Following the Light: Use of Multimodal Imaging and Fiber Optic Spectroscopy to Evaluate Aging in Daylight Fluorescent Artists' Pigments

Fiona Beckett [1] , Aaron Shugar ; Garman Art Conservation Department, Buffalo State College

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Introduction

Daylight fluorescent artists' colors (used by artists such as Frank Stella, Peter Halley, Andy Warhol, and James Rosenquist; Fig. 1) have been well established as fugitive. Upon exposure to light, these vibrant colors can fade and exhibit color shifts. Artwork containing these fluorescent colorants presents complex challenges for art conservators faced with conserving these inherently problematic materials.

Current study: Nine fluorescent colorants from Kremer Pigmente (Figs. 2, 3) were tested to quantify the visual and photographic observations of fading and color changes. Multimodal imaging was executed to visually assess the pigments before and after aging, and fiber optic spectroscopy (ultraviolet and visible light sources) was used to measure the spectral shifts before and after exposure to light.

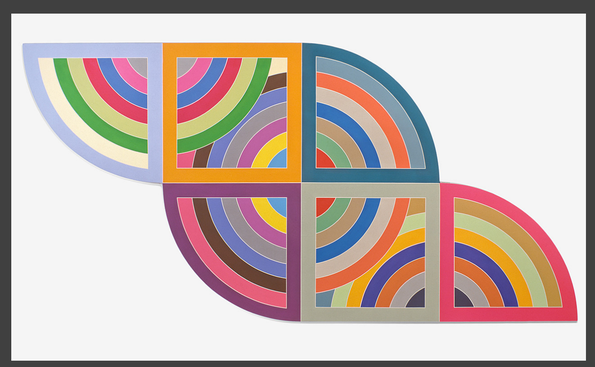


Figure 1: Frank Stella's 'Harran II', 1967. Polymer and fluorescent polymer paint on canvas, 120 x 240 inches. Solomon R. Guggenheim Museum

Figure 2: Sample preparation of the Kremer Fluorescent Orange (**left**) and all nine pigments (**right**) in Golden Acrylic Matte Medium prepared on white ceramic tiles.

Materials and Analysis

Materials:
Kremer Pigments (Fig. 3) Brick Red, Flame Red, Orange Golden Orange, Lemon, Yellow, Green, Blue, Violet, White; white ceramic tiles; Golden Acrylic Medium, aluminum foil, scotch tape.

Analytical Method for Fading:
Light exposure: Q-Sun xenon test chamber, ASTM D4303-06 Test Method D- 0.9W/(m^2 nm) at 420 nm; 36–44% RH, 60–65ºC, correlation to museum conditions is ~4 years.

Fiber Optic Spectroscopy Setup (Table 1):

Method 1: FORS Full Spectrum - Excitation Source, Geometry	Method 2: FOS UV-Induced Fluorescence - Excitation Source, Geometry	Capture and Geometry
Ocean Insights HL-2000-HP-FSHA tungsten halogen light source Vis–NIR (400–2400 nm) fiber optic cable, 90º angle	Ocean Insight LSM power source 365 nm LED UV–Vis–NIR (360–2400 nm) fiber optic with BG-38 filter, 90º angle, run between 2 mA and 5 mA	Ocean Optics SD-2000 Fiber Optic Spectrometer using a Vis–NIR fiber optic cable, 45º angle

Figure 3: Kremer fluorescent pigments in powder form, as imaged in normal illumination against a whitebox.

Multi Modal Imaging Setup (Table 2):

Technique (modified Nikon D810 UV-Vis-IR DSLR)	Illumination/Excitation Source	Filters on Apochromatic 60mm Lens
Normal (NORM)	Profoto D1 500 W electronic flash, 25° angle, both sides	X-Nite CC1
Ultraviolet-induced visible fluorescence (UVA–VIS)	UV Systems SuperBright UVA, peak 368 nm, 45° angle, both sides	Kodak 2E + PECA 918 + X-Nite CC1
Reflected ultraviolet (RUVA)	UV Systems SuperBright UVA, peak 368 nm, 45° angle, both sides	B+W 403 and X-Nite CC1
Reflected infrared (RIR)	Profoto D1 500 W electronic flash, 25° angle, both sides	X-Nite 715, X-Nite 850, and X-Nite 1000
Infrared luminescence (IRLUM)	1 Powersmith 50 W LED + Schott BG38 filter (6 mm-thick), axial position to subject	X-Nite 715, X-Nite 850, and X-Nite 1000

