Study of the degradation of an early synthetic dye, Crystal Violet

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ABSTRACT: The photo fading of crystal violet (CV), one of the earliest synthetic dyes and an ink component, is examined on different paper substrates (in the presence and absence of gum arabic as an example of ink additive) via HPLC-PDA, fiber optic reflectance spectroscopy (FORS), Xenotest and micro-fading-meter. The paper substrates chosen were pure cellulose paper, lignin containing paper and printing paper.

All samples were aged both with UV-Vis in a Xenotest and with Vis light with a micro-fading-meter [1]. In this way the effect of visible light exposure on the dye colour was taken into consideration in order to simulate actual indoor display conditions in which UV protection is applied.

The objective of the work is to fill the gap between model samples of CV on Whatman paper [2] and real objects (a drawing, a letter).

The final goal is to shed light on the discoloration of some drawings and letters by Van Gogh originally produced with a purple ink and showing at present either brownish discoloured areas or complete loss of colour.

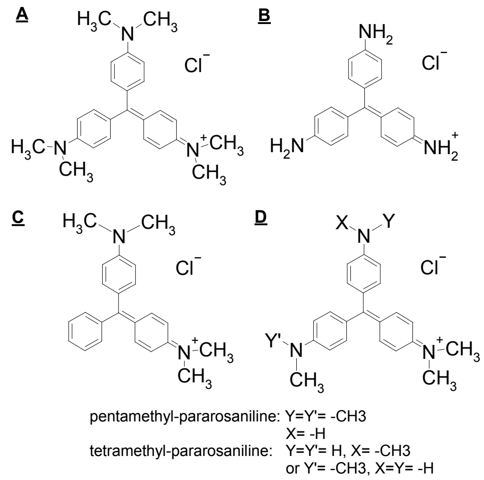

Figure 1: molecular structures for CV (A), pararosaniline (B), diamond green B (C) and penta or tetra-methyl-pararosaniline (D).

1. INTRODUCTION: Synthetic dyes have been used since XIX century as colouring matter in many inks. Triarylmethane dyes (also called aniline dyes) were among the first ones to be produced and marketed, Mauveine being the first synthetic aniline dye to be synthesized in 1856 by William Perkin. In particular, CV or hexamethyl pararosaniline (fig.1A) with its deep purple hue has had a wide diffusion for dyeing textiles, ball-point pens, as printing ink and on artists' palette as writing or drawing ink.

As many synthetic dyes, CV proved to be very light sensitive and the issue of discoloration of drawings and documents soon became evident.

As a prestigious example, some of Van Gogh's drawings and letters do show a purple ink; nonetheless discoloration to brown or in some cases complete fading of the ink strokes are affecting these precious works. Preliminary analysis of some of them has suggested the presence of CV or methyl violet (a mixture of CV, penta- and tetra-methyl pararosaniline) in the original ink.

In particular, the writing on a menu drawn and written by Van Gogh in 1886, still visible in 1958, was completely gone in 2001 (fig.2). This work shows some purple spots and FORS analysis performed on one of them detected the presence of CV or methyl violet.

For this reason the Van Gogh museum became concerned on the discoloration of triarylmethane dyes. This study and a previous one [2] are the result of a study on the photofading of CV carried out at the Netherlands Institute for Cultural Heritage (ICN, Amsterdam). The aims of the present study are the following:

- understanding the effect of light on the colour and chemical composition of CV on paper;
- finding out if it is possible to identify CV or methyl violet based inks from their degradation products present on discoloured documents;
- consequently, tracing the original colour of printings, writings or drawings.

After identifying degradation products of CV exposed to UV-Vis light on a model pure cellulose filter paper [2], more realistic paper samples were taken into account in order to both evaluate the behaviour of the dye on actual substrates and to probe the effect of different substrates on the degradation pathway.

The different substrates were chosen as follow:

- cotton linters paper as an example of high quality pure cellulose paper;
- lignin containing paper as an example of low quality paper;
- printing paper as an example of modern paper for digital printing.

