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Thermal Analysis Studies On Candidate Liner, Coating, and Sealer Materials For Thermally Protected Mark 80 Series Bombs

by
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ABSTRACT

The thermal stability of candidate liner, coating, and sealer materials for the Mk 50 series bombs was studied over a temperature range of -54 to about 700°C. The sealer and liner materials were also tested for compatibility with TNT, Composition B, and H-6 explosives. In addition to the laboratory-scale thermal studies, data from full-scale tests with Mk 82 bombs are included. All candidate liner materials failed as possible replacements for the present hot-melt liner material because they either did not exhibit any significant improvements or a compatibility problem existed. The candidate coating materials were tested thermally and their deficiencies were noted. The sealer material had serious compatibility problems and its use should be limited when in possible contact with explosives.

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AN ACTIVITY OF THE NAVAL MATERIAL COMMAND

W. J. Moran, RADM, USN Commander

H. G. Wilson Technical Director

FOREWORD

Because of the various types of explosives with unstable characteristics which can, during exposure to an enveloping flame, create a hazard aboard an aircraft carrier, there is a need to investigate various techniques that may alleviate or eliminate the disastrous consequences. This study evaluated various candidate liner, coating, and sealer materials that could possibly be used in Mk 80 series bombs to extend the cookoff time and to reduce the severity of the cookoff reaction.

This study was conducted during 1970 and 1971 and supported by AirTask W4703-02, Work Request 9-7197.

This report has been reviewed for technical accuracy by Gordon A. Greene.

Released by
N. L. Rumpp, Head
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15 February 1972

Under authority of
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INTRODUCTION

The purpose of this program was to study the thermal stability of candidate liner, coating, and sealer materials which could be used to extend the cookoff time of Mk 80 series bombs. If feasible, the liner material would replace the standard hot melt now used as an interface between the metal bomb case and the explosive. The coating would be applied on the outside of the bomb case. The candidate sealer material would replace the wax now used to seal the aft end of the Mk 80 series of bombs after they have been loaded with the explosive.

The candidate liner and sealer materials were tested for compatibility with TNT, Composition B, and H-6 explosives at the temperature range of ambient to above 700°C. This range covers the normal-temperature loading and the high-temperature storage of ordnance and also covers most of the decomposition reactions of the explosives and the candidate materials. In this way, the thermal stability and the compatibility aspects were studied simultaneously, since what effected the thermal stability of the explosive-liner/sealer interface was also part of the compatibility problem.

Stability, as used in this study, was defined as the ability of a material to remain unchanged, either physically or chemically, over extended periods of time even when exposed to rigorous environments. The study showed that there was no one single test that could effectively measure stability.

The materials used to coat, line, and seal Mk 80 series bombs are of a particularly complex nature. They are proprietary mixtures of organic and inorganic chemicals. Degradation of the original material can occur because of a change in their physical or chemical characteristics. It was shown in this study that the degradation process may create a hazardous condition when these materials come into contact with explosives, e.g., possible ignition. The degradation of the material was considered within the range of normal use conditions, in regard to the degree and rate of chemical reactions and changes in the physical state. In order to do this, overtests were performed, such as heating at temperatures higher than expected, so that long-term storage and loading results could be predicted from short-term tests. Again, compatibility was considered to be a type of stability, i.e., the tendency of an explosive to interact when in contact with other materials.

Six different candidate liner materials were studied both alone and in combination with explosives. One liner material, the standard hot melt (or black mix), was used as a comparison. Four coating materials were studied for thermal stability, but were not studied with an explosive for a compatibility evaluation. The coatings will not normally

come into contact with explosives; however, a contact is possible in the scrap collection area at a loading plant. Only one candidate sealer material was evaluated, alone and in combination with explosives.

The compositions of the candidate materials were only partially known or not known at all. This made compatibility and stability testing more difficult since the decomposition reactions had to be identified first in order to determine the specific problem areas. The candidate liner, coating, and sealer materials are listed in Table 1.

TABLE 1. Liner, Coating, and Sealer Material.

MATERIALS ^a	SOURCE
<p>Liners:</p> <p>Hot melt (black mix)</p> <p>Thiokol</p> <p>ISI (Plastonium 44)</p> <p>URP-2</p> <p>TSI</p> <p>Essex</p> <p>Unique (UPI-1000)</p>	<p>NAVWPNSTA Yorktown, Virginia</p> <p>Thiokol Chemical Corp. Trenton, New Jersey</p> <p>Insulation Systems, Inc. Santa Ana, California</p> <p>United Resin Products Brooklyn, New York</p> <p>Thermal Systems, Inc. Los Angeles, California</p> <p>Essex Chemical Company Clifton, New Jersey</p> <p>Unique Products, Inc. Santa Ana, California and Rocketdyne McGregor, Texas</p>
<p>Coatings:</p> <p>Pfizer</p> <p>Thermal lag</p> <p>CECO</p> <p>AVCO</p>	<p>Universal Propulsion Corp. Riverside, California</p> <p>Thermal Systems, Inc. St. Louis, Missouri</p> <p>Cheesman-Elliott Co. Brooklyn, New York</p> <p>AVCO Systems Division Wilmington, Massachusetts</p>
<p>Sealer:</p> <p>Tuffseal</p>	<p>H. H. Robertson Co. Ambridge, Pennsylvania</p>

^aThe citation in this report of the trade names of commercially available products does not constitute official indorsement or approval of the use of such products.

EXPERIMENTAL TECHNIQUES

ANALYTICAL

The Mettler Model No. 2 Thermoanalyzer¹ was used to obtain true simultaneous measurements on the effect of heat on a single sample under precisely defined conditions. Differential thermal analysis (DTA), thermogravimetric analysis (TGA), and derivative thermogravimetry (DTG) data were measured on one sample in one single run. The DTA covers the heat changes and the TGA covers the weight gained or lost while the sample is being heated at a constant rate. The DTG indicates the rate at which the weight is being lost at a given temperature. All Mettler runs were made under identical operational conditions. The heating rate was 5°C per minute, chart speed 6 inches per hour, temperature span 10-millivolt full scale, and runs made under atmosphere of air. (On the original chart, the distance between two numbered horizontal lines (e.g., 50 and 60) is 1 inch. This vertical distance is equal to ~1°C on the DTA curve and 1 mg on the TGA (10x) curve.) Indium metal was used in the reference cup to give a temperature calibration; it gave a small exothermic blip at 156°C.

The other analytical techniques employed were: differential scanning calorimetry (DSC), infrared spectrophotometry (IR), and mass spectrophotometry.

ISOTHERMAL

Isothermal analysis was accomplished by two different techniques. Both techniques were not always employed on each candidate material.

The first technique used small samples (5 to 8 milligrams) of explosives, alone and with sufficient quantities of liner and sealer materials. The decomposition rates of the explosives and mixtures were measured in various temperature regions ranging from 160 to 260°C. The differential pressure measurement results of these studies were used in part for the compatibility study (Ref. 1, 2, and 3).

The second technique used about 15 to 20 grams of material for each test. The sample was contained within a 45-milliliter stainless steel Parr general purpose test bomb. This small-scale pressure bomb (SPB) and heating block are shown schematically in Fig. 1. The heating block was machined from a 5 1/2-inch-diameter piece of solid cylindrical aluminum stock. The material sample container was a commercially available 45-milliliter T303 stainless steel general purpose bomb² with an A7AC7

¹Mettler Instrument Corp., Princeton, New Jersey.

²Part No. 4712, manufactured by the Parr Instrument Co., Moline, Illinois.

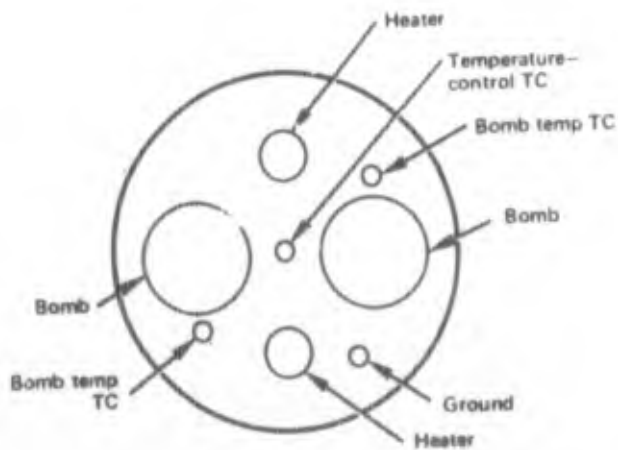
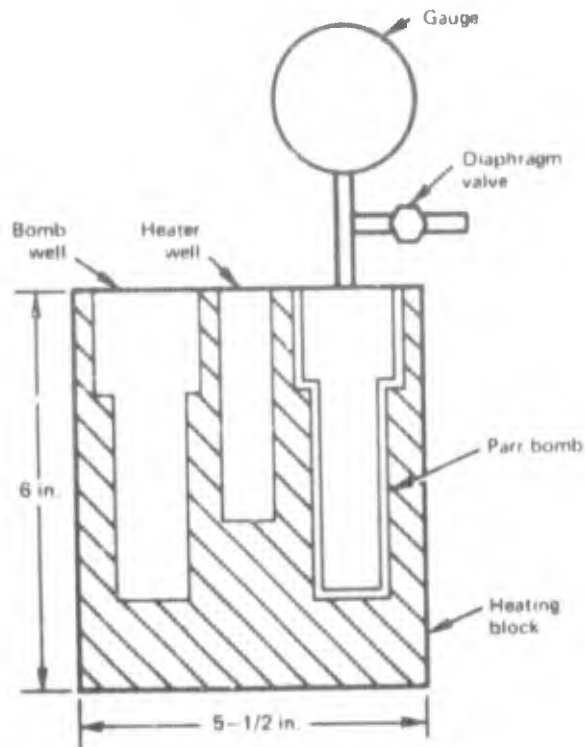


FIG. 1. Schematic Diagram of Small-Scale Pressure Bomb (SPB) Setup.

head. The overall length of the bomb was 4.6 inches. Two additional items are required for the basic bomb configuration: the Matheson No. 939-SS diaphragm valve and the Matheson No. 63-5307 precision pressure gauge³. The three items are connected to each other so that leakage will be eliminated. Two cartridge-type heaters rated at 250 watts 120 volts were used. The heating block was insulated by applying a 1/2-inch layer of asbestos ribbon around the side of the block and attaching a 1 1/2-inch-thick asbestos pad on the bottom. Additional insulation was provided by placing the completed assembly within a cylindrical enclosure of asbestos. A cover was placed on top of the enclosure, allowing the gauges and valves to be readily accessible above the enclosure. Pressure and temperature data were recorded continuously and decomposition products were analyzed periodically by transferring a gas sample from the bomb into the mass spectrophotometer. A more complete description of the SPB and its application is given in Ref. 4.

FAST COOKOFF

The fast cookoff tests were used to study the dynamic thermal characteristics of explosives when contained within a closed vessel and subjected to a rapid increase in temperature. Two different test vessels and techniques were employed.

The first technique used a small-scale cookoff bomb (SCB) to study the dynamic thermal characteristics of the explosives when confined within a closed container and subjected to a rapid temperature increase. The cylindrical container components along with a schematic view of the test setup are shown in Fig. 2. The bomb was electrically heated at a rate of about 1.6°C per second in the 100 to 200°C region. Each bomb was lined with a selected liner and filled with approximately 2 pounds of explosive, then heated until destruction. The time-temperature data were recorded for the inside metal wall of the bomb and for the liner/explosive interface. The bomb fragmentation was noted and recorded after each test. The type of reaction was reported in accordance with Ref. 5. The first technique was considered as a possible preliminary test that would be performed before employing a full-scale vessel in a fast cookoff test as described in the WR 50 publication (Ref. 6). A more complete description of the SCB and its previous applications can be found in Ref. 4.

The second technique used a full-sized Mk 82 bomb for the container and burning aviation jet fuel (JP-5) for the heat source. The bombs were lined with selected liners and then filled with H-6 explosive for the live tests and with sand for the inert tests. During the tests, the bombs were subjected to an enveloping flame per requirements stipulated in Ref. 6.

³Both items manufactured by Matheson Gas Products, Cucamonga, California.

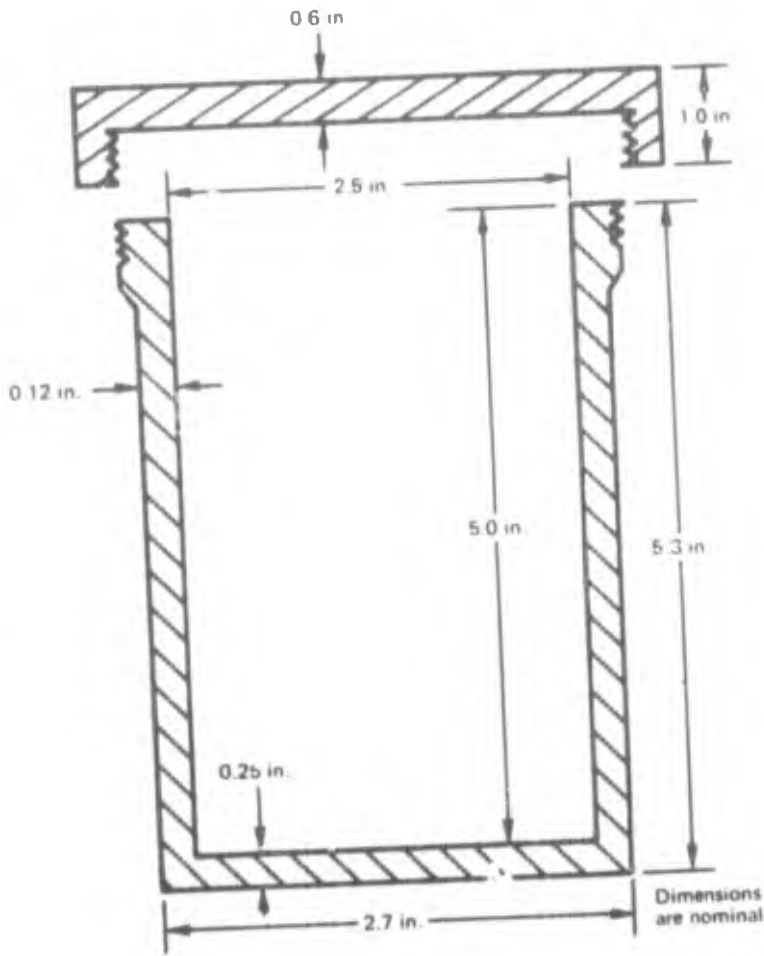


DIAGRAM OF BASIC BODY OF SCB

LOADED SCB READY FOR TEST

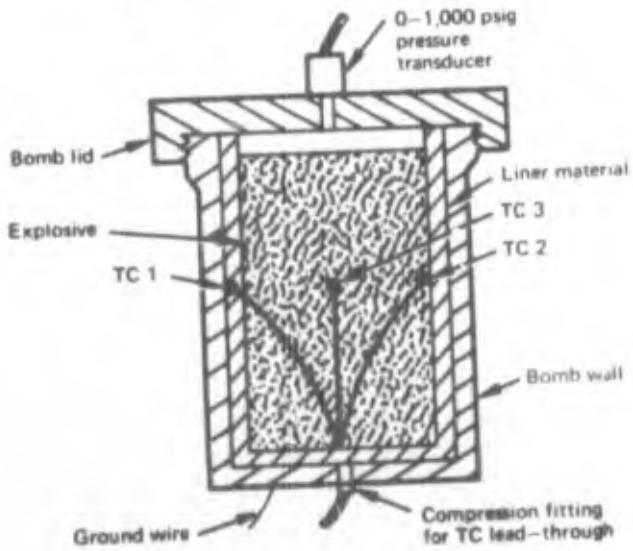


FIG. 2. Small-Scale Cookoff Bomb (SCB).

TEST PROCEDURES

The candidate liner, coating, and sealer materials were tested by all or some of the given experimental techniques. When the materials were tested with explosives, the tests were performed in such a manner that different problem areas could be uncovered. For example, the sample would be tested first with TNT to see what reactions might be encountered, then with Composition B, and finally with H-6 explosive. Reactions occurred with both TNT and RDX (a component of both H-6 and Composition B) and, if water came off from the material, there was a possibility of a reaction with the aluminum in the explosive. Each candidate material studied is reported separately and a comparison is made to standard materials wherever possible.

H-6 was the standard explosive used in these tests, except when it was felt that Composition B would be better since the aluminum present in the H-6 explosive could interfere with certain testing techniques. In some cases, TNT was used as the test explosive. The thermal stability of H-6 explosive is reported in Ref. 4; Composition B and TNT in Ref. 7.

The thermal decomposition of Composition B and TNT, when combined with the liner and sealer materials, is reported in Ref. 1, 2, and 3. This study was part of a compatibility investigation on the various materials when they were in contact with explosives. This established the kinetic parameters of the reactions. In general, accelerations in decomposition rates were observed and reported, and in some cases these reactions were extreme, i.e., explosions.

TEST RESULTS

HOT-MELT (BLACK MIX) LINER

The hot-melt (black mix) liner is the standard liner currently used as the interface material between the metal bomb case and the explosive. And since it was to be used as a comparison model against the candidate liners, a complete investigation was made of its thermal and physical properties.

The hot-melt material is a tar-like substance; it is soft and gummy at room temperature and has the characteristic odor of road tar. The average melting point was $140 \pm 6^\circ\text{C}$. The immersion density at 23°C was 0.999 grams per cubic centimeter, with a spread of 0.007.

The TGA-DTG-DTA thermal patterns of hot melt are shown in Fig. 3. The hot melt began to lose weight slowly at about 220°C and very rapidly at 360°C. There was a 12% weight loss to 360°C, then an additional 87% to the 550°C level leaving a residue of 1%. The onset to the exothermic action began at about 270°C and became more pronounced after 360°C. This exothermic action was probably the oxidation of the products coming off the hot melt.

