Alternatives to Conventional Methods of Reducing Discoloration in Works of Art on Paper

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Chemical bleaching has a detrimental effect on paper and conservators are quite concerned with the continued use of conventional chemical bleaching methods. This presentation is concerned with a search for alternative methods which would keep the use of chemical bleaching to a minimum, and eventually may make it possible to dispense with much of our worry.

The structure of paper tends to retain what it absorbs. Therefore, materials used to reduce discoloration of paper should ideally be harmless and not shorten its life. Magnesium bicarbonate, calcium carbonate and ammonia adjust the pH of wash water to a higher alkalinity and aid in releasing discoloration more effectively. Alcohols may be used as wetting agents for highly sized paper. Enzymes have a cleansing action. A vacuum suction table effectively draws dissolved substances out of the paper structure. Sunlight in the presence of moisture and magnesium bicarbonate may prove to be a safer, effective bleaching method, and further studies should be made of bleaching with alternative light sources.

Until recently, hardly anyone questioned the use of chemical bleaching as a standard procedure in the restorative treatment of paper objects. But today, as a result of having better information about the potential degrading effect of chemical bleaching in its immediate and latent actions on paper, the prevailing attitude among paper conservators is cautious and we tend to avoid the use of chemical bleaching in our work as much as possible. However, as conservators of works of art on paper, we are concerned with improving the visual effect of a damaged object in addition to enhancing its physical strength and longevity. If the object is disfigured by discoloration, we attempt to reduce it through our treatment to regain the visual coherence without which the art object falls short of the meaning it conveys. One challenge posed to us in treatment of works of art on paper, then, is how to achieve an effective reduction of discoloration with the safest possible means, minimizing the use of potentially dangerous chemical bleaching agents. The purpose of this paper is to discuss some methods with which we may meet this challenge.

Our standard procedure in the treatment of a discolored object is first to employ dry cleaning methods like brushing and erasures, and the application of some organic solvents which are safe to the paper and the media. When carried out with skill and ingenuity, these methods can considerably reduce certain stains and surface soil. The materials and methods for dry cleaning are discussed in various publications[1,2,3]. However, to reduce general discolorations in paper, we depend on the cleansing action of water. Water cleanses acidity, discoloration, and degradation products from paper and strengthens its structure by re-establishing bonding among fibres. Recent findings at the Library of Congress[4] caution us about the weakening effect of deionized and distilled water on paper. But the effect of water as a benign solvent for discolorations in paper is generally agreed upon.

Occasionally, chemical bleaches are resorted to prematurely when the effective limit of water's cleansing action seems to have been reached. But there are safe methods by which the cleansing action of water may be made more effective, and beyond this point there are still safe alternatives for the reduction of discoloration besides chemical bleaching. I will present three safe methods of increasing the effectiveness of water as a cleansing agent, and an organic alternative to chemical bleaching which is effective in certain instances. Many of you are already familiar with these procedures in your own practice. I will then present my observations on a traditional technique of non-chemical bleaching which I have also used experimentally in my work.

The Use of Safe Alkaline Substances in Water Cleansing: Since many of the discolorations in paper are acidic in nature, their reduction is achieved most effectively if the water used for the purpose is alkaline. Hey noted in her article on paper bleaching[5] that a deacidification procedure removes considerable discoloration from paper. She used solutions of calcium hydroxide and magnesium bicarbonate as immersion baths for this procedure.

The alkaline wash should follow a preliminary plain water wash in most cases to lessen the risk of shock to the paper. Paper conservators have observed that deacidification agents sometimes affect colours and binding of certain media, and occasionally leave a white crystalline deposit of carbonates that cloud the image surface. In cases where it is unsuitable to use a standard solution[6] of a deacidification agent, it should be used diluted in order to avoid these ill effects. Some reduction of paper discolorations can be achieved with a considerably diluted solution (e.g., magnesium bicarbonate to water 1:5, calcium hydroxide to water 1:10) used as an immersion bath. This is perhaps more effective in two baths with air-drying between each immersion. In view of the findings from the research at the Library of Congress[7], it is also important for conservators using deionized or distilled water to add a small quantity of either a calcium or a magnesium compound to their wash

[1]Plenderleith, H. J. & Werner, A. E. A., *The Conservation of Antiquities and Works of Art,* 2nd ed., London, 1971, pp. 78-79.

