Pictorial materials database: 1200 combinations of pigments, dyes, binders and varnishes designed as a tool for heritage science and conservation

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Tiziana Cavaleri[1*], **Paola Buscaglia**[1], **Simonetta Migliorini**[2], **Marco Nervo**[1], **Gabriele Piccablotto**[3], **Anna Piccirillo**[1], **Marco Pisani**[4], **Davide Puglisi**[1], **Dario Vaudan**[2], **Massimo Zucco**[4]

[1] Centre for Conservation and Restoration '*La Venaria Reale'* (CCR), via XX Settembre 18, 10078 Venaria Reale, province of Turin (Italy)
[2] Regione Autonoma Valle d'Aosta, Soprintendenza per i Beni e le Attività Culturali, Ufficio Laboratorio Analisi Scientifiche (LAS), P.zza Narbonne 1, 11100 Aosta (Italy)
[3] Laboratorio di Analisi e Modellazione dei Sistemi Ambientali (LAMSA), Departement of Architecture and Design, Polytechnic of Turin, corso Massimo D'Azeglio 42, 10125 Turin (Italy)
[4] National Institute of Metrological Research (INRIM), Strada delle Cacce 91, 10135 Turin (Italy).

* Corresponding author: tiziana.cavaleri@centrorestaurovenaria.it, +39 011 499 3031

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Abstract

The conservation of artworks requires a profound knowledge about pictorial materials, their chemical and physical properties and their interaction and/or degradation processes. For this reason, pictorial materials databases are widely used to study and investigate cultural heritage. At Centre for Conservation and Restoration *La Venaria Reale* (CCR) we prepared a set of about 1200 mock-ups with 173 different pigments and/or dyes, used across all the historical times or as products for conservation, 4 binders, 2 varnishes and 4 different materials for underdrawings. In collaboration with the Laboratorio Analisi Scientifiche (LAS) of Regione Autonoma Valle d'Aosta, the National Institute of Metrological Research (INRIM) and the Department of Architecture and Design (LAMSA) of the Polytechnic of Turin, we created a scientific database that is now available online (http://www.centrorestaurovenaria.it/en/areas/diagnostic/pictorial-materials-database) designed as a tool for heritage science and conservation. Here we present a focus on materials for pictorial retouching where the hyperspectral imaging (HSI) application, conducted with a prototype of new technology, allowed to provide a list of pigments that could be more suitable for conservation treatments and pictorial retouching. Then we present the case study of the industrial painting *Notte Barbara* (1962) by Pinot Gallizio where the use of the database including modern and contemporary art materials showed to be very useful and where the fibre optics reflectance spectroscopy (FORS) technique was decisive for pigment identification purpose. Later in this research, the mock-ups' will be exploited to study degradation processes, e. g. the lightfastness, or the possible formation of interaction products, e.g. metal carboxylates.

1. Introduction

The Centre for Conservation and Restoration *La Venaria Reale* (CCR) is a relatively young Italian institute dedicated to the research, conservation and valorisation of cultural heritage. The artworks shielded by the CCR present a number of different characteristics and hugely differ in techniques and historical periods spanning from Ancient Egypt textiles to art paintings by contemporary artists. Therefore, the CCR's main challenge is to cope with a wide range of different problems, diverse materials and conservation techniques.

In general, the conservation of artworks requires a profound, systematic knowledge about ancient and modern pictorial materials, their chemical and physical properties and their interaction and/or degradation processes [1-5]. In order to facilitate the knowledge of pictorial materials in artworks and the use of the right materials in conservation, the CCR created a wide pictorial database. The palette was prepared by CCR team using a set of about 1200 mock-ups with 173 different pigments and/or dyes used across all the historical times or as products for conservation, 4 binders, 2 varnishes and 4 different materials for underdrawings.

The scientific database, available online (http://www.centrorestaurovenaria.it/en/areas/diagnostic/pictorial-materials-database), was created by analysing materials and mock-ups. CCR worked in collaboration with the Laboratorio Analisi Scientifiche (LAS) of Regione Autonoma Valle d'Aosta for the examination with fibre optics reflectance spectroscopy (FORS). The National Institute of Metrological Research (INRIM) participated, with a new technology prototype based on the use of a Fabry-Perot interferometer [6], for the hyperspectral imaging (HSI), which is a very promising technique for heritage science [7-10]. The Department of Architecture and Design (LAMSA) of the Polytechnic of Turin collaborated for the colour rendering elaborations.

One of the main objectives of the project was to provide a widespread scientific tool for a better interpretation of data coming from the multispectral imaging techniques commonly used for investigating artworks. Through the HSI data and the colour rendering elaborations, a part of the project focused on materials for pictorial retouching and their effect on the artworks' colour appearance [11, 12]: specific mock-ups were designed to help the choice of products for conservation, which is decisive especially when one lacks information about the museum lighting. Finally, the paper presents the case study of *Notte Barbara*, a polychrome industrial painting by Pinot Gallizio (1902 – 1964 Alba, Italy) where a number of synthetic pigments were identified through the FORS database combined with complementary diagnostic techniques.

2. Materials and Methods

2.1 Material analysis and instrumentation, mock-ups preparation

A set of 139 inorganic pigments and 34 organic dyes supplied by the *Kremer Pigmente GmbH & Co. KG* company [13] were selected and divided in groups according to their use and diffusion in different historical periods [14-19]. In particular, 42 inorganic pigments were chosen to represent the palette of a long span of time, from Prehistory and Ancient Egypt to Ancient East and Classical Age, 21 inorganic pigments represent the early Christian age, medieval age and Renaissance up to the end of the 18th century and 76 pigments represent the 19th and 20th century art. With regards to the dyes, 13 are of organic nature, used since ancient times, and 21 are of synthetic nature, produced and diffused since the 19th century (tables 1, 2).

Before preparing the mock-ups, the chemical composition of each single material was analysed and compared to the datasheets [13]. These analyses were conducted on few grains of pigment/ dye and small amounts of resin/ binder with Fourier transform-infrared spectroscopy (FT-IR) in attenuated total reflectance modality (ATR) using a Bruker Vertex 70 FT-IR spectrophotometer along the 400 - 4000 cm^{-1} spectral range, with a 4 cm^{-1} resolution, and a Harrick MVP-2 Star single angle ATR unit.

In order to compensate the FT-IR spectroscopy limitations (see *Discussion and results*), further information was acquired later on the mock-ups with X-rays fluorescence spectrometry (XRF). We used a portable Micro-EDXRF Bruker Artax 200 spectrometer with a *fine focus* X-rays source and a Molybdenum anode, 4096 channel-ADC, 1.5 mm spot size, anodic voltage 30 kV and anodic current 1300 μA, purging helium gas in order to detect low atomic weight elements. For this technical reason, XRF analyses were not applied directly to the pigment powders.

The database of ATR FT-IR and XRF spectra is available online in the section “Material analysis” (http://www.centrorestaurovenaria.it/en/areas/diagnostic/pictorial-materials-database).

Once the colours were selected, the team (CCR, INRIM, LAS and LAMSA) defined what characteristics the mock-ups' should have had. First, the mock-ups had to simulate real artworks: support, preparation layer, underdrawing, pictorial layer and finishing. At the same time, their structure had to be as simple as possible in order to facilitate the interpretation of the analytical data. In addition, they had to be manageable both for technical and logistic reasons: for example, big size mock-ups would have complicated the transfer between the four institutes and would have been more sensitive to thermic and hygrometric environmental conditions.

Therefore mock-ups were prepared on four 50 x 70 cm multilayer wooden panels, 2.5 cm thick. The panels were evenly treated with a glue-based solution (water and animal glue in a 14: 1 ratio in weight) applied with a brush in order to reduce porosity, then they were prepared with a layer of *stucco* (gypsum added to saturate the glue-based solution, as before)and finally by smoothing the surface. In order to simplify the interpretation of data, we did not use coloured preparation layers, even if they can often be found in artworks [20]. As shown in figure 1, each rectangle (6 cm high, 5 cm wide) was designed to host one single pigment/ dye in six different combinations: it was divided into two columns, in order to present two different binders, and into three stripes, two of which corresponded to different varnishes and one left unprotected. This was particularly useful for comparing the UV fluorescence of the pigment-binder system with and without resin. Only some mock-ups presented particular combinations of colours, such as mixtures or glazing, well known and described in literature [17].

