

An investigation into the structure and color stability of Polaroid 20×24 prints

Paulina Miąsik, Sylvie Pénichon, Clara Granzotto, Ken Sutherland

The Art Institute of Chicago, 111 S. Michigan Ave, Chicago, IL 60603, USA

Corresponding author: Paulina Miąsik (paulinamiasikk@gmail.com)

ABSTRACT

Polaroid 20×24 prints, renowned for their distinctive large format and use by artists, have received limited attention within the conservation community. This study, conducted at the Art Institute of Chicago, examines the materials, structure, and stability of different generations of Polaroid 20×24 film, including Polacolor ER (P3), Polacolor Pro 100 (P6), Polacolor 7 (P7), and hybrid Chocolate prints. Utilizing a combination of non-invasive and micro-invasive analytical techniques, such as scanning electron microscopy with energy dispersive spectroscopy, Fourier transform infrared spectroscopy and pyrolysis gas chromatography mass spectrometry, the research aimed at characterizing the prints' structure and material composition, and investigates light stability through microfading testing (MFT). Complementary analyses showed some variations in the prints' structure and allowed the characterization of a specific degradation product; while comparative MFT analyses of various dye colors across generations revealed vulnerabilities to color fading. These findings contribute valuable insights into the material composition of Polaroid 20×24 prints and inform display and preservation strategies, ensuring the longevity of these culturally significant artworks.

KEYWORDS Instant Prints, Dye Diffusion, Polaroid 20×24, Polacolor, Microfading Testing, Light Stability, Polaroid Chocolate

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1. Introduction

The Polaroid 20×24 (inches, or 50×60 cm) revolutionized instant photography since the 20×24 camera, unlike smaller Polaroid formats, allowed for large-scale prints that captured exceptional detail. These qualities made it an attractive choice to notable artists such as Andy Warhol, William Wegman, Chuck Close, and David Levinthal, among many. Thanks to the Polaroid Artists Support Program [1]; artists embraced the format's combination of immediacy, size, and vibrant color to create iconic works that continue to be celebrated in fine art collections today. Despite their artistic significance, perhaps in part because of the complexity of the materials and processes involved in their creation, Polaroid 20×24 prints have received limited attention from the conservation community (Casto and Valverde, 2019; Pietsch and Gierstberg, 2016; Pénichon, 2013; Mesquit and Lemmen, 2005; Rebourt, 1997).

Research was undertaken at the Art Institute of Chicago to investigate the material and structural composition of three generations of Polaroid 20×24 color films: Polacolor ER (P3), Polacolor Pro 100 (P6), Polacolor 7 (P7), and the hybrid Polaroid Chocolate. In addition to characterizing the materials through thickness, texture, gloss and colorimetric measurements, scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), Fourier transform infrared spectroscopy (FTIR), pyrolysis gas chromatography mass spectrometry (Py-GCMS), and microfading testing (MFT) were used to investigate the nature of the materials, their layer structure, and the light stability of the prints.

2. Historical background and development of the Polaroid 20×24

The production of large Polaroid materials spanned approximately three decades, as shown in detail in Figure 1. Introduced by Polaroid Corporation in the late 1970s, the Polaroid 20×24 camera and films (Reuter, 2008, Reuter 2020) was initially conceived as a tool to demonstrate the capabilities of Polacolor 2 film during a shareholders' meeting (Bonanos, 2012).

Originally designed for smaller instant film systems, Polacolor 2 presented improvements over the previous generation of peel-apart color materials, including metallized dyes that had been developed for the Polaroid SX-70 integral film: specifically, chromium complexed azo dyes for the yellow and magenta and copper phthalocyanine for the cyan (Walworth and Mervis, 1989; Wilhelm, 1978). These dyes provided vivid and more stable colors, although the yellow dye still proved vulnerable to fading under prolonged exposure to light (Wilhelm and Brower, 1993; Adams and Baker, 1978).

With the advent of Polacolor ER (or P3) in 1980, additional modifications to the dyes further enhanced the longevity and stability of the P3 prints, offering more vibrant color reproduction, lower contrast, deeper blacks and increased saturation (Rebourt, 1997). P3 also possessed a distinctive property that the dye image layer could be separated from its support by soaking the print in warm water, enabling the transfer of the image layer onto alternative supports (Bonanos, 2012). This technique was embraced by artists to create unique Polaroid artworks.

