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EFFECTS OF DIFFERENT BINDERS ON TECHNICAL PHOTOGRAPHY AND INFRARED REFLECTOGRAPHY OF 54 HISTORICAL PIGMENTS

Antonino COSENTINO*

"Cultural Heritage Science Open Source" chsopensource.org
Piazza Cantarella 11, Aci Sant'Antonio, 95025, Italy

Abstract

Technical Photography (TP) is the collection of broadband spectral images in the range 360 - 1100 nm collected with a modified digital camera: visible (VIS), ultraviolet fluorescence (UVF), reflected ultraviolet (UVR), infrared (IR), infrared fluorescence (IRF) and infrared false color (IRFC). An InGaAs camera is sensitive to the 900-1700 nm range and provides infrared reflectography (IRR) images. It was previously shown that all these techniques used together allow a tentative identification of pigments laid with gum arabic. While the identification must be confirmed with analytical instruments, this flowchart method allows a fast and low-cost preliminary examination of polychrome works of art. This paper discusses the effects that other binders (egg tempera, linseed oil and fresco) can have on technical photos and on infrared reflectography images of 54 historical pigments. It is shown that only the UVF photos are considerably affected by these binders. The strong fluorescence emission of egg tempera and linseed oil dominate the UVF photos while the binders do not consistently affect the other technical photos, IR, IRF, IRFC and IRR. This study confirmed the validity of this comparative method for the tentative identification of pigments laid with the most common binders used on works of art.

Keywords: *Technical photography; Pigments identification; Infrared photography; Ultraviolet photography; Ultraviolet reflected photography; Infrared false color; Infrared fluorescence; IR; IRF; UVF; UVR; IRFC*

Introduction

Conservators and art historians need deep understanding of the materials, in particular pigments, and painting techniques used on works of art in order to select the proper conservation procedure and to reconstruct artists' workshop practices. Non-invasive examination methods are preferred since sampling is often forbidden.

Technical photography (TP) [1-5] represents a collection of broadband spectral images realized with a modified full spectrum digital camera, and using different lighting sources and filters in order to acquire images useful for art diagnostics. The seven TP methods presented in this study are: VIS (photography), UVF (Ultraviolet Fluorescence) [6], UVF254 (Ultraviolet Fluorescence with UV source 254 nm), UVR (Reflected Ultraviolet) [7], IR (Infrared) [8] IRFC (Infrared False Color) [9, 10] and IRF (Infrared Fluorescence) [11-13].

* Corresponding author: antoninocose@gmail.com

These TP techniques and infrared reflectography (IRR) [14-16] have been proposed as a comparative flowchart method for the tentative and non-invasive identification of pigments laid with gum arabic [17]. It was shown that the method is particularly effective on paints made of just one layer of pure pigment and that it can selectively discriminate some of the 54 pigments analyzed. This flowchart method doesn't provide conclusive pigments identification for two main reasons: pigments are often mixed and overlapped in layers (glazes) but the imaging methods are likely to succeed when applied on works of art painted with of simple mixtures and not layered paint such as miniatures and prints. While the results provided by the imaging methods must always be confirmed using analytical methodologies, nevertheless, this method plays a fundamental role in art examination because it allows the rapid and relatively low-cost preliminary examination of large areas of the art works. This simplified approach has the benefit of being accessible and easy to implement by professionals in the art conservation and examination field.

This paper broadens the scope of that previous study discussing the same flowchart method on the same collection of 54 historical pigments which have been laid also with egg tempera, linseed oil and fresco. It was necessary to assess the effects that these binders could have on technical photos and in particular on UVF since the two organic binders are strongly fluorescent. It was also necessary to evaluate if the infrared fluorescence emission of cadmium based pigments and Egyptian blue could be inhibited by the binders and if the UVR image could still distinguish the white pigments thanks to their absorbance in the UV region. IR and IRR images were also examined to assess any relevant change in the infrared absorbance due to the binder.

