Article: The Effects of Solvents on Early Color Transparencies
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*Topics in Photographic Preservation, Volume 17*
Pages: 140-152
Compiler: Jessica Keister and Marie-Lou Beauchamp


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The Effects of Solvents on Early Color Transparencies

Elsa Thyss

Presented at the 2017 PMG Winter Meeting in Kansas City, Missouri.

Abstract

This research was developed during the author’s Master’s thesis at the Institut national du patrimoine in Paris, for the purposes of the treatment of a corpus of thirteen color transparencies made by fashion photographer Henry Clarke. Henry Clarke was the main photographer for Vogue France from 1949 until 1973. When Clarke passed away in 1997, his entire collection was bequeathed to the Palais Galliera, the City of Paris Fashion Museum. Among the 90,000 images in the collection, there is a large number of color films. This study was focused on thirteen KODAK® Ektachrome transparencies made in the 1950’s that depict the New Look Style.

As the transparencies showed surface dirt and accretions, the goal of this research was to identify a cleaning procedure suitable for chromogenic color films with incorporated dye couplers produced in the 1950’s. We chose to apply eight different solvents, either by immersion or with a cotton swab, on Ektachrome transparency samples from the 1950’s and the 1960’s from various sources, and on recent 35 mm Ektachrome film. Visual observations were made and color measurements were carried out in order to track any color or surface changes. In parallel, a suitable imaging procedure with different lighting was set up, in order to document the artworks and the samples before, during, and after treatment.

The immersion tests allowed us to understand the effect of each type of solvent on the photographic materials (base, gelatin, dyes). Utilizing these results, and after testing the Clarke original materials, we decided to clean the transparencies with hydrocarbon solvents, as these presented lower risks and were efficient for removing some of the dirt when applied with a cotton swab.

Henry Clarke

Henry Clarke was an American photographer born in 1918, who started to work in the New York Conde Nast studios in the 1940’s. He left for France in 1949, where he spent his entire remaining career as a fashion photographer. In 1951, he signed a contract with the Conde Nast editions and became the primary photographer for Vogue France from 1949 until 1973, taking charge of covering the French Haute Couture collection for the magazine. He started to use color films very early in the 1950’s in order to keep up with the needs of the publication, which required glamorous images illustrating the “New Look” introduced by Christian Dior.

When Clarke passed away in 1997, his entire collection was bequeathed to the Palais Galliera, Musée de la mode de Paris (City of Paris Fashion Museum). Among the 30,000 chromogenic color films in the collection, a selection of them stood out with obvious surface
degradation as well as surface grime. We focused our study on thirteen KODAK® Ektachrome transparencies made in the 1950’s. They included two 20x25 cm portraits of the Duchess of Windsor Wallis Simpson, photographed by Clarke in 1952 and, eleven 4x5 inch fashion photographs made in 1957 and displaying various High Fashion designers’ creations. All these images were published in Vogue France and Vogue US a few months after they were taken.

**Technology of Ektachrome Transparencies**

Ektachrome films are chromogenic reversal films that were produced from 1947 until 2012 by KODAK® in different formats and types of sensitivity. If the technology of the films was improved throughout the second half of the century, the processing of the films was already very complex in the 1950’s. At the end of the processing, the image material is composed of cyan, magenta and yellow dyes in suspension in gelatin. These three distinct layers form the complete binder layer, which sits on a transparent support made of cellulose diacetate or triacetate, and is protected by a layer of transparent gelatin applied on top. On the other side of the support lies the anti-curl layer, also made of transparent gelatin. The overall thickness of such a transparency is around a third of a millimeter.

The transparencies required suitable photographic documentation, which was challenging because of the translucent nature of the objects. First, we photographed them in transmitted light, which enabled us to evaluate the condition of the color material. The documentation of the surface condition was more of a challenge. For that, we adapted a setup often used to document daguerreotype surfaces: A diffused light is placed in front of a Poly methyl methacrylate (PMMA) plate positioned at a 45° angle above the object. The light is partially reflected by the PMMA plate in an axial direction toward the surface of the object, and the specular reflection is captured by the camera. The result was not completely perfect, as there were a few shadows due to the slight distortion of the films, nevertheless, we found it a suitable method to document transparencies in a replicable way.

