Control of the colour evolution with time of a Luca Signorelli painting

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ABSTRACT
An oil panel painted by Luca Signorelli in the early years of XVI century was monitored non-invasively over a period of several years. Colour changes occurring in the painting were measured during conservation (before and after removal of old varnish and after the application of new varnish) and then during the course of display to the public. The effects observed are attributed mainly to the varnish layer. The results are used to identify likely sources of risk for the works of art on display that should be controlled.

1. INTRODUCTION
Light is one of the most powerful parameters in altering colour and so causing irreversible changes in works of art[1]. Indeed, it is by now widely recognised that several photo-induced deterioration mechanisms are enhanced, or accelerated through a co-operative action of the light with different physico-chemical factors (temperature, relative humidity, pollutants)[2,3]. Therefore, for conservation it is important to monitor possible colour changes of objects on display. Moreover, when a painting is conserved, it is as important to follow the evolution of the colour during the cleaning process, as it is to check the stability of the colour after the conservation. As a case study, the Predella by Luca Signorelli, an oil panel painted in the early years of XVI century, is considered. The painting, on display at the Uffizi Gallery in Florence, was initially monitored over a five-year period (1990 – 1995). In this period the painting was on public display in the Gallery's Leonardo room. In spite of the environmental control inside the room, significant colour changes were measured over this five years period[4]. Towards the end of the 20th century, the Uffizi Gallery management decided to restore the Signorelli's paintings belonging to the Gallery. This presented an opportunity for further investigations on this painting. Accordingly, two more measurements campaigns *in situ* were made: a) during the cleaning work in the conservator atelier (2000-2001), and b) during the new period of display to the public (2001-2004) in the museum, after the restoration and re-varnishing.

2. METHOD
The colour was measured repeatedly and non-invasively by means of Fibre Optics Reflectance Spectroscopy (FORS)[5] over several tens of selected areas (about 0.1 cm^2)

Figure 1: The Signorelli's Predella after re-varnishing. The investigated points are marked.

by means of a Zeiss, mod. MCS501, spectrophotometer. During the stage (a) of the investigation 62 points were investigated (see Figure 1). For stage (b), time constraints imposed by the fact that the painting was on display in a public gallery meant that the number of measurement points had to be reduced. As such, a subset of 23 points that nevertheless covered the entire palette was selected for this phase. For each point the measurement was repeated three times and the average reflectance spectrum was evaluated. A specially designed "Y shaped" probe head (manufactured in house at IFAC), with a measurement configuration 45°/0°/45° was used. The probe uses two fibre bundles (connected to the source) at 45° from the surface of the sample for incident light and a fibre bundle

(connected to the detector) normal to the surface to collect light diffused by the sample [6]. This configuration provides a highly homogeneous level of illumination of the surface of the sample under investigation and at the same time avoids the return of specular reflected light to the detector. This requirement is particularly pressing, when glossy or partially glossy surfaces, like a re-varnished painting, are investigated.
The selected points were measured at $t=t_0$ (immediately after re-varnishing with natural mastic from Chios), at $t=t_1$ (after 18 months) and at $t=t_2$ (after 30 months). Particular care was paid in relocating the areas of the painting previously analysed [7], by using a mask for the repositioning the probe.
The colour variations in time for each point measured were estimated using CIELAB 76 (ΔE) and CIEDE2000 (ΔE_{00}) colour systems[8,9]. Although the CIELAB 76 colour system is known not to be particularly well correlated to small-perceived colour variations, it was used to allow straightforward comparison of the results with other historical published data.
Moreover, an estimate of the global spectral changes with time was also attempted as follows. At two different times (for instance t_0, t_1) six reflectance spectra are available for each point (three at t_0 and three at t_1), from which nine values of the sum of the square differences over all the wavelengths in the range 400 nm – 700 nm can be evaluated. Then, the mean value was calculated together with the percentage error. The average Δ_i (i =1,2) of the above mean values extended to all the points investigated can be assumed, in the present case, as a good measure of the alteration of the painted/varnished layer.