On each rectangle, a sign simulating the *underdrawing*, represented with a letter, was applied directly on the *stucco*. Four different materials were chosen according to the historical period: charcoal (letter "A") and *sanguigna* (red ochre/hematite, letter "C") were used in panel n° 1; charcoal, *sanguigna* and iron gall ink (letter "D") were used in panel n° 2; charcoal and graphite (letter "E") were used in panels n° 3 and n° 4.

With regards to the pictorial layers, the binders were chosen according to the artistic techniques and the historical period. Binders in panel n° 1 are *Arabic gum*, in 1:10 (weight) water solution, and *egg tempera*, made by following the original recipe which requires adding 1/3 (volume) of vinegar and white egg to the yolk, beating until stiff and filtering. Binders in panel n° 2 are *egg tempera* and triple boiled *linseed oil*. Finally, *linseed oil* and *polyvinyl acetate*[1] were used in panel n° 3. For the natural and synthetic dyes, water-based binders (*Arabic gum* and *polyvinyl acetate*) were preferred for chemical compatibility[2]. The colour powders were grinded in a mortar, incorporated into the binder using a *spatula* and kneaded until homogeneous. Pictorial layers are thick enough to cover the underdrawing and generally thicker when the pigment/dye is not so opaque. In this step, conservators' competences were fundamental for using the correct pigment/binder ratio and obtaining the right opacity and saturation. With regards to the varnish, *mastic* was chosen to represent the natural terpene resins group and the acrylic *Vernis à Retoucher*[3] as an example of synthetic resin: both of them were applied with a brush.

Since one part of the project was dedicated to study materials for pictorial retouching and their effect on the artworks' colour appearance [11, 12], specific mock-ups were made with products for conservation[4].

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[1] Mowilith DM5: PVAc and acrylic ester in aqueous solution, plasticizer free, *Sinopia SAS* datasheet [21].

[2] Linseed oil was also used as binder for gamboge, madder and indigo, as reported in literature.

[3] Supplied by *Lefranc & Bourgeois* Company.

[4] Some examples: *Furnace Black* (n° 2, Kr. 26600), *Yellow ochre iron oxide* (n° 19, Kr. 40301), *Sienna Earth Italian* (n° 20, Kr. 40400), *Burnt Sienna Italian* (n° 22, Kr. 40451), *Burnt Umber reddish* (n° 23, Kr. 40700), *Bone Black* (n° 44, Kr. 47100), *Naples Yellow dark* (n° 51, 43125), *Prussian Blue* (n° 59, Kr. 45210), *Naples Yellow from Paris* (n° 61, Kr. 10130), *Titanium white* (n° 69, Kr. 46200), *Zinc white* (n° 70, Kr. 46300), *Artificial Ultramarine Blue* (n° 75, Kr. 45000; n° 79, Kr. 45010), *Cobalt Blue* (n° 81, Kr. 45714), *Cadmium Yellow* (n° 83, Kr. 21040), *Cadmium Orange* (n° 92, Kr. 21080), *Ultramarine violet medium* (n° 105, Kr. 45100), *Cobalt violet dark* (n° 107, Kr. 45800), *Cadmium Red* (n° 109, Kr. 21130), *Alizarine crimson dark* (n° 111, Kr. 23610), *Cobalt green* (n° 118, Kr. 44100), *Chrome oxide*

Once the mock-ups were dry, their interaction with different radiations was studied, trying to identify specific features or fingerprints for each material (i.e. significant absorption bands, particular UV fluorescence emissions).

Fig. 1 Portion of panel n° 3. Picture in visible light and mock-ups structure (see material description in **table 2**).

2.2 Mock-ups analysis and instrumentation

Multispectral, hyperspectral imaging and punctual non-invasive analyses were conducted on the mock-ups.
Two kinds of infrared reflectography (IRR) were adopted: the first one with an X-Nite Nikon D810 IRUV camera equipped with a R72 Hoya IR filter (IRR 950 nm) and the second one with an Art Innovation Artist Camera (IRR 1150 nm). For both, the mock-ups were illuminated with Ianiro Varibeam Halogen 800W lamps.
The ultraviolet fluorescence images (UVF) was recorded with an X-Nite Nikon D810 camera equipped with a Hoya IRUV-cut filter. The ultraviolet reflectography images (UVR) was recorded with an X-Nite Nikon D810 IRUV camera equipped with an X-Nite BP1 filter (i.e. 330 – 630 nm and 930 – 1400 nm bandpass filter) coupled to a Peca 900 filter (i.e. 250 – 400 nm and 675 – 775 nm bandpass filter). For both, the mock-ups were illuminated with Labino® UV FLOODLIGHT lamps (emission peak at around 365 nm).
For IRR, UVF and UVR, an XRITE Classic ColorChecker® of 24 colours and a 99% white ceramic tab were used as references.
False-colour (FC) images were elaborated following the British Museum's recommendations on survey methods, post-production and diagnostic applicability [22], using Adobe Lightroom and Adobe Photoshop software. In particular, the IR-FC images were obtained by combining the IRR 950 nm and the R and G channels of the RGB photograph and in particular by assigning the R to the G channel, the G to the B channel and the IR image to the R (empty) channel of the false colour image. The UVR-FC images were obtained by inserting the G and B channels of the picture and the UVR component respectively into the R, G and B channels of the false colour image.
Punctual analyses of fibre optics reflectance spectroscopy (FORS) were carried out on the mock-ups using a compact portable system based on two spectroanalysers (a MCS 601 UV and MCS 611 NIR 2.2 Zeiss Multi Channel Spectrometer system), one CLH 600 tungsten halogen lamp and optical fibres of 1 mm in core diameter. Measures were acquired in 0°/2x45° geometry along the 350 – 2200 nm wavelength range, with a spectral resolution of about 2.5 nm in the Vis range and 18 nm in the NIR range.
Colorimetric measurements were finally carried out with a Konica Minolta CM700d spectrophotometer that works in d/8° optical geometry in the range from 400 to 700 nm with a 10 nm step resolution. Measures were collected with the CIE D_{65} standard illuminant in the CIELAB 1976 (L*, a*, b*, C_{ab}*) colour space, where L* corresponds to the lightness, a* and b* represent respectively the green/red and the blue/yellow opposite colour components. Later in this research, the mock-ups' degradation processes, e.g. the lightfastness, will be monitored with further colorimetric analyses [23, 24] whereas the possible formation of interaction products, e.g. metal carboxylates [25], will be analysed with ATR FT-IR spectroscopy.
The hyperspectral imaging technique (HSI) was applied to those mock-ups considered interesting for the study of pictorial retouching materials. This allowed to acquire spectral data which can be exploited for colour rendering elaborations [11, 12]: the mock-ups' colour images were rendered with different light sources permitting to reveal some pictorial materials' metameric features. We used a hyperspectral imager

green (n° 120, Kr. 44200), *Permanent Green* (n° 122, Kr. 44280), *Phtalo blue* (n° 126, Kr. 23050), *Indanthren® blue* (n° 129, Kr. 23100), *Yellow lemon reseda* (n° 140, Kr. 36260) and *Cobalt violet* (n° 170, Kr. 45800). Many of them are normally sold also by to *Gambling Colors* and *Winsor & Newton Colors.*

prototype (HSI) based on a new technology. The prototype developed by INRIM has a Fabry-Perot interferometer inserted into the optical setup between the object and a monochromatic camera [6]: it provides the artwork's image in which the spectral reflectance factor of each pixel can be calculated with a Fourier transform-based algorithm. The imager works in the 400 – 720 nm range with a spectral resolution of about 5 nm at 500 nm; the spatial resolution depends on the optical system and on the number of pixels of the implemented camera sensor.

