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OPTICAL BRIGHTENERS-A STUDY OF WATER SOLUBILITY

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ABSTRACT:

Optical brighteners have been employed in photographic papers to enhance the visual qualities in the white areas of the image since the early 1950's. The aim of this experiment was to examine the water solubility of optical brighteners used in the photographic papers. A wide variety of historic samples from different manufactures were studied. Initially, the experiment set out to examine the degree of water solubility of optical brighteners in a simulated aqueous conservation treatment. A visual examination under normal and ultraviolet light would determine if any noticeable loss of optical brightening agents occurred by comparing a washed sample with an unwashed control. Upon initial development of these historic paper samples, other factors became evident that needed to be addressed before proceeding with the washing experiment. These issues are the focus of this paper.

1. HISTORY OF OPTICAL BRIGHTENERS

Optical brighteners, also known as fluorescent whitening agents, are organic dyes that are based on the cyclic compound stilbene. Their application to a material yields a brighter white surface by absorbing light in the ultraviolet range of the electromagnetic spectrum and emitting it in the blue end of the visible light spectrum. Their discovery has evolved from the desire to counteract the yellowing of aging materials. In 1852, G.G. Stokes described his discovery of the fluorescence produced by uranium glass. This glass, which is radioactive, could emit visible light from converted invisible ultraviolet light it absorbed. Following Stokes discovery in 1921, Lagorio was experimenting with fluorescent dyes and determined that the amount of reflected visible light is far greater than the amount absorbed (Anliker 1975). Shortly afterwards in 1929, Paul Karais discovered that the extract of horse chestnut bark (esculin) caused a blue fluorescence that would offset the yellowing of materials and hence the concept of optical whitening was born. (Mustalish 2000) These natural optical brighteners had limitations in that they would discolor with prolonged light exposure. Therefore, stilbene-based synthetic products were eventually developed to produce the effects of the natural whitening agents but with better aging and display properties. Synthetic optical brightening agents have had industrial applications since the mid 1930's as whiteners for papers, fabrics, plastics and laundry detergents (Anliker 1975). Today, optical brighteners have become a ubiquitous material (Mustalish 2000).

2. SAMPLE COLLECTION

Paul Messier provided a selection of unused, light sensitive vintage photographic papers for this experiment. Each of the papers was identified as containing optical brightening agents. Six papers by different manufacturers were chosen by Messier from each decade beginning with the 1950's and ending with the 1990's. The 1980's and 1990's decades had only three samples each and were subsequently consolidated into one study group. Altogether, there were 24 photographic paper samples used in this research.

Paper manufacturers included Agfa, Agfa-Gevaert, Ansco, Cachet, Dupont, Forte, Ilford and Kodak. Most of the papers were fiber based printing papers with the exception of one Resin Coated (RC) paper sample that appeared in the 1980's sample collection. All papers a gelatin silver halide emulsion layer and except for the RC paper, all papers had a baryta layer. All samples selected for this experiment contained optical brighteners on the emulsion side of the papers, most likely within the baryta layer. Not all of the papers contained optical brighteners in the paper base. This would suggest that the optical brighteners in the paper base are not likely to influence the fluorescence of the image due to the opacity of the barium sulfate.

3. DEVELOPING HISTORIC PAPERS

The historic paper samples used in this project were anywhere from ten to fifty years old and well beyond their recommended expiration dates. To check for fog and to determine the potential to develop an image on the papers, a small sample of each paper (approximately 1/8" x 2") was cut under a safelight and developed using Kodak Dektol developer according to archival standards (Fig. #1). Of the twenty- four paper samples, all but twelve samples exhibited fogging after development. These samples were then viewed under ultraviolet illumination to detect the presence of optical brighteners. The fluorescence of the optical brighteners in the paper samples that exhibited fogging was undetectable on the emulsion side of the paper under ultraviolet illumination.

DEVELOPER	STOP BATH	FIXER	WASH
Kodak Dektol 90 seconds	Acetic Acid (dil.) 15 seconds	Kodak Hypo 8 minutes	Tap Water 1 hour

Fig. #1 Developing Chemistry according to Archival Processing Standards

To gain a better sense of the intensity of the optical brighteners in 'fresh' paper, a similar sized piece of unexposed paper was cut under a safelight for each paper sample. That piece was placed side by side with the corresponding developed sample and immediately photographed under ultraviolet illumination. Knowing that optical brighteners are water-soluble, it was expected that the developed sample would show less fluorescence under ultraviolet illumination having been rinsed in water for an hour during development. However, the exact opposite results were consistently found showing the developed paper with a much greater fluorescence than the unexposed, undeveloped paper.

