A Survey of Recent Scientific Research which has Caused a Re-evaluation of Commonly Used Practices in Book and Paper Conservation

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(A copy of a talk given at the AIC Annual Meeting in New Orleans, Spring 1988. This article has been slightly edited to improve readability and has been updated since the Spring to include new research information.)

When I was first approached to give this talk I saw it as a wonderful opportunity to speak with my colleagues -- both scientists and practicing conservators -- and review the literature on new developments and old developments I had forgotten. It soon became apparent that in a twenty minute presentation I could not hope to discuss all of the scientific research that has affected paper conservation practice. As a consequence I plan to give a very personal overview of historic developments and current research in four areas: Bleaching, Washing and Deacidification, Encapsulation, and Fumigation.

However, before I talk about scientific research that has changed the way paper conservators do their work I would like to comment on research developments that are changing the way research is being conducted. Some of the most significant changes that have occured in the scientific evaluation of the nature of paper involve the manner in which experimental data are analyzed and interpreted.

In case you were not aware of it, the paper substrate is not a simple material to analyze. The whole cannot be evaluated without analyzing the parts, but the individual parts do not nescessarily describe the whole. Paper is a composite material. It is a mat of fibers. It has characteristics that are imparted to it because of its web construction, its individual fiber nature, its fiber to fiber chemical bonding, its molecular structure and a long list of factors which arise out of the manner in which it was manufactured including cooking, beating, forming, drying, and finishing. In addition the finished product often has fillers, brighteners, sizings and other additives that also contribute to the character of the sheet.

To simplify things, research into paper tends to focus on the substrate at its purest level and ignores the additives and certainly ignores the design medium on the surface. A lot of testing is done with something called Whatman Filter Paper -- the pure cellulose sample; and newsprint -- the woodpulp, lignin containing sample. Yet the composite nature of the paper objects we all work on as conservators limits the usefulness of tests which have focused on these isolated components.

In addition, it is often difficult for scientists to see a cause and effect relationship in the testing and evaluation of data. The paper matrix is complex, cellulose is quite resistant to chemical attack, and testing methods and analytical equipment must be sensitive enough to measure subtle changes. When changes are seen, a determination must be made whether they are significant and whether they are related to the experiment at hand.

The paper industry has been analyzing its own product for years, and yet EVEN IT does not completely understand all of the mechanisms for reactions in cellulose chemistry. Unfortunately, for our purposes, the industry's standards, and the questions the industry is trying to answer, can be quite different from what we need answered. The industry's orientation is towards the raw material and much of their testing is done at the vat, so to speak -- on raw pulp. Their experiments on bleaching and deacidification are evaluated before the sheet is cast and their strength tests are always on new material. Our questions, as paper conservators, revolve around the treatment of an already formed sheet of paper and we are actually talking about re-wetting, re-bleaching and treatments on papers that already possess very distinct characteristics.

Paper conservators want to ask scientists about the effects of particular treatments on paper, and yet before we can get an answer to a practical treatment question, we find that the scientists are still trying to clarify how to evaluate the degradation of cellulose. For example, one of the standard industry tools for evaluating paper strength, and one that has been widely used by conservators and conservation scientists, is the fold endurance test. In simple terms, this test is administered by a machine which literally folds a piece of paper until it breaks. Antoinette Dwan discusses the limitations of this test at length in her paper in the Spring, 1987 AIC Journal. While this test can be used as a quick indication of the state of degradation of a piece of paper, it is an imprecise measure and open to multiple interpretations. As a result it is not surprising that conservation scientists in recent years have moved away from fold endurance as the significant indicator of a paper's strength, and instead increasingly rely on a measure of the degree of polymerization or D.P.: a technique which looks at the length of the cellulose polymer chains. While this is not a new test, its application to paper conservation science for the analysis of degradation products is relatively new.

Another area that is being examined in detail is artificial aging conditions. The ideal artificial aging temperature for paper is an ongoing question -- as it is for many materials. Different cellulose breakdown products are formed dependent upon the temperature and humidity of the aging oven. Those products may not best represent the effects of natural aging. David Erhardt at the Conservation Analytical Lab of the Smithsonian, reported on his findings on the effects of artificial aging at the 1987 AIC Annual Meeting, and continues to research the problem. His research could change the future of paper testing and the meaning of previous research.