Experimental

A collection of swatches of 54 historical pigments (Table 1) has been prepared on 3 boards, hereafter called pigments checkers, using the 3 most common binders in art: gum arabic, egg tempera and linseed oil. Both gum arabic and linseed oil are commercialized by Winsor & Newton (Product Codes, respectively, 884955017708 and 884955015933). Egg tempera was hand-made mixing egg yolk with water. The support is a cellulose and cotton watercolor paper, acids and lignin free, commercialized by “Fabriano”, 270g/m^2. This paper is not treated with optical brighteners, it's slightly UV Fluorescent, and it reflects IR. Two cross-hair lines, 0,2mm (vertical) and 0.4mm (horizontal), were printed on each swatch of paper before the application of paint, in order to have a means to evaluate the pigment transparency in the IR and IRR imaging.

The pigments were mulled into the binder which was added as needed for each pigment and applied with brush. No other means to control and measure thickness of the paint and ratio binder-pigment was implemented. Among all the pigments and their varieties ever used in art these 54-pigments collection is not exhaustive but it attempts, at least, to be a selection of the most used from antiquity to early 1950'. A swatch of just the binder is added as a reference for each pigments checker. The pigments have also been applied with fresco technique on a preparation of marble powder and lime plaster ($Ca(OH)_2$) in ratio 2:1. Figure 1 shows the 4 pigments checkers.

All the pigments are distributed by Kremer Pigments and their relative information about composition and manufacturing can be found on the Kremer website [18]. The pigments checkers were aged by exposure to direct sun radiation for 2 months (Sept-October) at 37^{o}N.

Fig. 1. Pigments checkers. A collection of 54 historical pigments laid with gum arabic, egg tempera, linseed oil and fresco.

Table 1. List of pigments with the Kremer Pigments product code.

BLACKS	**BROWNS**	**WHITES**	
Ivory black, 12000	Burnt Sienna, 40430	Lead white, 46000	
Vine black, 47000	Burnt umber, 40710	Zinc white, 46300	
Bone black, 47100	Van Dyke brown, 41000	Lithopone, 46100	
Lamp black, 47250	Raw Sienna, 17050	Titanium white, 46200	
	Raw umber, 40610	Gypsum, 58300	
		Chalk, 58000	
BLUES	**GREENS**	**REDS**	**YELLOWS**
Azurite, 10200	Cadmium green, 44510	Alizarin, 23600	Cadmium yellow, 21010
Blue bice, 10184	Chrome green, 44200	Cadmium red, 21120	Cobalt yellow, 43500
Cobalt blue,45730	Cobalt green, 44100	Red lead, 42500	Lead Tin yellow I, 10100
Egyptian blue, 10060	Green earth, 11000	Red ochre, 11574	Lead Tin y. II, 10120
Indigo, 36005	Malachite, 10300	Vermilion, 10610	Massicot, 43010
Maya blue, 36007	Phthalo green, 23000	Madder lake, 372051	Naples yellow, 10130
Prussian blue, 45202	Verdigris, 44450	Lac dye, 36020	Orpiment, 10700
Smalt, 10000	Viridian, 44250	Carmine lake, 42100	Saffron, 36300
Ultramarine nat, 10510		Realgar, 10800	Yellow ochre, 40010
Phthalo blue, 23050			Yellow Lake res., 36262
Cobalt violet, 45800			Gamboge, 37050

Figure 2 shows the 7 TP methods and the IRR image of the pigments laid as fresco. The technical photography equipment and the calibration procedures are the same as described extensively on the previous paper [17] illustrating the flowchart method for the identification of pigments laid with gum arabic. It was used a Nikon D800 DSLR (36 MP, CMOS sensor) digital camera modified "full spectrum" (sensitivity between about 360 and 1100nm). The filters set was: a) For Reflected Ultraviolet (UVR) photography, B + W 403 filter plus X-Nite CC1; b) For Visible (VIS) photography, X-Nite CC1; c) For UV Fluorescence (UVF and UVF254) photography, B + W 420 plus X-Nite CC1; d) For Infrared (IR), Infrared Fluorescence (IRF) and Infrared Reflectography, Heliopan RG1000.