The DSC thermal pattern showed that the hot melt began to smoke and boil at ~ 440 to 450°C. This was observed on a 6-milligram sample that was run at a heating rate of 20°C per minute. The thermal pattern showed strong endothermic action beginning at about 443°C, which indicated the boiling of the hot melt. The smoking indicated that thermal decomposition was probably taking place as the material boiled. No exothermic action was observed since the DSC sample was protected from air.

The heat capacity (c) was determined at several temperatures from thermal patterns obtained on the DSC and the results were:

<u>Temperature, °C</u>	<u>c, cal/grsm</u>
57	0.39
77	0.40
127	0.43
177	0.48

The thermal diffusivity, α , was calculated from thermal analysis data and Eq. 1:

$$\alpha = \frac{a^2}{4\Delta T} \frac{dT}{dt} \quad (1)$$

where:

a = radius, cm

ΔT = differential temperature, °C

$\frac{dT}{dt}$ = heating rate, °C/sec

The sample was contained within a cylindrical metal tube which was closed at one end. The tubes were 8 inches long and had an inside diameter of either 2 or 3 1/2 inches. One thermocouple was installed inside the tube wall and one in the center of the sample, both at the same distance from the end. Heat was applied to the outer metal wall (via electrical heating ribbon) at a constant heating rate. The heating rate was obtained from the thermocouple in the tube wall and ΔT from the difference between the two thermocouples. Each sample size was tested several times and an approximate value was determined in the range of 20 to 113°C. The value for α was 1 to 2 x 10⁻³ square centimeters per second.

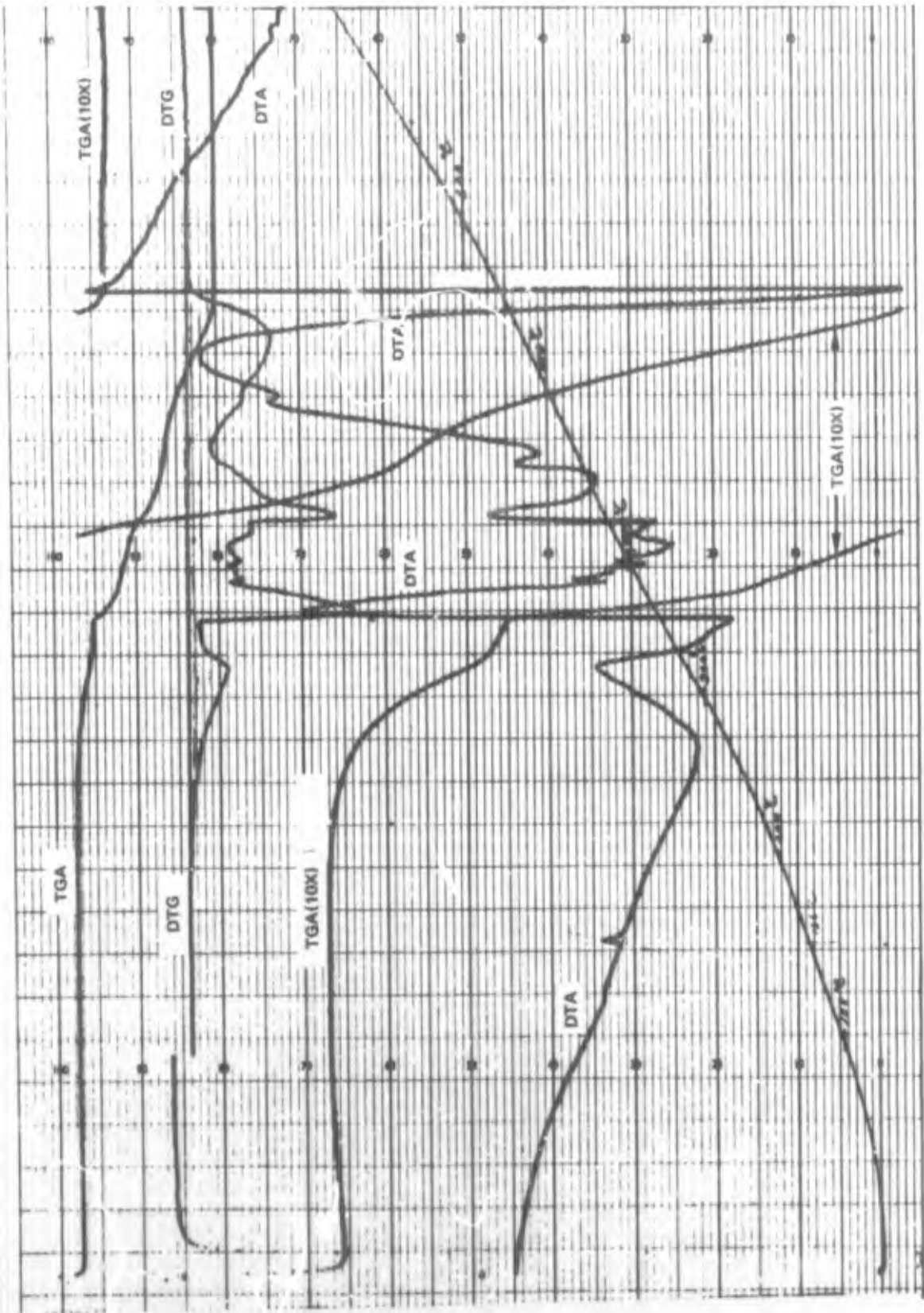


FIG. 3. Thermal Patterns of Hot-Melt Liner at Heating Rate of 5°C/min. (Sample wt: 17.437 mg; Run No. 1-15-3.)

A cookoff test was made with an SCB test unit. The small bomb had about a 1/4-inch-thick liner of hot melt and was loaded with H-6 explosive. Cookoff time was 3.7 minutes; the reaction was labeled as a deflagration (Ref. 5). This time value should correspond to the actual time to cookoff of a similarly loaded Mk 82 bomb.

Samples of both regular hot melt and high-temperature hot melt were aged under sealed conditions in an SPB test unit. The temperature was controlled isothermally at 200°F for about 6 days. Only a small pressure buildup of 5 to 10 psig was recorded. The decomposition gases were analyzed on a mass spectrophotometer. Both hot melts showed an absorption of mass 32 as compared to mass 28 and 16, with emission of masses 15, 18, 26, 27, 29, 39, 42, 43, and 58. Mass 18 was quite strong from the regular hot melt, indicating that water was coming off.

The compatibility of hot melt with Composition B and TNT explosives was studied in the temperature regions of 180 to 240°C and 160 to 270°C, respectively (Ref. 1 and 2). It was found that the hot melt increased the decomposition rate of the explosives.

THIOKOL LINER

This liner material was received from the Thiokol Chemical Corporation. The composition of the material was not known. A sample of this material was checked with the H-6 explosive and no action was observed in the ambient temperature region.

The TGA-DTG-DTA thermal patterns on this material are shown in Fig. 4. This material started to lose weight slowly at about 100°C, becoming rapid at 300°C. By 400°C, the weight loss was 74%, and by 475°C the sample was completely gone. The material started to go exothermic at about 300°C (apparent air oxidation). This would indicate a compatibility problem in the high temperature region.

The internal cavity of an SCB test unit was coated with approximately 1/4-inch-thick Thiokol liner material and then loaded with H-6 explosive. Cookoff time was 4 minutes. The bomb wall split open and the reaction was defined as a deflagration (Ref. 5).

A cookoff test was performed on a Mk 82 bomb which was similarly prepared and loaded. The bomb was subjected to an enveloping flame from burning jet fuel; cookoff time was 5.25 minutes. The predicted time to cookoff for the Mk 82 bomb was 7.6 minutes. This estimate was calculated from the data on a sand-filled Thiokol-lined Mk 82 bomb subjected to an enveloping flame. The heating rate and temperature data on the inner surface of the Thiokol liner were used for the calculations. At the heating rate of 0.8°C per second, the ignition temperature of H-6 explosive would be 263°C (from Fig. 34 of Ref. 8). Using the temperature-time data from the sand-filled bomb, it was determined that the H-6 explosive would require

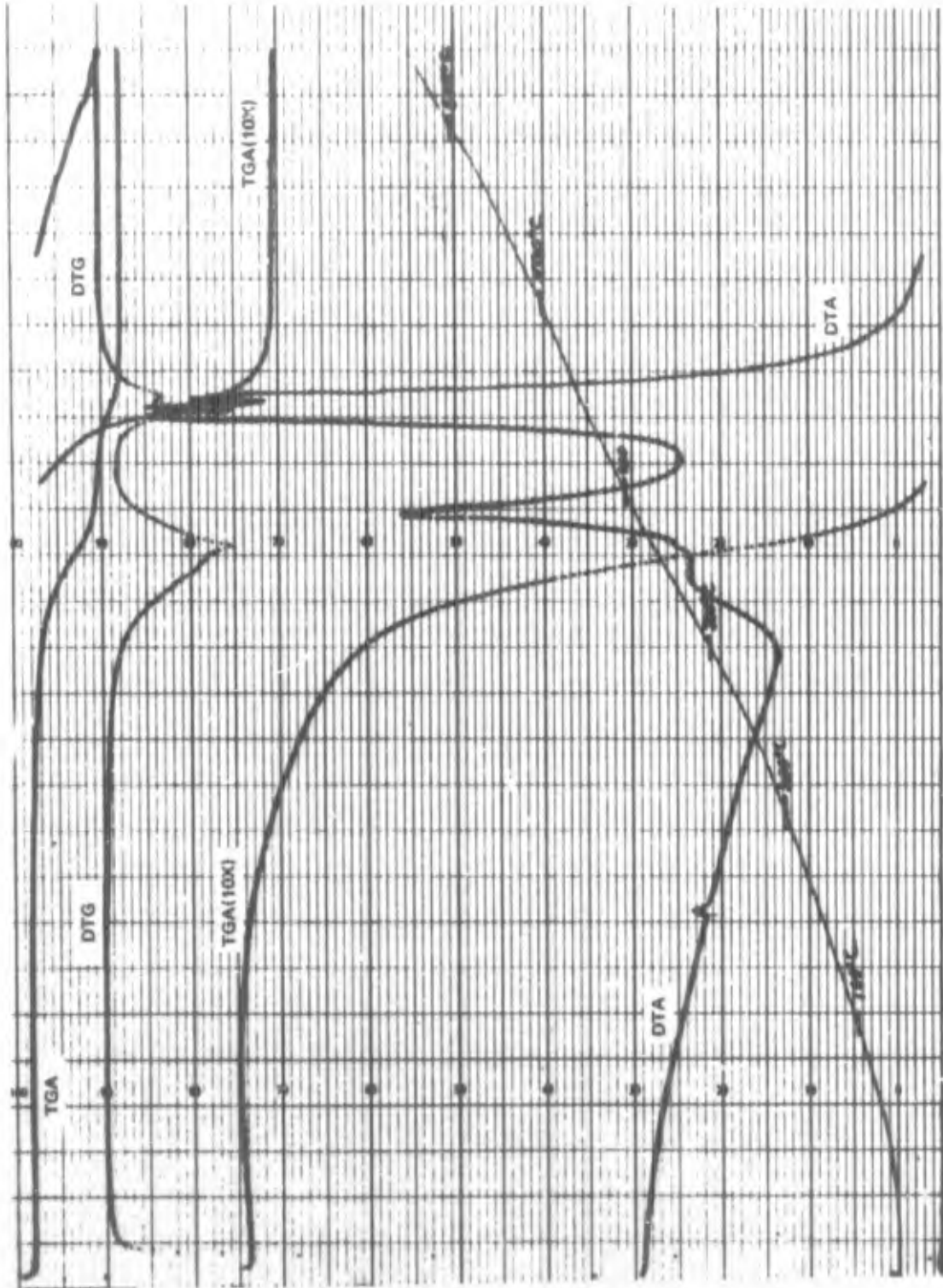


FIG. 4. Thermal Patterns of Thiokol Liner at Heating Rate of 5°C/min. (Sample wt: 10.33 mg; Run No. 1-18-3.)

7.6 minutes to reach the ignition temperature and consequently cook off. The "cookoff time" for the sand-filled bomb might have occurred sooner but a wind condition existed at the test site causing the flame envelope to momentarily move away from the bomb. Because of this, the heating rate was only 0.8°C per second in the 200 to 300°C temperature region at the inside surface of the Thiokol liner. This rate was much lower than the 1.9°C per second value in the same temperature region at the inside surface of the SCB. These tests indicated that the Thiokol liner was no better than the present standard or hot-melt (black mix) liner used in the Mk 82 bombs.

Studies on the decomposition of TNT and Composition B in the presence of the Thiokol liner are covered in Ref. 3. That report emphasizes the fact that the liner accelerates the decomposition reaction of the explosives.

No additional tests were made on this liner as the above studies indicated that this liner would not offer any significant advantages over the standard hot-melt liner.

ISI LINER

This liner material was received from Insulation Systems, Incorporated, and it was referred to as Plastonium 44. Some formulation changes were made by the supplier as testing was in progress. Therefore, data shown may not be actually representative of the final ISI product.

This liner material gave off water in the low temperature region, as shown in the TGA-DTG-DTA thermal patterns (Fig. 5). The elimination of water resulted in a weight loss of 8%. At about 300°C , this liner decomposed exothermally and incurred an additional weight loss of 12% (apparent air oxidation). The total weight loss was 20% for the entire run to 650°C . The water would be a compatibility problem with any explosive containing aluminum, i.e., generation of hydrogen gas.

The time to cookoff was 7.25 minutes for the SCB which contained H-6 explosive and a 1/4-inch-thick ISI liner. When a similarly loaded Mk 82 bomb was subjected to an enveloping flame, the cookoff time was 11.2 minutes. The heating rate in the 200 to 300°C region at the metal wall/liner interface in the small bomb was 1.2°C per second, and in the Mk 82 bomb the rate was 1.0°C per second. The results from both tests were considered explosions (Ref. 5).

Under isothermal test conditions the half-lives for the decomposition of Composition B and TNT, in the presence of the ISI liner, were reduced one-half at 170 and 190°C , respectively. This indicated that the ISI liner material accelerated the decomposition of both explosives (Ref. 3).



FIG. 5. Thermal Patterns of ISI Liner at Heating Rate of 5°C/min. (Sample wt: 12.415 mg; Run No. 1-24-4.)

The ISI liner showed a considerable improvement over the hot-melt (black mix), but it had one serious drawback. This material was somewhat water-soluble; about 25% of its original weight would dissolve and cause the material to disintegrate. Obviously, this material could not be used inside a Mk 82 bomb containing a water-slurry explosive, a candidate consideration for the alternate fill program.

URP-2 LINER

This liner material was received from United Resin Products. This material is designated URP-2 since a prior sample received from this company had a different composition.

The DTA-TGA-DTG thermal patterns showed that the URP-2 material had excessive exothermic heat generated above 200°C. It also started to lose weight rapidly above 200°C and by 500°C the sample had a weight loss of 97% (Fig. 6).

The time to cookoff was 4.1 minutes for the SCB which was loaded with H-6 explosive and had a 1/4-inch-thick URP-2 liner. The heating rate, in the 200 to 300°C region, was 1.5°C per second at the metal wall/liner interface. The cookoff reaction was considered a deflagration (Ref. 5).

Of all the liner materials tested, URP-2 was the most inert. It produced only small accelerations in the decomposition of Composition B and TNT (Ref. 3). The problem with URP-2 was the material itself in that it melted below 150°C and had exhibited rapid exothermic decomposition above 200°C. This is a rather low temperature to observe oxidation of a sample. The URP-2 material showed a marginal improvement over the hot-melt (black mix) liner now used in Mk 82 bombs. Although it has no apparent compatibility problems, URP-2 may have a low ignition temperature.

TSI LINER

This liner material was received from Thermal Systems, Incorporated. The composition of the material was unknown. A sample of the liner was checked for compatibility with H-6 explosive at ambient temperature. There were no apparent problems present.

The TGA-DTG curves show that the material started to lose weight at 150°C, the loss became rapid after 200°C, and by 350°C there was a weight loss of 50%. From 350 to 500°C, the sample had an additional weight loss of 36%. The DTA thermal pattern indicated strong exothermic action starting above 350°C (apparent air oxidation) (Fig. 7).

