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Original article

Identification of chromogenic colour photographic print brand by fiber optical reflectance spectroscopy and statistical analysis

Aurélie Tournié[a,1], Philippe Carré[b,2], Christine Andraud[a,1], Clotilde Boust[c,3], Bertrand Lavédrine[a,*,1]

[a] Centre de Recherche sur la Conservation (CRC, USR 3224), Sorbonne Universités, Muséum national d'Histoire naturelle, Ministère de la Culture et de la Communication, CNRS, 36, rue Geoffroy-Saint-Hilaire, 75005 Paris, France
[b] Laboratoire XLIM, UMR CNRS 7252, Université de Poitiers, Département XLIM-SIC, UMR CNRS 7252, Futuroscope, Bât. SP2MI, Téléport 2, 11, boulevard Marie-et-Pierre-Curie, BP 30179, 86962 Chasseneuil cedex, France
[c] Centre de Recherche et de Restauration des Musées de France, Palais du Louvre–Porte des Lions, 14, quai François-Mitterrand, 75001 Paris, France

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ABSTRACT

Over the last quarter of the 20th century, chromogenic colour process was the predominant photographic process on the market and has been used by the professionals, artists and the public at large. Today it represents a precious part of our photographic heritage. Unfortunately, some colour prints are very fragile and discolour during display or storage faster than others; it is well known that some brands and production times correspond to different thermal and light-ageing behaviour for prints. Being able to identify a colour process, a brand and possibly a period of printing may inform us not only about the provenance of the artefact but also its sensitivity to the environment. With this aim, this paper investigates the possibility of using near-infrared spectral signatures of chromogenic colour photographs combined with statistical analysis to identify photographic paper manufacturers. To carry out the study, a batch of a few hundreds of amateurs colour photographs printed on Agfa, Fuji or Kodak paper produced from the 1960's to the 2000's was gathered from private and public collections. Non-invasive fiber optical reflectance spectroscopy (FORS) in the range of 1000–2500 nm was performed on those images in order to implement a reflectance spectra database. Then statistical data treatments were tested to evaluate the possibility of retrieving a print manufacturer with the lowest error possible. The use of linear discriminant analysis (LDA) combined with principal component analysis (PCA) allows reaching from 82 to 96% of correct identification depending on the paper type. This shows a possibility of implementing automated attribution procedures for chromogenic colour photographic prints.

1. Research aims

This research aims to evaluate the possibility of using the near-infrared spectral signatures of chromogenic colour photographs combined with different statistical approaches to identify photographic paper manufacturers. The study was carried-out on a batch of a few hundreds of amateurs colour photographs printed on Agfa, Fuji or Kodak paper produced from the 1960s to the 2000s that were analysed with non-invasive fiber optical reflectance spectroscopy in the range of 1000–2500 nm images in order to implement a reflectance spectra database.

2. Introduction

2.1. Classification of photographs and materials characterisation

Technical history has always been of central importance in the field of photographs conservation. Earliest publications from the 1980's dealing with preservation of photograph collections have made a great deal of photographic process identification since it provides the crucial information that will underlie all subsequent decisions about conservation. Process identification based on visual observation or microscopic inspection of the layered structure of the prints does not always allow discrimination between

* Corresponding author.
E-mail addresses: aurelie.tournie@mnhn.fr (A. Tournié), carre@sic.sp2mi.univ-poitiers.fr (P. Carré), candraud@mnhn.fr (C. Andraud), clotilde.boust@culture.gouv.fr (C. Boust), lavedrin@mnhn.fr (B. Lavédrine).
[1] +33 (0)140795300.
[2] +33 (0)549496576.
[3] +33 (0)140205652.

