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Study on the XPS-ESCA of Aluminum Phosphide Products

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Abstract: XPS-ESCA analysis showed small signal for phosphorus in fresh specimens of aluminum phosphide (AlP). After removal of a layer of about 0.5 – 1.0 µm by argon ion sputtering, it was observed that signal intensities from oxygen and aluminum increased. The oxygen signal decreased as a function of sputtering time, synchronously with the increase of the phosphorous signal from the AlP nucleus. The aluminum signal, which was considered to be mainly due to AlP and $Al(OH)_3$, remained constant. Other impurity elements including N, Mg, etc., were identified in the technical 85% AlP and AlP tablet formulated products.

Keywords: XPS, ESCA, aluminum phosphide.

Introduction

X-ray Photoelectron Spectroscopy (XPS) is a technique for determining the binding energies of core-electrons [1]. The ESCA spectrum measures the kinetic energies of electrons ejected from a molecule by a mono-energetic beam of X-radiation. Aluminum phosphide and its formulated products are important insecticides still used in stored products and agricultural fields [2,3]. Up to now, the impurity elements and their forms among these products are unknown due to the analytical difficulties with either chromatography or common chemical analysis. Thus, XPS-ESCA determination was undertaken to characterize aluminum, phosphide and other impurity elements in the technical aluminum phosphide and formulated products.

Results and Discussion

The binding energy data for Al(2p) and P(2p) were as shown in Table 1.

Table 1. The binding energies for Al(2p) and P(2p) in aluminum phosphide

Atom	Al(2p)	P(2p)
FWHM	2.069	1.883
Binding energy (eV)	74.1	129.6

The sensitivity and peak areas of the characteristic elements in the full scan spectrum and that obtained by the argon ion sputtering method were compared. Four samples were submitted to this study, including AlP technical powder (85%), AlP tablets (55%), aluminum powder (95%) and red phosphorus (96%).

XPS for aluminum

94% Aluminum powder was used for the full scan analysis by XPS. Al (2p) has a binding energy of 74.1, 71.4 eV. Very minor impurities were found in this 94% powder, aside from the peaks of C1s and O1s (Figure 1).

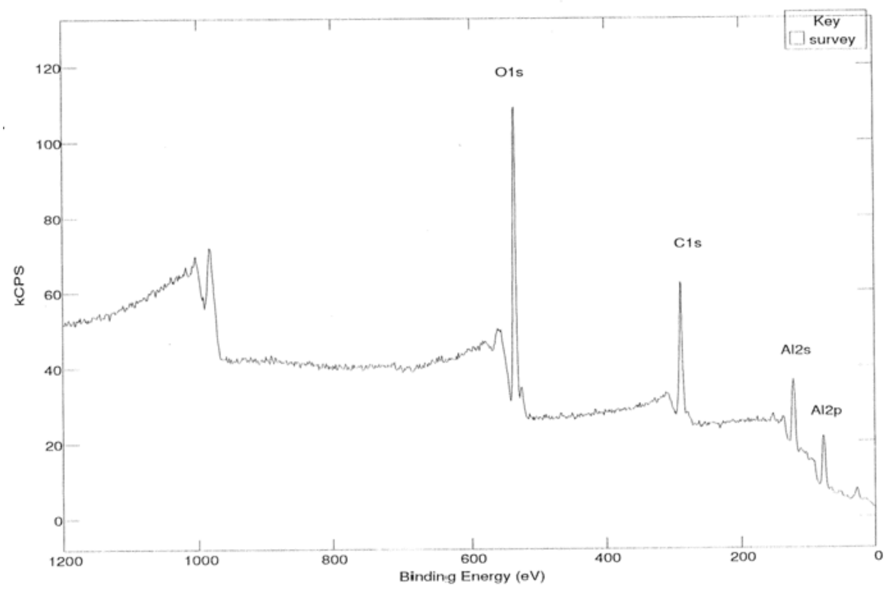

Figure 1. XPS full scan spectra of Al power (94%) by argon ion sputtering.