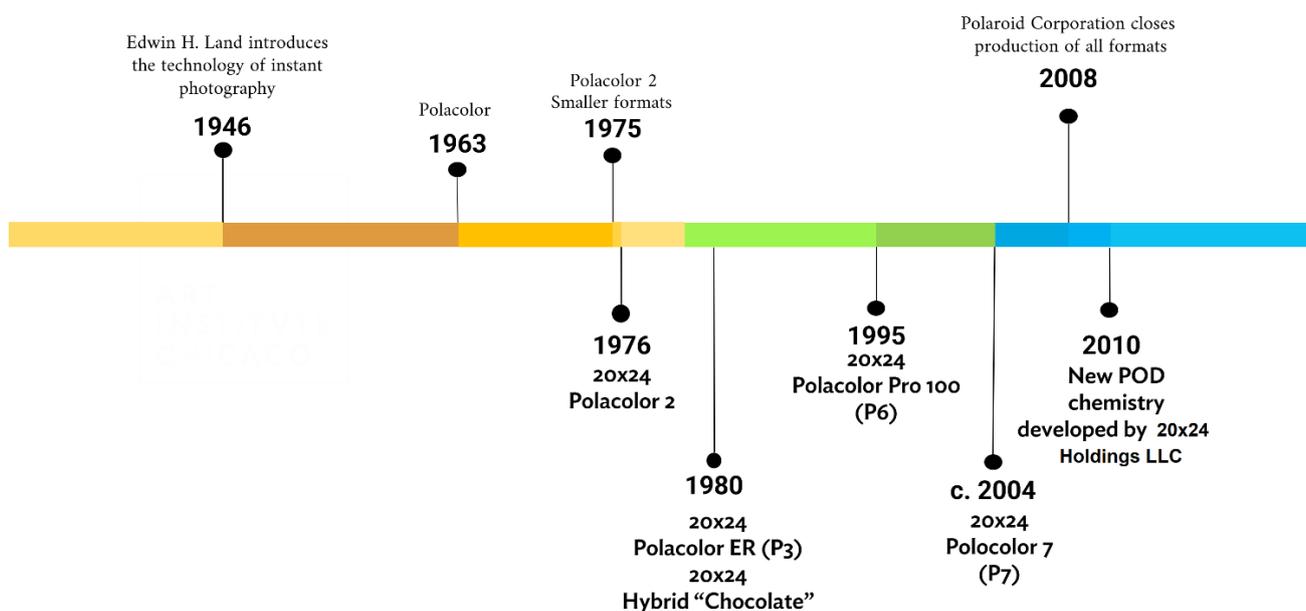


Fig. 1. Timeline for 20×24 peel-apart Polaroid film (Walworth and Mervis, 1989; Image Permanence Institute, 2010; Pénichon, 2013).

Chocolate prints, characterized by their split-tone effect and sepia tones, emerged as a hybrid system combining color and black-and-white peel-apart materials. This cross-process was the result of an accidental combination of Polacolor ER negative with Polapan 100 positive and reagent (Pryme Magazine, 2015). With the 20×24 format, Chocolate prints were produced by combining Polapan 400 black-and-white positive support with P3 negative sheet (Holmquist, 2024).

In 1995, Polaroid introduced Polacolor Pro 100 (P6) that incorporated over thirty functional consumer-driven improvements, including three new emulsions, four new developers (in negative), and a new receiving layer (Rebourt, 1997). According to Polaroid literature, this new generation of material featured higher concentrations of metalized dyes, particularly in the cyan and magenta layers, which resulted in enhanced image clarity and more precise color reproduction (Polaroid Corporation, 2002; Rebourt, 1997). A significant development was the modification of the reagent chemistry where hybrid formulations with temperature-sensitive inhibitors acting as molecular thermostats were introduced, allowing for greater chemical stability under varied environmental conditions (Rebourt, 1997).

Polacolor 7 (or P7), released in the early 2000s, was the last iteration of Polaroid 20×24 film. This generation incorporated numerous technical improvements, including increased brightness and contrast in the final images (Gomes, LaPointe and Manning, 2005). It also featured further enhancements to the structure of both positive and negative, and to the processing chemistry. However, P7 proved to be more chemically unstable than its predecessors, particularly in humid environments, as discussed further below (Gomes, 2024; Miąsik and Pénichon, 2024).

The production of 20×24 film and all other Polaroid materials came to an official halt in 2008, when the Polaroid Corporation filed for bankruptcy. The company 20×24 Holdings LLC acquired the remaining rolls of film and some production equipment, allowing artists to continue using the format long after production ceased (Reuter, 2012; Panzer, 2008). Through the efforts of the 20×24 Studio in New York, led by John Reuter, and the 20×24 Studio Berlin, operated by Markus Mahla, the 20×24 format continues to live on today (Asto, 2019; Reuter, 2008).

3. Materials characterization

3.1. General physical properties

A total of 87 prints, including identified samples of various 20×24 print generations (P3, P6, P7 and Chocolate) from the Art Institute's photography conservation study

collection and prints of undetermined generation from the collections of the Art Institute of Chicago, the Museum of Contemporary Photography in Chicago, and the Museum of Fine Arts Boston, were examined, measured and compared. Measurements consisted of colorimetric values, thickness, texture, and gloss. Because of the lack of Polaroid 2 samples in the study collection and their rarity in museums' collections, this generation was not included in the study.

