X-Ray Photoelectron Spectroscopic analysis of CCA treated wood.

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Summary

Ponderosa pine and Douglas-fir wood sections were treated with CCA preservative. To elucidate the mechanism of fixation of the CCA, the wood surface was analyzed by X-ray photoelectron spectroscopy (XPS). The C1s spectra allowed the chemical state of the carbon atoms in the surface region of unextracted wood to be allocated: 44-47% to C1 (carbon bonded to carbon and/or hydrogen), 45-47% to C2 (carbon bonded to one oxygen), and 8-9% to C3 (carbon bonded either to a carbonyl oxygen or to two oxygen atoms). CCA treatment of unextracted wood increased the C1 (47-63%) component and decreased the C2 fraction (28-44%). However a similar change was observed at the wood surface when wood samples were wetted and then allowed to air dry. This was interpreted as being due to a redistribution of extractives to the wood surface during drying. Since this effect will occur during the drying of treated wood, it will influence the XPS spectra of the CCA reacted samples. Extractive-free sections resulted in a decrease in C1 (18-25%), and an increase in C2 (65-74%). The C3 component was unchanged at 9-10%. CCA treatment of the extracted sections caused a slight increase in the C1 (24 - 28%) and decreased slightly the C2 component (63 - 68%). The changes in C1 (increase) and C2 (decrease) could be explained by the oxidation of hydroxyl group on cellulose (C2 decrease) to form carbonyl and carboxyl, followed by decarboxylation (C1 increase). The large changes in the state of the carbon atoms recorded during CCA treatment of unextracted wood would appear to be due to migration of extractives to analyzed surfaces as well as to the oxidation of hydroxyl group in wood by CCA.

Introduction

X-ray photoelectron spectroscopy (XPS) is one of the most effective and sensitive tools for the surface analysis of solid wood. A number of XPS studies have been carried out on cellulose, lignin, modified wood, wood pulp, and paper (Dorris and Gray 1978, Mjöberg 1981, Young *et al.* 1982, Williams and Feist 1984, Hon 1984, Ahmed *et al.* 1988,

Ostmeyer *et al.* 1988, Yamamoto and Inoue 1990, Kiguchi 1990). The application of XPS to wood treated with chromated-copper-arsenate (CCA) should give an indication of the extent of chemical change in the treated wood during the fixation. However, difficulties due to surface contamination and the migration of extractives to the surface during sample preparation remain to be solved.

The focus of this paper is on the production of reproducible surfaces carefully prepared using ultrathin microtomed sections to minimize contamination. In addition to examining how the carbon state in the wood components changes due to treatment with CCA, an investigation of the movement of extractives to the surface was also undertaken. This was done to investigate the influence of extractive movement during CCA fixation on the XPS spectra. By comparing the spectral results of extractive free wood sections with those of unextracted samples, their interaction with CCA during preservative fixation could be better understood. Future papers will present the information on the interaction of extractives and CCA. Surface characteristic determined by XPS were related to water repellency which is an important factor affecting surface performance.

Materials and methods

(i). Sectioning

Ponderosa pine (*Pinus ponderosa* Ait.) sapwood and Douglas-fir (*Pseudotsuga menziesii*) sapwood were used in the study. Radial sections in 50μm thickness and 8x8 mm area were serially microtomed from dry wood blocks having a moisture content of approximately 8 percent. A new disposable microtome blade, cleaned with acetone to remove oil, was used to create the sections. The blades were replaced after preparation of ten sections. In addition, extreme care was taken through all steps of specimen preparation and storage to minimize surface contamination.

(ii). Extraction procedure

Previous studies have shown that the surfaces of unextracted wood and extracted wood gave somewhat different XPS spectra and O/C ratio (Mjöberg 1981, Yamamoto and Inoue 1990, Kiguchi 1990). Therefore, half of the samples were pre-extracted with organic solvent (TAPPI T264 om-88, 1988). The sections or small wood blocks (8x8x8mm) were extracted in a soxhlet apparatus with ethanol-toluene (1:2) for 8 hours. This was followed by ethanol extraction for 8 hours and extraction with distilled water at 100°C for 2 hours. The residue was washed several times with hot distilled water.