Results

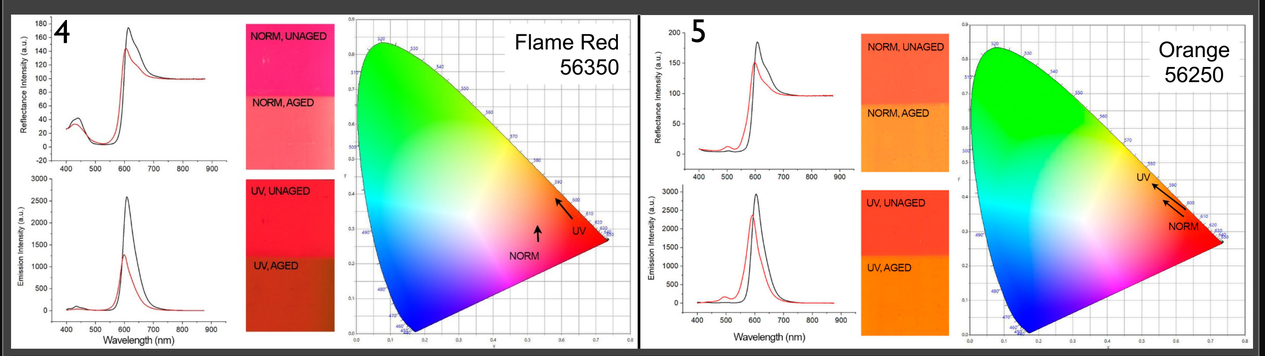
Fiber Optic Spectroscopy:

All pigments except White displayed a shift in their primary peak wavelength position under both methods of illumination (tables 3,4; Figs. 5-9). Typically, there was a blue shift and a reduction in intensity in the primary peak after fading, except for the Blue under full-spectrum illumination which had a red shift in the primary peak (+14 nm). The peak shift was less than 20nm (except for White and Violet), with significant spectral alteration. The largest spectral shift occurred in the Violet with the smallest shift occurring in the Green.

Fluorescent Colorant	Maximum Intensity in a.u. (Unaged, Aged)	Percent Difference (%)	Highest Peak (nm) (Unaged, Aged)	Total Shift in nm
Brick Red 56300	170 147	− 13.53	619 608	−9
Flame Red 56350	174 144	−17.24	613 604	−9
Orange 56250	188 151	−19.68	608 598	−10
Golden Orange 56200	182 146	−19.78	596 585	−11
Lemon Yellow 56150	159 137	−13.84	524 513	−11
Green 56100	121 107	−11.57	517 514	−3
Blue 56050	83 57	−31.33	454 468	14
Violet 56450	87 123	13.89	652 612	−40
White 56000	123 123	0	443 443	0

Fluorescent Colorant (λexc. = 365 nm)	Maximum Intensity in a.u. (Unaged, Aged)	Percent Difference (%)	~Highest Peak (nm) (Unaged, Aged)	Total Shift in nm
Brick Red 56300	2850 1626	− 42.95	615 607	−8
Flame Red 56350	2592 1275	−50.81	608 599	−9
Orange 56250	3049 2372	−22.20	604 591	−13
Golden Orange 56200	3788 3342	−11.77	591 573	−18
Lemon Yellow 56150 Aged (3 mA *)	3620 2926	−19.17	520 501	−19
Green 56100	806 1991	147.02	516 511	−5
Blue 56050 aged (3 mA *)	3819 104	−97.28	453 443	−10
Violet 56450	242 423	74.79	636 608	−28
White 56000 aged (2 mA *)	3832 3832	0	441 441	0

Tables 3 and 4: Summary of Fiber Optic Spectroscopy results (LEFT Table - full-spectrum illumination, RIGHT - emission results (exc. = 365 nm)) for each pigment sample (unaged and aged): maximum intensity, percent difference (in a.u., arbitrary units), highest peak, and total shift of the highest peak.



Figures 4 – 9: For each colorant: (**Left**) Spectra of Kremer colorant unaged (black line) and aged (red line) showing a visible-induced spectral shift and UV-induced (λ exc. = 365 nm) spectral shift. (**Center**) Corresponding images of the samples realized using an RGB imaging system. (**Right**) CIE 1931 (x, y) color space chromaticity diagram detailing the visual color change shift indicated by the direction of arrows.

Light Exposure:

Exposure indicated a lightfastness equivalent to ISO BWS 2 or lower (poor / not lightfast) for all colorants except White.

Figure 10: Sample of Kremer Fluorescent Orange after aging the right side of the sample.

Multi Modal Imaging:

(Figs. 10-12)
NORM: perceptible fading and loss of fluorescence observed in all aged samples except for the White.

UV-VIS: upon aging, Brick Red, Flame Red, Orange, Golden Orange, Lemon Yellow, and Blue exhibited decreased fluorescence. Blue exhibited dramatic decrease in fluorescence. Green and Violet appeared brighter after aging, likely due to preferential fading of one colorant.

