TNT tests HGT-39 and HGT-38 (gaps of 0.5 and 0.75 inches, respectively) with results for aqueous solution tests HGT-84 and HGT-85 (gaps of 0.5 and 1 inches, respectively) reveal that there is no great difference between the velocity traces of the TNT and the solution. In both TNT and the sodium nitrate solution at gaps of 0.5 to 1 inches velocities are relatively high, at 2,100 to 2,550 m/sec, and then they decay to 1,400 to 1,500 m/sec at about a third

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(11)Hay, J.E. and R.W. Watson, Description of a Shock Sensitivity/Detonation Propagation Test for Defining Class 1 Explosive Substances Which are Liquids, Pittsburgh Research Center Report No. 4301.

of the way down the length of the pipe. The above results indicate that the velocities recorded for the TNT tests at gaps of 0.5 to 3 inches (with the exception of 130ºC TNT at a 0.5-inch gap, which undergoes high velocity detonation) cannot be unambiguously attributed to a low-velocity detonation reaction in the molten TNT. The velocity probe may be recording the low-velocity detonation of the TNT or merely the booster-produced shock wave. It is possible that the velocity of the low-velocity detonation and that of the booster-produced shock wave are so close that we cannot discern the difference without further study. In the 1/2- to 3-inch gap range the molten TNT is clearly reacting very energetically, as evidenced by the damage to the test pipe and witness plate.

As mentioned above, the pure TNT and the TNT contaminated with 2 pct asphalt behaved similarly in these tests. Since the asphalt did not mix well with the molten TNT but rather floated on the top when loaded in the gap test pipe, this result is not too surprising . Some component of the asphalt had mixed with the TNT since the color of the TNT was changed from yellow to light brown but this was apparently not enough to change the shock sensitivity significantly.

A review of the results in terms of high-velocity detonation reveals a small effect of temperature on the shock sensitivity of molten TNT. At 90 to 125ºC, the molten TNT will detonate at high velocity for gaps of 0.25 inches and less, but will not detonate at high velocity for gaps of 0.5 inches and greater. At 130ºC, however, the molten TNT will detonate at high velocity at a gap of 0.5 inches. TNT at 130ºC is more sensitive to shock than it is at the lower temperatures.

Conclusions

This project was initiated due the concerns over the safety of the autoclave meltout operation for recovering TNT from Mk-9 depth bombs. In melting out TNT from the depth bombs, the asphalt liner material would also melt and contaminate the TNT, possibly sensitizing the TNT and creating a hazardous situation. Based on the research reported here we see that contamination by asphalt somewhat adversely affects the thermal and impact sensitivity of the TNT at higher temperatures, above ~110ºC. Gap test results indicate that the shock sensitivity of molten TNT, though not affected by asphalt contamination, must also be considered. Hay and Watson(12) have shown that molten TNT will detonate at gaps of up to 3.5 inches with the addition of bubbles and we have shown that molten TNT can explode at gaps up to 3 inches without added bubbles. These results put molten TNT in the sensitivity range of nitromethane and monomethylamine nitrate solutions (detonations at 2.5 and 4.5 inches, respectively, with added bubbles), both of which have been involved in serious accidental explosions.

Care must also be taken in controlling the temperature of the TNT because the asphalt affects its thermal sensitivity. The thermal analysis test results show that when asphalt is present in TNT, it greatly accelerates the exothermic decomposition of TNT, starting at temperatures near 200ºC. In the thermoanalytical tests reported here, asphalt was deliberately used in excess, to assure good contact with TNT. It is quite probable that during loading of the original explosive devices, some of the TNT mixed with the asphalt coating and formed intimate mixtures of high asphalt concentration. If, somehow, the molten TNT heated to temperatures near 200ºC, it may undergo accelerated reaction.

Table 1. Impact sensitivity test results for pure TNT (Key Number X-4530A). (Each value of H_{50} is based on 10 trials.)

Temperature, °C	H_{50}, cm	Standard Deviation, cm
90	7.8	1.2
100	7.8	1.2
110	6.5	1.3
120	4.9	1.2
125	4.2	1.8
130	4.5	1.4

Table 2. Impact sensitivity test results for TNT contaminated with 2 pct asphalt (Key Number X-4530C). (Each value of H_{50} is based on 10 trials.