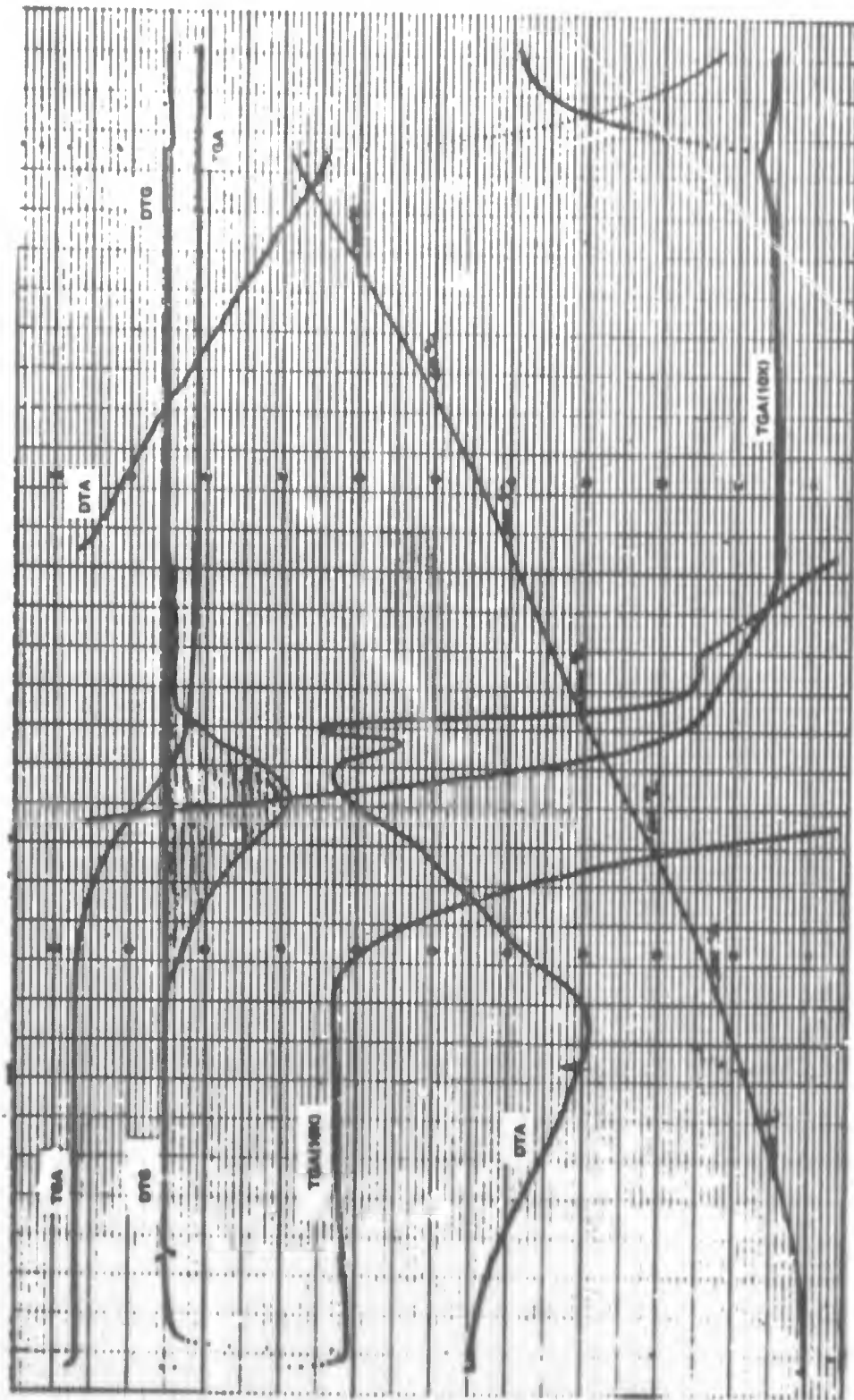


FIG. 6. Thermal Patterns of URP-2 Liner at Heating Rate of 5°C/min. (Sample wt: 16.11 mg; Run No. 1-15-4.)

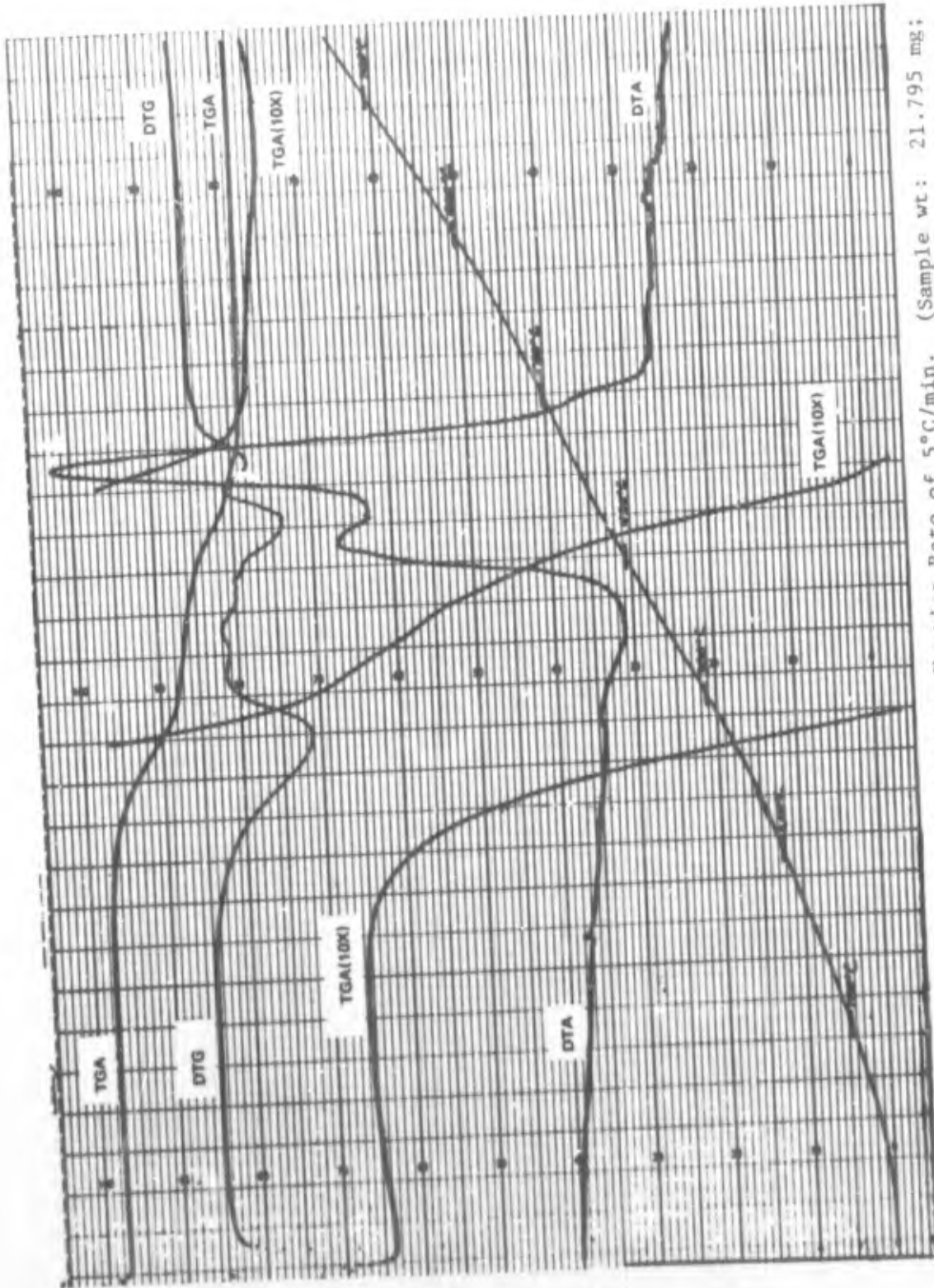


FIG. 7. Thermal Patterns of TSI Liner at Heating Rate of 5°C/min. (Sample wt: 21.795 mg; Run No. 1-16-3.)

A cookoff test was made with an SCB which was lined with about a 1/4-inch-thick layer of TSI material and loaded with H-6 explosive. The time to cookoff was 4.45 minutes and the reaction was labeled a deflagration (Ref. 5).

It was reported in Ref. 3 that this material softened at about 138°C and melted completely to a black viscous fluid at 160°C, with general breakdown starting at 150°C. It was also stated that the TSI liner increased the decomposition of Composition B and TNT by a factor of 10 at 170 and 190°C, respectively. The results indicated serious compatibility problems.

From its chemical, physical, and compatibility properties, the TSI liner material would be inferior to the hot-melt (black mix) liner now in use in Mk 82 bombs.

ESSEX LINER

This liner material was received from the Essex Chemical Company.

The TGA-DTG-DTA thermal patterns on the Essex liner are shown in Fig. 8. The material started to lose weight at about 200°C. The weight loss became rapid after 250°C and by 450°C it was a weight loss of 90%. The liner material exhibited strong exothermic reaction above the 300°C level.

An SCB was lined with a 1/4-inch-thick layer of Essex material and loaded with H-6 explosive. The time to cookoff was 3.2 minutes. For a similar test with a hot-melt (black mix) liner, the time to cookoff was 3.7 minutes.

In Ref. 3, the Essex liner was found to greatly accelerate the reaction of Composition B and TNT explosives. It rated among the top of the group as being the least compatible liner with these explosives.

The above data indicated that the Essex liner material would be an undesirable replacement for the standard hot melt (black mix) now used in Mk 82 bombs.

UNIQUE LINER

The Unique (UPI-1000) liner material was received from Unique Products, Inc. (later represented by Rocketdyne). This material is made from a two-part system (referred to as Part "A" and Part "B"). It was studied in both the cured and uncured state; the individual parts were analyzed also. Since this product showed promise in the preliminary screening tests, an intensive study was made on this material. The study covered the physical, chemical, and compatibility properties of this material.

As shown by the DTG and TGA curves in Fig. 9, the cured Unique material seemed to decompose by one minor and two major steps when heated at a constant rate. In the minor step region preceding the start of the first major step (260°C), the TGA curve shows that the sample had a weight loss of 3% due to water and other volatiles. During the first major step (260 to 450°C), the sample lost 75% of its weight. During the second major step (450 to 500°C) it lost an additional 15%, leaving 7% of residue after 500°C. Between 350 and 400°C, the material underwent endothermic decomposition; after 400°C, the reaction became exothermic.

An isothermal weight loss study was carried out to investigate the first two steps involved in the decomposition. The first step (minor) was the loss of water, which was going on from ambient temperature to about 190°C. The heat of vaporization or decomposition of this first step is shown in Fig. 10, with a value of 10.2 kcal per mole. This proved to be water by the use of the mass spectrophotometer and IR analysis, and also that the heat of vaporization (assuming water) was 565 cal per gram. The water, coming off in such large amounts at a temperature below the loading temperature of an aluminized explosive (H-6), would cause serious storage problems. The second step (first major) was the loss of a "liquid" which separated from the remaining solid material. The composition of this liquid was not known but IR analysis indicated that it was from Part "A" of the original two-part system. The heat of vaporization or decomposition of the "liquid" from Part "A" was 13 kcal per mole in the 200 to 300°C temperature region (Fig. 10). This material appeared to be reactive with the TNT explosive as indicated by the formation of a reddish compound.

If this Part "A" and water could be generated on the hot steel inside surface of the Mk 82 bomb during a fire, the water would act as the "carrier" for Part "A". They would then migrate through the liner to the explosive interface and a cookoff would occur on contact with the explosive.

To demonstrate this point, a 1-inch-diameter by 1/2-inch-thick sample of UPI-1000 was cured on top of a 1/4-inch-thick piece of 3- by 4-inch steel plate. A guard ring of insulation material was used to protect the sides of the UPI-1000 material. Thermocouples were located at the steel/UPI-1000 interface and on top of the UPI-1000. Heat was applied to the bottom of the steel plate. A schematic drawing of the setup for the fast-heat test is shown in view A of Fig. 11. A plot of the log heating rate versus temperature for the steel plate was compared to that of a sand-filled Mk 82 bomb in a standard cookoff fire; the heating rates were similar. The experimental data showed that the surface temperature of the UPI-1000 did not exceed 100 to 110°C during the test period of 5 to 7 minutes.

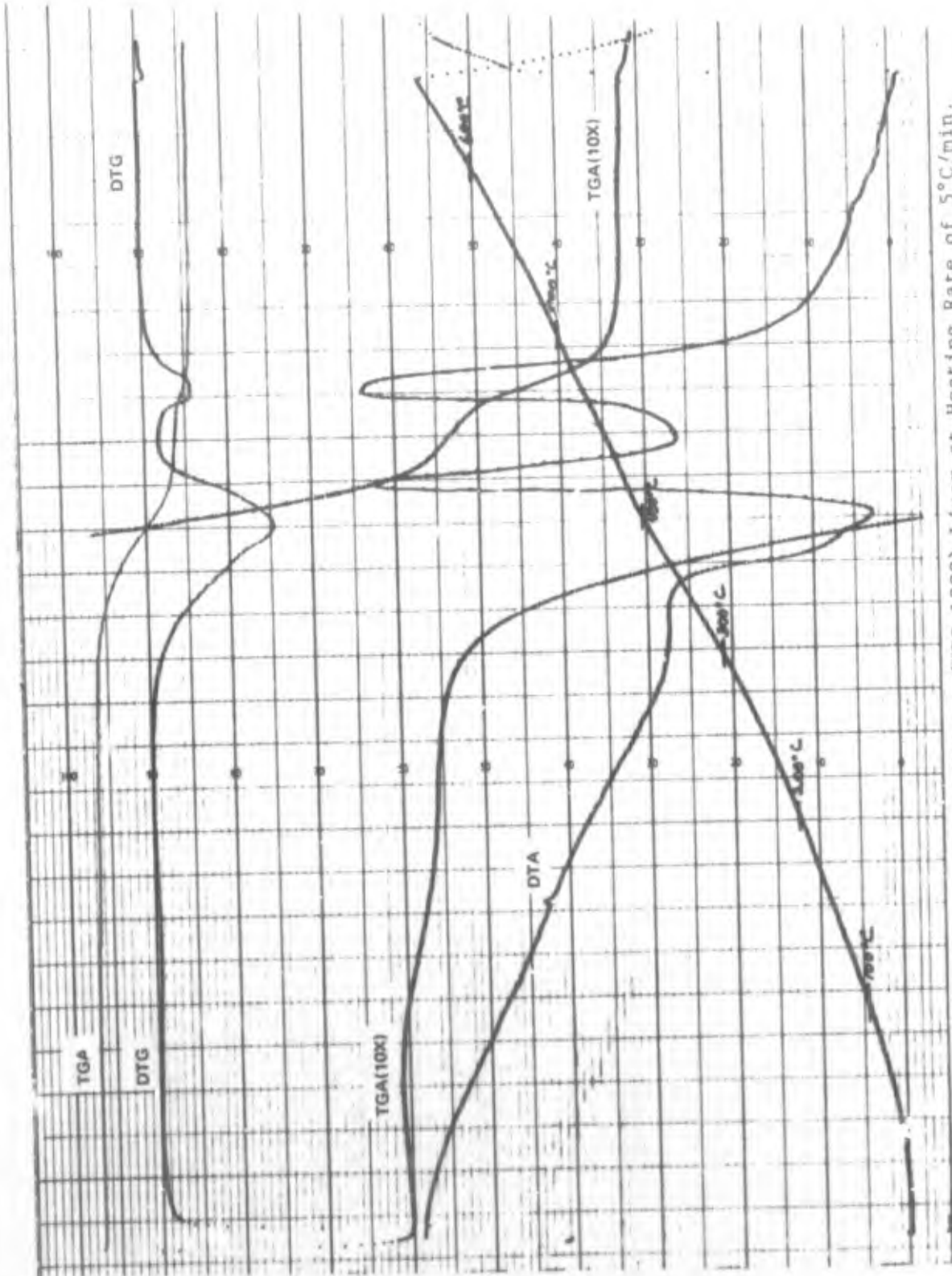


FIG. 9. Thermal Patterns of Unique (UPI-1000) Liner at Heating Rate of 5°C/min.
(Sample wt: 13.74 mg; Run No. 1-25-3.)

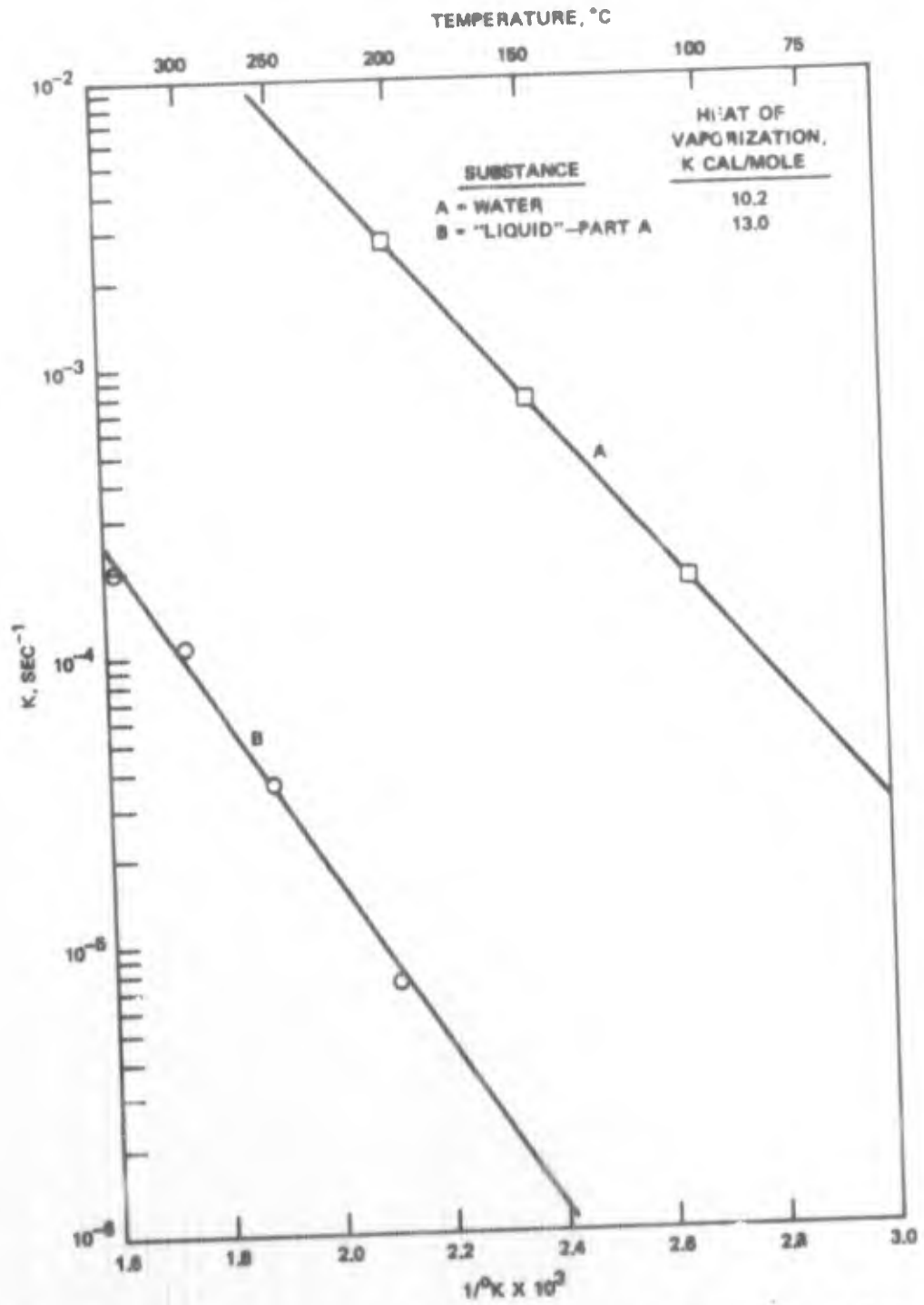


FIG. 10. Plot of Specific Rate Constant Versus Temperature for Decomposition Products of Unique Liner Material.

