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Investigation of the MK83 Bomb Ablative Coating Failures

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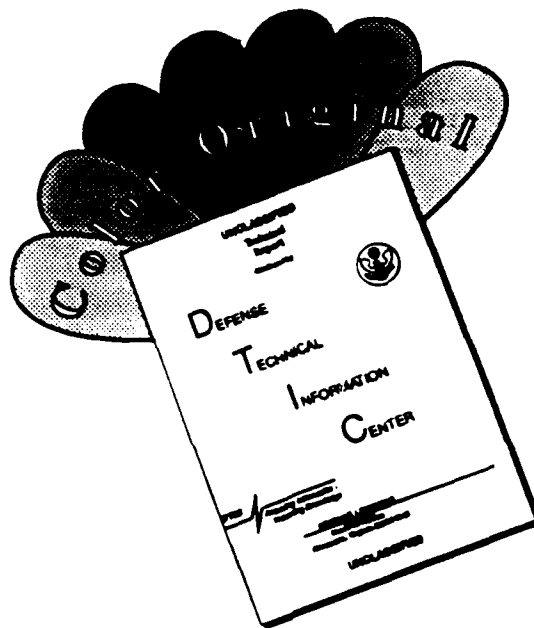
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13. ABSTRACT (Maximum 200 words) This investigation determined the cause of an ablative coating adhesive failure on MK83 bombs that were stored for approximately five to seven years at the McAlester Army Ammunition Plant (McAAP). An inspection of the contracting manufacturer's facilities revealed white products on the bomb surfaces resulting from the zinc phosphate procedure. This affected the bonding of a subsequent epoxy primer. The handling of bombs prior to complete curing of the primer caused the primer to adhere to worktable surfaces. A lack of process control was observed at the McAAP where the polyester ablative was sprayed on top of the primer. The resin gun clogged for short periods causing a burst of resin to deposit onto the bomb while the catalyst gun continued to spray. In addition, the ratio of catalyst to resin was adjusted manually only when the coating was observed to be sagging because there were no automatic controls to regulate the ratio. The storage conditions at the McAAP were hot and humid during the summer and resulted in water condensation on the ablative coating surface. The palletized bombs were stored five high causing high stress on the ablative which lead to blistering. Spectroscopic characterization indicated that spots on the interior surface of the failed coatings were similar in composition to a viscous fluid that exuded from the ablative. Mechanical testing revealed that an ablative sample displaying a relatively high degree of exterior surface tack had an average hardness below the minimum serviceable level required by the governing specification. Based on observations made at the production and storage facilities and the test data collected, poor processing and high stress adversely affected the adhesive, mechanical, and barrier properties of the coatings. It was also concluded that the adhesion of the primer and ablative coatings may have been affected by the viscous exudant from the polyester ablative.				
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Contents

	Page
Introduction	1
Inspection at McAAP	1
Inspection of the Contracting Manufacturer's Facilities	2
Visual Inspection of the Failed Coatings	2
Infrared Spectroscopy	3
Tensile Testing	3
Hardness Testing	4
Biological Examination	4
Conclusions	5
Recommendations	5

Figures

1. Predominant failure mode of coating was at the primer and zinc phosphate interface. Note the dark spots on both the interior primer surface and corresponding bomb surface	7
2. Second type of coating failure occurred at ablative and primer interface. Ablative surrounding primer in center still adheres to the bomb	7
3. Bomb pallet saddle with viscous fluid in center that had exuded from a bomb coating	9
4. The dark spots on the interior primer surface were crystalline in appearance	9
5. Interior surface of a fractured coating blister	11
6. Schematic of the blister fracture face	11
7. Infrared spectrum obtained from a crystalline spot on the interior primer surface of Specimen No. 2	13
8. Infrared spectrum obtained from the leached viscous fluid found on Specimen No. 4, the bomb pallet saddle	13
9. Infrared spectrum obtained from an acetone extract of the polyester ablative	15

