JOURNAL OF MATERIALS SCIENCE **24** (1989) 1533–1538

Surface characterization of 1,3,5-triamino-2,4,6-trinitrobenzene by X-ray photoelectron spectroscopy and Fourier transform nuclear magnetic resonance

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X-ray photoelectron spectroscopy (XPS) and Fourier transform nuclear magnetic resonance (FT-NMR) were used to characterize 1,3,5-triamino-2,4,6-trinitrobenzene. The XPS results showed approximately equal signal intensities of N 1s electrons from NO_2 and NH_2; this agrees well with the theoretically calculated values. An increase in the NH_2/NO_2 ratio was observed after ultraviolet or X-ray irradiation. FT-NMR at proton frequency showed a characteristic Pake's doublet due to strong proton dipole–dipole interaction in solids. Surface moisture absorption was observed when the samples were exposed to a humid environment. The moisture molecules were found to be partially bonded to the surfaces or diffused into the crystal lattice after an extended exposure period.

1. Introduction

1,3,5-Triamino-2,4,6-trinitrobenzene has been the subject of several recent studies [1–7]. The technique of X-ray photoelectron spectroscopy (XPS) has been used in two of these studies to show changes in the molecule which occur as a result of ultraviolet (UV) irradiation, thermal decomposition or shock impact [4, 5]. In all cases, the stimulus to the sample was of a magnitude that was less than that required to cause detonation. However, the XPS data did give clear evidence that there was a decrease in the proportion of nitro-nitrogen to amine-nitrogen. In another study, infrared (IR) analysis has shown that there is secondary amine production as a result of UV irradiation [7]. The XPS data support these IR results.

In the present study, we have used XPS to characterize both uncoated samples as well as polymer-coated samples. A polymer coating is routinely used in order to control certain physical properties such as sensitivity to ignition. XPS was applied to coated samples in order to discern the completeness of coating coverage and in order to compare the susceptibility of coated and uncoated powders to irradiation-induced decomposition. We also report in this paper the results of a study of powder surface moisture by FT-NMR at proton frequency.

2. Experimental details

The 1,3,5-triamino-2,4,6-trinitrobenzene used in this study is either an "ultrafine" powder or a thermally purified powder. The coated sample is a composite of 95 wt % 1,3,5-triamino-2,4,6-trinitrobenzene and 5 wt % Kel-F (chlorotrifluorethylene/vinylidine fluoride copolymer).

The XPS spectrometer is a modified AEI-ES-100 instrument. The modifications to this instrument include the addition of a Heinke X-ray gun for sample excitation as well as the addition of a 110 litre sec^{-1} ion pump and a 220 litre sec^{-1} turbo-molecular pump for evacuation of the sample chamber. A vacuum of 1×10^{-9} torr is achievable in the sample chamber. A magnesium X-ray anode was used for all of the XPS measurements.

The NMR spectrometer used in this study is a Bruker CXP-200. The probe is 5 mm diameter designed for high-power proton observation. A superconducting magnet supplies a 47 kG field for proton observation at 200.1200 MHz with an offset of 10^4 Hz and a sweep width of 10^6 Hz. No field lock was used in observing this broadline signal. A typical 90° pulse-width for proton was between 1.0 and 1.2 μsec depending on the tuning of the probe. A recycling time of 300 sec was used for a single pulse experiment; 200 free-induction-decays (FID) were accumulated for each sample and then Fourier transformed.

3. Results and discussion

3.1. XPS results

One of the first problems encountered in our efforts to characterize 1,3,5-triamino-2,4,6-trinitrobenzene with XPS was the surface colour change from yellow to green which was observed in samples which had been

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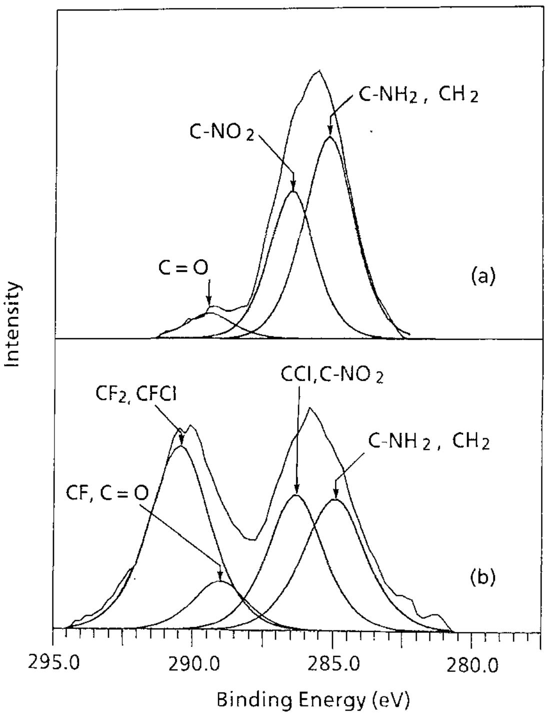

