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**Ageing of thin films used in explosives detection**

 T. Caron<sup>a\*</sup>, P. Montméat<sup>a</sup>, E. Pasquinet<sup>a</sup>, P. Prené<sup>a</sup>, F. Serein-Spirau<sup>b</sup>, J. P. Lère-Porte<sup>b</sup>
<sup>a</sup>CEA DAM Le Ripault, F-37260 Monts, France

<sup>b</sup>Ecole de Chimie Laboratoire AM2N, F-34000 Montpellier, France

**Abstract**

The ageing of fluorescent materials (phenyleneethynylene) has been studied to evaluate their lifetime as chemical sensors and to identify the ageing mechanism.

*Keywords:* Ageing; phenyleneethynylene; sensor; fluorescence; Infrared; XPS

**1. Summary**

During the last 10 years counterterrorism activities have been strengthened and various explosive detection technologies have been developed (e.g.: HPLC, GC/MS, NMR and IMS). Chemical sensors, especially fluorescent ones, seem to fill the need in terms of reliability, cost and handling ability. We have developed an optical device based on the capability of  $\pi$ -conjugated fluorescent materials (phenyleneethynylenes) to detect explosives vapors, in particular nitroaromatic compounds (TNT and DNT) [1,2,3]. As far as we know the ageing of phenyleneethynylenes is the subject of only few studies and none of them linked the ageing to the performances of the device [4, 5]. This paper is focused on the ageing of these materials studied by two means. First, we evaluated the influences of oxygen and light on the performances and the lifetime of the Polyimine compound (Fig. 1). Secondly, we undertook an accelerated ageing by the means of UV lamps to characterize (by FT-IR, Raman and XPS) the degradation process of the fluorescent part of the molecule: the Phenylene (Fig. 1).

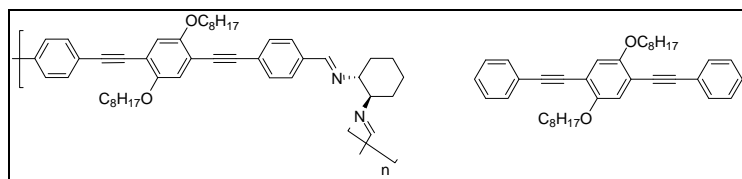


Fig. 1: Polyimine (left) and Phenylene (right)

\* T. Caron, CEA Le Ripault, BP 16, F-37260 MONTS, France, Tel: ++33-(0)2-47-34-56-78, Fax: +33-(0)2-47-34-51-58, E-mail: Thomas.caron@cea.fr

## 2. Lifetime evaluation of fluorescent sensors.

To validate the lifetime of the chemical sensor, it is essential to evaluate its performance in the larger range of time and, to identify the best way to store it. To do so, we evaluated the performances of a polymer by the way of a routine detection test of DNT using a prototype and a testing bench at different time intervals.

### 2.1. Testing bench and detection test description

The bench described in Fig. 2 was used to distribute either dry air to the prototype or air contaminated with 2,4-dinitrotoluène (DNT). The DNT concentration (120 ppb) was measured by spectroscopy after bubbling in a reactor full-up with HPLC grade acetonitrile.

The general testing procedure was:

- 30 minutes of stabilisation under air to obtain the signal base-line.
- 10 minutes of DNT exposure, the quenching of the fluorescence is then observed.
- 45 minutes of dry air to get the original signal back.

The sensitivity of the material is then defined as the percentage of fluorescence inhibition after 10 minutes.

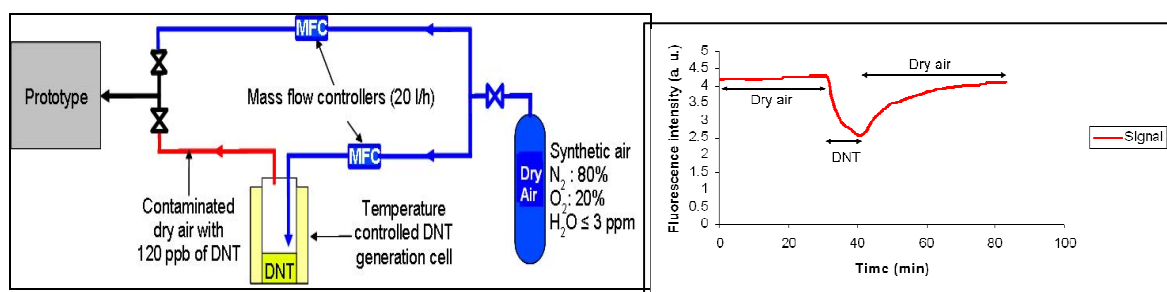


Fig. 2: DNT vapour generation bench (left) and typical detection test (right).