Tables

1. Tensile Test Results	3
2. Hardness Test Results	4

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Introduction

The Army Research Laboratory (ARL) was requested by the Navy Pacific Missile Test Center (PMTTC) to determine the cause(s) of the MK83 ablative coating failure. The ablative coating system had failed to adhere to MK83 bombs after approximately five to seven years of storage at the McAlester Army Ammunition Plant (McAAP). These general purpose, low drag, 1000 pound, steel bombs were forged, blasted, and machined by a single manufacturer. After forming, the manufacturer conversion coated the MK83 bombs by a dip zinc phosphate process before applying an epoxy primer. Then, the bombs were shipped by rail to the McAAP where they were charged with explosive and coated with a styrene cross-linked polyester ablative. After coating, the bombs were placed on steel pallets and stored, without fuses, in earth covered concrete *igloos*. The problem with the coatings was discovered only after the bombs were pulled from the magazines and depalletized for fusing.

Inspection at McAAP

The first and predominant failure occurred between the primer and zinc phosphate interface. Large sections of the coating, when peeled away, revealed a dull gray surface on the bomb. The peeled sections of coating consisted of the ablative topcoat with the primer adhered to the interior side. Often times the bomb surface and the corresponding interior primer surface were covered with dark spots which had the appearance of oil stains (see Figure 1). A second type of failure occurred at the ablative and primer interface. In these instances, the primer remained intact on the bomb surface (see Figure 2). This second type of failure occurred most often near the bomb pallet saddles. No correlation was found between the coating failures and production lot numbers.

In addition to the adhesion failures, anomalies were observed on the exterior of the ablative coatings. Most of the bombs had a tacky exterior ablative surface and were discolored with black spots. Some of the coatings had a viscous liquid bleeding from random locations along the length of the bombs. This viscous liquid accumulated on the bomb pallet saddles that the bombs were set on (see Figure 3).

A concrete storage igloo was inspected. The igloos were constructed completely above ground and covered with earth. Two large unventilated doors opened outward to reveal a hot and humid igloo interior. The only ventilation appeared to be a ceiling vent at the rear of the igloo with vegetation extending in through its screen. About the cracked igloo floor, the concrete was wet and discolored. The gutters that ran the length of the igloo on each side were filled with standing water. Pallets of bombs were stacked up to five high.

The application of the ablative on the MK83 bombs was observed. The coating process utilized a separate spray gun for the catalyst and resin components. The resin gun was often clogged for short periods while the catalyst continued to flow. The ratio was manually adjusted whenever the ablative coating sagged and ran after application.

Inspection of the Contracting Manufacturer's Facilities

The zinc phosphate and primer coating processes of the MK83 bomb manufacturer were reviewed. Although these inspections were held five to seven years after the failed bombs had been produced, the only change in processing was the substitution of a solvent based, zinc rich, blue pigmented, epoxy primer for the red iron oxide pigmented, epoxy primer.

The MK83 bombs were processed in a five tank conversion coating procedure after forming was complete. The five tanks, in order of operation, contained, respectively, an alkaline cleaner, a tap water rinse, the zinc phosphate solution, a tap water rinse, and a chromic acid sealer. After removal from the last tank, large white powdery deposits were observed on the surfaces of many of the bombs. These poorly phosphated bombs were not rejected upon inspection. Interviews with company employees revealed that the rinse water utilized in the rinse baths was local tap water. Laboratory records on the chemistry of the baths were reviewed. Instances where the pH exceeded specifications in some of the baths were found.

After zinc phosphating, many of the bombs were not dried prior to application of the primer. An inadequate amount of time was allowed for the primer to cure, too, before final assembly. Contaminants from the assembly table adhered to the primed surface of the bomb. Table surfaces were left blue (the color of the primer) as the bombs were rolled along. Shoe prints were observed on primed bomb surfaces. The assembled bombs were transported to holding areas by forklifts with hard steel forks to lift and lower the bombs. Examination of these bombs revealed long scuff marks down to bare metal where the steel forks had been in contact.