[2]Clapp, F., *Curatorial Care of Works of Art on Paper,* 3rd ed., revised. Oberlin, Ohio, 1978, pp. 59-61.

[3]Banks, N., Paper cleaning, *Restaurator,* Vol. 1, No. 1, 1969, pp. 52-55.

[4]Tang, C. & Jones, N. M. M., The effects of wash water quanlity on the aging characteristics of paper. *Journal of the American Institute for Conservation,* Vol. 18, No. 2, Spring 1979, pp. 61-81.

[5]Hey, M., Paper bleaching: its simple chemistry and working procedures, *The Paper Conservator,* Vol. 2, 1977, pp. 10-23.

[6]It appears that there are various "standard" solutions according to the way these deacidification solutions are prepared. The standard solutions here are: Magnesium bicarbonate *c.* .2%; calcium carbonate, a saturated solution diluted with water 1:1.

[7]Tang, L. C. & Jones, N. M. M., *op. cit.*

water, which will prevent the over-purified water from weakening paper and may increase its effectiveness as a cleansing agent through its mild alkalinity.

Ammonium hydroxide is a weak, volatile alkali, and its salts are soluble in water. Used in weak concentrations, it is considered harmless to paper. Paper washed in water containing a small amount of ammonium hydroxide (droplets of a concentrated NH_4OH, or less than .05% of the volume of the wash water) normally looks brighter than paper washed in diluted deacidification solutions.

The same, safe alkaline substances can be used for local application to discolored areas such as foxing marks, mat burn, and other stains which respond to alkalinity. In local applications, the standard solution of magnesium bicarbonate and calcium hydroxide can be used, and a slightly stronger concentration of ammonium hydroxide solution (e.g., twice the amount used for general washing) can be employed, brushed on to discolored areas a few times in succession. Additional moisture is then used to flood the area and the released discoloration is leached away with blotting paper or a vacuum suction table (see below). The released discoloration can also be washed away in an immersion bath, but this method of local application is especially useful for objects that cannot be exposed to excess moisture.

A word of caution about groundwood paper. It darkens in alkaline water, and although its acidity is more efficiently reduced by these alkaline substances, its brightness is not enhanced.

The Use of Alcohols in Water Cleansing: Among various wetting agents available for our use in the treatment of works of art on paper, alcohols appear to be the safest and most generally applicable to objects. Although alkaline water penetrates into the paper structure better than plain water, highly sized papers, especially those sized with alum rosin, and areas in paper with certain water-repellent stains will often refuse to wet thoroughly. By brushing or spraying an alcohol on the paper, or by mixing some amount in the water, the paper readily allows water to penetrate into its structure, and the cleansing effect of water is enhanced as the result.

Alcohol is particularly useful as a wetting agent when an object is cleansed by flotation over a water bath so long as no friable medium will dislodge and no colour will suffer ill effects from the more effective penetration of water.

Alcohol can be mixed in the water which is applied to discolored areas of an object that does not allow an excess use of moisture. It helps to prevent the formation of tide marks, and aids in the more effective release of discoloration as well as in faster drying of the areas.

The most common alcohol used as a wetting agent is ethyl alcohol. Methanol is more powerful and quicker in its action than other alcohols and is used in situations where such properties are called for as long as it is safe to the object.

The Use of Vacuum Suction Table in Cleansing Procedures: The vacuum suction table, which was introduced by Marilyn Weidner in 1974[8], greatly extended the range of possible treatment of paper objects. Vacuum suction tables are particularly valuable in the removal of discoloration because of their capacity to evacuate solubilized matters efficiently out of paper without immersion in a water bath, allowing water or organic solvents to flow through the paper structure by the draw caused by the vacuum suction. They are also useful in localizing moisture and solvents to areas under treatment without affecting other areas with fugitive colours or very friable medium, for example, where treatment should be avoided.