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different prints produced with the same process including slight variations in the chemical treatment or in the process technology. Recent issues have promoted the development of researches on "technical art history" for photographs of the 19th and 20th century including the use of analytical equipment for physical or chemical characterization. In 2000, the Getty conservation Institute launched a project [1] on photographs that resulted 13 years later in publishing online the "Atlas of Analytical Signatures of Photographic Processes". Its "purpose was to aid in the formulation of analytical questions related to a particular photograph and to assist scientists unfamiliar with analysis of photographs when interpreting analytical data" [2]. Based on the use of non invasive analytical equipment techniques such as X-ray fluorescence spectroscopy and attenuated total reflection Fourier transform infrared (ATR-FTIR), this Atlas provides reference spectra to assist the conservator, curator or scientist to identify materials – such as image material substances, binder, support – and processes in order to avoid misidentification or misinterpretation of analytical results. This was a significant step in setting a common knowledge platform that was not existing or scattered in the grey literature. Those authors indicate that the Atlas is a "living document" that should be upgraded whenever new quality data on signatures of photographic processes. However, this technical information, beyond constituent identification, does not allow to answer yet to more focused problems such as the authenticity or authorship of a particular artefact or group of artefacts. To address those issues, more specific approaches have been implemented in consisting to a precise characterization of twentieth-century photographic paper print. The study of the baryta layer – a mineral substratum coated on most of the industrial photographic paper produced from the end of the 19th century to today – has been chosen as a mean to identify the provenance of those photographic papers thanks to a fine analytical characterisation of chemical markers ratio (such as baryum/strontium) and the implementation of a database so called "barytome" [3]. Indeed the examination of the baryta layer could provide some information such as the provenance of the barium sulfate but unfortunately often not enough to solve complex issues of authenticity. Later methodological developments have encompassed a broader approach gathering the main tangible and intangible clues that are the basis of connoisseurship and include paper fiber analysis, manufacturer marking, optical brighteners and fluorescence, texture studies, elemental composition, etc. Paul Messier lead this innovative approach by investigating a batch of more than 5000 well-documented photographic baryta paper [4]. Such studies resulted in the production of a large number of data that requires a methodology in order to retrieve relevant information for identification. The development of proper algorithms is on-going in order to provide a fully automated computer-based classification system [5]. The statistical approach to extract the significance of a batch of data for characterization is very promising. Recent works have investigated the possibility of dating plain paper [6] and fibre-based photographic prints [7] by the use of a chemometric approach based on NIR spectra. That research focused on the paper support since it may contain relevant clues for discriminating one type of black and white photographic print from another while the image forming substance itself, metallic silver, might not allow to make a difference. On the contrary, for colour photographs, the image forming substances are proprietary dyes that potentially can serve as a marker of provenance (brand). So far, no study has been yet devoted for applying statistical approaches to colour photographic prints for brand identification purposes.

2.2. Chromogenic colour prints

The use of the colour photographic prints began in 1942 when Kodak introduced on the market the first negative/positive colour print process followed by Agfa in 1949. The poor quality of colour rendition, the lack of dye stability and the cost slowed down the spread of this process in its early years. Gradual improvements in colour photographic paper quality and the decrease in the cost lead colour photography to replace gradually the black and white photography in the mass market in the 60s. Over the last quarter of the 20th century, chromogenic colour was the predominant photographic process on the market and has been used by the professionals, artists and the public at large. By the 1980s, more than 95% of photographic prints market was chromogenic colour prints [8] and today it is an important part of our photographic heritage. From a technical point of view, chromogenic photography is based on silver halide technology. It uses chromogenic development, wherein the dyes that form the final image are chemically synthesized during development from colourless precursors initially present in the film layers. These precursors are known as dye couplers and this technology constitutes one of the major innovations of the chromogenic process [9]. The first supports in the 40s were baryta fiber-based paper, they were replaced by resin-coated (RC) or polyester supports in the 70s. The top surface of a print is mainly protective and usually made with gelatin and hardeners. In between this and the support, prints mainly contain three separated emulsion layers, one sensitive to red light, the second to green light and the last to blue light. Those layers form respectively the cyan, magenta and yellow layers of the print after development. The other layers in the paper print have the role of filters: gelatin to avoid dye layer bleedings and UV or coloured layer that correct imperfect dye colour absorption. During the processing, the oxidized developer, formed with the reduction of silver bromide, reacts with the adjacent molecules of colour coupler present in the layer to produce azomethinic dyes. Discovered by Rudolf Fisher in the 1910s, such a way of producing colour photographs was originally limited due to technical problems such as dye bleeding in the gelatin layers. To overcome those difficulties manufacturers devised different solutions. Agfa used couplers with long hydrocarbon chains that anchor the molecule within the gelatin layer, while Kodak or Fuji encapsulated the couplers in oily droplets. Other chemicals are present in a print, depending on technological choices made by the manufacturers. All technologies were proprietary and differ from one manufacturer to another. Furthermore all complex formulations have been improved over the last 50 years. Such technological differences for dye molecules, couplers and layer composition might help to differentiate and characterize a manufacturer and a period of production by using spectral signatures.

2.3. Chromogenic colour prints characterization

Priority in the field of technical art history focussed on black and white photography since it was the most significant part of collections and the main focus of inquiry. However since the turn of the century similar questions are being asked about colour photographs, as they are increasingly collected, especially concerning brand identification. The name of the manufacturer is often printed on the back of colour prints with sometimes the year of production, however date or names are sometimes lacking and many prints in museums are permanently mounted on a polymer or aluminium support without access to the information written on the back and no proper documentation. Actually, being able to identify a colour process, a brand or even a period of printing may inform us about the history of the artefact and also its sensitivity to the environment. It is well known that some brands correspond to different thermal and light ageing behaviours. For instance some manufacturers have improved chromogenic colour print stability in the 1980's [10]. Identifying a print manufacturer may help to define an exhibition strategy by referring to existing – or future –

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