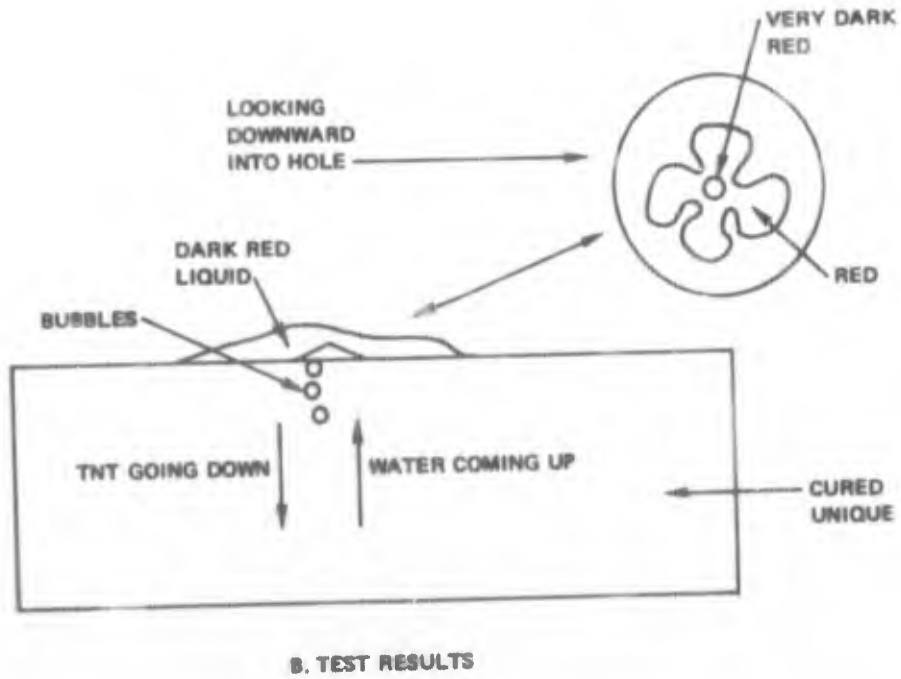
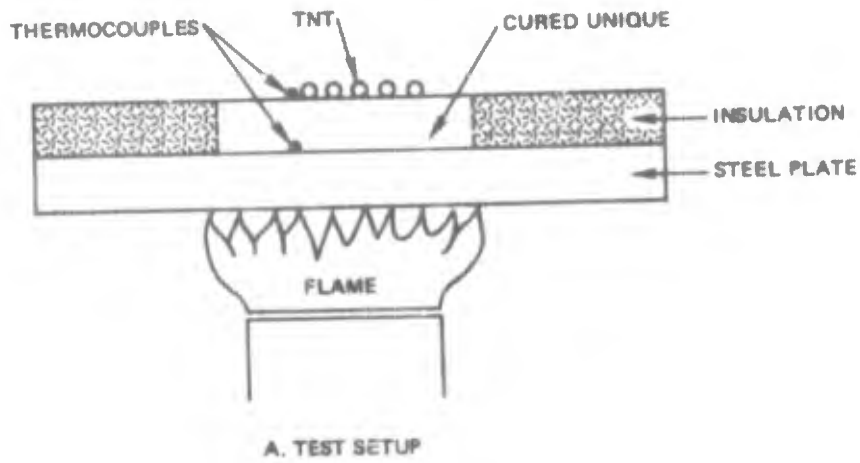


FIG. 11. Schematic Drawing of Fast-Heat Test on Cured Unique Liner Material.

For subsequent tests, 30 to 50 milligrams of TNT were placed on top of the Unique disc. During each test, the TNT started to melt when a liquid formed on the top surface of the disc. The boiling liquid appeared to form "mud pots" on the surface of the Unique material. The melted TNT appeared to go down the "mud pot holes" caused by the bubbling liquid. The TNT would change color to bright red. On cooling, a reddish colored waxy material was present. A schematic drawing of the test results is given in view B of Fig. 11.

A related fast-heat study was made at the NASA Ames Fire Test Facility. First, a 1-inch-diameter hole was machined in the center of a 3- by 3- by 1/4-inch steel test plate. Then, a 7/8-inch-diameter by 1/4-inch-thick steel button was potted in the 1-inch hole, using a high-temperature potting material. The test plate was held in a horizontal position. A 7/8-inch-diameter wafer of the Unique liner material was placed on top of the button and a thermocouple bead was placed on top of the wafer. An approximately 3-inch-thick piece of foam was used to insulate the wafer and top of the test plate. The fire side of the test plate was coated with carbon black to provide better heat conduction through the steel.

Three Unique wafers were tested at Ames; the samples were 0.150-, 0.242-, and 0.305-inch-thick. A log plot of time versus the reciprocal temperature is shown in Fig. 12. For comparison, a plot of data for a bare steel reference point from a sand-filled Mk 82 bomb is included. Data from an SCB cookoff test and a 1/16-inch bare steel plate are also shown. As can be seen, the lines are approximately parallel when the heat input is the same. Any change in the slope is due to a change in heating rate, e.g., the Mk 82 steel temperature, or decomposition of the Unique liner material.

Because of the results obtained from the two fast-heat studies, additional tests were made on UPI-1000. The cured Unique material was tested at various temperatures from ambient to about 120°C, alone and with TNT. At ambient temperatures the compatibility of the cured Unique liner material appeared to be good, but the uncured material, and particularly Part "A" of this system, reacted with TNT to form a reddish-type compound. However, at temperatures between 90 and 120°C, even the cured Unique material would break down and produce a red colored "liquid" as one of the end products. The original materials and the end products of the cured and uncured Unique material were analyzed by the DSC, IR, and mass spectrophotometer. This chemical study indicated the presence of serious compatibility and aging problems.

The various studies showed that parts of this system reacted with TNT to form a reddish-type compound. It is known that TNT will react very easily, with amines or alkaline material, yielding compounds that are no longer TNT. Numerous investigations, carried out to elucidate the possible structures of these substances, have given no definite

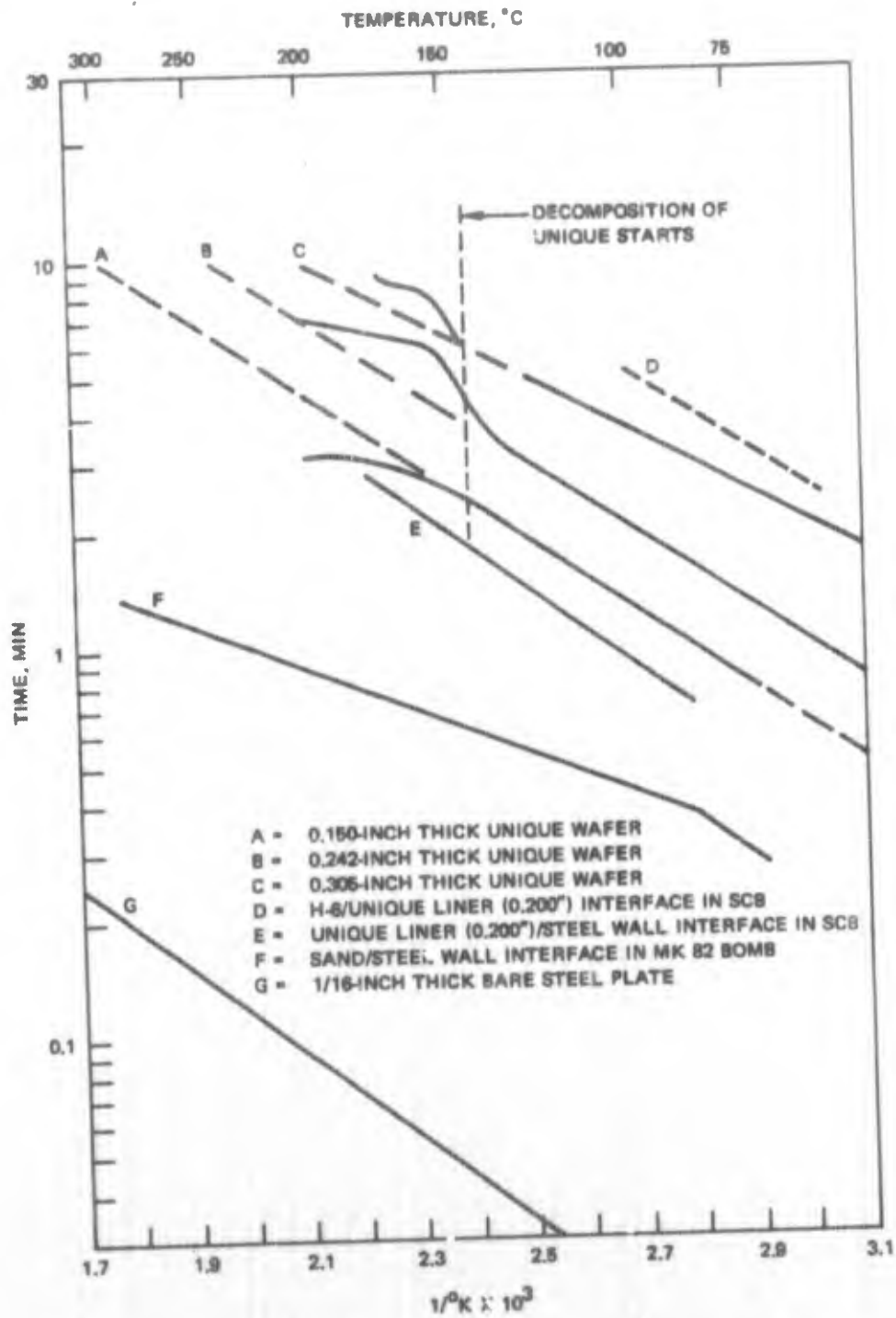


FIG. 12. Results of Ames Fast-Heat Study on Cured Unique Material.

answer as yet. Although no definite answer is known, it has been stated repeatedly that these products are much more sensitive to heat, impact, and friction than TNT by itself. Their high sensitiveness is of greatest practical importance, and it is a warning that great care should be taken to avoid bringing TNT into contact with these materials, especially in the presence of organic solvents (Ref. 9).

The hand-mixed material had problems at low temperatures. In the temperature range of -40 to -54°C , the material cracked badly. The machine-mixed material was better and only showed some cracking after four days at -54°C and 8 days at -34°C (Fig. 13). The DSC thermal pattern and the 3-inch-diameter solid cylinder both showed endothermic action at -35 to -39°C and at 0 to -12°C (melting-freezing). The melting-freezing temperature point (0 to -12°C) was due to the water present in the material. It was not known what caused the endothermic action at -33 to -30°C .

The thermal diffusivity (α) was calculated by Eq. (1) and the thermal data from a 3-inch-diameter by 8-inch-long solid cylinder of the material. The value for α was 9.4×10^{-4} cm^2 per second in the temperature range from ambient to about 140°F .

After aging in an SPB at 75°C (165°F) for a total of 37 days, the Unique material caused the development of ~ 5 pounds of pressure within the vessel. A bomb with no sample showed about 1.5 pounds of pressure in the same time period. After the first 4 days, the material apparently absorbed oxygen from the air because the mass 32, when compared to mass 38 or mass 40, had been reduced by about one-third or less over normal air. After 37 days, some of the oxygen had de-absorbed; the oxygen measured about one-half that of normal air. Masses 17, 18, and 44 were present over the air background. Mass 17 is due to OH^+ and possibly NH_3^+ , mass 18 is due to water, and mass 44 is due to carbon dioxide. The latter two were confirmed by IR analysis.

The SCB study was done with sealed containers lined with the Unique material, of various thickness, and loaded with H-6 explosive. Pressure and temperature data were recorded while the bombs were electrically heated. The results are given in Table 2. The pressure did not get too high (~ 35 to 250 pounds) probably due to the water coming off. The water had a cooling action and this behavior was noted in the thermocouple data in each time-temperature plot; usually, the time-temperature curve showed a "dip" in the 100 to 200°C region. In the 300 to 400°C temperature region, the "liquid" was apparently separating and coming off and this may have accounted for the majority of the samples having about the same cookoff time regardless of the liner thickness. This would not be seen in the compatibility study by Joyner (Ref. 1, 2, and 3) since his tests were 100 to 200°C lower in temperature. These studies indicate that when the inside steel temperature of a container (Mk 82, etc.) reaches about 400 to 450°C cookoff would occur.

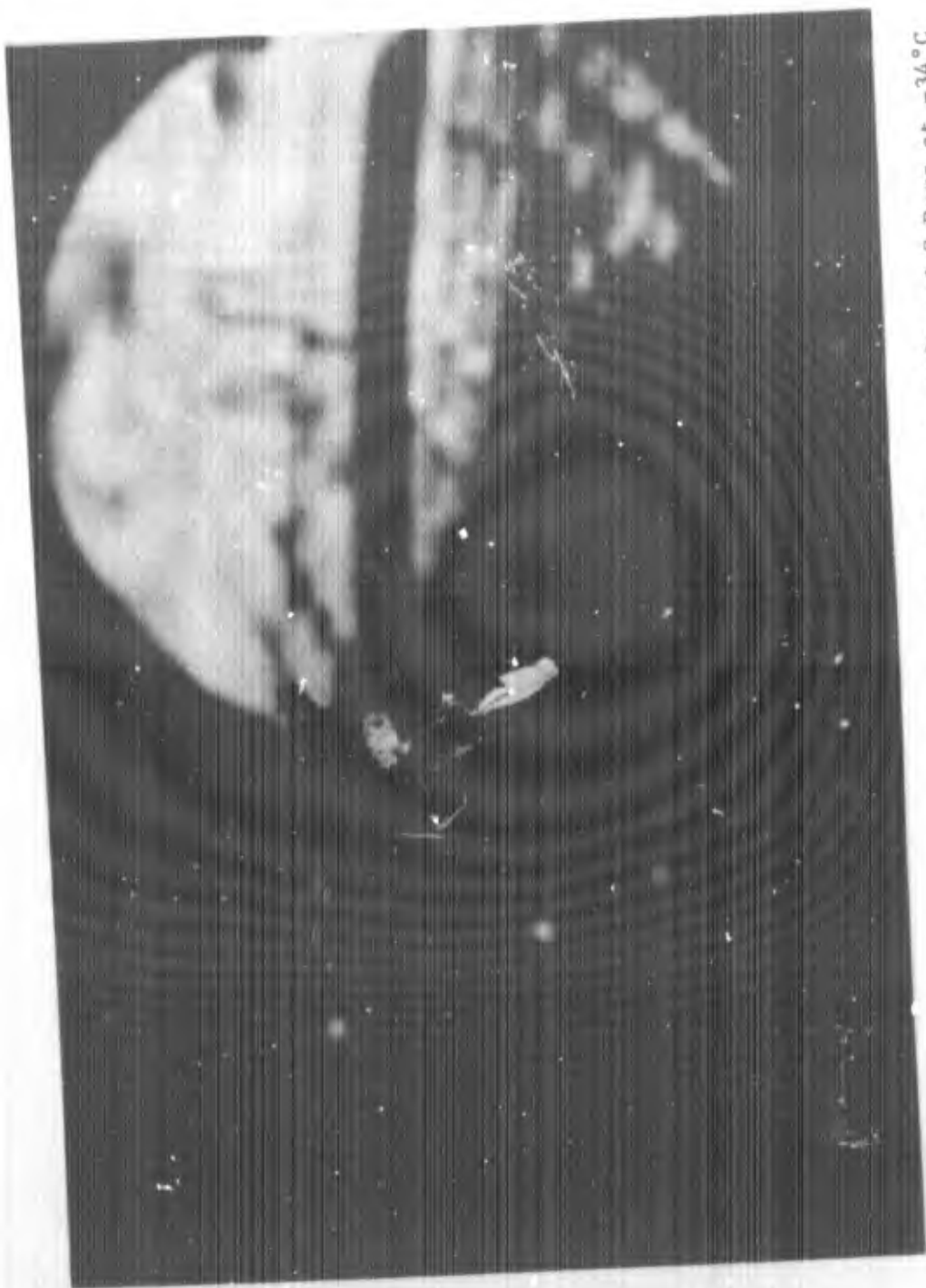


FIG. 13. UPI-1000 Liner in a Mk 82 Bomb After 4 Days at -54°C and 8 Days at -34°C (LHL-153485).

TABLE 2. SCB Results with H-6 Explosive and Unique Liner.

Liner thickness, in.	T_0^a , °C	T_1^b , °C	T_m^c , °C	ϕ^d , °C/sec	Cookoff, min.	Press, ^e PSIG	Steam, ^f °C
0.188	20	45	115	1.58	3.30	---	---
0.200	35	61	194	2.65	5.00	190	195
0.200	29	33	108	1.32	4.77	---	---
0.250	30	29	162	2.20	4.15	246	207
0.250	35	37	177	2.37	4.78	85	164
0.300	36	37	144	1.80	2.10	33	137
0.300	30	30	93	1.05	5.25	62	154

^aTemperature at zero time

^bTemperature at liner/explosive interface after 1 minute

^cTemperature at metal/liner interface after 1 minute

^dHeating rate at metal/liner interface during first minute

^eFinal pressure at time of cookoff

^fTemperature of steam at final pressure

A test was made on a sand-filled Mk 82 bomb with a 0.215-inch-thick Unique liner and that had Tuffseal as a sealer between the sand and the aft end plate. There were 20 thermocouples located internally and four located adjacent to the outside skin to record the flame temperature. The time-temperature plots of the thermocouples were made for their first 10-minute exposure to the enveloping flame. Theoretically, by using the above data and assuming that the liner acts as a true insulator until it breaks down, then cookoff should not occur until after about a 7- to 10-minute exposure to an enveloping flame. However, if the liner material gives off a "liquid" at about 400 to 450°C, which is not compatible with TNT, then cookoff would occur in about 4 to 6 minutes.

