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Effects of Thermal Cycling on Trinitrotoluene and Tritonal Explosive Compositions

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ABSTRACT

The effects of thermal cycling of Trinitrotoluene (TNT) and tritonal were studied using unprocessed virgin TNT, reclaimed TNT and laboratory prepared tritonal. Small quantities of explosives were temperature cycled through ranges designed to simulate aerodynamic heating. The thermal chemical kinetics at isothermal temperatures were investigated using differential scanning calorimetry methods. Physical and Chemical changes were studied using Scanning Electron Microscopy, X-ray diffraction, and Thin-Layer Chromatography (TLC) techniques.

INTRODUCTION

Aerodynamic heating has been shown to induce temperature rises on the surface of munitions flown on the exterior of aircraft. A study already completed by the Air Force at Armament Laboratory (AFSC) on cyclotri-methylenetrinitramine (RDX)[1] has established thermal profiles for surface temperatures encountered by ordnance during flight. In the AFSC experiment, samples of RDX were cycled several times from ambient temperature to $177^{o}C$ and back again in order to simulate this aerodynamic heating. Changes in the explosive were determined by measuring the kinetic constants before and after cycling. Conclusion of the study was that small quantities of temperature cycled RDX gave test results indicating a lowering of the thermal decomposition temperature.

As in the case of RDX, bombs loaded with trinitrotoluene (TNT) and tritonal, a TNT aluminum explosive, are subjected to aerodynamic heating while being carried externally. Until now, no kinetic experiments have been conducted on unpurified military grade TNT. Investigators use recrystallized TNT purified because it is free of the low-melting impurities which are not

entirely removed during manufacturing[2]. This process may eliminate any effects these trace components might have on the thermal decomposition of the TNT. It has been shown that TNT which has been exposed to elevated temperatures for many hours will become less sensitive[3], but under those conditions the breakdown products formed may have masked a change in sensitivity caused during the initial increased temperature exposure. In aerodynamic heating, the munitions will only see elevated temperatures for short time periods. Therefore any decomposition reactions which were encountered in extended heating may not occur; however, the explosive may become unstable.

Rodgers[4] has evaluated the stability of explosives by using kinetic parameters such as the activation energy and the collision frequency factor to calculate the critical temperature at which any size and shape of explosive can self heat to explosion. Thus, the kinetic constants are related to explosive sensitivity in such a way that a decreased activation energy and frequency factor suggest a change in thermal stability. A lowered activation energy would be indicative of lower thermal stability.

OBJECTIVES

The purpose of this investigation was to determine if thermal cycling affects the stability and sensitivity of TNT and TNT based explosives. This was to be accomplished by measuring:

     1. Kinetic parameters such as energy rate constants, pre-exponentials and activation energy by using isothermal calorimetry.

     2. Impact sensitivity

     3. Heat capacity

There were other factors which were to be considered but were not completely pursued. These involved physical and chemical changes which may have occurred during temperature cycling, such as crystal changes or the formation of compounds. Analytical techniques to study these changes included scanning electron microscopy, X-ray diffraction, and chromatography.

EXPERIMENTAL

Theory

Explosive materials decompose exothermally at a temperature dependent rate. If this rate is first order, that is without any complex secondary reactions, the activation energy can be calculated by using the isothermal DSC techniques developed by Rodgers[5] for determining rate constants. He established that for the fraction (a) reacted during the isothermal decomposition, the DSC defection (b) above the baseline is directly

proportional to the rate (dq/dt) of energy evolved or absorbed by the sample. This rate is also proportional to rate of reaction, da/dt. Therefore,

$$ab = Bdq/dt = da/dt = k (1-a) \qquad (1)$$

where a and B are proportionality constants and k is the rate constant. By mathematical manipulation and definition, the following are obtained:

$$\ln b = \ln k/a + \ln (1-a) \qquad (2)$$

$$-\ln (1-a) = kt + c \qquad (3)$$

where c is a constant. By combining equations 2 and 3, the result is:

$$\ln (b) = \ln K/a - (kt + c) = C - kt \qquad (4)$$

where c is the combined constants. For a first order reaction, the rate constant is obtained from the negative slope of a plot of deflection vs time.

It must be demonstrated that the decomposition is first order. To do this a more general form of equation (1) is used:

$$b = k (1-a)^n \qquad (5)$$

where n is the order of the reaction. Now equation (4) becomes:

$$\ln b = \ln (1-a)^n + \ln (k/) = n \ln (1-a) + C.$$

The value of n for a first order reaction should be one.

The activation energy (E_a) and the collision frequency factor (Z) can then be calculated using the experimentally determined rate constants from the Arrhenius Equation:

$$K = Ze^{-E_a/RT}$$

where R is the universal gas constant and T is the temperature in degrees <u>Kelvin</u>.

<u>Experimental Set Up</u>

The experiment required that small quantities of explosive be sealed in DSC sample pans and subsequently temperature cycled. The pans would then be

perforated with a 0.15mm hole, so that isothermal decomposition could be conducted. The kinetic parameters would be determined from triplicate analyses on each explosive.

