



Separating pigments and fillers from the polymer matrix in acrylic colors subjected to natural aging

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Abstract Upon aging and exposure to ambient conditions, acrylic colors get dry and the degree of polymerization of the polymer matrix increases due to progressive cross-linking. When interested in studying acrylic colors, separation of the different components, namely matrix, pigments, and fillers, may be particularly useful for their identification and characterization. In the case of aged acrylic colors, as found in artworks themselves or in materials present in artist studios, the separation approaches requiring chemical treatments of fluid samples cannot be applied. To overcome this limit, here a controlled combustion strategy is developed for eliminating the polymer matrix from the color and then recovering a powder made of pigments and fillers, which is analyzed by optical spectroscopy and demonstrated to display the same chromatic/chemical properties of the original color. As a case study, the new method is successfully applied to acrylic colors used by the Italian artist Domenico “Ico” Parisi (1916–1996), found in the original tubes in his studio.

1 Introduction

In the field of cultural heritage, the study of the materials of artworks in terms of chemical composition and physical properties often gives worthy insights in view of conservation, restoration of deteriorated objects, and in general for art history studies. Optical spectroscopy offers a wide variety of techniques for in situ, non-invasive, sensitive analysis, and in recent years has been applied to many art objects and materials. In the literature, the capability of different analytical techniques in characterizing the pictorial materials has been discussed [1–6]. Nonetheless, when acrylic colors are concerned, the separation of the different components, first of all the pigments from the polymeric matrix, is often a fundamental step in view of their identification and study. Certainly, when acrylic colors are subjected to aging, as in the artworks or on the palette or in the original tubes by the artists, separation can become difficult, being often based on specific treatments of fluid colors [7, 8] or on rather complex techniques, e.g., the analytic pyrolysis [2, 7]. The availability of an easier, more straightforward, and more widely applicable separation method, then enabling a comprehensive spectroscopic analysis of the color components, should therefore be worthy in several cases. For example, when it is forbidden to directly sample a cross section from the artwork, the comparison between the data acquired on the original pigment separated by the filler with our method and the data obtained by non-invasive analyses on the artwork gives useful information of materials if a restoration is planned.

Here, we present a simple separation method consisting of a controlled thermal treatment of acrylic color samples leading to the combustion of the polymer matrix and to the recovering of the original pigment. The strategy is highly versatile and applicable even in the case of aged colors, where the polymer matrix is crosslinked and, as such, difficult to treat by the conventional chemical techniques. The controlled combustion of the acrylic paints is carried out using an apparatus for thermogravimetric analysis (TGA), equipped with a Fourier transform infrared (FTIR) spectrometer which permits to monitor the species produced during the thermal degradation process. The spectroscopic analysis of aged acrylic colors is carried out by diffuse reflectance (DR) in the ultraviolet–visible–near infrared (UV–Vis–NIR) spectral range and by attenuated total reflection FTIR (ATR-FTIR) in the mid-IR range, before and after applying the thermal treatment to different samples, and it demonstrates the full reliability of the method. Three aged colors are analyzed, namely Raw Siena (pigment PBr7), Cobalt Blue (pigment PB28), and Phthalocyanine Green (pigment PG7), as found in the studio by Ico Parisi, an Italian artist of the XX Century.

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2 Materials and methods

Different acrylic colors used by Ico Parisi, collected in his studio as bulk dry materials and untouched since the 1970 s, have been studied. The first color is Raw Siena made by Liquitex, an acrylic polymer matrix containing the inorganic pigment PBr7 (various Fe oxides). The second one is a Cobalt Blue by Liquitex, which contains the inorganic pigment PB28 (Co aluminate blue spinel, CoAl_2O_4); the good preservation of the tube permits to recover some fluid samples, already analyzed [8], but, for the purpose of the present study, we took some aged, dry samples. The third color is Phthalocyanine Green, containing the organic pigment PG7 (chlorinated Cu-phthalocyanine). It is known [9] that Liquitex used aqueous acrylic emulsions with principally two different mixtures of polymers: in earlier times a blend of methyl methacrylate (MMA) and ethyl acrylate (EA) that polymerize in p(EA/MMA), and later a blend of MMA and *n*-butyl acrylate (nBA) that polymerize in p(nBA/MMA).