A second test was made with a Mk 82 bomb which had a Unique liner and was filled with H-6 explosive. This bomb also used Tuffseal as a sealer between the bomb load and the aft end plate. The live bomb cooked off in less than 4.5 minutes. Evidently, the bomb cooked off as predicted previously, i.e., a "liquid" was generated and it caused an early cookoff time.

An H-6 explosive-filled Mk 82 bomb, with a UPI-1000 liner, was subjected to 28 days of temperature/humidity cycling from -54 to $+74^{\circ}\text{C}$ (-65 to $+165^{\circ}\text{F}$) in accordance with Ref. 6. After the test, the bomb was cut open and inspected. The UPI-1000 liner had rusted the steel bomb and had become easily separated from the metal shell. The liner had a top coating of black cavity paint as a potential interface barrier to the explosive. This paint had little, if any, effect on keeping the explosive from reacting with the UPI-1000 or on keeping the two surfaces together. A graphic view of this surface is shown in Fig. 14. An IR analysis of a sample, taken from the UPI-1000 surface, showed that it contained TNT. After aging for about a month, the UPI-1000 surface appeared to contain evidence of TNT crystal growth.

In summary, the UPI liner suffered from the following: low-temperature cracking, short cookoff times, raw material incompatibility with explosives, reactivity with Composition B and TNT (Ref. 3), and thermal breakdown of liner material at temperatures of 40°C and above. On accelerated aging, it easily gave off water and a "red liquid"; this "red liquid" appeared to react with TNT. The liner material became brittle at low temperatures (-54°C to ambient), soft at temperatures above 93°C , and the liner would burn in a fire. There was a quality control problem, e.g., the amount of water loss varied from sample to sample, the liner thickness varied from about $1/4$ inch to more than 1 inch in the Mk 82 bombs, and Parts "A" and "B" hardened and separated on storage. It is possible that other undiscovered problem areas may be encountered with this liner material. The above data indicated that it should not be used as a liner in a bomb where contact with an explosive is possible.

NO LINER

To compare the data from small cookoff bombs, H-6 explosive was cast into an SCB which did not contain any liner material. For this test, the time to cookoff was 1.75 minutes. The results of this test and all tests with liners are shown in Fig. 15. The approximate power curve was taken as an average value from the individual tests. The heating rate was about 1.6°C per second in the 50 to 300°C region. All liner materials offered an improvement over the bare steel. Of all liners, the ISI material showed the most improvement. However, the ISI liner contains water and is water soluble and it would not be compatible with a water-slurry explosive or H-6 explosive.

PFIZER COATING

This coating material was received from the Universal Propulsion Corporation.

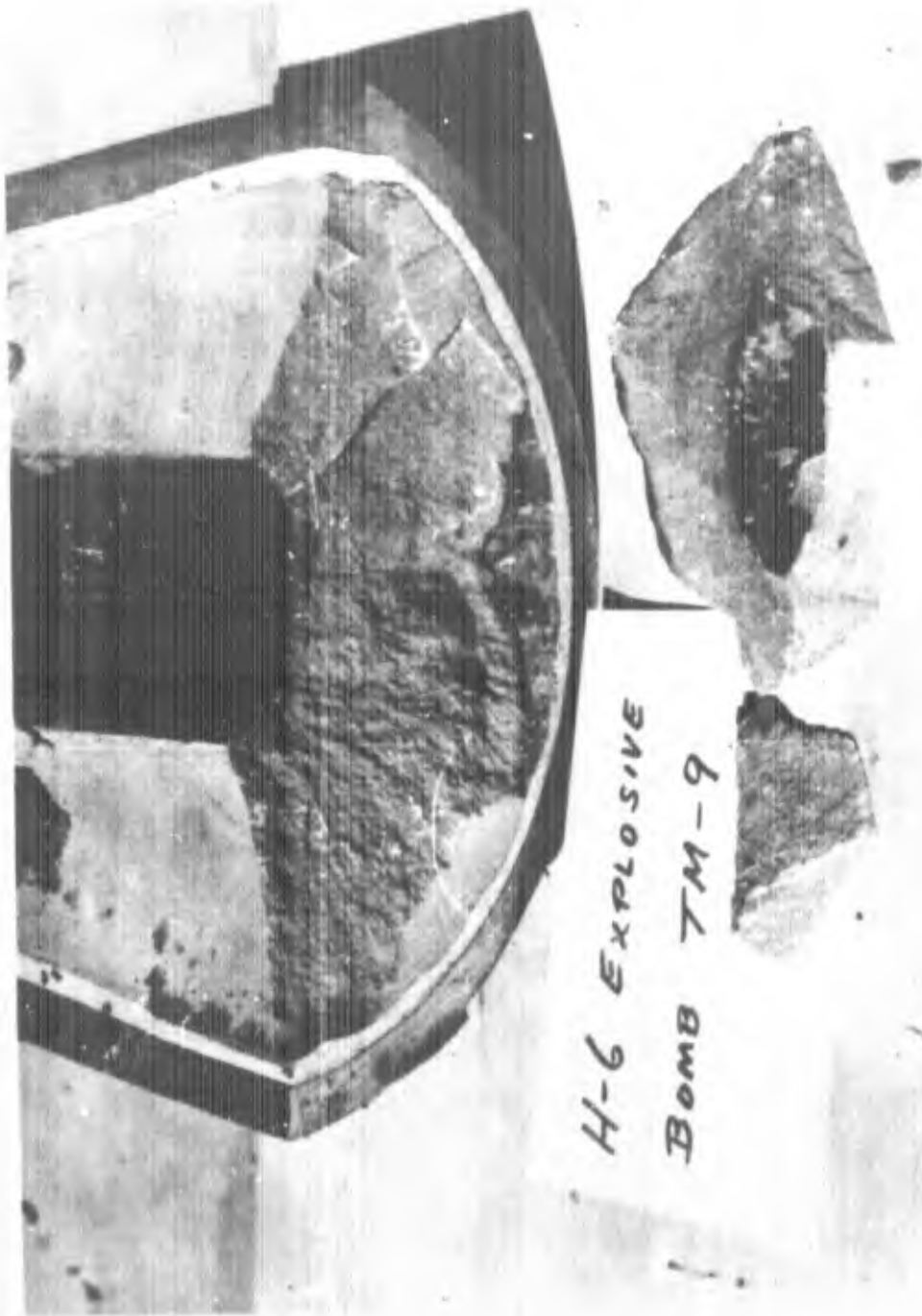


FIG. 14. Mk 82 Bomb With UT-I-1000 Liner After 28 Days Cycling from -54 to $+74^{\circ}\text{C}$ (LHL-156249).

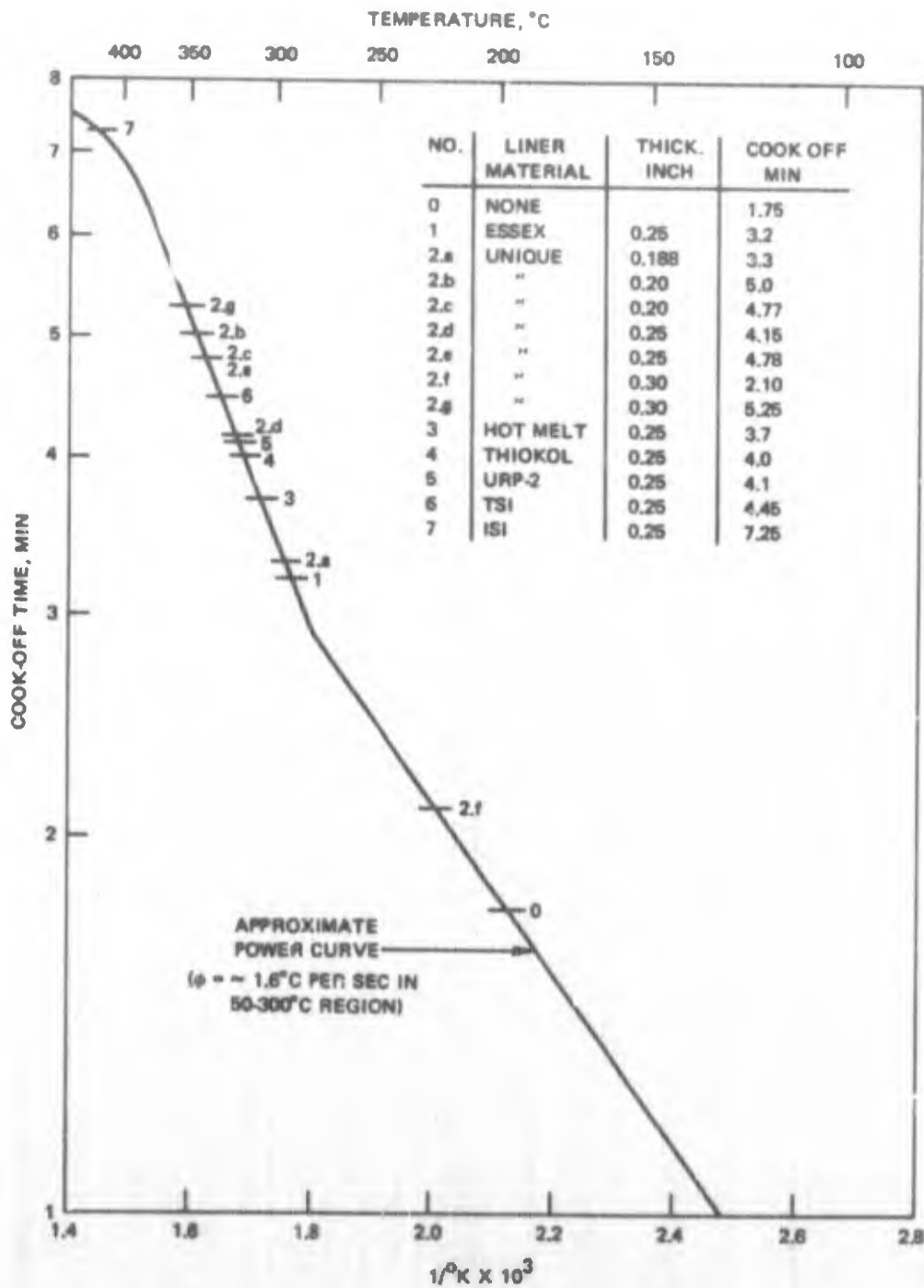


FIG. 15. Comparison of SCB Cookoff Data Using H-6 Explosive.

As shown in the TGA-DTG-DTA thermal patterns (Fig. 16), the coating material started to lose weight at 70 to 75°C. Above the 100°C level the weight loss rate increased and the sample had a weight loss of 63% at the 700°C level. The DTA curve showed that the decomposition reaction was endothermic to 275°C, thereafter becoming exothermic, due to the burning of the binder. At the end of the test run, there was about 37% residue in the sample holder.

An IR pattern was obtained on a sample which had been pyrolyzed at 500°C for a 1-minute period. Absorption peaks were present at 1,730, 1,360 and 1,210 cm^{-1} , which indicated the thermal breakdown of the binder. An IR run was made on a sample which had been pyrolyzed at 900°C for a 1-minute period. The spectrum had absorptions peaks at 3,300 (broad), 3,000, 2,310, 2,170, 2,105, 2,080, 1,730, 1,360, 1,210 and 950 cm^{-1} , which indicated burning (formation of CO_2 , CO , and H_2O) and binder decomposition.

Two Mk 82 bombs, loaded with H-6 explosive and coated with the Pfizer material, were subjected to a fast cookoff in accordance with Ref. 6.

For the first Mk 82 bomb, the cookoff time was 20 minutes 2 seconds. The flame temperature reached 982°C (1800°F) for about 2 minutes, but the average temperature was about 777°C (1430°F) for the overall test. This was below the minimum specification temperature of 899°C (1650°F) required in Ref. 6. Since there were no internal thermocouples, the heating rate could not be determined at the inside metal surface. The results of this test were considered to be a detonation since only small fragments could be found (Ref. 5). The fragment size was about 1 inch on an estimated average. The biggest piece measured about 5 inches long by 1.5 inches wide (Fig. 17). The thickness of the coating was not measured on this bomb.

The second Mk 82 bomb had a coating thickness of 0.193 inch at the nose, 0.178 to 0.188 inch at the middle, and 0.184 inch at the aft end. This exceeded the 0.150-inch specification limit. The time to cookoff was 13 minutes plus. The average temperature of the fire was above the specification temperature of 899°C (1650°F). Evidently, the higher average flame temperature caused the bomb to cook off in a shorter time period, even though it had a thicker coating of material on the outer skin. The test result was determined to be a deflagration (Ref. 5). Figure 18 shows a section of the bomb case.

THERMAL LAG PAINT (Coating)

This coating material was received from Thermal Systems, Inc.

A TGA curve showed that the freshly mixed paint, aged 1 hour, lost weight rapidly from ambient to 100°C and leveled off to a weight loss of about 80% between 150 to 350°C. Then there was a 17% stepwise weight

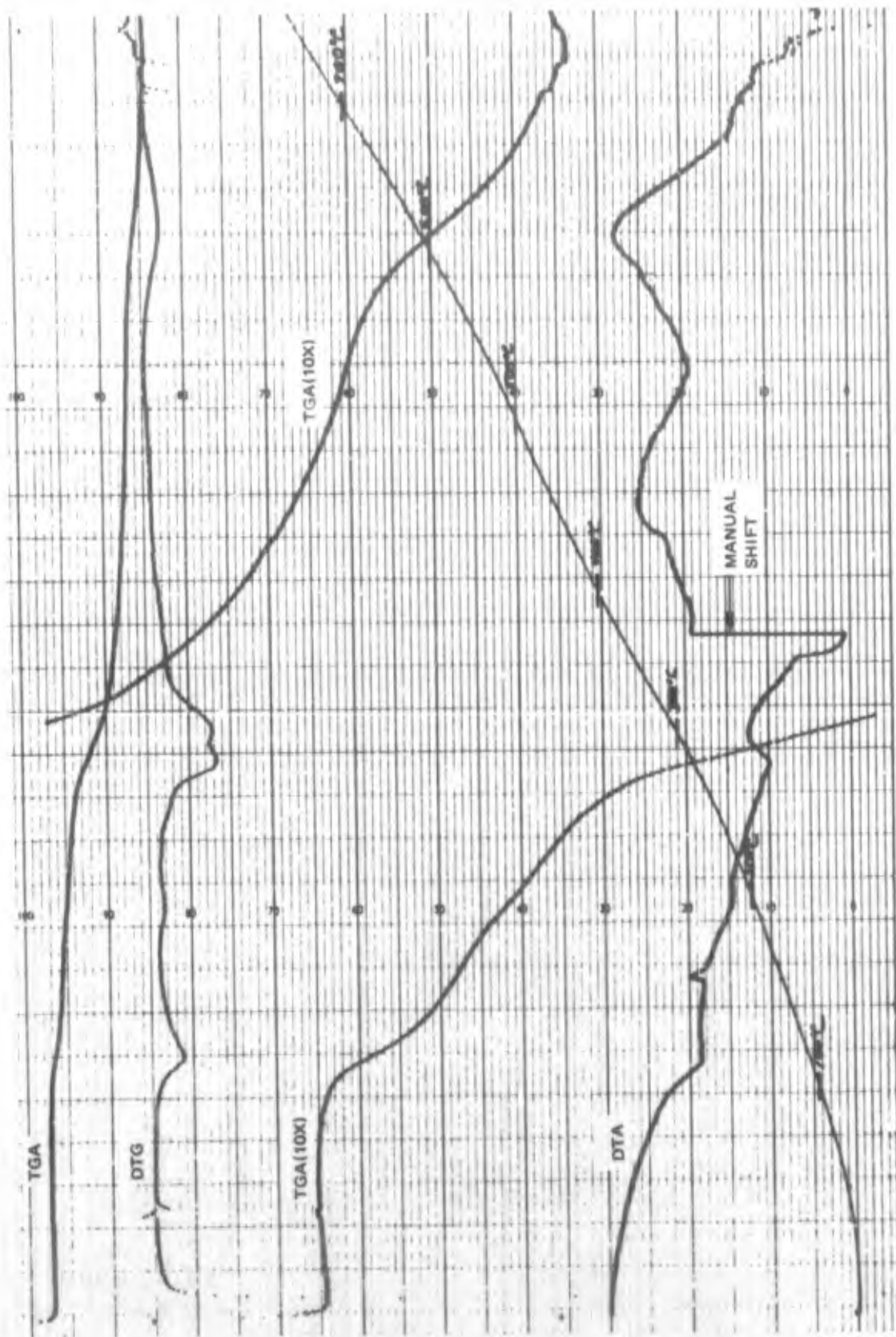


FIG. 16. Thermal Patterns of Pfizer Coating at Heating Rate of 5°C/min. (Sample wt: 20.42 mg; Run No. 1-17-2.)



FIG. 17. Metal Fragments Recovered After Fast Cookoff Test of First Mk 82 Bomb Coated With Pfizer Coating (LHL-160794).