The temperature cycling was accomplished by weighing 2.00mg of TNT, and in the case of Tritonal 2.25mg, in Mettler TA2000B sample pans and cold weld sealing. These pans were placed in the Mettler and cycled through the following temperature profiles:

    a. Ambient to 150°C to ambient at 5°C/min, once

    b. Ambient to 150°C to ambient at 5°C/min, twice

    c. Ambient to 200°C, hold 30 minutes, return to ambient at 30°C/min

The pans were then perforated using a commercially available pivot drill bit measuring 0.15mm diameter. This type of drill bit made the hole size reproducible.

The design of the Mettler instrument does not easily permit dropping the pans on the sensors at elevated temperatures. However, the instrument can heat the samples from ambient to the isothermal temperature at a rate of 100°C/min. This was done for each kinetic analysis. A typical thermogram is shown in Figure 1. The first of the thermal parameters to be measured was
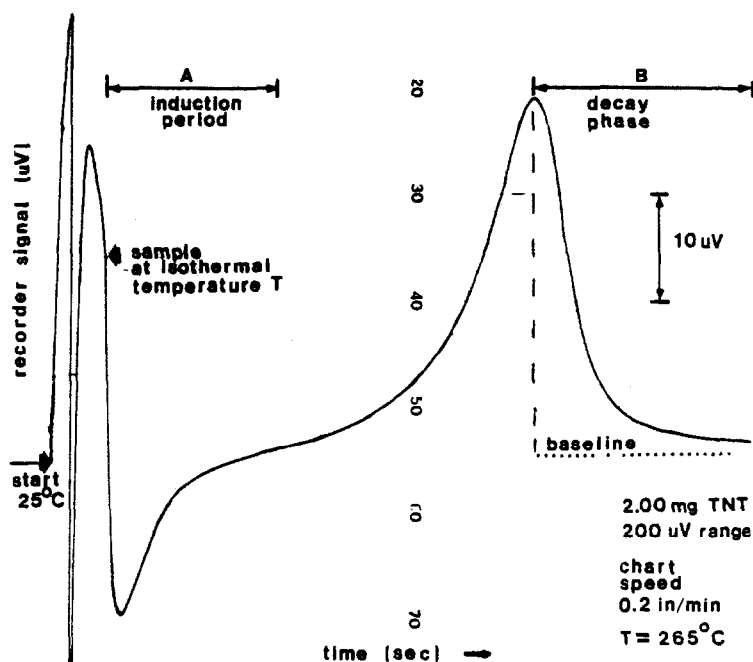

Figure 1. DSC thermogram of the isothermal decomposition of TNT

the induction period (A). This quantity was defined in this study as the difference between the time required for the sample to reach the isothermal temperature and the time the curve departed from the baseline established by the isothermal decomposition. Unlike RDX, the TNT induction period could not be measured reliably by visual means. The difficulty was in recognizing a deflection from the baseline. This was solved by using a computer to analyze the data collected by a digital to analog converter. A program was devised to pick a point where the curve begins to change significantly. The computer examined the data stored for the induction period as a series of sets of points. Each set consisted of 30 points. The value of each set was compared with the set before it, and when the value was equivalent to one and one-half divisions of the chart the computer established that value as the end of the induction period. The next thermal parameter was the decay phase (B) which began when the curve reached a maximum and ended when a baseline could be established.

The impact sensitivities were calculated by using the maximum no fire height because the 50 percent fire method would not give usable data. Approximately 2gms of explosive was cycled in a modified Dupont thermal analyzer cell. The test samples were then ground and impact sensitivity was determined. No attempt was made to do impact on chunks of explosive.

The heat capacity data was obtained using the Mettler TA2000B. Explosive samples weighing 30mg were temperature cycled. The heat capacity was determined by conducting a blank scan over the desired temperature range using an empty sample pan. The instrument recorder chart paper was then returned to the starting point and another scan was done over the same temperature range using the cycled explosive. No data was collected between 60 and $120^{o}C$ because of the drastic change in the thermal curve due to the melting of TNT.

Data Collection and Reduction

The data was collected using a combination system of a Canberra digitizer and dual counter/timer with a DEC PDP 11-05 minicomputer. The stored digital information was then converted back to analog form for display on a multichannel analyzer. In Figure 2a every tenth point was enhanced by the multichannel analyzer so that points could be quickly selected for calculating the rate constant. The computer stored the data from the decomposition curve indicated by the arrows in Figure 1a. A linear portion of this plot was chosen to determine the slope for the rate constant. In Figure 2c, a plot of ln b vs ln (1-x) resulted in the reaction order (n) from the slope.

The confidence limits for the kinetic constants were obtained using confidence levels for linear regression calculation as outlined by

Middlebrooks[6]. For 95 percent confidence, the Y value for any given X value is:

$$Y \pm \Phi_{[.05]\ [n-2]} \times S_y$$

Tables were used for the Φ value and two degrees of freedom were assumed. S_y represents the Y variance and is dependent on the X value.
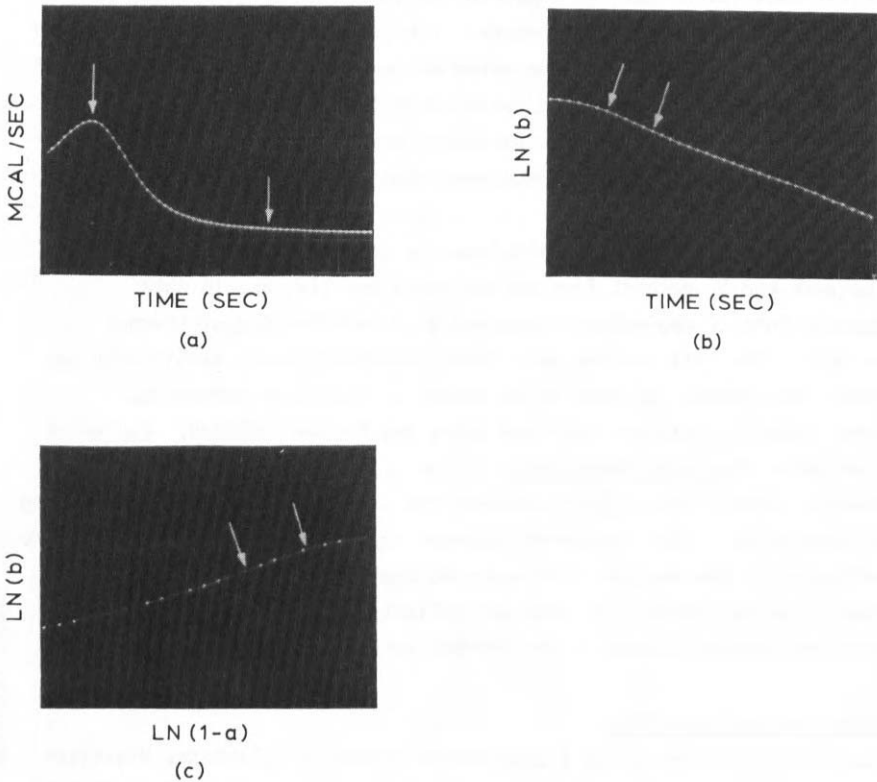

Figure 2. Multichannel Analyzer Data Display-arrows indicate sets of data used in determining:

    (a) "b" deflection
    (b) rate constant, K = slope
    (c) reaction order

DISCUSSION

Kinetics

Figures 3 and 4 were made from plots of the induction periods in Table 1 as a function of the isothermal temperature used in each kinetic analysis. The induction period (I_p) for flaked TNT decreased slightly after each successive cycle. The graph obtained for tritonal (Figure 4) would seem to indicate that (I_p) had increased after cycling. When you plot (I_p) measured for the virgin TNT used in making the tritonal and ignore the data from the uncycled tritonal, the result is a decrease in the induction period. This comparison is valid because after the first cycle the TNT tended to migrate away from the aluminum. The cycled tritonal could be treated like cycled virgin TNT. The powdered aluminum was inert material bound to the pan by a thin layer of melted TNT.

The validity of the activation energy depends upon whether the thermal decomposition is the result of a first order reaction. An examination of the reaction orders experimentally determined for the decomposition of TNT and tritonal listed in Table 2 confirm that they are first order. The nominal

TABLE 1

TNT Thermal Decomposition Induction Periods (Sec)*

TNT Sample	Temperature (^{0}C)					
	255	260	265	270	275	280
Flake, Uncycled	725	526	469	394	344	300
Flake, Cycled Once at 150^{0}C, 5^{0}C/min	537	488	444	412	313	281
Flake, Cycled Twice at 150^{0}C, 5^{0}C/min	785	463	382	288	250	213
Flake, 200^{0}C Hold for 30 min	719	513	375	388	269	256
Virgin, Uncycled	881	563	488	420	319	281
Tritonal, Uncycled	563	425	369	325	275	206
Tritonal, Cycled Once at 150^{0}C, 50^{0}C/min	506	444	381	350	343	225
Tritonal, Cycled Twice at 150^{0}C, 5^{0}C/min	788	556	475	412	337	250
Tritonal, 200^{0}C Hold for 30 min	800	604	531	425	337	232