XPS for red phosphorus

Red phosphorus (96% technical) was used for the full scan analysis by XPS. P (2p) has a binding energy of 129.6eV (133.9, weak). Minor impurities including sodium, calcium and magnesium were found in this 96% powder, excepting for the normal peaks of C1s and O1s (Figure 2).

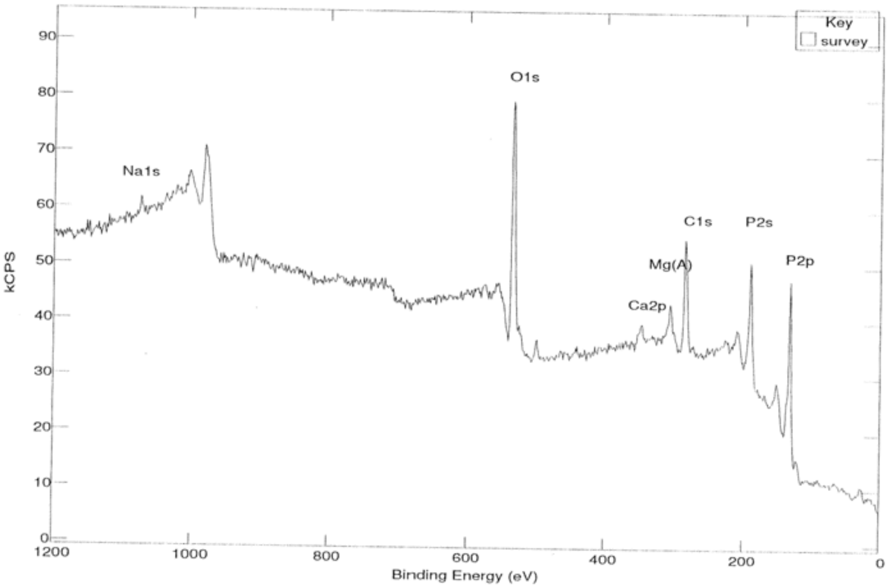

Figure 2. XPS full scan spectra of P power (95%) by argon ion sputtering.

XPS for Aluminum Phosphide technical

An 89% technical AlP was used for the full scan analysis by XPS (Figure 3). P (2p) has a binding energy of 133.7eV. Al (2p) has a binding energy of 74.4 eV (single peak). Minor impurities including sodium, calcium, magnesium, nitrogen and oxygen, etc. were found in this 89% powder.

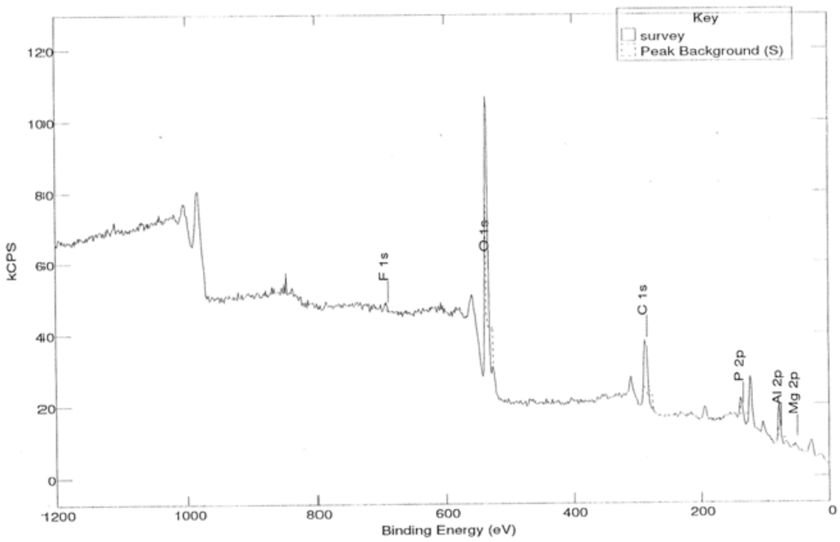

Figure 3. XPS full scan spectra of AlP technical (85%) by argon ion sputtering.