Temperature, °C	H_{50}, cm	Standard Deviation, cm
90	7.9	1.2
100	7.4	1.1
110	7.8	1.2
120	6.8	1.1
125	5.4	1.5
130	3.3	1.1

Table 3. DSC test results for TNT.

Sample	Figure No.	Heating rate, °C/min	Sample, weight, mg	Weight loss, pct	Final test temperature °C
M-7601	2	10	2.4	100	280
M-7601	N.S.	20	4.4	95	347
M-7601	N.S.	20	2.5	100	351
X-4530A	N.S.	20	3.7	100	435
X-4530A	N.S.	50	5.5	100	477

N.S.: Not Shown.

Table 4. DSC test results for asphalt and for TNT-asphalt mixtures.

Sample	Figure No.	Heating rate, °C/min	Sample Weight, mg	Weight loss, pct	Onset temp, °C	Final test temp, °C	Comments
Asphalt, X-4530B	4	10	2.6	-	260	405	Sample leaked out
Asphalt, X-4530B	5	20	4.0	-	230	485	Sample leaked out
Flake TNT + asphalt	6	10	-	-	200	402	-
Flake TNT + asphalt	7	10 (to 135°C) then 50	-	-	230	497	-
Flake TNT +asphalt	8	10 (to 130°C) then 20	8.1 TNT 3.6 asphalt (30.8 pct)	-	235	389	-
Flake TNT + asphalt	9	5 (to 165°C) then 10	7.1 TNT 1.0 asphalt (12.4 pct)	65	225	296	-
TNT + asphalt	10	10	2.5	84	240	304	
TNT +asphalt	11	10	3.9	72	245	294	
M-7601 + rust	12	50	3.3 0.7	88	300	407	TNT weighed first; rust sprinkled on top
X-4530A + rust	13	10 (to 90°C) then 50	-	-	280	435	Rust placed first; TNT on top of rust

Table 5. Summary of gap test results for TNT (X-4530A).

Gap, in	90ºC	100ºC	110ºC	120ºC	125ºC	130ºC
4.00	HGT-45 NR	HGT-64 NR	HGT-47 NR	HGT-61 NR	HGT-49 NR	HGT-43/67 NR
3.00	HGT-44 EXP	HGT-65 EXP	HGT-46 EXP	HGT-62 EXP	HGT-48 EXP	HGT-42/68 EXP
2.00		HGT-6 EXP				
1.50		HGT-8 EXP				
1.00		HGT-7 EXP				HGT-15 EXP
0.75	HGT-30 EXP	HGT-38 EXP	HGT-32 EXP	HGT-63 EXP	HGT-36 EXP	HGT-12/69 EXP
0.50	HGT-31 EXP	HGT-39 EXP	HGT-33 EXP	HGT-71 EXP	HGT-37 EXP	HGT-11/70 DET
0.25	HGT-34 DET	HGT-40 DET	HGT-35 DET	HGT-66 DET	HGT-41 DET	HGT-9 DET

NR - No Reaction
EXP - Explosion, possibly a low velocity detonation
DET - Detonation, high velocity

Table 6. Summary of gap test results for asphalt-contaminated TNT (X-4530C).

Gap, in	90ºC	100ºC	110ºC	120ºC	125ºC	130ºC
4.00	HGT-51 NR	HGT-72 NR	HGT-60 NR	HGT-53 NR	HGT-56 NR	HGT-19/77 NR
3.00	HGT-50 EXP	HGT-73 EXP	HGT-52/57 NR/EXP	HGT-54 EXP	HGT-55 EXP	HGT-20/78 EXP
2.00						HGT-18 EXP
1.50						
1.00						
0.75	HGT-21 EXP		HGT-24 EXP	HGT-58 EXP	HGT-26 EXP	HGT-16/79 EXP
0.50	HGT-22 EXP	HGT-74 EXP	HGT-25 EXP	HGT-76 EXP	HGT-27 EXP	HGT-17/80 DET/EXP
0.25	HGT-23 DET	HGT-75 DET	HGT-28 DET	HGT-59 DET	HGT-29 DET	

