

AD-A276 595



ARMY RESEARCH LABORATORY



Condensed-Phase Processes During
Solid Propellant Combustion
III: Preliminary Depth-Profiling Studies
on XM39, JA2, M9, M30, and HMX2

Michael A. Schroeder
Robert A. Fifer
Martin S. Miller
Rose A. Pesce-Rodriguez
Claire J. Selawski
Gurbax Singh

RECEIVED
JAN 02 1994
E D

ARL-TR-346

January 1994

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

94 3 01 020

3096

94-06794



NOTICES

Destroy this report when it is no longer needed. DO NOT return it to the originator.

Additional copies of this report may be obtained from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

The findings of this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The use of trade names or manufacturers' names in this report does not constitute indorsement of any commercial product.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing the instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Service, General Services Administration, Paperwork Project, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE January 1994	3. REPORT TYPE AND DATES COVERED Final, Nov 90-Oct 91		
4. TITLE AND SUBTITLE Condensed-Phase Processes During Solid Propellant Combustion III: Preliminary Depth-Profiling Studies on XM39, JA2, M9, M30, and HMX2			5. FUNDING NUMBERS PR: 1L161102AH43	
6. AUTHOR(S) Michael A. Schroeder, Robert A. Fifer, Martin S. Miller, Rose A. Pesce-Rodriguez, Claire J. Selawski, and Gurbax Singh				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRL-WT-PC Aberdeen Proving Ground, MD 21005-5066			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRL-OP-CI-BC (Tech Lib) Aberdeen Proving Ground, MD 21005-5066			10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARL-TR-346	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This report describes preliminary depth-profiling studies on the chemical changes in the burned layers of propellant samples that have been burned in air, then quenched by dropping them into water. The changes studied described here are mainly those observable by infrared spectroscopy using an infrared microscope. Depth-profiling is obtained either by examining the cross section of a burned propellant sample or by abrasive blasting small amounts of material from the burned surface and examining the remaining surface in the infrared microscope. The propellants and compositions studied include XM39, JA2, M9, M30, and HMX2. For the nitramine-binder compositions XM39 and HMX2, the surface layers seem to consist of a layer of molten oxidizer (RDX or HMX) tens to hundreds of micrometers thick, overlaid by a 10- or 20- μ m-thick layer of binder and/or its decomposition products. In the case of the nitrate ester compositions JA2 and M9, the chemical changes observable by infrared spectroscopy seem to be very near the surface, within approximately 10 μ m. This is in agreement with our scanning electron microscope observations and with results in the literature.				
14. SUBJECT TERMS infrared spectroscopy, nitramines			15. NUMBER OF PAGES 27	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR	

INTENTIONALLY LEFT BLANK.

TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES	v
1. INTRODUCTION	1
2. EXPERIMENTAL	3
3. RESULTS	5
4. DISCUSSION	6
4.1 Cross-Section Examination	6
4.1.1 JA2	6
4.1.2 HMX 2	6
4.1.3 Formulation X	7
4.2 Abraded-Surface Examination	7
4.2.1 XM39	7
4.2.2 JA2	8
4.2.3 M9	8
4.2.4 M30	8
5. CONCLUSIONS	9
5.1 Nitramine-Binder Compositions	9
5.2 Nitrate Ester Compositions	9
5.3 M30	9
6. FUTURE PLANS	10
7. REFERENCES	17
DISTRIBUTION LIST	19

Accession For	
NTIS CR-31	<input checked="" type="checkbox"/>
DFC 773	<input type="checkbox"/>
Unpublished	<input type="checkbox"/>
By	
Date	
Availability Codes	
Dist	Avail and/or Special
A-1	

INTENTIONALLY LEFT BLANK.

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Apparatus used for abrasive blasting of extinguished samples	11
2. FTIR microscope spectra of JA2 propellant	11
3. FTIR microscope spectra of HMX-PEGA composition (HMX2)	12
4. FTIR microscope spectra of Formulation X	12
5. FTIR microscope spectrum of burned/quenched surface of XM39 propellant	13
6. FTIR microscope spectrum of virgin unburned XM39 propellant	13
7. FTIR microscope spectra of XM39 propellant surfaces	14
8. FTIR microscope spectra of JA2 propellant surfaces	14
9. FTIR microscope spectra of M9 propellant surfaces	15
10. FTIR microscope spectra of virgin M9 propellant	15
11. FTIR microscope spectra of M30 propellant surfaces	16

INTENTIONALLY LEFT BLANK.

1. INTRODUCTION

This is a progress report on work aimed at understanding the nature and importance of condensed-phase reactions in the combustion of solid nitramine and other gun propellants. Information on the nature and importance of condensed-phase reactions is needed as input for modeling studies. This information could also be very important in understanding the relationship of chemical structure and of physical properties such as melting point, phase transition temperatures, etc., to explosive and propellant behavior.

Our initial work has been described previously (Schroeder et al. 1990, 1992). Burning propellant samples were quenched, and the burned surfaces were examined microscopically and by chemical analysis. Studies were carried out on a series of propellants including XM39, M30, JA2, RDX, and on the HMX/binder composition HMX2. Preliminary results on XM39 are consistent with the idea that, at least at low pressures, there is a liquid layer approximately 100–300 μm thick present during the combustion of nitramine propellants; scanning electron microscope (SEM) examination revealed little if any evidence of degradation below this layer. Gas chromatography mass spectrometry (GCMS) results suggest that the stabilizer/plasticizer ratio is reduced considerably in the surface layers presumably either by reaction of stabilizer with nitrogen oxides formed by decomposition of RDX and nitrocellulose (NC) or by accumulation of plasticizer at the surface. High performance liquid chromatography (HPLC) results suggest that there is a significant increase in concentration of the mechanistically significant nitrosoamines MRDX and DRDX over the very small amounts possibly present as impurities in RDX. These results are consistent with the idea that RDX decomposition under propellant combustion conditions involves primarily (1) vaporization followed by gas-phase decomposition and/or (2) decomposition in the liquid phase to products that are almost entirely gaseous. Fourier transform infrared photoacoustic spectrometry (FTIR-PAS) examination of the burned surfaces also provided evidence for condensed-phase reaction in the compositions studied. Results of SEM examination of the burned surfaces of quenched samples of HMX2, HMX/PU, RDX, M30, and JA2 were also presented.

In the course of this work, samples have been obtained in two ways: (1) The propellant grains are ignited with a flame in air at ambient pressure and burning is interrupted by dropping the burning grain into a beaker of water (Schroeder et al. 1990); and (2) the propellants are burned in a low-pressure strand burner at different pressures (Schroeder et al. 1992); the sample is mounted on a massive copper block and burning is interrupted by conduction of heat away from the burning surface as the burning surface

approaches the copper block, as described by Novikov and Ryzantsev (1970). Previous reports (Schroeder et al. 1990, 1992) described preliminary results on a series of burned samples including XM39, M30, JA2, and RDX, on HMX-polyester (HMX2), and on HMX/PU compositions. In the future, we plan to investigate quenching by rapid depressurization caused by the breaking of a rupture disk in the strand burner; the various quenching methods will then be compared.

In the previous work, the samples were cleaved parallel to the grain axis and the cleaved surfaces were examined with an SEM. In addition, the surface layers were removed from the extinguished propellant grains by scraping with a small, sharp knife. The resulting scrapings were analyzed by spectroscopic methods such as FTIR-PAS, nuclear magnetic resonance (NMR), GCMS, and HPLC.

In this report, we describe our preliminary attempts at obtaining information on depth profiling (i.e., obtaining information on the variation with depth within the surface layers) to identify chemical changes caused by combustion. To date, results have been obtained by burning the samples in air and quenching by dropping them into water. The samples are then either (1) split as described above, after which the infrared spectra of portions of the cross section are obtained on an infrared (IR) microscope (cross-section examination); or (2) the IR microscope spectra are obtained on the top burned and abraded surface of the sample (abraded-surface examination).