In an attempt to meet more realistic experimental conditions also for the dyeing substance, every paper was dyed with CV both in the presence and absence of gum arabic as an example of one of the possible additives in an actual ink.

2. EXPERIMENTAL: *2.1 Degradation of CV in the presence and absence of gum arabic on different kinds of paper.*

Three kinds of paper (printing Staples, cotton linters and lignin paper) were dyed with an aqueous solution of CV (Acros, pure, certified) and then left to dry horizontally. Other three samples of the same kinds of paper were dyed with an aqueous solution of CV and gum arabic (Fluka).

Other three samples of the same kinds of paper were written with an aqueous solution of CV using a fountain pen.

As for the ageing with Xenotest (Alpha High Energy by Atlas®. filtered Xenon-Arc-lamp (UV-Vis light present);

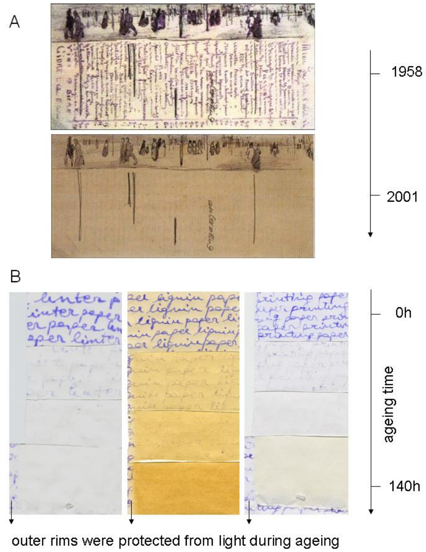

Figure 2: A. Menu drawn and written by Van Gogh in 1886 in Paris as it appeared in 1958 (top) and in 2001 (bottom). Van Gogh museum, Amsterdam. B. model samples written with CV on cotton linters, lignin and printing paper (from left to right) before ageing and after 7h, 14h and 140h in the xenotest (from topo to bottom).

105 Klux, T 50°C, 40 %RH.), samples were taken before and after different irradiation intervals and the dye was extracted from each sample with methanol (Fluka, for HPLC, gradient grade, ≥99.8% (GC)) at 70 °C for 10 minutes. Previous studies showed that the dyes and degradation products are stable under these conditions [2].

Samples of undyed paper (with and without gum arabic) were treated the same way and used as a reference.

As for micro-fading, same samples as before were exposed to Vis light and reflectance spectra were recorded before and during fading.

2.2 HPLC-PDA analysis: All extracted solutions were analysed via HPLC-PDA. All dyeing solutions used were also analysed.

For technical details on instrumentation and experimental conditions see [3].

2.3 FORS and micro-fading-meter analysis: FORS analysis were performed with a home-assembled equipment as the one described in [4].

The micro-fading-meter used is a modified version (by H. Neevel) of the one described in [1].

Reflectance spectra were collected in the range 380-800 nm.

Reflectance spectra for CV were recorded before and after exposure to UV light of a dyed disc of paper.

Colorimetric L*a*b* values were calculated using a software available online at www.brucelindbloom.com and selecting the D65 illuminator and the 10° Supplementary Standard Observer.

The colour change ΔE was calculated both for samples from the Xenotest and from micro-fading.

3. RESULTS : In a previous study [2] a series of degradation products for CV exposed to UV and UV-Vis light were identified both for the dye in aqueous solution and on model cellulose paper. Degradation was demonstrated to involve de-methylation (loss of $-CH_3$) and de-amination (loss of $-N(CH_3)_2$) reactions. Oxidation at the central carbon atom is considered likely to occur.

In this work, more realistic samples of cotton linters, lignin and printing paper dyed or written with CV were aged with Xenotest (fig.3) and the products formed were analysed with HPLC-PDA.