### 2.2. Results

The effects of day-light and oxygen were evaluated on four spin casted Polyimine thin films for different time intervals. The effectiveness for a day corresponds to the sensitivity of the film reported to its initial performance, as for the remaining fluorescence. As can be seen in Fig. 3, both the effectiveness and remaining fluorescence of films decreased quickly under light. The presence of light is thus critical for the ageing of the material. The storage under inert atmosphere (Argon) seems to nearly stop the ageing of the Polyimine. According to these results, we believe photo-oxidation to be the ageing process of the films.

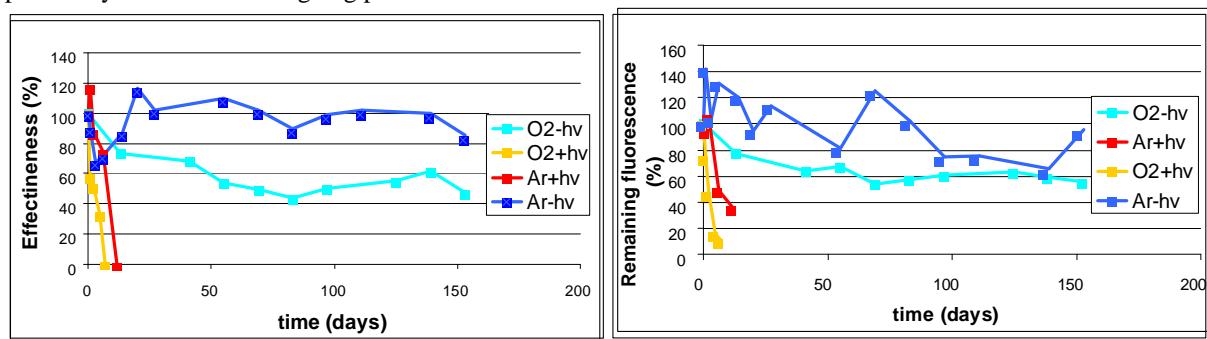


Fig. 3: Effectiveness (left) and remaining fluorescence (right) of four thin films. Storage conditions: O2+hv: Air and light, O2-hv: Air without light, Ar+hv: Argon with light, Ar-hv: Argon without light.

### 3. Ageing comprehension.

To better understand the ageing process, we used a model compound, the Phenylene, which is the fluorescent part of the Polyimide. As a smaller compound, we believe its degradation to be easier to study.

#### 3.1. Infra-red studies.

Phenylene was deposited on silicon wafer and an Epiq6000 UV Fusion lamp was used to produce a quick degradation. As can be seen on Fig. 4 (left), the compound loses its fluorescence after each irradiation, transmission IR spectra were recorded, but we obtained no significant results.

On Fig. 4 (right), we reported an IR spectrum for a fresh film and two spectra (ATR and transmission) after fourth irradiation, we can notice that the two transmission spectra are quite the same, revealing no noticeable degradation. Huge differences can be noticed on the ATR spectrum: a large band at  $1730\text{ cm}^{-1}$  (carbonyl band) and at  $3200\text{ cm}^{-1}$  (OH groups), the alkoxy signal ( $2950\text{ cm}^{-1}$ ) is doubled as well as the majority of the bands found between  $700$  and  $1500\text{ cm}^{-1}$ . The comparison of these spectra led us to the conclusion that only a small part of the film thickness seems to be engaged in the degradation process, with the creation of carbonyl or ester chemical functions.

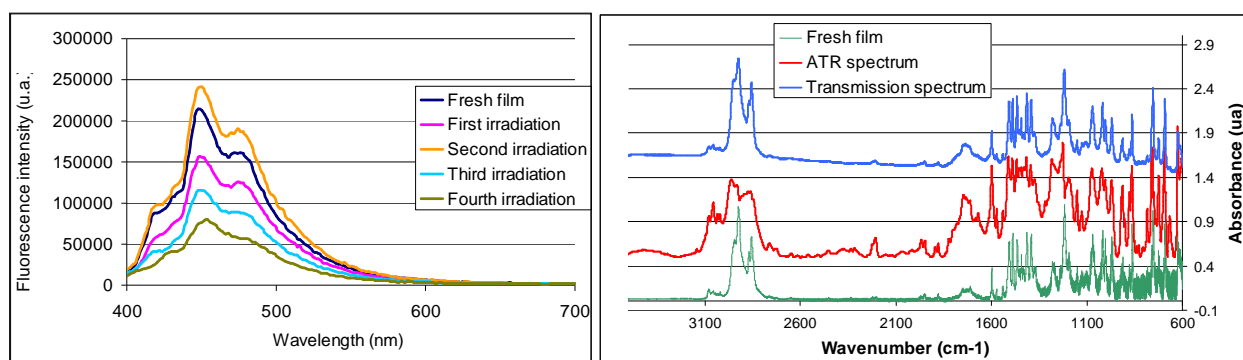


Fig. 4: Phenylene fluorescence spectra after several irradiations under an UV-Fusion lamp (left) and Transmission IR spectrum of fresh Phenylene as well as ATR and transmission spectra after four irradiations (right).