Multispectral imaging data and FORS spectra (one per each pigment/dye) are available online in the "Panel" sections (http://www.centrorestaurovenaria.it/en/areas/diagnostic/pictorial-materials-database): the scientific database was designed as diagnostic tool for future research on polychrome artworks.

The paper presents the case study of a polychrome industrial painting by Pinot Gallizio (1902 – 1964 Alba, Italy) belonging to the Gallery of Modern Art of Turin (GAM) where a number of synthetic pigments were identified through the new FORS database, combined to further complementary techniques such as XRF and ATR FT-IR spectroscopy.

3. Discussion and results

3.1 Materials chemical composition

FT-IR spectroscopy can give information about organic and inorganic compounds, with some limitations [26]. For example, it cannot identify oxides and sulphides because they have no signals in the instrumental range (MIR spectral range: from 4000 cm^{-1} to 400 cm^{-1}). Moreover, it is difficult to identify some organic compounds when carbonates, sulphates and silicates are present, since the latter have strong signals in the MIR range.

In this project, the FT-IR analyses were useful to verify the chemical composition of pigments, dyes, binders and resins reported in the datasheets and supplied by the *Kremer Pigmente GmbH & Co. KG* Company. They allowed to identify the chromophores of pigments and dyes, but also to reveal further compounds such as barium sulphate, calcite and talc used as additives or fillers [27]. Figure 2 reports two examples: *Studio yellow* (n° 86, Kr. 23850) results to be a pure organic compound, classified with Color Index Pigment Yellow 3 (C. I. PY3) corresponding to the Hansa Yellow 10G group [28]. *Studio pigment yellow* (n° 90, Kr. 55100) results instead an organic compound classified with the C. I. PY74 and named Arylide Yellow 5GX [28], filled with calcite and talc as reported also on the technical datasheet [13].

FT-IR analyses revealed the presence of unexpected compounds in some pigments: figure 3 shows the example of *Cadmium yellow n° 6* (n° 83, Kr. 21040) which is described as "cadmium zinc sulphide yellow" in the datasheet [13]. Actually, barium sulphate, kaolin and cadmium sulphate were detected, explaining why it is classified as C.I. PY35:1 instead of C.I. PY37, which is the pure cadmium sulphides' group. In this case, since the sulphides cannot be detected by FT-IR, the presence of Zinc and Cadmium was confirmed with the XRF analysis later on the mock-up.

Fig. 2 ATR FT-IR spectra of *Studio yellow* (n° 86, Kr. 23850, black line) identified as PY3 and *Studio pigment yellow* (n° 90, Kr. 55100, red line) identified as PY 74: the latter shows also signals ascribable to calcite (2510, 1796, 872, 711 cm^{-1}) and talc (1018, 667 cm^{-1}).

Fig. 3 ATR FT-IR spectra of *Cadmium yellow n° 6* (n°83, Kr. 21040): some signals can be ascribed to the presence of barium sulphate (1182, 1138, 1065, 984,637 cm^{-1}) and kaolin (3691, 1113, 805 cm^{-1}) used as fillers. Other signals indicate the presence of cadmium sulphate (1639, 1182 cm^{-1}).

3.2 Underdrawing detectability

In several mock-ups, the infrared reflectography did not allow to detect the underdrawing: this happened, for example, in the *Copper blue*-based mock-ups (fig. 4 *a*) because the pigment strongly absorbs the radiation along the 800 – 1400 nm spectral range (fig. 5). On the contrary, the underdrawing can be detected for example in the *Madder lake*-based mock-ups (fig. 4 *b*), which reflect the 600 – 1300 nm spectral range (fig. 5).

Only a few mock-ups' spectral behaviour strongly differs in the 750 – 1150 nm range: one example is the *Natural azurite*, which in fact appears very dark in the IRR 950 nm and very light in the IRR 1150 nm (fig. 4 *c*). This means there is a possibility of discovering the drawing under an azurite-based layer by acquiring an IRR 1150 nm of the painting.

As known, the possibility of detecting the underdrawing through an IRR depends also on its own chemical nature [29]: a stronger absorption of the underdrawing in the considered IR region (750 – 1150 nm) leads to a higher contrast between the underdrawing and the pictorial layer. Charcoal and graphite absorb the IR radiation almost completely so they are generally easier to detect, while *sanguigna* is often difficult to reveal. In our database, in fact, a very small number of mock-ups allowed to detect the *sanguigna* underdrawing, in particular through IRR 950 nm and not through IRR 1150 nm. Two examples which perfectly explain this behaviour are the mock-ups made of *Purple red* and *Brazilwood* (figg. 4 *d, e* and 5): *sanguigna* iron oxides have high reflection percentages towards the longer wavelengths and a large absorption band centred at about 870 nm. In correspondence of this absorption band, *Purple red* and *Brazilwood* have high reflection percentage, so they permit, at least in theory, the underdrawing detection: obviously, other materials in the overall composition of the painting, such as varnishes and binders or the dust on the surface, can affect the IRR outcomes depending on their chemical nature.

In general, thanks to the FORS and of IRR data integration, the database is able to indicate which material combinations might require the use of an IRR 950 nm, or 1150 nm, for detecting the underdrawing.

Fig. 4 Mock-ups of *(a) Copper blue, (b) Madder lake, (c) Natural azurite, (d) Purple red, (e) Brazilwood*. Pictures, IRR 950 nm and 1150 nm. Examples of mock-ups with different spectral behaviour in the 750 – 1150 nm range *(a, b, c)*. Examples in which the *sanguigna* underdrawing (*letter "C")* is detectable through IRR 950 nm and not 1150 nm *(d, e)*.

Fig. 5 FORS spectra of the mock-ups shown in figure 4. *Copper blue* (red curve), *Madder lake* (green curve) and *Natural azurite* (blue curve) show different spectral behaviours in the 750 – 1150 nm range (paints in PVAc without varnish); FORS spectra of the *Purple red* (orange curve) and *Brazilwood* (purple curve) –based mock-ups (in Arabic gum without varnish) compared to *sanguigna* (black curve).

3.3 Pigment characterization process

In this research, the UVF showed to be a useful tool for facilitating the pigment identification process on mock-ups of similar colour. Considering for example orange mock-ups made of *Cadmium orange n.2* (n° 92, Kr. 21080), *Paliogen® orange* (n° 94, Kr. 23560) and *Irgazin® yellow light orange* (n° 95, Kr. 23670), their FORS spectra are not very distinctive: as many other yellow, orange and red pigments, they show similar *"S"* shaped curves [30-32]. Nevertheless, the mock-ups made of *Paliogen® orange* show a characteristic (red) UV fluorescence, mainly due to the pigment, with a feeble intensity difference ascribable to the different binder (fig. 6 *b*, see UVF: left and right column corresponds respectively to oil and PVAc). With regards to the other orange mock-ups, the difference in UV fluorescence seems to depend especially on the binder (fig. 6 *a, c*).

Moreover, the UV region can be decisive for distinguishing two classical blue pigments, *Smalt* (n° 13, Kr. 10000) and *Lapis Lazuli* (n° 47, Kr. 10562), which can appear very similar in visible light and IRR 950 nm. Since they absorb differently the UV radiation, they can be distinguished from each other through an UVR or an UVR-FC elaboration (fig. 6 *d, e*).

Fig. 6 Mock-ups made of *(a) Cadmium orange n.2* (92, Kr. 21080), *(b) Paliogen® orange* (94, Kr. 23560) and *(c) Irgazin® yellow light orange* (95, Kr. 23670): pictures in visible light and UVF. Mock-ups made of *(d) Smalt (13, Kr. 10000)* and *(e) Lapis Lazuli (n° 47, Kr. 10562)*: pictures in Vis light, IRR 950 nm, IRR 950 nm-FC, UVR and UVR-FC.

3.4 Pictorial retouching: metameric features and survey on paintings

In conservation treatments, pictorial retouching is a decisive step: materials selected for treatment might hugely differ in colour appearance from the conservation laboratory to the museum, depending on the lighting; consequently, the chromatic harmony between original painting and pictorial retouching might drastically change. As mentioned, part of this project focused on these materials, considering that one often lacks information about museum lighting. The mock-ups' spectral behaviours were easily acquired, pixel by pixel, with the HSI technique and they were employed to evaluate metameric features under specific light sources: this is just one of the feasible applications of the HS cubes and consists in calculating colour images of the same object rendered with different lightings.