Visual Inspection of the Failed Coatings

Four specimens were taken from McAAP and examined at ARL. Specimen No. 1 was a tacky ablative coating to which the primer still adhered. The degree of tackiness was typical of most of the bombs. The exterior ablative surface did not display much discoloration and no anomalies were found on the inner primer surface.

Specimen No. 2 was an ablative coating that did not display as much tack as Specimen No. 1. The primer adhered to the interior of the ablative. Dark spots resembling oil stains were found on the interior epoxy surface while the exterior surface of the ablative was dotted with black spots. At higher magnification, the topography of the spots on the interior epoxy primer surface had a crystalline appearance (see Figure 4).

Specimen No. 3 was an ablative coating that was blistered by a bomb pallet saddle (see Figure 5). This blister consisted of ablative only with traces of the primer on its interior surface. The interior showed the failure initiation region as a thumbnail-shaped area (see Figure 6). The crack propagated along the ablative and primer interface (Zone 2) with no signs of flow or deformation until it finally reached Zone 3 where the local stress field exceeded the ablative's yield strength and the ablative flowed until rupture was complete. The high local stresses were due to the weight of the bomb concentrated on the area of two bomb pallet saddles.

Specimen No. 4 was a saddle removed from a bomb pallet (see Figure 3). A puddle of viscous brown fluid formed in the center of the saddle; this fluid had exuded from the bomb that had been resting on the saddle.

Infrared Spectroscopy

Attenuated total reflectance infrared spectroscopy was used to identify the crystalline spot on the interior primer surface of Specimen No. 2 and the fluid found on Specimen No. 4. Analysis of the crystalline spot on Specimen No. 2 (see Figure 7) revealed a spectrum that was similar to the spectrum obtained from the leached viscous fluid found on the bomb pallet saddle (see Figure 8). The peaks at 1580 cm⁻¹ and 1400 cm⁻¹ are typical of organic acid salts. These species may have formed when carboxylic acids generated by the oxidation or hydrolysis of a plasticizer (Dimethyl Phthalate) followed by reaction with aqueous salts. The aqueous salts would have originated from the contaminated zinc phosphate coatings and/or the dirty environments the bomb pallets were exposed to.

Further evidence supporting the presence of an organic acid salt was the decrease in the pH of distilled water from 6.1 to 5.6 when the leached viscous fluid from the bomb pallet saddle was dissolved in the water.

In a comparison of the spectra of an acetone extract of the ablative (see Figure 9), the leached viscous fluid and crystalline spot were similar as well; this suggests that the leached viscous fluid probably came from the polyester.

Tensile Testing

Five *dog bone* tensile coupons were cut from coating specimens No. 1 and 2 and tested in accordance with ASTM D 638. Table 1 compares the average measured ultimate tensile strength (UTS) of the specimens to the minimum 500 pound per square inch (psi) UTS (at room temperature) specified by MIL-C-81904.

Table 1. Tensile test results

Ultimate Tensile Strength (UTS), psi, $\pm$ Standard Deviation			
Tensile Coupon ID	Specimen No. 1	Specimen No. 2	MIL-C-81904
1	530	680	—
2	570	650	—
3	560	710	—
4	490	630	—
5	550	720	—
Average	520 $\pm$ 36	680 $\pm$ 41	500

Both specimens No. 1 and 2 exceeded the minimum UTS requirement at room temperature. Specimen No. 2 displayed less tack and was 31% stronger than Specimen No. 1.

Hardness Testing

Hardness readings were performed on Specimens No. 1 and 2 according to ASTM 2240. Five Shore D scale readings were taken for each of the ablative coatings, each reading held for 10 seconds. Table 2 compares the average measured Shore D reading with the minimum working hardness value specified by MIL-C-81904.