Upon further investigation, it was found that the Kodak Dektol developer contains a fluorescing agent that was visible when Dektol was mixed with water, but not in the dry powder form. It was possible that the Dektol developer intensified the reflectance of the blue light associated with optical brighteners in the paper by adding an additional amount of optical brightener during processing. This would only be possible if optical brighteners could transfer via an aqueous means, but this remained undetermined at this point. A second explanation for the difference in fluorescence between the papers implies that the optical brighteners migrate to the surface of the paper when moisture is introduced. By redistributing themselves at the surface interface upon drying, the fluorescence would increase proportionally to the concentration of optical brighteners on the surface.

4. TEST FOR TRANSFER OF OPTICAL BRIGHTENERS

Knowing that an optical brightener or some other fluorescent agent was present in the Dektol developer, it was necessary to see whether or not it had the potential to transfer to the photographic paper during development. This phase of the preliminary testing investigated the potential transfer of optical brightener from the developer to the paper, from paper to paper, and from tray to tray within the development setup. This test was conducted using a contemporary paper that contains ample amounts of optical brighteners (Kodak Polymax c. 2000) and comparing it with a historic paper (Kodak Azo c. 1940) that pre-dates the use of optical brighteners in the photographic paper industry.

Samples of both the Kodak Polymax and Kodak Azo papers were cut under a safelight to the size of approximately 2" x 4". Three sets of developing chemistry were set up in small plastic trays that contained approximately 300 mL of each developing solution. The samples were documented photographically under ultraviolet illumination during each step of development.

The first test set of chemistry exhibited the development of the non-fluorescent Kodak Azo paper in the fluorescent Dektol developer. After full processing and drying, the presence of optical brightening agents was not visible under ultraviolet illumination. This indicated that the fluorescent agent in the Dektol developer did not transfer to the Kodak Azo paper by aqueous means. The second set of chemistry employed the development of the modern Kodak Polymax paper followed by the development of the Kodak Azo paper, but never in the same tray at the same time. Upon development and drying, no fluorescence was detected on the Kodak Azo paper under ultraviolet illumination despite the fact it remained for an hour in a bath of water that contained optical brighteners washed out of the Kodak Polymax paper developed before it. The final set of chemistry showed the simultaneous development of the Kodak Azo and Kodak Polymax paper in the same tray where they were allowed contact. After development and drying, distinct rectangular patterns of optical brightening agents were present on the Kodak Azo paper where a point of contact occurred with the Kodak Polymax paper.

These experiments were conducted several times and the results were found to be consistent. Some conclusions could be drawn about the movement of optical brighteners during photographic development: The optical brighteners can only transfer from paper to paper when allowed direct contact between the paper sheets. This finding could be useful information when bulk washing photographs during conservation treatment or examining photographs that have been bulk processed by the photographer. The optical brighteners in the developer do not exhibit aqueous transfer to a sheet of paper or between trays during development. This finding would suggest that the fluorescing agent in the Dektol developer does not intensify the fluorescence of a paper that already contains optical brighteners. Hence, it is likely that the migration of optical brighteners to the surface interface following development and drying contributes to the intensified fluorescence the papers exhibit under ultraviolet illumination. Aqueous transfer of optical brighteners does not occur between the developer and a paper processed in it or from processing another paper in the same chemistry. The fluorescent agents deposited in the rinse water bath of the developing chemistry are solely comprised of the optical brighteners removed from the paper washed in that bath and not from the Dektol developer.

5. WASHING EXPERIMENT.

A sheet of each photographic paper was cut under a safelight to a size of approximately 4 x 4.5 inches. In the cases where the preliminary development showed no fogging, an additional sheet of paper cut to a size of approximately 4 x 3.5 inches was used.

One third was cut from each sheet of the 4 x 4.5 inch sized paper and was rapidly fixed (in Kodak Rapid Fixer without the hardener) and washed (in tap water) for 30 seconds each. This step was performed to stabilize the paper to light so that it could be used outside of the darkroom. With minimal aqueous exposure, it would simulate the unexposed, undeveloped paper used in the preliminary testing. This third was used as the control and labeled A.

The other two thirds of the paper sample (labeled B¹ and C¹) were “developed” with water as a replacement for the Kodak Dektol to avoid fogging. The development of the papers needed to be uniform and therefore all paper samples, regardless of whether they fogged or not, were developed in water. However, to most accurately replicate actual development of a photographic print, the additional sample of the twelve papers that did not experience fogging were labeled B and C and developed under normal conditions using the Kodak Dektol developer.

