

AN INVESTIGATION OF POLYMER COATINGS USED IN  
HYDROGEN MASER STORAGE BULBS

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ABSTRACT

X-ray photoelectron spectroscopy has been used to investigate the surface composition (top 50 Å) of some fluorinated polymers that either have been, or could be, used to coat the storage bulbs in hydrogen masers. The results indicate inadequacies of some of the coatings, and the long term effect of exposure to hydrogen atoms. Recently developed fluorinated polymers have been investigated also as possible coating materials.

INTRODUCTION

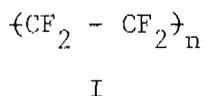
With hydrogen masers under consideration as a timing standard in the NAVSTAR Global Positioning System, this paper will report the results of a study of some of the fluorinated polymer surfaces that have been used in hydrogen maser storage bulbs. The possibility of the use of some fluorinated polymers recently developed at the Naval Research Laboratory (NRL) has been considered also. The surface of the hydrogen maser storage bulbs may play an important role in both the short term and long term stability of the maser. For example, it has been reported that the lowest surface hydrogen atom recombination coefficient observed (by about two orders of magnitude) is that in which the surface has been coated with Teflon (1); this effect could be somewhat larger, but precision of the reported results was poor. This comparison was made with a wide number of surface treatments (2). Hydrogen atom recombination would take away hydrogen atoms that could be involved in the maser action. Thus, the surface of the hydrogen maser storage bulb could contribute to the poorly understood temperature effect on frequency changes that have been noted with hydrogen masers.

Over the past several years many new techniques for the investigation of surfaces have become widely available. One of these recent methods is X-ray Photoelectron Spectroscopy (XPS), and it has been used to investigate the surfaces of a large number of materials including polymers. A thorough review of XPS with an emphasis upon fluorocarbon polymers has been made by Clark and Feast (3), but a few highlights will be given here. A low intensity X-ray source (usually about 1253 or 1486 eV)

impinges upon the material of interest. Both orbital and valence electrons are ejected, and the kinetic energy of these electrons is measured. The binding energies of the various levels of an element can be determined from the following equation:

$$E_{BE} = h\nu - E_{KE} - \phi_{SP} \quad (1)$$

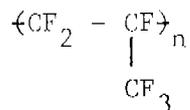
$E_{BE}$  is the binding energy of the level of interest,  $h\nu$  is the photon energy,  $E_{KE}$  is the kinetic energy of the ejected electron, and  $\phi_{SP}$  is the work function of the spectrometer. XPS spectra can be observed for all of the elements except hydrogen and helium, and each element has a unique spectrum. The mean escape depth for X-ray induced photoelectrons is about 20 Å, but with carbonaceous material the mean escape depth may be greater. Changes in the atomic environment can be followed by the observation of shifts in the binding energy. For example, the shift in the binding energy for the C 1s line is about 7 eV between polytetrafluoroethylene (PTFE, compound I) and polyethylene (3).



## EXPERIMENTAL

### Materials

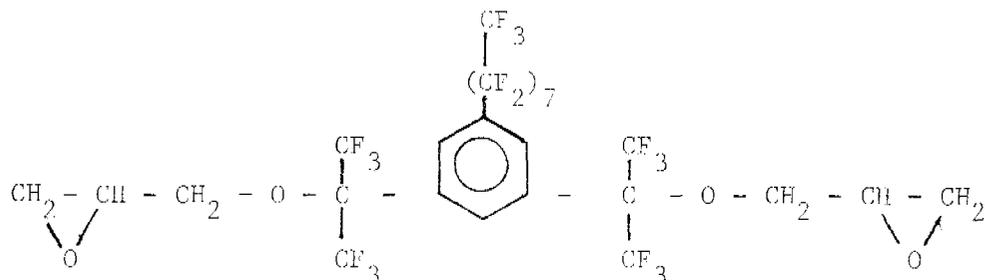
Three different types of fluorinated polymer samples have been investigated. All of the samples were put onto 2 by 1 cm stages. The first set of samples was a FEP Teflon coating of various configurations on gold-coated Al and quartz stages, and was prepared under the direction of Dr. R. Vessot of the Smithsonian Astronomical Observatory (SAO), Cambridge, Mass. The coatings covered either part or all of the underlying substrate and were thought to be on the order of a few thousand Å. Au was selected as one substrate so that the  $4f_{7/2}$  photoelectron line could be used as a standard, and quartz was chosen to simulate a substrate used in a maser. The coatings were made from an FEP-120 dispersion, an aqueous dispersion of FEP Teflon containing a volatile wetting agent; FEP Teflon is a mixture of polytetrafluoroethylene (PTFE) and polyhexafluoropropylene (HFP), Compound II.