The literature contains a number of papers describing microscopic examination of burned surfaces of propellant grains of HMX and compositions derived therefrom; these are listed in Schroeder et al. (1992). Wilmot et al. (1981) and Sharma et al. (1991) describe the chemical analysis of the burned surface of nitrate ester propellants. However, as far as we are aware, chemical analysis of burned surfaces has not been applied to nitramines or nitramine propellants, although in one study (Zimmer-Galler 1968), the surface layers of a quenched RDX-polyester composition were extracted with benzene and acetone, and the presence or absence of a residue under various conditions was noted. It was suggested that variations with particle size in the appearance (no spectra were reported) of material extracted with benzene and with acetone from the extinguished surface indicated an increase in surface temperature with decreasing particle size. Also, nitrosoamines have been detected in drop-weight impacted RDX (Hoffsomer, Glover, and Elban 1985).

2. EXPERIMENTAL

Table 1 shows the compositions of the various propellants studied. Samples were ignited with a candle, burned in air, and quenched by dropping into water as described previously (Schroeder et al. 1990, 1992). Cross sectioning was carried out as described in Schroeder et al. (1990, 1992). Formulation X was a propellant with the indicated composition; the structure of the plasticizer is proprietary. XM39, M9, JA2, and M30 propellants were from a series of standard propellants made up at the former U.S. Army Ballistic Research Laboratory (BRL) (now the Army Research Laboratory) for use in research studies. The lot numbers were as follows: XM39, IH-XM39-0988-100A1; M9, RAD-PE-792-77; JA2, RAD-PDI-002-1F; and M30, RAD-PE-792-82. HMX2 had the composition indicated in Table 1; it was prepared by a contractor for Dr. John Vanderhoff of BRL, to whom we are grateful for providing a generous sample.

Abrasive blasting was carried out using an abrasive blaster manufactured by S. S. White Dental Mfg. Company and referred to in the literature accompanying it as "Industrial Airbrasive Unit, Model C." The sample was mounted (Figure 1) with its burned surface uppermost on a platform rotated by a small electric motor; the rotation of the sample in the stream of abrasive provided more even and reproducible abrasion, at least with regard to angular variations in the intensity of the abrasive stream. The propellant sample was centered under the nozzle of the abrasive blaster. It was possible to vary the nozzle-to-sample distance and the flow of abrasive so that the amount of sample removed by each blasting is in the range of 5–20 μm . The depth of material removed was estimated from the weight change and the density and diameter of the unburned propellant, as given by the appropriate propellant description sheets. The abrasive was propelled by Matheson ultra-high-purity nitrogen. After abrasive-blasting, a stream of the same nitrogen was used to remove any leftover abrasive from the abraded surface. Note the possibility of error due to (a) the weight of any still-unremoved abrasive; and (b) radial or temporal variations in the intensity of the abrasive stream. Note also that the burned layers are often overlain by a layer of lower density foam, with the result that it is difficult to speak precisely about depths removed.

Microreflectance Fourier transform infrared (FTIR) spectra were obtained with 8 cm^{-1} resolution and 1024 scans, using a Spectra-Tech IR-Plan infrared microscope, operating in reflectance mode and interfaced to a Mattson Polaris FTIR Spectrometer operated through a PC running Mattson FIRST software. Where necessary, the Kramers-Kronig transformation was used to remove spectral distortions.

Table 1. Compositions of Propellant Formulations Studied

Propellant	Approximate Oxidizer Particle Size (μm)	Composition	Percentage of Total (%)
XM39	20	RDX Cellulose Acetate Butyrate Acetyl Triethyl Citrate Nitrocellulose (NC) (12.6% N) Ethyl Centralite (EC)	76.0 12.0 7.6 4.0 0.4
HMX2	100	HMX Polyester (PE)	80.0 20.0
M30	>50 long 1-5 wide	Nitroguanidine (NQ) Nitrocellulose (NC) (12.68% N) Nitroglycerine (NG) Ethyl Centralite (EC) Cryolite	47.7 28.0 22.5 1.5 0.3
JA2	N/A	Nitrocellulose (NC) (13.04% N) Nitroglycerine (NG) Diethylene Glycol Dinitrate Ethyl Centralite (EC) Magnesium Oxide Graphite	59.5 14.9 24.8 0.7 0.05 0.05
M9	N/A	Nitrocellulose (NC) Nitroglycerine (NG) Ethyl Centralite (EC) Potassium Nitrate	57.75 40.00 0.75 1.50
Formulation X	<20	RDX Cellulose Acetate Butyrate Nitrocellulose (NC) Proprietary Plasticizer	

Spectra were obtained on either the top of the burned surface or on the cross sections of the split pieces. The area examined (spot size) (specified in the captions to the figures) was 20 by 140 μm , 40 by 140 μm or 40 by 40 μm .

3. RESULTS

Results obtained to date are summarized in Figures 2–11 and in Table 2. Figures 2–4 show IR microscope reflectance spectra as a function of depth for cleaved samples of the indicated propellant and compositions. Figures 5–11 show IR microscope reflectance spectra of unburned propellant surfaces for burned/quenched surfaces before and after abrasive blasting.

Table 2. Summary of Conclusions for Compositions Studied

Propellant	Melt Thickness (μm)	General Conclusions (This Study)
XM39	100–300 ^a	<u>Abraded-Surface Examination:</u> Molten CAB/decomposition products in top 10–20 μm ; remainder is mostly molten RDX.
HMX2	25–100 ^a	<u>Cross-Section Examination:</u> Polyester/decomposition product decreases with increasing distance from surface, most change is in the top 40 μm .
M30	5–10 ^a	<u>Abraded-Surface Examination:</u> Top of surface depleted in nitroguanidine; top 10 μm or so shows signs of nitrocellulose decomposition; depth of nitroguanidine depletion is uncertain.
JA2	<5 ^a	<u>Cross-Section Examination:</u> Chemical changes go no lower than the top 40 μm of the subsurface region. <u>Abraded-Surface Examination:</u> Chemical changes go no lower than the top 11 \pm 9 μm of the subsurface region.
M9	Probably similar to JA2	<u>Abraded-Surface Examination:</u> Chemical changes less noticeable than for JA2, and go no lower than the top 9 μm of the subsurface region.
Formulation X	80	<u>Cross-Section Examination:</u> Surface shows far more binder and plasticizer than does unburned propellant; most binder and plasticizer confined to the top 20 μm (~25%) of melt layer. Relative amounts of plasticizer and binder are similar at surface and in the virgin material.

^a Source: Schroeder et al. 1990, 1992.

Column 2 of Table 1 shows the particle sizes of the oxidizers of the propellants under study; this information was obtained by SEM examination of the propellant in question, either in the course of the work described in this report, or in previous reports (Schroeder et al. 1990, 1992). This information is furnished so that, in combination with the area examined (see Section 2), the reliability of the IR microscope spectra as average representations of the samples can be evaluated.

4. DISCUSSION

In this section, conclusions are drawn about the individual samples and conditions examined from the actual experimental data obtained.

4.1 Cross-Section Examination

4.1.1 JA2. Figure 2 shows IR microscope spectra of a burned/quenched sample of JA2 propellant. Note the presence of a small peak at about $1,730\text{ cm}^{-1}$ in the spectrum of the extinguished surface and the increased intensity, relative to the rest of the spectrum, of the C-O-C stretching bands in the $1,000$ to $1,200\text{ cm}^{-1}$ region of the spectrum of the burned surface (spectrum(a)). These changes are barely, if at all, discernible in the spectrum of the region $0\text{--}40\text{ }\mu\text{m}$ below the surface (spectrum(b)) and are totally absent from the spectrum(c) of the region $40\text{--}80\text{ }\mu\text{m}$ below the surface CF (spectrum(d)). This suggests that these chemical changes are confined to the region $40\text{ }\mu\text{m}$ below the surface and, quite possibly, to the top few micrometers of that region.

4.1.2 HMX2. Figure 3 shows similar IR microscope spectra of a burned/quenched sample of HMX2 composition. The quenched surface shows an intense carbonyl peak ($1,730\text{--}1,750\text{ cm}^{-1}$) and aliphatic CH stretch peaks ($2,800\text{--}3,000\text{ cm}^{-1}$) assignable to the polyester binder. As the distance below the surface increases to $0\text{--}40\text{ }\mu\text{m}$ and then to $40\text{--}80\text{ }\mu\text{m}$, the relative intensities of these peaks decrease and the relative intensities of the HMX peaks begins to increase. The melt layer of this sample was about $80\text{--}100\text{ }\mu\text{m}$ thick; this is in agreement with a previous report which described SEM examinations indicating a melt-layer thickness of $25\text{--}100\text{ }\mu\text{m}$ for HMX2 under these conditions. These results are consistent with the idea that the concentration of binder in the melt layer is greatest near the surface and decreases with increasing distance from the surface, with most of the changes in the first $40\text{ }\mu\text{m}$ below the surface.

