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Material Characterization: A Contribution to Reduce Fake Practices in Contemporary Prints

ABSTRACT

Prints are one of the most widespread artistic processes. Owing to their relatively simple manufacture, prints are easy to reproduce and falsify, and the ensuing danger of forgery affects some contemporary artists. Given this problem, the capability to differentiate and distinguish between originals, fakes, and frauds is improved by better knowledge both of the chemical composition of the constituent materials of prints (inks, papers, and pencils), and the classical approach to their manufacture, based on historical and aesthetic information obtained through catalogues raisonnées.

We studied two print series of a contemporary artist, including prints of different origins. Material characterization using Fourier transform infrared spectrometry (FTIR) and scanning electron microscopy (SEM), together with printing order determination by micro-Raman spectroscopy, made it possible to differentiate original from nonoriginal prints and to establish the relationship between the different elements of each print. The methodology proposed is micro- or nondestructive and yields useful information to contribute to the resolution of an important part of doubtful attributions.

INTRODUCTION

Prints are based on the production of multiple versions of an original design. The design consists of an image stamped on a support. Sticky ink is spread on a matrix, where the design had previously been made; this ink is then transferred by pressure to the paper. When a colored impression is made, the artist usually prints each separate color one after the other.

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In view of their popularity and production, prints are widespread on the artistic market. Due to this popularity of prints, a huge number of forgeries and fakes have appeared. Whereas copies are not misattributed, fakes and frauds are made with willful deceit. Nowadays, the most widespread procedure to differentiate originals from forgeries is artistic style, as described in catalogues raisonnées (Gallego 1996; Zweite 1999; Warncke 1995) and it is interesting to complement this information by adding the chemical composition of the constituent materials used and the printing order. Moreover, especially when very common materials are used, it is important to identify the order.

The aim of this study is the material characterization of prints and, based on the information obtained, the differentiation between originals and copies, fakes, and reproductions. The study is applied to a real print series and comprises two sections. The first part is based on the establishment of the physico-chemical composition of prints' constituent materials and aims to obtain discriminative criteria among the different inks and the papers used as support. The second part is based on the determination of the printed order of inks in engravings.

EXPERIMENTAL

Samples

Two different print series were studied, *Boys and Bike* and *Elephant*. These series are by a contemporary artist, Elies Plana. Both series are composed of unnumbered prints produced using relief processes. Linoleum matrices and different colored inks were used.

The areas analyzed in the two different series are: *Boys and Bike*: blue, yellow, and black particles, and the paper (fig. 1); and *Elephant*: gray monolayer, yellow monolayer, and the overlapped gray-yellow area (fig. 2).

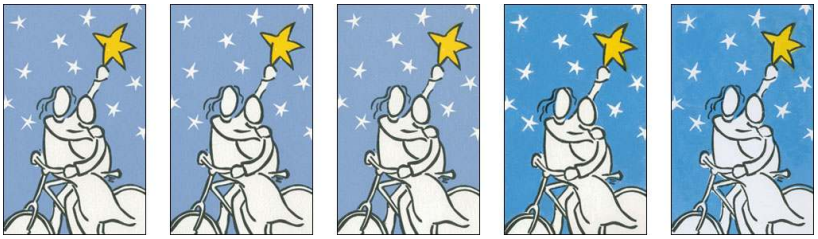

Fig. 1. The five prints examined from the series *Boys and Bike* (Elies Plana).

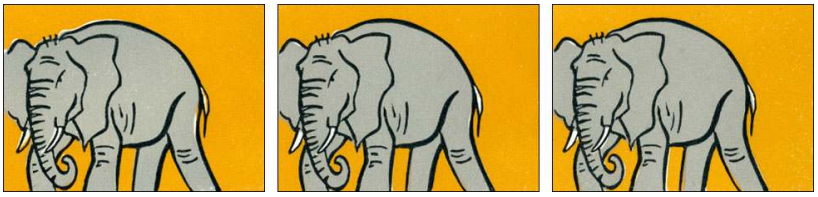

Fig. 2. The three prints examined from the series *Elephant* (Elies Plana).