*Average from three analyses per temperature
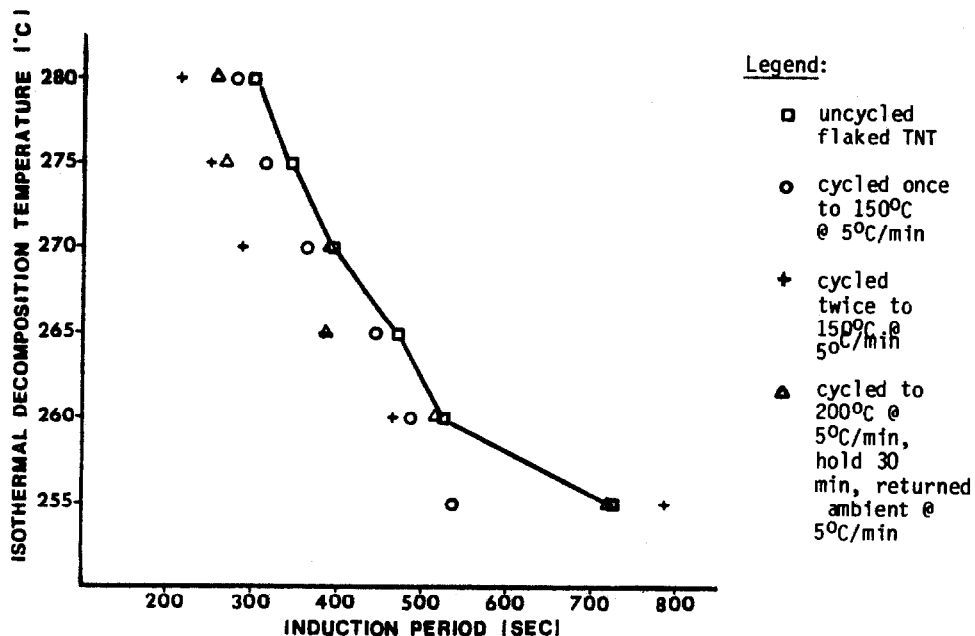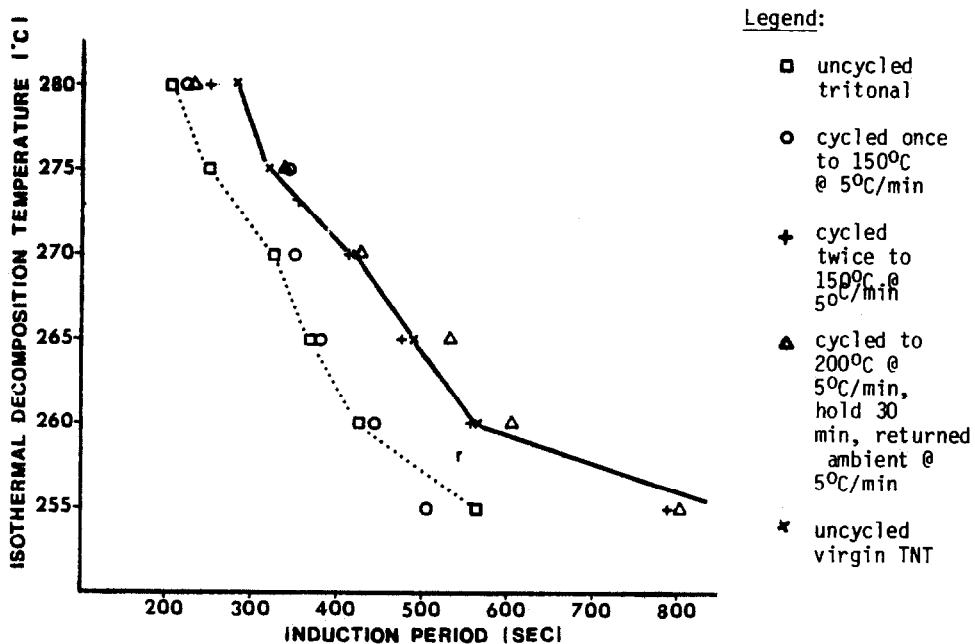
Figure 3. Induction Period of Flaked TNT vs Temperature

Legend:

▫ uncycled
   flaked TNT

○ cycled once
   to 150°C
   @ 5°C/min

✛ cycled
   twice to
   150°C @
   5°C/min

▲ cycled to
   200°C @
   5°C/min,
   hold 30
   min, returned
   ambient @
   5°C/min

Figure 4. Induction Period of Tritonal vs Temperature

Legend:

▫ uncycled
   tritonal

○ cycled once
   to 150°C
   @ 5°C/min

✛ cycled
   twice to
   150°C @
   5°C/min

▲ cycled to
   200°C @
   5°C/min,
   hold 30
   min, returned
   ambient @
   5°C/min

✱ uncycled
   virgin TNT

TABLE 2

TNT Thermal Decomposition Reaction Orders *

TNT Sample	Temperature (°C)					
	255	260	265	270	275	280
Flake, Uncycled	.91	.92	1.02	1.04	1.07	1.08
Flake, Cycled Once at 150°C, 5°C/min	.88	.98	1.06	1.06	1.14	1.15
Flake, Cycled Twice at 150°C, 5°C/min	.90	.97	1.05	1.06	1.11	1.20
Flake, 200°C Hold for 30 min	.89	.97	1.04	1.08	1.16	1.19
Virgin, Uncycled	.89	.98	1.03	1.07	1.12	1.23
Tritonal, Uncycled	.93	.97	.99	1.09	1.14	1.15
Tritonal, Cycled Once at 150°C, 50°C/min	.88	.97	1.04	1.08	1.13	1.16
Tritonal, Cycled Twice at 150°C, 5°C/min	.83	.93	1.03	1.09	1.14	1.14
Tritonal, 200°C Hold for 30 min	.85	.93	1.03	1.05	1.11	1.14

*Average from three analyses per temperature

TABLE 3

TNT Thermal Decomposition Rate Constants (Sec -1)*

TNT Sample	Temperature (°C)					
	255	260	265	270	275	280
Flake, Uncycled	.0070	.0110	.0118	.0148	.0187	.0229
Flake, Cycled Once at 150°C, 5°C/min	.0080	.0092	.0118	.0147	.0184	.0220
Flake, Cycled Twice at 150°C, 5°C/min	.0080	.0095	.0112	.0144	.0181	.0222
Flake, 200°C Hold for 30 min	.0081	.0098	.0113	.0154	.0189	.0223
Virgin, Uncycled	.0085	.0096	.0133	.0148	.0192	.0222
Tritonal, Uncycled	.0085	.0104	.0135	.0158	.0192	.0236
Tritonal, Cycled Once at 150°C, 50°C/min	.0090	.0108	.0128	.0158	.0189	.0228
Tritonal, Cycled Twice at 150°C, 5°C/min	.0097	.0115	.0138	.0161	.0197	.0250
Tritonal, 200°C Hold for 30 min	.0090	.0110	.0131	.0164	.0196	.0227

*Average from three analyses per temperature

value was one. The rate constants in Table 3 were used in the Arrhenius Equation to calculate activation energy for each of the uncycled and cycled explosives. The values obtained (Table 4) are for the temperature range 255 to 280°C. The reduced E_a value after cycling TNT and tritonal connotes that they both became more sensitive to thermal degradation. It also appears that the initial cycle was the most critical one. Additional cycles resulted in no further decrease in the activation energy.

