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LES SCIENCES DE LA CONSERVATION DU PATRIMOINE ET LE DÉVELOPPEMENT DURABLE
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Using the different analytical techniques to study on the degradation of toned motion picture films

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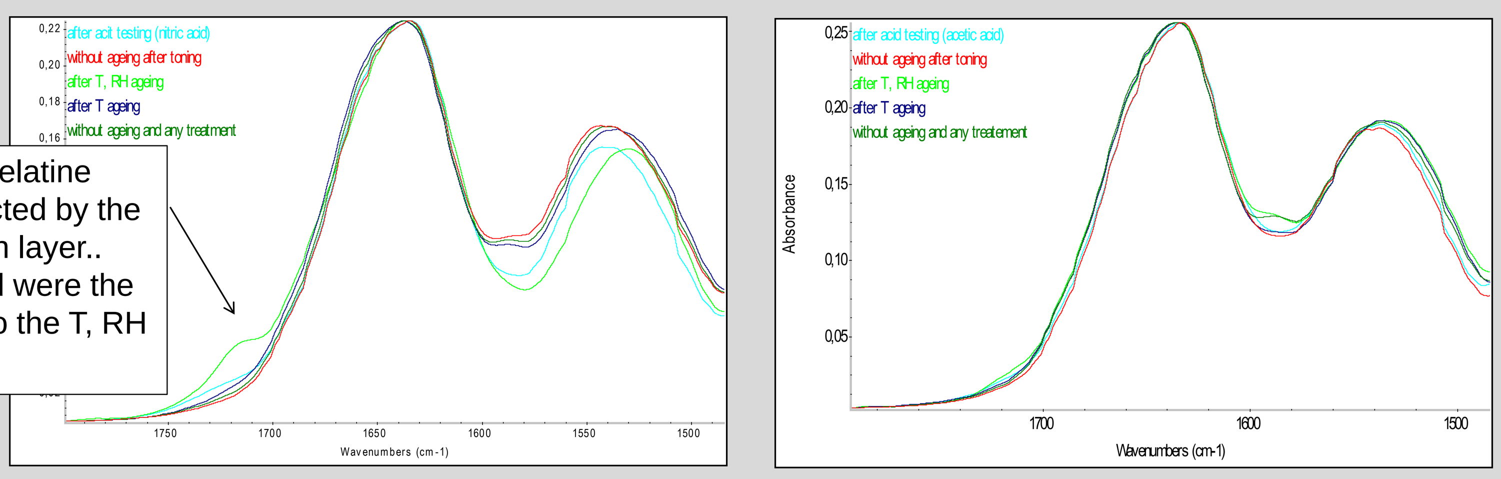
Introduction

This work presents some of the results of the investigation of degradation processes occurring during the ageing of toned motion picture films.

In the case of color motion picture films the unsuitability for projection can be caused by two kinds of degradation. One of them is the material destruction, brittleness of the film base or stickiness of the emulsion layer. The second kind of degradation includes color changes, which occur together with material degradation during the years of storage and as the effect of projections. The understanding of the original colors of the motion picture films is fundamental when they are duplicated.