Figures 2B and 3 show the colour change during the Xenotest for all three kinds of paper, written or dyed with CV, without gum arabic (similar result were obtained with gum arabic as additive). Written samples (fig.2B) completely discoloured after the ageing, reproducing the phenomenon observed in the menu. As for dyed samples (fig.3), the colour change was significant for all three samples, and particularly for CV on lignin and printing paper. The protected areas did not fade, so one can conclude that temperature an RH do not affect the fading.

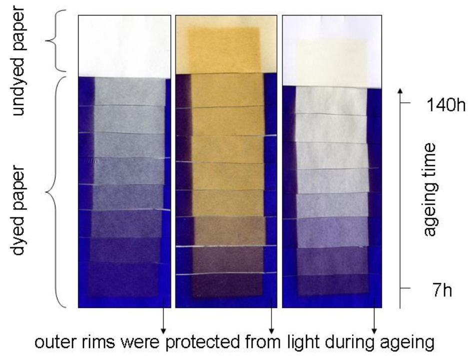

Figure 3: colour change during the Xenotest for cotton linters, lignin and printing paper (from left to right) dyed with CV. Reference samples of undyed paper after a 140h ageing are also shown on top.

Samples of undyed paper were also aged and a more or less strong yellowing was obtained for lignin and printing paper respectively. Cotton linters paper did not yellow.

Samples of cotton linters, lignin and printing paper dyed with CV and exposed to UV-Vis light for 140 hours were all extracted with methanol and the solutions were analysed with HPLC-PDA. As expected, cotton linters paper showed the same chromatograms as model Whatman paper previously analysed, demonstrating that exactly the same degradation products are formed [2].

Interestingly, chromatograms for CV on printing and lignin paper are also very similar to the one for Whatman paper except for few differences (the most interesting being the formation on printing paper of a diamond green-like compound different from the ones found on Whatman paper). The same considerations can be made for the samples containing gum arabic.

A plot of the relative peak area (proportional to the relative concentration) for CV as a function of ageing time in the xenotest is reported in fig.4 for all three kinds of paper both in the presence and absence of gum arabic.

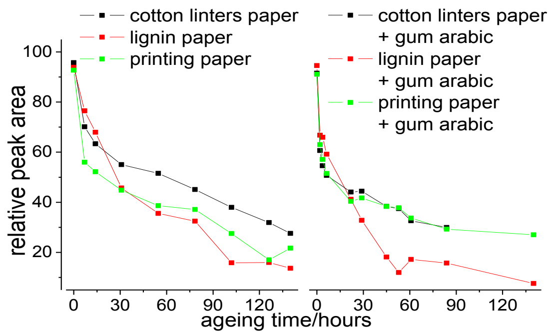

Figure 4: relative peak area for CV on different papers during ageing in the xenotest.

A reproducible trend was obtained both in the presence and absence of gum arabic: during the first hours of ageing, consumption of CV on lignin paper was always slower than on cotton linters and printing paper; but at the end of the ageing, degradation of CV was more pronounced on lignin paper. Interestingly, fading CV on a pre-yellowed sample of lignin paper one obtains again a curve shape (not shown) similar to the ones for cotton linters and printing paper. This demonstrates that lignin does play a role in CV degradation.

The same samples were analysed with FORS and the colour change ΔE were calculated from the L*a*b* values measured. A plot of ΔE as a function of ageing time in the Xenotest is reported in fig.5.

As for the samples without gum arabic, there is a consistency with the result of the HPLC analysis: the smallest colour change was measured for cotton linters paper. As for lignin and printing paper, despite the very different colours obtained after 140 h in the xenotes (brown for the former and with-bluish for the latter), the colour change trends were similar.

As for lignin paper, the strong colour change can be explained both with a higher reactivity of CV on lignin paper and with a stronger yellowing of the paper substrate itself (fig.3).

As for printing paper, an explanation has still to be found.

In the presence of gum arabic the discoloration on cotton linters paper slightly increased while on lignin and printing papers it appreciably decreased. In no case a browning of the ink was observed: consequently for now gum arabic can not be considered responsible for the brown discoloration of some of Van Gogh's works and further studies are necessary.