All examined Polaroid 20×24 prints share a glossy surface finish and exhibit no discernible differences in texture, maintaining a consistent aesthetic and tactile quality across generations. The thickness of P3, P6 and P7 supports is remarkably consistent, varying between 0.260 and 0.273 mm. Their visual appearance under magnification is also similar, although the Chocolate print exhibits a linear pattern of blurry dots.

The colorimetric values taken from the 87 prints were used to create scatter plot diagrams of $L^*a^*b^*$ readings from the white margin on the recto and the backcoat of the verso, shown in Figure 2a and 2b respectively. For some prints it was not possible to perform both readings due to the absence of white margins or to the presence of mounts which hindered access to the verso.

Figure 2a shows broadly scattered groups that do not separate as cleanly as when using data from the verso. The greatest spread is in the vertical (b^*) axis, with the Chocolate prints (indicated by red dots) forming a distinct group at the top left of the diagram with highest b^* values (most yellow). P3, P6, and unidentified prints (blue, pink and black dots) are scattered in the middle of the diagram, with P6 showing the lowest b^* values (least yellow). P7 print samples (green dots) created a group on the lower left side of the diagram, with slightly higher L^* values (greater lightness).

Figure 2b shows data obtained from the verso of the prints. Three distinct groups can be discerned: a first one including samples from the Chocolate prints (red dots) at the bottom; a second one including the prints of unknown generations (black dots) in the upper left; and a relatively more scattered third group that includes P3, P6, and P7 prints (blue, pink, and green dots) and a few unidentified (black) in the upper right. This distinction is expected as three different colors of the backcoat were observed: Chocolate prints are characterized by a dark gray backcoat, while most of the unknown samples have a light gray backcoat. The generation of Polaroid 20×24 associated with the light gray backcoated prints requires further investigation.

This method is therefore promising for the differentiation of undetermined generations of prints, but an extended database including data from more samples of known types of 20×24 Polaroids is required.

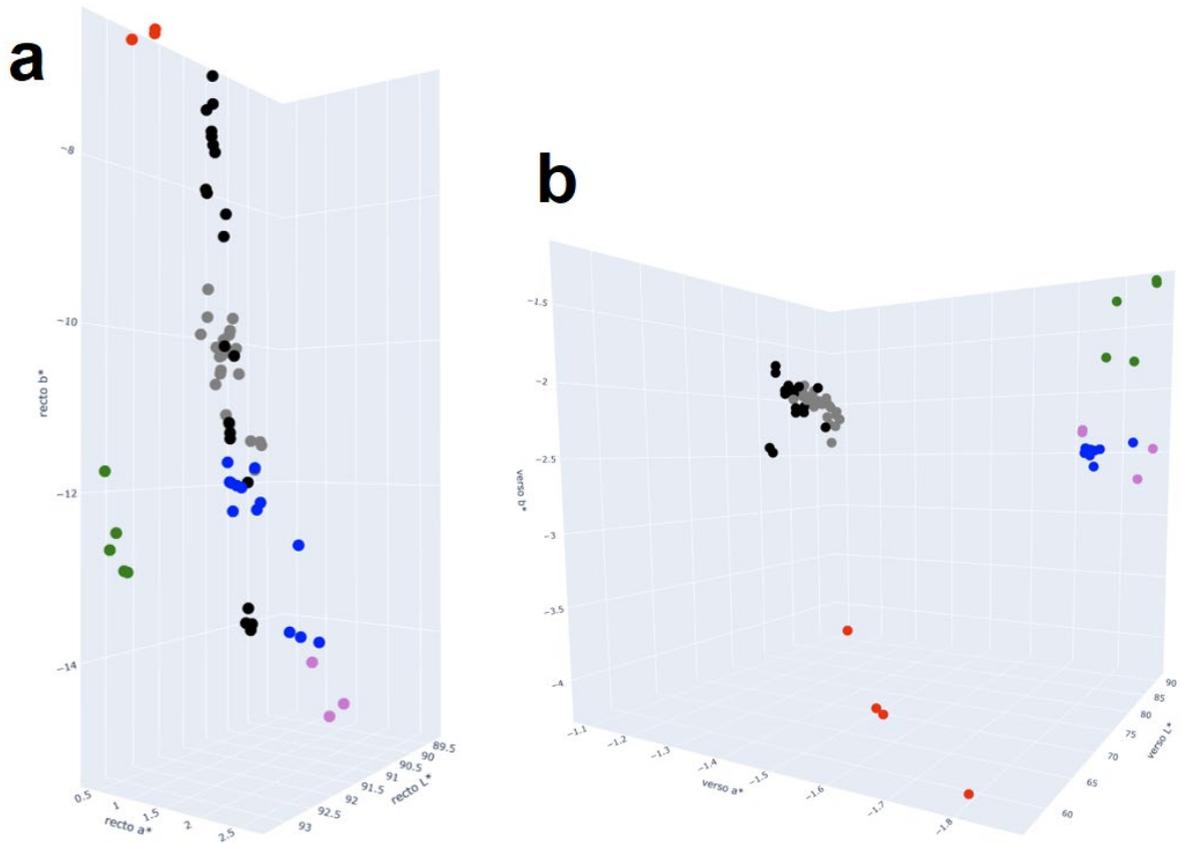


Fig. 2. Colorimetric values ($L^*a^*b^*$) taken from Polaroid 20×24 photographs (a) in the white margins, recto, and (b) on the backcoats, verso; (blue) P3, (pink) P6, (green) P7, (black) unknown generation, (red) Chocolate.