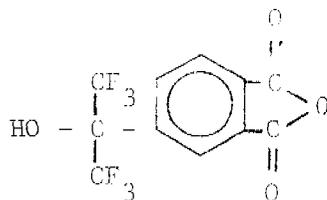
### II

The second set of samples was from a film of FEP Teflon that came from

the storage bulb of a used maser from SAO. This thick film had been removed from the maser bulb by an overnight soaking with a few cc of water. After receipt at NRL, the sample was manipulated with cleaned tweezers and placed on fresh, clean aluminum foil; plastic gloves were used also in the handling of the film. When the sample was unfolded, two distinct regions of the film were observed; one region was clear and the other, much smaller in area, had a brown color. The third set of samples was a fluorinated diglycidyl ether, compound III, and the coupling agent compound IV, a fluorinated anhydride, which form a very high molecular weight cross-linked polymer. Fluorinated amines have been employed as coupling agents also.



III



IV

Some of the specimens of this set contained about 50%, by weight, PTFE. These fluorinated polymers have the ability to "wet" PTFE, whereas most polymers do not have this property.

#### EXPERIMENTAL PROCEDURES

Spectra were obtained with a Physical Electronics XPS/AES electron spectrometer operating in the  $10^{-6}$  Pa region. The X-ray source was MgK $\alpha$  radiation (1253.6 eV) at 10 KV and 30 or 40 ma and a pass energy of either 100 or 25 V was used for all spectra. The area of analysis is a few mm<sup>2</sup>. Elemental ratios were determined from the model developed by Carter, Schweitzer, and Carlson (4), as given in equation (2).

$$\frac{n_1}{n_2} = \frac{N_1 \tau_2 \lambda_2 S_2}{N_2 \tau_1 \lambda_1 S_1} \quad (2)$$

$N$  is the area under the curve of the photoelectron peak,  $\sigma$  is the photoelectron cross section (5),  $\lambda$  is the mean escape depth of the photoelectron (4), and  $S$  is the spectrometer response, as a function of energy (6). More detailed consideration of this model for the determination of elemental ratios in polymers will be given elsewhere (7).

## RESULTS AND DISCUSSION

### A. Thin FEP Film from SAO

In Figure 1 is shown the XPS spectrum of a thin film made from FEP-120 dispersion on a quartz substrate. From known binding energies (8), the various peaks in Figure 1 have been identified and the atomic levels

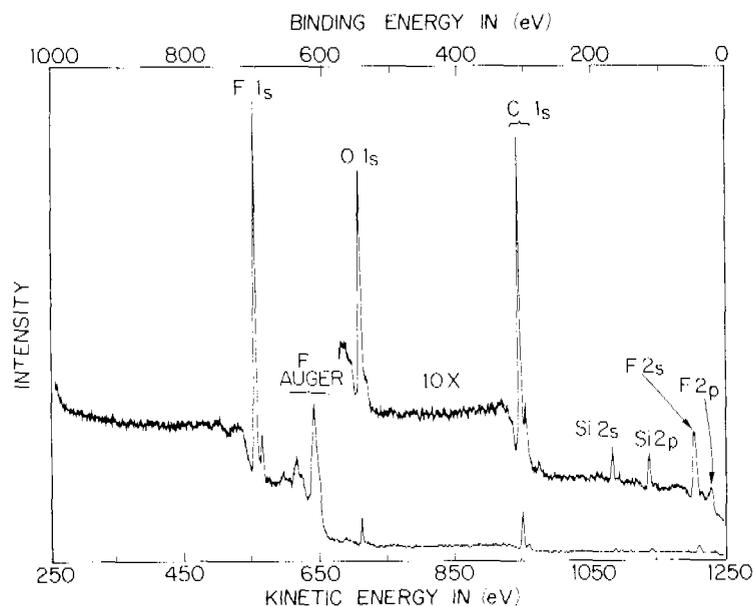


Figure 1: XPS spectrum of a quartz stage coated with FEP 120 Teflon dispersion. Elemental peaks are identified on the figure.