Figure 1 C 1s XPS spectra of (a) an uncoated 1,3,5-triamino-2,4,6-trinitrobenzene sample, and (b) a coated sample.

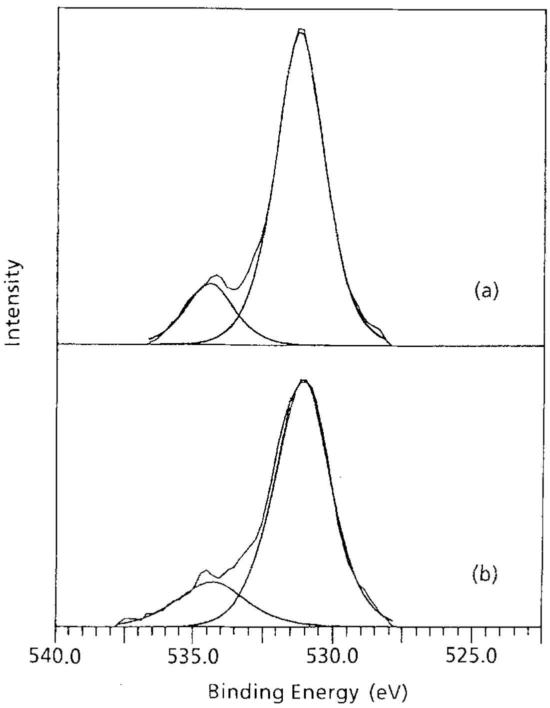

Figure 2 O 1s XPS spectra of (a) an uncoated sample, and (b) a coated sample.

irradiated with X-rays for periods of 1 h or more within the XPS instrument. This colour change has been reported by other workers for the samples irradiated with UV light [4]. The colour change due to X-ray irradiation could be minimized by obtaining the XPS data within a shorter period of time (~ 20 min).

Figs 1a, 2a and 3a show the C 1s, O 1s, and N 1s XPS spectra for a sample which had been exposed to less than 20 min Mg X-radiation (anode power = 120 W). The C 1s spectrum has an intense asymmetrical peak at approximately 286 eV, which has been resolved into two components, one of which is believed to be due to C–NH_2 carbon (285.0 eV), while the other is due to C–NO_2 carbon (286.6 eV). The shoulder at 289 eV may be due to a C=O impurity.

The O 1s spectrum shows a peak at 531 eV due to NO_2 oxygen as well as a peak at 534 eV which may be due to water. The N 1s spectrum shows peaks due to both NH_2 (398 eV) and NO_2 (404 eV). The NO_2 peak has a shoulder of higher binding energy (407.2 eV). This shoulder is a satellite of the NO_2 peak which is due to a complex multiple excitation process described in a recent theoretical and experimental study of para-nitroaniline [8].

The approximate atom per cent surface compositions of several samples were determined from the XPS data using empirical sensitivity factors measured on our photoelectron spectrometer. Table I gives the composition of three different uncoated samples: (1) with < 20 min Mg X-radiation; (2) with > 1 h Mg X-radiation; (3) UV irradiated with < 20 min X-radiation. This table shows that the nitro-nitrogen to amine-nitrogen ratio is slightly lower on both the UV irradiated sample and on the sample with extended X-irradiation. This is in agreement with the results of Sharma *et al.* [5].