Table 2. Hardness test results

Hardness Measurements (Shore D Scale), $\pm$ Standard Deviation			
Reading No.	Specimen No. 1	Specimen No. 2	MIL-C-81904
1	40	50	—
2	47	54	—
3	50	55	—
4	46	56	—
5	43	52	—
Average	45 ± 3.8	53 ± 2.4	50

Specimen No. 1 failed to meet the minimum working hardness required by MIL-C-81904 indicating it was structurally softer than Specimen No. 2.

Biological Examination

Light optical microscopy performed on the exterior surface of the ablative coatings revealed areas covered with a brown fibrous growth. Several fibers were extracted from the surface and identified visually as fungal mycelium, the genus *Cladosporium*. This is a common airborne organism found on all types of organic acids that convert organic compounds (such as the polymeric ablative and epoxy) into a nutrient solution. The combination of water and polymeric ablative is enough to keep *Cladosporium* viable.

Conclusions

The inspections performed at McAAP and the contracting manufacturer uncovered coating, handling, and storage conditions that contributed deleteriously to the integrity of the coating system. The zinc phosphate procedure yielded a white powdery coating and was not allowed to dry prior to primer application. This blocked the primer from wetting and bonding to the surface of the zinc phosphate.

The bombs were handled after primer application before sufficient time had been allowed for curing. This caused the primer to bond to surfaces other than the zinc phosphate; i.e., work tables. The bombs were then scratched to bare metal when handled by the metal fork lifts exposing the surface to the environment during storage and shipment.

After the ablative coating was applied, the coating system was subjected to high loads from the stacking of bomb pallets on each other. This caused blisters to form by the areas of highest stress adjacent to the bomb pallet saddles. The cumulative effects of years of humid, hot summers coupled with the high stress while in storage at McAAP caused the viscous fluid to exude from the ablative. Infrared spectroscopy identified similarities in the composition of the viscous fluid, the spots on the interior surface of the primer, and the polyester ablative indicating the fluid may have diffused to the zinc phosphate/primer interface affecting primer adhesion. The humid storage conditions were also conducive to attack of the ablative coating by a *Cladosporium* species of fungus. The mechanical properties of the failed ablative coating examples did not always meet specification requirements.

Hardness and tensile testing revealed that a tacky ablative coating (that had failed at the primer/zinc phosphate interface) could be below the minimum hardness of 50 Shore D and still exceed the minimum UTS of 500 psi. An ablative coating exhibiting less tack had a 31% greater UTS value.

Recommendations

- All steps of the coating process should be carried out within the guidelines of the pertinent government and coating supplier specifications to achieve the desired properties of the coating system. A good zinc phosphate coating can be obtained by regular testing and maintenance of the baths utilized. There are simple titrations that can be performed to insure that the constituents of the baths are at prescribed levels. Routine cleaning of the baths is needed to minimize contamination that accumulates with normal production. To increase the interval of maintenance, deionized water should be utilized in the rinse baths as well as in the phosphate and chromic acid rinse.
- When powdery deposits do occur on the bombs, the surfaces should not be simply wiped. Wiping has been observed and found to spread the deposits. Instead, the bombs should be reworked. Bombs that have been successfully zinc phosphated should be allowed to dry adequately before

priming is executed. Drying of the zinc phosphated surface will also allow for proper inspection of the conversion coating.

- The primer, applied after zinc phosphating, should be allowed to dry adequately before handling. A dry primer will have optimal mechanical and adhesive properties and will not bond to other surfaces; i.e., tables and other bombs. Care should be taken when handling the properly primed and cured bomb bodies at the contracting manufacturer's facility, in rail cars, and at McAAP. Deep gouges were observed along the length of some MK83 bomb bodies when they were at the manufacturer's facility which had been mishandled by forklift machinery and were being prepared for shipment. Corrosion was observed in the areas where surface scratches ran deep into the metal substrate. All of these defects can contribute to coating failures during storage or in the field.
- The bomb pallets utilized for storage of the bomb bodies should be redesigned to lower the stress distributed on the ablative coating adjacent to the pallet saddles. The level of stress can be reduced by enlarging the surface area of the pallet saddles and eliminating any sharp machined edges.
- Reduce the humidity in storage igloos by increasing ventilation, repairing cracked floors, and draining standing water in gutters.