(iii). CCA treatment

The extractive-free and unextracted thin sections were immediately soaked in a 3% solution of CCA type C (CrO_3:CuO:As_2O_5=47:18:35) for ten minutes. After treatment the samples were dried either a) on the bench under normal conditions at room temperature, or b) using accelerated fixation method which required two minutes under

humid conditions (Ruddick 1991). The XPS analyses were performed after 5-7 days storage of all samples in dark clean glassware at room temperature to allow for complete fixation.

(iv). XPS analysis

The spectra were measured in a Leybold MAX200 spectrometer at an operating pressure of 6×10^{-9} mbar (base pressure 3×10^{-10} mbar). The unmonochromatized MgKα excitation source was operated at 15 kV and 20 mA; the emited photoelectrons were collected from a 2 x 4 mm^2 area. Initial survey spectra for use in qualitative analysis were obtained with the analyzer pass energy set at 192 eV; high-resolution narrow-scan spectra for quantitative analysis were measured for the C1s and O1s core levels at a 24 eV pass energy. For the latter, peak areas determined after background subtraction were taken to measure relative elemental amounts after correction with the appropriate sensitivity factors.

Curve fitting of C1s spectra was done by the following method. Peak synthesis was performed using mixed Gaussian and Lorentzian functions with a nonlinear base line. The full width at half maximum height of C1, C2, and C3 were restricted to 1.89 +/- 0.12 eV in individual spectra. The binding energy of C1 was referenced to 285.0 eV. The chemical shift was fixed at 1.7 eV for C2 and 3.7 eV for C3 respectively, in all spectra. Computor curve fitting gave chi square values between 2-6%.

(v). Water repellency

A 5 µl water drop was added to the surface of each section. The time for the water droplet to disappear and be absorbed into the wood was measured (Hemingway 1969). Five observations were made each on a different section. The time for extracted sections on which no droplet formed was counted as 0 seconds. Where the time exceeded 60 minutes, the observation was recorded as not wetting the sections.

Results and discussion

(i). Unextracted and extracted wood

The surface of sections cut from untreated wood blocks showed the same trend of O/C ratio and C1, C2, and C3 percentages in ponderosa pine and Douglas-fir (Table 1). The XPS C1s spectra of ponderosa pine is illustrated in Fig. 1. Dorris and Gray (1978) have classified carbon atoms in woody materials into four categories which correspond to C1 being carbons bonded to other carbons or hydrogen ie. C-C or C-H; C2 being carbons bonded to a hydroxyl group, C-OH; C3 being carbons bonded to two oxygen atoms (eg. HO-C-OH) or to a carbonyl group, C=O; and C4 a carbon bonded in a carboxylic structure O-C=O. The O/C ratios of both species were a little higher values than those in

the literature but were similar to those of the extracted wood surface of Scots pine and Japanese cedar (Table 2).

The higher O/C ratio obtained in this experiment may be due to less surface contamination and/or less extractive migration during sample preparation. The contamination in normal laboratory air due to light oils is mainly C1 rich (Takahagi *et al.* 1990) while extractives are rich in C1 and low in O/C ratio (Young *et al.* 1982, Rowell 1984). The chemical state of the carbon atoms at the surface of the untreated wood was almost equally divided between carbons bound to one oxygen and carbons bonded to no oxygen atoms. The percentages of C1 and C2 were similar to those of redwood and southern pine reported by Williams and Feist (1984), although quite different from other literature data which were characterized as high in C1.

Surface smoothed wood blocks were impregnated with water and dried at room temperature to accelerate the extractive redistribution to the surface. The XPS spectra observed for the surface of the water dipped block was markedly different from that of the unextracted control (Table 1). Water soluble extractives migrating to the surface would be expected to increase the C1 percentage and decrease O/C ratio during drying. It is known that water soluble extractives such as the tannin-polyphenol components migrate from the inner layer to the outer layer of timber during drying (Anderson *et al.* 1960). Water soluble nitrogen based nutrients have also been shown to move to the surface during drying (King *et al.* 1974, Yamamoto and Rokova 1991). This suggested the interpretation of XPS spectra will be complicated by extractives migrating to the surface during chemical treatment. The movement of extractives to the specimen surface during surface preparation may account for the variations in results reported by different workers (Table 2). The surface of unextracted controls will contain different amounts of extractives. In this study this was overcome by preparing extractive-free specimens in the shape of section or small block. It was also recognized that removal of extractives may interfere with the fixation mechanism and research continues on this aspect. Extraction of sections with methanol and toluene decreased C1 and increased O/C ratio strongly in both species (Table 1). The extent of extraction differed depending on the specimen size and depth of analysis from the block surface. Extracted thin sections showed higher O/C ratio and lower C1 percentage than extracted blocks.