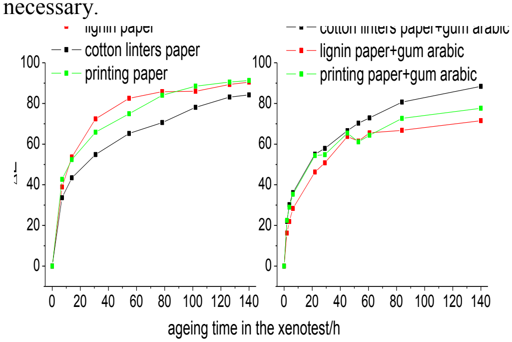

Figure 5: ΔE for CV on different papers during ageing in the xenotest.

Eventually, a micro-invasive artificial ageing of the samples was performed via micro-fading-meter selecting only the visible portion of the light source and the colour change was calculated (fig.6).

Interestingly, a discoloration of CV was observed even in the absence of UV radiation. This observation, of particular importance when dealing with objects in display even if indoors, highlights the need of a better understanding of the photo-fading of drawings, writings or printings containing triarylmethane dyes.

As for the samples without gum arabic in the absence of UV, discoloration on lignin paper seems to be slower than for printing paper. This is probably due to a smaller yellowing of lignin paper in the absence of UV. Moreover, in the presence of gum arabic the same behavior observed in fig.5 is reproduced in fig.6: discoloration for lignin and printing paper appreciably decreased.

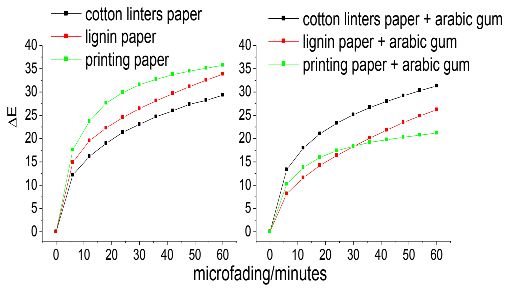

Figure 6: ΔE for CV on different papers during micro-fading.

Summarizing, for cotton linters and printing paper the results of HPLC-PDA analysis are consistent with the colorimetric measurements: the higher the CV consumption the bigger colour change and vice versa. On lignin paper, although CV consumption was slightly bigger in the presence of gum arabic, the colour change was smaller.

Although the composition for the inks used by Van Gogh is not known yet, since the presence of an additive proved to play a role in determining the colour change of the samples, a more comprehensive evaluation of the possible additives present in Van Gogh's inks would be necessary to shed light on the different kinds of discoloration found on Van Gogh's drawings and letters.

4. CONCLUSION: Discoloration of crystal violet exposed to UV-Vis and Vis light was studied on cotton linters, lignin and printing paper with HPLC-PDA, Xenotest, FORS and micro-fading-meter.

The same degradation products formed on a model sample of Whatman filter paper were obtained on all three kinds of papers studied. In addition, on printing paper a new diamond green-like compound was detected.

Despite the consistency in the degradation products formed, different degradation rates were observed on different paper substrates. On the long term, lightfastness of CV on lignin paper and cotton linters paper seems to be the worst and the best respectively.

The colour change during ageing was measured with FORS and micro-fading-meter for all samples: it was demonstrated that the spectral range of the light source and the presence of an ink additive as gum arabic play a role in the colour change. In particular, it was obtained a strong discoloration of CV also with only Vis light. Moreover, an additive such as gum arabic proved to influence the colour change differently according to the different paper substrate, underlining the importance of studying more realistic composite samples where the interaction of different components can be taken into account.

To conclude, the complete loss of readability occurred in the case of the menu by Van Gogh may be well explained with a complete fading of a CV-based ink. On the other hand, the browning of some originally purple drawings can not be due to the presence of gum arabic in the ink used and further study is required.

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