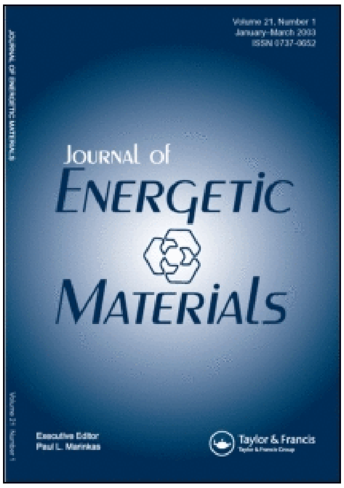

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Pu Sen Wang[a]; T. N. Wittberg[b]
[a] Monsanto Research Corporation Mound Facility, Miamisburg, Ohio [b] University of Dayton Research Institute Dayton, Ohio

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X-RAY PHOTOELECTRON SPECTROSCOPY AND ION SCATTERING SPECTROSCOPY CHARACTERIZATION OF COATED AND UNCOATED PETN

Pu Sen Wang
Monsanto Research Corporation
Mound Facility *
Miamisburg, Ohio 45342

and

T. N. Wittberg
University of Dayton Research Institute
Dayton, Ohio 45469

ABSTRACT

Surface structures of PETN and plastic bonded PETN were studied by high resolution X-Ray Photoelectron Spectroscopy (XPS) and Ion Scattering Spectroscopy (ISS). The coating material is a copolymer of vinyl chloride and chlorotrifluoroethylene. Specimen with 4 wt. % coating material on PETN were used in these studies. High resolution elemented XPS spectra of F 1s, N 1s, C 1s, and Cl 2p indicate that the surface of coated PETN (LX-16) show the surface layer to be thinner than 100A. $^3He^+$ ISS data on LX-16 suggest that the coating on PETN is not uniform and is, in fact absent in some regions.

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INTRODUCTION

The reasons for coating a chosen explosive powder with a specific surface binder are:

1. to improve the mechanical strength of the powders and thus increase the rigidity of the pellets into which the powders are pressed;

2. to control the physical characteristics of the powder surfaces for easy handling;

3. to maximize the energy output of the explosive per unit volume; and

4. to control the sensitivity of the explosive for safety or other reasons.

Whether the above advantages can be achieved depends critically upon the choice of the binder for a specific explosive, the percentage of the binder, and the thickness as well as the uniformity of the coating in plastic bonded explosive (PBX).

If the chosen explosive has both a high surface energy and a specified number of acidic sites, the ideal binder to form a PBX would be one with roughly an equivalent surface energy and a complementary basicity.[1, 2] It was also believed that in order to minimize the sensitivity of the composite, a low modulus coating should be used, otherwise a stiff, crack-susceptible, highly sensitive composite will be formed.[1, 3]

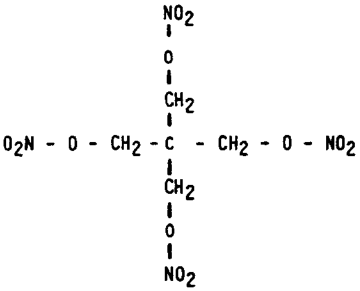
XPS, a surface sensitive technique, has been applied to analyze the surface coating of explosives with a certain degree of success. However, the overall application of this method to PBX was found to be doubtful.[4] The factors contributing to this limitation are:

1. sample charging due to the insulation inherent in organic samples; and
2. relatively limited resolution of XPS with respect to the small chemically shifted binding energy differences for carbon and oxygen.

In this paper, we report surface analysis results of coated and uncoated PETN characertized by XPS and ISS.

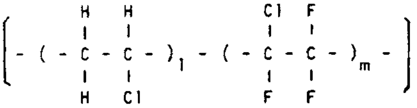
SAMPLES AND SPECTROMETERS

The explosive, pentaerythritol tetranitrate (PETN, $C_5H_8N_4O_{12}$) has the following molecular structure:



$$\begin{array}{c} NO_2 \\ | \\ O \\ | \\ CH_2 \\ | \\ O_2N-O-CH_2-C-CH_2-O-NO_2 \\ | \\ CH_2 \\ | \\ O \\ | \\ NO_2 \end{array}$$

and the coating material is a copolymer of vinyl chloride and trifluorochloroethylene (trade named FPC 461), which has the following structure:



$$\left[-(-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-)_{l}-(-\underset{F}{\overset{Cl}{C}}-\underset{F}{\overset{F}{C}}-)_{m}-\right]$$

PETN was dispersed into water and PFC 461 dissolved in toluene. FPC 461/toluene solution was added into the PETN/water mixture and stirring. Toluene was then evaporated and coated PETN dried at 60C for 100 hours. The surface area of this powder was measured to be 4110 cm^2/g. The composition of coated material is 96 wt. % PETN and 4 wt. % FPC 461. A small amount of each sample was sprinkled on a piece of Fullum copper adhesive tape prior to spectroscopic analysis.