4.1.3 Formulation X. Figure 4 shows similar IR microscope spectra of a partially burned sample of Formulation X. The quenched surface shows increased absorption at about $1,750\text{ cm}^{-1}$, due to the carbonyl group of the cellulose acetate butyrate (CAB) or its decomposition products, as well as a greatly increased absorption at about $2,100\text{ cm}^{-1}$, possibly due to undecomposed sp-hybridized functional groupings in the plasticizer or binder. In the region within approximately $20\text{ }\mu\text{m}$ of the surface, the $1,750\text{-cm}^{-1}$ and $2,100\text{-cm}^{-1}$ absorptions may decrease somewhat but remain quite strong. By the time the region $20\text{--}40\text{ }\mu\text{m}$ below the surface is reached, however, these absorptions have decreased greatly, almost to the levels present in virgin bulk material. Since SEM examination of the split samples shows a melt layer approximately $80\text{ }\mu\text{m}$ thick, these results are also consistent with the idea that the concentration of binder/plasticizer, etc., in the melt layer is greatest near the surface and drops off with increasing distance from the surface. Nearly all of the binder/plasticizer and decomposition products are in the upper $20\text{ }\mu\text{m}$, the remainder of the melt layer being primarily RDX.

4.2 Abraded-Surface Examination

4.2.1 XM39. Figure 5 shows an IR microscope spectrum of the quenched surface of a burned, extinguished grain of XM39. Figure 6 shows an IR microscope spectrum of virgin XM39 propellant. The spectrum of the quenched surface (Figure 5) is very similar, with the exception of the RDX band at $1,574\text{ cm}^{-1}$, to that of the CAB binder used in XM39 (spectrum not shown). Earlier FTIR-PAS spectra (Schroeder et al. 1990) of quenched and virgin samples of XM39 show the burned sample as looking basically like a CAB-enriched sample of XM39. This discrepancy can be explained if, as expected, the FTIR microscope reflectance spectra are representative of the surface while the FTIR-PAS (Schroeder et al. 1990, 1992) spectra are average spectra representative of the material not only on the surface but for some distance into the sample. Thus, the IR microscope spectra have contributed insight: the enrichment in CAB noted previously (Schroeder et al. 1990) appears to be mainly on the surface of the sample and probably does not extend very far down into the sample.

This is confirmed by the spectra shown in Figure 7. This figure shows FTIR microscope spectra of quenched and virgin surfaces of XM39 and of the quenched sample after removal of portions of the surface material. Even after removal of only $17\text{ }\mu\text{m}$ (estimated) by a single abrasive blasting, the spectrum resembles the virgin material much more than the quenched, unabraded sample. Our previous report (Schroeder et al. 1990) included SEM photographs which indicated a melt layer approximately $100\text{--}300\text{ }\mu\text{m}$ thick for samples burned/quenched under the conditions used here. Thus, it appears that only

the very top part of the quenched layer was CAB and its decomposition products. The remainder appears to be mostly RDX; this is consistent with its apparent crystalline nature (Schroeder et al. 1990, 1992) and with the low melting point (204° C) of RDX.

4.2.2 JA2. Figure 8 shows FTIR microscope spectra of quenched and virgin samples of JA2 propellant and of the quenched sample after removal of portions of the surface material. The quenched sample shows a carbonyl band approximately $1,730\text{ cm}^{-1}$ and an increase in the C-O-C bands at $1,000\text{--}1,200\text{ cm}^{-1}$ relative to the NO_2 bands at $\sim 1,650$ and $1,280\text{ cm}^{-1}$. After removal of an estimated $2\text{ }\mu\text{m}$ by a single abrasive blasting, the $1,730\text{ cm}^{-1} > \text{C} = \text{O}$ peak is still present, but after $19\text{ }\mu\text{m}$ (estimated) have been removed, the spectrum resembles the virgin material, except for bands at about $1,500\text{--}1,550\text{ cm}^{-1}$ and 880 cm^{-1} . These bands may be due to the abrasive since they increase with the number of blastings for both JA2 and the similar composition M9. (See Section 4.2.3).

4.2.3 M9. Figure 9 shows FTIR microscope spectra of quenched and virgin samples of M9 propellant and of the quenched sample after removal of portions of the surface material. The behavior here is similar to that for JA2, except that the differences due to the burning seem to be smaller. Note also the peaks at $1,530\text{ cm}^{-1}$ and 890 cm^{-1} ; these peaks do not match the spectrum of the abrasive. However, they appear to be associated with the abrasive-blasting process since they become more intense with each successive abrasive-blasting, even on unburned samples (Figure 10).

4.2.4 M30. Figure 11 shows FTIR microscope spectra of quenched and virgin samples of M30 propellant and of the quenched sample after removal of portions of the surface material. As expected, the spectrum of the virgin material appears to be the sum of the individual spectra for NC and NQ. The spectrum of the quenched surface shows a reduction in the amount of NQ, as well as what appears to be a very small amount of carbonyl absorption in the $1,730\text{ cm}^{-1}$ region; this last apparently results from NC decomposition as described previously for M9 and JA2. The small carbonyl absorption is gone after only one blasting, with removal of an estimated $2\text{ }\mu\text{m}$. However, even after removal of approximately $106\text{ }\mu\text{m}$ in six blastings, the spectrum still is not the same as that of virgin material; the NQ peak at $1,412\text{ cm}^{-1}$ still appears weaker than in the virgin material, and the peaks at $1,667\text{ cm}^{-1}$ (NC, NQ) and $1,640\text{ cm}^{-1}$ (NQ), and at $1,285\text{ cm}^{-1}$ (NC) and $1,330\text{ cm}^{-1}$ (NQ) do not appear to be split as strongly as in the virgin material. This seems surprising, since in previous work (Schroeder et al. 1992) the melt layer for M30

under these conditions appeared to be quite thin (5–10 μm). This is discussed further in Section 5. See Section 4.2.3 for a discussion of the peaks at $1,530\text{ cm}^{-1}$ and at 890 cm^{-1} .

5. CONCLUSIONS

In Section 4, the experimental observations were translated into information on the individual propellants obtained by the two methods that have been employed (cross-section examination and quenched/abraded-surface examination). These observations are summarized in Table 2. In this section, an attempt will be made to generalize for the various propellants and types of propellants studied.

5.1 Nitramine-Binder Compositions. For most of the nitramine-binder compositions (XM39, HMX2, and Formulation X) studied here, and possibly for nitramine-binder compositions generally, the surface layers seem to consist of a layer of molten oxidizer (RDX or HMX) tens to hundreds of micrometers thick, overlaid by a much thinner, 10- to 20- μm -thick layer of binder and/or its decomposition products. This conclusion stands out most clearly for XM39 (Figures 5–7, Table 2) and for Formulation X (Figure 4, Table 2). Since HMX2 and Formulation X were studied by the method of cross-section examination and XM39 was studied by the method of abraded-surface examination, it can be said that these two methods have produced results in qualitative agreement with each other.

5.2 Nitrate Ester Compositions. In the case of the nitrate ester compositions, JA2 (Figures 2 and 8, Table 2) and M9 (Figure 9, Table 2), the chemical changes observable by IR spectroscopy seem to be very near the surface, within 10 μm or so. This is in agreement with our earlier SEM observations (Schroeder et al. 1992) and with previous studies (Sharma et al. 1991) on a closely related formulation. In the case of JA2, the method of abraded-surface examination indicated that the changes due to burning occur within approximately 10 μm of the surface, while the method of cross-section examination indicated that the changes due to burning occur within approximately 40 μm of the burning surface. Since the resolution of the cross-section examination method as applied to this sample was 40 μm , it does not seem unreasonable to say that the two methods agree, although the resolution of the cross-section examination method was less precise in this particular case.