(ii). CCA treatment of pre-extracted section

Studies of the CCA treatment of extracted wood may not represent the complete interaction with wood, because extractives have been suggested as playing a role in CCA fixation (Pizzi *et al.* 1986). However since the primary reactions appear to involve the structural components, it was considered important to distinguish the reaction with these components first. It was noted that CCA treatment for pre-extracted sections slightly increased C1 and decreased C2 in both species (Table 3). The XPS C1s spectra of Douglas-fir is shown in Fig. 2.

A decrease in the C2 component could be explained by the oxidation of hydroxyl groups (C2) during reaction with CCA. It resulted in a slight increase of C3 in air dried sections

indicating formation of carbonyl bonds and resulted in a slight decrease of C3 in rapidly fixed CCA treated samples suggesting a stronger oxidation of carbonyl or carboxyl groups resulting in the decarboxylation proposed by Williams and Feist (1984). Ostmeyer *et al.*(1989) showed that treatment of southern pine with CCA - C resulted in a decrease in both the aromatic and carbonyl peaks of the infrared spectra. The CCA treatment followed by accelerated fixation caused more extensive oxidation, producing higher percentages in the C1 component than by fixation at ambient temperatures. The lower C3 component in the rapidly fixed sections than in the conventionally fixed samples was consistent with the formation of more unoxidized carbons (ie. C1) and a lower O/C ratio. This suggested that accelerated fixation enhanced the decarboxylation reaction. The decarboxylation from cellulose treated with CrO_3 was reported using mass spectroscopy (Williams and Feist 1984). The lower value of O/C ratio in the rapidly fixed sections than that in the conventionally fixed sections supported the interpretation that decarboxylation occurred more in former specimens in both wood species. Research is in progress to confirm that CO_2 is evolved during CCA fixation.

(iii). CCA treatment of unextracted section

In unextracted sections of ponderosa pine, surface hydroxyl concentration (C2) markedly decreased with the 3% CCA treatment (Table 4). The same behavior was observed with Douglas-fir. The XPS C1s spectra of ponderosa pine is shown in Fig. 3. The increase of C1 could be due to mainly the migration of acid soluble extractives to surface and partly due to the oxidation of hydroxyl groups on cellulose followed by the decarboxylation, as proposed by Williams and Feist (1984). The migration of extractives as indicated by the incease in C1, occurred less in rapidly fixed CCA treated sections than in those allowed to fix at ambient temperatures, possibly because the moisture gradient within sections during drying might be flatter in the former process. Ostmeyer *et al.* (1988) reported that CCA treatment of southern pine decreased the C1 component and increased C2. They suggested that non-substituted carbon atoms in the aromatic ring reacted with chromic acid to form chromate esters, as described by Pizzi (1980, 1990). In the current investigation, there was no indication of the increase of C2 component with CCA treatment in either the unextracted or pre-extracted sections.

The C1s peak showed a decrease in carbon-oxygen bonding(C2) after CCA treatment although O/C ratio increased. This may be attributed to added oxygen atoms from the CCA. An additional constituent appeared in the O1s peak following CCA treatment.