#### 3.2. XPS studies

To corroborate the previous observation, XPS analyses were carried out on fresh Phenylene films and on deteriorated ones, the XPS carbon signals are reported in Fig. 5.

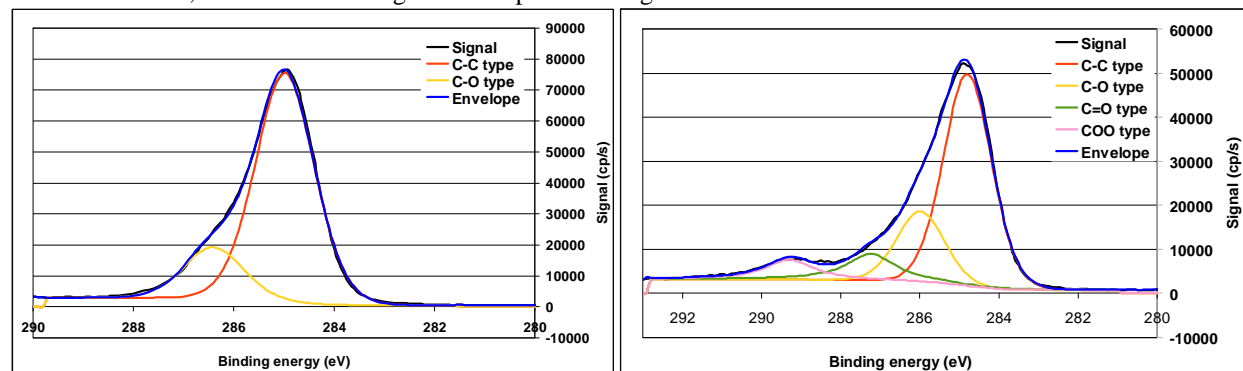


Fig. 5: XPS carbon signals of a fresh Phenylene film (left) and a deteriorated one (right)

The carbon signal of the deteriorated Phenylene exhibits carbonyl and ester (or carboxylic acid) signal contrary to fresh film. Moreover, after Ar<sup>+</sup> bombardment, the XPS signals were the same as the one obtained on fresh films. These observations suit with the infrared results and the hypothesis that only a few nanometers of the film thickness are engaged in the degradation process.

To clarify the location of the degradation (the alkoxy chains or the  $\pi$ -conjugated part) we carried-out the XPS analyses on a non-substituted Phenylene derivative. The presence of two contribution from ester (or carboxylic acid) and carbon-oxygen single bond proves the oxidation of the  $\pi$ -conjugated part of the material (on the triple bonds or phenyl rings).

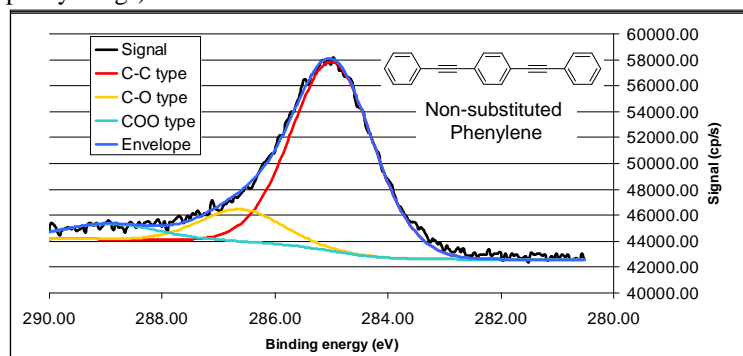


Fig. 6: XPS carbon signal and chemical formula of non-substituted Phenylene

#### 4. Conclusion

The ageing of phenyleneethynylene compounds has been studied. Photo-oxidation seems to be the ageing process, but kept safe from day-light, films were able to detect nitroaromatic compounds 150 days after being spin casted.

The XPS and IR analyses showed that only a small part of the film thickness was involved in the ageing process with creation of carbonyl functions.

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