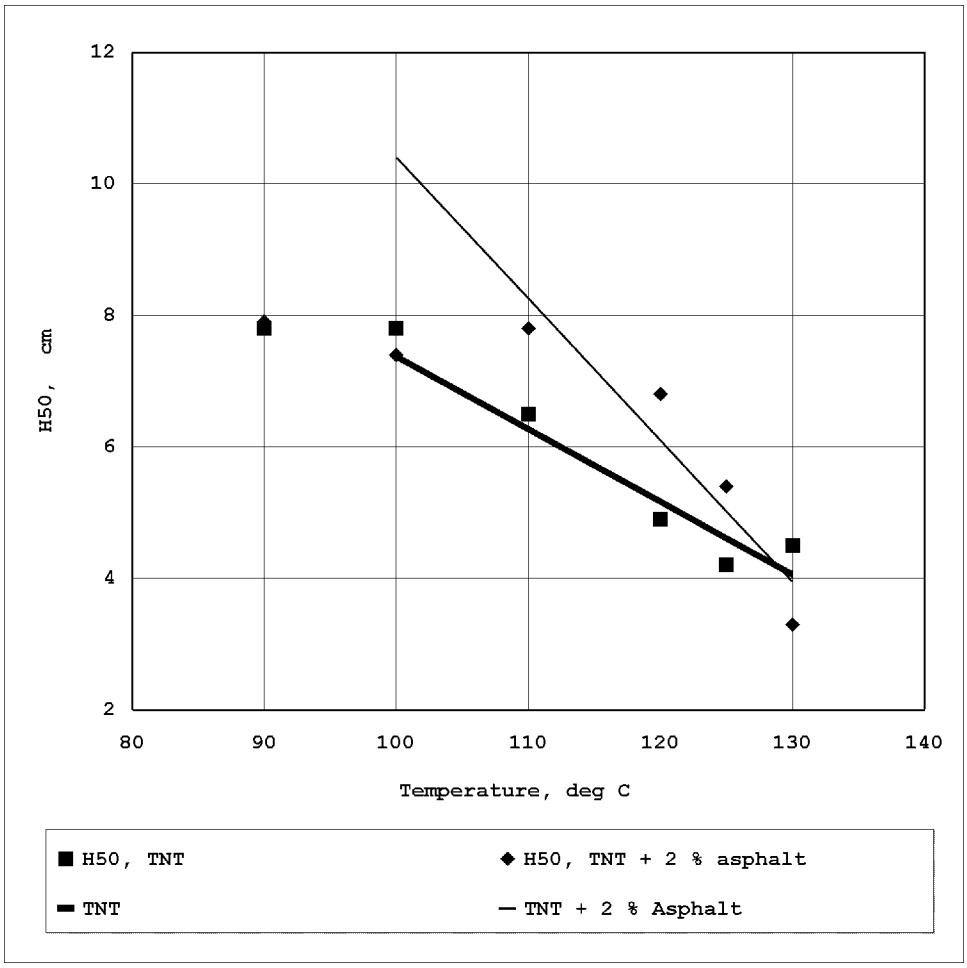


Figure 1. Drop weight impact sensitivity test results for pure and asphalt-contaminated TNT.

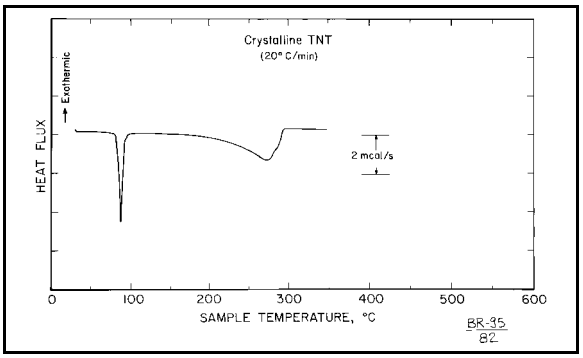


Figure 2. DSC thermogram for crystalline TNT (20°C/min, 4.4-mg sample).