(iv). Water repellency of wood surfaces

Dipping the samples for a short time in water and allowing them to air drying at room temperature significantly increased their water repellency (Table 5). It is proposed that this increase in water repellency was due to the migration of water soluble extractives to the wood surface. This interpretation was supported by the XPS spectra in which the C1 component of the C1s spectra increased markedly (Table 1). Hemingway (1969) has shown that the unsaturated fatty acid and esters undergo considerable oxidation under

heating to produce water repellency. Removal of the extractives with ethanol and toluene resulted in complete loss of water repellency. CCA treatment improved water repellency more in the unextracted surface than in the extracted surface. It was interesting to note that extractives were responsible for changes in the water repellency of wood surface induced by CCA treatment. This would suggest that interaction between extractives and CCA should be an important factor influencing the increased water repellency during fixation. Crosslinked chromium complexes with alcohol groups as ligands in wood components, including extractives, could contribute the increase in water repellency (Duncalf and Dunn 1964).

Conclusions

The migration of extractives to the wood surface during CCA treatment caused major changes to the XPS spectra, resulting in incorrect interpretation of fixation reactions. CCA treatment increased C1 and decreased C2 in XPS C 1s spectra, both in unextracted and extracted sections. This suggested oxidation of hydroxyl groups on cellulose or lignin by CCA occurred, followed by the decarboxylation of carbonyl and carboxyl groups. CCA fixation resulted in a higher water repellent surface, especially in the presence of extractives. Future work on the investigation of chromium and copper complexes formed with wood should give a more complete picture of CCA fixation.

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Table 1. O/C ratio and fractional contribution to C1s peak in unextracted, water dipped, and extracted wood.

Specimen	O/C	C1	C2	C3
Ponderosa pine				
Unextracted, section	45.3	44.2	46.6	9.2
Water dipped and dry, block,	32.6	57.4	33.6	9.0
Extracted, section	58.5	25.2	65.0	9.8
Extracted, block, surface	48.8	36.6	54.9	8.5
0.2mm deeper	57.0	32.0	59.5	8.5
Douglas-fir				
Unextracted, section	42.5	46.6	45.4	8.0
Extracted, section	66.1	17.5	73.6	8.8

Table 2. O/C ratio and fractional contribution to C1s peak in literature

Specimen	O/C	C1	C2	C3	Reference*
Redwood, heartwood	33	43	44	13	(1)
Southern pine, sapwood	37	46	47	7	(1)
Yellow poplar, sapwood	26	64	26	10	(2)
Suger maple	15	50	43	7	(3)
Populus tremuloides	24	72	22	6	(4)
Scots pine	26				(5)
Scots pine, extracted	42				(5)
Japanese cedar	26	76	21	3	(6)
Japanese cedar, extracted	54	20	77	3	(6)
Redwood, 5% CrO_3 treatment	49	70	17	13	(1)
Southern pine, 5% CrO_3	40	70	18	12	(1)

* (1) Williams and Feist, 1984; (2) Hon, 1985; (3) Young *et al.*, 1982; (4) Ahmed *et al.*, 1985; (5) Mjöberg, 1981; (6) Kiguchi, 1990.

Table 3. O/C ratio and fractional contribution to C 1s in pre-extracted wood treated with 3% CCA

Specimen	O/C	C1	C2	C3
Ponderosa pine				
Extracted	58.5	25.2	65.0	9.8
Pre-extracted, 3%CCA, Air dry	67.1	25.8	63.6	10.6
3%CCA, Accelerated dry	65.9	28.0	62.7	9.3
Douglas-fir				
Extracted	66.1	17.5	73.6	8.8
Pre-extracted, 3%CCA, Air dry	67.0	23.7	66.6	9.7
3%CCA, Accelerated dry	65.8	24.0	68.0	8.0

Table 4. O/C ratio and fractional contribution to C1s in unextracted wood treated with 3% CCA.

Specimen	O/C	C1	C2	C3
Ponderosa pine				
Unextracted	45.3	44.2	46.6	9.2
Unextracted, 3%CCA, Air dry	45.8	63.1	27.5	9.4
3%CCA, Accelerated dry	51.4	53.8	36.6	9.6
Douglas-fir				
Unextracted	42.5	46.6	45.4	8.0
Unextracted, 3%CCA, Air dry	53.1	55.1	36.2	8.7
3%CCA, Accelerated dry	49.2	47.6	43.9	8.5

Table 5. Change in surface water repellency of thin sections after extraction, water dipping, and CCA treatment