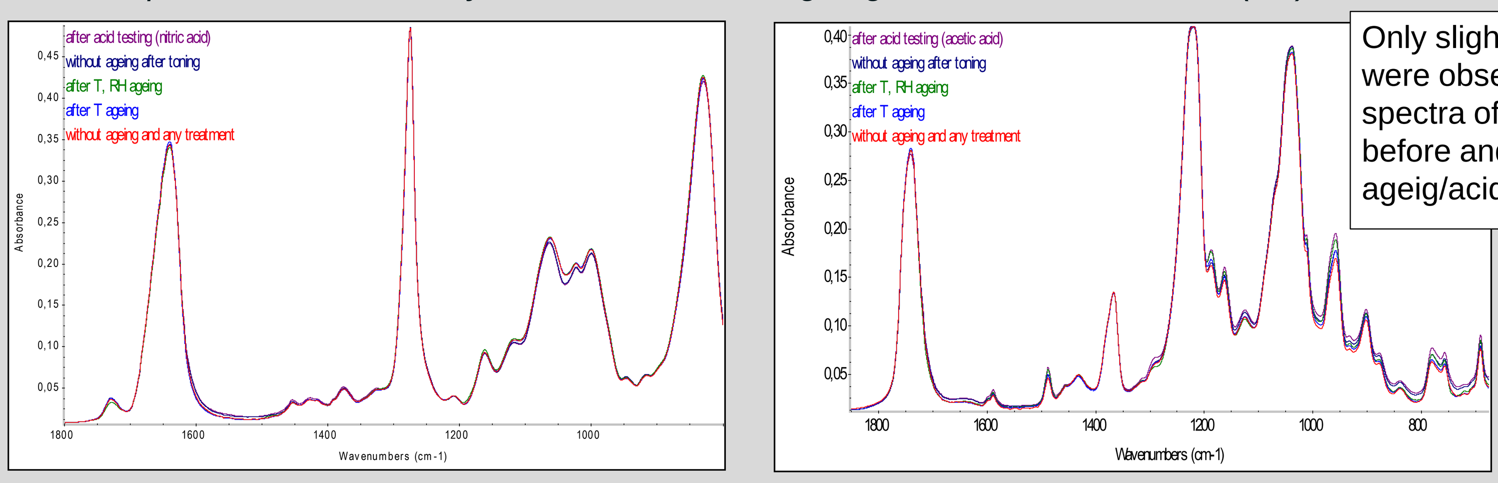
Samples of motion picture films toned by dye toning were prepared for the further analysis. The process of dyeing included mordating of the film, during which the metal silver was converted to the silver iodide, and dyeing of the film in the solutions of different basic dyes (methyl violet, malachite green, fuchsine, rhodamine B, safranine). Afterwards, the toned films were subjected to an accelerated ageing in the conditioning chamber with elevated temperature and high relative humidity, and to an acid vapor testing, which included an exposure of the films to the diluted acetic acid or nitric acid vapors.

The study of the degradation of the motion picture films was done by means of different analytical techniques, using UV/VIS, infrared and Raman spectroscopy. This complementary approach was used to relate the observed color changes with the changes in chemical composition of support and emulsion layer with color component.



Different degree of gelatine hydrolysis was detected by the study of the emulsion layer.. The most hydrolyzed were the samples subjected to the T, RH ageing.

Infrared spectra of emulsion layer before and after ageing/acid treatment: nitrate (left) and acetate (right) film.



Only slight differences were observed in the spectra of film bases before and after the ageig/acid treatment.

Infrared spectra of film bases before and after ageing/acid treatment: cellulose nitrate (left) and acetate (right).

Analytical techniques used

UV/VIS spectroscopy and color changes

Using the colorimetric measurements the color changes occurring during the artificial ageing were quantified. Measurements were done by colorimeter Datacolor Mercury (Datacolor) and the CIELab space were used for determining the L, a, b coordinates from which ΔL, Δa, Δb and total color diference ΔE were calculated.

Infrared spectroscopy

For the analysis FTIR microscope Nicolet iN10 (Thermo Scientific) in ATR mode (Ge crystal) was used. Measurements were performed using the fixed setting: resolution of 4 cm^{-1}, accumulation of 64 scans. By this technique changes in the composition of film base and emulsion layer were detected.

Raman spectroscopy

Raman spectra were collected on Raman microscope (Bruker) using the laser diode with the wavelength of 785 nm. This technique was used for the analysis of organic dyes in the emulsion layer. For the measurement samples were mordated in a non-complete way due to which some of the silver particles remain inside the emulsion layer. Enhancement of the signal by means of SERS (surface enhanced Raman spectroscopy) was noted. Analyses were done using a limited illumination extending at the same time the interval of the accumulation.