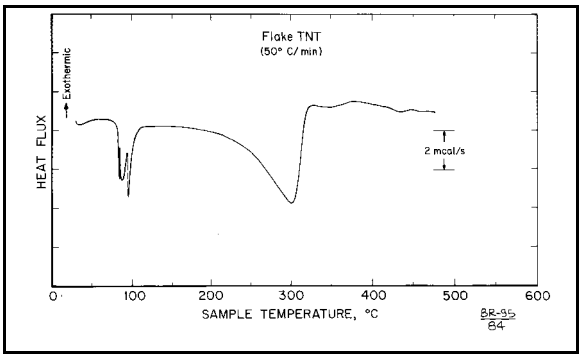


Figure 3. DSC thermogram for flake TNT (50°C/min, 5.5-mg sample).

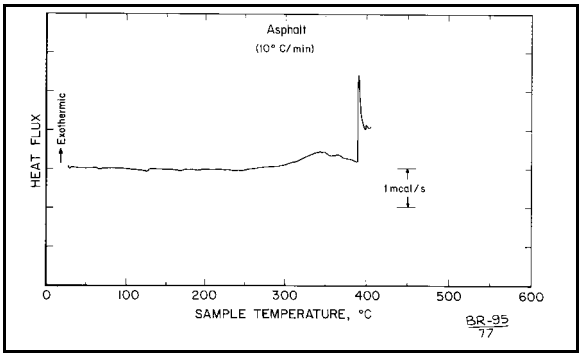


Figure 4. DSC thermogram for asphalt (10°C/min, 2.6-mg sample).

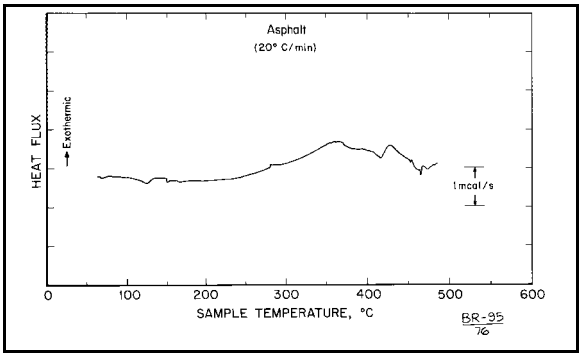


Figure 5. DSC thermogram for asphalt (20°C/min, 4.0-mg sample).

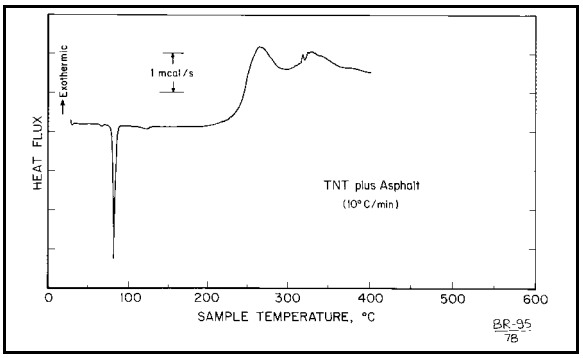


Figure 6. DSC thermogram for a mixture of flake TNT with asphalt (10°C/min, not weighed).

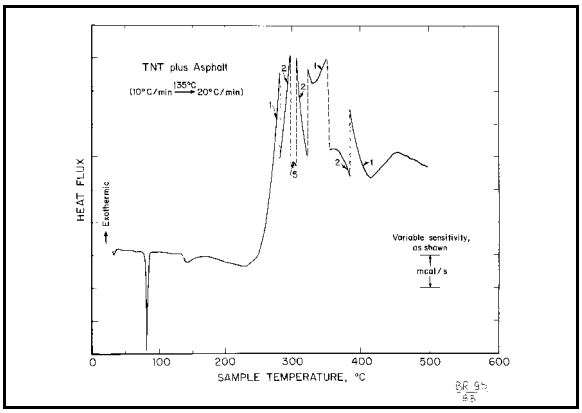


Figure 7. DSC thermogram for a mixture of flake TNT with asphalt (variable heating rate, not weighed).

