Title: Colour and changes of composition of materials used in conservation and restoration of graphic documents

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1.- Introduction

The use of synthetic polymers is widespread in the conservation of cultural heritage [1]. Thanks to the great advances developed by the chemical industry, it has emerged a great range of products. Depending on their technical method of polymerization and their own processing method they can be used as sheet, supports, foams, composites, adhesives etc. Usually, these products have been initially developed for other industrial uses (transport, packaging, industrial design, construction, etc). So, the information available concerning their composition is quite limited and, in some cases, inaccurate. For this reason it is necessary to analytically characterize such materials. On the other hand, they should have to be previously studied to know their long-term behaviour. ATR-FTIR spectroscopy has provided excellent results in the characterization of polymers used in conservation [2]. Photochemical and thermal aspects have to be considered in accelerated aging [3]. In this paper it is reported the methodology applied and the first results obtained in relation to some materials very used in conservation. The main objective has been to study the chemical changes promoted on samples subjected to photochemical aging. They have also been quantified the colour changes associated to these chemical changes.

2.-Experimental

Samples. The materials analyzed include adhesives (Archibond), archival pockets (Secol and JCR) and one kind of foam core board archival quality. All of them have been previously analyzed to identify its components: polymeric matrix and additives. Some materials are multilayer, so in these cases the analyses have been performed on each layer. In the same way each layer has been subjected to photochemical aging conditions. Intervals aging times have been controlled. Into these time ranges spectrophotometric measurements have been performed and analyses by ATR-FTIR have been made on each sample.

Photochemical aging

It has been used a chamber Xenon arc Suntest XLS+ with light source filtered for λ<295nm and having a constant irradiation at power of 765W/m^2. The maximum temperature into the chamber was 45ºC. Aging cycles have been applied attending to ISO 4892-2 ("Methods of exposure to laboratory light sources using Xenon-arc lamps"). Cycle 1: 120 hours of exposure and 24 hours of darkness; Cycle 2: 240 hours of exposure and 48 hours of darkness; Cycle 3: 480 hours of exposure and 48 hours of darkness, and so on. Three samples were prepared for each material tested. On each of these samples were taken at least five calorimetrical measurements and two ATR-FTIR analyses.

Analytical Techniques

ATR-FTIR spectroscopy: An ATR- FTIR spectrometer (Thermo Nicolet 380) with a DTGS temperature-stabilized coated detector was used (4000-400 cm-1). This was equipped with an attenuated total reflection diamond crystal accessory (ATR). The spectra were obtained in absorbance mode from 64 scans at 4 cm^{-1} resolution. The spectra were analyzed usin Omnic v 7.3 and processed with Origin v 7.0.

Colour measurements: A Konica Minolta CM 2600d spectrophotometer was used. Measurement spot: 3mm, SCE mode, CIELAB space, range 400nm to 700nm, step size of 10nm, light source D65, standard observer 10º. Average values were obtained from at least five measurements.

3.- Results and Discussion

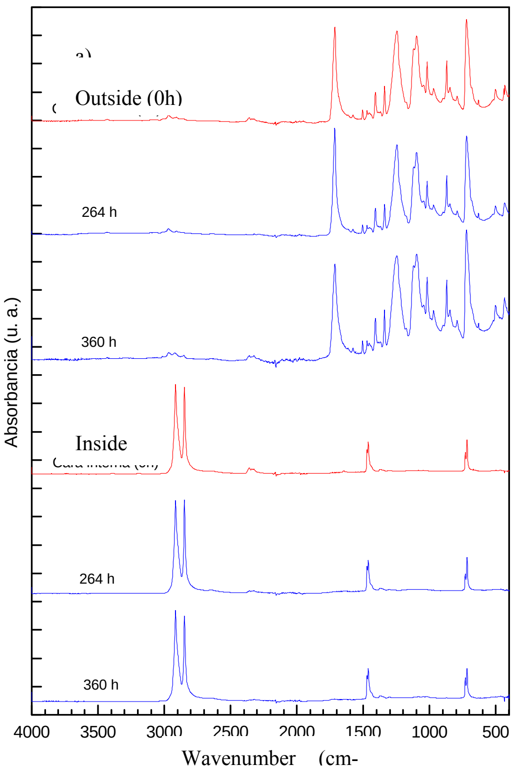
In the first stage of this investigation all materials have been analyzed by ATR-FTIR spectroscopy. The obtained spectra were interpreted with respect to the bands from the characteristics groups of the polymers and additives [4]. Finally, the spectra were compared with those of polymers in FTIR spectral libraries (polymers and additives) [4, 5]. From the results obtained, it has been characterized the chemical nature of each one material investigated. It has also been obtained the colorimetric measurements. In the case of transparent sheets (Archival Pockets) these measurements have been achieved using as ground the white reference used for calibrate the spectrophotomether.