The physical process designed and applied to all samples to eliminate the polymer matrix consists of the polymer combustion by a controlled thermal treatment. A small amount of about 10 mg of the original color was put into an alumina sample holder of a TGA apparatus Mettler-Toledo TGA/DSC1 STARe SYSTEM and subjected to a controlled heating ramp. Such a sample amount is enough for reliable treatment and analysis; in some cases, when studying real artworks, 10 mg could be too much, but this depends on the artwork worth, type, size, and state of conservation. The treatments were carried out from 50 to 350 °C at 5 °C/min, at constant air flow (mL min^{-1}); the process was repeated with a ramp up to 850 °C at 5 °C/min on both the same samples already subjected to treatment and on new samples. To better understand the process occurring during TGA, the release of different products was monitored by analyzing the gaseous emissions from the TGA by a FTIR spectrometer during the entire TGA process. FTIR spectra were registered with a Thermo Fisher Nicolet™ iS20 spectrometer, in the region between 4000 and 650 cm^{-1} (16 scans, 4 cm^{-1} resolution spectra), collecting about 4 spectra per minute.

For the spectroscopic studies of the colors before the heat treatments, all the bulk samples were analyzed directly as recovered. In one case, the Phthalocyanine Green color, the original color sample was too bulky and irregular, so that it looked almost black and DR resulted featureless. It was therefore used as a sort of pencil on a piece of paper and the DR measurements collected on the colored paper (then using white paper as a reference); this strategy gave very good spectra. For all the pigment powders obtained after heat treatment, thin films were deposited for spectroscopic analysis: at first, a dispersion of the powder was prepared in 5 ml of tetrahydrofuran and sonicated to obtain a homogeneous suspension; then, thin films were deposited by drop casting on glass slides, with the possibility of tuning film thickness by repeated drop depositions.

DR spectra were collected in the UV–Vis–NIR range (300–2500 nm) with 1 nm step by using a PerkinElmer Lambda 900 spectrometer, equipped with a 15 cm integrating sphere; for all the colors, the samples prepared on glass substrates were mounted on one of the sphere ports to collect the total reflected light (diffuse + specular), checking the full reproducibility of the measurements and performing the proper background correction. ATR-FTIR spectra were collected in the mid-IR range (600 to 4000 cm^{-1}) with 1 cm^{-1} resolution and averaging 8 scans, using a PerkinElmer Spectrum 100 instrument equipped with a diamond crystal, a KRS5 beam splitter, and a DTGS detector.

3 Results and discussion

The DR spectra of the Raw Siena color, before and after the thermal treatment up to 350 °C, are reported in Fig. 1a. The broad absorption over the complete Vis range corresponds to the typical response of brown colors, including, e.g., ochre, with Fe^{3+} -related broad bands around 650 nm and 850 nm [10] (minima in the DR spectrum, corresponding to absorption maxima). In the NIR, the typical low intensity bands due to the polymer matrix [8, 11, 12] are visible before treatment around 1700 nm, 1900 nm, and 2200 nm, related to the second overtones of strong chemical bonds like –CH and –OH. After the sample treatment, the same spectrum is clearly observed in the UV–Vis range, while the response of the polymer in the NIR range is no longer detectable. The chemical and chromatic properties of the Raw Siena color are therefore preserved by the thermal treatment, which, on the contrary, is demonstrated to lead to the successful elimination of the acrylic polymer. Figure 1b shows the ATR-FTIR spectra of the same Raw Siena samples, before and after the thermal treatment, definitely confirming the elimination of the polymer component after the thermal treatment. Indeed, the characteristic sharp peak at 1740 cm^{-1} , attributed to the stretching mode of the $\text{C}=\text{O}$ bond of the acrylic group [13], as well as several minor peaks at lower wavenumbers and wider bands at higher wavenumbers, again related to the polymer matrix [8], are strongly reduced. Some bands are still detected, to be attributed to inorganic fillers (in particular calcite [8, 14, 15], with the known three main peaks at 713 cm^{-1} , 874 cm^{-1} , and 1400 cm^{-1}).

By applying the same method to the Cobalt Blue color, some differences in the spectra collected before and after treatment are observed, as illustrated in Fig. 2. The DR spectrum of the untreated sample in Fig. 2a, full line, shows the known response in the UV–Vis, with a broad band displaying a minimum around 400 nm, a sharp peak at 480 nm, and a composite deeper band from 550 nm to about 680 nm, where the sharp edge is observed [11]. In addition, the NIR band from about 1000 to 1800 nm is detected, also attributed to Cobalt Blue and masking most of the polymer-related NIR response [11].