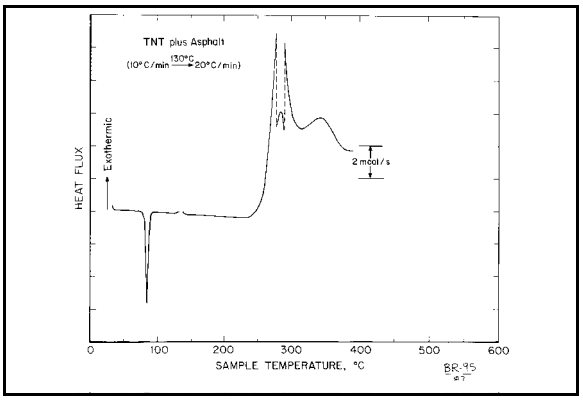


Figure 8. DSC thermogram for a mixture of flake TNT with asphalt (variable heating rate, 11.7 mg total weight).

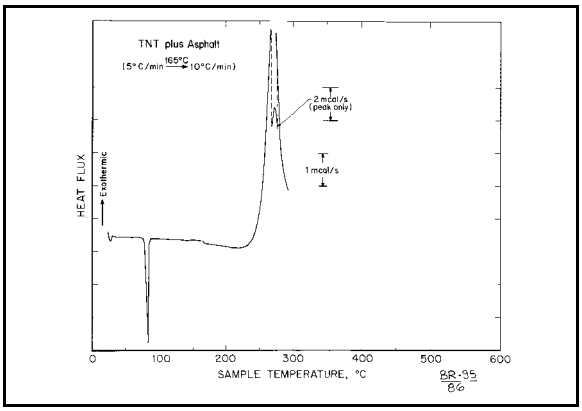


Figure 9. DSC thermogram for a mixture of flake TNT with asphalt (variable heating rate, 8.1 mg total weight).

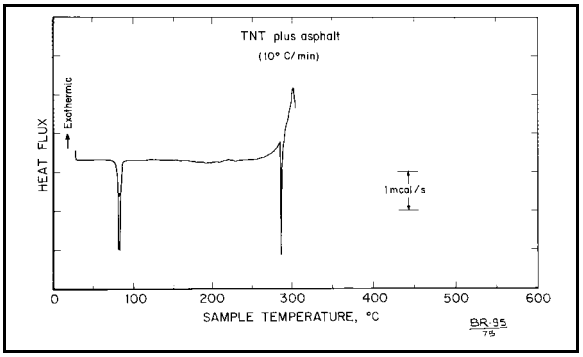


Figure 10. DSC thermogram for a sample of premelted TNT with asphalt (10°C/min, 2.5-mg sample).

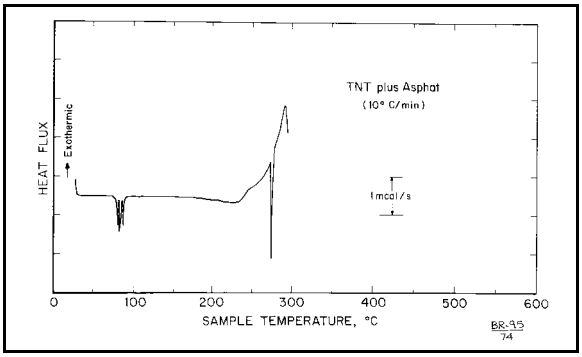


Figure 11. DSC thermogram for a sample of premelted TNT with asphalt (10°C/min, 3.9-mg sample).

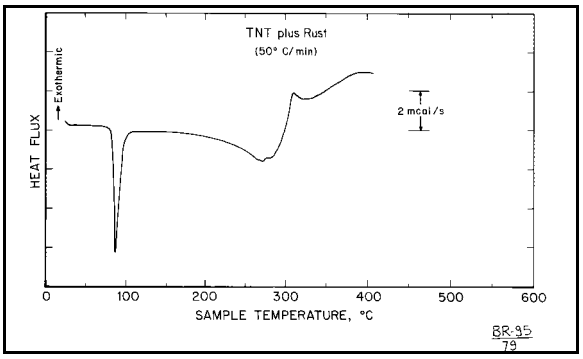


Figure 12. DSC thermogram for a mixture of crystalline TNT with rust (50°C/min, 4.0 mg total weight).