ISS spectra were obtained with a 3M Model 525 ion scattering spectrometer which uses a 138° backscatter collection geometry. In this system a 3M minibeam ion gun is concentric with a single pass cylindrical mirror analyzer. Spectra were recorded using an incident ion beam of $^3He^+$ at an energy of 2500 eV. The spectrometer was backfilled with ^3He to 5×10^{-5} torr. A charge neutralization filament was used to provide a source of low energy electrons to reduce the effects of positive charge buildup on the nonconductive specimen.

The XPS spectrometer is a modified AEI ES-100 instrument. This spectrometer with the accompanying argon ion sputtering system is pumped by a 110 liter/sec ion pump and a 220 liter/sec turbomolecular pump. The vacuum achievable in the sample chamber is 10^{-8} torr. The anode used for all the XPS measurements was magnesium. The XPS binding energies were referenced to the C 1s peak from $-CH_2-$ at 285.0 eV.

RESULTS AND DISCUSSION

Illustrated in Figures 1, 2, and 3 respectively, are the overall XPS spectra of uncoated PETN (the explosive), FPC 461 (the coating material), and coated PETN (LX-16). Nitrogen, oxygen, and carbon were detected in PETN, as expected; fluorine, chlorine, oxygen, and carbon were detected in FPC 461. In the LX-16 sample, all these elements were observed. In Figure 4, high resolution F 1s and Cl 2p XPS spectra of these three samples are shown. These two signals can be observed at binding energies of 687.5 eV and 203.2 eV, respectively, in both FPC 461 and LX-16. No F or Cl signals were observed for PETN. The most interesting XPS data are the C 1s spectra which are shown in Figure 5. These spectra were deconvaluated using a DuPont 310 Curve Resolver. Figure 5 (a) indicates that in PETN, three types of carbon at binding energies of 285.0 eV, 286.8 eV, and 289.2 eV with respective signal areas of 22%, 64% and 14% were observed. These signals can be primarily attributed to the carbon of the central -C- atom, of the $-CH_2-$ groups, and of contaminants containing CO_x groups, respectively. In PETN, the theoretical ratio of $-CH_2-$ to -C- should be 4. We measured this ratio to be 3, probably due to the presence of carbon contamination from the adhesive tape used to support sample. Figure 5 (c) illustrates the C 1s signal of FPC 461; no residual carbon impurity was observed. This signal can be deconvoluted into three peaks at 285.5 eV, 288.0 eV and 291.3 eV with relative intensities of 45%, 29%, and 26%, respectively. The highest binding energy peak is due to $-CF_2-$; the peak at 288.0 eV is due to the -CFCl-; and the lowest binding energy is probably due to the sum of $-CH_2-$ and -CHCl- groups. These areas agree closely with theoretical values based on the formula of the binder being $[(-CF_2CFCl-)_3\text{-}\ (-CH_2CHCl-)_2]$. Figure 5 (b) shows C 1s XPS of LX-16. The peak at 285.0 eV indicates surface contaminant of residual carbon remaining on the surface of the PBX; probably this residual carbon is toluene, the solvent used in dissolving FPC 461 during coating. The peaks at 291.5 eV (18% of total signal) and 289.8 eV (19% of total signal) can be assigned to $-CF_2-$ and -CFCl- of the plastic. The peak at 287.0 eV (38% of total signal) can be interpreted as a combination of $-CH_2-$ of PETN and $-CH_2CHCl-$ of FPC 461. The fact that the intensity ratios of the photopeak at 287.0 eV to that of both the 291.5 eV and 289.2 eV signals are ~ 1 rather than 1.5 suggests that the $-CH_2-$ of the PETN contributes part of the 287.6 eV peak. These data on the composite suggest two possible explanations:

1. The plastic coating film thickness of the LX-16 composite is less than 100Å, because the mean free path, λ, for the C 1s photoelectron is 27Å; thus 95% of the total intensity will come from 3 λ or 81Å.

2. The plastic coating on the PETN particles is incomplete.

The C 1s XPS data of PETN, FPC 461, and LX-16 are listed in Table 1.

These two possible explanations are supported by the N 1s XPS data given in Figure 6. The binding energy of the N 1s from the PETN is 408.2 eV as shown in Figure 6 (a). Weak peaks at 399.8 eV and 398.0 eV are satellite signals that can be associated with the main peak at 408.2 eV. The fact that an N 1s signal was also observed in an LX-16 sample, as shown in Figure 6 (b), is evidence that the surface coating is either thinner than 100Å, or incomplete, or both.

Figure 6 shows that the signals in the satellite region are broader in the composite (b) than in the PETN (a). This change in peak shape indicates that a new nitrogen structure at 400.3 eV binding energy is present in the composite but not in the explosive. Three N 1s spectra from an LX-16 sample that has been irradiated with Mg X-rays for an extended period of time are shown in Figure 7. These results show that X-ray induced decomposition of PETN forms the new structure at a binding energy of 400.3 eV. Possible nitrogen structures observed at this binding energy are $C\text{-}NH_2$ or C-N=N-C.

Residual gas analysis (RGA) of LX-16 during irradiation showed the main gaseous products to be 30, 44, 46 and 76 a.m.u. The possible assignments for these products are as follows:

30 - No, C_2H_6
44 - CO_2, N_2O
46 - NO_2
76 - $CH_2\text{-}O\text{-}NO_2$

The most intense peak was observed at mass = 30.