I raise these matters by way of an extended preamble because it is important that we all recognize at the outset that there are few truly settled issues in the areas I will be discussing. There are no easy answers. Paper conservators and scientists do not all agree on what techniques best achieve safe but effective treatments. Moreover, given the research now ongoing, what I have to say today may be moot by the time you read this article.

BLEACHING

The first area I would like to explore is bleaching.

Bleaching is probably the most talked-about treatment in paper conservation. "To Bleach, or not to Bleach", that is the question. Once the decision is made to remove a discolored material, then the words of Helen Burgess (among others) begin to ring in your ears. As Helen says: "It is difficult to conceive of a process which has more potential for the sheer destruction of artifacts."

Nevertheless, we do bleach! Over the last decade, chemical bleaches have been examined pretty closely and the general parameters of their safe use seem to be well defined. Bleaching must be done with the greatest respect for the artifact AND with the greatest attention to the method of application in order to make it as "safe" as possible.

The reactions which take place during bleaching are either chemical oxidation or reduction of the colored materials. It is difficult to confine this process solely to the stains you want to remove. Other components which make up the artifact, both the substrate and the medium, may be damaged by these same reactions. In additon to whitening, oxidizing agents cause changes that include a decrease in the degree of polymerization of the cellulose molecule, increase in carbonyl oxidation products, and the loss of a wide variety of physical strength properties. Nonetheless, oxidizing agents are often the only effective treatment against severe discoloration and have long been used in conservation treatments.

Some oxidizing bleaches which have fallen out of favor over the years are, potassium permanganate and Chloramine-T. The problem with Chloramine-T is that it bonds very strongly to paper fiber and can be extremely difficult if not impossible to remove -- there are better oxidizing bleaches available which do not have this problem. As for potassium permanganate, I do not know how widely it was used -- I experimented with it once -- it turned the paper sample bright purple-brown, then I added the acid which was the second step, and it became white again. It was 4th grade chemistry at its best. Chemically and aesthetically it was terrorizing to consider it as a conservation treatment.

Some of the oxidizing bleaches which are in use today include the following:

- -hydrogen peroxide
- -chlorite/chlorine-dioxide solutions, both as a gas and a liquid
- -and with great care, hypochlorites.

Recently, considerable attention has shifted to reducing bleaches. Helen Burgess has done research on reducing bleaches and has found sodium borohydride and tetramethyl and ethyl ammonium borohydride to be the safest for use in paper conservation. According to her research there have been no scientific results which show negative chemical effects on cellulose as a result of bleaching with reducing agents. In fact, when particular reducing agents are used after oxidizing bleaches, as one would expect, they can actually reduce the state of oxidation of the paper making it less vulnerable to future oxidation.

However, there are some very practical problems with the use of reducing bleaches in conservation. While they may be safe for the cellulosic polymers of paper, they can wreak havoc with the media and can pose serious problems to the physical structure of the sheet through the evolution of hydrogen gases. This can often be minimized by the use of the vacuum suction table and adjustment of the bleach mixture.

Needless to say, the easy answer to what bleach to use does not exist, and the limitations of any bleaching agent can be quite troubling. Despite the limitations of reducing bleaches, I have noticed that many conservators are using them more now than in the past, especially for spot bleaching.

I could not finish my discussion of bleaches without telling all of you who are not paper conservators why it is that paper conservators all carry dark glasses in their tool bags. No its not just because we are "cool" -- which of course we are... It is because the bleach that has really captured the interest of paper conservators in the last few years is light bleaching. The process basically involves the bleaching of paper with light -- either sunlight or artifical light -- in the presence of water, either a bath or locally wet paper. Light bleaching is an oxidizing process. In the 18th Century it was also the only bleach available. Now light bleaching is back, inspite of, or perhaps because of, the advances of chemistry.

Wholely apart from its scientifically provable merit, many conservators use light bleaching for very simple reasons: it is non-chemical, it is easy to control, and it is amazingly effective. Of course it is photo-energy and while it may seem more wholesome to humans, we already know that photo-enery can be a source of degradation when paper is exposed to it in dry conditions.