XPS for Aluminum Phosphide tablets

A 55% AlP tablet was used in duplicate for the full scan analysis of XPS. P (2p) has a binding energy of 133.7eV. Al (2p) has a binding energy of 74.4 eV (single peak) Minor impurities including sodium, calcium, magnesium, nitrogen and oxygen, etc. were found in this 55% tablet formulation.

Aluminum (2p) has a binding energy of 74.5, while P (2p) (133.7eV) has a weak signal on the spectrum due to contamination(s) of the sphere.

The qualitative and quantitative composition of technical aluminum phosphide was studied employing X-ray photo-electron spectroscopy as well as gravimetric and gas volumetric methods in this research. AlN, Al, $Al(OH)_3$, Mg^{2+} and As (below 0.04%) were found to be present, in addition to AlP, in the technical and formulated AlP products. $Al(OH)_3$ is produced by the reaction of AlP with H_2O. Some impurities are from the the raw materials. This conclusion was supported by analysis of the aluminum and red phosphorous. Additionally, Na (1s in XPS) and Ca (2p in XPS) etc were found in some amount in the raw materials.

The reaction of aluminum phosphide with water produces a white power and gaseous PH_3. No reaction was observed between AlP and dry air. The solid reaction product could therefore be Al_2O_3, AlO(OH), and $Al(OH)_3$. It is assumed that reaction with water vapor causes the growth of concentric layers of $Al(OH)_3$. The mass of $Al(OH)_3$ was determined by the thickness of these layers in XPS spectroscopy. The values of the concentration of $Al(OH)_3$, and other impurities of the analyzed specimens in AlP technical were: $Al(OH)_3$: 12%, Al: 1.1% and AlN: 3.5%, respectively.

X-ray photoelectron analysis showed a small signal for phosphorus in fresh specimens. This indicated that the presence of absorbing coatings that were thicker enough than 50 Angstroms. To determine precisely the phosphorus concentrations, the grains of the specimens were stripped of surface contaminations by argon ion sputtering. These results were consistent with the reporting of Mantler [1], Moffitt [4] and Chuan [5] for similar researches for multi-layer films. It's observed that signal intensities from oxygen and aluminum increased at first accompanying with the removal of the layer by about 0.5 – 1.0 μm. Oxygen signal decrease as a function of sputtering time, synchronously with the increase of the phosphorous signal from the AlP nucleus, while the aluminum signal which was considered to mainly due to AlP and $Al(OH)_3$, remains constant. Thus, by the argon ion sputtering technique, the main differences between the technical AlP and AlP products were identified semi-quantitatively as described.

Experimental

General

An ESCALAB-220ixl, VG Co double focusing iron-free electron spectrometer of split coil solenoid type was used. Reagents used were AlP technical, 85%; AlP tablets power, 55%; Aluminum power, 95%; Red Phosphorus, 96%. Operating conditions: $AlK_{\alpha 1/2}$ X-ray line at 2000eV; X-ray power run at 15Kv and 25ma; Instrumental resolution: 0.04%; CAE=40ev, STEP=50mev, SCAN=2

Procedure

Photoelectron spectra were obtained on a double focusing iron-free electron spectrometer of the split coil solenoid type. Samples were introduced by a probe approximately 10 cm from the target chamber. 2 mg of sample was weighed and the sample was run as powders dusted onto a backing of double-backed cellophane tape. The experiments were carried out at room temperature and the sample pressure was adjusted to about 0.07 Torr to give optimum spectral conditions. The binding energies were measured for the Al(2p) electrons and for P(2p) electrons. All measurements were referenced to the C (12) line.

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