Contributions for the preservation of plastic negatives

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Abstract

Cellulose esters film-based negatives are known for their autocatalytic and irreversible decay. Over time, the ephemeral nature of these negatives became one of the most challenging issues for manufacturers, photographers, scientists, conservators, and overall caretakers that strive to foresee the decay of those composite materials and to develop preservation solutions.

The aim of this study is to introduce an analytical methodology that can inform the conservator not only about the nature of the film base but also about its condition in a non-invasive way. For this purpose, three hundred and sixty-one cellulose nitrate and cellulose acetate film-based negatives (1930s-1950s) from Portuguese institutions were selected. The selection of the cases studies relied on three main criteria: historical framework of the collection, film characteristics (type of support, format, producers/brands) and preservation condition. The selected negatives are representative of European and North American producers. The objects were studied using infrared and Raman microspectroscopies (μ-FTIR and μ-Raman), pH and hardness measurements, and Near infrared spectroscopy.

μ-FTIR analysis allowed to identify three types of film supports: cellulose nitrate, cellulose acetate and cellulose acetate butyrate. Based on the μ-FTIR analysis a correlation between molecular identification of the film base and notch codes was accomplished. For the set of negatives with cellulose acetate butyrate support no significant molecular changes were obtained, indicating that this type of negatives is considerably stable. Concerning cellulose nitrate and acetate-based negatives, μ-FTIR allowed to assess very different preservation conditions, ranging from Very Good to Severely degraded. A careful observation of the results obtained for cellulose nitrate-based negatives allowed concluding that negatives with spectral changes associated with severe degradation may have different degradation pathways according to thickness. Concerning cellulose acetate-based negatives, similar results were obtained. Moreover, the FTIR results enabled to identify a degradation trend associated with a film typology characterized by 'U' notch code and blue and brown anti-halation dyes.

Different plasticizers, namely camphor, phosphates and phthalates, were also identified by μ-FTIR and μ-Raman analysis.
pH and hardness measurements supported the spectral results obtained. It was confirmed that the de-esterification and chain-scission may be detected by their decrease. To confirm the chemical behaviour of cellulose nitrate-based negatives, an artificial ageing experiment (80^0C, 90% RH) was carried out, followed by the same analytical methodology. The results obtained for samples artificially aged support the findings obtained from the study of historical films.
These findings contribute for a review of the preservation strategies currently used, establishing a novel and non-invasive methodology which could provide accurate tools for the identification of early degradation stages of negatives with cellulose nitrate and cellulose acetate supports.

Keywords: cellulose esters, photographic negatives; condition assessment; hardness, preservation.