The time dependence of LX-16 decomposition is given in Table 2 and is plotted in Figure 8. These data show the X-ray induced decomposition of LX-16 to be a first-order process. It should be noted that similar X-ray induced decomposition has been observed for uncoated PETN. Figure 9 illustrates a plot of the C 1s and O 1s signals ratioed to the N 1s signal. These data show nitrogen decreasing more rapidly than carbon or oxygen as the time of X-irradiation increases. Table 3 lists the data plotted in Figure 9. We conclude from the RGA and XPS data taken during X-irradiation that nitrogen-containing gaseous components, such as NO_2, evolve from the LX-16.

With ISS the composition of the outermost atomic layer of a sample surface can be determined. With this technique a sample is bombarded with a beam of noble gas ions, and some of these ions will experience binary elastic collisions with surface atoms. From the laws of conservation of momentum and energy, the energy of these scattered primary ions can be computed in terms of the masses of the sample atoms, the probe ions, and the scattering angle. By measuring the ratio of scattered primary ion energy (E) to primary ion energy (Eo), the mass of the sample atoms can be determined.

The probe gas used for ISS measurements was $^3He^+$ at 2.5 KeV energy. The sputter rate with $^3He^+$ is very low, probably about 1A/min. Two different areas of an LX-16 specimen were analyzed and, in both instances, the ion beam covered several particles. The ISS data given in Figure 10 are representative of one of the two areas where the sample has been exposed to 5, 10, 12 and 45 min. of $^3He^+$ exposure. In both cases, the elements fluorine, oxygen, and nitrogen were detected initially. Exposing for longer periods of time did not change the relative amounts of these elements appreciably. The scan taken after 45 min. of exposure on the first spot did show a slight increase in the carbon energy region. The initial detection of the N signal in the coated powder suggests that the surface of LX-16 powders are not completely coated with FPC 461. This is possibly due to the low percentage (only 4%) of coating material used in the manufacutring of the LX-16 composite.

There are a couple of points about the data which are not explainable at this time. First, chlorine was detected using XPS, yet it was not detected with ISS. It should appear at $E/E_0 = 0.74$. Secondly, very little carbon was detected with ISS. It could be that these elements actually are not present in the first few monolayers, although this does not seem likely.

ACKNOWLEDGEMENTS

The authors thank Mr. Walter J. Moodie for his donation of PETN and LX-16.

TABLE 1

XPS DATA FOR C 1s IN PETN, LX-16, AND FPC 461

SAMPLE	BINDING ENERGY (eV)	INTENSITY (%)	IDENTIFICATION
PETN	285.0	22.0	$(-\overset{|}{\underset{|}{C}}-)$
	286.7	64.0	$-CH_2-$
	289.2	14.0	(CO_x)
FPC 461	285.5	45	-CHCl- and $-CH_2-$
	288.0	29	-CHCl-
	291.3	26	$-CF_2-$
LX-16	285.0	25	$(-\overset{|}{\underset{|}{C}}-)$ and Residual carbon
	287.0	38	$-CH_2-$ and -CHCl-
	289.2	19	(CO_x) and -CFCl-
	291.5	18	$-CF_2-$

TABLE 2

PETN DECOMPOSITION AND NEW NITROGEN-CONTAINING PRODUCT FORMATION IN LX-16 INDUCED BY X-IRRADIATION

TIME OF X-IRRADIATION (min)	$\frac{I_N 408}{I_N 400}$	$\ln \frac{I_N 408}{I_N 400}$
29	8.1	2.09
79	7.3	1.99
129	5.2	1.65
179	3.0	1.10
229	2.2	0.80
279	1.7	0.53
367	1.1	0.04

TABLE 3

NITROGEN CHANGE IN PETN SURFACE INDUCED BY X-IRRADIATION

TIME OF X-IRRADIATION (min)	$\frac{I_c(286)}{I_N}$	$\frac{I_o(O1s)}{I_N}$
24	1.15	4.77
177	1.55	5.50
250	1.98	6.99
326	2.32	9.25