3.2. Print structure and composition

Cross-sections from P3, P6, and P7 prints were examined using optical and electron microscopy to provide a better understanding of their respective layering structures (Figure 3). The cross-section of P6 is not shown, being very similar to that of P7.

A comparison of the cross-sections revealed that the three generations of Polaroids consist of the same number of layers. However, the image receiving layer (1) and polymeric acid layer (2) in P7 (and P6) are thinner than in P3.

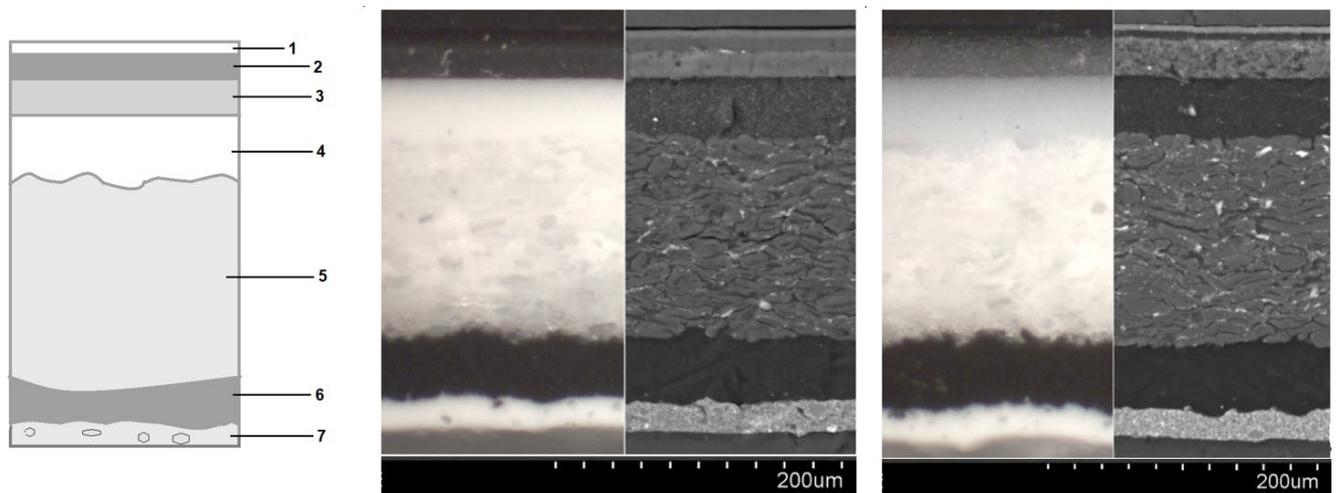


Fig. 3. Left: Schematic diagram of Polaroid cross-section showing (1) Image receiving layer, (2) Polymeric acid layer, (3) Timing layer, (4) Polyethylene layer, (5) Paper support, (6, 7) backcoats. Center: Micrograph and SEM backscatter image of P3 sample. Right: Micrograph and SEM backscatter image of P7 sample.

SEM-EDS spot analysis and elemental mapping of the cross-sections provided information on the inorganic materials used in some of the Polaroids' layers (Figure 4). In both P3 and P7 samples, titanium (Ti) was detected in multiple layers: the polyethylene layer (4), the paper support (5), and the backcoat (7). This suggests the presence of titanium dioxide (TiO_2), or titanium white, a material commonly used in photographic paper as a filler and brightener (Stulik and Kaplan, 2012). It might have been added to the polyethylene layer possibly as an opaque barrier (Fujita, 2004). Silicon-rich particles in the paper support (5) and backcoat (7) suggest an additional clay filler. Bromine (Br) was detected in correspondence with the image receiving layer (1), possibly transferred from the silver bromide (AgBr) emulsions in the negative or coming from the other bromine-based compounds used as counter ions in the positive and negative sides. Potassium (K) appeared predominantly in the timing layer(3) as well as the image receiving layer (1), confirming the use in Polaroid films of potassium hydroxide (KOH) as a developing chemical and as mordant (Wilker, 2004; MSDS No. M-0579, 1998). Chromium (Cr) was detected at trace levels in the image-receiving layer (1) of both samples, likely corresponding to the metallized organic dyes used in these films (Walworth and Mervis, 1989). One of the major differences between the two generations is the presence of blue particles in the polyethylene layer (4) of Polaroid P7 (Figure 3). SEM-EDS analysis detected the presence of sodium (Na), aluminum (Al), silicon (Si) and sulfur (S) in these particles, which suggest the presence of ultramarine blue, a complex sodium-silicate, likely used as an optical brightener. In comparison to cross