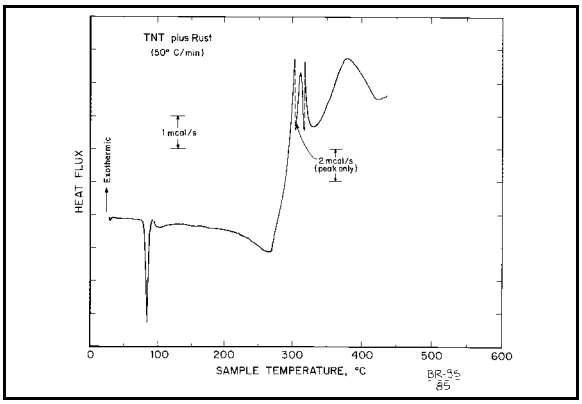


Figure 13. DSC thermogram for a mixture of flake TNT with rust (variable heating rate).

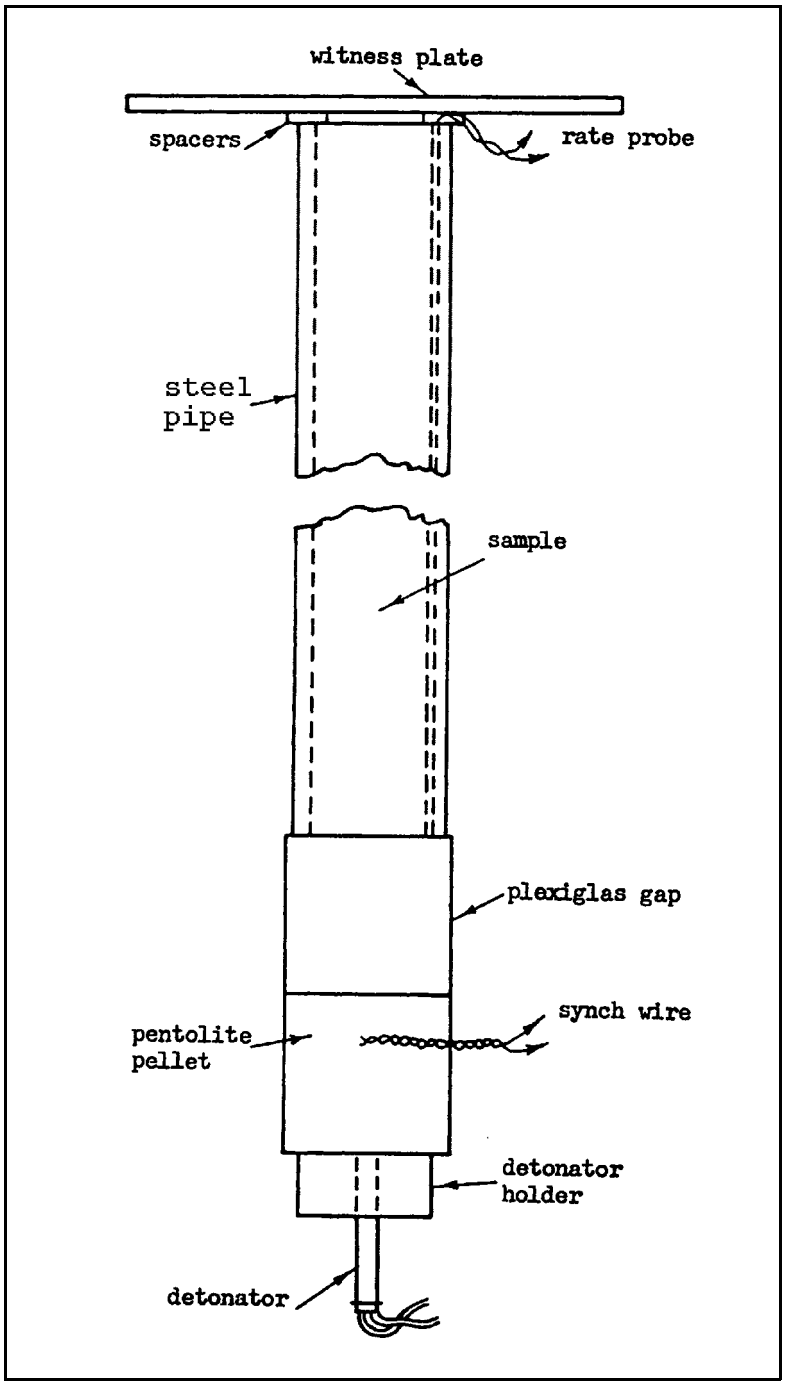
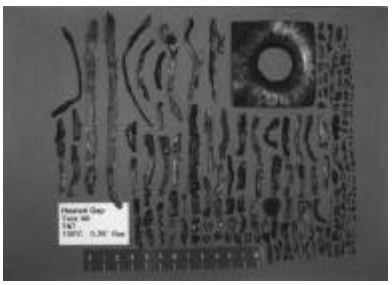