5.3 M30. The triple-base, NQ-containing propellant, M30 (Figure 10, Table 2), also contains NC and NG. The unabraded surface of the burned sample is noticeably depleted in NQ, and, in addition, has gained a weak absorption in the $1,730\text{-cm}^{-1}$ region, apparently due to NC decomposition. The $1,730\text{-cm}^{-1}$

peak disappears upon removal of approximately 2 μm ; but the NQ has not regained its original intensity even after removal of $\sim 106\ \mu\text{m}$ of material. This seems surprising, since in our previous work (Schroeder et al. 1992), the melt layer for M30 under these conditions appeared to be quite thin (5–10 μm). Possibly, the NQ decomposes to a greater depth than the other ingredients; this might have something to do with the fact that the NQ in M30 is in the form of long crystals oriented perpendicular to the burned surface. Another possibility might be that some of the NQ softens before melting, changing its spectral intensities.

6. FUTURE PLANS

Runs will be carried out in a strand burner with depressurization quenching, and the results will be compared with those from the two conductive-quenching methods used to date.

Also, optical examination of the quenched surfaces will be carried out, particularly in view of the possibility that studies of color changes and variations may yield information on the occurrence (or lack thereof) of chemical changes in the solid below the liquid layer.

Additional ways of obtaining improved depth profiling of the burned layers are also being explored; these include microabrasive blasting, microtoming, solvent-dipping, and improved scraping procedures. Depth profiling will be applied to the nitrosoamine-formation and stabilizer-depletion results reported previously (Schroeder et al. 1990, 1992). Additional binders, oxidizers, and compositions will be studied. Other propellant formulations will also be examined.

Isotope-scrambling studies on burning (rather than merely decomposing) samples are needed. These would involve use of unlabeled RDX or HMX with RDX or HMX labeled with nitrogen-15 in all nitrogens, both in the ring and in the nitro groups. Use of these mixtures would lead to scrambled nitrosoamines if the recombination mechanism were operating, and to unscrambled nitrosamines if the oxygen-abstraction mechanism were operating (Schroeder et al. 1990). Partial scrambling would mean that both mechanisms were operating to some degree. Note, however, that while formation of fully scrambled nitrosoamines would provide no evidence for oxygen abstraction, it would not necessarily rule it out, since the scrambling could have taken place by further N-N cleavage equilibria before or after formation of the nitrosoamines.

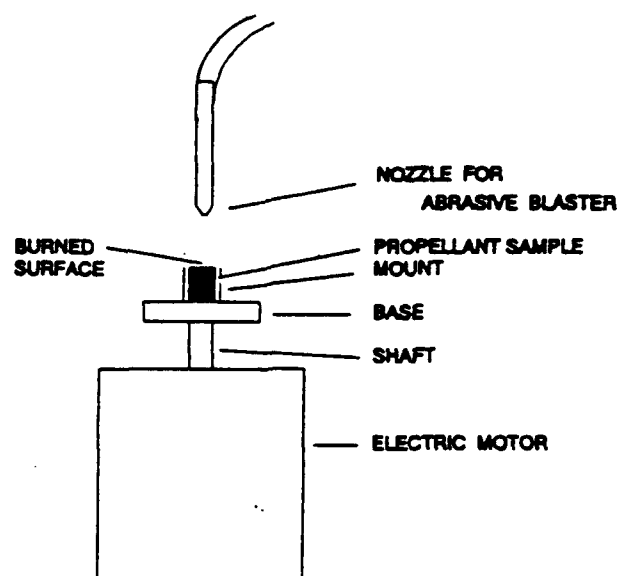


Figure 1. Apparatus used for abrasive blasting of extinguished samples.

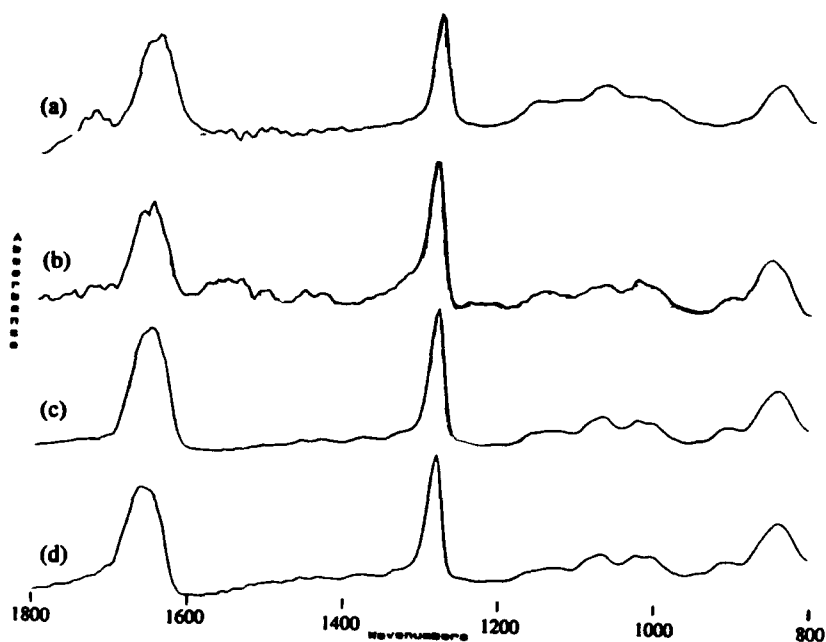


Figure 2. FTIR microscope spectra of JA2 propellant (area sampled $40 \times 140 \mu\text{m}$): (a) extinguished surface; (b) $0\text{--}40 \mu\text{m}$ below burned/quenched surface; (c) $40\text{--}80 \mu\text{m}$ below burned/quenched surface; (d) virgin, unburned bulk material.

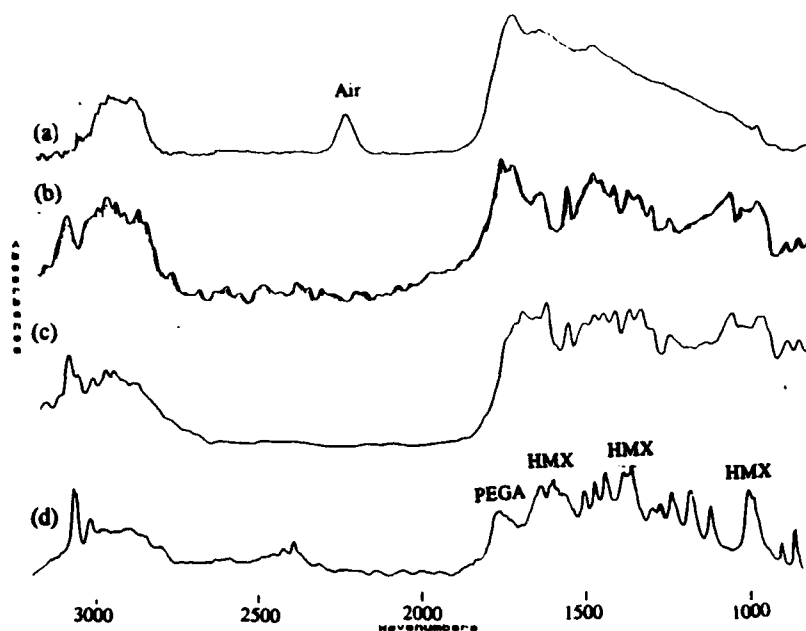


Figure 3. FTIR microscope spectra of HMX-PEGA composition (HMX2) (area sampled $40 \times 140 \mu\text{m}$): (a) extinguished surface; (b) 0–40 μm below burned/quenched surface; (c) 40–80 μm below burned/quenched surface; (d) virgin, unburned bulk material.