After sample treatment at 350 °C, the sample looked like a black powder and indeed the UV–Vis spectrum shows some differences (dashed line). The most relevant one is an altered line shape, with a monotonic background in the region of the two main bands, from about 400 to 500 nm, as well as between 700 and 1000 nm, where the absorption edge results much more smoothed; in

Fig. 1 **a** Diffuse reflectance spectra and **b** ATR-FTIR spectra of Raw Siena aged acrylic color, before (full lines) and after (dotted black lines) the heating ramp up to 350 °C; the step at 860 nm in **a**) is an instrumental artifact

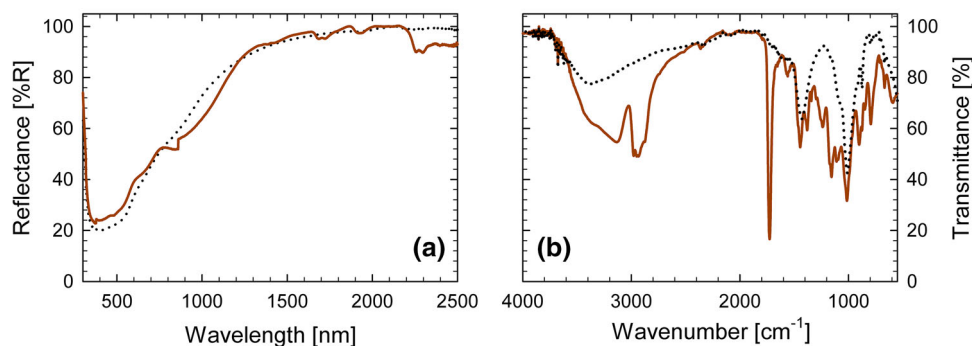
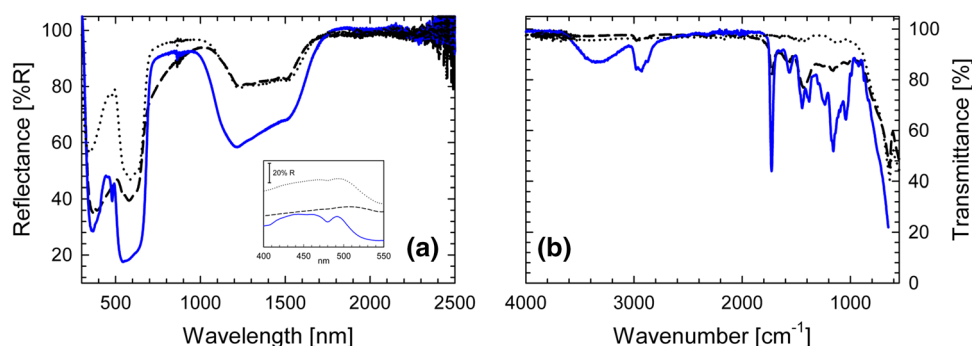


Fig. 2 **a** Diffuse reflectance spectra and **b**) ATR-FTIR spectra of Cobalt Blue aged acrylic color, before any treatments (blue full lines), after the heating ramp up to 350 °C (black dashed lines), and after the heating ramp up to 850 °C (black dotted lines); the inset in **a**) shows the region around the peak at 480 nm, discussed in the text; the spectra are shifted with respect to each other for sake of clarity