**Condition of the Clarke Transparencies**

Local dirt and accretions were present throughout the surface of the films. Many fingerprints were noted on both sides of all the films as well as accretion rings along the edges of the two larger films. We observed numerous abrasions and scratches on the surface, some in particular reaching the support and thus visible in transmitted light. Two of the films also displayed handling creases.

The films displayed a significant overall color shift toward the red. This was particularly visible when the photographs were compared to the corresponding publication printed in offset – even if they likely represented a certain color interpretation. We noticed local dye deterioration along the bottom and right edges, either in blue-ish lines or in brighter magenta lines. On the majority of the films, there were white matte undulating lines present on the surface, reaching from the edges to the center of the film (see Figure 1). Finally, on five of the transparencies, we noticed the presence of a whitish haze overall on the surface, which was visible only in reflected light and particularly in axial light, with many disruptions throughout. It was associated with an
oily texture detected when handling the films. Mold was present along the top edge of five films, where it had penetrated the binder and deteriorated the dyes turning them red.

Figure 1: White matte undulations on the surface of the transparency (GALH121E5)

**Diagnosis and Understanding of the Degradation Processes**

It appeared that certain types of deterioration were related to the handling of the films, others to the photographic materials themselves, or to the environment. We decided to investigate more closely the ones that seemed to have been induced by the material of the original housing sleeves, in order to better understand the deterioration processes involved.

**Interactions Between the Transparency and the Sleeve**

When we started our research, the transparencies were stored in paper sleeves, as they had been rehoused at their arrival in the Galleria museum in the early 2000’s. However, prior to this, and for more than fifty years, the transparencies were housed in plastic sleeves. These sleeves were produced by KODAK® and packed with the transparencies, so that the customer could protect them after the processing. Thankfully, the Galleria museum staff saved several original sleeves, from which we were able to make some observations and on which we performed scientific analysis:

1. The sleeves were made of a sheet of transparent plastic folded and sealed with an adhesive applied along the side and bottom folded edges.
2. The plastic displayed regular undulations, particularly along the folded edges (see Figure 2).
3. The sleeves material was identified by infrared spectroscopy as being cellulose acetate.

Our impression was that the local dye deterioration and the white matte lines had a shape that evoked the undulations of the deteriorated sleeves. Therefore, in order to better understand how these deteriorations interacted, we superimposed:

- the digital annotated image of the transparencies showing the dye deterioration and the matte undulated lines on the transparencies;
- and the digital capture of the sleeve in raking light, that showed the areas of contact with the transparency.

After a close examination of the stacked images, it appeared that the local dye deterioration overlapped with the areas where the film was in contact with the sleeve. In contrast, the white matte accretions in lines seemed to be located where there was no contact between the transparency and the sleeve (see Figure 3).

Figure 2: Original cellulose acetate sleeve of a transparency showing planar distortions in raking light
Local Color Deterioration

We went further in understanding the local color change, as manifest in small bluish stripes (less than 3 mm wide), and particularly visible in transparencies that were reddish overall. To learn more, we conducted color measurements with a reflectance spectrophotometer adapted from a Fiber Optic Reflectance Spectroscopy (FORS) instrument in areas with and without local dye deterioration (respectively the blue and red areas). These measurements showed that:

- Red and blue areas show the same low level of reflectance in the 450-550 nm range (blue-green light);
- In contrast, blue areas show less reflectance than red areas in the 550-700 nm range (red-yellow light) (see Figure 4).

This means that the reflectance of the upper layers of the emulsion – yellow and magenta – is lower in the blue areas, whereas the reflectance of the lower layer – cyan – is the same in both areas.
These two modest investigations led us to conclude that, there may be deterioration of the upper layers of the binder containing the magenta and yellow dyes in the areas where the cellulose acetate sleeve was in contact with the binder.

The Haze

The last conservation issue that we investigated was the overall whitish haze associated with an oily surface texture. Fourier Transform Infra-Red (FTIR) spectroscopy analysis conducted on the surface of the films did not identify any coating other than gelatin, and X-ray fluorescence analysis (XRF) eliminated the possibility of it being a layer of residual silver resulting from imperfect bleaching or fixing during the processing. The haze may be due to the presence of degradation products coming from the cellulose acetate of the sleeve, although this has not been checked yet, but could be confirmed with separation analysis of a sampling of the haze (see Table 1).