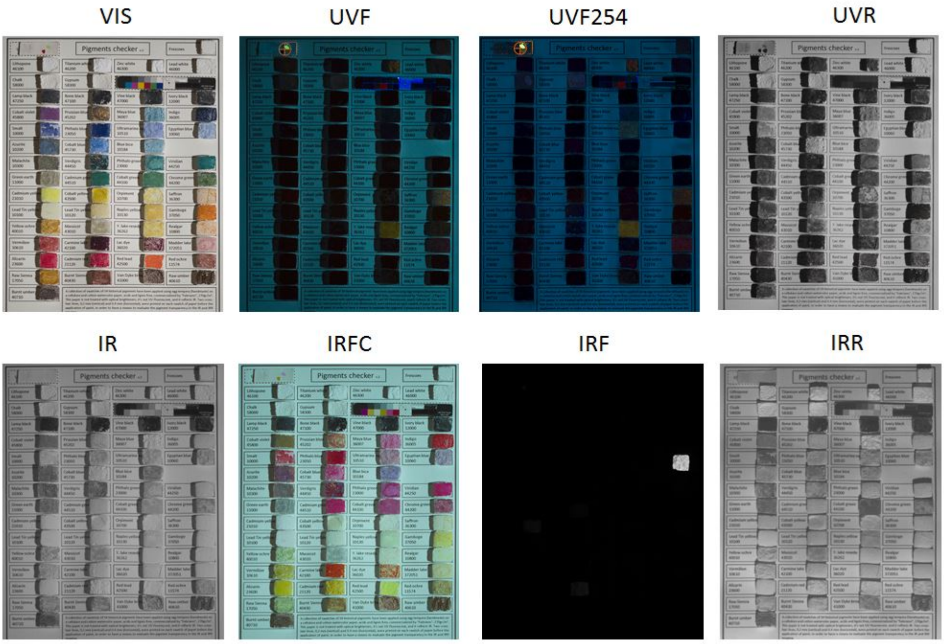

Fig. 2. Technical photos of fresco pigments checker.

Halogen lamps (2 x 400 W) were used for VIS and IR photography while one Xenopus Electronix UV high-Flux 365nm LED (filtered with UV-pass glass) provided UV light for UVF and UVR photography. UVF254 was performed with a 254nm UV lamp, Spectroline MiniMAX UV-5F (5W lamp complete with UV-pass glass). A white light LED lamp filtered with the X-Nite CC1 filter provided the visible light for infrared fluorescence photography. The camera has been calibrated with the X-rite ColorChecker Passport and its bundled software to create a camera profile for Adobe Camera Raw ®. A Nikon Nikkor 50mm f/1.8D AF lens was used for all the TP photos. The American Institute of Conservation Photo Documentation (AIC PhD) target [19] was used for calibration of the technical photos. The images were shot RAW and they were then color corrected using the camera profile above mentioned and white balanced using the N8 neutral grey patch in the AIC target. The grey patches are identified by the following designations (white to black): white; N8; N6.5; N5; N3.5; and black. They were also exposure corrected: N8 patch 150 +/- 5 for VIS. The same patch is also used for correcting the other images: 100 +/- 5 for IR and IRR, and 50 for UVR. The AIC PhD target was coupled with 3 UV activated emitters: a section of a card for forensic UV photography (orange fluorescence), a swatch of zinc white (yellow fluorescence), and a fluorescent paint (green fluorescence). These 3 UV emitters together with the red fluorescence emission of the red square of the AIC PhD target itself are used for color balancing of UVF and UVF254 photos.

The images are also exposure corrected using the red fluorescence of the red patch: Red channel 70 +/- 5, Green 0, Blue 0. In order to check the correct exposure for IRF photography a swatch of cadmium red was also added to the UV emitters, and the IRF images are exposure corrected with the red cadmium swatch at RGB 30. The Infrared False Color image is made by digitally editing the VIS and IR images. A copy of the VIS image is edited to become the IRFC image. The VIS green channel substitutes the blue channel and the red channel the green channel. Then, the IR image constitutes the red channel of the edited VIS. Infrared Reflectography (IRR) was performed with an InGaAs camera (320x256pixels) Merlin NIR by Indigo Systems using the same Nikon Nikkor 50mm f/1.8D AF lens and an adaptor for Nikon F-mount to C-mount.