Exceptionally discolored papers and papers with thick or absorbent structures often retain dissolved discolorations within themselves even after repeated soaking in immersion baths. If these papers are simply dried, the discolorations will remain in their structure. By placing such papers over a vacuum suction table, it is possible to evacuate the discolorants out of its structure. This procedure is quite effective on objects which have been floated over a water bath. In these cases, the diffusion of discoloration into water is not as effective as in immersion baths since the mobilized discoloration on the surface of the object often cannot penetrate downward to the water through the structure of the paper. The object is placed on a vacuum suction table face upward immediately after the removal from the flotation bath, and the discoloration is evacuated by the vacuum suction, with additional water applied from the surface by spray or brush application as the object allows. This procedure avoids tide marks and the mottling effect of discoloration which often are a problem in flotation cleansing.

Localized areas of discoloration on vulnerable objects with fugitive or friable media may be treated on a vacuum suction table. Discolored areas are brushed with alkaline water, mixed with an alcohol if necessary, and evacuated through the table, and additional fresh water is applied for final cleansing.

As yet vacuum tables are not commercially available. Those in use are made with various

[8]Weidner, M. K., A vacuum table of use in paper conservation, *Bulletin of the American Institute for Conservation,* Vol. 14, No. 2, 1974, pp. 115-22.

methods and materials which reflect the needs and ingenuity of their individual makers and users. My own table was designed by Robert Futernick of the Achenbach Foundation Conservation Laboratory using a vacuum-sealed aluminium Hexal panel and a wet-and-dry vacuum cleaner as the suction pump. I have used various other methods based on the same working principles outside of my studio; and in all instances I felt it helpful to use enough cushioning material between the object and the table surface so that the pressure from the vacuum suction would not distort the textures of paper and the medium. A sheet of blotting paper on top of a felt approximately ⅛" thick creates enough cushioning for my table.

Enzymal Reduction of Discolouration: Hardened and discolored adhesives are very tenacious and difficult to remove by ordinary means from the porous, retentive structure of paper; so is the engrimed soil which is trapped among the interstices of paper fibres. Here, the mere cleansing action from water falls short of its function. High temperature often increases the cleansing effectiveness of water in these cases, and steam heat often helps remove adhesives that react to high temperatures. But in these cases enzymes are generally a more effective cleansing agent than water.

The recent articles by Segal and Cooper[9] and by Hatton[10] describe their practical working procedures in the use of enzymes to release adhesives and to reduce adhesive stains and trapped soil in paper. More information is needed to establish the safety of enzymes in the treatment of paper, but the specificity of enzymes and the ease with which they can be denatured suggest a good safety potential for use not only as agents to facilitate the delicate and often time consuming procedure of removing the backing from an object, but also to reduce discoloration that is difficult to treat with other means.

The parameters of safety vary according to the nature of objects to be treated, and whether or not water and other agents may be used to eliminate residues and by-products of chemical substances utilized. The foregoing methods are by no means an exhaustive list of treatments possible for safe reduction of discolorations in paper, but are primary measures safe even for media that cannot withstand extensive cleansing. However, combining these means with skill and ingenuity can reduce discolorations considerably. And often in objects with fugitive or friable media, these are the only possible treatments we can apply to achieve any improvement in their visual effect.

As paper tends to retain substances or their harmful by- products to which it is exposed during the course of treatment, a large concern in using chemical bleaching agents is the elimination of harmful residues from the paper. If a bleaching method is available which does not employ a chemical bleaching agent, much of this concern may be eliminated. Bleaching with light is a method that does not employ chemical bleaching agents.