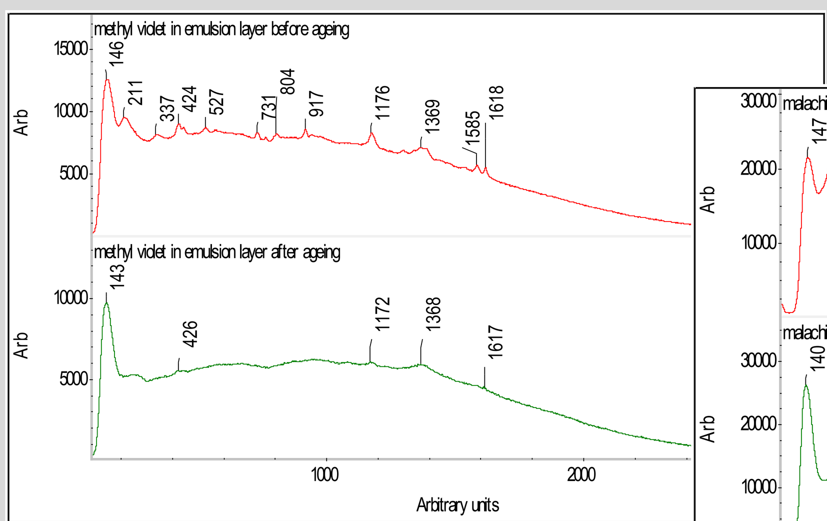
Accelerated ageing and acid vapor treatment

Type of ageing	Condition used	Simulates…
T ageing	T=80°C, RH<10%	unsuitable storage conditions
T, RH ageing	T=80°C, RH=60%	unsuitable storage conditions
acid vapor testing	acetic or nitric acid, conc. 30%	accumulation of degradation products from film bases

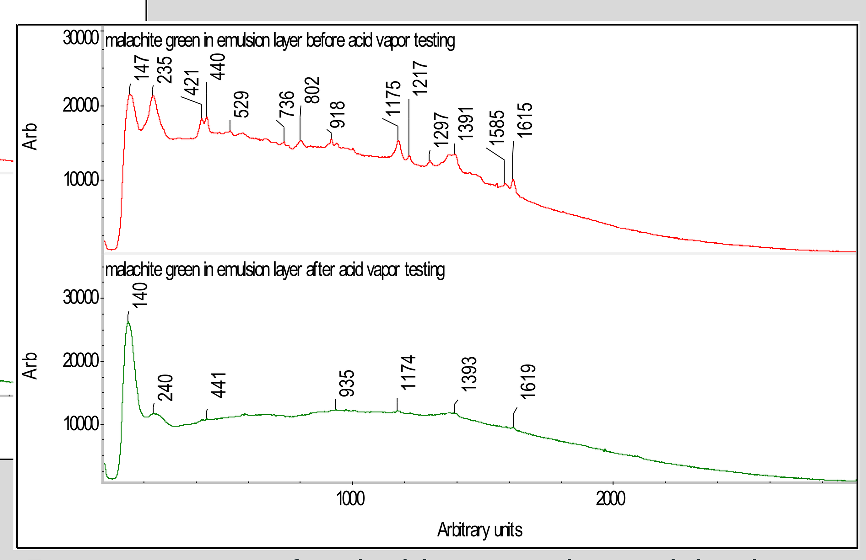
ΔE	acetic acid	nitric acid	T,RH	T
Malachite green	50,31	56,46	4,62	9,26
Methyl violet	8,13	35,37	5,34	6,05
Fuchsine	12,44	44,43	3,98	5,36
Rhodamine B	26,29	22,23	1,38	6,54
Safranine	6,35	22,20	4,70	6,52

Color changes differ whithin the ageing condition used. The most significant changes were observed in the samples treated by acid vapors, in particular the impact of nitric acid.

Figure 1: Total color diference ΔE of aged films as determined by UV/VIS spectrometry



Raman spectra of methyl violet in emulsion layer: methyl violet before (red) and after (green) acid treatment.



Raman spectra of malachite green in emulsion layer: methyl violet before (red) and after (green) acid treatment.

Raman spectroscopy could be useful for the identification of the dyes used for toning if the residual silver remains in the emulsion layer. After the acid treatment the silver particles became sensitive to the laser illumination and only the decrease in the dye concentration was observed.

Conclusions

During the ageing and acid vapor testing small changes in film bases and emulsion layers occurred. Color changes differ with the different kind of ageing. The most significant color changes were observed in the samples treated by acid vapors. The most hydrolyzed gelatine in emulsion layer was detected in the samples treated by T, RH ageing, which indicates that the color change of the film depends more likely on the possible accumulation of the acid vapors in the storage box. The use of Raman spectroscopy in this study was limited on the original dye identification and partial quantification.

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