The measured surface composition of a coated sample is also given in Table I. The C 1s, O 1s, and N 1s spectra for this coated sample are shown in Figs 1b, 2b and 3b. Several observations can be made

TABLE I Summary of XPS data for 1,3,5-triamino-2,4,6-trinitrobenzene

	Binding energy (eV)									
	C 1s				O 1s		N 1s		Cl 2p	F 1s
	285	286	289	291	531	534	398	404	200	687
Functional group	CNH_2 CH_2	CNO_2	C=O CFCl	CF_2	NO_2	OH	NH_2	NO_2	CCl	CF_2
Sample 1 (< 20 min X-rays)	17.5	14.3	2.4	–	27.3	5.0	15.8	17.7	–	–
Sample 2 (60 min X-rays)	18.8	14.0	2.0	–	28.1	5.2	16.2	15.8	–	–
Sample 3 (UV + < 20 min X-rays)	19.5	15.1	1.9	–	27.9	3.6	15.9	16.1	–	–
Theoretically calculated	16.7	16.7	0.0	0.0	33.3	0.0	16.7	16.7	0.0	0.0
Sample coated with 5% Kel-F	8.3	7.2	3.6	10.3	13.3	1.9	8.9	9.2	7.6	29.7

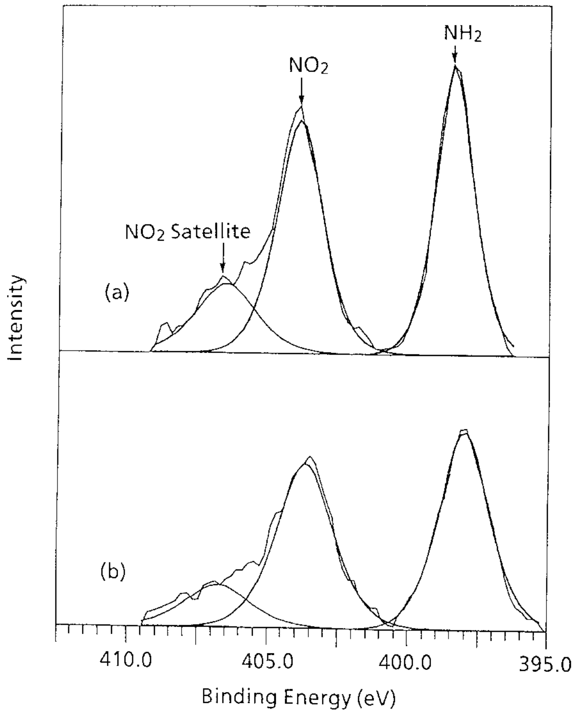

Figure 3 N 1s XPS spectra of (a) an uncoated sample, and (b) a coated sample.

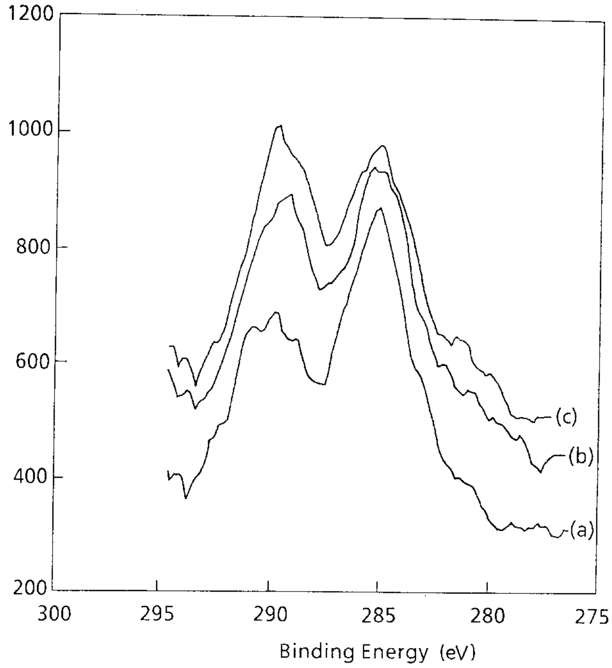

Figure 4 C 1s XPS scans of coated samples after (a) 3 min, (b) 30 min, (c) 60 min X-irradiation.

from the data in this table. Note that the fluorine and chlorine which are detected are from the Kel-F coating material. The C 1s peak at 290 eV is also due to the coating and is from CF_2 and CFCl-type carbon. The fact that nitrogen is detected on the surface of the coated sample indicates that the coating is either incomplete or very thin. The C 1s and O 1s data from this sample also support this conclusion. From the known Kel-F composition, the fluorine-to-chlorine ratio on the coated sample is expected to be 3.7. This is in good agreement with the measured ratio of 3.3.