After development using either water or Dektol and drying between blotters and spun polyester webbing, the sample was then cut in half. All portions labeled C and C¹ were washed in a small tray of approximately 300 mL of deionized water for 1 hour to simulate an aqueous conservation treatment. The trays were agitated intermittently to assure proper water coverage, as most of these papers had a distinct curl and would not stay immersed. Photo documentation of the trays was taken under ultraviolet illumination every fifteen minutes. After one hour of washing, the samples were dried between blotters and spun polyester webbing. Following washing, a sample of water from each of the bath trays was stored and labeled in a glass and examined under ultraviolet illumination for the presence of any fluorescence. This would indicate if the optical brighteners had washed out of the paper. All samples showed fluorescence, yet the degree varied throughout the samples.

5.1. VISUAL COMPARISON

Following the washing step, all A,B,C and A,B¹,C¹ samples for each paper were placed side-by-side and evaluated on their relative intensity of whiteness under normal museum-type lighting (with little to no ultraviolet content) and near ultraviolet illumination. The results showed that in most cases, no noticeable change occurred between the unwashed and washed samples in either lighting condition. In some cases only a minimal change was detected, bearing in mind that these visual evaluations are subjective. Another observation seen on some of the samples was an uneven redistribution of the optical brighteners on the surface of the papers, resulting in a splatter pattern on the paper visible only under ultraviolet illumination.

The paper samples were all mounted to acid-free paper and stored in a closed binder for six months, at which point they were re-evaluated. Normal illumination showed no change in the appearance of these samples. However, upon visual examination near a window where the ultraviolet content of the sun was quite significant, the washed samples (C and C¹) appeared to fluoresce greater than the unwashed samples (A, B, or B¹) in all twenty-four samples.

6. DISCUSSION OF RESULTS

General Effects of Water on Optical Brighteners

Immersion or other means of prolonged contact with water will alter photographic papers that contain optical brightening agents. The general tendency is that water-soluble optical brighteners become mobile when an aqueous medium is present. The length of time the photographic paper is exposed to water determines the degree of loss of optical brighteners within the paper. Shorter exposures to water can result in the migration of these materials during drying to the air-surface interface of the photographic paper. Longer exposure to water can result in the migration and overall reduction of optical brightening agents. When concentration of the optical brighteners at the surface occurs upon drying, photographic papers that have been exposed to water may have a greater fluorescence and hence can appear to be a brighter white when viewed under near ultraviolet illumination. Sometimes, migration and loss of optical brightening agents in water-exposed photographic papers can cause tide lines or uneven surfaces from unequal distribution. Fortunately, these changes in fluorescence are primarily visible only under ultraviolet illumination or in direct daylight.

Development of Papers

Modern developers may contain optical brightening agents that may influence the fluorescence that a photographic paper already has. However, the fluorescing agent in the developer used in this experiment had no detectable effect on the photographic paper during development. There was no visual difference in the degree of fluorescence between the paper samples that had been developed with water versus the samples developed using Kodak Dektol. Optical brighteners can transfer from paper to paper when wet papers are brought into contact. This finding could be a concern to conservators when bathing several photographic papers in the same tray simultaneously.

Visual Evaluation

While bathing a photographic print, a degree of loss of optical brightening agents is to be expected. Fortunately, the visual impact under normal lighting or museum-type lighting is minimal if not non-existent. The resulting visual impact of aqueous treatment can only truly be seen in lighting where the ultraviolet content is very high. In most cases, the result of the movement of the brighteners to the surface interface results in an even layer of optical brightening agents, as was the case in this experiment. However, some irregularities can occur. In some cases, the optical brighteners that migrate to the surface can redistribute themselves in an uneven manner on the surface. Once again, these irregularities are not visible under normal lighting conditions.

7. CONCLUSION

While it is not possible at this point in time to come to any definitive conclusions whether or not the aqueous treatment of photographs containing optical brighteners is detrimental to their visual aesthetic, it can be stated that aqueous treatment will render change in a photograph. Bathing can be responsible for the redistribution of the brighteners or for diminishing of the quantity of optical brighteners in photographic paper. On one hand, the redistribution of optical brighteners on the emulsion side of the paper could possibly replenish lost or exhausted optical brighteners, regaining the original brightness or perhaps making the photographs seem fresher or crisper. On

the other hand, if the redistribution is uneven, then the visual impact may not be so desirable if the optical brighteners have an opportunity to be excited by ultraviolet light. This matter is complicated by the fact that typical museum and gallery lighting conditions suggest that the ultraviolet source of the lighting be filtered out. Without an ultraviolet excitation source, the optical brighteners are essentially ineffective.

Since little research has been conducted on these materials, it leaves the floor open for further discussions on whether light may also have an effect on the breakdown of these materials. Additionally, being synthetic product optical brighteners have the potential to break down or lose their ability to fluoresce. These are all factors, in addition to water solubility, that could benefit from further research in order to best understand the nature of optical brighteners.

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