Figure 1 Predominant failure mode of coating was at the primer and zinc phosphate interface. Note the dark spots on both the interior primer surface and corresponding bomb surface.



Figure 2 Second type of coating failure occurred at ablative and primer interface. Ablative surrounding primer in center still adheres to the bomb.



Figure 3 Bomb pallet saddle with viscous fluid in center that had exuded from a bomb coating

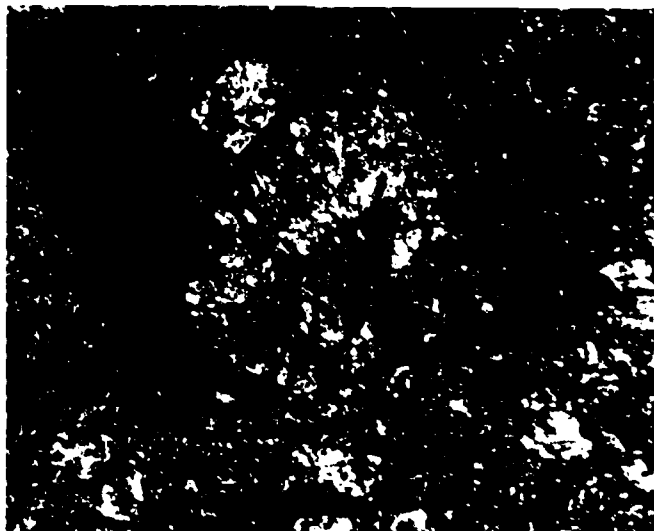


Figure 4 The dark spots on the interior primer surface were crystalline in appearance Mag 30X