Apparatus

This study was conducted using scanning electron microscopy (SEM) (to study inorganic materials), Fourier transform infrared spectroscopy (FTIR) (to study organic and inorganic materials), and Raman spectroscopy (to study the printing order). All of these are well-established techniques in museums and centers related to the study of artworks (Romero and Ferrer 1999; Bruni et al. 1999; Schaening et al. 2004; Ferrer and Vila 2006; Vila et al. 2006; Wise et al. 2004).

Scanning electron microscopy (SEM): The scanning electron microscope used was the Cambridge Instruments Stereoscan 360, equipped with the Inca Energy 200 microanalysis apparatus. The spectrum was recorded with conditions of 20 kV, 1 nA, and 20–35 mm distance from sample to detector. The areas analyzed were between 20 x 20 and 50 x 50 μm. All results were processed using Oxford Inca software.

Fourier transform infrared spectroscopy (FTIR): A Bomem MB–120 Fourier transform infrared spectrometer, equipped with a Spectra-Tech Analytical Plan microscope, was used with the diamond cell as a sample holder. The spectrometer has a KBr beamsplitter and a glowbar source. The microscope has its own mercury-cadmium-telluride (MCT) detector refrigerated with liquid nitrogen. The spectrum was recorded between 4000–720 cm^{-1} with a resolution of 4 cm^{-1} and an accumulation of one hundred scans. The areas analyzed were around 100 x 100 μm in size. All results were processed using Grams 32 software

Raman spectroscopy: The Raman spectrometer used was a Jobin Yvon T64000 instrument equipped with an argon ion laser as illumination source. The T64000 consists of a subtractive dispersion double monochromator combined with a spectrograph that disperses the scattered light onto a bidimensional charge-coupled device (CCD) detector cooled at 140 K. The Raman instrument is coupled to a BH2 Olympus optical microscope, and the collection optics system is used in the backscattering configuration. The laser frequency is the 514.5 nm line, and the laser power at the sample was 1.5 mW (50x) and 0.7 mW (100x). The laser spot diameter on the sample, obtained with 50x objectives, was about 2 μm. Spectra were recorded with an acquisition time of sixty seconds and two scans. The samples had been analyzed without any previous treatment or preparation. All results were processed using Grams 32 software.

Sampling and Sample Preparation

The sampling procedure was done with fine tools (tungsten needles and scalpels) under the magnification lenses (50x) to obtain small amount of fibers and ink particles. These fiber and ink particles were around 100–200 μm in size; while this procedure is microdestructive, it does not really modify the artwork.

For SEM analysis, the particles removed from the prints were deposited on carbon adhesives stuck on stubs of aluminum, and then recovered by carbon.

For FTIR analysis, it is very important to correctly separate ink from the fibers. The particles extracted from the prints were laid on the diamond cell, which was covered by another cell of the same material and pressed in order to obtain as thin a layer as possible to facilitate infrared radiation transmission.

The region studied using Raman spectroscopy was viewed directly and analyzed through the 50x or 100x magnification views of the microscope (Wise et al. 2004; Burgio et al. 2000; Vila, Jawhari, and Garcia 2007). A nondestructive sampling technique and previous treatment of the sample are not required.

Due to the minimal size of the fragments extracted, and the potential heterogeneity of the material, triplicates of each sample were analyzed to ensure representative results.

RESULTS AND DISCUSSION

This study is focused on the analysis of inks, papers, and the printing order of inks as the basis to discriminate between different prints of a series.

In previous studies, the chemical composition and the discriminative capability of this approach was evaluated by analyzing different fine-quality papers as well as black and colored inks of different brands. Database and discriminative criteria of the different materials studied have been published (Vila et al. 2007; 2007a; 2010). It was expected that a similar percentage of success would be obtained when the same methodology was applied to two unstudied series of prints. Two different series, *Boys and Bike* and

Elephant, by the contemporary artist Elies Plana were studied for this purpose.

BOYS AND BIKE SERIES

In this first case, five prints were studied. One of these prints is of known origin and was used as reference. The other prints show some stylistic and visual differences (fig. 1). Samples from the blue, yellow, and black areas, together with paper fibers, were analyzed by SEM and FTIR.