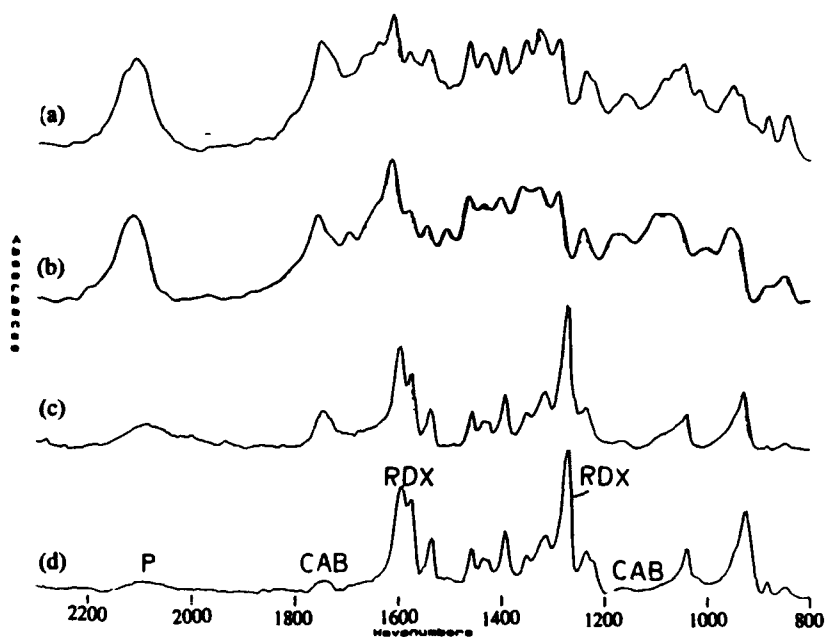


Figure 4. FTIR microscope spectra of Formulation X (area sampled $20 \times 140 \mu\text{m}$): (a) extinguished surface; (b) 0–20 μm below burned/quenched surface; (c) 20–40 μm below burned/quenched surface; (d) virgin, unburned bulk material.

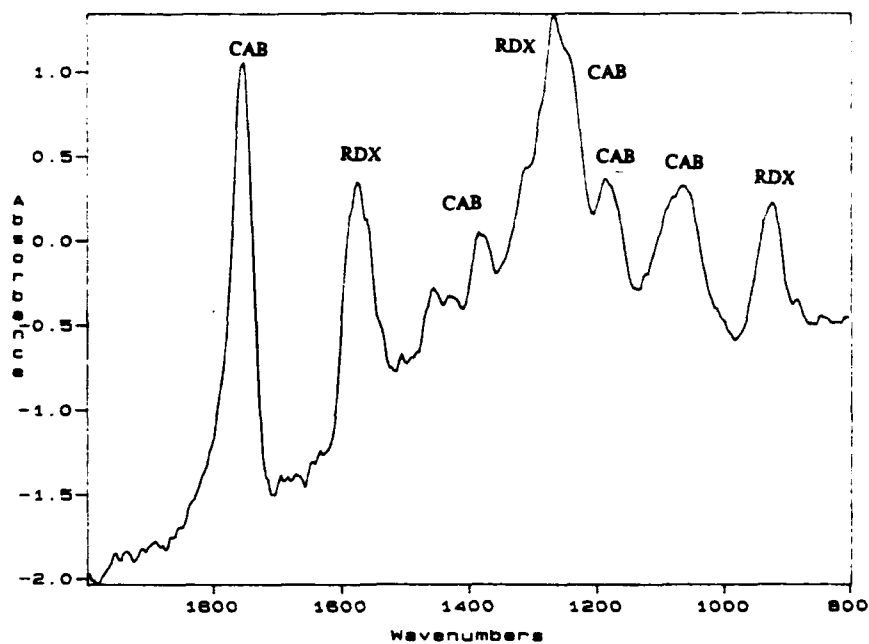


Figure 5. FTIR microscope spectrum of burned/quenched surface of XM39 propellant (area sampled 40 x 40 μm).

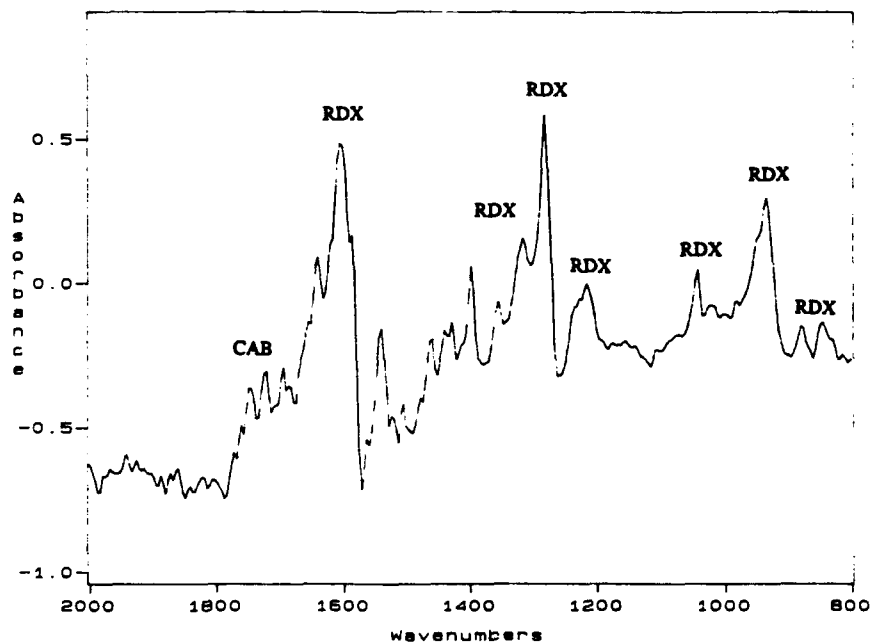


Figure 6. FTIR microscope spectrum of virgin, unburned XM39 propellant (area sampled 40 x 40 μm).

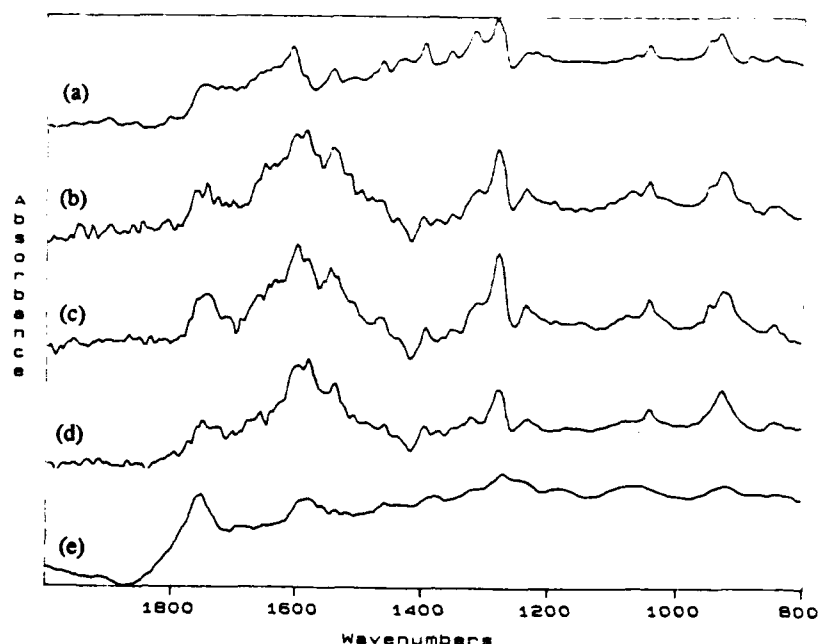


Figure 7. FTIR microscope spectra of XM39 propellant surfaces (area sampled $40 \times 40 \mu\text{m}$): (a) virgin, (b) virgin, blasted once with abrasive; (c) burned/quenched, $367 \mu\text{m}$ removed; (d) burned/quenched, $17 \mu\text{m}$ removed; (e) burned/quenched, unblasted.

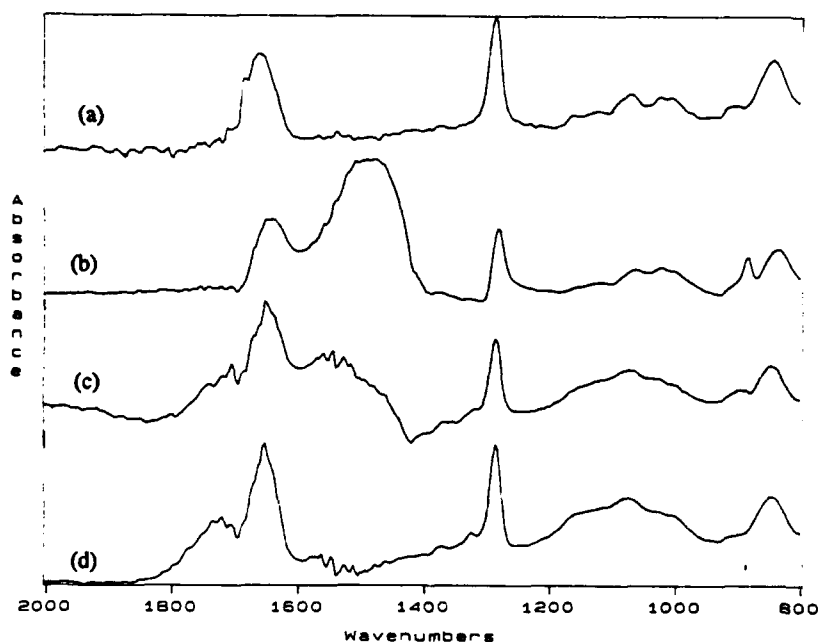


Figure 8. FTIR microscope spectra of JA2 propellant surfaces (area sampled $40 \times 40 \mu\text{m}$): (a) virgin; (b) burned/quenched, $19 \mu\text{m}$ removed; (c) burned/quenched, $2 \mu\text{m}$ removed; (d) burned/quenched, unblasted.