indicated. The identification of the X-ray-induced F Auger peaks was made on the basis of the observed kinetic energy. In addition to the expected C and F XPS peaks, both Si and O XPS lines were observed. Thus, it appears that the coating is either in the form of "islands," or that portions of the coating are so thin (perhaps 10-20 Å at the most) that the underlying quartz substrate can be observed. If the peaks ascribed to O and Si are not considered, the spectrum in Figure 1 is very similar to that reported by Clark and Feast (3) for PTFE.

From a detailed analysis of the small peaks due to the Mg K $\alpha_{3,4}$  radiation (9) it was concluded that the minor peak on the high kinetic energy side of the main Cls peak, was due, in part, to some hydrocarbon present in the coating, possibly the residue of the wetting agent in the FEP-120 dispersion.

Table 1 gives the elemental ratios determined for the quartz sample covered by the FEP-120 coating as determined by the use of equation 2.

Table 1  
Elemental and Group Ratios of FEP-120 Teflon-Coated  
Quartz, as Determined by XPS

<u>Ratio</u>	<u>Experimental</u>	<u>Theoretical</u>
C(1s)/F(1s)	0.47 $\pm$ 0.04	0.5
C(1s)/F(2s)	0.46 $\pm$ 0.02	0.5
Si(2s)/O(1s)	0.6 $\pm$ 0.1	0.5
CF <sub>2</sub> /SiO <sub>2</sub> (First location on sample)	9.0 $\pm$ 0.6	
CF <sub>2</sub> /SiO <sub>2</sub> (Second location on sample)	15 $\pm$ 2	

The observed Si/O and C/F (C ascribed to C-F bonds) ratios agree well with the theoretical ratios. These results are gratifying considering the approximations made and some of the small signals observed. For the analysis of the C/F ratio, the contribution by the different C-F bonds in HFP to the C 1s signal has been neglected (9). The results show that little, if any, O is present, except that from the quartz. On a completely polymer coated gold-covered Al stage, only a very faint O signal was observed. Thus, it appears that the coating or surface contamination contributes very little O to the surface region.

After these encouraging results were obtained from the Si/O and C/F ratio measurements, an attempt was made to find the amount of the fluorocarbon coating relative to the quartz substrate. For this purpose the number of apparent CF<sub>2</sub> groups vs. the number of SiO<sub>2</sub> groups is of interest. The C/Si, F/O, C/O, and F/Si ratios were determined with the proper consideration to stoichiometry, and the results are given also in Table 1. Unfortunately, these ratios do not help answer the question of whether there are blank spots in the coating or just some very thin sections.

B. Thick FEP Film From SAO

In Figure 2 (clear portion) and Figure 3 (brown portion) the XPS spectra of the film obtained from a used hydrogen maser are shown. The