Results and Discussion

Visible (VIS)

The VIS photos of the pigments checkers are a useful tool for painters, conservators and art historians because they show the appearance of these 54 pigments when applied with the four binders. The hiding power of pigments depends on the difference between their refractive index (R.I.) and that of the binder [20] and they become more opaque when this difference increases, while they can results much transparent when their R.I. is very close to that of the binder. This phenomenon was known to painters and they mixed pigments with specific binders in order to prepare an opaque paint or transparent glazes. The R.I. of the two aqueous media, gum arabic and egg tempera, are similar and are both smaller than that of linseed oil. The R.I. of red lake pigments are close to that of linseed oil (about 1.5) and, consequently, they are transparent in oil and were used as red glazes. The R.I of ultramarine (c. 1.6) is sufficiently far from that of linseed oil and it becomes just a bit more saturated and dark in oil than in the aqueous media. On the other hand, the R.I. of azurite (c.1.8) is far from those of all the three binders and therefore the difference is minimal, but azurite loses its brightness and it can have a greenish color in oil. Eventually, pigments, such as red lead, with even higher R.I. are not affected by the binder (Fig. 3). The fresco board shows the pigments that don't stand the lime alkaline environment (Fig. 4).

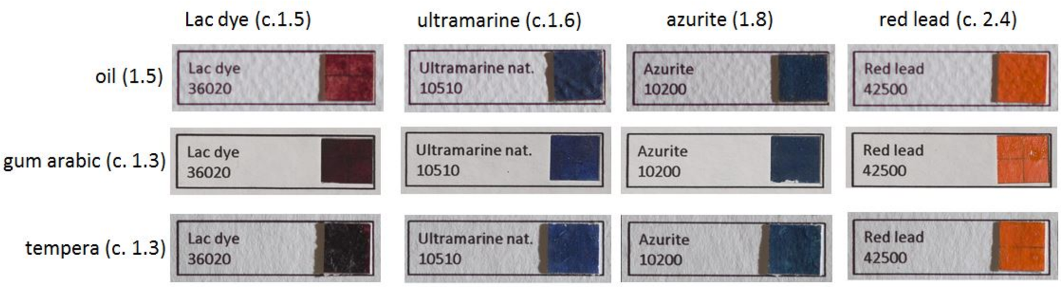

Fig. 3. Examples of pigments and binders with increasing R.I. distances.

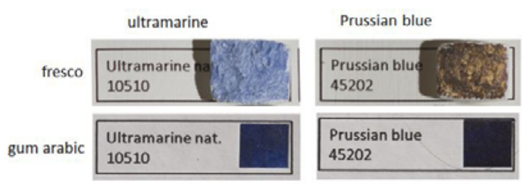

Fig. 4. Most pigments do not stand the alkaline environment of lime in fresco technique. While ultramarine maintains its color, Prussian blue reacted with the lime and turned brown.

Ultraviolet Fluorescence (UVF and UVF254)

UV fluorescence images are the most affected by the binders. Among the two aqueous media, egg tempera is the one responsible for the intense blue-whitish fluorescence which dominates the UVF and UVF254 images of some of the pigments laid with this binder. On the other hand, linseed oil is responsible for a yellowish fluorescence and fresco doesn't contribute any emission (Fig. 5).

White pigments. Zinc white is recognizable among the four white pigments thanks to its characteristic yellow emission which is observed in all the binders. Lead white and lithopone feature intense fluorescence due to the binders they are mixed with. Among the four white pigments only titanium white is characterized by the lack of fluorescence in any of the binders, thanks to its strong absorption band in the UV region.

Black pigments. The four black pigments do not show any fluorescence, regardless of the binder.

***Blue pigments*.** Cobalt violet, smalt, Maya blue, indigo, ultramarine, Egyptian blue and cobalt blue are dominated by the fluorescence of the tempera and oil binders. On the other hand, Prussian blue, phthalo blue, azurite and blue bice don't show any fluorescence, regardless of the binder. (Fig. 6) shows as an example the UVF images of ultramarine and azurite.

Green pigments. The eight green pigments are slightly affected by the binder or don't present any fluorescence.

Yellow pigments. Cadmium yellow features a red UV fluorescence in gum arabic and fresco while it has a yellow fluorescence in tempera and oil. Orpiment features only yellowish fluorescence in tempera and oil. Saffron and yellow lake reseda shows a yellow fluorescence in all the binders. Lead tin yellow I and II, cobalt yellow, Naples yellow, realgar, massicot, yellow ochre and gamboge show fluorescence due just to the tempera and oil binders.

***Red pigments*.** Carmine lake, alizarin, cadmium red, red ochre, don't feature any fluorescence regardless of the binder. Vermilion and lac dye are weakly dominated by the egg tempera fluorescence. Red lead has an intense fluorescence when laid in egg tempera. Madder lake shows its characteristic fluorescence across all binders but the colors are different, ranging from red, to orange to purple.