Original print

Blue particles: The infrared spectra of particles from the print's blue area show basically the characteristic bands of cellulose (3337, 2900, 1638, 1430, 1373, 1320, 1247, 1156, 1107, 1063, and 898 cm^{-1}) and the carbonyl peak at 1732 cm^{-1}. SEM results show the presence of calcium, aluminum, and a large amount of titanium.

Yellow particles: The infrared spectra obtained from yellow particles are similar to those obtained on the blue area: the characteristic bands of cellulose and the carbonyl peak at 1732 cm^{-1}. SEM results show a high amount of titanium and, in a smaller proportion, calcium, aluminum, and chloride.

Black particles: Particles extracted from the print's black area show, again, infrared spectra similar to the yellow and blue particles. Results show the presence of cellulose and the 1732 cm^{-1} carbonyl band. SEM results, in this case, show the presence of calcium, silicon, and sulfur.

Paper fibers: The infrared spectra obtained from fibers of the print paper show the characteristic cellulose bands; SEM results show the presence of calcium.

Prints 2 and 3

Analysis obtained from prints 2 and 3 of the blue, yellow, and black particles and paper fibers show the same composition as the original print. With the naked eye, these two prints match aesthetically to the original print.

Print 4

Blue particles: The infrared spectra of particles from the blue area show detailed bands at 2925 and 2853 cm^{-1}. It also shows peaks at 1733, 1462, 1032, 1012, 940, 912, and 874 cm^{-1} and, in a smaller proportion than in the blue area of the original print, some peaks that could be related to the cellulose of the paper. SEM results show a high amount of titanium and also the presence of zinc, aluminum, silicon, calcium, sulfur, and sodium.

Yellow particles: Results obtained from the infrared spectra of yellow particles show, together with the cellulose bands, characteristic peaks at 1741, 1536, 1502, 1478, 1374, 1336, 1281, 1259, and 875 cm^{-1}. SEM spectra contain a high amount of aluminum and also silicon, sulfur, calcium, chloride, and titanium.

Black particles: The infrared results from black particles show the typical bands at 2925 and 2852 cm^{-1} related to CH_2-CH_3 and the carbonyl band at 1741 cm^{-1}. The 2013 and 1040 cm^{-1} peaks are also present and are characteristic of phosphates. In the infrared spectra, some other small peaks also appear, and these are probably related to the cellulose. SEM results show, basically, presence of phosphorous and calcium, and this, together with the infrared results, corroborates the presence of bone black pigment (calcium phosphate).

Paper fibers: The infrared spectra of paper show the cellulose characteristic peaks. SEM results contain calcium.

Print 5

Blue particles: Infrared and SEM results obtained from the blue area of print 5 show the same results as those obtained from the same area of print 4.

Yellow particles: The infrared spectra from yellow particles show the same bands obtained in print 4 (1741, 1536, 1502, 1478, 1374, 1336, 1281, and 1259 cm^{-1}) together with the typical cellulose bands and a large amount of calcium carbonate (1429 and 875 cm^{-1}). SEM analyses corroborate the infrared results with the presence of a high amount of calcium and the elements detected on the yellow area of print 4 (aluminum, silicon, sulfur, chloride, and titanium).

Black particles: The infrared spectra, obtained from black particles extracted from print 5, show the same bands of CH_2-CH_3, carbonyl and phosphates identified on print 4. On print 5 the presence of calcium carbonate is also detected. SEM results show, basically, phosphorous and calcium that, as in the previous print, corroborate the presence of a bone black pigment in the ink composition.

Paper fibers: The infrared spectra of paper fibers show the characteristic bands of cellulose and also a large amount of calcium carbonate. SEM results contain calcium.

Distinguishing Criteria for *Boys and Bike* Prints

The infrared and SEM results from the four areas analyzed (blue, yellow, and black particles, and the paper fibers) do not show differences between the original print and prints 2 and 3; therefore, from the material point of view, they could be considered as part of the original series.

Compared with the original, print 4 shows some differences in the results obtained from the blue, yellow, and black areas by infrared and SEM. Otherwise, the paper composition of print 4 seems to be the same as that used in the original print. In this case, print 4 would not belong to the original series but was probably printed onto an equivalent paper to that used initially.