A surface colour change from yellow to green was also noted for the coated sample following X-irradiation. This was found to correlate with a decrease in the nitro-nitrogen to amine-nitrogen ratio. A change in the C 1s spectrum was also noted during X-irradiation. This can be seen in Fig. 4. The peak at 290 eV, due to CF_2 and CFCl groups in the Kel-F coating, increases with respect to the carbon peak at

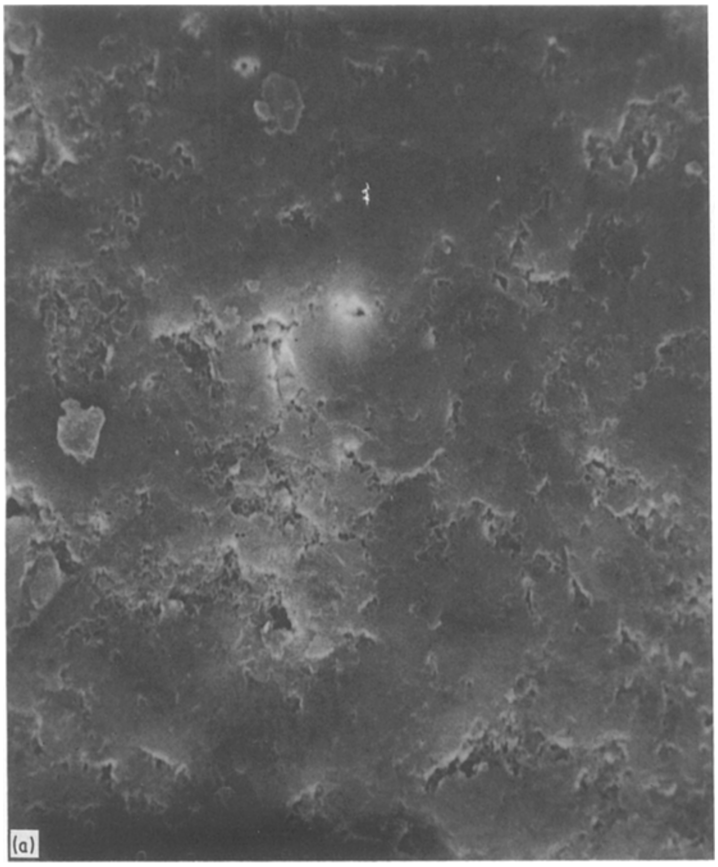

Figure 5 Scanning electron micrograph of coated samples (a) as-received (b) after 1 h Mg X-irradiation.

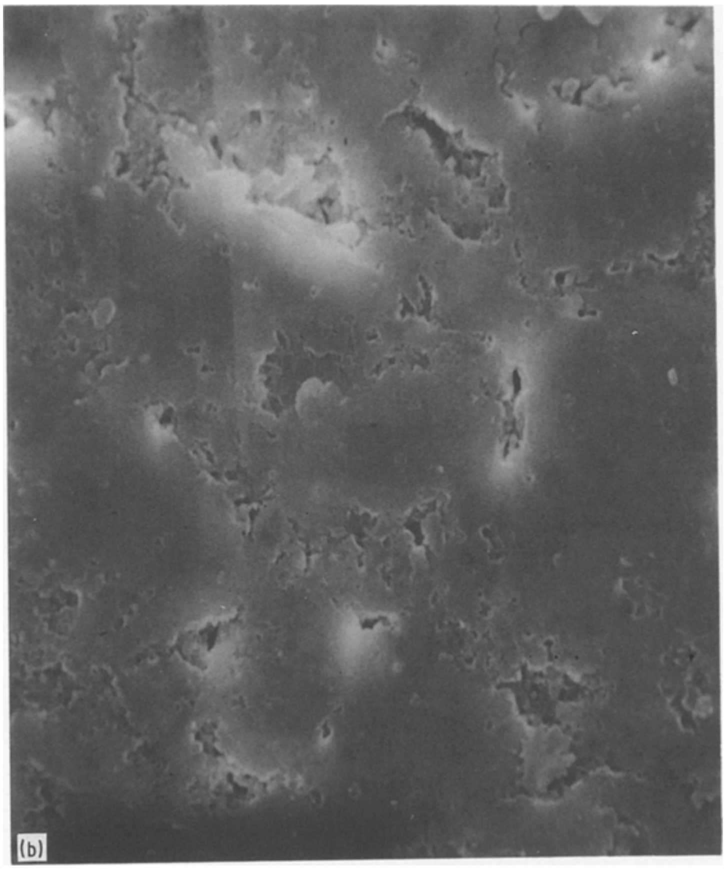

Figure 5 Continued

285 eV which is due to 1,3,5-triamino-2,4,6-trinitrobenzene. The reason for this change can be ascertained from the scanning electron micrographs shown in Fig. 5. In Fig. 5b the photomicrograph of the coated sample particle that had been irradiated shows that its surface is smoother than that of the unirradiated particle. Apparently, there is some flow of the Kel-F coating due to heating of the sample during irradiation. This redistribution of the coating then masks the underlying substrate particles.