***Brown pigments*.** All the browns, raw sienna, burnt sienna, Van Dyke brown, raw umber, burnt umber remain dark in all of the four binders.

Fig. 5. UVF photos of the four pigments checkers.

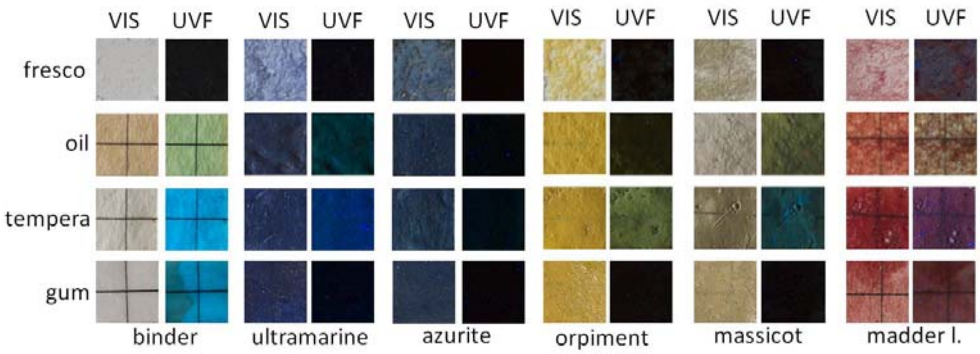

Fig. 6. UV fluorescence of binders and 5 representative pigments.

It must be pointed out that the UVF examination becomes useless if a layer of dirt or a varnish cover the paint since the UV light will be absorbed by the external layer and will not reach the paint. A 14th century icon, *the Virgin with the Child and a Saint*, unknown author (Public Library of Taormina, Sicily), was examined with UVF before and after its cleaning. The UVF image of the painting before the restoration doesn't reveal any fluorescence because of the thick layer of dirt. Once this is removed, the whitish fluorescence of lead white laid with tempera becomes apparent. The same UVF image also shows the inpaints with titanium white (dark spots) (Fig. 7).

Eventually, for mural paintings the UV fluorescence due to the aqueous media is helpful to identify *a secco* technique (Fig. 8). The UV excitation at 254nm enhances the intensity of the UV fluorescence of the pigments but also that of the binders. Consequently, the UVF254 images of the pigments are affected by the bluish and yellowish UV fluorescence, respectively, of the egg tempera and of the linseed oil. As for the UVF images cadmium yellow exhibits a reddish fluorescence when laid with fresco and gum arabic and yellow when mixed with egg tempera and oil (Fig. 9).

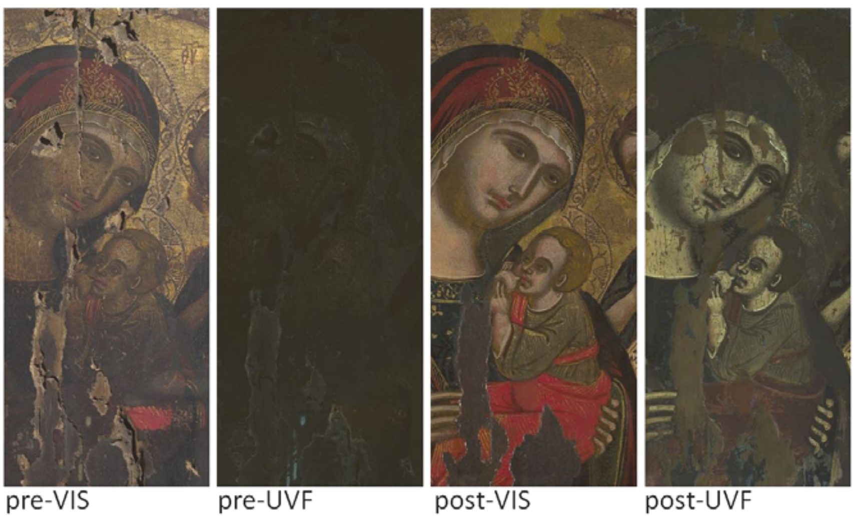

Fig. 7. 14th century icon, the Virgin with the Child and a Saint, unknown author (Public Library of Taormina, Sicily). VIS and UVF photos before (pre) and after cleaning (post).