sections reported in the literature (Image Permanence Institute, 2010), the application of SEM-EDS analysis provided enhanced insight into the Polaroids' structure and material composition. FTIR was used to better characterize some of the layers, in cases where it was possible to physically separate them for analysis, complementing the SEM-EDS information. Results from the white backcoats, which were observed to contain titanium dioxide, showed the use of polyvinyl alcohol (PVA) in P3, and a combination of PVA and polyethylene in both P6 and P7 generations, as suggested by the sharper C-H bands at 2919 and 2851 cm^{-1} (Figure 5). The presence of polyethylene in P6 and P7 was also supported by the detection of a series of straight-chain alkanes and alkenes by pyrolysis gas chromatography mass spectrometry (Py-GCMS) (Tsuge, 2011). Different materials, including PVA and polyethylene, often in combination with other compounds, can be used in the support, depending on the desired nature of the final print (Fehervari and Manning, 2002; Walworth and Mervis, 1989). Despite analyzing only one sample per generation, the FTIR results suggest a variation in the backcoat material choice between generations. The image-receiving layer was also investigated by FTIR. Besides the confirmation of PVA in all three generations, the likely presence of multiple dyes and other materials made the spectral interpretation complicated and hindered the conclusive identification of individual components. These results seem promising to differentiate the various generations; however, non-invasive techniques such as reflectance-FTIR should also be explored when investigating prints held in collections.

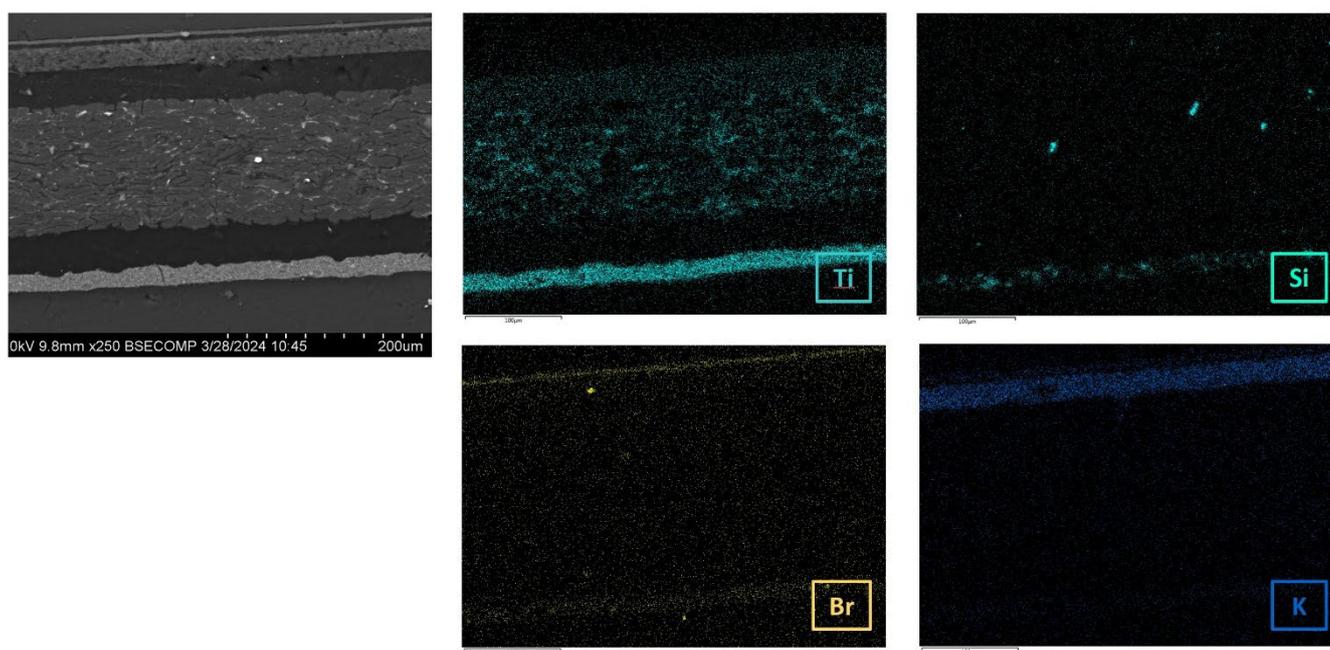


Fig. 4. SEM backscatter image of cross-section sample from Polaroid P3 (left) and EDS elemental maps for titanium (Ti), silicon (Si), bromine (Br) and potassium (K).