In order to verify that the O 1s peak at ~ 534 eV was due to the moisture, the uncoated samples were aged in a desiccator and then analysed with XPS. Fig. 6 shows the O 1s spectra for an unaged sample and for a sample aged for 9 days in a desiccator. On the aged sample, there is a reduction in the intensity of the peak at ~ 534 eV as well as a shift to higher binding energy for this peak. Fig. 7 shows the change in the intensity ratio of the two oxygen peaks as a function of ageing time. Clearly, the oxygen peak at ~ 534 eV must be due to bound water in the sample which is slowly removed while ageing in the desiccator. The reason for

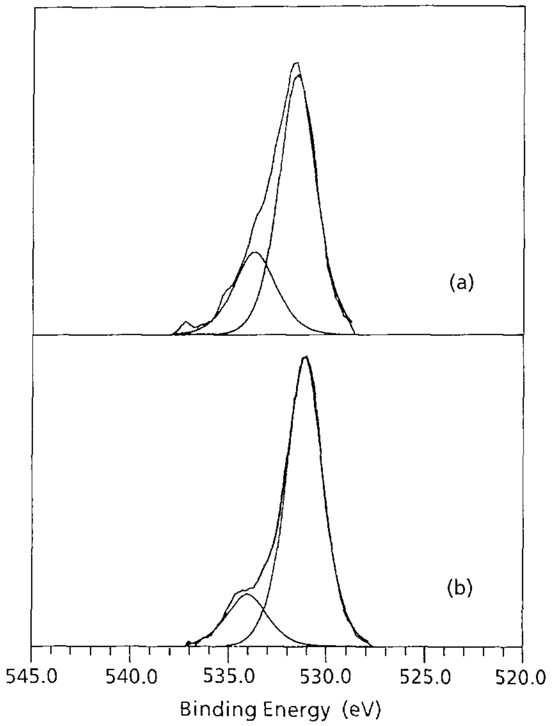

Figure 6 O 1s XPS spectra of an uncoated sample (a) before ageing in a desiccator, (b) after 9 days in a desiccator.

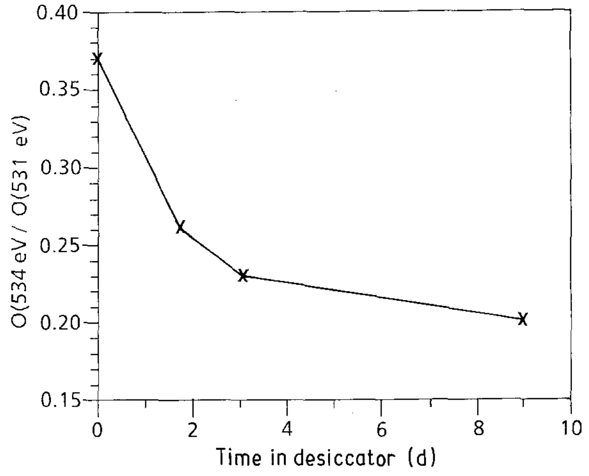

Figure 7 Plot of O 1s ratio of as a function of ageing times in a desiccator. O 1s peak at 534 eV is due to the moisture and the peak at 531 eV is from the 1,3,5-triamino-2,4,6-trinitrobenzene.

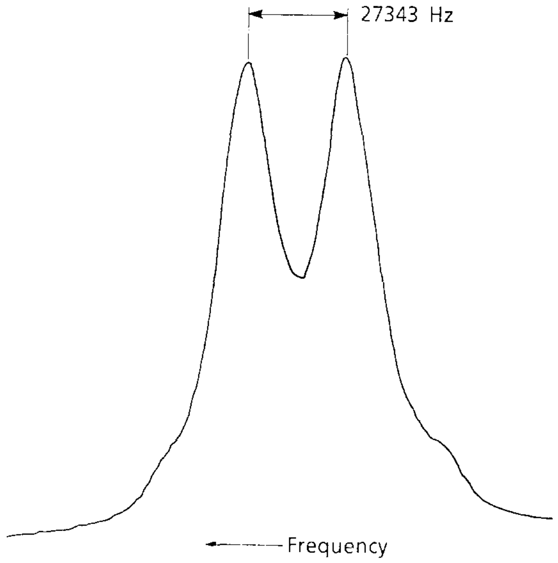

Figure 8 Proton FT-NMR spectrum of a thermally purified 1,3,5-triamino-2,4,6-trinitrobenzene sample at room temperature.

the shift in this oxygen peak due to water will be clarified by the NMR results discussed in the following section.