Fig. 8. Crucifix chapel, mother church, Aci Sant'Antonio (Sicily). The 18th century mural paintings were executed with a secco technique, using an aqueous binder.

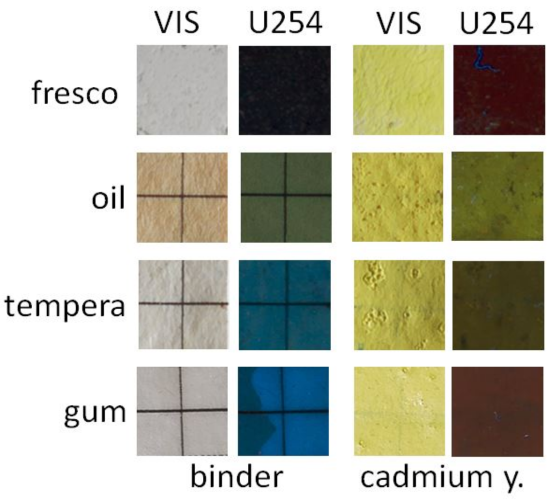

Fig. 9. UVF254 images of binders and cadmium yellow.

Reflected Ultraviolet (UVR)

Compared to gum arabic, egg tempera and linseed oil absorb more UV and they affect accordingly the brightness of the UVR images but no other differences respect to the gum arabic swatches are noticeable in both egg tempera and linseed oil. For example, among the whites, in all the binders, lead white reflects in the UV region while titanium white appears dark (Fig. 10). On the other hand, some differences are observed in the fresco swatches. Some pigments reflect much more UV when laid in fresco than with the other binders. Among the blues, these are Maya blue, smalt, ultramarine, cobalt blue and Egyptian blue. This increased reflectance in the UV region is also confirmed by the reflectance spectra of the same swatches, available on the online database [21] (Fig. 11). All the green, yellow, red and brown pigments absorb UV and they maintain the same behavior across all the binders.

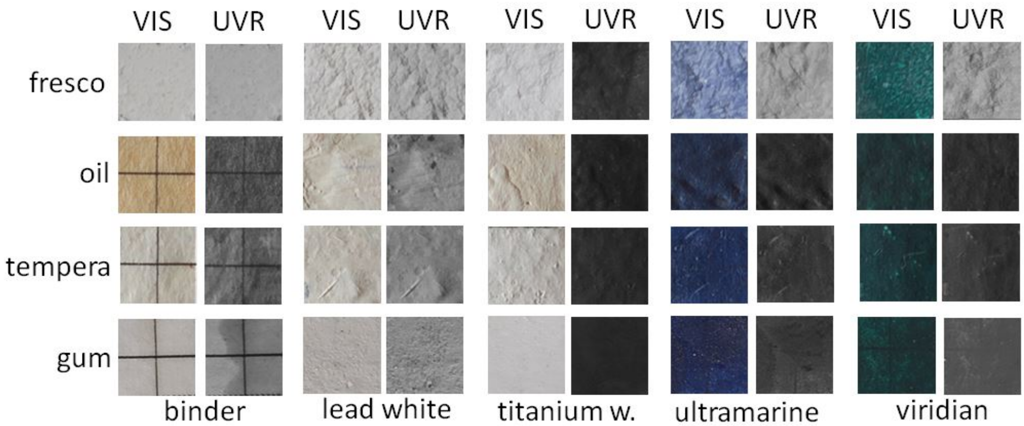

Fig. 10. UVR images of binders and some pigments. Lead white and titanium white maintain their respective UV reflectance across all the binders while ultramarine and viridian become more reflective when laid with fresco.