Whether or not light bleaching is the safest of the oxidizing bleaches has not been finally determined. Several scientists have been researching the effects of light on paper from different angles:

Robert Feller has been trying to identify what the components are that are being bleached or darkened by light in mostly dry conditions. He has been looking at model compounds that are representative of the components which would be reactive to light and heat in a paper substrate. Subjecting known sugars and known lignin-like compounds to light, he has been able to determine the effects of wavelength, temperature, and pH on brightening and on post irradiation darkening. His testing in dry conditions, however, have not proven to be representative of light bleaching under wet conditions. Dr. Feller most recently reported on results from light bleaching paper samples immersed in water (Ottawa CCI Conference, Fall 1988). His experiments indicate that light bleaching of lignin-free papers in wet conditions does not cause damage to the cellulose structure. The light degradation which is seen on dry paper may in fact be significantly attributable to thermal causes.

Further testing is still necessary, but Dr. Feller's work confirms some earlier informal tests done by Keiko Keyes with Santucci that have not been published. Their results which were analyzed using D.P. tests on good quality, non-lignin containing papers, exposed to the California sun, showed that there was no appreciable degradation of the fibers. Their test did not examine wood-pulp or severely degraded papers.

Dr. Feller's results also follow on the heels of Daine Van der Reyden's work at CAL. Risking oversimplification here, I request that the reader read her results as published elsewhere in this Annual. She examined the effects of light bleaching in water baths on paper of mixed fiber content. Tensile strength measurements were taken on test samples and no significant change in strength was found that could be attributed to light exposure. The tests did find a significant change in strength characteristics between samples which had been placed in water and those which had not been water treated. Whether this is due to the buffer material present in the water or just the effects of washing is not clear and is reminiscent of the results of Tang and Jones on wash water quality.

Paper conservators can not get information fast enough about the effects of bleaching. At times we feel that we have so few tools in our arsenal to improve the state of a badly damaged work of art. More relevant scientific data would certainly make us feel more secure about our treatments.

WASH WATER QUALITY AND DEACIDIFICATION

I now want to turn to the area of water quality and deacidification.

Everyone knows that paper conservators wash paper. In fact a great number of paper conservation treatments involve the use of aqueous solutions. As basic as water always has been to the work of paper conservators, one of the pivitol papers on wash water quality was only done as recently as 1979. In 1979 Tang and Jones published an article on the effects of wash water quality on the aging characteristics of paper. Their study concluded that highly purified water actually shortened the life of paper by stripping it of buffering agents such as calcium.

As a result of their research, and subsequent research, paper conservators have taken a much closer look at the use of pure water in the treatment of objects. Today, "pure" water for routine washing is considered to be water which is free of iron, copper, chlorine, and organic materials but water which contains some salts, usually in the form of calcium or magnesium.

Aqueous deacidification can be seen as an extension of washing -- whether we are neutralizing or buffering is only a matter of solution concentration. Washing removes discoloration and degradation products and thereby can stabilize a paper. If the concentration of calcium or magnesium salts in the wash water is high enough, the end result is a deposition of the salts in the paper and buffering action which protects against future acid hydrolysis.

Pioneering work on deacidification was done 50 years ago by

Schierholz and in the 1950's by Barrows when he introduced the two-step deacidification process. In 1979, the National Archives and Records Service did a thorough examination of the various ways of making magnesium bicarbonate solutions and the effectivenss of those solutions. Their conclusion was: "There is still no 'Best' deacidification solution because very little quantitiative data is available on the effect of various deacidification solutions on typical papers."

While they may have been speaking only about magnesium bicarbonate solutions in 1979, that fact still holds true for the state of knowledge about most deacidification agents today. While research to date indicates that the presence of an alkaline reserve is beneficial to the cellulose polymer, testing has been limited in scope: few paper types have been examined, and solution concentration and make-up have not been fully explored. The amount of research currently going on in this area is a real indication of how many questions remain unanswered. Past research has not necessarily been consistent with treatments that are actually being used. The extremely low alkaline reserves which Tang and Arney examined, are not comparable to the 2%-3% reserve which the Library of Congress has recommended.

In the next year, Helen Burgess' research will be focusing on the effects of washing and deacidification on naturally aged paper, rather than Watman filter paper commonly used for such experiments. She has collected paper samples from Canadian archives which will be washed in low and high alkaline waters. She will be comparing the effects of calcium to magnesium, looking at concentration factors, and aqueous and non-aqueous deacidification treatments.