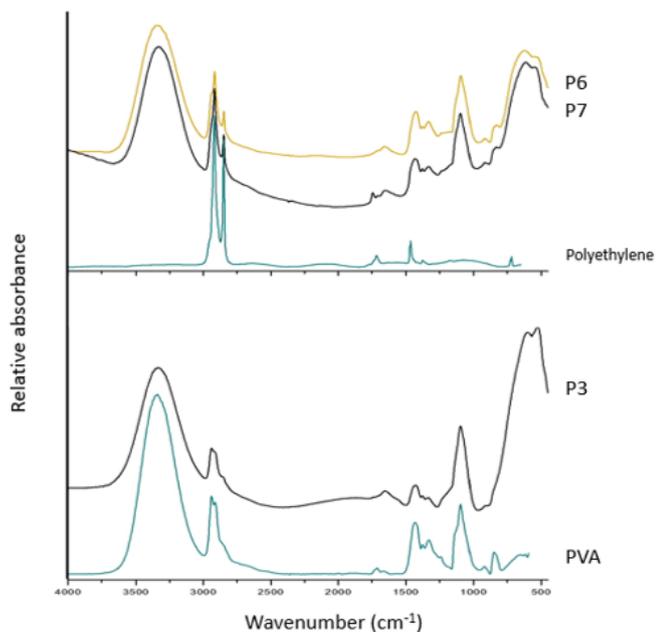


Fig. 5. FTIR spectra of the white backcoats from P3, P6, and P7, compared with reference spectra of polyvinyl alcohol (IRUG database, SR00092) (Price, 2007) and polyethylene (Fiveash Data Management, Polymers FTIR database).

Fiber analysis of the samples' paper cores revealed that the composition across generations P3, P6, and P7 was largely consistent, with slight differences attributable to different batches. The core of the samples was composed primarily (80 to 82%) of bleached hardwood fibers, such as maple, beech, or eucalyptus, with smaller amounts (18 to 20%) of bleached softwood fibers, including white or red pine, spruce, and hemlock (Bushner and Ranten, 2024).

Close examination of P6 and P7 prints from the study collection revealed the presence of a white powder formation on their surface (Figure 6a). P7 prints are notably susceptible to chemical instability and are known to develop a white haze within two years after the prints were made. This degradation, first noted by Reuter, manifested itself as small, salt-like particles embedded in the surface, giving it a matte and uneven appearance (Reuter, 2024). FTIR spectra of the white powder showed features that closely resemble those of the purine compound hypoxanthine (Figure 6b). Together with inosine, hypoxanthine was a component of the aqueous alkaline processing solution and was involved in the image transfer and development (Eckert et al., 1998; Kliem and Mass 1988; Gomes, LaPointe and Manning 2005). It is soluble in alkaline environments and insoluble in a neutral one. The detection of potassium (K), as well as bromine (Br), chlorine (Cl) and sulfur (S), in the white powder sample by SEM-EDS analysis suggests that hypoxanthine

may be present as its potassium salt, or in combination with other salts, possibly resulting from re-solubilization and crystallization of hypoxanthine on the surface of the final image. This phenomenon might have been triggered by a change in pH and/or humidity in the Polaroid micro and macro environment (Gomes, 2024). More research is necessary to better understand the exact mechanism behind the crystal formation.

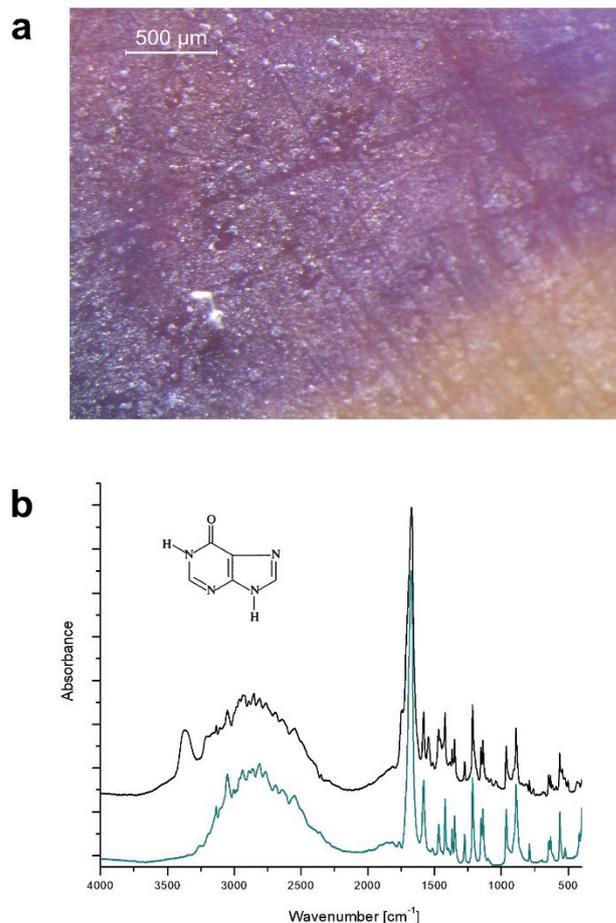


Fig. 6. (a) micrograph of the white powder formation on the surface of a P7 print; (b) FTIR spectra of the white powder (top) and a reference hypoxanthine (bottom) (Sigma, H9636).