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Figure 4: Percentage of reflectance on the red and blue areas of a Kodak Ektachrome made by Clarke in the 1950s
Table 1: Results of analysis performed to identify the composition of the whitish haze

<table>
<thead>
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<th>Hypothesis</th>
<th>Analysis</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Varnish?</td>
<td>FTIR</td>
<td>Undetected</td>
</tr>
<tr>
<td>Residual silver from processing?</td>
<td>XRF</td>
<td>Undetected</td>
</tr>
<tr>
<td>Degradation products (plasticizers) from cellulose acetate sleeves?</td>
<td>Separative analysis (GC-MS) (not performed)</td>
<td>?</td>
</tr>
</tbody>
</table>

**Technical Study**

Our plan was to find a suitable method to remove the different types of dirt and accretions on the transparencies in order to improve the readability of the images and to ensure a better chemical and physical preservation of the photographic materials. Since no cleaning method emerged from our conversations with photograph conservators and in the photograph conservation literature, we needed to identify a suitable cleaning procedure to treat the films.

Trichloroethane 1-1-1 used to be the standard cleaner for most photographic films but it was phased-out in 1996. We went through the results of the many tests conducted by several photograph conservators since then, which show that:

- the effects of water can vary a lot depending on the type of sample and the application procedure;
- acetone has a destructive effect on the support;
- and most hydrocarbons seem not harmful for the photographic materials.

However, the results seemed to vary depending on the chromogenic material, e.g. a chromogenic print of the 1990’s versus a reversal film of the 1960’s.

We chose to apply eight solvents on seven samples of Ektachrome transparencies from the 1950’s and 1960’s, and on a recent 35 mm Ektachrome roll film. The latter, though a more recent product, was helpful in evaluating the reliability of our tests. The solvents selected were: water, ethanol, isopropyl alcohol, ethyl acetate, acetone, methyl-ethyl-ketone, toluene and cyclohexane. These were applied alone or in mixtures, and with two different methods. Half of the samples were immersed in solvents for five days. Solvents were applied with a cotton swab gently rubbed onto the surface in a circular motion of the other half. Visual observations and color measurements were then carried out to evaluate color and/or surface change. In parallel, using suitable capture set ups, digital documentation was performed on the samples before, during, and after treatment.
Results: Immersion Tests

After the immersions, we noticed that:

- water and alcohols made the binder swell temporarily, and left irreversible distortions and halos;
- a water-ethanol mixture extracts the dyes from the binder, and also left irreversible distortions and halos;
- ketones and ethyl acetate resulted in the dissolution or the distortion of the film base;
- hydrocarbons had very few visible effects on the samples.

The color measurements conducted with a spectrophotometer (X-RITE® SP64, D65 Illuminant, Specular Component Excluded, 2 Degree Standard Observer) before and after the tests allowed us to evaluate the color change for each sample. On the modern samples, immersion in water-ethanol clearly led to the highest color difference ($\Delta E$) (see Figure 5). The $\Delta E$ was around 25 (in CIELAB 1976 color space), whereas it was below 6 with the other solvents. On the other hand, on the historic samples from the 1950’s to the 1970’s, the results were more varied. Water-ethanol was still the one that induced the most color change, but with a less significant color change than with the modern samples (see Figure 6). From all these measurements, including the reflectance spectra, all immersion tests resulted in an unacceptable amount of color change.

![Figure 5: Average color change of modern samples from the 2000s after a 5-day solvents immersion ($\Delta E$ measured in CIELAB 1976 color space)]
Figure 6: Average color change of older samples from the 1950’s-1960’s after a 5-day solvents immersion ($\Delta E$ measured in CIELAB 1976 color space)

**Results: Cotton Swab Tests**

After the cotton swab test we did not observe any color change when comparing the treated with the untreated samples. The color measurements indicated a much lower color change on all the samples than after the immersion tests. Low visible color changes were measured with a $\Delta E$ values all below 2.