3. RESULTS AND DISCUSSION

By an inspection of the reflectance spectra related to the different points of the Predella, a tentative identification of the used pigments was made. Azurite, cinnabar, ochre and earths, lead white and a copper-based green pigment were identified. All the above pigments have been reported in the literature to have a good light fastness, at least in oil binding medium, much higher than that of the upper varnish, which can therefore be assumed to provide the main contribution to the colour changes. Results from measurements made during and after restoration confirm such an interpretation. In fact, the removal of the old varnish layer in the stage (a) is accompanied by strong colour variation, especially in the parameters b* (Figure 2) and L* as predicted by theoretical analysis[10].

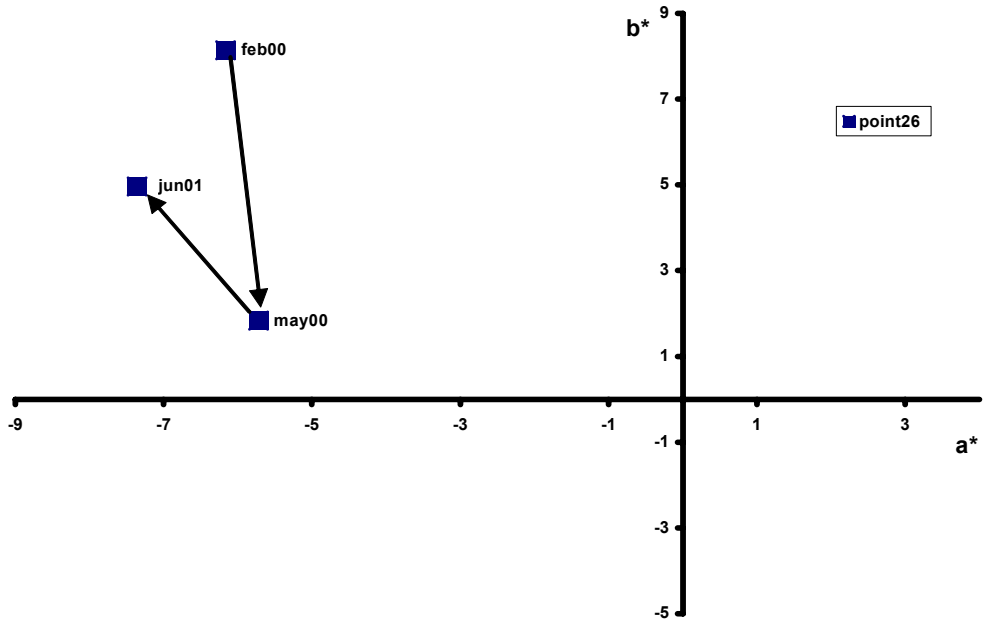

Figure 2: Movement in the (a*, b*) plane of the representative point of one of the investigated areas (blue mountain in the background). feb00: before restoration; may00: after varnish removal; jun01: after new varnishing.

Successively (stage (b)), after re-varnishing, the colour of the painting was monitored when it was exposed again in the Gallery (June 2001). The checks were made after 18 months (January 2003) and 30 months (January 2004). The colour variations, though limited (Figure 3), show a constant increasing trend (Figure 4). Only one of the points (number 33) shows an anomalous large colour change. Considering that the point 33 corresponds to a *chiaroscuro* area, small inaccuracies in repositioning could be responsible of such an anomalous result. Quite interestingly, colour variations were found to be larger for the second (shorter) period (January 2004 - January 2003) than for the initial (longer) period (January 2003 – June 2001).