4. Light Stability

Polaroid marketed its materials as being “among the most permanent and fade resistant ever developed in photography” (Wilhelm and Brower, 1993). However, this assertion was effectively debunked by Henry's Wilhelm's research on the light stability of photographic materials (Wilhelm and Brower, 1993; Wilhelm, 1978). Results of accelerated tests published by Wilhelm revealed that Polacolor 2 and P3 exhibit relatively low light stability, with Polacolor 2 being especially prone to yellowing, even in dark storage. P3 showed improved resistance, though it

remained susceptible to light-induced fading, particularly in yellow dye areas (Wilhelm and Brower, 1993). Wilhelm's research did not address later generations, such as P6, P7, or Chocolate prints. Observations by Reuter indicate that Chocolate prints are especially sensitive to light exposure, thus requiring careful display practices (Reuter, 2024).

MFT was employed in this study to assess the light sensitivity of materials with minimal damage, by inducing controlled, localized color fading in microscopic areas [2] (Beltran et al., 2021; Łojewski and Grzelec, 2020; Pesme, 2016; Whitmore and Bailie, 1999). Overall, results suggest that dyes across generations may fade at slightly different rates, but all exhibiting curves between blue wool BW2 and BW3 references, indicating a sensitivity to light.

The yellow staining residue, typically found along the lower edge of each Polaroid 20×24 print as a result of processing chemistry outside the image area during development, was also tested. This area proved to be the least stable, with high susceptibility to color shifts over time, across all tested generations. The hybrid Chocolate print was also tested; both light and dark areas were tested near the BW3 standard. Further studies on 20×24 chocolate prints in museum collections would be necessary to validate these results.

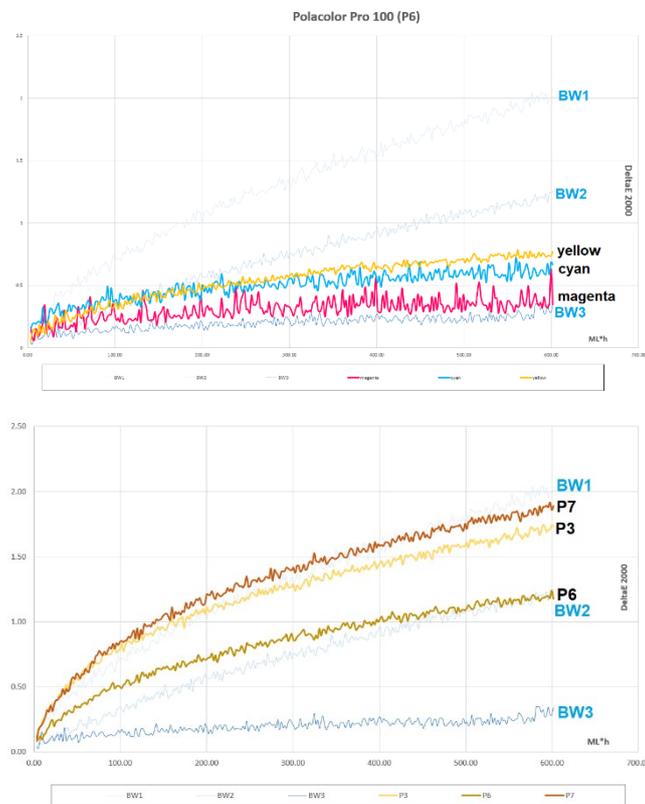


Fig. 7. Above: Representative graph for P6 showing MFT results for yellow, cyan, and magenta dyes. Below: MFT results for yellow stain for P3, P6, and P7.

5. Conclusion

This research is the first scientific study to comprehensively analyze the material composition and light sensitivity of Polaroid 20×24 prints across multiple generations, as well as a specific degradation phenomenon observed in the P7 prints. Because P3, P6 and P7 generations of materials have been used concurrently, one cannot rely on the dates artworks were created for the identification of individual generations, and so analysis of their physical properties and chemical constituents provides critical evidence. Measurements of thickness, gloss and texture showed a remarkable consistency of these physical attributes across generations, precluding their differentiation. On the contrary, color measurements of the white margins of the images or of the versos of the prints showed potential in distinguishing one generation from another, but a more extensive dataset of known Polaroid generations is needed to further develop these preliminary results.

Microphotographs of cross-section samples, combined with SEM backscatter images and EDS elemental mapping, facilitated discrimination of the various layers and gave insights on their chemical composition. The presence of ultramarine pigment in the polyethylene layer of the P7 sample, and the detection by FTIR of polyethylene in combination with PVA in the backcoat of the P6 and P7, were distinctive features in this study, but would require analysis of a wider sample set to confirm their diagnostic value. FTIR analysis also allowed the identification of hypoxanthine as a degradation product on P7, which can be related to residues of the chemical processing solution. MFT analysis showed that light sensitivity, while showing some variation among the samples tested, remains consistent across Polaroid 20×24 generations.