The Experimental Use of Sunlight in Bleaching of Paper Objects: The first chemical bleach, chlorine, was discovered by Karl Wilhelm Scheele in 1774. Before the use of chlorine, sun bleaching was the only method of whitening the linen and cotton cloths that were used as fiber sources for papermaking. Cloth was soaked in extract of wood ashes and in sour milk, then was spread over a grassy meadow and exposed to sunlight with frequent sprinkling of water. Nascent oxygen emanating from the grass aided in the bleaching action[11,12]. Sunlight has been used to bleach discolorations in the restorative treatment of paper objects for some time. Wätcher[13] used sunlight effectively to bleach black and white graphics and Egyptian papyri, spraying the objects intermittently with water to keep them moist. Plenderleith[14] describes a method to reduce tea and coffee stains by exposing the affected areas to sunlight after applying an aqueous solution of potassium perborate. Annis and Reagan[15], in their recent study, describe the effect of sun bleaching on an old, undyed cotton fabric, exposing dry samples to the sun up to 32 hours, and report good results. The fabric samples noticeably brightened without a detrimental effect on fibre properties.

Over the past three years, I have experimented with the use of sunlight in bleaching discolored paper and would like to report my method and observations here. I generally use an immersion bath to irradiate paper with sunlight. Water mixed with magnesium bicarbonate solution (*c.*2%) in the ratio of 5:1 is placed in a white photo-developing tray which is large enough to keep the shadow cast by the rim away from the paper. The paper should rest approximately 1" or 2.5 cm below the surface of the water. For paper objects which cannot be placed in an immersion bath, I use a "moistening sandwich". A blotting paper slightly larger than the dimension of the paper object is moistened with the mixture of water and magnesium bicarbonate solution and placed on a Plexiglas support. The paper object is also sprayed with the mixture and placed on the moistened blotting paper and a medium weight sheet of Mylar film is placed over its surface. The entire sandwich is then placed in the sunlight. The blotting paper supplies, and the Mylar film retains, the necessary alkalinity and moisture. Although frequent spraying is not necessary since the sandwich remains moist, sunlight warms the sandwich considerably if left alone during the course of irradiation, and occasional spraying on the surface of the paper object is necessary to keep

[9]Segal, J. & Cooper, D., The use of enzyme to release adhesives, *The Paper Conservator,* Vol. 2, 1977, pp. 47-50.

[10]Hatton, M., Enzymes in a Viscous Medium, *The Paper Conservator,* Vol. 2, 1977, p. 9.

[11]Barrow, W. J., *Permanence/Durability of the Book—III: Spray Deacidification,* Richmond, Virginia: W. J. Barrow Research Laboratory, 1964, p. 9.

[12]Clapp, V. W., The story of permanent/durable book-paper, 1115-1970, *Restaurator,* Supplement No. 3, 1972, pp. 12-13.

[13]Wätcher, O., The Cleaning and Bleaching of Prints, Graphic Arts and Water-Colours. English translation. *Einband-und Grafik-Pflege.* Date unknown. pp. 156-166.

[14]Plenderleith, *op. cit.,* p. 86.

[15]Annis, Z. K. & Reagan, B. M., Evaluation of selected bleaching treatments suitable for historic white cottons, *Studies in Conservation,* Vol. 24, No. 4, November 1979, pp. 171-178.

it cool. The Mylar film also avoids the harmful effect of evaporating water to cellulose at a cellulose-water-air interface[16].

The exposure time in the sunlight varies according to the season and to the degree of discoloration of the paper but normally ranges between 2 to 4 hours. During this time the object should be turned to expose both sides.

As bleaching procedes, the solubilized discolorants are leached away into the bath or moistened blotting paper, but after the irradiation is completed the paper object is further cleansed by immersion in a clean water bath or, for objects which cannot be immersed in water, by the application of moisture by spray or brush on a vacuum suction table to remove the solubilized substances remaining in paper. Deacidification procedure should follow.

Magnesium bicarbonate solution is added to the water because the presence of the magnesium ion retards the degradation of cellulose in oxidative bleaching processes by deactivating the catalytic action of metal impurities such as iron and copper present in paper[17,18]. Richter[19] found that paper treated with magnesium hydroxide solution was well-preserved after 100 hours of dry exposure to direct sunlight in Florida.

UF-3 Plexiglas, or a similar filtering material should be placed over the paper if the ultraviolet radiation in the sunlight is feared to cause an adverse effect. UF-3 filters all the ultraviolet radiation and a portion of the violet and blue range in the sun's spectrum. Even with this filtering, discoloration is reduced, although the bleaching action is slower and paper objects must be exposed to sunlight for a longer time (approximately 1 to 3 hours longer depending on the time of year and the degree of discoloration in paper) to achieve a satisfactory result.