TABLE 4

TNT Thermal Decomposition Kinetic Parameters (255-280 o) DSC Isolthermal Method

TNT Sample	Activation Energy, Ea (Kcal Mol^1)	Log Pre-Exponential Factor, Log Z (sec^1)
Flake, Uncycled	26.6 $\pm$ 2.0	8.9 $\pm$ .8
Flake, Cycled Once at 150°C, 5oC/min	24.5 $\pm$ 1.7	8.0 $\pm$ .7
Flake, Cycled Twice at 150°C, 5°C/min	24.0 $\pm$ 2.1	7.8 $\pm$ .9
Flake, 200°C Hold for 30 min	24.0 $\pm$ 2.1	8.0 $\pm$ .9
Virgin, Uncycled	23.3 $\pm$ 2.0	7.5 $\pm$ .8
Tritonal, Uncycled	23.6 $\pm$ 1.4	7.7 $\pm$ .6
Tritonal, Cycled Once at 150°C, 50°C/min	21.7 $\pm$ 1.0	6.9 $\pm$ .4
Tritonal, Cycled Twice at 150°C, 5°C/min	21.5 $\pm$ 1.9	6.7 $\pm$ .8
Tritonal, 200°C Hold for 30 min	21.7 $\pm$ .9	6.9 $\pm$ .4

Impact Sensitivity

The impact sensitivity data in Table 5 suggest that temperature cycling has reduced the sensitivity of virgin TNT and flaked TNT, whereas the tritonal remained about the same. Since the explosives were ground for the impact testing, it is believed that the grinding may have altered the results. Kinetic analyses should have been conducted on the ground material in order to evaluate any changes which the grinding may have caused.

A possible method to improve on the impact test might be to use the DSC sample pans and perform impact directly on the pans after temperature cycling.

TABLE 5

Heat Capacity For TNT and Tritonal
Units In Calories/Gram-^{o}C
Values Within + 0.015

Temperature ^oC	Flake TNT Uncycled	Flake TNT Cycled to 150^oC @ 5^oC/min	Virgin TNT Uncycled	Virgin TNT Cycled to 150^oC @ 5^oC/min	Tritonal Uncycled	Tritonal Cycled 150^oC @ 5^oC/min
20	.247	.255	.270	.278	.237	.247
30	.257	.266	.280	.290	.246	.255
40	.265	.274	.289	.299	.254	.262
50	.276	.286	.300	.311	.264	.271
60	.286	.296	.311	.321	.273	.278
120	.359	.372	.386	.392	.333	.338
130	.361	.374	.388	.395	.335	.340
140	.367	.381	.396	.402	.341	.346
150	.369	.384	.398	.404	.343	.349
160	.375	.387	.405	.411	.349	.354

Heat Capacities

The heat capacity data is provided in Table 6. A slight increase in heat capacity was measured after thermal cycling. A possible explanation for this increase may be due to the presence of liquid TNT in the crystal latice of the cycled explosive. There is no evidence to confirm this theory. Scanning electron microscopy cannot detect liquid materials since sample preparations force the crystallization of the liquid. The more likely reason is during the melting a change in the pan-to-sample contact caused a better energy transfer to the Mettler TA2000B sensors.

Figure 5 curve 1 is a thermogram of TNT used to determine its heat capacity. Curve 2 (Figure 5) is the same sample of TNT which has been supercooled to 40^oC and then heated up again. The significance of these two curves is the large differences between the heat capacity of the liquid and solid TNT below the melting point.

TABLE 6

Impact Sensitivity, 2 Kg Weight
Data is Maximum
No Fire Height in CM

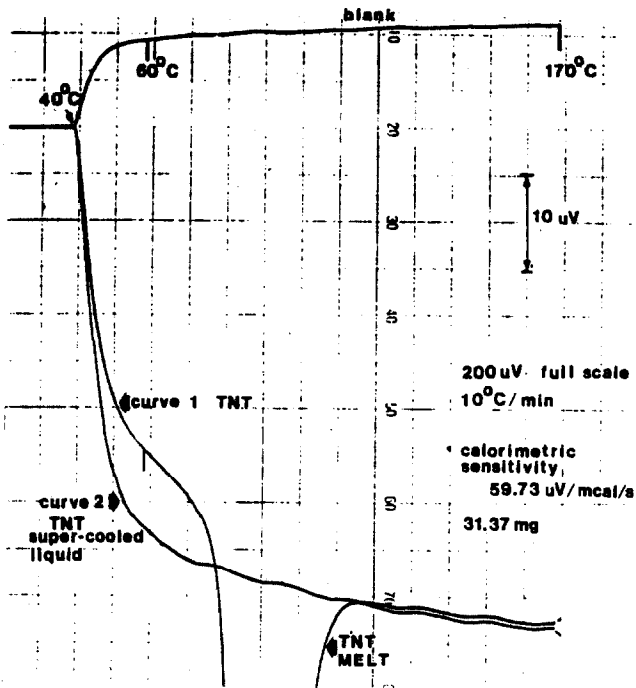| Sample	Uncycled	Cycled Once to 150^oC at 5^oC	Cycled Twice to 150^oC at 5^oC	Ambient to 200^oC at 40^oC/min Hold for 30 min
Virgin TNT	42	58	56	84
	42	52	64	60
Reclaimed	50	58	54	-
Flake TNT	52	64	60	
Tritonal	74	82	60	70
	64	72	74	56