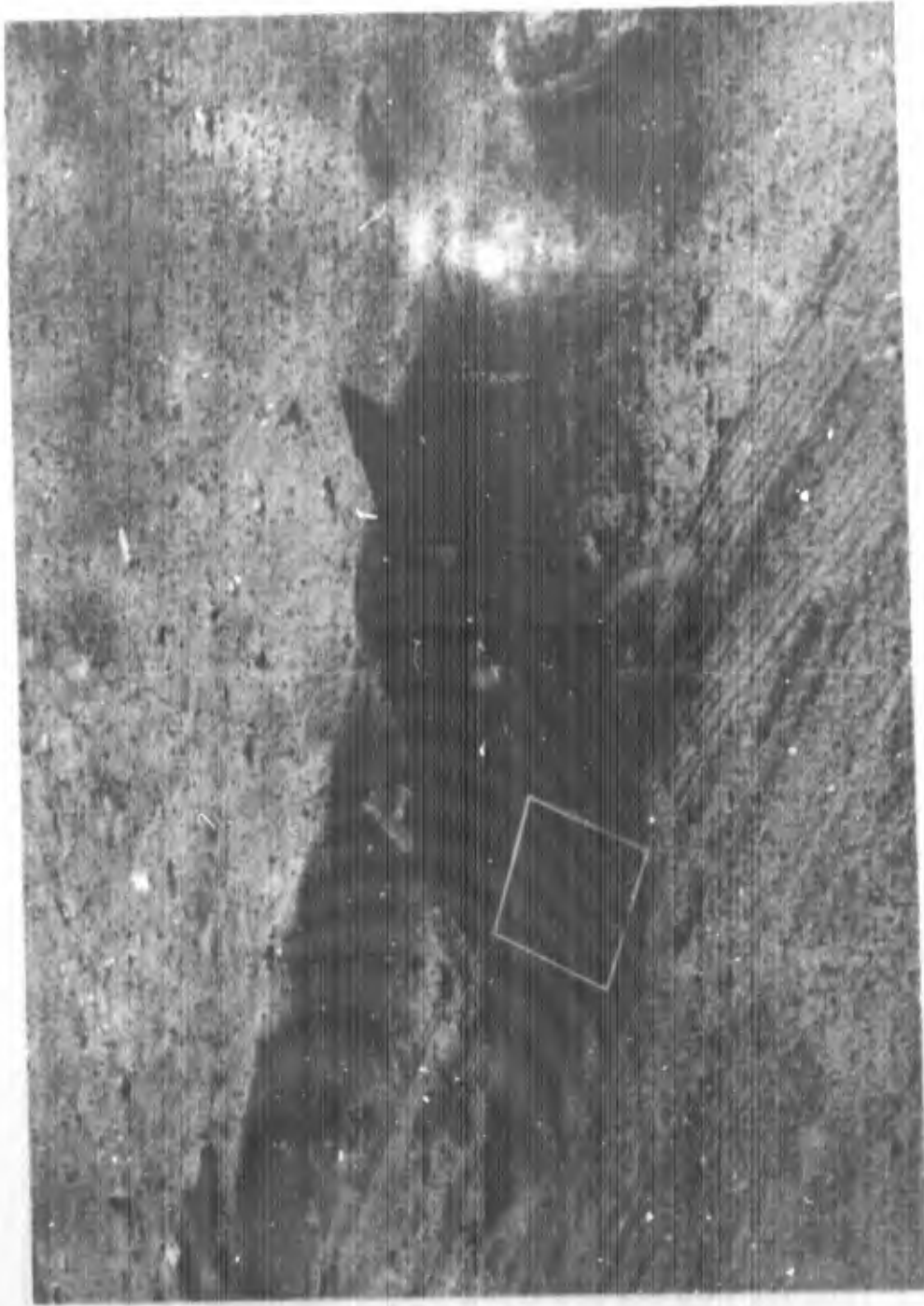


FIG. 18. Section of Bomb Case After Fast Cookoff Test of Second Mk 82 Bomb Coated With Pfizer Material (LHL-153037).

loss to about 425°C, leaving a 3% residue by the end of the run. The TGA-DTG-DTA thermal patterns on this paint, dried for 1 week, are shown in Fig. 19. As shown by the DTG and TGA curves, the decomposition occurred in two steps. During the first step, the material started to lose weight at 100°C and by 250°C it had lost 24%. The second step ranged from 250 to 450°C, where the sample lost an additional 63%. The DTA curve showed a strong exothermic reaction starting at 156°C and attaining a peak at 400°C. The two test runs indicated that the paint would suffer weight loss on aging.

CECO PAINT (Coating)

This coating material was received from the Cheesman-Elliott Co. This paint was used in the Naval Ordnance Laboratory (NOL), White Oak, Maryland, "Quick Fix" for the Mk 82 Bomb System.

The TGA-DTG-DTA thermal patterns are shown in Fig. 20. The paint showed a gradual weight loss from ambient to about 70°C, then a rapid loss to 125°C. There was a 50% loss in weight to this level. Then at 210°C the sample started to lose weight again and by 600°C it had lost an additional 36%. The thermal patterns show that the decomposition reactions of this paint appear to be quite complex.

AVCO COATING

This material (FM-26) was received from the AVCO Systems Division.

The TGA-DTG-DTA thermal patterns are shown in Fig. 21. The material first showed a gradual weight loss in the 100 to 225°C temperature region. This may have been due to unbonded water in the material. The weight loss in this region was about 7%. The second weight loss region was from about 225 to 350°C, which accounted for about 20% of the sample. Both of these regions were endothermic. The third region, 350 to 450°C, was exothermic; the material was apparently "burning" in the air atmosphere. The weight loss in this region was about 35% of the sample weight. The last region, 450 to 550°C, was similar to the third region in that apparent "burning" was taking place, with about 6% of the sample weight being lost. The residue was about 32% of the original weight, after being heated to 550°C.

A sample of the material was pyrolyzed at 400 and 900°C and the residual gas-liquid was analyzed by IR. Water, carbon dioxide, carbon monoxide, and some organic material (at 1,720 to 1,760 cm^{-1}) was observed in the IR spectrum.

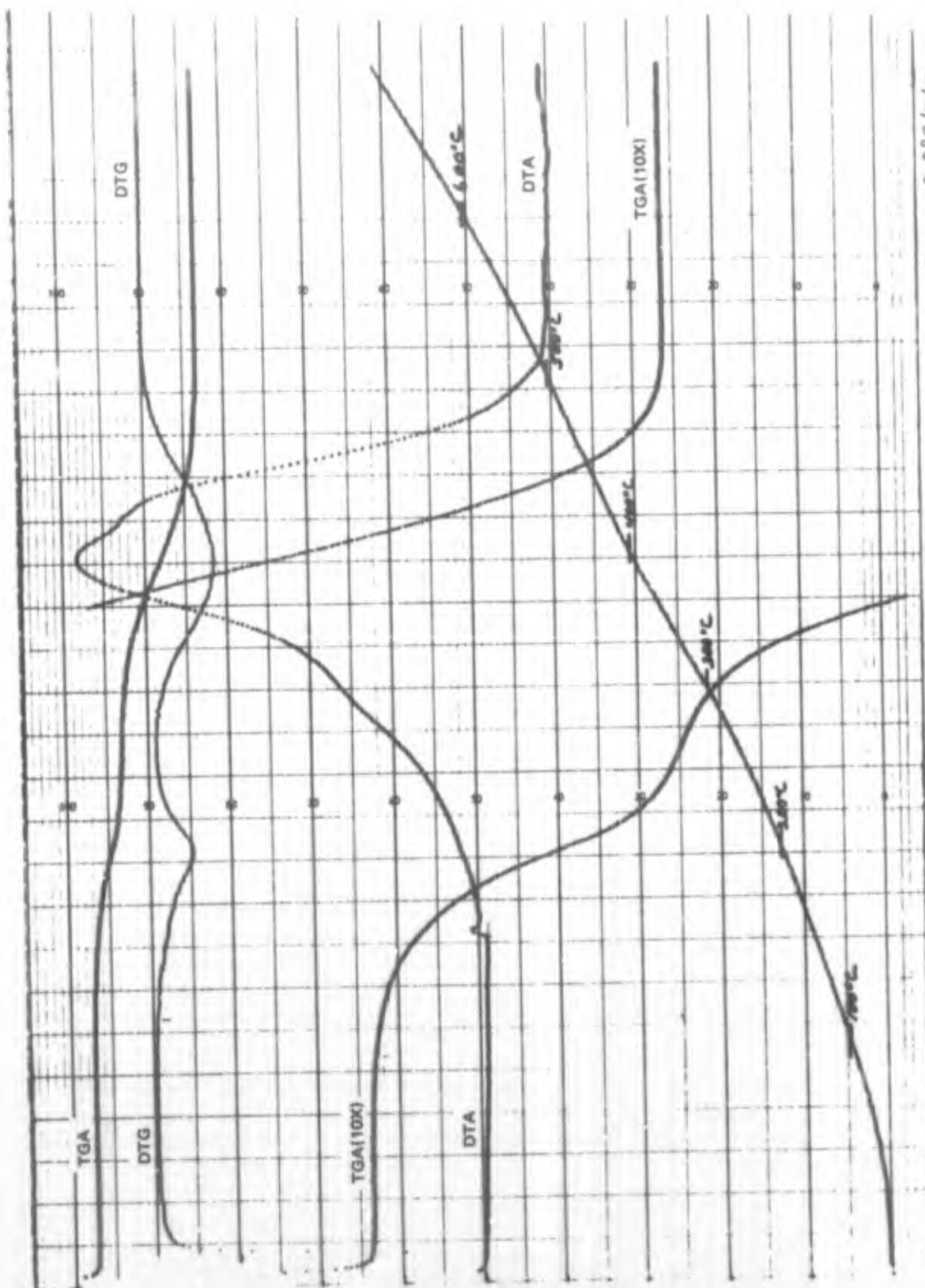


FIG. 19. Thermal Patterns of Thermal Lag Paint (dried 1 week) at Heating Rate of 5°C/min. (Sample wt: 15.73 mg; Run No. 1-30-3.)

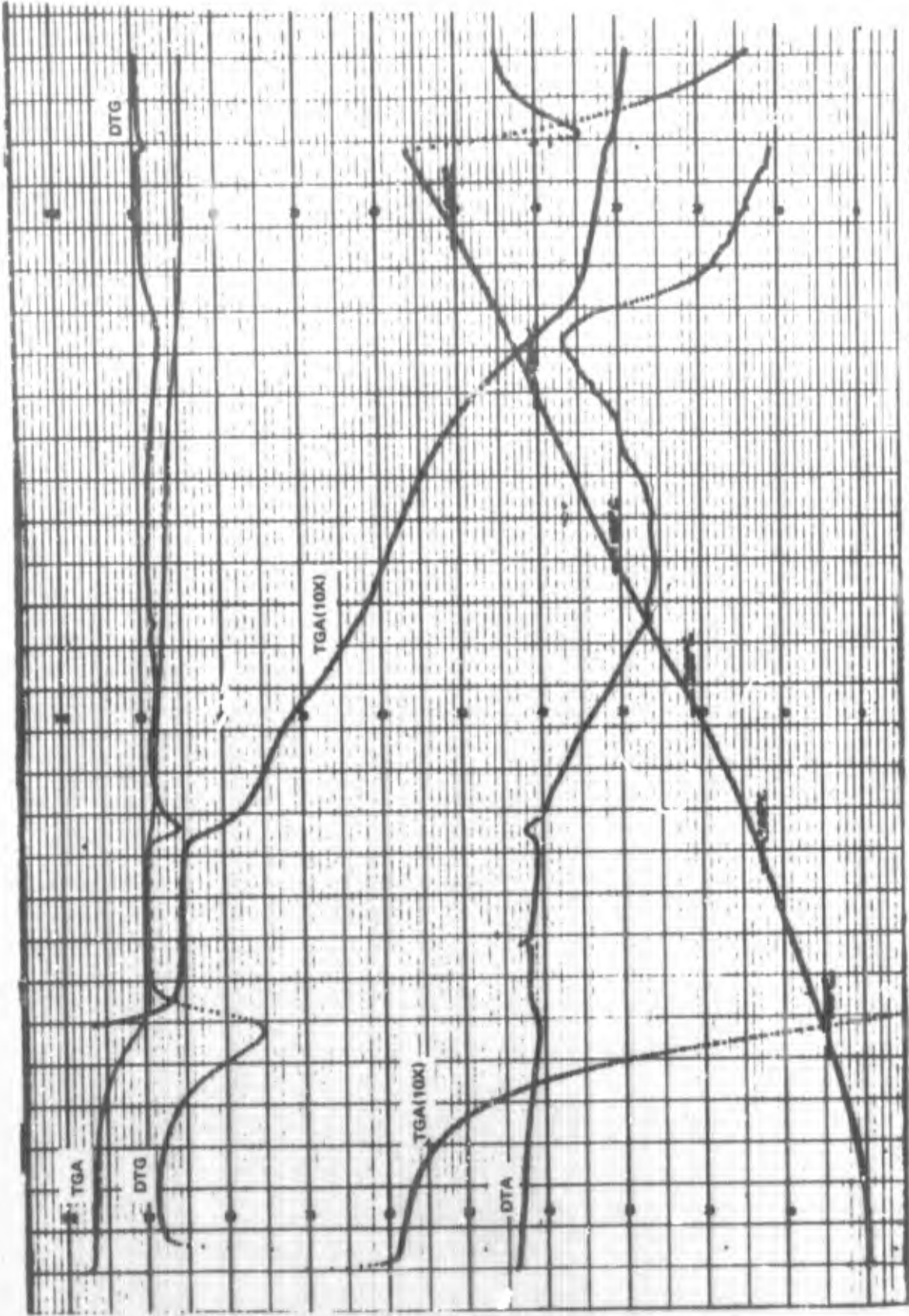


FIG. 20. Thermal Patterns of CECO Paint at Heating Rate of 5°C/min. (Sample wt: 14.66 mg; Run No. 1-25-2.)

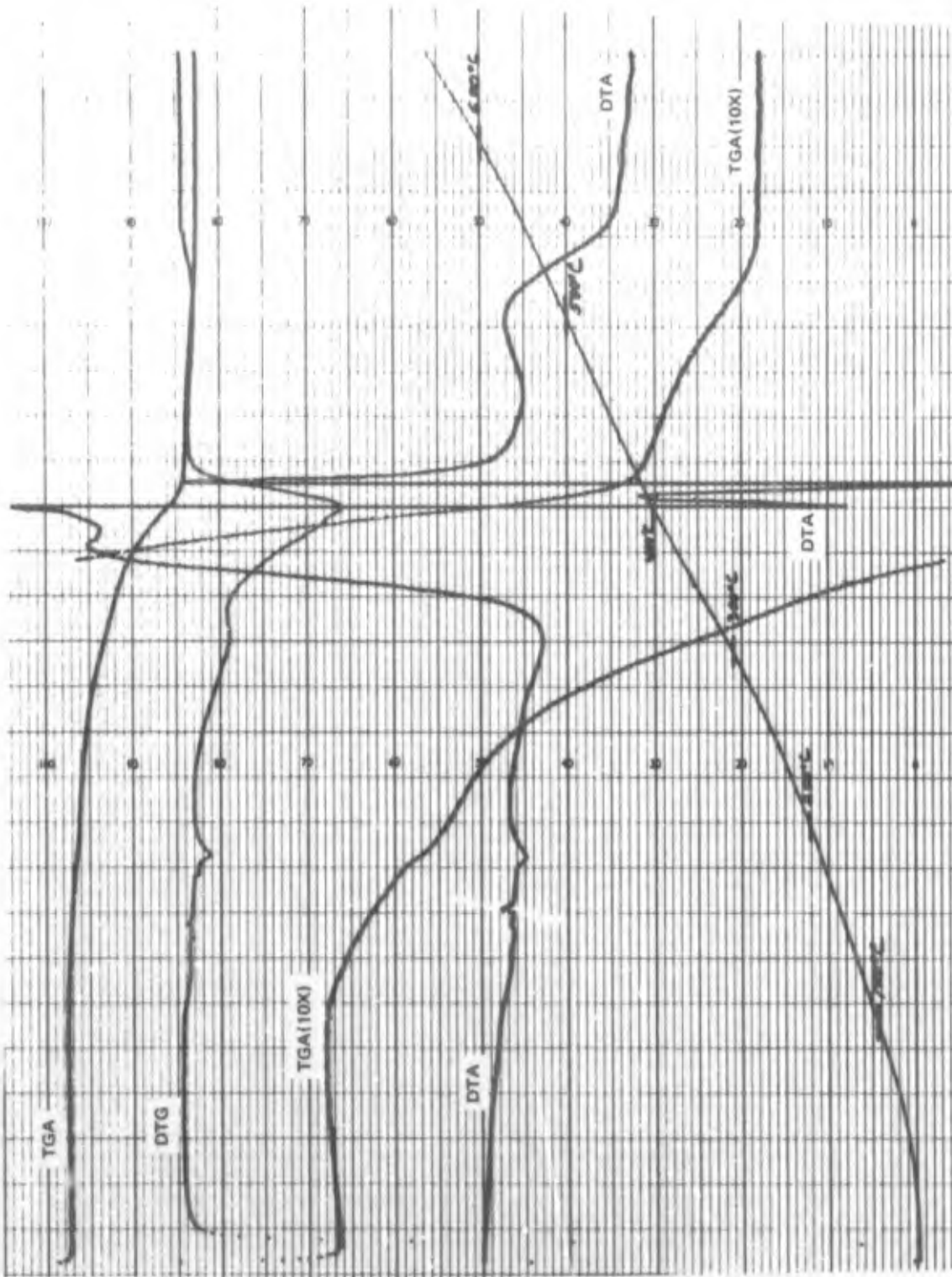


FIG. 21. Thermal Patterns of AVCO Coating at Heating Rate of 5°C/min. (Sample wt: 22.01 mg; Run No. 1-16-1.)