	Time for the absorption of a water droplet(sec)	
Treatment	**Ponderosa pine**	**Douglas-fir**
Unextracted	8	98
Drying after water dipping	36	167
Extracted	0	0
Pre-extracted, 3%CCA treatment	694	544
Unextracted, 3%CCA treatment	>3600	>3600

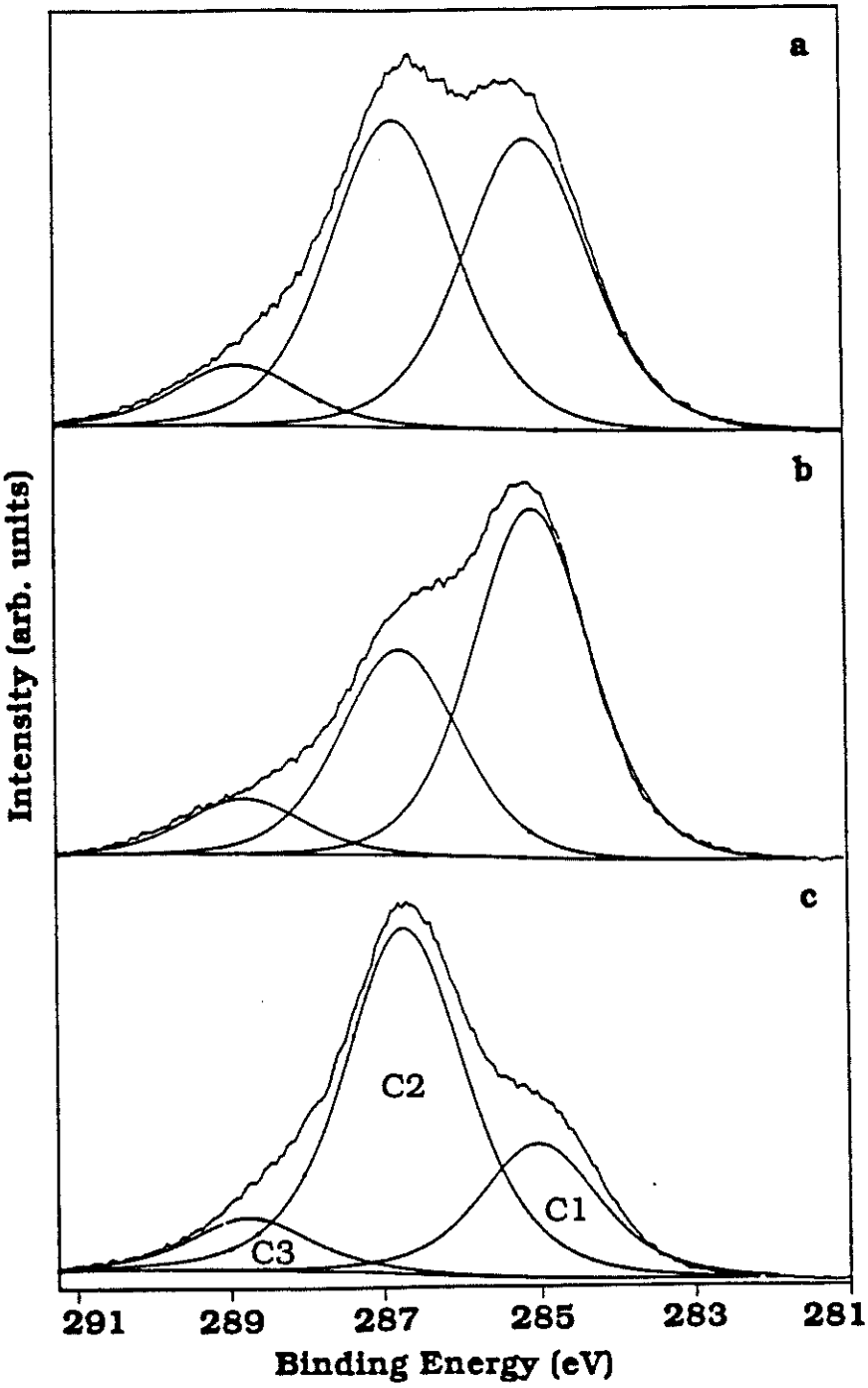

Fig. 1 XPS C1s spectra of ponderosa pine; a) unextracted section, b) block surface dried after water impregnation, c) ethanol and toluene extracted section.