However, we noticed the presence of faint traces that corresponded with the area of application on five of the transparencies, visible upon close examination under raking light (see Figure 7). These traces were completely absent on the other three transparencies, which means that their presence depended on the sample rather than on the nature of the solvents or application method, which made us believe it perhaps could be due to the removal of surface dirt.
Conclusions From the Technical Study

The tests completed do not provide a definite answer for the cleaning of all color transparencies and many other tests could be conducted to refine the results. However, they do provide major clues to help us find appropriate solvents for the Clarke transparencies as well as a suitable way to apply them. Indeed, the local application with a cotton swab gently rolled or rubbed is a method that has already proven itself in the cleaning of photographic materials and seems appropriate for the color transparencies as well, since any potential visible effects on the surface can be checked immediately. Furthermore, the extreme immersions have confirmed our common knowledge that “like dissolves like”. They allowed us to compare the potential effects of each solvent on the materials, so that we can choose the least harmful among them. Whereas hydrocarbon solvents have the least effects on the transparency materials, aqueous solutions cause damage on the emulsion layers, and ketones and ethyl acetate alter the acetate base. Immersion in water-ethanol causes significant dye extraction. Cotton swabs do not provoke any dye change, but the surface appears to be altered on 60% of the samples.

Treatment of the Clarke Ektachrome Films

In treating the transparencies in the Clarke collection, the goal was to eliminate the external materials that could lead to further degradation of the photographs, especially dirt, grime, accretions and fingerprints, and the white areas that seem to be related to the local dye deterioration. While the harmfulness of the whitish haze has not been proven, we agreed with the curator that it would be completely removed in the course of cleaning the other types of dirt.

The transparencies were first progressively dusted, with an air blower, a goatshair brush, and a soft microfiber tissue. Then we conducted preliminary solvent tests with a cotton swab on...
the edges of the transparencies – except for the ketones and the MEK that were applied further in from the edges. Only water had a noticeable impact on the gelatin when applied at a higher percentage than at 10% in ethanol, and the other solvents did not have any visible effect. Their respective efficiency was then tested, and was confirmed for some of them on a portion of the accretions and dirt, but seldom on the fingerprints. Following the previous results, and after testing the artworks’ surfaces, we decided to clean the transparencies with hydrocarbon solvents, as they presented lower risks and were efficient for removing some of the dirt when applied with a cotton swab. The whitish haze was very easily disrupted with the cotton swab. It was decided to remove it completely in order to remove the other types of dirt and accretions, and also to leave a clean and homogeneous surface. For that, we tested first the two hydrocarbons approved in our technical study, and as they seemed both, equally efficient, we chose to use the cyclohexane – which is the less toxic of the two.

Finally, the transparencies were housed in hand-made sleeves with non-buffered paper and placed in conservation boxes. We chose to use non-buffered paper to make the sleeves, because of the potential risk of damaging the dyes in case of a significant increase in humidity.

The Clarke transparencies were then returned to the vaults of the Galliera Museum, which have stable climate conditions, though no cold storage at present. Handling will be permitted only with nitrile gloves, and occasional consultations on a LED light table allowing strict control of the heat and the light level.

Conclusion

This study has provided proof that an intake of solvent on a color transparency, which is such a complex and fragile material, is a significant intrusion that has multiple effects. Due both to their inevitable deterioration and their great quantity in collections, color transparencies are sure to receive our preventive attentions in the future.

Acknowledgments

I want to thank warmly my thesis supervisors Caroline Barcella, photograph conservator; Marie-Angélique Languille, research engineer CNRS, Doctor of Physical Chemistry, Centre de Recherche sur la Conservation (CRC); Claire Tragni, photograph conservator at the Atelier de Restauration et Conservation des Photographies de la Ville de Paris (ARCP); and Sylvie Lécallier, curator in charge of the photography collection of the Palais Galliera, Paris.

My sincere gratitude goes to scientists Nathalie Balcar, conservation scientist at the C2RMF in Paris, who performed the FTIR spectroscopy analysis on the transparencies and the sleeves; Céline Daher, conservation scientist at the CRCC in Paris, who conducted the FORS spectroscopy analysis on one of the transparencies; and Anne Genachte Le-Bail, conservation scientist at the Inp in Paris, who performed the XRF analysis on the transparencies.
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Papers presented in Topics in Photographic Preservation, Volume Seventeen have not undergone a formal process of peer review.