TUFFSEAL SEALER

The Tuffseal sealer material was obtained from the H. H. Robertson Company. This material was a candidate as a replacement for the wax normally used to seal the bomb after explosive loading. Therefore, the major concern was with the chemical and thermal stability of the sealer and the compatibility of the sealer with explosives.

The sealer is primarily a polyurethane binder with an asphaltic filler. Tuffseal is cured from a two-part system and the nonproprietary composition of each is:

Part A

1. Petroleum asphalt
2. Hydroxy-modified polydiene
3. Plasticizer mineral oil
4. Catalyst-alkyl tin

Part B

1. Petroleum asphalt
2. Plasticizer mineral oil
3. Nonvolatile isocyanate-terminated polymer
4. Molecular sieve compound

The general thermal stability may be pictured from Fig. 22, which is a TGA-DTG-DTA thermal pattern on the cured Tuffseal. The decomposition of the Tuffseal appeared to be in four steps, starting at about 150°C. During the first step, it lost about 8% of its original weight, with some exothermic action at 228 to 290°C. This could be an endothermic reaction, but since air was flowing over the top of the sample, this could be a "burning" of the organic material coming off. The second step was very abrupt in reacting, but was probably similar to step one. The third step gave the greatest weight loss, but it was not a simple decomposition reaction, as indicated from the DTG thermal pattern. The weight loss was about 63% in the temperature range of about 350 to 450°C. The fourth step was in the 450 to 575°C region and the weight loss was an additional 24%.

A sample of the cured Tuffseal was pyrolyzed at about 700°C for 30 seconds and the residual gas-liquid was analyzed by IR. The spectrum showed absorption peaks corresponding to petroleum asphalt and carbon dioxide. This should be related to the asphaltic filler and to the thermal decomposition of the polyurethane binder.

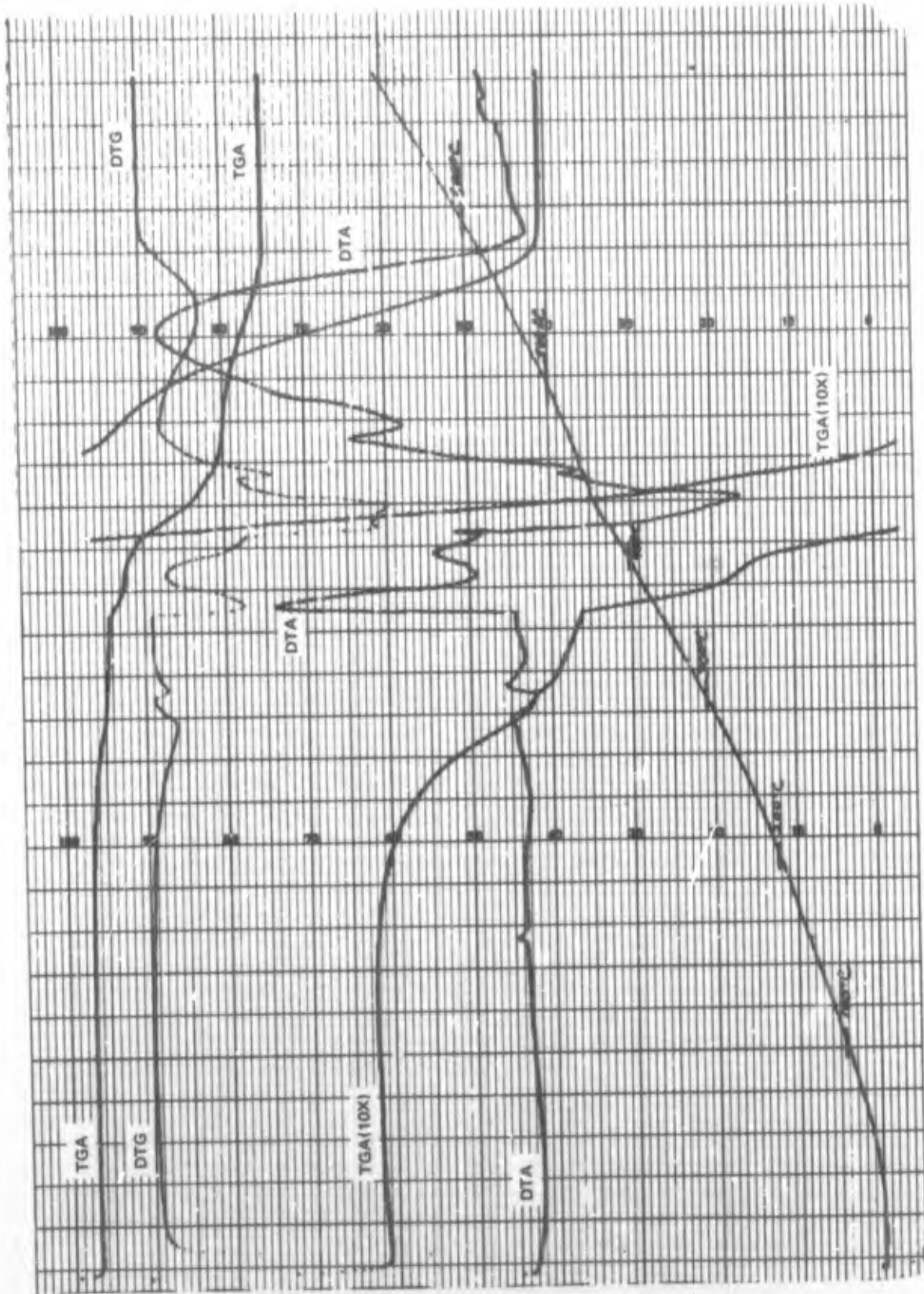


FIG. 22. Thermal Patterns of Tuffseal Sealer at Heating Rate of 5°C/min. (Sample wt: 22.565; Run No. 1-33-2.)

The isothermal decomposition of Composition B and TNT in the presence of cured Tuffseal has been studied by Joyner (Ref. 3). In this study, it was shown that Tuffseal produced very serious accelerations on the decomposition of the explosives, the worst being with TNT. It was also reported that TNT, in the presence of Tuffseal, produced pressure bursts at relatively low temperatures in the temperature range studied. Although Tuffseal is mainly an asphaltic filler (estimated at 80 to 90%), the acceleration of Tuffseal on TNT was greater than the asphalt on TNT. To show the acceleration, a plot of log half-life ($t_{1/2}$ in seconds) versus temperature was taken from the data in Ref. 2 and 3 and is shown in Fig. 23. And, as Joyner suggested, something other than the asphalt present in the Tuffseal was entering into the reactions. Additional studies indicated that this was true.

Compatibility tests were made on the components present in Tuffseal in an attempt to identify the component(s) responsible for increasing the decomposition rate of TNT. This explosive was chosen since it was readily available and it is common to many explosive formulations. The Tuffseal components were received from the H. H. Robertson Company.

The first component tested with TNT was a combination of petroleum asphalt plus a plasticizer mineral oil. This component is common to both the A and B parts of Tuffseal. Asphaltic mixtures with TNT are known to increase the decomposition rate of TNT (Ref. 2). This component appeared to dissolve the TNT and form a reddish-tint substance. However, any color change cannot always be accounted for because of the black color of the asphalt. An IR pattern, on this component and TNT mixed together, showed absorption bands of each and they could be separated by solvent action. The melting point, onset to exothermic action, and the exothermic peak temperatures determined on the DSC for TNT alone were 75, 308, and 331°C, respectively. For TNT and this component, the temperatures were 76, 255, and 292°C, respectively, a drop in the last two temperatures. For comparison, a sample of regular hot melt with TNT gave 79, 236, and 274°C, a greater decrease in the last two temperatures.

The next component tested was a hydroxy modified polydiene, a colorless oil. It appeared to lighten the color of the TNT, with some possible solvation action. The DSC results were 76, 211, and 247°C, for the melting point, onset temperature, and exothermic peak temperature, respectively.

The third component was a nonvolatile isocyanate terminated polymer. This polymer is a liquid which readily dissolved the TNT. This was confirmed by IR analysis. The polymer appeared to react with the TNT at 95°C, after a period of less than 4 hours. The new compound may be an addition-complex with the TNT. The new complex was insoluble in carbon tetrachloride, whereas the polymer was soluble and the TNT was sparingly soluble. The IR pattern showed that both the polymer and TNT were present in the apparent complex. The DSC data did not show a melting

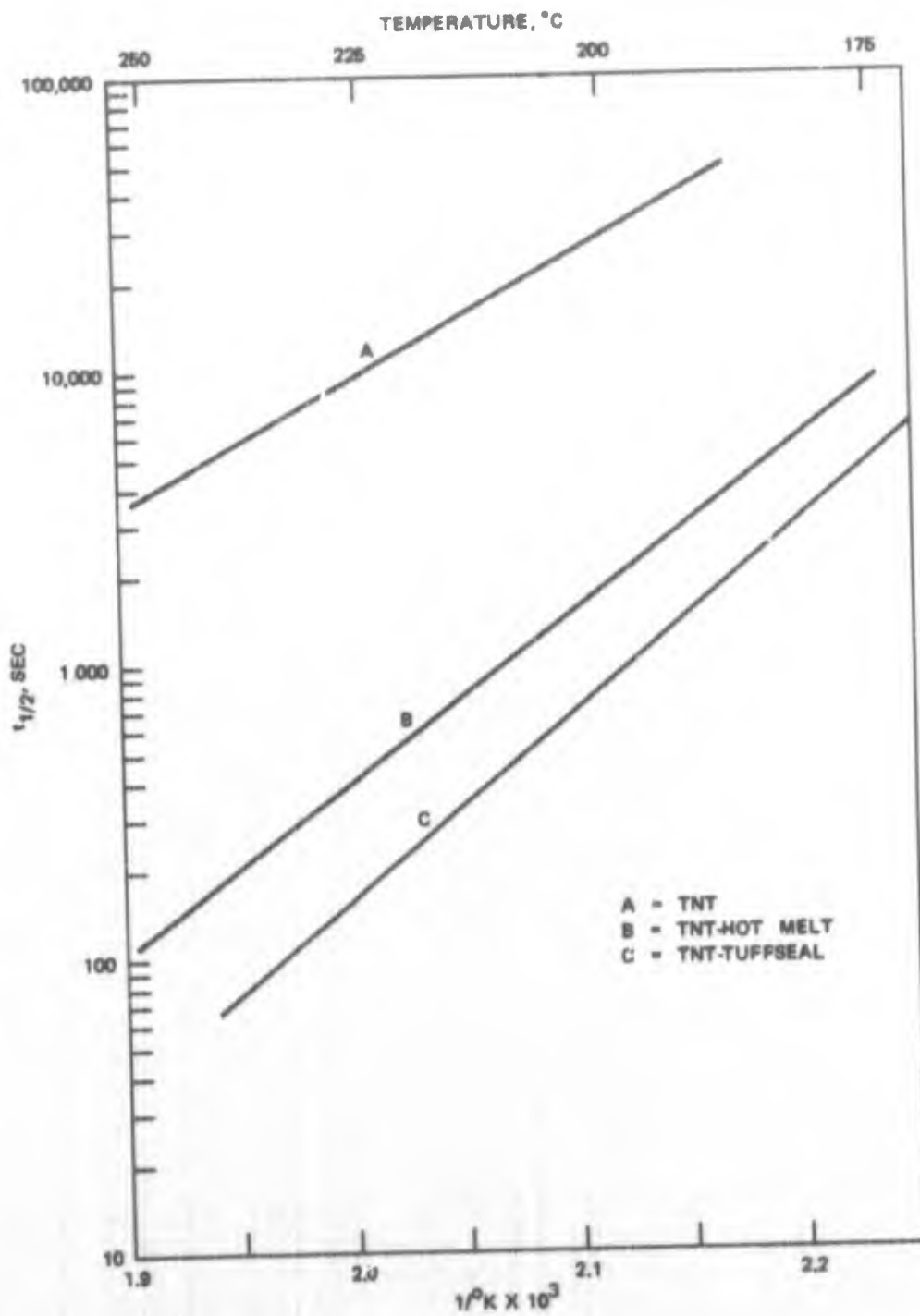


FIG. 23. Half-Lives for the Decomposition of TNT, TNT-Hot Melt, and TNT-Tuffseal.

point, since a one-to-one ratio of polymer-plus-TNT mixture is a liquid at room temperature. The onset temperature was 240 to 263°C and the peak temperature was 284 to 288°C. After a chemical separation of the apparent complex, the melting point was 67 to 73°C (very broad), onset temperature was 256°C, and the peak temperature was 298°C. No attempt was made to purify the apparent complex. This polymer alone appeared to dissolve the dried black cavity paint but not the Super Gem wax (a product of the Tetrolite Corp., New York, N.Y.). This wax is one of the end sealers used in the production of explosive-loaded Mk 82 bombs.

Some additional studies were made on a purified sample of a non-volatile isocyanate-terminated polymer which was received from the H. H. Robertson Company. The TNT and the isocyanate polymer were placed together in a flask (fitted with water traps) for approximately 5 hours over a boiling water bath. The resulting material was thrice recrystallized from carbon tetrachloride; the product was an off-yellow waxy looking substance. The melting point was about 2°C lower than the TNT used, with the softening point about 6°C lower. The exothermic peak was about 14°C lower than the TNT alone. From the heat of fusion and weight loss data, it was estimated that the composition of this material was about three parts of TNT to one part of the isocyanate polymer by weight. The IR pattern on this material showed the presence of both the TNT and the isocyanate polymer. The plot of specific rate constant (zero order) versus temperature data, determined from the DTG curve, gave the same value for the heat of vaporization with either the TNT or this material. The value was 17.0 kcal per mole. Laboratory tests have shown that the TNT is presumably dissolved far faster by the isocyanate than by the other components in Part B.

The fourth component was the catalyst, which is an alkyl-tin compound. The alkyl tin appeared to dissolve the TNT (confirmed by IR analysis) and to lighten the color of the TNT. The DSC data gave 76, 228, and 257°C for the melting point, onset temperature, and peak temperature, respectively.

The fifth component tested was a molecular sieve compound. This component was a white powder. It did not appear to react with the TNT at room temperature, but it did form a pinkish color with melted TNT. The IR spectra showed nothing unusual, with or without the TNT present. The DSC data showed temperatures at 79, 233, and 257°C, for the melting point, onset temperature, and peak temperature, respectively.

All of the components lowered the exothermic onset and peak temperature, which was due, in part, to the heat transfer involved in each mixture. They also accelerated the decomposition of the TNT.

The nonvolatile isocyanate component also was reacted with Composition B and H-6 explosives and the results were similar to that for TNT. This component would readily dissolve the TNT in both Composition B and H-6 explosives. The wax present in each explosive did not stop this component from dissolving the TNT.

A study was made on Tuffseal taken from two Mk 82 bombs which had been temperature-cycled. The bombs were loaded with H-6 explosive and contained Tuffseal (50/50 parts by weight of A and B) between the explosive charge and the aft end plate. One bomb was coated with Pfizer material and the other with AVCO material.

The Pfizer-coated bomb was aged according to a modified WR-50 safety test. The bomb was temperature-cycled for 14 days between +60 and -40°C (+140 and -40°F). Then the aft end of the bomb was cut off and sectioned. A picture of the section shows the explosive and Tuffseal (Fig. 24). A piece was taken of the Tuffseal that was between the explosive and the back plate of the bomb. The DSC thermal pattern showed that the loose powder, removed from the surface of the piece of Tuffseal which had been backing the explosive, was just RDX with no TNT present. A sample of Tuffseal was then taken every 0.2 inch from the Tuffseal-explosive interface. An IR analysis of the first 0.4 inch showed the presence of TNT in the Tuffseal. Using a microscope (20 - 100 power), it was observed that small red crystals were located throughout the Tuffseal. Tuffseal that was cured without being in contact with explosive did not have these red crystals. The assumption that the red crystals were associated with the TNT was confirmed by IR analysis. Pockets of red crystals were also found in the Tuffseal.

The AVCO-coated bomb was cycled according to a standard WR-50 safety test, 28 days between +74 and -54°C (+165 and -65°F). Then, the aft end of the bomb was cut off and sectioned, as shown in Fig. 25. An examination of a piece of the Tuffseal showed that TNT was present for about 1 inch into the sealer material. It is possible that the TNT extended further into the Tuffseal, since the IR analysis was limited to a minimum value of about 1%. There was loose powder at the surface and red crystals were present throughout the piece of Tuffseal.

Studies were also made on Mk 82 bombs, containing Tuffseal in different ratios of Parts A and B, to determine the extent of the migration of TNT from the H-6 explosive into the Tuffseal. Six aft half-sections of Mk 82 bombs were examined. The three AVCO-coated (AV) bombs had been subjected to temperature cycling (WR-50) from -65 to +160°F in an air atmosphere that had a relative humidity value of 95%. The three Pfizer-coated (PF) bombs were stored at ambient temperature. The sections were identified as follows:

Bomb No.	Tuffseal A/B, parts	Loaded	Cut	Sampled
AV-10-5	57/50	4/71	7/20/71	8/13/71
AV-10-3	50/50	4/71	7/21/71	8/13/71
AV-10-6	50/57	4/71	7/21/71	8/13/71
PF-4-1	57.5/50	12/70	7/20/71	8/13/71
PF-4-3	50/50	12/70	7/20/71	8/13/71
PF-4-4	50/57	12/70	7/20/71	8/13/71



FIG. 24. Tuffseal and Explosive Within a Pfizer-Coated Mk 82 Bomb After 14 Days Cycling Between +60 and -40°C (LHL-157112).

