THE IDENTIFICATION OF PHOTOGRAPHIC DYES IN CULTURAL MATERIALS USING RAMAN SPECTROSCOPY

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Abstract: The role of film archivists is becoming increasingly important as the amount of film in archival collections continues to rise. The detection and identification of photographic dyes using non-destructive methods such as Raman spectroscopy is explored. Interference from fluorescence appears to be a major problem during the analysis procedure and initial results will be presented detailing progress to date.

Film archives all over the world own huge collections of color motion picture films. ScreenSound Australia, the Australian national screen and sound archive, for example, owns about 200,000 motion picture films of which 70,000 are in color. To preserve this important part of our cultural heritage, film archivists are confronted daily with the problem of the fading of the colors in these films. In a film, color arises from the selective absorption of the illuminating white light from the three colored layers composing the film. In the initial stage these layers are not colored but they contain colorless couplers that are converted to colored dyes of the azomethine family during the processing of the film.

Figure 1 shows a typical cross section of an unprocessed color print film. Whilst this basic structure has been slightly changed since the production of the first incorporated-color coupler films in the 1930s, the specific nature of the color couplers used, and therefore of the resulting dyes, has undergone major changes in the last 50 years. Apart from economic factors, the driving forces to modify the nature of the color couplers have been the need of improving the quality of the photographic product by selecting dyes that absorb only in a relatively narrow spectral range and the need to improve the stability of the dyes.

In the blue sensitive layer, yellow forming couplers are present and they are of the α-pivaloylacetanilide and α-benzoylacetanilide type. In the green sensitive layer, magenta forming couplers are present of the 5-pirazolinone-, indazolone-, pyrazolobenzimidazole- and pyrazolotriazole-type. Finally in the red sensitive layer, cyan forming couplers of the substituted phenol- or naphthol type are present. Groups can be attached to the couplers mainly to anchor the coupler in a certain layer, to modify the spectral absorption of the resulting dye and to improve the stability of the resulting dye.

Dye degradation can occur as a result of the exposure to light or, in the dark, as a result of heat, humidity or environmental pollutants. In this work, we are interested in the former mechanism of dye degradation and specifically in the acid hydrolysis of the azomethine dyes. Tuite [1] has shown that under acidic conditions the dissociation of the azomethine linkage of the dye takes place resulting in a colorless leuco dye.

This degradation pathway is interesting because it is connected to a widely spread type of degradation of motion picture films: the autocatalytic acidic hydrolysis of the cellulose triacetate

This drawing illustrates only the relative layer arrangement of the film and is not drawn to scale.
base which results in the production of acetic acid (therefore the common name “vinegar syndrome”) and in the rapid destruction of the film. Ram et al. [2] have shown that, although yellow dyes are more vulnerable, also magenta and cyan azomethine dyes are prone to acid hydrolysis degradation.

To better understand the mechanism of dark dye degradation and to be able to detect early dye fading in color motion picture films it is necessary to identify the dyes present in the emulsion and their degradation products. The techniques usually used for dye identification in photographic materials are gas or liquid chromatography coupled with mass spectroscopy. Raman spectroscopy offers the important advantage in that it is a non-destructive technique applicable to archival objects. Bristow et al. [3] have shown that the use of FT-Raman spectroscopy on solid phase concentrated samples allows the successful identification of the photographic dyes in effluent streams. In these types of measurement, the problem of the fluorescence signal arising from the dyes themselves, from the gelatin matrix, and from the cellulose acetate base, can interfere with the Raman peaks, this is somewhat circumvented by using an infrared laser source of 1064nm.

Preliminary investigations using a Renishaw 2000 Raman Microscope have shown that interference due to fluorescence in conventional collection mode can dominate the detection of the dyes even with an excitation laser wavelength of 785nm. This was established by analysing the edge area of a film where we know that the dyes are absent. So methods are required to discriminate against this component of the signal.

A technique dependent on the subtraction of “fixed pattern non-uniformity” and known as Subtracted Shifted Raman Spectroscopy or SSRS [4] has been previously applied to ancient printed manuscripts [5-7]. The basic idea comes from shifting the spectrum of a sample by a small amount of about 20 cm\(^{-1}\) by changing the angle of the diffraction grating in the spectrometer. This overcomes the noise limiting non-uniformity of adjacent pixels in a CCD detector that has been assessed at ±1% [4]. The two spectra are subtracted and the Raman peaks appear as derivative waveforms. Curve fitting is then applied and the original Raman spectrum is reconstituted without the fluorescence background. All sources of fluorescence are removed by this procedure because the fluorescence signals are usually much broader than Raman signals. However, care must be taken if broad Raman signals such as those emanating from various forms of elemental carbon are analysed but this is not generally the case when analysing photographic dyes.

Results will be presented that demonstrate the first application of this technique to photographic media.

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