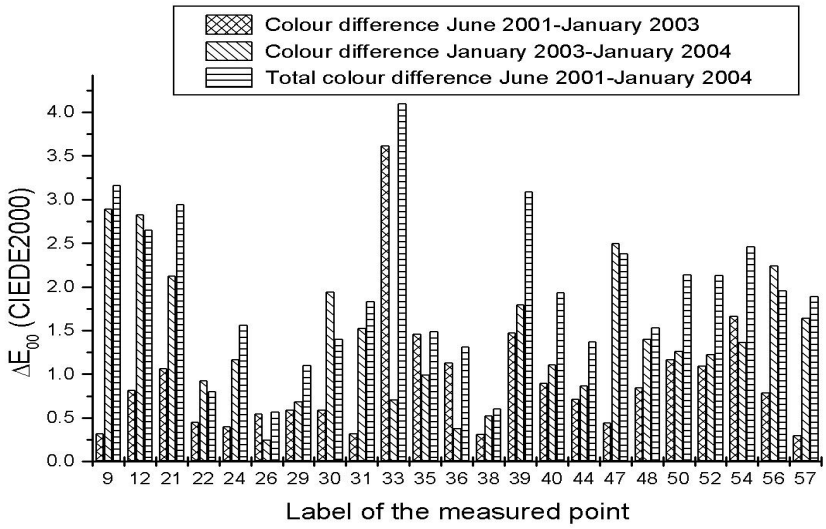

Figure 3: Colour change according to CIEDE2000 formulas for the selected 23 points during the period of exhibit to the public.

As regards the different contributions to the colour change, lightness plays a prominent role: the general trend is towards an increase of L*, even if the situation was not so clear in the period January 2003 – June 2001. Probably, variation of the varnish refraction index with time together with some surface modification due to the loss of the varnish solvent and natural ageing could account for the observed behaviour.

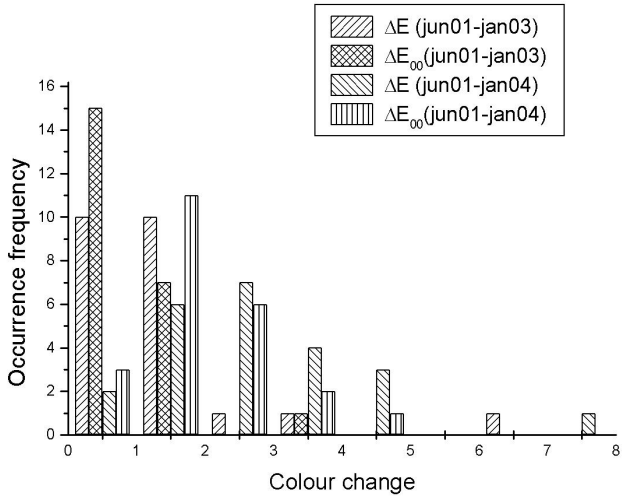

Figure 4: Global colour change for the period of exhibit to the public (June 2001-January 2004) evaluated according to CIELAB76 and CIEDE2000.

To confirm the colorimetric results, the global spectral changes of the painting were evaluated by the method described above. A statistically significant positive trend with time (Δ_1 = 82.6 a.u., mean percentage error = 17%; Δ_2 = 157.5 a.u., mean percentage error = 18%) was found, which compares well with the measured colour change ($\Delta E_{00(jan03\text{-}jun01)}$ = 0.91±0.15; $\Delta E_{00(jan04\text{-}jun01)}$=1.93±0.18). Of course, the above figures have only an indicative meaning, because spectral changes (and, accordingly, colour) depend on the spectral features of each pigment as well as the extent of surface levelling by the varnish.[10,11]

4. CONCLUSIONS

In spite of the very fact that the Predella is stored in one of the most important Galleries in the world, where the microenvironment is monitored and controlled, non-negligible colour variations are measured even after relatively short periods of exhibit. Though the observed effects can be attributed, at least partially, to some curing of the varnish layer, the present results, together with the ones of our previous work[4], demonstrate the need to reconsider the chemical and physical factors that are possible sources of risk for the works of art on display.

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