3.2. Proton FT-NMR results

The nuclear spin of the two protons in NH_2 of triaminotrinitrobenzene is triplet state. The total Hamiltonian operator of this two spin system in an external magnetic field can be a sum of Zeeman effect, proton-proton dipolar interaction, and nuclear exchange interactions [9–12]. However, it is mainly the nuclear dipolar term that is responsible for the line-broadening in the solid NMR spectroscopy. In our case, the line splitting of the FT-NMR signal forms the well-known Pake's doublet [13].

Fig. 8 shows such a proton FT-NMR spectrum of the uncoated powders separated by thermal gradient sublimation. This sample should not contain any residual solvent or surface moisture because it was handled in a nitrogen box immediately after separation. The spectrum was taken at 200. 1200 MHz and the two peaks with a splitting of 27 343 Hz can be observed. The two weak signals at the side of the spectrum are due to partial orientation of the sample which formed flakes after sublimation.

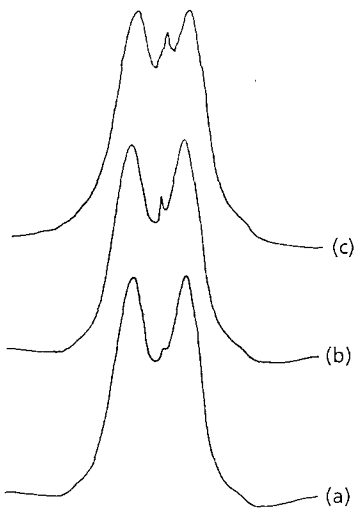

Figure 9 Proton FT-NMR spectra of "ultrafine" triaminotrinitrobenzene powders at room temperature (a) as-received; and after (b) 66 h, (c) 114 h exposure to 100% relative humidity condition.

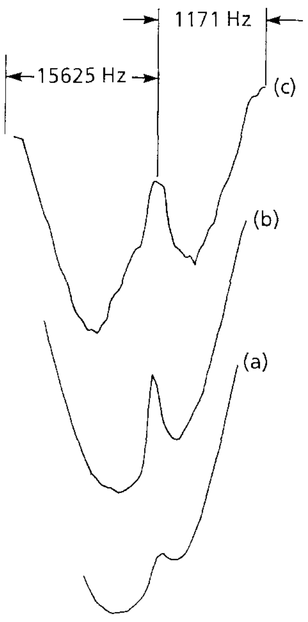

Figure 10 Enlarged proton FT-NMR spectra of surface moisture portion in Fig. 9.

Fig. 9 shows spectra of our "ultrafine" powders exposed to moisture for various times. In Fig. 9a, the small signal observed between the doublets (11 718 Hz from the lower frequency peak) is due to surface moisture in the as-received sample. As the sample is exposed to 100% humidity at room temperature for 66 h, the surface moisture increases, as can be seen from Fig. 9b. Exposure for 114 h gives even stronger moisture signal (Fig. 9c). One interesting feature about the surface moisture in Fig. 9c is that when the moisture reaches a certain amount, the line-broadening in H_2O starts to develop. This is probably due to the diffusion of surface moisture into the solid crystal lattice or the formation of partially bonded water on the surface. In either case, the water molecules lose a certain degree of freedom and thus a broader line from the moisture is measured. This agrees very well with the XPS result which shows an increase in O 1s binding energy in the bound water after ageing in the desiccator. Fig. 10 is the expanded moisture region of Fig. 9; note the line-broadening in Fig. 10c.

Acknowledgements

The authors thank D. W. Firsich of Mound for his thermally sublimated powders. Mound is operated by Monsanto Research Corporation for the United States Department of Energy under Contract no. DE-AC04-76DP00053.

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Received 9 March
and accepted 27 July 1988