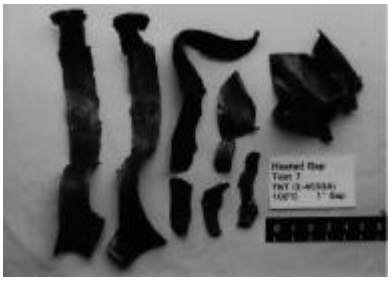
Figure 14. Card gap test setup.



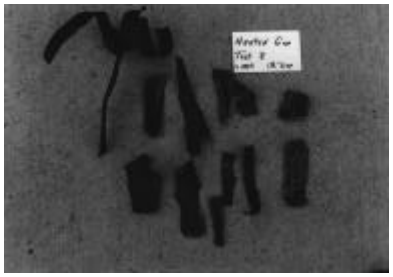
HGT-40. TNT, 0.25-inch gap, 100ºC.

HGT-39. TNT, 0.5-inch gap, 100ºC.

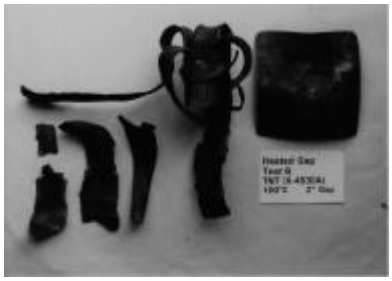
HGT-38. TNT, 0.75-inch gap, 100ºC.



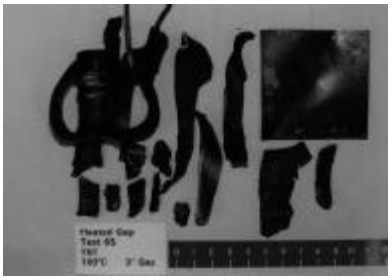
HGT-7. TNT, 1-inch gap, 100ºC.



HGT-8. TNT, 1.5-inch gap, 100ºC.



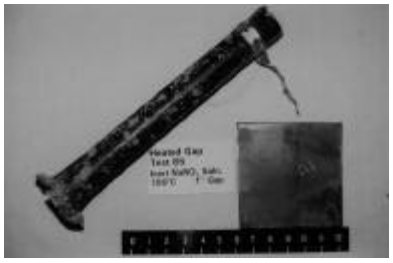
HGT-6. TNT, 2-inch gap, 100ºC.



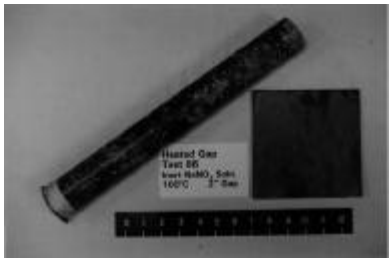
HGT-65. TNT, 3-inch gap, 100ºC.

HGT-64. TNT, 4-inch gap, 100ºC.

HGT-84. Inert, 0.5-inch gap, 100ºC.

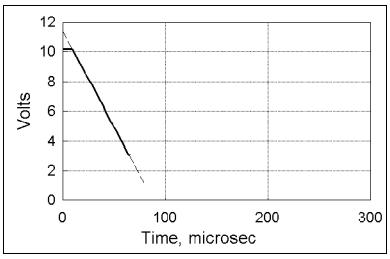


HGT-85. Inert, 1-inch gap, 100ºC.

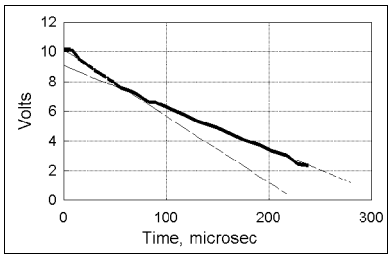


HGT-86. Inert, 2-inch gap, 100ºC.