The database makes thus a list of pigments with the lowest colour variability under different light sources. Starting from the HS cubes' spectra, this variability was obtained by calculating the mock-ups' chromatic values and images (fig. 7) for different light emission spectra, included the ones of lamps normally used in museums or art galleries. We used a low-voltage Multifaceted Reflector halogen lamp (*Halogen 3000K*) as reference light source, a "Warm White" LED (*LED - XICATO 3000 old*), which has a spectrum designed to mimic halogen lamps, typically used in museums, and two "Neutral White" LEDs (*LED - XICATO 2700 and 4000 new*).

Just to make one example, *Chrome Oxide Green* (120, Kr. 44200) in PVAc without varnish showed to have a lower colour variability than *Cobalt Green* (118, Kr. 44100): the average values of its colorimetric coordinates, calculated for the different emission spectra, show in fact lower standard deviations (table 3). Because both green pigments are normally used in conservation, we can consider the *Chrome* one more appropriate for pictorial retouching; nevertheless, only by really knowing the lighting systems of both the museum and the laboratory, the operator can make the right choice.

Fig. 7 Hyperspectral images of the *Cobalt Green (n° 118, Kr. 44100)* and *Chrome Oxide Green (n° 120, Kr. 44200)*-based mock-ups rendered with different lamps.

3.5 FORS database and the case study of a contemporary art painting

This project provided an implementation of the FORS data available in the scientific literature [24, 30, 31, 33-37] and on the web [1-5, 32], in particular with regard to a large number of synthetic dyes and pigments of Contemporary Art. For this reason the database was exploited for studying, for example, an industrial painting by Pinot Gallizio (1902- 1964 Alba, Italy): this was a very challenging case study because of the big size of the painting and the number of pictorial materials.

As anthropologist, chemist, pharmacist and expert in alimentary field, the artist took from his experience by experimenting innovative materials such as liquid plastics of polyvinyl chloride and acetate, and by producing many sorts of shade by himself. The painting entitles *Notte Barbara* (fig. 8) and dates back to 1962. Born from the Artistic Movement for Industrial Painting, it measures 220 per 985 cm but belongs to one of the long rolls of canvas that were painted, cut and sold by the meter in the markets [38].

Among the many pictorial materials of *Notte Barbara* we identified lithopone, titanium white, artificial ultramarine blue and Prussian blue, Permanent green, Phtalocyanine green and ochres of different hues through the comparison with the FORS database. As usual, each result was supported and confirmed by other complementary analyses (XRF, FT-IR spectroscopy).
For example, lithopone (mixture of zinc sulphide and barium sulphate) was identified for the triple absorption in the 650 – 750 nm range (fig. 9) due to the Co(II) ion in coordination with the sulphide, since cobalt was usually added to the pigment for improving the photostability [35]. Titanium white (TiO_2) was identified from the flex at about 400 nm (fig. 9 *a*) due to the 3 eV energy gap between valence and conduction bands of this semiconductor [36]. Since lithopone's discovering and diffusion date back respectively to 1847 (France) and 1874, and the one of titanium white to 1916-1919 [14], we can assert that both whites are chronologically compatible with the Gallizio's time.
At the same way, ultramarine blue was identified for the bell-shaped curve centred at around 475 nm and the absorption band centred at around 600 nm: high XRF signals of aluminium, sulphur and silicon supported this result whereas the XRF signal of chlorine suggested something about the binding medium, then characterized by FT-IR spectroscopy as liquid PVC.
With regards to the greens, phtalocyanines were identified by the triple absorption at around 635 nm, 725 nm and 785 nm (fig. 9 *b*), with reflection centred at around 505 nm and flex at around 800 nm [37]: this result was supported by the feeble XRF signals of copper. Also phtalocyanines, which were used as pigments since the 1930s [14], can be considered compatible with the artwork's age.
Different hues of mustard yellow showed instead the typical absorption bands of iron hydroxides, such as goethite, placed in the FORS spectrum at around 380 nm and 420 – 435 nm (fig. 9 *c*) and due to the charge transfer among OH^- ions and Fe^{3+} ions [39].
In general, when the non-invasive techniques showed not to be sufficient, in particular for reds and yellows, which have FORS *S*-shaped curves, some micro-samplings were taken and analysed by FT-IR spectroscopy. For example, the composition of some red paints results to be a mixture of red (*Permanent red R, PR4*) and yellow (*Hansa Yellow G,* PY1) organic pigments [28], with barium sulphate as filler (fig. 10 *a*). Also, one of the yellow paints is composed of *Hansa Yellow G* (PY1) with kaolin as filler (fig. 10 *b*).

Fig. 8 Picture of the industrial painting *Notte Barbara* by Pinot Gallizio (220 per 985 cm), GAM Turin.

Fig. 9 FORS spectra of the painting *Notte Barbara* compared to the database mock-ups. *(a)* White areas of paint (red, black curves) compared to *lithopone* (*68, Kr. 46100*, green curve) and *titanium white rutile* (*69, Kr. 46200*, blue curve). *(b)* Green areas (red, black and blue curves) compared to *Permanent green* (*122, Kr. 44280*, green curve) and *Phthalo green yellowish (137, Kr. 23010*, orange curve*). (c)* Yellow area of paint compared to *Yellow Ochre iron oxide (25, Kr. 40301*, orange curve*).*

Fig. 10 ATR FT-IR spectra of the *Notte Barbara*'s micro-samplings compared to the database. *(a)* The red paint (black spectrum) is a mixture of red (PR4, green spectrum) and yellow (PY1, pink spectrum) organic pigments in drying oil, with barium sulphate (purple spectrum) as filler. *(b)* The yellow paint (in black) contains an organic pigment (PY1, pink) in alkyd resin (in grey), with kaolin (in red) as filler.

4. Conclusions

The set of about 1200 mock-ups, simulating real artworks of a long span of time and presenting different combinations of pictorial materials, allowed to build an important database of scientific analyses.

Through the combination of infrared reflectography (IRR) and fibre optics reflectance spectroscopy (FORS), we could demonstrate that some material combinations can hinder the underdrawing detectability (causing possible misunderstandings in the data interpretation), depending also on the range of investigation.
The ultraviolet fluorescence (UVF), traditionally used for example for mapping the varnish distribution on the painting, showed to be an interesting tool in the identification process of some Contemporary Art materials.
By means of FT-IR and XRF analyses, the project provided a full investigation on the chemical composition of about 190 pictorial materials, supplied by the well-known *Kremer Pigmente GmbH & Co. KG* company, which can be helpful for tests and experimentations in the field of heritage science and conservation.
The hyperspectral imaging (HSI) application, conducted with a prototype of new technology, allowed to provide a list of pigments that could be more suitable for conservation treatments and pictorial retouching. This step required the elaboration of images and the calculation of chromatic coordinates of some selected mock-ups, in order to evaluate the colour variability under different lightings (metamerisms). For this reason, we also selected pigments used in conservation for the palette.
The study of mock-ups with preparation layer, underdrawing, painting layers and varnishes revealed important features of each group of materials and combinations, which proved to be useful for the diagnostic investigation on polychrome artworks. In particular, the FORS database allowed the implementation of the data available in the scientific literature and on the web, especially with regard to a large number of synthetic dyes and pigments of Contemporary Art, as demonstrated by the case study of the industrial painting *Notte Barbara* by Pinot Gallizio.
Thanks to the colorimetric data, it will be possible to monitor the natural ageing of the palette by means of further measurements during time, paying specific attention to some lightfastness pigments. At the same time, mock-ups will be exploited for studying the possible formation of interaction products, i. e. metal carboxylates, in ATR FT-IR spectroscopy.
We believe that all the collected data might be a helpful diagnostic tool for future research on polychrome artworks and for evaluating and preserving our cultural heritage.