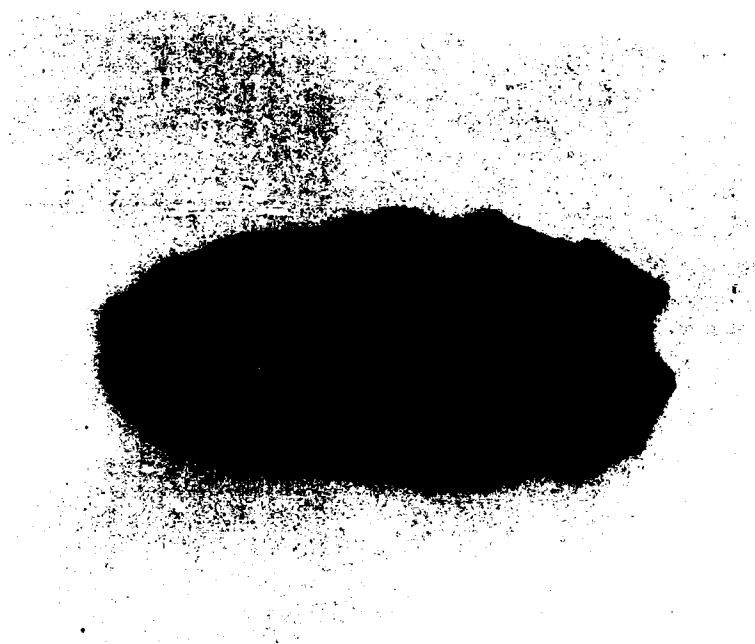


Figure 5. Interior surface of a fractured coating blister

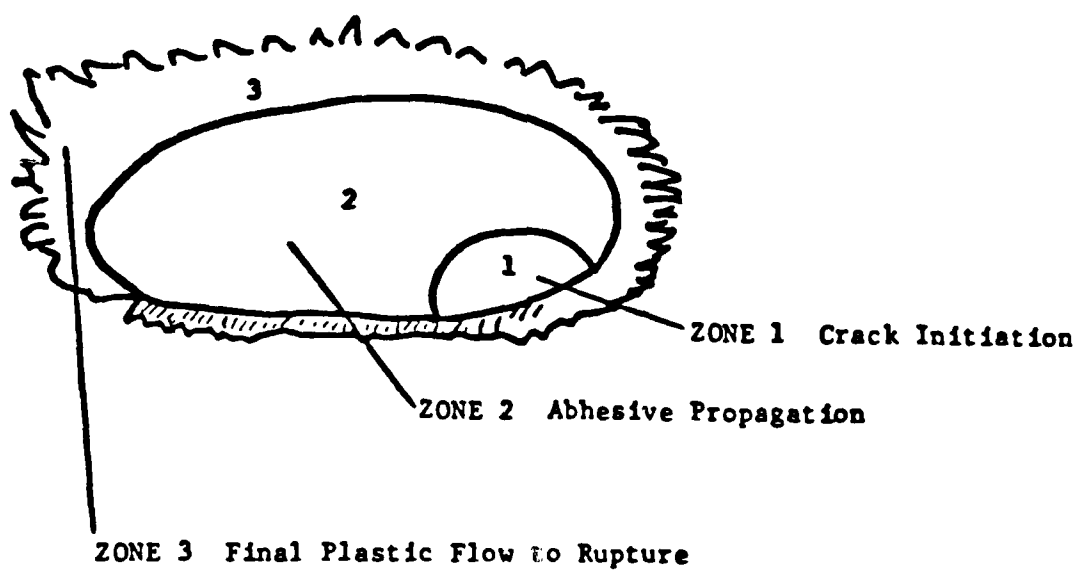


Figure 6. Schematic of the blister fracture face.

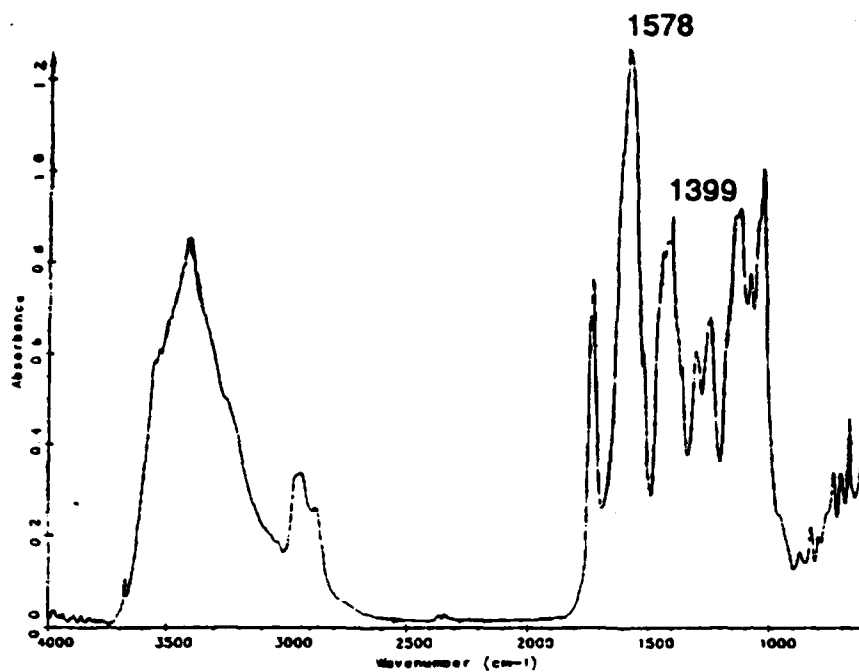


Figure 7. Infrared spectrum obtained from a crystalline spot on the interior primer surface of Specimen No. 2.