Figure 5. Heat Capacity Thermograms

Scanning Electron Microscope (SEM) Evaluation

SEM micrographs of uncycled and thermally cycled TNT material are presented in Figures 6 through 10. Four samples were analyzed: recrystallized TNT, uncycled; flake TNT, uncycled; flake TNT, cycled once to 150°C; and flake TNT, cycled twice to 150°C. Figure 6 includes low power 100X magnification photographs of the four samples. The recrystallized TNT appears broken into several irregular, plate-like crystals. The reclaimed flake TNT (having undergone steam processing), uncycled, reveals smaller crystals compressed together. This is indicative of the steaming process, melting smaller crystals and smoothing those larger. The cycled flake TNT appears continuous with noticeable cracks and voids, which is characteristic of material that has melted. There is more evidence of voids in the twice cycled material than once cycled.

Figures 7 and 8 contain photographs of the four samples at magnifications of 400X and 1000X, respectively. Again, the uncycled flake TNT has more compact, indiscrete crystals than the recrystallized material. Crystallization sites appear on the surface of cycled TNT, which were formed during the solidification

Recrystallized, Uncycled
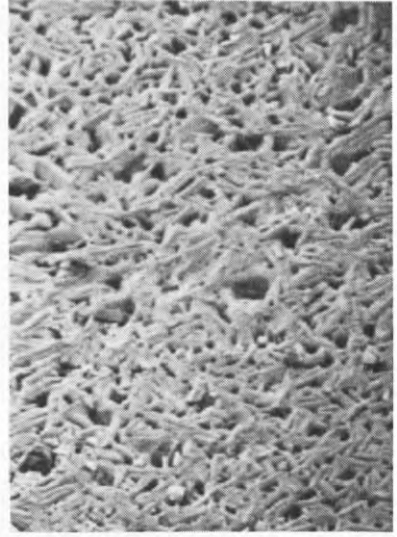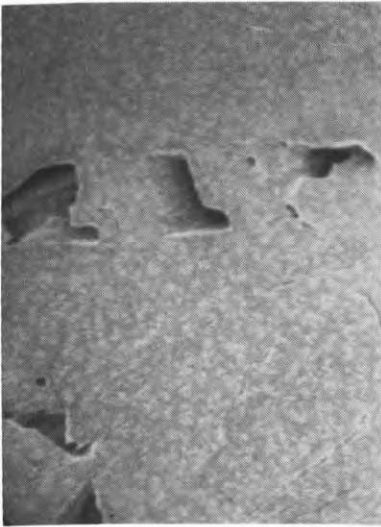
Flake, Uncycled

Flaked, Cycled Once
at 150°C, 5°C/min
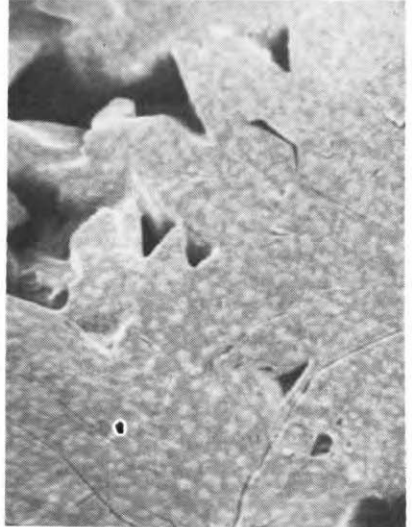
Flaked, Cycled Twice
at 150°C, 5°C/min

Figure 6. SEM Photographs of TNT Samples, 100X

Recrystallized, Uncycled
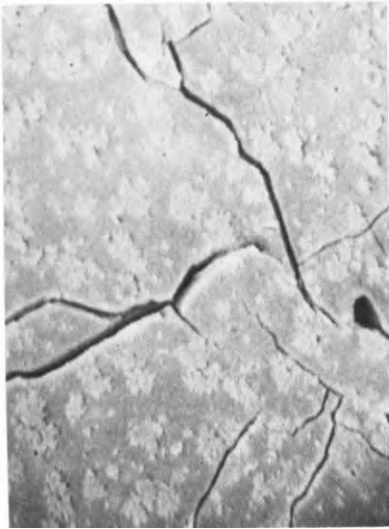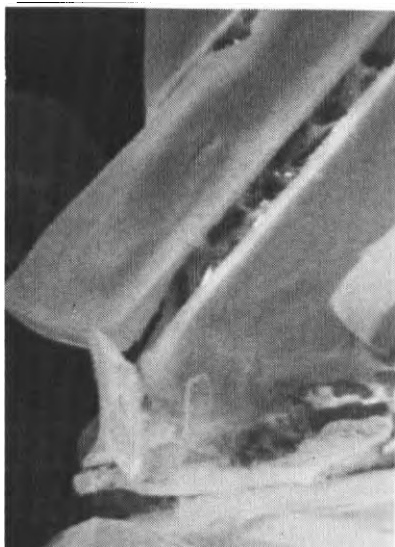