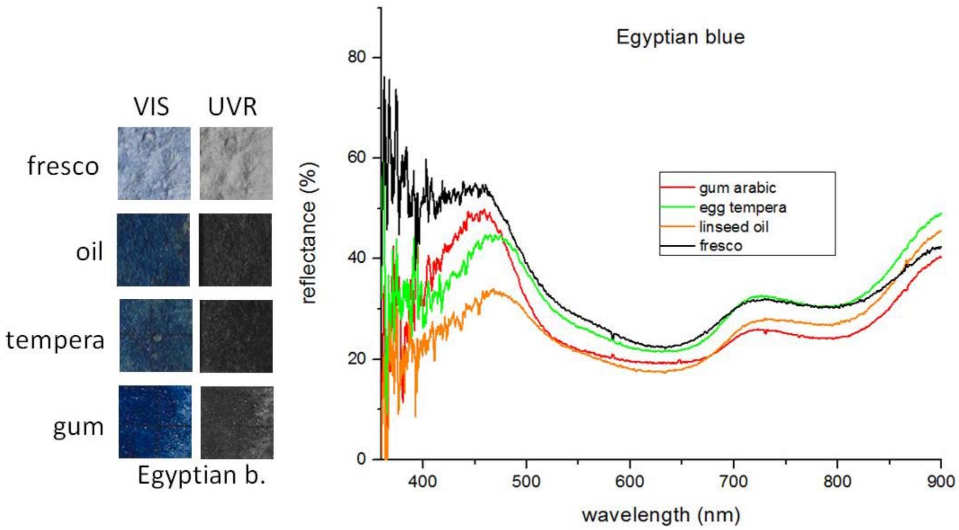

Fig. 11. The Reflectance spectrum of Egyptian blue laid with fresco shows the increased reflectance in the UV region compared to the other binders.

Infrared (IR, IRFC, IRF, IRR)

In the IR and IRR images there are no significant changes due to the binders but only the increased brightness of the fresco swatches which is responsible for the difference in the resulting IRFC. The brighter infrared images are responsible for the shift of the IRFC images into more intense red component. For example, depending on the binder Maya blue can have red or pink false color, while indigo maintains its red false color across all binders. Vermilion and chrome green are examples of pigments which maintain a consistent false color on different media, respectively, yellow and purple. As an example, chrome green was identified through pXRF on the mural painting cycle in the Crucifix chapel in Aci Sant'Antonio [22] and its false color is compatible with that attribution (Fig. 12). The infrared fluorescence images of cadmium pigments and Egyptian blue are not affected by the binders.

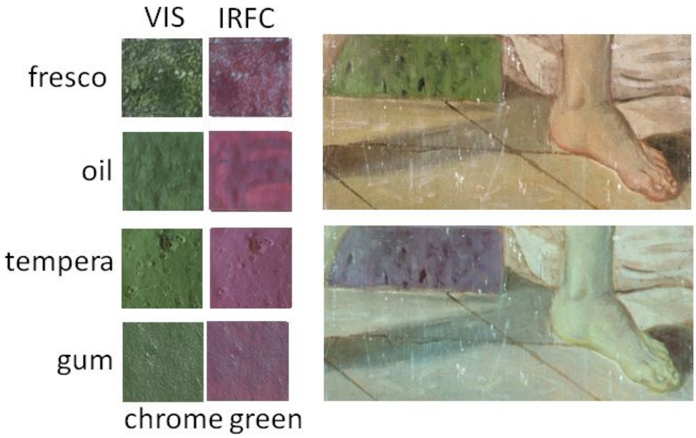

Fig. 12. Crucifix chapel, Aci Sant'Antonio (Sicily). IRFC of chrome green and detail from the fresco where chrome green has been identified with XRF.

Conclusions

This work discussed the effect that four widely used binders for works of art have on the technical photos and infrared reflectography images of the pigments they are laid with. Ultraviolet images (UVF and UVF254) are the most affected by egg tempera and linseed oil since they feature strong fluorescence emission, respectively, bluish and yellow, which can dominate that of the pigments. It was noted that those pigments that are known to have their own characteristic fluorescence still show it even when mixed with these binders, such as zinc white, whose yellow emission is distinct in each of the binders and madder lake. It was interesting to observe that cadmium yellow features a red UV fluorescence in gum arabic and fresco while it has a yellowish fluorescence in tempera and oil. The information collected on UVF and UVF254 showed that the interpretation of these images must be careful since binders have a strong influence and other factors can influence the resulting fluorescence of the paint, such as aging and layer of dirt or varnish.

On the other hand, the other technical photos (UVR, IR, IRF, IRFC) and infrared reflectography were just slightly affected by the binders which are responsible only for a small change in the overall brightness. This study confirmed the efficacy of the flowchart method as a valid tool for the preliminary identification of some pigments if the issues regarding the UV fluorescence are taken into account.

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