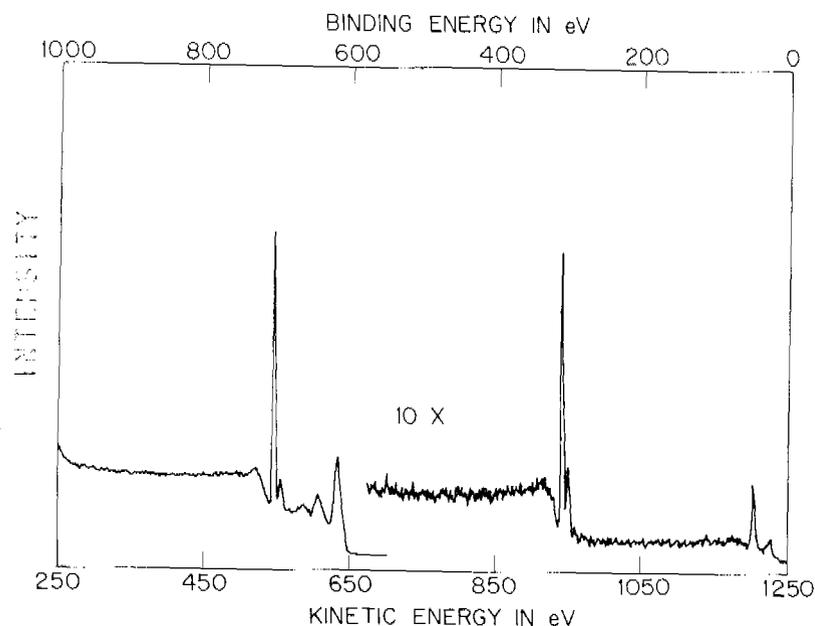


Figure 2: XPS spectrum of the clear portion of the FEP Teflon from a used hydrogen maser.

spectra were from the side of the film that was believed to be exposed to hydrogen atoms (this tentative suggestion was prompted by the shape of the film). All of the films appeared to be continuous, since peaks from the substrate beneath the films were not detected, and the C/F ratio (C ascribed to C bonded to F) was close to the expected ratio (0.5) for FEP Teflon. By the same type of analysis mentioned previously it was concluded that the clear part of the film indicated a small hydrocarbon contribution to the C 1s signal, while on the other side of the film there appeared to be little, if any, hydrocarbon type C present. Oxygen was not detected on either side of the clear portion of the film.

The spectrum in Figure 3 (brown film) has marked differences from the spectrum of the clear portion of the film. The spectra from both sides of the brown colored film were similar. The C signal due to non-fluorine bonded C was about one third of that due to F bonded C, while the O present had about one sixth the intensity of the non-fluorine bonded C. These results definitely show that there are differences