The SEM and infrared results from print 5 were also compared with those obtained from the original print. Print 5 shows differences in the three colored areas and also in the paper. Therefore this print does not belong at all

to the original series. However, comparing results obtained from prints 5 and 4, it can be observed that the ink composition (on the three areas) is the same in both prints, although in some cases print 5 shows the presence of calcium carbonate. This difference probably comes from the paper substrate of print 5, which contains a larger amount of calcium carbonate. Despite the fact that both prints (4 and 5) were probably made with the same types of ink, neither of them is original.

In summary, the study of the material composition of prints makes it possible to establish which are originals (2 and 3) and which are not (4 and 5) as well as the similarities between the elements of each of the groups.

This methodology, based on the use of SEM and FTIR, does not identify all of a print's components, but it provides enough information to differentiate, in general, between prints of an original and a nonoriginal series.

ELEPHANT SERIES

In this second case, three different prints were analyzed. One of these prints is of known origin and was used as reference. The three prints are stylistically and aesthetically equivalent (fig. 2).

In the *Elephant* series, the three prints show the same chemical composition. For this reason the chemical information obtained about the component materials is complemented by the determination of the printing order of the inks. The knowledge of this order will contribute to establishing which prints were printed following the procedure of the original series.

Different techniques were used to establish the relative position of the different ink layers on the prints.

The use of SEM to analyze the inks' strata requires the extraction of a small amount of sample; thus, it is a destructive technique and, in the end, the results obtained are not quite satisfactory.

On the other hand, the laser-induced breakdown spectroscopy technique does not require a sample extraction. However, due to the laser ablation process, results are also destructive (a 1 mm crater appears on the surface of the print).

Finally, Raman spectroscopy does not need a prior sampling process and analyses can be performed directly on the artwork. Due to the low laser power used, it can be classified as a nondestructive technique.

The proposed procedure to identify the printing order, using Raman spectroscopy, is based on spectral determination: first of the monochrome areas, and then of the overlaid area. Data treatment of signals from the different inks (standardization, normalization, and comparison using a "paired test") was done to establish the relative position of the different ink layers on prints.

Gray monolayer: The gray ink Raman spectra contain two broad bands at 618 and 450 cm^{-1}. The results obtained for the three prints are the same. The mean Raman intensity signal (similar in both peaks) is around 61.8 ±12.2 cps.

Yellow monolayer: The yellow ink shows Raman spectra with sharp peaks. It includes a 1600 cm^{-1} band with a very important Raman intensity signal and other important sharp peaks at 1400, 1289, 1259, and 1249 cm^{-1}. The results obtained for the three prints are similar. The mean Raman intensity signal for the 1600 cm^{-1} peak (reference band for this ink) is around 1554.4 ± 446.5 cps.

The relatively important dispersion on the registered intensities (in both monolayers) is a consequence of the lack of instrument stability, together with heterogeneity of the print's materials.

Overlapped gray-yellow area: The three prints have the same behavior in the overlapped gray-yellow areas (fig. 3). Results obtained from the monolayer ink show that the intensity of the Raman signal from the gray ink is smaller than the one from the yellow ink. On comparison of the intensities obtained in the gray-yellow overlapped areas of the reference signals (once it has been standardized and normalized), only eight of sixty measurements indicate that yellow ink is on the surface. The other fifty-two measurements indicate that gray ink is on top. The explanation of these eight measurements can be related to the heterogeneous distribution of inks on the soft paper surface. By using a paired test to compare the complete set of the dif-

Fig. 3. Detail (20-60x) from the area of overlapped inks in a print from the *Elephant* series.

ferences between the analyzed intensities of the reference peaks of each ink, it can be established that, with a probability of greater than 99%, the yellow ink was printed before the gray ink. These results have been confirmed by the artist.

To summarize, micro-Raman spectroscopy is a nondestructive technique capable of determining the printing order on graphic artworks. This information will contribute to their characterization as original versus nonoriginal.

CONCLUSION

The physico-chemical characterization of the component materials of prints, together with the establishment of the printing order of the different inks used, is an important contribution to the process of differentiating among original prints and copies, fakes, and reproductions.

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