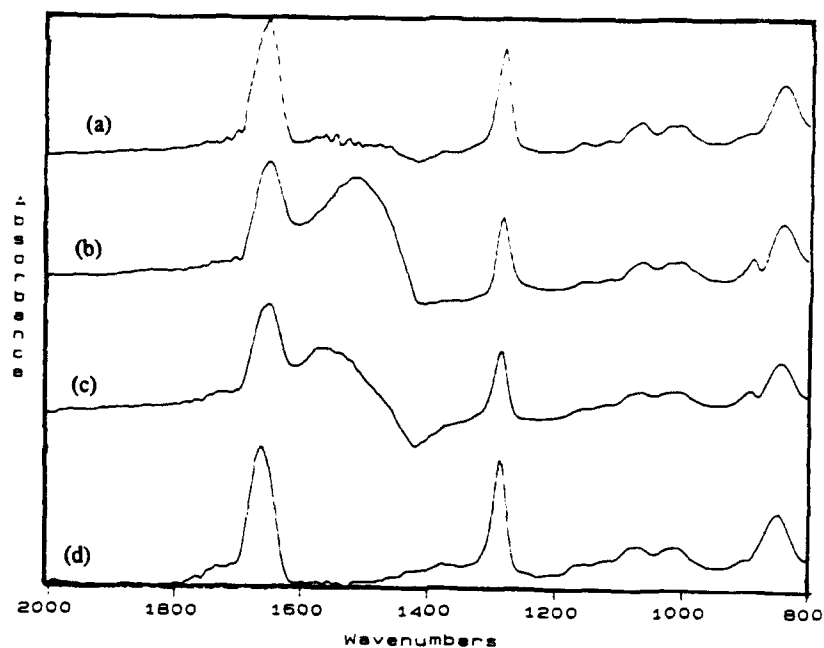


Figure 9. FTIR microscope spectra of M9 propellant surfaces (area sampled $40 \times 40 \mu\text{m}$): (a) virgin; (b) burned/quenched, $9 \mu\text{m}$ removed; (c) burned/quenched, $7 \mu\text{m}$ removed; (d) burned/quenched, unblasted.

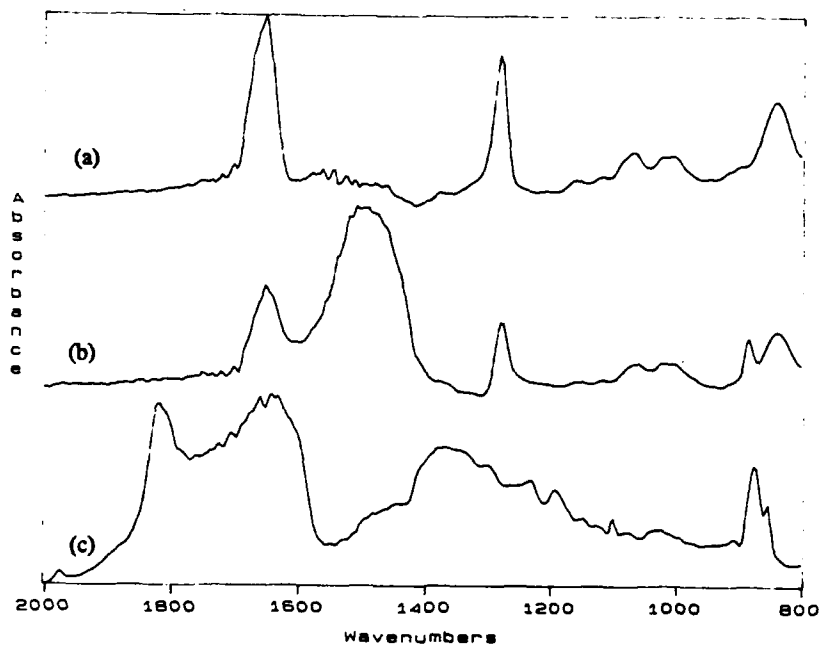


Figure 10. FTIR microscope spectra (area sampled, $40 \times 40 \mu\text{m}$) of: (a) virgin M9 propellant; (b) virgin M9 propellant sandblasted once; (c) abrasive used for sandblasting.

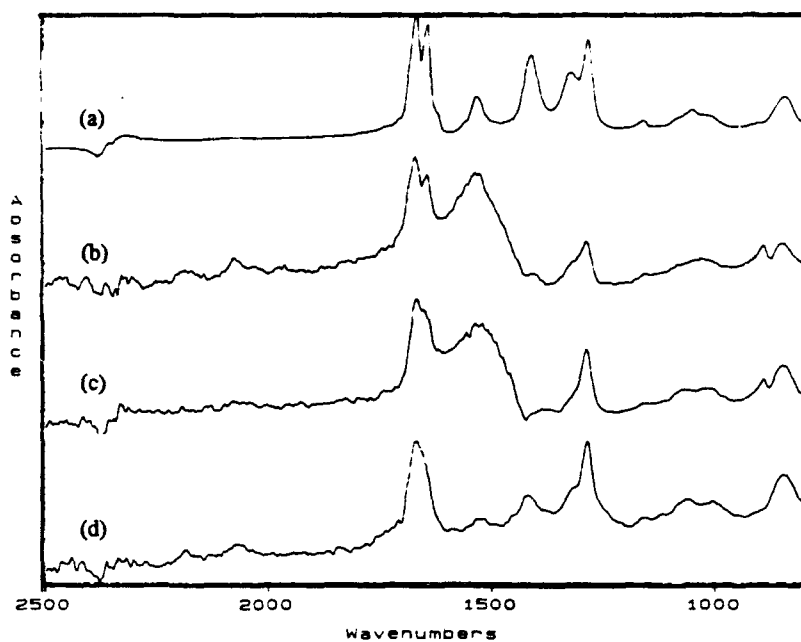


Figure 11. FTIR microscope spectra of M30 propellant surfaces (area sampled $40 \times 40 \mu\text{m}$):
(a) virgin; (b) burned/quenched, 106 μm removed; (c) burned/quenched, 2 μm removed;
(d) burned/quenched, unblasted.

7. REFERENCES

- Hoffsommer, J. C., D. J. Glover, and W. L. Elban. "Quantitative Evidence for Nitroso Compound Formation in Drop-Weight Impacted RDX Crystals." Journal of Energetic Materials, vol. 3, pp. 149-167, 1985.
- Novikov, S. S., and Y. S. Ryzantsev. "Extinction of Propellant Near the Contact with a Metal." AIAA Journal, vol. 8, pp. 358-359, 1970.
- Schroeder, M. A., R. A. Fifer, M. S. Miller, and R. A. Pesce-Rodriguez. "Condensed-Phase Processes During Solid-Propellant Combustion. I. Preliminary Chemical and Microscopic Examination of Extinguished Propellant Samples." BRL-MR-3845, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD, June 1990. (AD-A225 581)
- Schroeder, M. A., R. A. Fifer, M. S. Miller, R. A. Pesce-Rodriguez, and G. Singh. "Condensed-Phase Processes During Solid-Propellant Combustion. II. Chemical and Microscopic Examination of Conductively-Quenched Samples of RDX, XM39, JA2, M30 and HMX-Binder Compositions." BRL-TR-3337, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD, May 1992. (AD-A250 799)
- Sharma, J., G. B. Wilmot, A. A. Campolattaro, and F. Santiago. "XPS Study of Condensed Phase Combustion in Double Base Rocket Propellant With and Without Lead Salt Burning Rate Modifier." Combustion and Flame, vol. 85, pp. 416-426, 1991.
- Wilmot, G. B., E. G. Powell, J. Sharma, and D. Carlson. "Combustion Mechanisms of Lead-Salt-Catalyzed Double-Base Propellants." Proceedings of the 18th JANNAF Combustion Meeting, CPIA Publication No. 347, vol. 3, pp. 297-306, October 1981.
- Zimmer-Galler, R. "Correlations Between Deflagration Characteristics and Surface Properties of Nitramine-Based Propellants." AIAA Journal, vol. 6, pp. 2107-2110, 1968.