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Table 1. Mock-ups composition of Panels n° 1-2: each pigment has a number and the *Kremer Pigmente* (Kr.) code [13].

PANEL n° 1 *Prehistory, Ancient Egypt, Ancient East, Classical Age*	**Support:** multilayer wooden panel treated with glue-based solution. **Preparation layer:** *stucco.* **Underdrawing**: charcoal (letter "A"), *sanguigna* (letter "C"). **Pigments' Binders**: Arabic gum (left column), egg tempera (right column). **Pigments**: Lead white (1, Kr. 46000), Furnace Black (2, Kr. 26600), Gesso (3), Calcium carbonate (4), Vine Black (5, Kr. 47000), Magnetite Black (6, Kr. 48800), Egyptian blue (7, Kr. 10060), HAN-Blue fine (8, Kr. 10071), Azurite MP, Sky-Blue light (9, Kr. 10207), Azurite natural fine, (10, Kr. 10210), Turquoise Sky-Blue (11, Kr. 103800), Vivianite (12, Kr. 104000), Smalt (13, Kr. 10000), Maya blue (14, Kr. 36007), Orpiment (15, r. 10700), Realgar (16, Kr. 10800), Jarosite (17, Kr. 11520), Burgundy Yellow Ochre (18, Kr. 11573), Yellow Ochre iron oxide (19, Kr. 40301), Raw Sienna Italian (20, Kr. 40400), Massicot Litharge (21, Kr. 43010), Burnt Sienna Italian (22, Kr. 40451), Burnt Umber reddish (23, Kr. 40700), Haematite-Chrome Oxide Spinel (24, Kr. 49700), French Ochre SOFOROUGE (25, Kr. 40090), HAN-Purple fine (26, Kr. 10074), Purple-Red (27, Kr. 23490), Pozzuolana Red Earth (28, Kr. 31230), Extract of Brazilwood (29, Kr. 36160), Madder Lake genuine (30, Kr. 37202), Red ochre English (31, Kr. 40351), Pompeii Red (32, Kr. 40440), Red bole (33, Kr. 40503), Minium (34, Kr. 42500), Hematite (35, Kr. 48651), Malachite natural standard (36, Kr. 10300), Chrysocolla (37, Kr. 10350), Verona Green Earth (38, Kr. 11000), Copper resinate (39, Kr. 12200), Sap Green (40, Kr. 37391), Verdigris synthetic (41, Kr. 44450), Sodalite (42, Kr. 104200). **Finishing**: terpene resin (upper stripe), acrylic (middle stripe), unprotected (lower stripe).
PANEL n° 2 *Early Christian age, medieval age, Renaissance, up to 18th century*	**Support:** multilayer wooden panel treated with glue-based solution. **Preparation layer:** *stucco.* **Underdrawing:** charcoal (letter "A"), *sanguigna* (letter "C"), iron-gall ink (letter "D"). **Pigments' Binders**: egg tempera (left column), linseed oil (right column). **Pigments**: Barium Sulfate (42, Kr. 58700), Sepia fine (43, Kr. 12401), Bone Black (44, Kr. 47100), Asphaltum (45, Kr. 47600), Blue Bice (46, Kr. 10184), Lapis Lazuli sky-blue (47, Kr. 10562), Ultramarine Ash (48, Kr. 10580), Lead Tin Yellow light (49, Kr. 10100), Indian Yellow imitation (50, Kr. 23350), Naples Yellow dark (51, Kr. 43125), Van Dyck Brown (52, Kr. 41000), Natural Cinnabar (53, Kr. 10620), Lac Dye (54, Kr. 36020), Vermilion (54, Kr. 42000), Caput Mortuum reddish (56, Kr. 48700), Caput Mortuum violet (57, Kr. 48750), Green Earth light (58, Kr. 40800), Prussian Blue (59, Kr. 45210), Lead Tin Yellow II (60, Kr. 10120), Naples Yellow from Paris (61, Kr. 10130), Venetian Red (62, Kr. 40510), Cremnitz White (1, Kr. 46000), Calcium Carbonate (4), Vine Black German (5, Kr. 47000), Azurite MP Sky-Blue light (9, Kr. 10207), Smalt (13, Kr. 10000), Orpiment (15, r. 10700), Realgar (16, Kr. 10800), Yellow Ochre iron oxide (19, Kr. 40301), Raw Sienna Italian (20, Kr. 40400), Massicot Litharge (21, Kr. 43010), Burnt Sienna Italian (22, Kr. 40451), Burnt Umber reddish (23, Kr. 40700), French Ochre SOFOROUGE (25, Kr. 40090), Pozzuolana Red Earth (28, Kr. 31230), Madder Lake genuine (30, Kr. 37202), Red ochre English (31, Kr. 40351), Red bole (33, Kr. 40503), Minium (34, Kr. 42500), Malachite natural standard (36, Kr. 10300), Sap Green (40, Kr. 37391), Verdigris synthetic (41, Kr. 44450) **Special paints:** Madder Lake Kr. 37202 glazing on Natural Cinnabar Kr. 42000 (A); Azurite Kr. 10207 (B) glazing on Madder Lake Kr. 37202; Lapis Lazuli Kr. 10562 glazing on Azurite Kr. 10207 (C); Copper resinate Kr. 12200 glazing on Verdigris Kr. 44450 (D); Bisso (mixture of Madder Lake Kr. 37202 and Lapis Lazuli Kr. 10562 (E); mixture of Azurite Kr. 10207 and Lead Tin Yellow light Kr. 10100 (F). **Finishing**: terpene resin (upper stripe), acrylic (middle stripe), unprotected (lower stripe).

Table 2. Mock-ups composition of Panels n° 3-4: each pigment has a number and the *Kremer Pigmente* (Kr.) code [13].