Flake, Uncycled

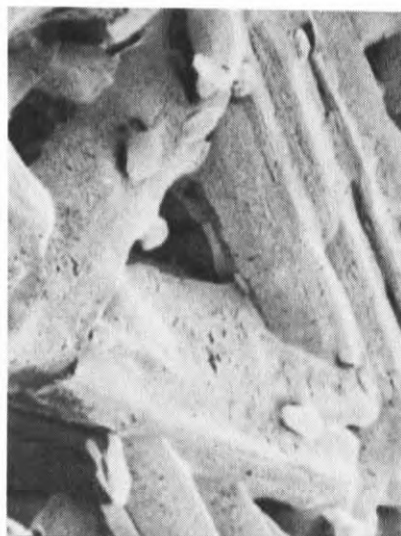Flaked, Cycled Once
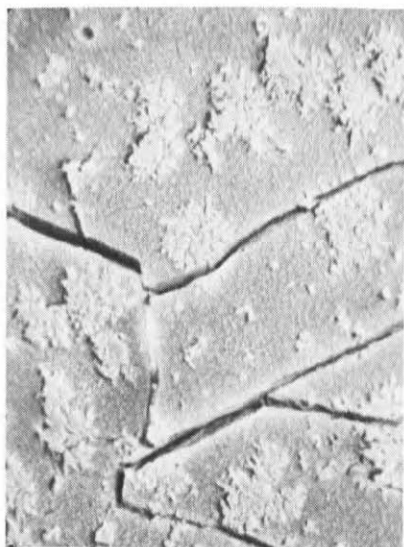at 150°C, 5°C/min
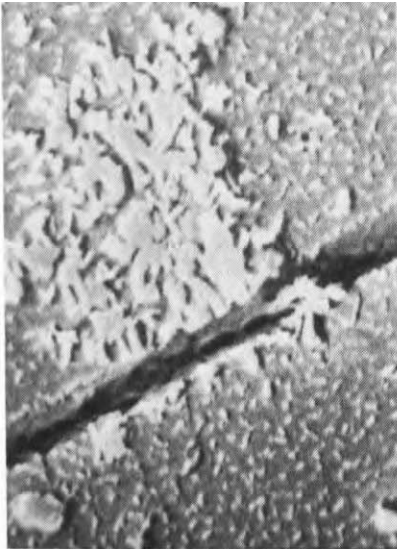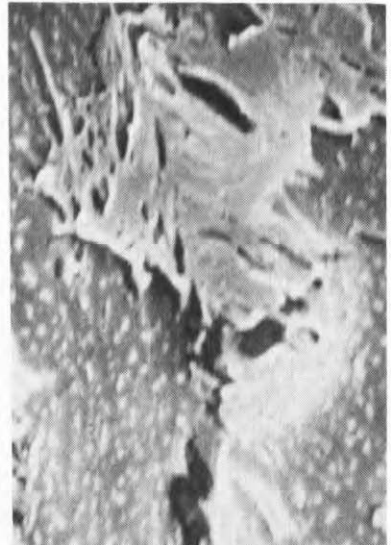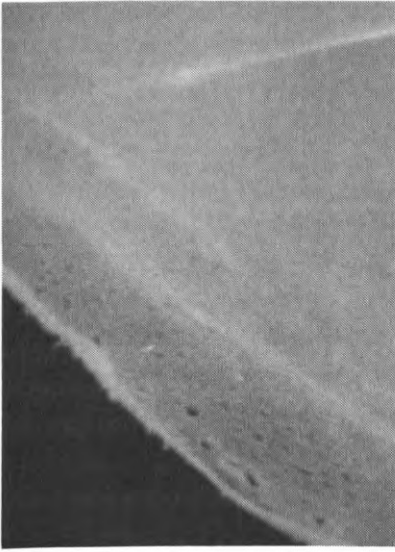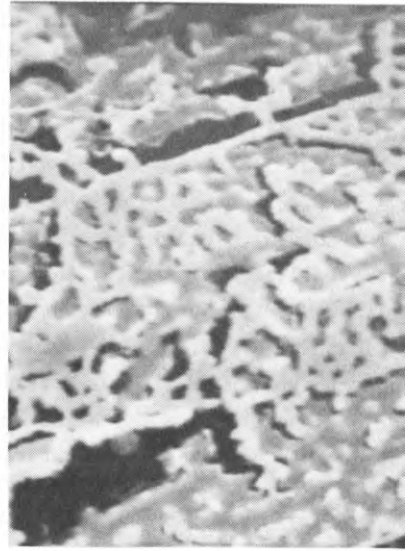