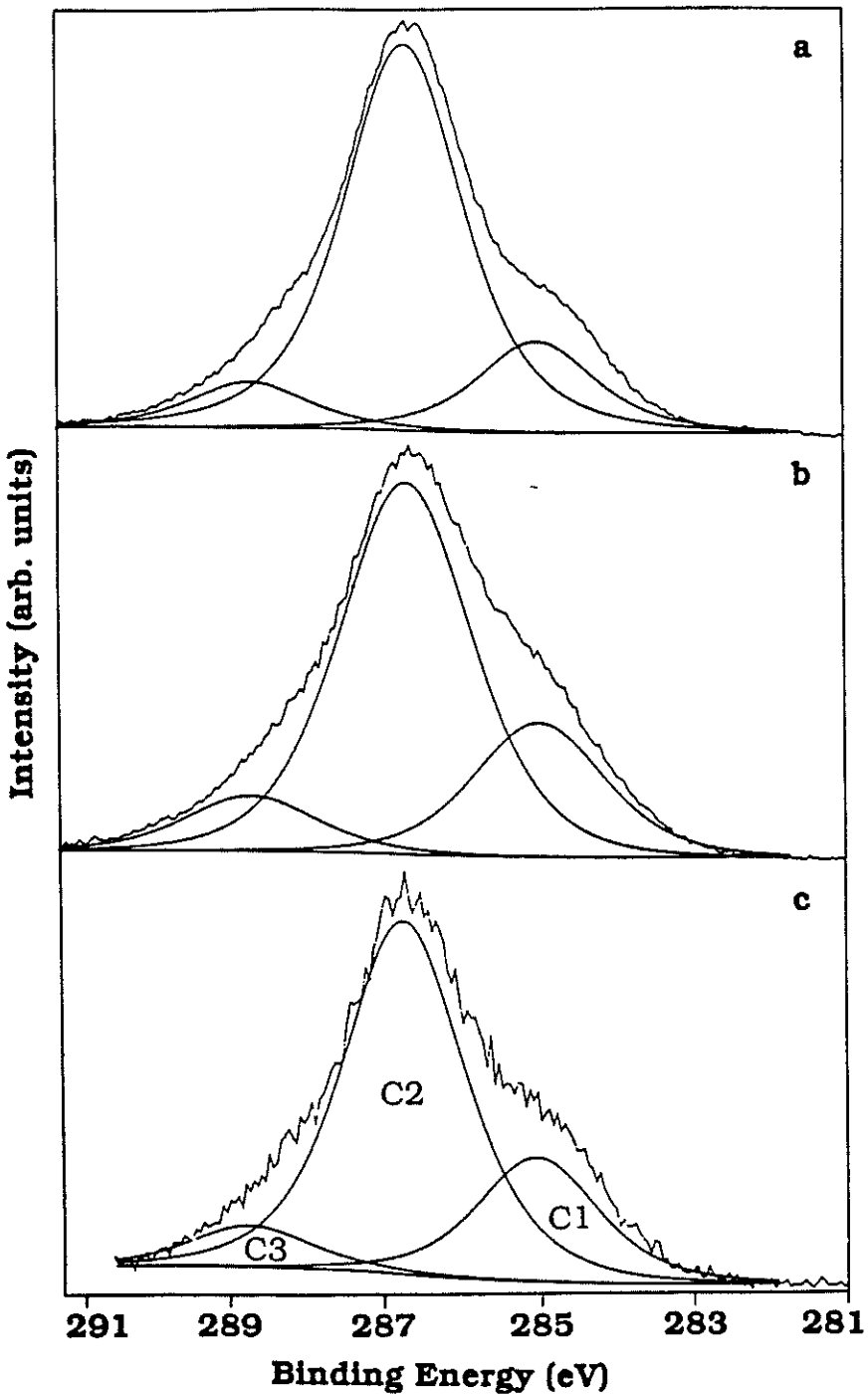

Fig. 2 XPS C1s spectra of douglas-fir; a) pre-extracted section, b)pre-extracted section treated with 3%CCA followed by air dry, c)pre-extracted section treated with 3%CCA followed by accelerated dry.