In relation to the analytical characterization, the results have been: *Standard Archival Pocket (Secol)* is a polyester sheet, more specifically poly(ethylene terephthalate) (PET). *Archival Pocket (JCR)* is a multilayer sheet. Inside layer is a high-density poly(ethylene) (HDPE) and outside layer is poly(ethylene terephthalate) (PET). *Archibond* is a heat seal adhesive (film). Its composition corresponds to a acrylic polymer, more specifically poly(methyl acrylate-etylmethacrylate) (Paraloid B-72). *Foam core board* analyzed is a sandwich paperboard with foamed plastic. So it is a multilayer material. In the board have been identified cellulose, lignine and calcite ($CaCO_3$). It should be noted that the composition of the board can vary. In some ones this layer is e composed of cellulose and calcite (without lignine) and others one have a coating of poly(vinyl acetate) [2, 7]

During and at the end of each aging cycle the ATR-FTIR spectra have been again obtained. In the two aging cycles applied (Cycle 1 and 2) the materials Standard Archiva Pocket (Secol), Archival Pocket (JCR) and Archibond do not show any compositional changes: Their colour do not have appreciable changes (Fig. 1). However, the foam core board studied shows noticeable changes, specially in foam core (polystyrene). These changes are in relation to chemical composition and colour (Fig.2a and 2b). In the Figure 2a can be appreciate bands corresponding to carbonyl group νC=O (1717 cm^{-1}). From this peak and taken the band at 695 cm-1 (assigned to aromatic ring) as reference peak, the carbonyl index has been calculated [$I_{co}=(A_{1717}/A_{695})\cdot 10$]. These values have been used to compare changes of colour (ΔE_{ab}) and the formation of carbonyl group (Fig. 2c). Finally, It has to be note that the board has experimented yellowness; this behaviour could be promoted by the lignin present in its composition.

4.- Conclusions

The methodology applied has allowed to establish a relationship between chemical and colorimetrical changes inmaterials used in conservation.



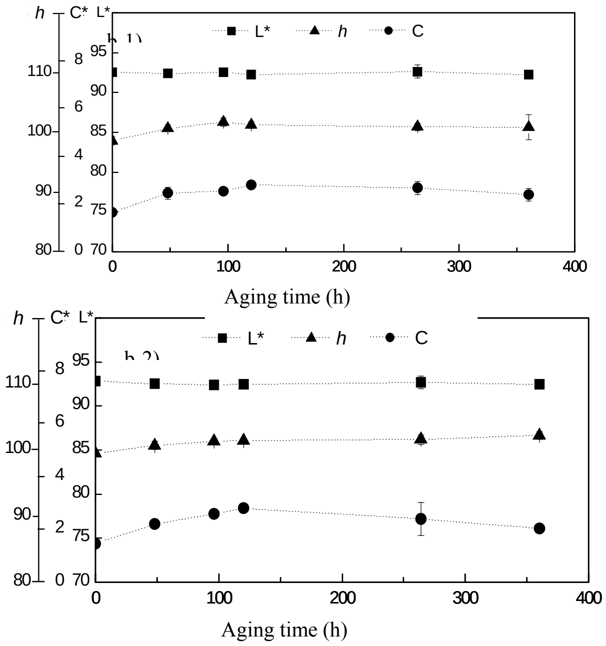
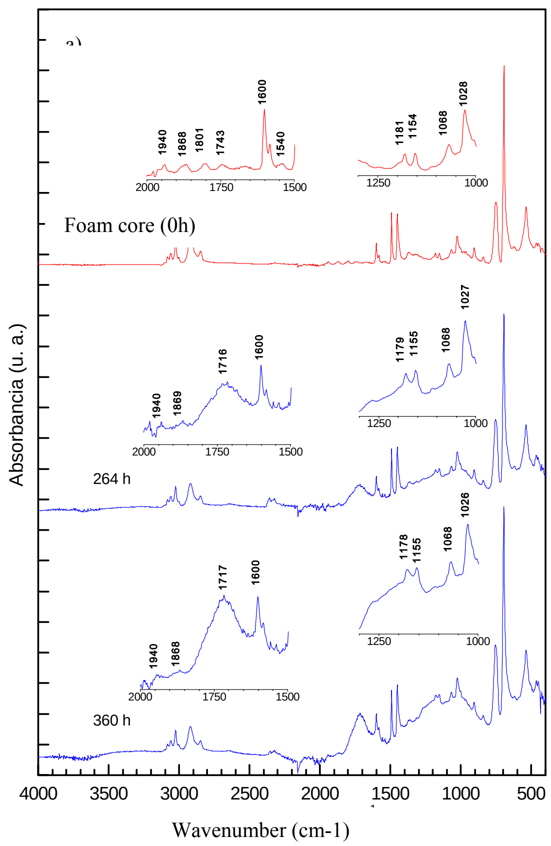
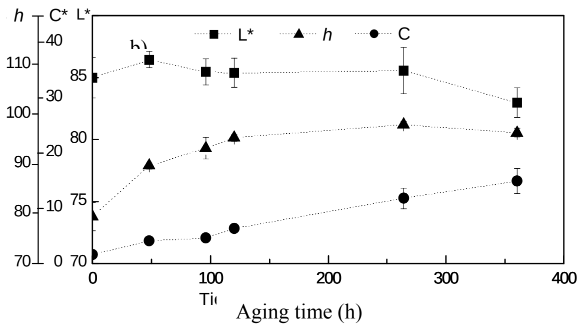


Fig 1. *Archival pocket (Secol)* (outside and inside layer). Evolution with photochemical aging a) ATR-FTIR spectra; b) Changes of lightness (L), chroma (C) and hue (h): outside (b-1) inside (b-2).





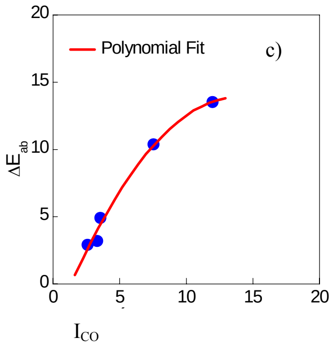


Fig. 2. *Foam core board:* foam core–poly(styrene). Photochemical aging evolution a) ATR-FTIR spectra; b) Changes of lightness (L), chroma (C) and hue (h); c) Relation ΔEab - I_{CO}

5. References

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