With all bleaching methods, there is a risk of fading if colours are exposed to sunlight. However, it is possible to expose a local discolored area to sunlight and block the penetration of light to undesirable areas by masking these areas with opaque paper or aluminium foil. If the colours present are not water-soluble, such as in western colour prints, the "moistening sandwich" unit can be used after masking areas where exposure is to be avoided. If any colours are water-soluble, the moistening should be limited to the stain and the adjacent areas. Care should be taken not to form tide marks in this case by leaching away the solubilized discoloration from the surface from time to time with dry blotting paper and applying additional moisture by "feathering" toward the adjacent areas. This method may give conservators a wider latitude in treating discolorations on objects with moisture-vulnerable media since the subsequent cleansing with water is far less compared to that required when a chemical bleaching agent is applied locally. The exposure time varies tremendously, but much shorter than that of overall bleaching so as not to cause unevenness of the paper tone.

Sun bleaching is not suitable for all papers. In fact, sun bleaching should be used principally for rag papers made before the middle of the 19th century. Pure cellulose is a stable material and direct degradation of cellulose by sunlight is minimal[20,21], and early papers were relatively free from light-sensitive impurities. But from about 1850, wood pulp was in prevalent use in papermaking. Lignin is an impurity in wood pulp and is known to be very unstable in light. It absorbs light, decomposes, and in so doing degrades paper. Papers with a high lignin content, such as groundwood papers, should not be subjected to sun bleaching as they darken rather than brighten. The presence of lignin can be tested by a simple colour reaction of phloroglucinol solution applied to a fibre sample obtained from the paper in question[22]. About the same time as the use of wood pulp, alum rosin sizing came to be used in papermaking. Richter[23] reported that the presence of rosin endangered the stability of paper in dry exposure to the sun for 100 hours. Although it is not certain that alum rosin sized papers will be appreciably affected in the short irradiation time required in this method, it is a good policy to avoid sun bleaching them. Rosin size in paper can be detected by a characteristic ring when ether or a similar solvent is dropped in a spot on the surface of paper, or by observing the resistance of ink from feathering when applied to a crease[24].

Most papers industrially manufactured in the 20th century contain mixtures of various fibres and chemical additives used as sizing, coating and filler, and it is impossible to detect what substances may exist in a given paper without a specialist's knowledge in paper analysis. Titanium dioxide, for example, is a pigment that came into use in the 1920s, and subsequently has come into wide use as a filler to increase the brightness and opacity of industrially made papers. This substance can cause photochemical degradation of cellulose. The detection of titanium dioxide filler requires more involved chemical tests than are feasible in a normal paper conservation laboratory. Since titanium dioxide and other photosensitive substances are found in modern papers, sun bleaching should be used cautiously with ultraviolet filtering. Further studies would be helpful to establish whether potentially harmful substances are in fact harmful during the short period of filterable irradiation required in sun bleaching.

[16] Bogarty, H., Campbell, K. S. & Appel, W. D., Some observations of the evaporation of water from cellulose, *Textile Research Journal*, 2, 1952, pp. 75-81.

[17] Gilbert, A. F., Pavlovova, E. & Rapson, W. H., Mechanism of magnesium retardation of cellulose degradation during oxygen bleaching, *Tappi*, Vol. 56, No. 6, June 1973, pp. 95-99.

[18] Isbell, H. S., Parks, E. W. & Naves, R. G., Degradation of reducing sugars and related compounds by alkaline hydrogen peroxide in the presence and absence of iron and magnesium salts, *Carbohydrate Research*, 45, 1975, pp. 197-204.

[19] Richter, G. A., Relative permanence of papers exposed to sunlight: II. *Industrial and Engineering Chemistry*, Vol. 27, No. 4, April 1935, p. 437.