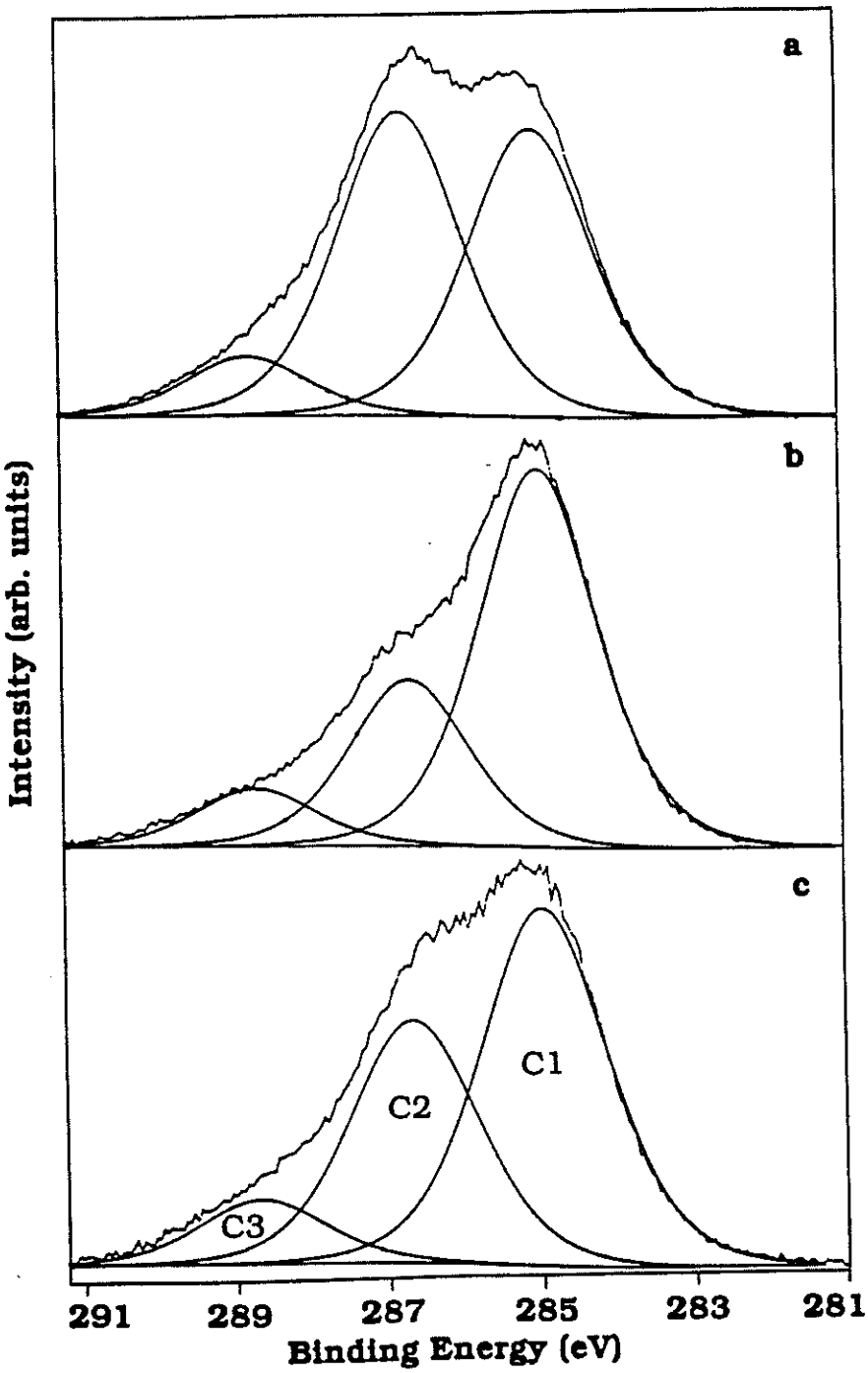

Fig. 3 XPS C1s spectra of ponderosa pine; a) unextracted, b) unextracted section treated with 3%CCA followed by air dry, c) unextracted section treated with 3%CCA followed by accelerated dry.