Flaked, Cycled Twice
at 150°C, 5°C/min

Figure 7.   SEM Photographs of TNT Samples, 400X

Recrystallized, Uncycled

Flake, Uncycled

Flaked, Cycled Once
at 150°C, 5°C/min

Flaked, Cycled Twice
at 150°C, 5°C/min

Figure 8.   SEM Photographs of TNT Samples, 1000X

Recrystallized, Uncycled

Flake, Uncycled

Flaked, Cycled Once
at 150°C, 5°C/min

Flaked, Cycled Twice
at 150°C, 5°C/min
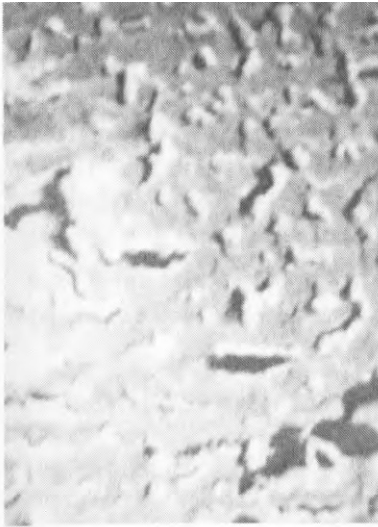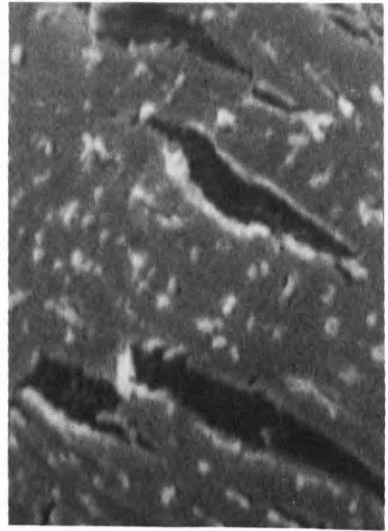
Figure 9. SEM Photographs of TNT Samples, 4000X

Recrystallized, Uncycled

Flake, Uncycled

Flaked, Cycled Once
at 150°C, 5°C/min

Flaked, Cycled Twice
at 150°C, 5°C/min

Figure 10.   SEM Photographs of TNT Samples, 10,000X

transition. No analytical method was available to determine composition of these particular sites. The high magnification photographs of 4000X and 10,000X (Figures 9 and 10), reveal a smooth topography for recrystallized TNT. This is in contrast with the minute speckled formations on the surface of flake TNT, uncycled or cycled. These bump-like features appear to be bubbles or gas-relief pores on the surface, rather than separate crystals.

The morphological information from SEM examination can reveal differences between recrystallized TNT and TNT that has been subjected to thermal conditions above the melting point. No significant difference is noticed between material thermally cycled once or twice. Crystal nucleation during the solidifying process forms a topography with small crystallization sites covering the surface. It is believed these structures are the result of TNT crystal formations during soldification, rather than any change in chemical composition due to thermal treatment.

X-Ray Diffraction Studies

X-ray diffraction patterns were obtained for virgin TNT using 12 and 24 hour exposures because at 24 hours some of the lines which appeared broad were better resolved. Extra lines which showed in cycled TNT were very faint. They occurred near the same D spacing which might indicate a formation of something during cycling, but with only two very faint lines it is not possible to learn the nature of the material.

The laboratory prepared tritonal had several lines which could not be attributed to TNT or aluminum. These lines may be shifted from their true position, but no cause for such a shift is apparent at this time. Faint lines similar to those found in the virgin TNT lines were encountered in tritonal. These weak lines do not constitute sufficient evidence to support the conclusion that similar changes have occurred in both explosives.

The computer search of the patterns of TNT and cycled TNT samples revealed a large number of possible matches. The compound which seemed to be most probable from the search was p-dinitrobenzene.

Thin-Layer Chromatography

The results of the analysis in two solvent systems indicate that the source TNT sample itself contains as many as four relatively nonpolar contaminants detectable at the 10,000 ppm level; the reclaimed TNT contains two detectable contaminants at 10,000 ppm; and the tritonal sample at 10,000 ppm contains five contaminants. No additional products were detected in any of the samples after they were cycled once or twice at $150^{\circ}C$. However, all samples cycled at $200^{\circ}C$ yielded an additional product (with an R_f value of 0.38). The product apparently is polar in nature, since it was detected only after development in the polar solvent system. This

experiment did not attempt to identify the material or estimate any increase in any of the contaminants after each cycling. Further tests are planned to confirm these products.

SUMMARY AND CONCLUSIONS

This study suggests that thermal profiles experienced on current munitions either during capture flight or storage may result in the alteration of the decomposition mechanisms and cause sensitivity changes.

The thermal cycles studied under this phase were similar to a temperature profile of an aircraft traveling mach 1.5 - 2.0 at various altitudes on a standard hot day.

Decomposition kinetics on explosives having undergone an evaluated heat profile showed a drop in the activation energy (E_a) which may mean an increase in sensitivity to thermal decomposition.

A rise in the heat capacity for TNT and tritonal over the temperature range of $20^{\circ}C$ - $160^{\circ}C$ was noted. No physical changes were observed by scanning electron microscopy under the test conditions. However, the drop hammer impact tests were suggestive of a decrease in sensitivity to impact. It should be noted this test data was very erratic and could have been affected by sample homogeneity; i.e., particle size and sample spread.

Preliminary thin-layer chromatography experiments found an unidentified material in the explosives cycled to $200^{\circ}C$ which was not present in the other cycled samples.

ACKNOWLEDGEMENTS

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