PANEL n° 3 *19th and 20th centuries*	**Support:** multilayer wooden panel treated with glue-based solution. **Preparation layer:** *stucco.* **Underdrawing:** charcoal (letter "A"), *graphite* (letter "E"). **Pigments' Binders**: PVAc (left column), linseed oil (right column). **Pigments**: Lead sulphate (67, Kr. 46050), Lithopone (68, Kr. 46100), Titanium white rutile (69, Kr. 46200), Zinc white (70, Kr. 46300), Zinc sulphide (71, Kr. 46350), Manganese black (72, Kr. 47500), Ploss blue (73, Kr. 10170), Blue verditer (74, Kr.10180), Ultramarine blue very dark (75, Kr. 45000), Copper blue (76, Kr. 45364), Zirconium cerulean blue (77, Kr. 45400), Cavansite (78, Kr. 104602), Ultramarine blue dark (79, Kr. 45010), Cobalt blue dark (80, Kr. 45700), Cobalt blue pale (81, Kr. 45714), Natural chromium yellow or crocoite (82, Kr. 10850), Cadmium yellow n.6 medium (83, Kr. 21040), Permanent yellow medium (84, Kr. 23310), Brilliant yellow (85, Kr. 23650), Studio yellow (86, Kr. 23850), Cobalt yellow (87, Kr. 43500), Bismuth-vanadate yellow lemon (88, Kr.43910), Baryte yellow (89, Kr. 43940), Studio pigment yellow (90, Kr. 55100), Studio pigment yellow sun gold (91, Kr. 55140), Cadmium orange n.2 (92, Kr. 21080), Paliotol® orange (93, Kr. 23540), Paliogen® orange (94, Kr. 23560), Irgazin® yellow, light orange (95, Kr. 23670), Isoindolol orange (96, Kr. 23800), Titanium orange (97, Kr. 43300), Iron oxide orange 960 (98, Kr. 48060), IWA-Enogu® Shinsia (99, Kr. 15253), IWA-Enogu® Iwamomo (100, Kr. 15261), IWA-Enogu® Usukuchi-Murasaki (101, Kr. 15311), Côte d'Azur violet(102, Kr. 11350), Thioindigo red lightfast (103, Kr. 23700), Cinquasia® violet RT 201 D (104, Kr. 23710), Ultramarine violet medium (105, Kr. 45100), Manganese violet (106, Kr. 45350), Cobalt violet dark (107, Kr. 45800), Pinkcolor (108, Kr. 10150), Cadmium red n.2 medium (109, Kr. 21130), Irgazine® scarlet DPP EK (110, Kr. 23179), Alizarine crimson dark (111, Kr. 23610), XSL Irgazine® red DPP (112, Kr. 26310), Rosso sartorius (113, Kr. 40490), Aegirine fine (114, Kr. 11140), Andeer green fine (115, Kr. 11181), Phthalo green dark (116, Kr. 23000), Chromite (117, Kr. 40650), Cobalt green (118, Kr. 44100), Cobalt green bluish A (119, Kr. 44151), Chrome oxide green (120, Kr. 44200), Viridian green (121, Kr. 44250), Permanent green (122, Kr. 44280), Cadmium green light (123, Kr. 44500), Cadmium green dark (124, Kr. 44510), Fluorescent pigment blue (125, Kr. 56050), Phthalo blue (126, Kr. 23050), Phthalo blue royal blue (127, Kr. 23060), Phthalo blue reddish (128, Kr. 23070), Indanthren® blue (129, Kr. 23100), XSL Phthalo blue royal blue very lightfast (130, Kr. 26405), Indigo blue lake (131, Kr. 36005), Indigo red-violet (132, Kr. 36006), Studio pigment sky blue (133, Kr. 55500), Studio pigment dark blue (134, Kr. 55600), XSL translucent yellow (135, Kr. 26120), IWA-Enogu® Iwabeni (136, Kr. 15222), Phthalo green yellowish (137, Kr. 23010), Heliogen® green (138, Kr. 23000). **Finishing**: terpene resin (upper stripe), acrylic (middle stripe), unprotected (lower stripe).
PANEL n° 4 *Natural and synthetic dyes*	**Support:** multilayer wooden panel treated with glue-based solution. **Preparation layer:** *stucco.* **Underdrawing:** charcoal (letter "A"), *graphite* (letter "E"). **Dyes' Binders**: Arabic gum (left), PVAc (right) for synthetic dyes; Arabic gum for natural dyes. **Natural dyes**: Gamboge powder (161, Kr. 37050), Turmeric powder (162, Kr. 37220), Wild Saffron (163A, Kr. 36300), Grains d'Avignon immature (163B), Stil de Grain (164, Kr. 37394), Dragon´s Blood powder (165A, Kr. 37000), Logwood Extract powder (165B, Kr. 36110), Madder Lake genuine (166, Kr. 37202), Sandalwood (167A, Kr. 36180), Cochineal (167B, Kr. 42100), Indigo Indian genuine (168, Kr. 36000), Indigo made of Woad (169A, Kr. 36003), Nettle (169B, 36316). **Synthetic dyes**: Paliotol® Yellow-Orange (139, Kr. 24000), Yellow lemon reseda (140, Kr. 36260), Translucent Yellow (141, Kr. 52200), Orange ingarzin (142, Kr. 23168), Hostaperm® Pink (143, Kr. 23152), Quindo® Pink D (144, Kr. 23402), Dioxazine Violet (145, Kr. 23451), Irgazine® Scarlet DPP EK (146, Kr. 23179), Irgazine® Red DPP BO (147, Kr. 23180), Irgazine® Ruby DPP TR (148, Kr. 23182), Scarlet Red (149, Kr. 23200), CPT-Scarlet Red (150, Kr. 23202), Permanent Red dark (151, Kr. 23250), Permanent Red (152, Kr. 23290), Permanent Red FRLL (153, Kr. 23291), CPT–Red (154, Kr. 23293), Quindo® Red R6713 (155, Kr. 23410), Hostaperm® Red (156, Kr. 23720), Studio Red-Helio (157, Kr. 23950), Dye black Cibacron (158, Kr. 345170), Cibacron® Blue FN-G (159, Kr. 345160). **Finishing**: terpene resin (upper stripe), acrylic (middle stripe), unprotected (lower stripe).

Table 3. CIELAB 1976 chromatic coordinates of the mock-ups shown in fig. 10 (in PVAc without varnish).

Light source	***Cobalt Green* (n° 118, Kr. 44100)**			***Chrome Oxide Green* (n° 120, Kr. 44200)**		
	D65 / 10°			**D65 / 10°**		
	L*	**a***	**b***	**L***	**a***	**b***
Halogen 3000K	35.61	-23.76	17.26	33.34	-13.40	17.85
LED - XICATO 2700 (new)	34.87	-24.05	17.31	32.94	-13.55	18.56
LED - XICATO 3000 (old)	35.86	-25.12	19.29	33.33	-14.54	19.82
LED - XICATO 4000 (new)	35.79	-25.32	20.42	33.20	-14.91	20.12
average values	35.53	-24.56	18.57	33.20	-14.10	19.09
dev. st.	0.45	0.77	1.55	0.18	0.74	1.07

Figure 1

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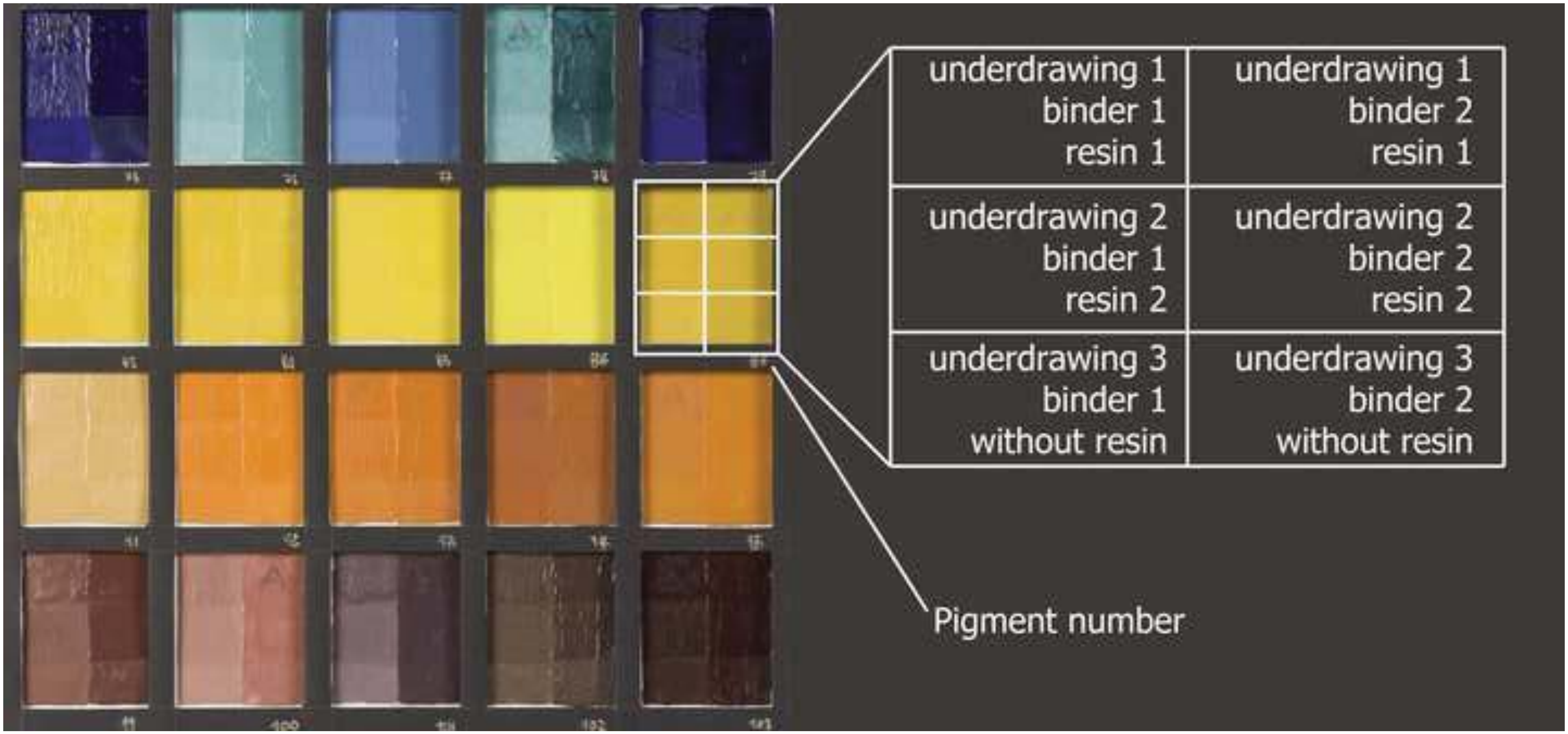