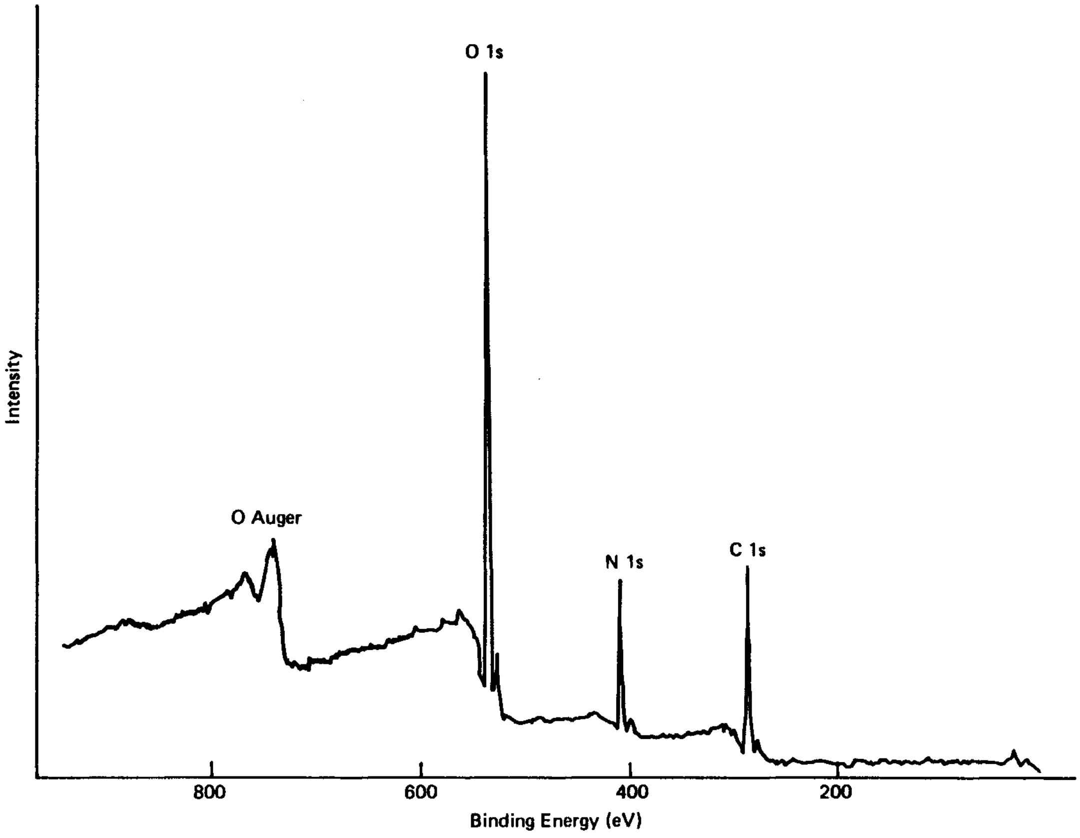


Figure 1. Overall XPS spectrum of PETN

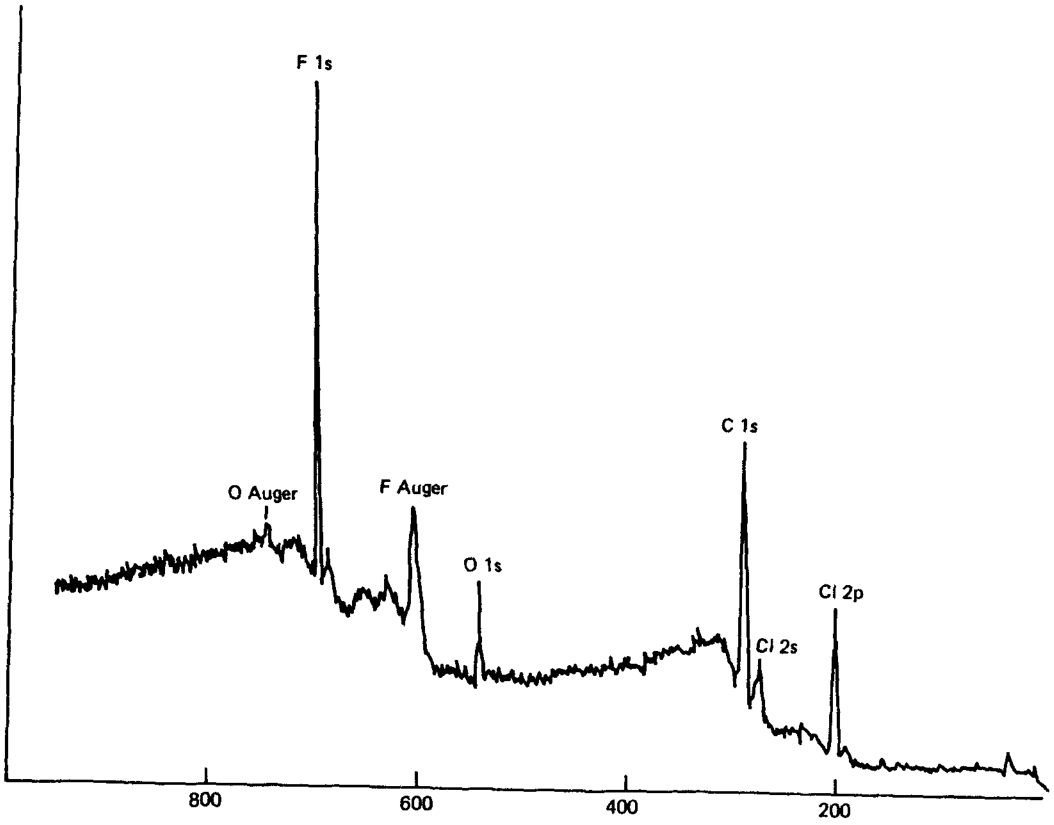


Figure 2. Overall XPS spectrum of *FPC 461*