addition, the 480 nm peak disappeared (see inset). On the contrary, the typical NIR band of Cobalt Blue between about 1000 nm and 1700 nm remains almost unchanged (remind that absolute values are meaningless in DR spectra of highly diffusive materials). In the ATR-FTIR spectra of the same samples, reported in Fig. 2b, after thermal treatment all the polymer-related peaks are strongly reduced, indicating partial degradation of the polymer matrix (the filler-related bands are still clearly detectable). In other words, the polymer combustion occurs, together with some other phenomena altering the sample response in the visible range. The most likely attribution of the spectra modification lies in the formation of carbon black during heating, indeed a common process. Trying to solve the problem, contemporarily looking for a support to this hypothesis, a higher temperature treatment up to 850 °C was performed on both the already treated sample and a new Cobalt Blue sample, with the aim of inducing the total combustion of the matrix and carbon black sublimation. At first sight, the new, high-temperature process leads to a blue coloration of both samples, i.e., their color, lost after the 350 °C treatment, is back. As a quantitative confirmation, the results of the spectroscopic analysis of the already treated sample are reported in Fig. 2 as dotted curves. (High-temperature treatment of the new, untreated sample gives exactly the same results.) After the 850 °C treatment of the sample, the DR spectrum is now matching with the one collected before any treatment also in the UV–Vis range: The line shape between 400 and 500 nm is recovered, as well as the sharp edge around 680 nm. Moreover, the two main bands are clearly detected at about 400 nm and from 550 to 680 nm (the latter with the components much better resolved), together with the tiny sharper peak at 480 nm (see inset). For this sample, after the high-temperature treatment the polymer-related response in the ATR-FTIR spectra is absent; at the same time, the peaks attributed to calcite are also reduced, since, given the high temperature of the treatment, calcite is partially converted into CO₂ and released [16].

The results in Fig. 2 confirm the success of the method for Cobalt Blue, where the polymer matrix is eliminated, even when crosslinked, just by heating the color sample at a higher temperature. In other words, considering the results in Figs. 1 and 2, the proposed method is fully reliable, after a proper tuning of the heating treatment for the specific colors, as could be expected. Indeed, given the variety of the industrial formulation produced since the late XIX Century, the polymer blend can be different from acrylic paint to acrylic paint, and this may alter their processability.

To fully support the hypothesis about polymer degradation, carbon black formation and subsequent sublimation, the analysis of the products formed during the color treatment by TGA and monitored by FTIR [17] is presented. In Fig. 3a, the TGA curve related to thermal degradation of Cobalt Blue is shown (full line), together with its first derivative (dotted line). In the first 80 min of treatment, a first weight loss occurs, identified by the peak at 357 °C (59 min) in the derivative and consisting of about 90% of the total weight loss. Looking at the corresponding FTIR spectrum recorded after 59 min (Fig. 3b), three peaks at 2976 cm⁻¹, 2950 cm⁻¹, and 1744 cm⁻¹ are detected, to be attributed to the acrylic polymer degradation, as well as the typical peaks of CO₂ (2359 cm⁻¹ and 2312 cm⁻¹), indeed a combustion product. After longer times and temperatures approach 850 °C, a further weight loss occurs (peak at 648 °C in the derivative, 120 min), to be mainly related to sublimation of C black and, possibly, to the filler

Fig. 3 **a** TGA curve (full line) obtained on Cobalt Blue aged acrylic color by a ramp up to 850 °C and its derivative (dashed line); **b** two of the FTIR spectra collected during the treatment, namely at 357 °C and at 648 °C (see labels)

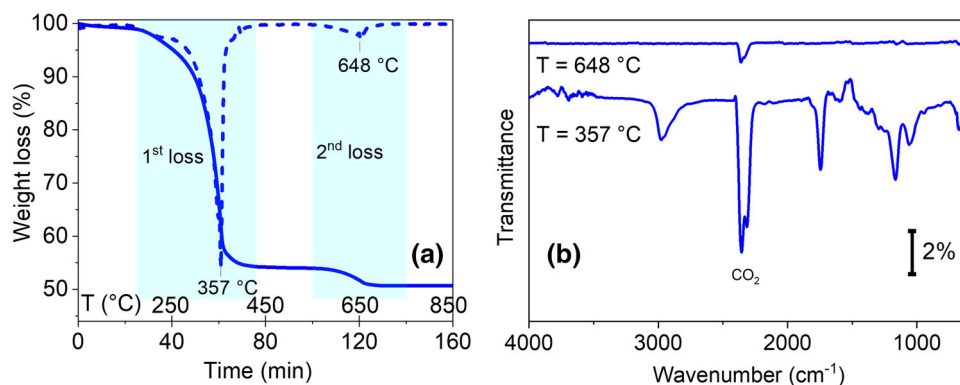
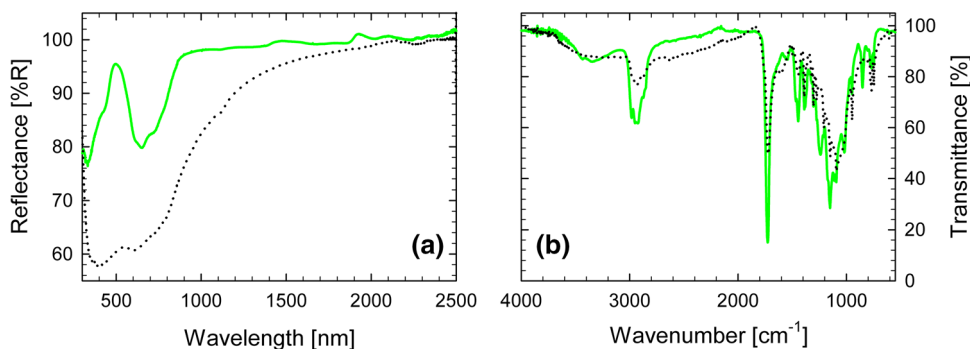