These findings underscore the necessity of careful light management when displaying 20×24 prints. Given that light-induced degradation is cumulative and irreversible, conservators and curators should interpret this data as a strong recommendation for exhibition conditions appropriate for light sensitive objects, for all generations. The necessity of proper storage conditions is also emphasized, ideally a cold storage environment, to preserve color stability and minimize chemical deterioration.

6. Conflict of interest declaration

The authors declare there is no conflict of interest concerning the research presented in this paper.

7. Funding source declaration

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9. Short biography of the authors

Paulina Miąsik - Current Mellon Conservation Fellow in the Conservation and Science Department at the Art Institute of Chicago. She holds a master's degree from the Faculty of Conservation and Restoration of Works of Arts of the Academy of Fine Arts in Warsaw, Poland, where she trained in the conservation and restoration of books, paper objects, and photographs. Her professional experience includes positions as a paper and photograph conservator at The Museum of Warsaw and The Central Military Library, Warsaw, as well as internships at the Museum of Photography in Krakow and at the Memorial and Museum Auschwitz-Birkenau German Nazi Concentration and Extermination Camp.

Sylvie Pénichon - William E. Urschel Family Director of Paper, Photography and Media Conservation at the Art Institute of Chicago. She is the author of *Twentieth-Century Color Photographs: Identification and Care* (2013), a comprehensive guide to understanding color photographs. In 2024, she joined Barbara Flueckiger as co-curator of the website *Timeline of Historical Colors in Photography and Film*.

Clara Granzotto - Associate Conservation Scientist in the Conservation and Science department at the Art Institute of Chicago. She received her Ph.D. in chemical sciences from the University of Venice, Italy, and the University of Lille, France. Clara conducted post-doctoral research at Northwestern University, the Metropolitan Museum of Art and the University of Copenhagen. She specializes in the analysis of traditional binding media by mass spectrometry, with a focus on polysaccharides and proteins.

Ken Sutherland - Andrew W. Mellon Director of Scientific Research in the Department of Conservation and Science at the Art Institute of Chicago. His main research interests concern the characterization of organic materials in works of art, using mass spectrometric and other analytical techniques, to inform an understanding of their technique, condition and appearance.

Notes

[1] The Polaroid Artists Support Program was an initiative by the Polaroid Corporation to engage artists in exploring and expanding the creative possibilities of instant photography. Established in the 1960s, the program provided selected artists with access to Polaroid cameras, film, and studio time, enabling them to experiment with the medium and offer feedback on Polaroid products. In return, many artists contributed their works to the Polaroid Collection, which eventually amassed over 16,000 fine-art photographs.

[2] MFT results are typically compared to the ISO Blue Wool Scale (BW1 to BW8, BW1 being the most fugitive and BW8 the most stable) to measure the permanence of colored materials. By analyzing these effects, conservators can effectively forecast the potential risks of light exposure to materials and formulate preventive conservation strategies (Whitmore, 1999, Michalski, 2017).

Experimental

1. Visible and fluorescence light microscopy: Samples were prepared as cross sections using a methacrylate resin (Technovit 2000 LC) and examined using a Zeiss Axioplan 2 research microscope with reflected light and UV fluorescence illumination; images were captured using a Zeiss AxioCam MRc5 digital camera.

2. Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS): An Hitachi S-3400N was used in the EPIC facility of the NUANCE Center at Northwestern University (Evanston, IL). The uncoated cross-sections were analyzed in low-vacuum mode at 80 Pa pressure and 20 kV accelerating voltage.

3. Fourier transform infrared spectroscopy (FTIR): Micro-samples were mounted on a diamond cell. Analysis was performed with a Bruker Hyperion 3000 FTIR microscope with a mercury cadmium telluride D315 detector interfaced to a Tensor 27 spectrometer. Samples were analyzed in transmission mode between 4000-400 cm^{-1} at 4 cm^{-1} resolution and collecting 128-512 scans per spectrum.

4. Pyrolysis gas chromatography mass spectrometry (Py-GCMS): Micro-samples were analyzed via direct pyrolysis in splitless mode, using an Agilent Thermal Separation Probe, which was inserted in an Agilent 7890B GC interfaced to a 5977B mass spectrometer. For analysis parameters see Sutherland et al. (Sutherland 2022).

5. Micro Fading Tester (MFT): The Micro Fading Tester manufactured by Instytut Fotonowy with LED light source (3200 K), spot diameter 0.5 mm, spectral resolution 2.50 nm.

6. Color: Color of the prints was measured using the X-Rite Exact spectrophotometer. This instrument produces color measurements using the L*a*b* color space (CIELAB, The International Commission on Illumination, 1976), where L* measures lightness (0 = black, 100 = white), a* measures green and red (positive values for red, negative values for green), and b* measures yellow and blue (positive values for yellow, negative values for blue). The reported results represent an average of three measurements.

7. Thickness: Thickness of the photographs was measured using a Mitutoyo Digimatic Micrometer Series 293 with a resolution of 0.001mm. Six measurements were made on each print at the top and bottom edges. Reported values are the averages of these measurements.

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