Figure 4

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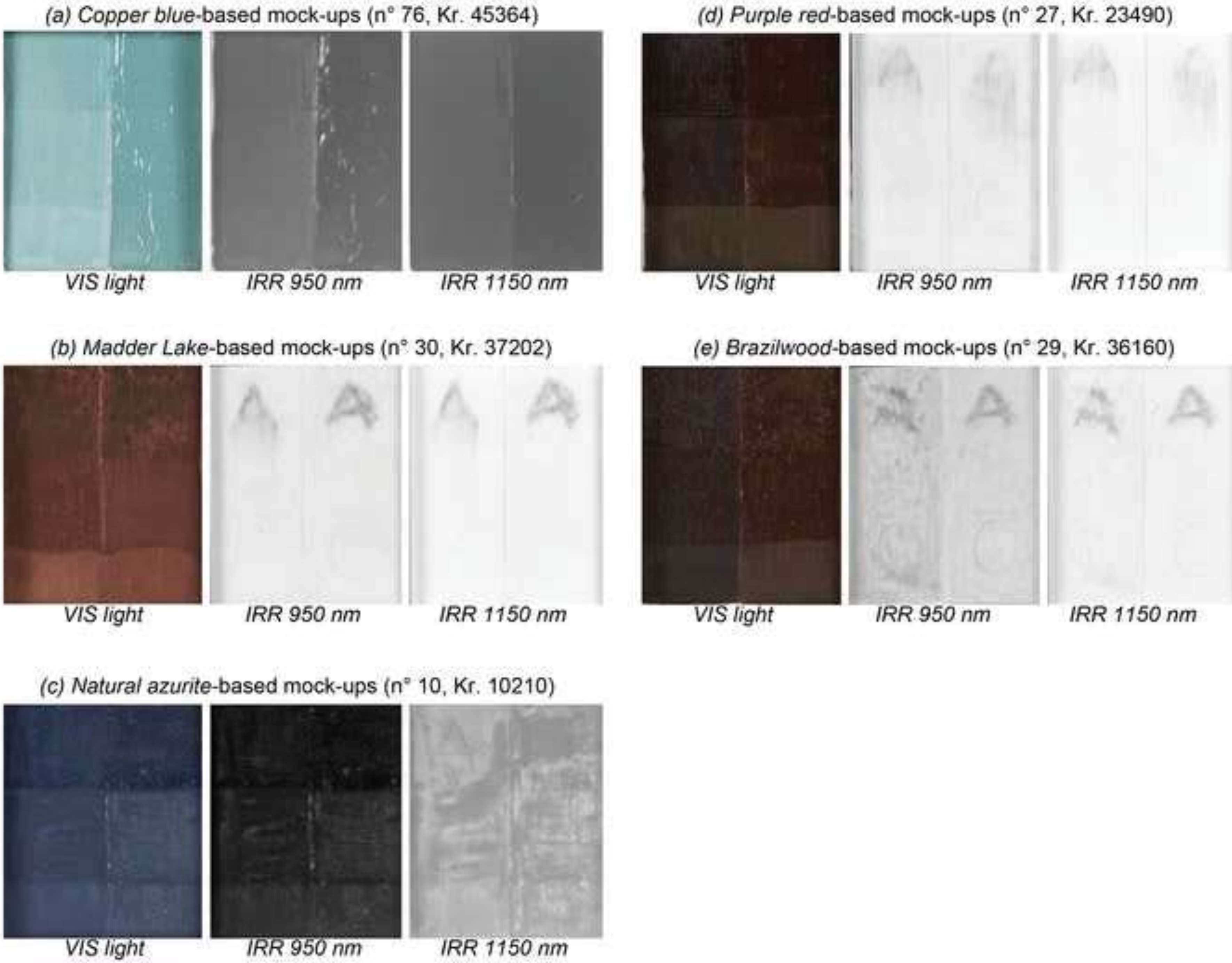

Figure 5

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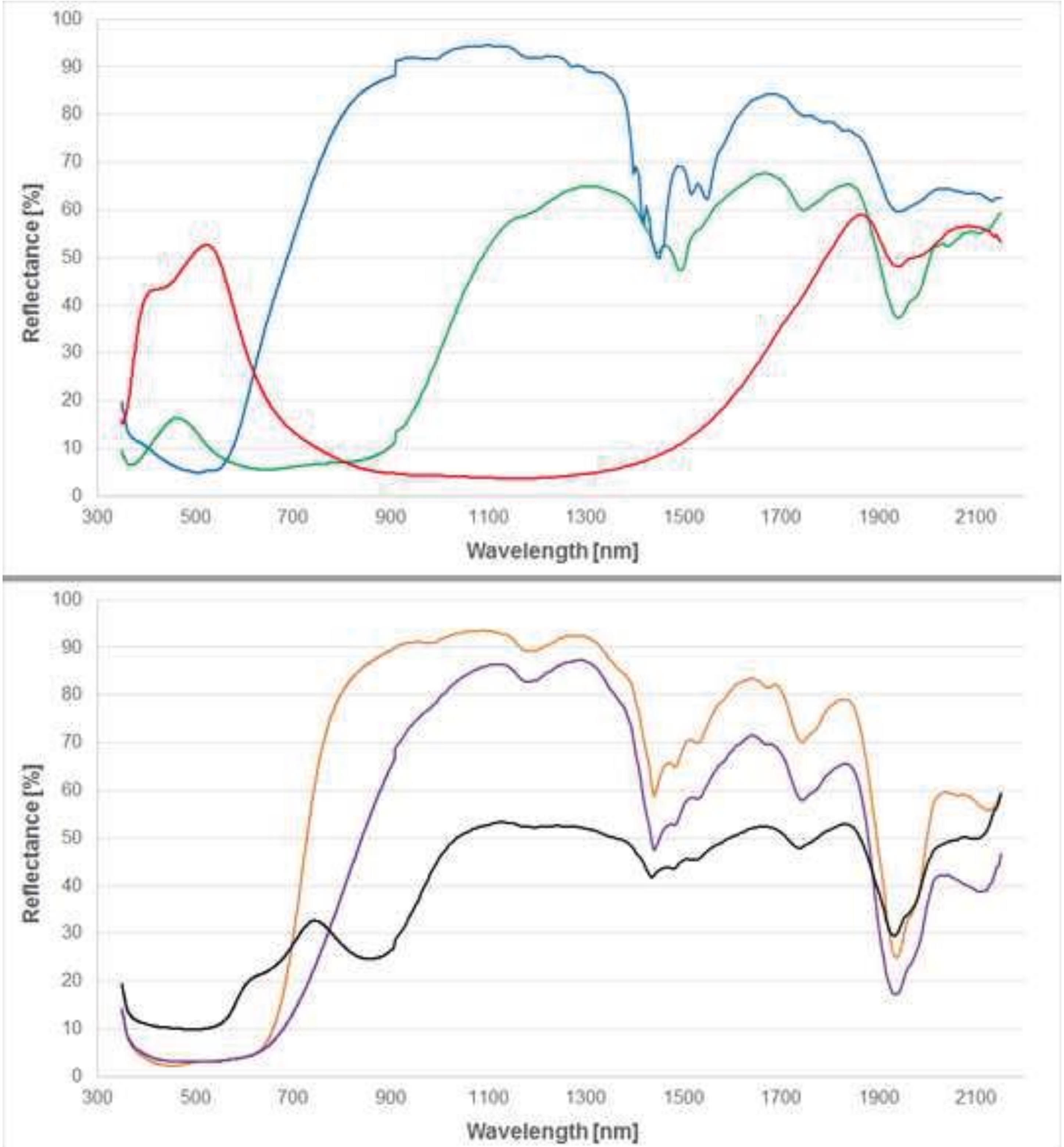