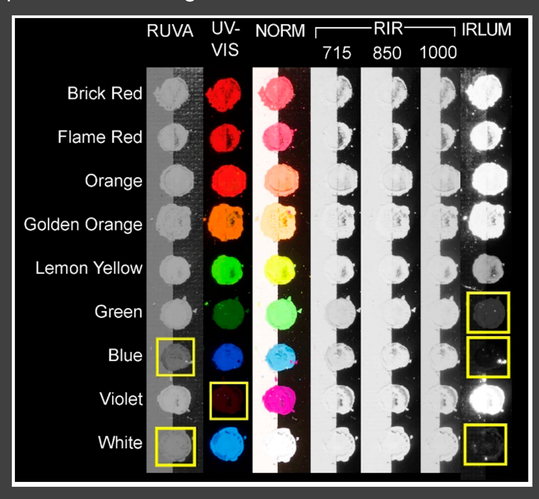


Figure 11: Kremer dry pigments (**unaged**) with no binder arranged by imaging technique (including filter cut-off in nm for RIR and IRLUM) and pigment color. Significant differences in spectral response captured by the camera indicated by yellow rectangles.

RUVA : Orange, Golden Orange, Lemon Yellow, and Green exhibited less reflected UVA upon aging. Blue exhibited an increase in reflectance upon aging.

RIR: All pigments had similar reflected infrared reflectance**.** At 715 nm, slight absorption was noted in Green and Blue samples, possibly related to the inclusion of phthalo pigments in the composition.

IRLUM: Green, Blue, and White exhibited very weak luminescence. Lemon Yellow exhibited weak luminescence. Brick Red, Flame Red, Orange, Golden Orange, Lemon Yellow, and Violet exhibited strong infrared luminescence, with Violet exhibiting the strongest.

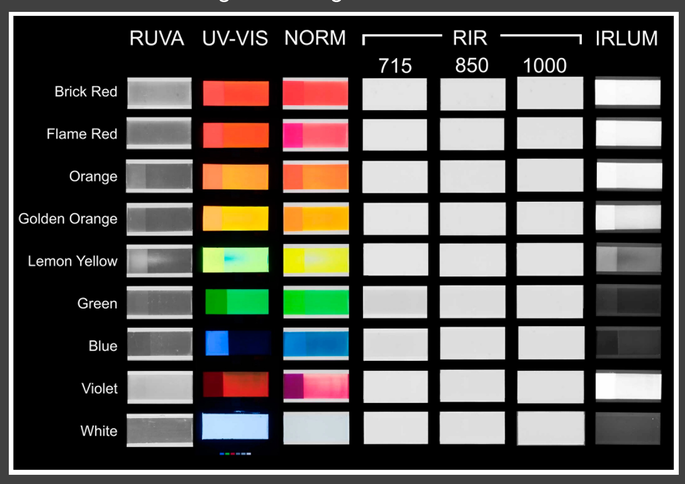


Figure 12: Imaging results showing tiles with fluorescent pigments arranged by imaging technique and by color (each tile consists of the unaged section on the left and the aged section on the right).

Conservation Implications

MMI and fiber optic spectroscopy results highlight the problems in considering conservation documentation and treatment. Paint film thickness and concentration of fluorescent colorants can affect the resulting reflectance, particularly those with several dyes. Documenting inpainting in fluorescent artwork is problematic as fluorescent colorants are necessary to achieve a match (Figs. 13-14). Fiber optic spectroscopy analysis combined with CIE diagrams provide indications as to the direction of fading and potential future color shift. Artists combining fluorescent paints with non-fluorescing artists' materials will invariably cause changes in color upon fading and in spectral response.

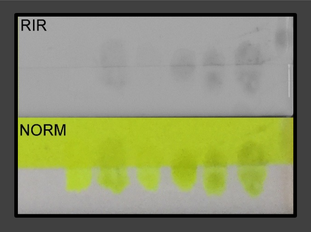


Figure 13: Inpainting test using carbon black in Aquazol binder over the top of Kremer fluorescent Lemon Yellow (RIR (upper) and NORM (lower)).

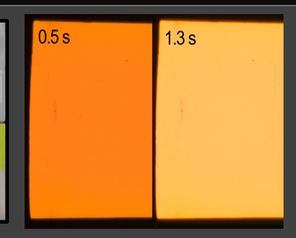


Figure 14: UV-induced visible fluorescence images of the same sample of Golden Orange with the only difference being the exposure time (0.5 s left; 1.3 s right).

Conclusions:

The fiber optic spectroscopy results provide possible ways to predict the direction of the color shift as the pigments fade, and to quantify the results obtained by imaging. Regardless of the exposure time adjustments required for imaging, fiber optic spectroscopy clearly determined the characteristic spectral peak changes that occurred.

Plotting the resulting spectra on a CIE 1931 (x, y) color space chromaticity diagram suggests the potential overall color change due to fading. MMI identified the absorption and reflectance of the colorants in the regions of the spectrum from RUVA, UV–Vis, NORM, RIR, and IRLUM. Particularly useful are the results observed using RIR and IRLUM.

This study provides unique spectral and imaging information that serves to better the understanding of fluorescent materials used in artwork, and highlights the difficulties related to documentation and preservation. It serves to inform conservation practices and reveals the need for continued future study of fluorescent artists' materials.

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Contact: becketft@buffalostate.edu

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