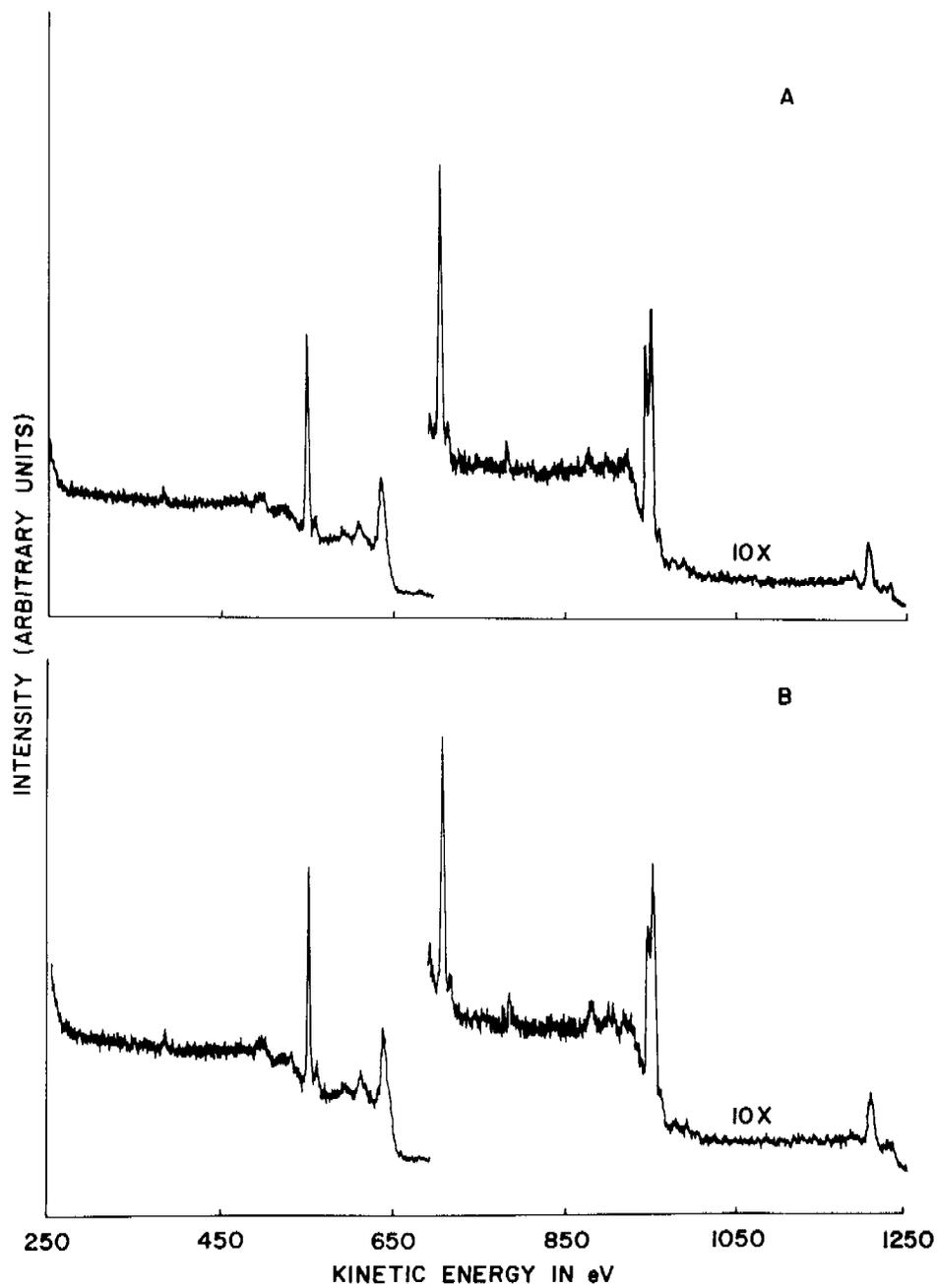


Figure 4: Spectrum A. XPS spectrum of compounds III and IV with 50 percent by weight powdered PTFE. Spectrum B. XPS spectrum of compounds III and IV.

result of a simple scraping of the polymer mixture used in Figure 4 (spectrum A), the XPS spectrum of the resultant film that was observed is shown in Figure 5. As can be seen this spectrum is vastly different

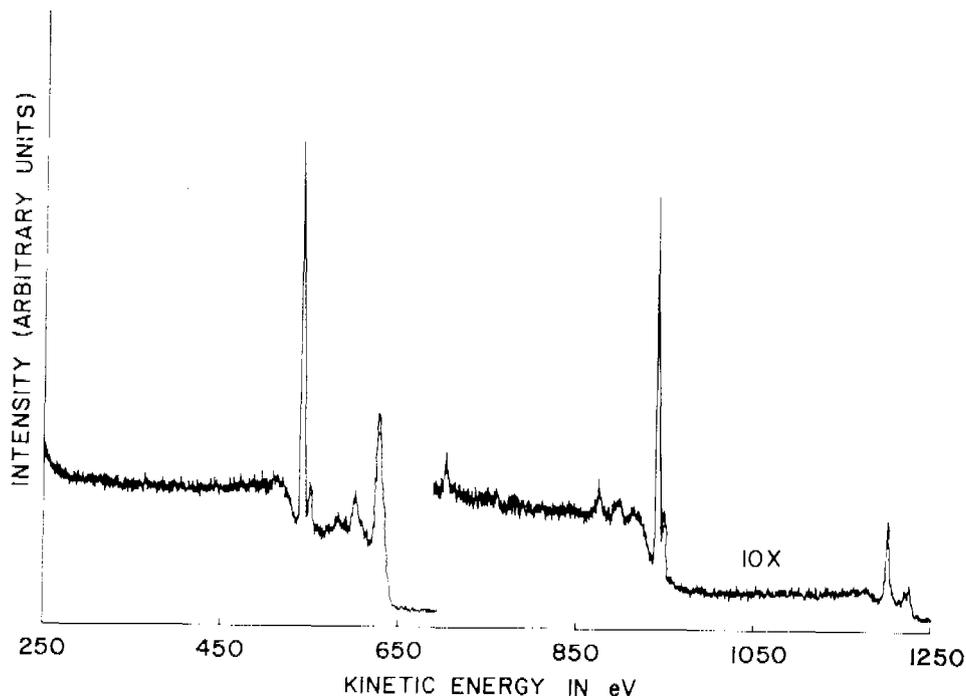


Figure 5: XPS spectrum after scraping of the mixture used in spectrum A, Figure 4.