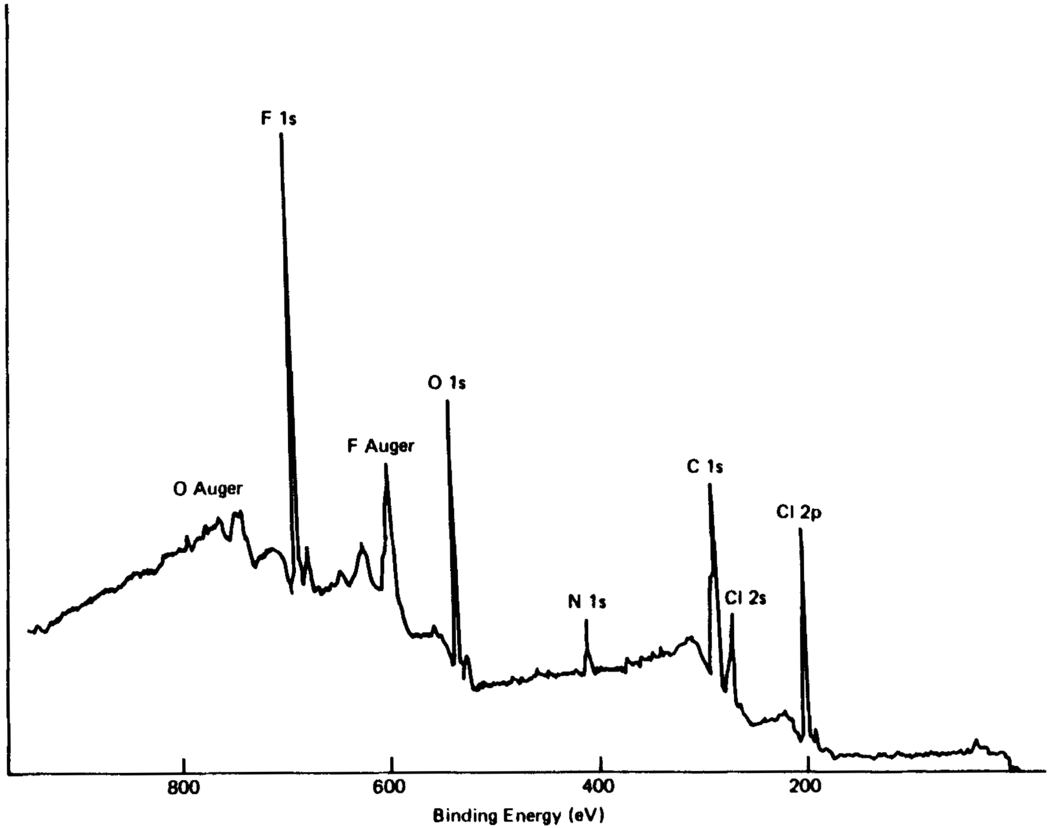


Figure 3. Overall XPS spectrum of LX-16

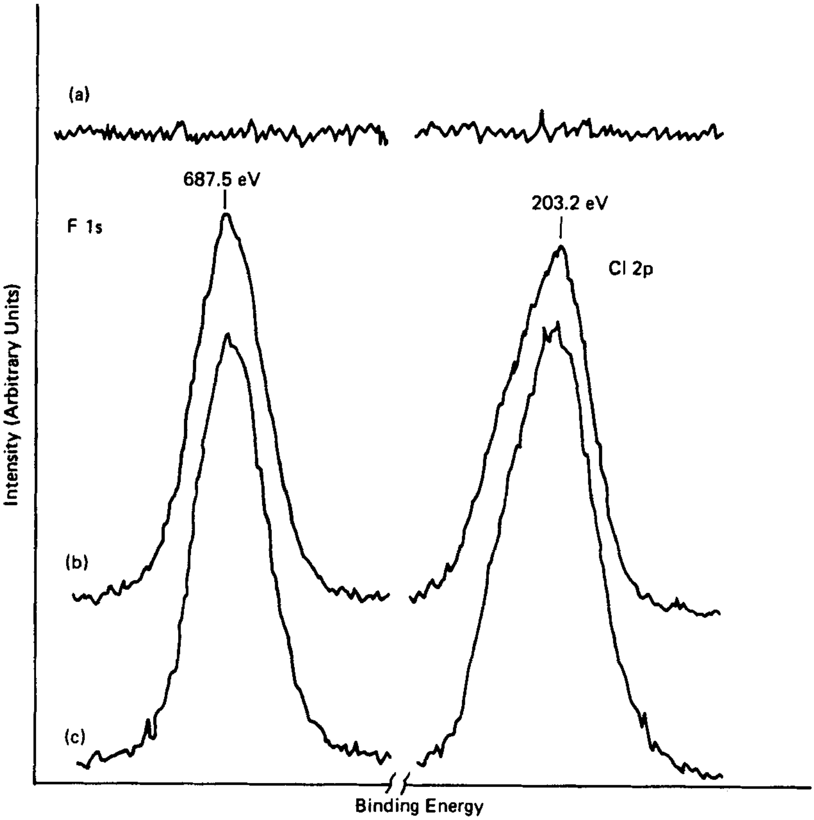


Figure 4. F 1s and Cl 2p XPS spectra of (a) PETN (b) LX-16 (c) FPC 461