Figure 6

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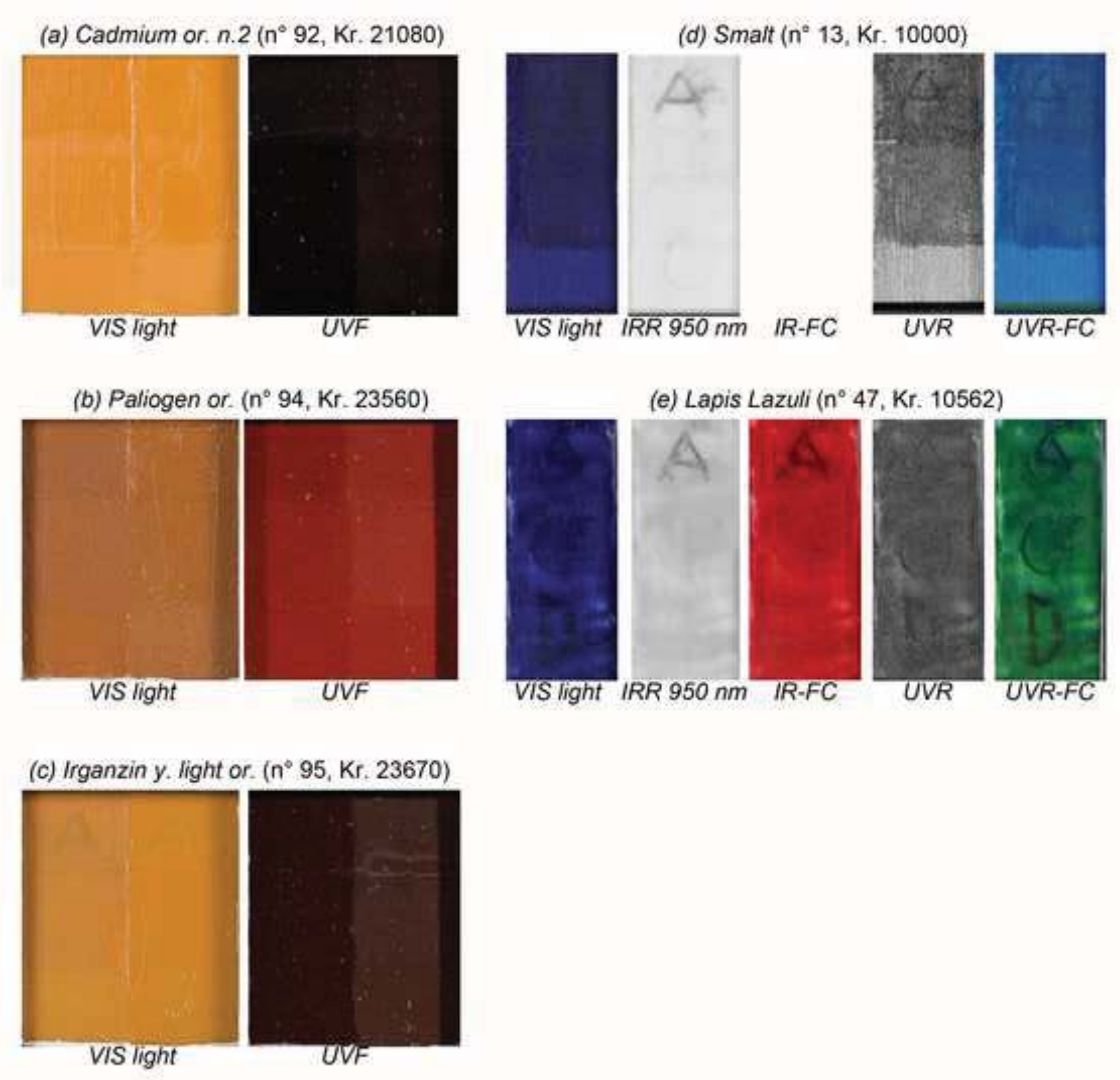

Figure 7

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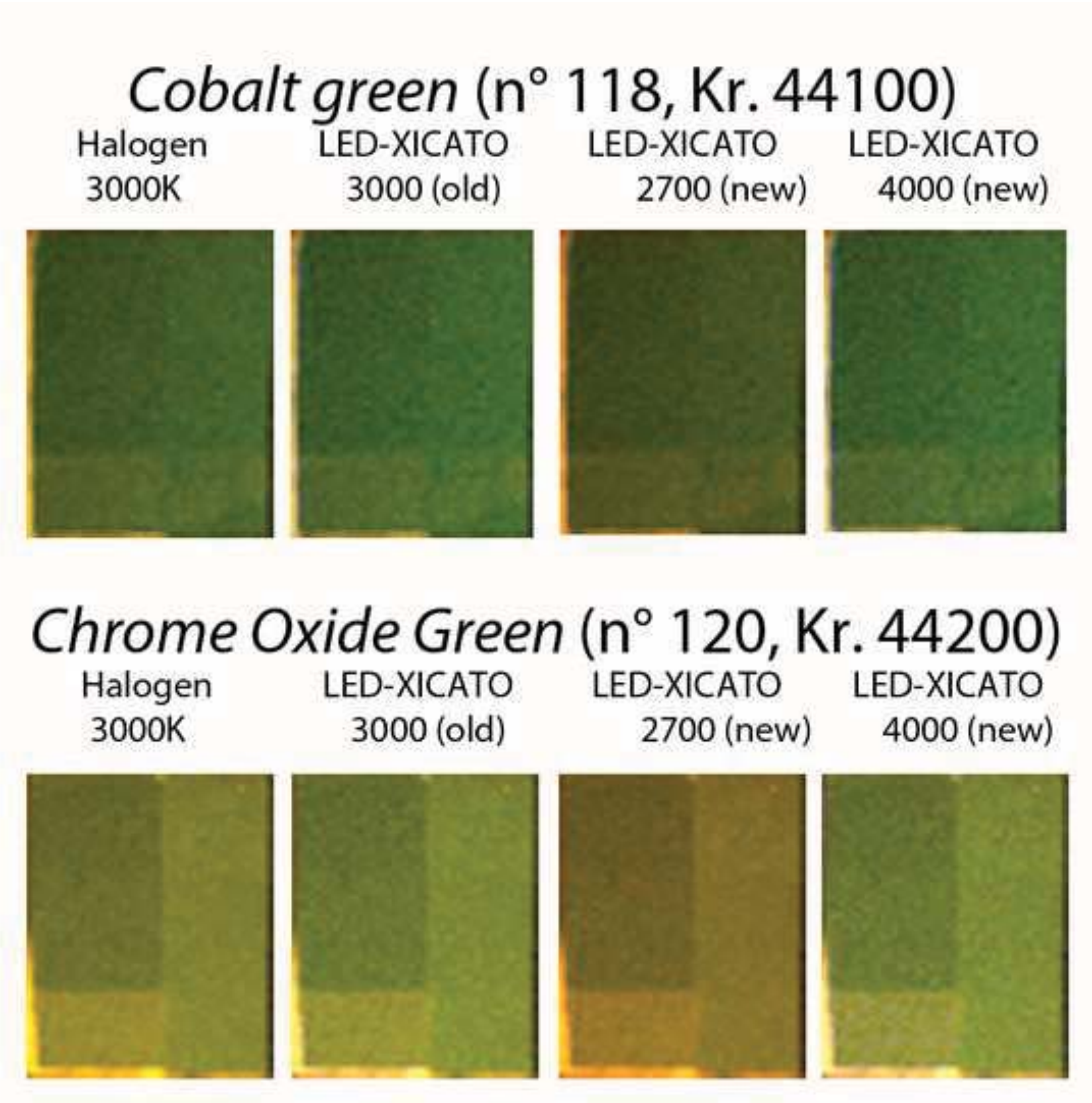

Figure 8

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Figure 9

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