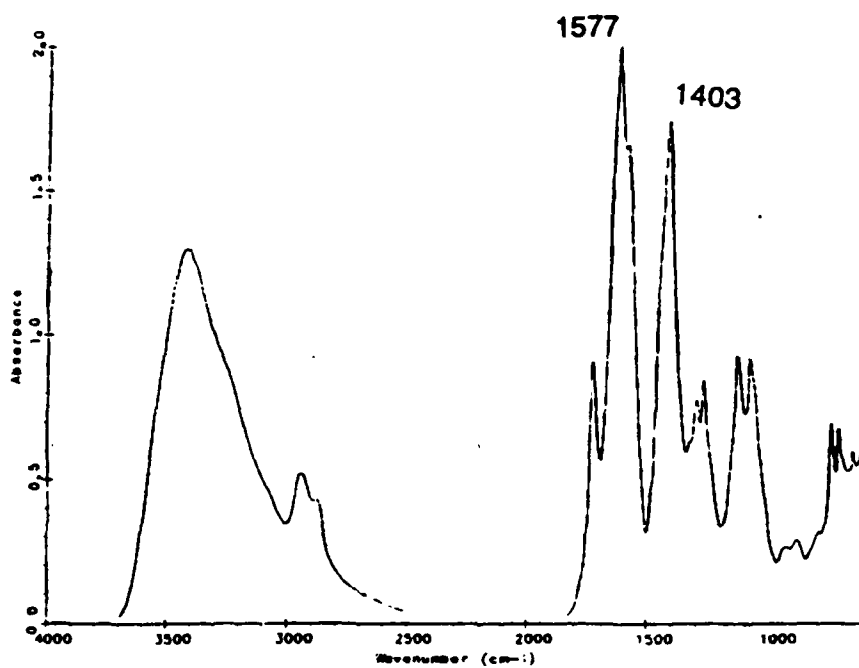


Figure 8. Infrared spectrum obtained from the leached viscous fluid found on Specimen No. 4, the bomb pallet saddle.

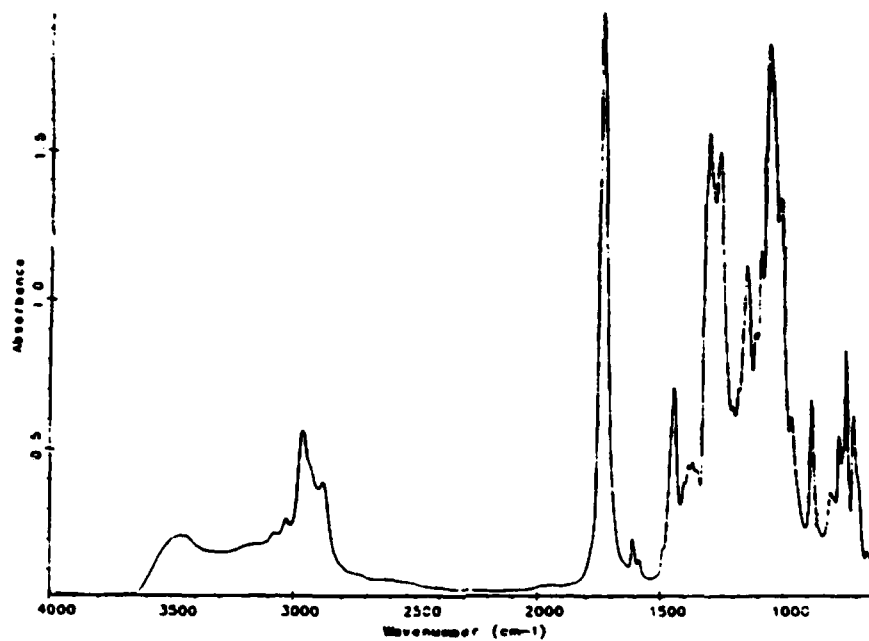


Figure 9. Infrared spectrum obtained from an acetone extract of the polyester ablative.

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