from the spectra in Figure 4. The O and the non-fluorine bonded C peaks have been reduced quite markedly. The C (bonded to F) to F ratio is close to that expected for PTFE. These results suggest that it is possible to form a film similar to PTFE from mixtures of PTFE and compounds III and IV. (Compounds similar in chemical structure to III and IV probably could also be used equally as well). Thus, it appears that PTFE films could be produced in configurations that would be difficult to fabricate from commercially available films or dispersions.

#### CONCLUSIONS

XPS can be used to examine the fluorocarbon polymer coatings used in hydrogen masers both before and after use in a maser. Films that appear to be similar to PTFE can be made from powdered PTFE combined with compounds such as III and IV.

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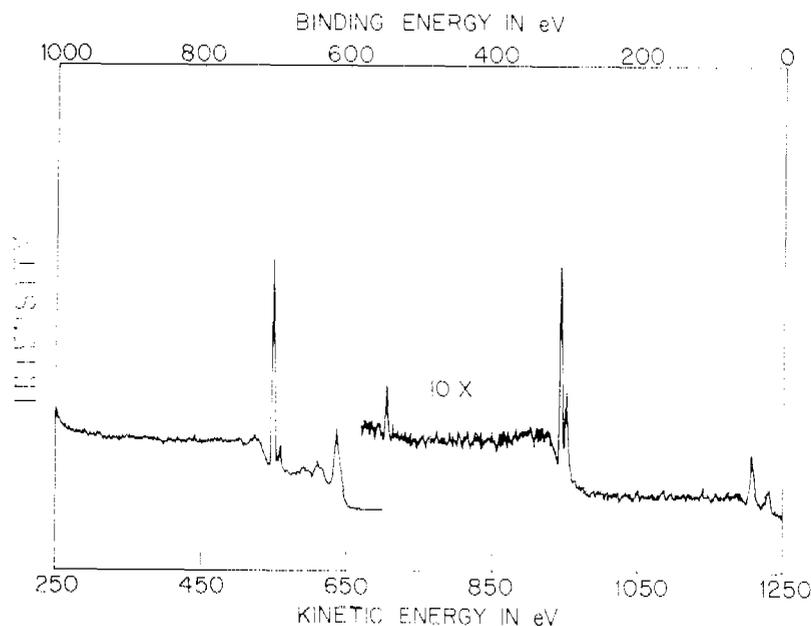


Figure 3: XPS spectrum of the brown portion of the FEP Teflon from a used hydrogen maser.

between the clear and the brown portions of the film. It seems reasonable to suggest that the brown portion of the film was exposed directly to the hydrogen atom source, and that the changes extended throughout the extent of the film. Due to the prior handling and treatment of the film the absolute results of these analyses cannot be given with certainty; however, the differences between the clear and brown portions of the film do appear to be real.

#### C. NRL Developed Fluorocarbon Polymers

In Figure 4 (spectrum B) the XPS spectrum of the epoxy polymer mixture derived from compounds III and IV is shown. Detailed consideration of these spectra will be given elsewhere (7) but a few comments will be made. The surface composition, as determined by XPS, appeared to be close to that of the expected bulk composition. The two peaks in the C region are expected also. Spectrum A in Figure 4 is the spectrum of the polymerized mixture of compounds III and IV containing 50 percent by weight of powdered PTFE. As can be seen, the difference between the spectra in Figure 4 is minimal. In a polymer system similar to that in spectrum A of Figure 4, Hunston, Griffith, and Bowers (10) found that the frictional behavior closely resembled that of pure PTFE. As a