INTENTIONALLY LEFT BLANK.

<u>No. of Copies</u>	<u>Organization</u>
2	Administrator Defense Technical Info Center ATTN: DTIC-DDA Cameron Station Alexandria, VA 22304-6145
1	Commander U.S. Army Materiel Command ATTN: AMCAM 5001 Eisenhower Ave. Alexandria, VA 22333-0001
1	Director U.S. Army Research Laboratory ATTN: AMSRL-OP-CI-AD, Tech Publishing 2800 Powder Mill Rd. Adelphi, MD 20783-1145
1	Director U.S. Army Research Laboratory ATTN: AMSRL-OP-CI-AD, Records Management 2800 Powder Mill Rd. Adelphi, MD 20783-1145
2	Commander U.S. Army Armament Research, Development, and Engineering Center ATTN: SMCAR-IMI-I Picatinny Arsenal, NJ 07806-5000
2	Commander U.S. Army Armament Research, Development, and Engineering Center ATTN: SMCAR-TDC Picatinny Arsenal, NJ 07806-5000
1	Director Benet Weapons Laboratory U.S. Army Armament Research, Development, and Engineering Center ATTN: SMCAR-CCB-TL Watervliet, NY 12189-4050
1	Director U.S. Army Advanced Systems Research and Analysis Office (ATCOM) ATTN: AMSAT-R-NR, M/S 219-1 Ames Research Center Moffett Field, CA 94035-1000

<u>No. of Copies</u>	<u>Organization</u>
1	Commander U.S. Army Missile Command ATTN: AMSMI-RD-CS-R (DOC) Redstone Arsenal, AL 35898-5010
1	Commander U.S. Army Tank-Automotive Command ATTN: AMSTA-JSK (Armor Eng. Br.) Warren, MI 48397-5000
1	Director U.S. Army TRADOC Analysis Command ATTN: ATRC-WSR White Sands Missile Range, NM 88002-5502
(Class. only) 1	Commandant U.S. Army Infantry School ATTN: ATSH-CD (Security Mgr.) Fort Benning, GA 31905-5660
(Unclass. only) 1	Commandant U.S. Army Infantry School ATTN: ATSH-WCB-O Fort Benning, GA 31905-5000
1	WL/MNOI Eglin AFB, FL 32542-5000 <u>Aberdeen Proving Ground</u>
2	Dir, USAMSAA ATTN: AMXSY-D AMXSY-MP, H. Cohen
1	Cdr, USATECOM ATTN: AMSTE-TC
1	Dir, USAERDEC ATTN: SCBRD-RT
1	Cdr, USACBDCOM ATTN: AMSCB-CII
1	Dir, USARL ATTN: AMSRL-SL-I
5	Dir, USARL ATTN: AMSRL-OP-CI-B (Tech Lib)

<u>No. of Copies</u>	<u>Organization</u>
1	HQDA, OASA (RDA) ATTN: Dr. C.H. Church Pentagon, Room 3E486 WASH DC 20310-0103
4	Commander US Army Research Office ATTN: R. Ghirardelli D. Mann R. Singleton R. Shaw P.O. Box 12211 Research Triangle Park, NC 27709-2211
1	Director Army Research Office ATTN: AMXRO-MCS, K. Clark P.O. Box 12211 Research Triangle Park, NC 27709-2211
1	Director Army Research Office ATTN: AMXRO-RT-IP, Library Services P.O. Box 12211 Research Triangle Park, NC 27709-2211
4	Commander US Army Armament Research, Development, and Engineering Center ATTN: SMCAR-AEE-WW, S. Bulusu SMCAR-AEE-WE, T. Chen SMCAR-AEE-B, D.S. Downs SMCAR-AEE, J.A. Lannon Picatinny Arsenal, NJ 07806-5000
1	Commander US Army Armament Research, Development, and Engineering Center ATTN: SMCAR-AEE-BR, L. Harris Picatinny Arsenal, NJ 07806-5000
2	Commander US Army Missile Command ATTN: AMSMI-RD-PR-E, A.R. Maykut AMSMI-RD-PR-P R. Betts Redstone Arsenal, AL 35898-5249

<u>No. of Copies</u>	<u>Organization</u>
1	Office of Naval Research Department of the Navy ATTN: R.S. Miller, Code 432 800 N. Quincy Street Arlington, VA 22217
1	Commander Naval Air Systems Command ATTN: J. Ramnarace, AIR-54111C Washington, DC 20360
2	Commander Naval Surface Warfare Center ATTN: R. Bernecker, R-13 G.B. Wilmot, R-16 Silver Spring, MD 20903-5000
5	Commander Naval Research Laboratory ATTN: M.C. Lin J. McDonald E. Oran J. Shnur R.J. Doyle, Code 6110 Washington, DC 20375
2	Commander Naval Weapons Center ATTN: T. Boggs, Code 388 T. Parr, Code 3895 China Lake, CA 93555-6001
1	Superintendent Naval Postgraduate School Dept. of Aeronautics ATTN: D.W. Netzer Monterey, CA 93940
3	AL/LSCF ATTN: R. Corley R. Geisler J. Levine Edwards AFB, CA 93523-5000
1	AFOSR ATTN: J.M. Tishkoff Bolling Air Force Base Washington, DC 20332

<u>No. of Copies</u>	<u>Organization</u>
1	OSD/SDIO/IST ATTN: L. Caveny Pentagon Washington, DC 20301-7100
1	Commandant USAFAS ATTN: ATSF-TSM-CN Fort Sill, OK 73503-5600
1	University of Dayton Research Institute ATTN: D. Campbell AL/PAP Edwards AFB, CA 93523
1	NASA Langley Research Center Langley Station ATTN: G.B. Northam/MS 168 Hampton, VA 23365
4	National Bureau of Standards ATTN: J. Hastie M. Jacox T. Kashiwagi H. Semerjian US Department of Commerce Washington, DC 20234
2	Director Lawrence Livermore National Laboratory ATTN: C. Westbrook W. Tao, MS L-282 P.O. Box 808 Livermore, CA 94550
1	Director Los Alamos National Lab ATTN: B. Nichols, T7, MS-B284 P.O. Box 1663 Los Alamos, NM 87545
1	National Science Foundation ATTN: A.B. Harvey Washington, DC 20550

<u>No. of Copies</u>	<u>Organization</u>
2	Princeton Combustion Research Laboratories, Inc. ATTN: N.A. Messina M. Summerfield Princeton Corporate Plaza Bldg. IV, Suite 119 11 Deerpark Drive Monmouth Junction, NJ 08852
5	Director Sandia National Laboratories ATTN: R. Cattolica, Div. 8354 S. Johnston, Div. 8354 P. Mattern, Div. 8354 D. Stephenson, Div. 8354 R. Skyocypec, Div. 1513 Livermore, CA 94550
1	Brigham Young University Dept. of Chemical Engineering ATTN: M.W. Beckstead Provo, UT 84058
1	California Institute of Tech. Jet Propulsion Laboratory ATTN: L. Strand/MS 125-224 4800 Oak Grove Drive Pasadena, CA 91109
1	California Institute of Technology ATTN: F.E.C. Culick/MC 301-46 204 Karman Lab. Pasadena, CA 91125
1	University of California Los Alamos Scientific Lab. P.O. Box 1663, Mail Stop B216 Los Alamos, NM 87545
1	University of California, Berkeley Chemistry Department ATTN: C. Bradley Moore 211 Lewis Hall Berkeley, CA 94720
1	University of California, San Diego ATTN: F.A. Williams AMES, B010 La Jolla, CA 92093