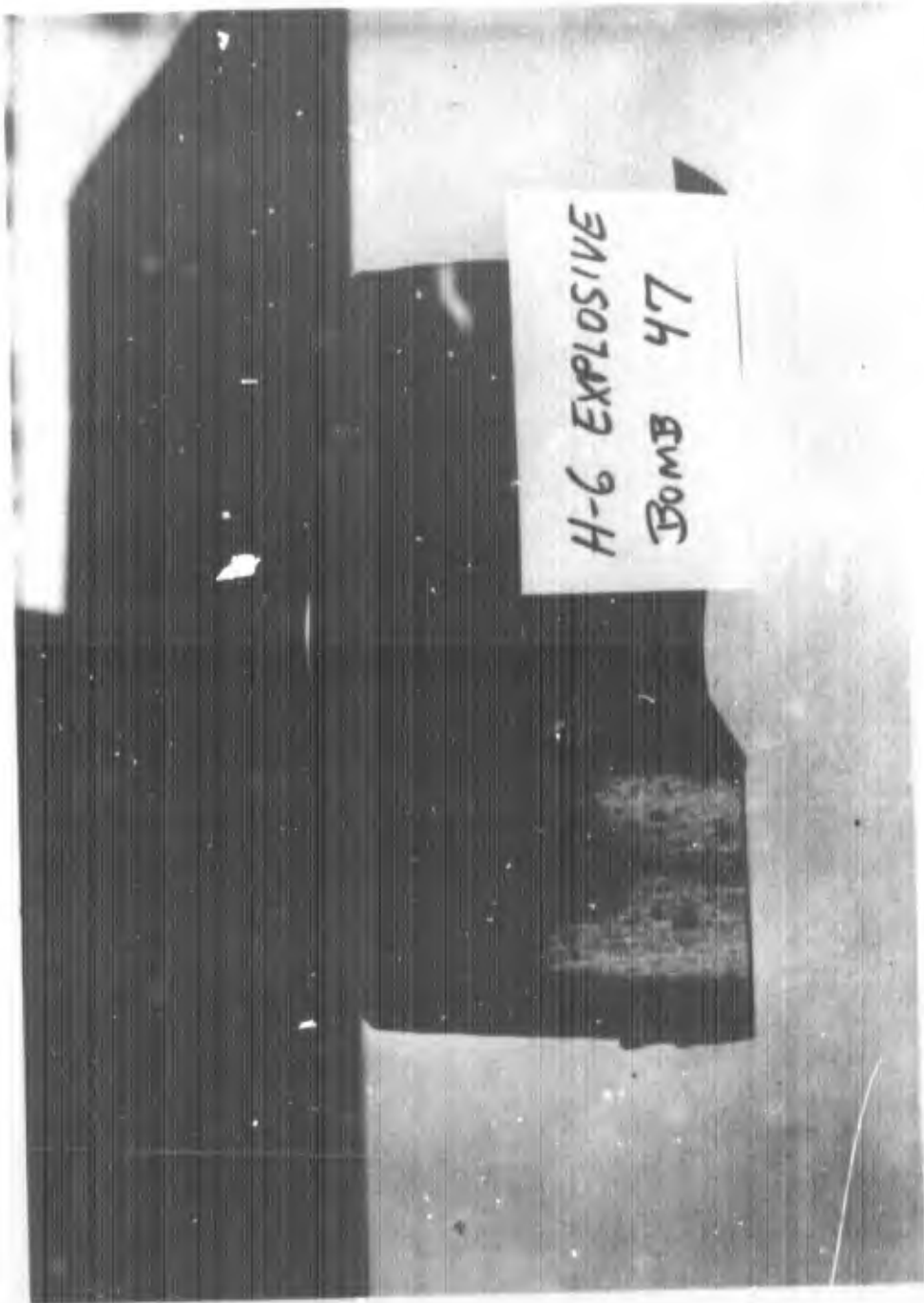


FIG. 25. Tuffseal and Explosive Within an AVCO-Coated Mk 82 Bomb After 28 Days Cycling Between +74 and -54°C (LHL-157115).

A piece of Tuffseal was taken from each section. Then, 1/4-inch-thick slices were cut from a 1/2-inch-wide by 1/4-inch-thick slab that extended from near the Tuffseal/H-6 interface to near the Tuffseal/aft metal ring interface. Slice No. 1 was nearest to the H-6. The slices were analyzed for the presence of TNT by the procedure described in Ref. 10. There were two modifications to the technique: (1) acetone, instead of dimethylsulfoxide (DMSO), was used as the solvent, and (2) the peak at 505 μ was measured 15 minutes after adding the ethylenediamine (EDA). The quantitative results are given in Table 3.

A second piece of Tuffseal was taken from the six bombs and similar 1/4-inch-thick slices were obtained from the small test slabs. The slices were qualitatively analyzed for the presence of TNT by the use of the IR. Each piece was soaked for 4 to 6 hours in warm acetone to extract any TNT present in the sealer material. A small amount of liquid was placed on an IR window and allowed to evaporate. An IR spectrum was obtained on the extract from each slice. The IR spectra also showed the presence of TNT in the slices of Tuffseal. The indication was positive for the samples that contained more than 1% of TNT. Because of the operational limitations of the instrument, it was not possible to positively identify TNT in quantities less than about 1%.

TABLE 3. Analysis of TNT in Tuffseal^a.

Bomb no.	Tuffseal		TNT, % by wt					
	A	B	Slice no. ^b					
			1	2	3	4	5	6
AV-10-5	57.0	50.0	13.4	7.7	2.2	0.5	0.9	0.2
AV-10-3	50.0	50.0	15.2	5.8	3.6	2.1	0.6	0.2
AV-10-6	50.0	57.0	11.5	4.4	0.6	0.2	0.2	0.7
PF-4-1	57.5	50.0	3.0	1.2	0.2	0.3	X ^c	X ^c
PF-4-3	50.0	50.0	3.1	2.7	1.3	0.2	0.1	0.3
PF-4-4	50.0	57.0	4.6	1.7	1.0	1.2	1.0	1.4

^aRef. 10 used acetone instead of DMSO for solvent. Peak at 505 μ measured 15 minutes after adding EDA.

^bEach slice \sim 1/4-inch-thick.

^cX = only 4 slices in this section.

NOTE: The AVCO-coated bombs (AV) were temperature/humidity cycled in accordance with WR-50.

Previous tests on an unaged bomb showed that the TNT migrated about 1/2 inch through the Tuffseal. During aging, small salt-like crystals were deposited as a powdery residue at the Tuffseal/explosive interface. DSC tests indicated that these loose crystals were RDX. Little or no TNT was found in the boundary layer. The studies have shown that the TNT migrated slowly after initial loading at ambient conditions and migrated rapidly during accelerated aging.

To illustrate this migration phenomena, a photomicrograph was taken of a piece of Tuffseal which came from an H-6 explosive-loaded Mk 82 bomb. Under 20-power magnification, three distinctly different types of colored crystals were observed; the colors were yellow, red, and clear white. The yellow crystals were TNT, the red were TNT which had reacted with one or more of the components of Tuffseal, and the white crystals were RDX (Fig. 26). The crystals were identified by the use of IR and DSC.

Samples of H-6 explosive were taken from an area just below the explosive/Tuffseal interface. The results of the chemical analysis are given in Table 4. A significant difference was observed in the RDX content in the samples from the two differently coated bombs. The accelerated-aged bombs (AVCO-coated) had a lower content of RDX (~ 1%) than the unaged bombs (Pfizer-coated). Presumably, the RDX had migrated to the explosive/Tuffseal interface.

TABLE 4. Chemical Analysis of H-6 Explosive.

Bomb no.	Percent by weight ^a		
	RDX	TNT + wax	Al
AV-10-5	42.88	35.67	21.45
AV-10-3	42.45	37.15	20.40
AV-10-6	42.40	35.81	21.79
PF-4-1	43.39	35.33	21.28
PF-4-3	43.59	35.93	20.48
PF-4-4	43.47	35.09	21.44

^aAverage of three trials, except average of two trials on Bomb no. AV-10-3.

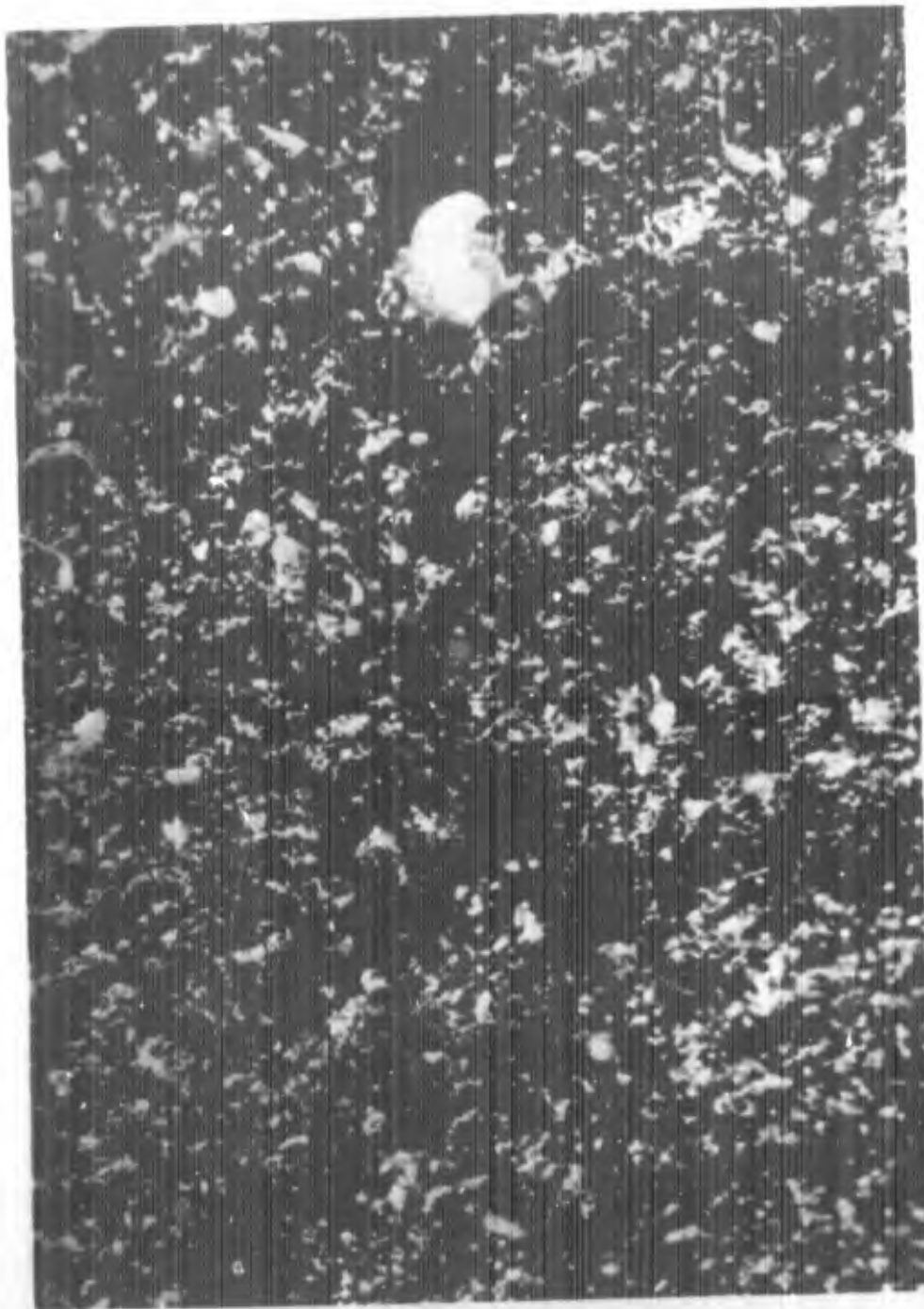


FIG. 26. Photomicrograph of a Piece of Tuffseal From an H-6 Explosive-Loaded Mk 82 Bomb (LHL-161545).

SUMMARY

The liner materials, as a lot, did not offer much improvement over the present hot-melt liner. In some cases, such as Unique, a great number of other problems were present. To be acceptable, a liner should be nonmelting, be a good insulator, be compatible with explosives, and have good chemical stability by resisting oxidation for example.

The coating materials may have problems in hot climates; thermal analysis data showed appreciable weight loss at low temperatures. The AVCO coating appeared to be the best.

The one sealer, Tuffseal, offered the needed protection for a Mk 82 in a fire, but it had compatibility problems when it came in contact with explosives. Tuffseal absorbs TNT and apparently some RDX from the H-6 explosive during loading and on accelerated aging. The red crystals of TNT are present throughout the Tuffseal and also clear white crystals are present which appear to be RDX.

An outline of the relative compatibility of the candidate materials to hot melt, stability to air oxidation and the type of reaction on fast cookoff is tabulated in Table 5.

TABLE 5. Summary of Evaluated Candidate Materials.

Material (liner/coating/ sealer)	Compatibility ^a	Exothermic ^b onset temp, °C	Type of reaction ^c
Hot melt	0	270	Deflagration
Thiokol	0	300	Deflagration
ISI	+ (water)	300	Explosion
URP-2	+	200	Deflagration
TSI	0	350	Deflagration
Essex	-	300	Deflagration
Unique	0 (water)	400	Deflagration
No liner	NA ^d	NA	Deflagration
Pfizer	NA	275	Detonation/ deflagration
Thermal lag	NA	155	(Not tested)
CECO	NA	430	Deflagration
AVCO	NA	350	Deflagration
Tuffseal	-	230	NA

^aCompatibility with explosives based on a comparison to hot melt. 0 = same, - = worse, + = better (Ref. 3 and this study for data). The presence of water would be a problem with aluminized explosives.

^bStart of air oxidation (DTA-TGA data) and not the degree of burning.

^cAs defined in Ref. 5, using H-6 explosive, SCB, and/or Mk 82 bomb data.

^dNA = Not applicable.

For the data in Table 5, i.e., the compatibility of liner and sealer materials with explosives, other tests were performed in addition to the standard compatibility tests such as DTA, vacuum thermal stability, color change, etc. These additional tests were employed in the following studies on the effect of the liner and sealer materials on the explosives:

A. Effect on thermal decomposition rate of the explosive in the presence of different liners and the sealer. In Ref. 3, it was shown that the liners varied in their effect on the decomposition of TNT and Composition B; e.g., the URP-2 liner having little effect to that of the Essex liner having a larger effect. The accelerations in the decomposition rates of the explosives can shorten the time to cookoff. The kinetic data from the decomposition studies can be used in the heat flow equations to predict the critical temperature of the explosive and, consequently, the time to cookoff can be calculated for specific temperature levels (Ref. 4 and 7).

B. Effects on chemical stability of the explosive. Water present in the liner may react with any aluminum in the explosive to form hydrogen gas. The hydrogen gas may cause excessive pressure buildup or the gas may contribute to a hazardous/flammable situation.

C. Reactions of TNT with bases. Several of the liners and the sealer material had an alkaline nature. It has been reported in Ref. 9 that TNT reacts with bases (Meisenheimer's reaction) to form addition compounds or new compounds. These products are usually much more sensitive to mechanical and thermal shock than TNT.

D. Migration of explosives. It has been observed that explosives readily migrated into and throughout a liner and sealer material (Fig. 26). Individual components in the material can react with the explosives to form new or addition-type products which are not very stable.

REFERENCES

1. Naval Weapons Center. *Thermal Decomposition of Explosives. Part 1. Effect of Asphalt on the Decomposition of RDX-Bearing Explosives* (U). by Taylor B. Joyner. China Lake, Calif., NWC, March 1969. (NWC TP 4709, Part 1, publication CONFIDENTIAL.)
2. ----- . *Thermal Decomposition of Explosives. Part 2. Effect of Asphalt on the Decomposition of TNT* (U), by Taylor B. Joyner. China Lake, Calif., NWC, April 1969. (NWC TP 4709, Part 2, publication CONFIDENTIAL.)
3. ----- . *Thermal Decomposition of Explosives. Part 8. The Reactions of Composition B and TNT in the Presence of Various Potential Cavity Liners and Sealants* (U), by Taylor B. Joyner. China Lake, Calif., NWC, 1971. (NWC TP 4709, Part 8, publication UNCLASSIFIED.)
4. ----- . *Thermal Analyses Studies on Gelled Slurry Explosives* (U), by Jack M. Pakulak, Jr., and Edward Kuletz. China Lake, Calif., NWC, May 1971. (NWC TP 5023, publication CONFIDENTIAL.)
5. Naval Ordnance Systems Command, Navy Department. *Standard Terminology for Ordnance Explosive Reactions Obtained by Cookoff* (U). (NAVORDNOTE 8020, ORD-93221, 23 April 1969, publication UNCLASSIFIED.)
6. Bureau of Naval Weapons, Navy Department. *Naval Weapons Requirements. Warhead Safety Tests, Minimum for Air, Surface and Underwater Launched Weapons (Excluding Mine and Nuclear Warheads)*. (WR-50, dated 13 February 1964, publication UNCLASSIFIED.)
7. U. S. Naval Ordnance Test Station. *The Thermal Decomposition Characteristics of Explosives* (U), by C. D. Lind. China Lake, Calif., NOTS, February 1962. (NAVWEPS Report 7798, NOTS TP 2792, publication CONFIDENTIAL.)
8. Naval Weapons Center. *Temperature Data on Mk 82 Bombs Used in CASS Mini-Deck Tests*, by Jack M. Pakulak, Jr., and Edward Kuletz. China Lake, Calif., NWC, Oct. 1970. (NWC TP 4967, publication UNCLASSIFIED.)
9. Urbanski, T. *Chemistry and Technology of Explosives. Volume 1*. New York, Pergamon Press, 1964. Pp 290-311.
10. Glover, D. J., and E. G. Kayser. *Quantitative Spectrophotometric Analysis of Polynitroaromatic Compounds by Reaction with Ethylenediamine*. ANAL. CHEM., Vol. 40, No. 13 (November 1968), pp 2055-58.

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
THERMAL ANALYSIS THERMAL STABILITY LINERS COATINGS SEALER MATERIAL COMPATIBILITY/EXPLOSIVES MK 80 SERIES BOMBS						

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