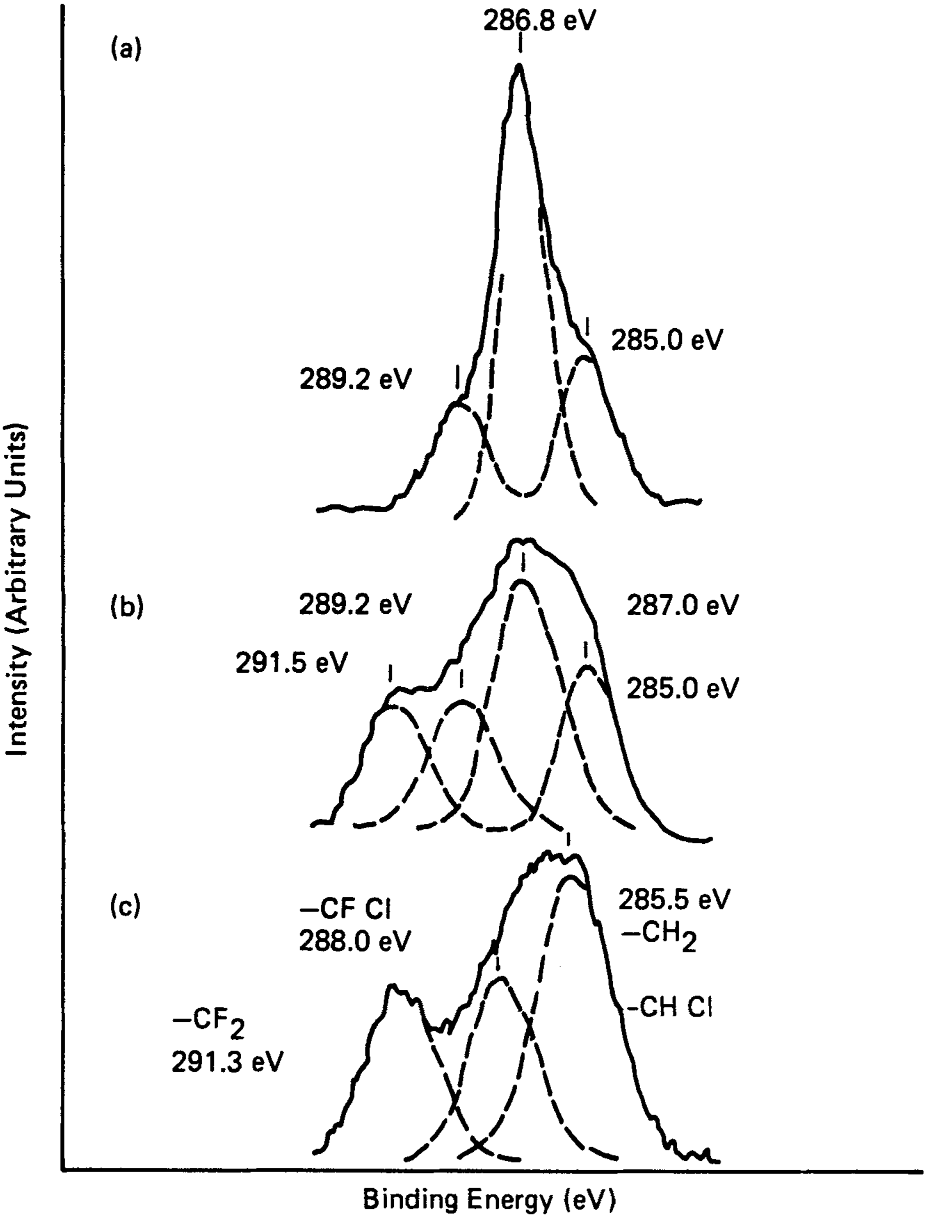


Figure 5. C 1s XPS spectra of (a) PETN (b) LX-16 (c) FPC 461

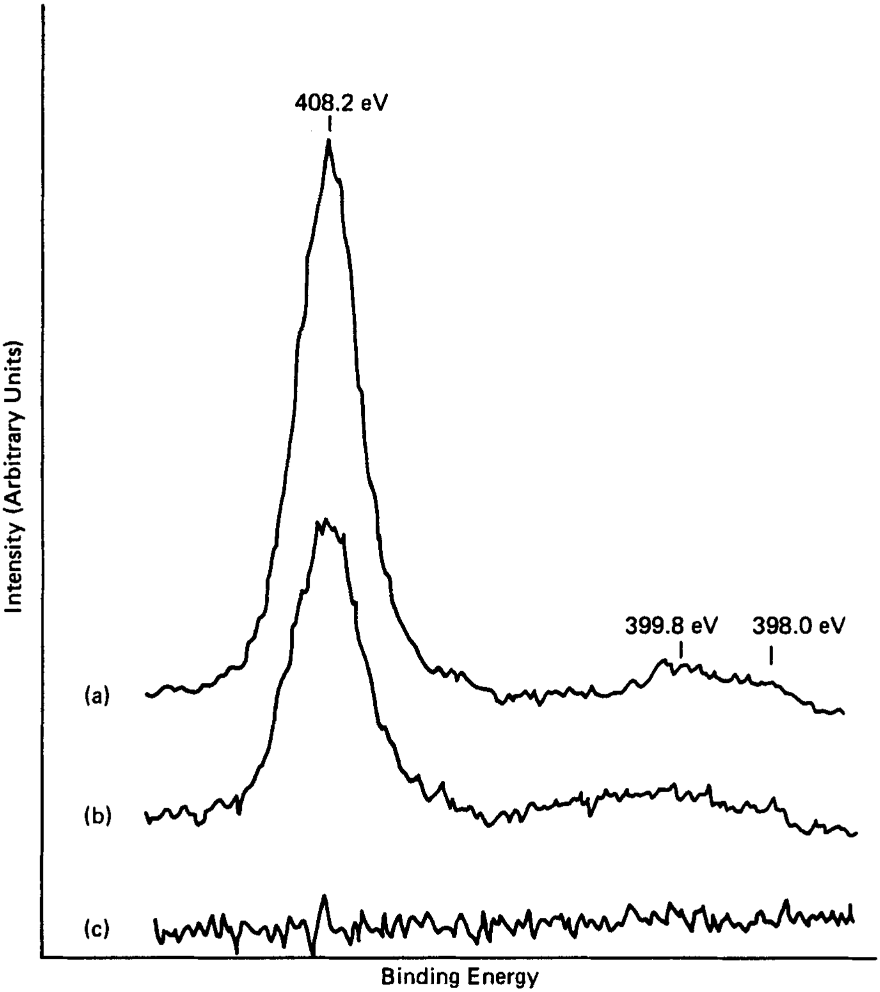


Figure 6. N 1s XPS spectra of (a) PETN (b) LX-16 (c) FPC 461

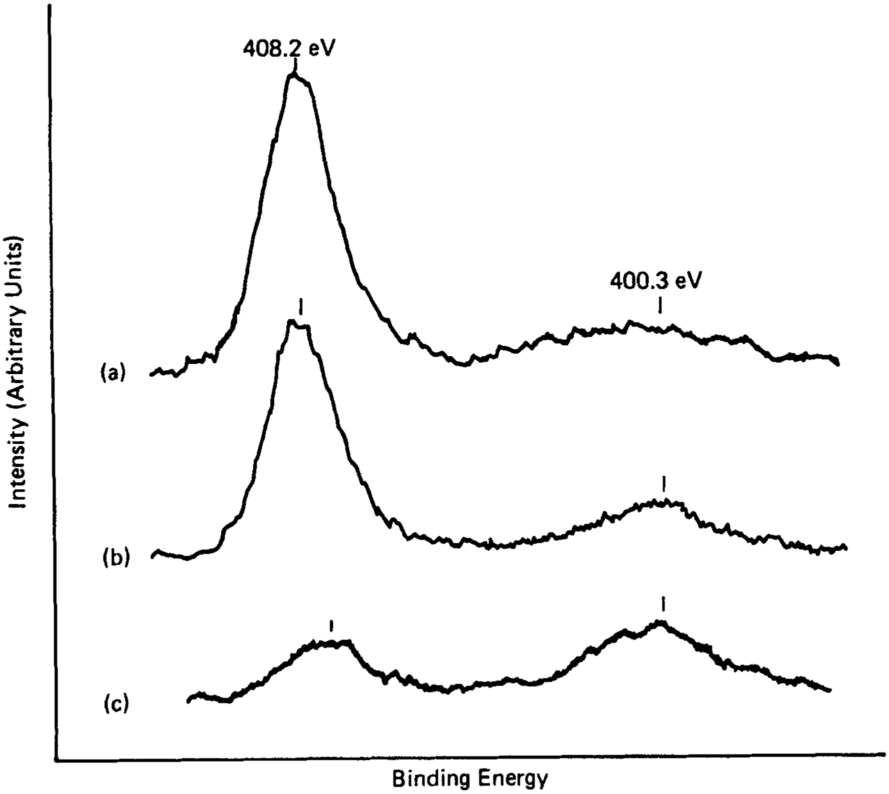


Figure 7. N 1s XPS spectra of LX-16 caused by (a) 1/2 hr. (b) 3 hrs. and (c) 6 hrs. of x-ray decomposition