<u>No. of Copies</u>	<u>Organization</u>	<u>No. of Copies</u>	<u>Organization</u>
2	University of California, Santa Barbara Quantum Institute ATTN: K. Schofield M. Steinberg Santa Barbara, CA 93106	1	The Johns Hopkins University Chemical Propulsion Information Agency ATTN: T.W. Christian 10630 Little Patuxent Parkway, Suite 202 Columbia, MD 21044-3200
1	University of Colorado at Boulder Engineering Center ATTN: J. Daily Campus Box 427 Boulder, CO 80309-0427	1	University of Maryland, Eastern Shore Department of Natural Sciences ATTN: G. Singh Princess Anne, MD 21853-1299
3	University of Southern California Dept. of Chemistry ATTN: R. Beaudet S. Benson C. Wittig Los Angeles, CA 90007	1	University of Michigan Gas Dynamics Lab Aerospace Engineering Bldg. ATTN: G.M. Faeth Ann Arbor, MI 48109-2140
1	Cornell University Department of Chemistry ATTN: T.A. Cool Baker Laboratory Ithaca, NY 14853	1	University of Minnesota Dept. of Mechanical Engineering ATTN: E. Fletcher Minneapolis, MN 55455
1	University of Delaware ATTN: T. Brill Chemistry Department Newark, DE 19711	4	Pennsylvania State University Dept. of Mechanical Engineering ATTN: K. Kuo M. Micci S. Thynell V. Yang University Park, PA 16802
1	University of Florida Dept. of Chemistry ATTN: J. Winefordner Gainesville, FL 32611	1	Polytechnic Institute of NY Graduate Center ATTN: S. Lederman Route 110 Farmingdale, NY 11735
3	Georgia Institute of Technology School of Aerospace Engineering ATTN: E. Price W.C. Strahle B.T. Zinn Atlanta, GA 30332	2	Princeton University Forrestal Campus Library ATTN: K. Brezinsky I. Glassman P.O. Box 710 Princeton, NJ 08540
1	University of Illinois Dept. of Mech. Eng. ATTN: H. Krier 144MEB, 1206 W. Green St. Urbana, IL 61801	1	Purdue University School of Aeronautics and Astronautics ATTN: J.R. Osborn Grissom Hall West Lafayette, IN 47906

<u>No. of Copies</u>	<u>Organization</u>
1	Purdue University Department of Chemistry ATTN: E. Grant West Lafayette, IN 47906
2	Purdue University School of Mechanical Engineering ATTN: N.M. Laurendeau S.N.B. Murthy TSPC Chaffee Hall West Lafayette, IN 47906
1	Rensselaer Polytechnic Inst. Dept. of Chemical Engineering ATTN: A. Fontijn Troy, NY 12181
1	Stanford University Dept. of Mechanical Engineering ATTN: R. Hanson Stanford, CA 94305
1	University of Texas Dept. of Chemistry ATTN: W. Gardiner Austin, TX 78712
1	Virginia Polytechnic Institute and State University ATTN: J.A. Schetz Blacksburg, VA 24061
1	Applied Combustion Technology, Inc. ATTN: A.M. Varney P.O. Box 607885 Orlando, FL 32860
2	Applied Mechanics Reviews The American Society of Mechanical Engineers ATTN: R.E. White A.B. Wenzel 345 E. 47th Street New York, NY 10017
1	Atlantic Research Corp. ATTN: R.H.W. Waesche 7511 Wellington Road Gainesville, VA 22065

<u>No. of Copies</u>	<u>Organization</u>
1	Textron Defense Systems ATTN: A. Patrick 2385 Revere Beach Parkway Everett, MA 02149-5900
1	Battelle ATTN: TWSTIAC 505 King Avenue Columbus, OH 43201-2693
1	Cohen Professional Services ATTN: N.S. Cohen 141 Channing Street Redlands, CA 92373
1	Exxon Research & Eng. Co. ATTN: A. Dean Route 22E Annandale, NJ 08801
1	General Applied Science Laboratories, Inc. 77 Raynor Avenue Ronkonkoma, NY 11779-6649
1	General Electric Ordnance Systems ATTN: J. Mandzy 100 Plastics Avenue Pittsfield, MA 01203
1	General Motors Rsch Labs Physical Chemistry Department ATTN: T. Sloane Warren, MI 48090-9055
2	Hercules, Inc. Allegheny Ballistics Lab. ATTN: W.B. Walkup E.A. Yount P.O. Box 210 Rocket Center, WV 26726
1	Hercules, Inc. ATTN: R.V. Cartwright 100 Howard Blvd. Kenvil, NJ 07847

<u>No. of Copies</u>	<u>Organization</u>
1	Alliant Techsystems, Inc. Marine Systems Group ATTN: D.E. Broden/MS MN50-2000 600 2nd Street NE Hopkins, MN 55343
1	Alliant Techsystems, Inc. ATTN: R.E. Tompkins 7225 Northland Drive Brooklyn Park, MN 55428
1	IBM Corporation ATTN: A.C. Tam Research Division 5600 Cottle Road San Jose, CA 95193
1	IIT Research Institute ATTN: R.F. Remaly 10 West 35th Street Chicago, IL 60616
1	Lockheed Missiles & Space Co. ATTN: George Lo 3251 Hanover Street Dept. 52-35/B204/2 Palo Alto, CA 94304
1	Olin Ordnance ATTN: V. McDonald, Library P.O. Box 222 St. Marks, FL 32355-0222
1	Paul Gough Associates, Inc. ATTN: P.S. Gough 1048 South Street Portsmouth, NH 03801-5423
1	Hughes Aircraft Company ATTN: T.E. Ward 8433 Fallbrook Avenue Canoga Park, CA 91303
1	MBR Research Inc. ATTN: M. Ben-Reuven, Suite C-22 801 Ewing Street Princeton, NJ 08540

<u>No. of Copies</u>	<u>Organization</u>
1	New Mexico Institute of Mining and Technology Department of Chemistry ATTN: J. Oxley Socorro, NM 87801
1	Rockwell International Corp. Rocketdyne Division ATTN: J.E. Flanagan/HB02 6633 Canoga Avenue Canoga Park, CA 91304
1	Science Applications, Inc. ATTN: R.B. Edelman 23146 Cumorah Crest Woodland Hills, CA 91364
3	SRI International ATTN: G. Smith D. Crosley D. Golden 333 Ravenswood Avenue Menlo Park, CA 94025
1	Stevens Institute of Tech. Davidson Laboratory ATTN: R. McAlevy, III Hoboken, NJ 07030
1	Sverdrup Technology, Inc. LERC Group ATTN: R.J. Locke, MS SVR-2 2001 Aerospace Parkway Brook Park, OH 44142
1	Sverdrup Technology, Inc. ATTN: J. Deur 2001 Aerospace Parkway Brook Park, OH 44142
3	Thiokol Corporation Elkton Division ATTN: R. Biddle R. Willer Tech Lib P.O. Box 241 Elkton, MD 21921

<u>No. of Copies</u>	<u>Organization</u>
3	Thiokol Corporation Wasatch Division ATTN: S.J. Bennett P.O. Box 524 Brigham City, UT 84302
1	United Technologies Research Center ATTN: A.C. Eckbreth East Hartford, CT 06108
1	United Technologies Corp. Chemical Systems Division ATTN: R.R. Miller P.O. Box 49028 San Jose, CA 95161-9028
1	Universal Propulsion Company ATTN: H.J. McSpadden 25401 North Central Avenue Phoenix, AZ 85027-7837
1	Veritay Technology, Inc. ATTN: E.B. Fisher 4845 Millersport Highway P.O. Box 305 East Amherst, NY 14051-0305
1	Freedman Associates ATTN: E. Freedman 2411 Diana Road Baltimore, MD 21209-1525

USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. ARL Report Number ARL-TR-346 Date of Report January 1994
2. Date Report Received _____
3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.) _____

4. Specifically, how is the report being used? (Information source, design data, procedure, source of ideas, etc.) _____

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate. _____

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.) _____

CURRENT ADDRESS

Organization

Name

Street or P.O. Box No.

City, State, Zip Code

7. If indicating a Change of Address or Address Correction, please provide the Current or Correct address above and the Old or Incorrect address below.

OLD ADDRESS

Organization

Name

Street or P.O. Box No.

City, State, Zip Code

(Remove this sheet, fold as indicated, tape closed, and mail.)
(DO NOT STAPLE)