Fig. 4 **a** Diffuse reflectance spectra and **b** ATR-FTIR spectra of Phthalocyanine Green aged acrylic color, before (full lines) and after (dotted black lines) the heating ramp up to 350 °C



decomposition (CaCO_3 indeed at high temperature decomposes [16] as $\text{CaO} + \text{CO}_2$); this is fully confirmed by the corresponding FTIR spectrum recorded after 120 min (Fig. 3b), where only the CO_2 peaks are still visible.

To go deeper and explore possibilities and limits of the method, aged acrylic colors containing organic pigments, damageable upon heating, were also subjected to the heating treatment and then analyzed by DR and ATR-FTIR spectroscopies. In Fig. 4, the DR and ATR-FTIR spectra of the Phthalocyanine Green color, containing an organic pigment, are shown, as collected before and after the heating ramp up to 350 °C. After the treatment, the UV–Vis response presenting the characteristic bands of the phthalocyanines, including the weak band at 1100 nm typical of Cu-phthalocyanine acrylics and related to electronic transitions of the Cu ions [18, 19], is smoothed and the overall line shape altered; in other words, the same effects are observed as for Cobalt Blue after the 350 °C treatment. In the DR spectrum after treatment the response of the polymer matrix in the NIR range is almost undetectable, while it is still present in the ATR-FTIR spectrum, even if reduced in intensity with respect to the other peaks. The thermal degradation of the polymeric matrix may therefore have started and, possibly, the pigment itself deserves partial degradation contributing to the formation of carbon black. As a check of the strategy applied to Cobalt Blue, the Phthalocyanine Green color was finally treated by TGA up to 850 °C; in spite of the high stability of phthalocyanine, the remaining sample is a black powder, demonstrating that the high-temperature treatment induces full combustion of the pigment itself, carbon black formation and sublimation. The TGA curve (Fig. S1 in the Supporting Information) shows that at 850 °C almost the whole sample has been degraded and combusted (weight loss of about 95%), as further demonstrated by the corresponding FTIR spectra, therefore fully supporting the present discussion. In the Supporting Information (see Fig. S2), the analysis of another organic-based acrylic color is reported as a further example, as it shows a similar behavior demonstrating pigment degradation.

4 Conclusions

A completely new and feasible method is proposed here to separate pigments and fillers from aged acrylic colors where the polymers in the matrix are crosslinked and for which chemical methods fail. Even if the method proposed here is invasive, the original mixture of pigment and fillers is recovered as a powder and can be studied, and possibly also reused, e.g., in view of restoration. In addition, our technique, invasive but applied to very small amount of colors of historical interest, may add extremely worthy details to the results obtained directly on artworks by non-invasive techniques.

The comparison between DR spectra and ATR-FTIR spectra recorded on the original samples and those recorded on the powders extracted after the treatment shows that for colors containing inorganic pigments, the chromatic/chemical properties are fully preserved, therefore completely assessing the method. In any case, the treatment parameters need to be tuned for each specific commercial color, where the polymeric matrix may be different. When colors containing organic pigments are concerned, after

thermal treatment the spectra can be altered by the formation of carbon black, which cannot be easily removed, as well as by the pigment degradation. For colors containing organic pigments, therefore, separation and analysis by different, more complex techniques are necessary. To show direct application of the new method to real cases, different acrylic colors recovered as dry, hard samples from the studio by Domenico “Ico” Parisi have been treated and their spectroscopic properties successfully studied.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1140/epjp/s13360-022-03117-4>.

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Data Availability Statement The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request. This manuscript has associated data in a data repository. [Authors’ comment: Our experimental data can be provided to researchers working in the field interested in discussion or collaboration.]

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