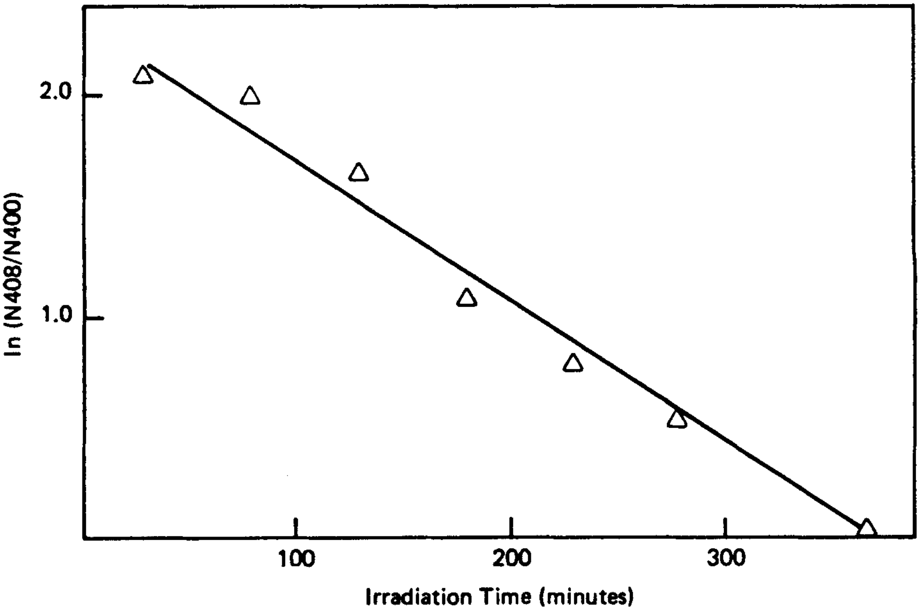


Figure 8. N 1s XPS Intensity changes due to Mg anode irradiation in LX-16

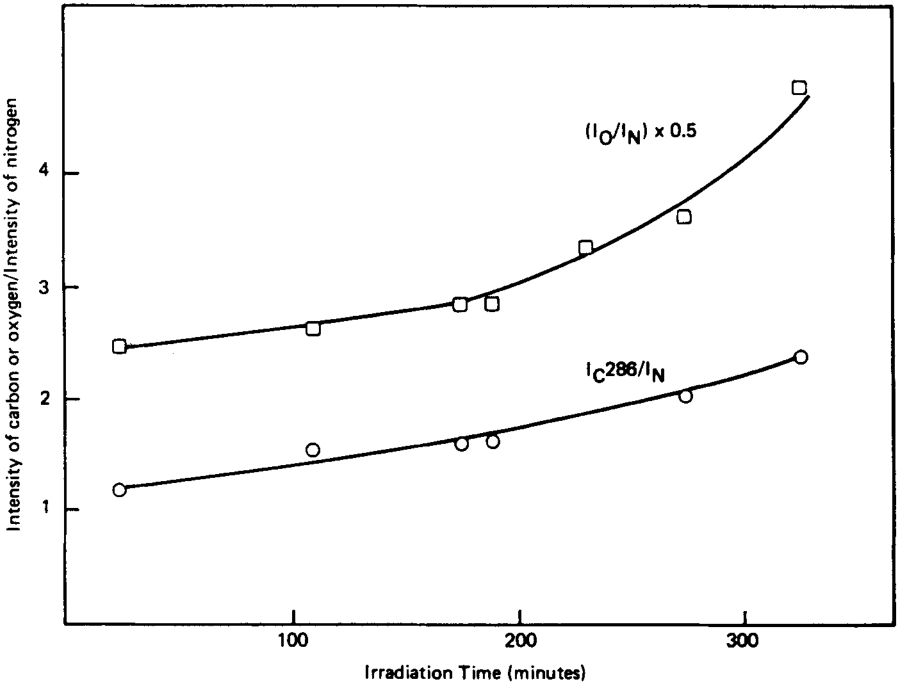


Figure 9. Nitrogen decrease in LX-16 during x-irradiation

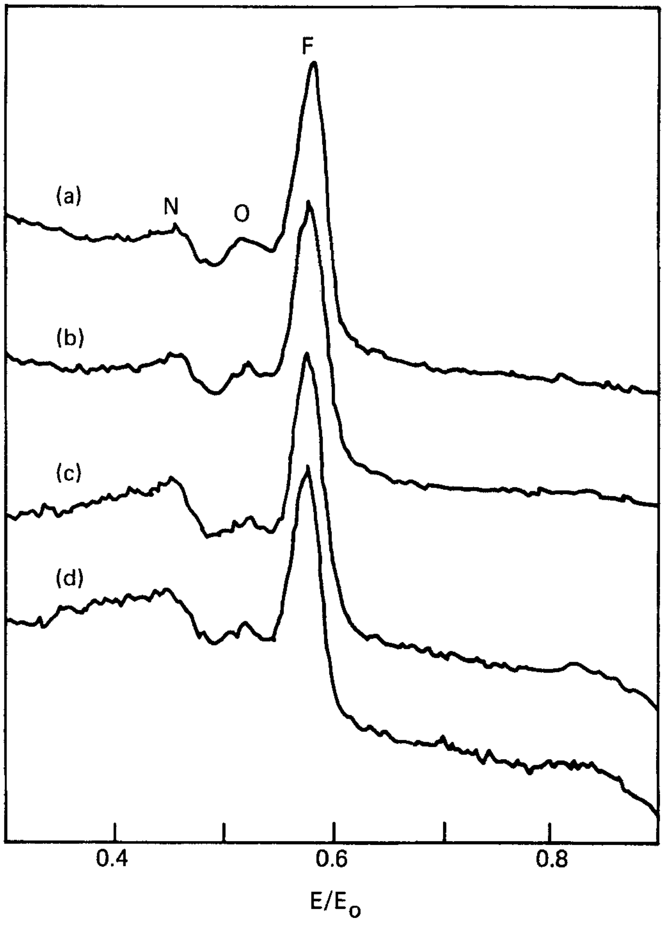


Figure 10. ISS spectra of LX-16 after (a) 5 min. (b) 10 min. (c) 12 min. and (d) 45 min. sputtering.

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