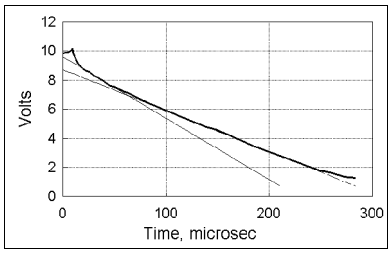
Figure 15. Comparison of pipe and witness plate damage for TNT and aqueous sodium nitrate solution at 100ºC.



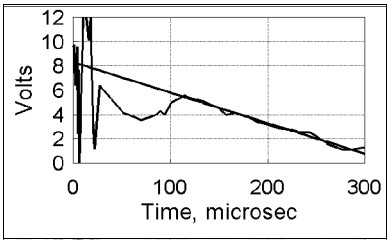
HGT-40. TNT, 0.25-inch gap, 100ºC. V=6,400 m/sec.



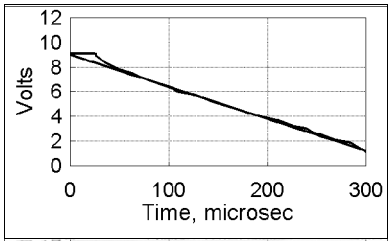
HGT-39. TNT, 0.5-inch gap, 100ºC. V=2,200/1,400 m/sec.



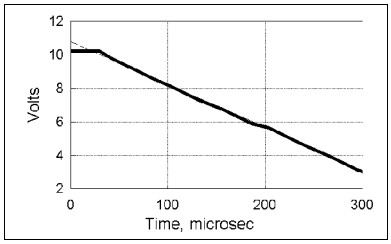
HGT-38. TNT, 0.75-inch gap, 100ºC. V=2,100/1,400 m/sec.



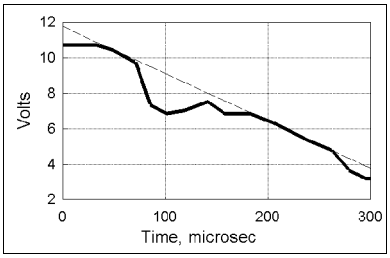
HGT-8. TNT, 1.5-inch gap, 100ºC. V=1,250 m/sec.



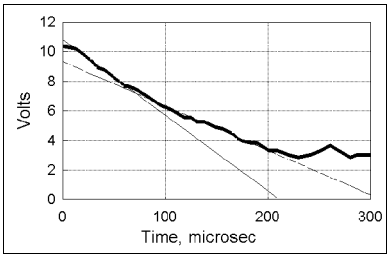
HGT-6. TNT, 2-inch gap, 100ºC. V=1,300 m/sec.



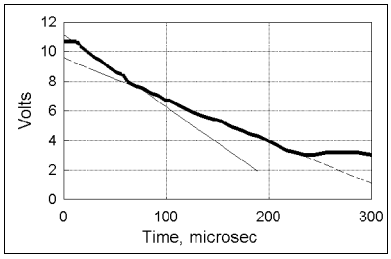
HGT-65. TNT, 3-inch gap, 100ºC. V=1,250 m/sec.



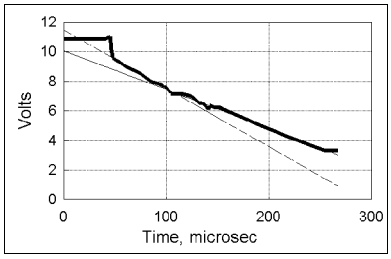
HGT-64. TNT, 4-inch gap, 100ºC. V=1,300 m/sec.



HGT-84. Inert, 0.5-inch gap, 100ºC. V=2,550/1,500 m/sec.



HGT-85. Inert, 1-inch gap, 100ºC. V=2,400/1,400 m/sec.



HGT-86. Inert, 2-inch gap, 100ºC. V=1,300/1,950 m/sec.

Figure 16. Comparison of velocity traces for TNT and aqueous sodium nitrate solution at 100ºC.