[20] Padfield, T., The deterioration of cellulose: The effects of exposure to light, ultra-violet and high energy radiation, *Problems of Conservation*, London, 1969, pp. 119-120.

[21] Annis and Reagan., *op. cit.*, p. 177.

[22] Browning, B. L., *Analysis of Paper*, 2nd. ed., New York, 1977, p. 73.

[23] Richter., *op. cit.*, p. 436.

[24] Browning., *op. cit.*, p. 83.

Without forgetting the cautions and limitations mentioned above, I would like to present some observations on the remarkable results of bleaching accomplished by sunlight. My observations are necessarily subjective, but some scientific tests on sun bleached paper samples are now being performed at the Cooperstown Graduate Program by Thomas Branchick under the supervision of Dr. F. Christopher Tahk, and these may result in some corroborative quantified data.

1. The use of sunlight is a very effective bleaching method. Stains such as distinct matburns, dark foxing marks, wood stains, and other pronounced discolorations that would require strong solutions of various chemical bleaching agents are satisfactorily reduced by single exposure. Since these tenacious discolorations are reduced simultaneously as the overall bleaching of the paper takes place, I have not found it necessary to expose only the local discolored areas. The only stains that do not reduce satisfactorily in sun bleaching appear to be those of metallic origin and dark pigmentation from mould growth.
2. Paper treated by this method of sun bleaching regains considerable physical strength, increasing its body and elasticity. Degraded paper that was weak and brittle before treatment is more handleable and supple, regaining its "rattle" in most instances. The recovered elasticity is observed in the ability of paper to flex more, and in the regained textural qualities of paper. The three-dimensional quality of relief and intaglio prints returns quite well. It is quite remakable to see portions of paper which have been particularly weakened by wood stains and other highly degrading discolorations regain their normal strength and recover the appearance of the rest of paper. In chemical bleaching these areas most often persist in their weakness, and sometimes shatter in the presence of strongly alkaline bleaching agents or become spongy from the effervescence of certain bleaching agents like sodium borohydride that disrupts the already weakened fibre bonding.
3. The visual effect of sun bleached paper is most pleasing. Paper has a warm white tone rather than the staring white brightness often observed in chemically bleached paper. The brilliant appearance of ink in black and white graphics is often remarkable. This probably is due to the fact that the binding medium of the ink remains intact in the sun bleaching method, whereas in chemical bleaching the medium may be affected by the strong alkalinity of the initial bleaching agent or by the antichlor subsequently used, or by both, which cause the ink to "gray" slightly. It is also partly due, no doubt, to the congenial warm new tone of the paper interacting with the ink to create this lustrous effect. Additionally, the regained textural quality of the paper contributes to the subtle three-dimensionality of the image, enhancing its visual effect. The end result after necessary repair and gentle pressing is an object that appears natural without the forced whitened appearance of chemical bleaching. The restored object looks as it should and as it was meant to be.

No study has yet been made to my knowledge to assess the effect of sunlight on paper under the conditions I have discussed and evaluate its use as a bleaching agent for paper objects. Sunlight is a much feared light source in conservation and its degrading effects to papers and textiles have been considerably studied[25]. However, these studies are normally carried out over long irradiation period (often 100 hours or more), and usually in dry exposure conditions. We must await for future studies to fully evaluate the soundness of this bleaching method which employs a short irradiation time and is carried out in the presence of water and magnesium bicarbonate. Until it can be proven safe, I present this method simply as an alternative possibility to be considered in paper bleaching.

The use of sunlight as an irradiation source may pose a problem for many conservators who do not have an access to it year-around as I do in California, and even where sunlight is present, air-pollution may pose a problem in urban areas. But xenon arc lamps produce a spectrum close to that of sunlight, and investigation of an artificial light source that would be practical for the use in a conservation laboratory is now underway in the project at the Cooperstown Graduate Program.

[25] Padfield., *op. cit.*, List of publications as of late 1960s, pp. 159-165.

This paper was first presented to the Cambridge 1980 International Conference on the Conservation of Library and Archive Materials and the Graphic Arts and published in the preprints of that conference. It will be published in revised form in the Cambridge 1980 Proceedings.