Tim Vitale at CAL is also looking into wash waters. He is examining the interaction of water with paper and the effects of calcium and sodium hydroxides and carbonates as washing aids. He is trying to find the experimental techniques which can characterize the changes that occur in the chemical and physical structure of cellulose without having to resort to artificial aging -- although he already thinks that artifical aging will ultimately have to be done. Among other things he will be looking at hydrogen bonding between fibers, and the size and distribution of amorphous and crystalline regions in the polymer.

Santucci is also conducting research in Italy on the nature of the products formed and the changes occuring in buffered papers.

Meanwhile for the mass deacidification of books and archives, research continues at the Library of Congress to determine how much of an alkaline reserve is sufficient for the longest term protection of paper. LC's Diethyl Zinc pilot plant is now operating in Texas. This ambitious project is one of the stickier subject among those in the mass deacidification business, so I refer any questions you might have to Peter Sparks who has been tending the fires in this area (so to speak).

Wei t'o is also available as a non-aqueous agent for individual and mass deacidification projects. Because of its ease of application, it is the principle non-acqueous treatment available to smaller labs. However, it continues to raise questions among some conservators because of its high alkaline deposition in the paper and some uneven mottling that can occur during use.

It is interesting to note in conclusion, that the approaches of conservators who do individual treatments and those who confront mass deacidification projects seem to be on dramatically divergent paths. At the same time that we have seen a push to deacidify general collection materials through mass efforts, many conservators who treat individual objects continue to be hesitant about routine deacidification. Where acidic materials are involved in libraries and archives, the need for long term preservation is often paramount and mass deacidification with the deposition of an alkaline reserve in the paper is one of the few options available. Meanwhile, the same does not hold true for the treatment of individual objects. Paper conservators are very aware of the fact that washing and buffering are not casual treatments, but rather irreversible treatments causing permanent chemical alteration of the paper. While preservation is still the goal, concerns about immediate or future aesthetic alteration of the artifact due to the effects of deacidification may take precedence -- media can be altered, the paper surface and handle can be changed and deposition of the buffering solutions evenly through the paper substrate can sometimes be problematic.

All of the ongoing research into deacidification will hopefully produce some answers for conservators in the near future. However, the most that we can probably hope for in the treatment of individual works of art -- whether we are talking about decisions involving deacidification or any treatment -- is that with enough hands-on experience and perhaps some background information about the pH, age and strength of the paper, we may be able to judge the so-called "needs" of the paper. There will always be a need for the conservator's sixth sense.

ENCAPSULATION

Polyester Film, often called by its brand names of Mylar or Melinex, has been a boon to the world of conservation. As an encapsulating material it has been widely used in paper and book conservation. By using mylar, the single fragile leaf can be physically protected in a clear, supportive, flexible, non-acidic material which is not bonded to the surface of the artifact and can easily be removed. Mylar's static charge can be used to one's advantage and its flexibility will allow for whole books to be encapsulated and rebound -- dramatically changing the structure, but nevertheless preserving the physical structure of the individual leaves.

When Mel Brooks, in his role as the 2000 year old man, was asked what was the most significant invention of mankind in two thousands years -- he said "Saran wrap -- it clings, you can see through it, and you can take your lunch to work in it...." Same with mylar...it's great.

Initially Mylar was used with great zeal. In recent years questions have arisen about how it should be used. Must an object be deacidified before encapsulation? Only washed? Both washed and deacidified? If not, are we creating small incubators for the action of acids? Should buffering sheets be enclosed in an encapsulation? Should the mylar be completely sealed or open a little or a lot? What about the problems of dust and pollution versus the problems of acid content in the long term preservation of an encapsulated object?

I could not possibly discuss all of these recent concerns in detail in this limited article. Instead I will focus on just a few examples of research on encapsulation that have started us thinking about current usage.

When we deal with the environment for books and paper we must continually evaluate the advantages and disadvantages of holding something IN versus keeping something OUT. Early testing on materials in enclosures included tests done by Browning at the Institute of Paper Chemistry in the 1960's. He found that paper samples enclosed in glass containers aged more quickly than those that were not enclosed. Yet we also know that there can be benefits to a microenvironment in providing protection to an object -- protection from the effects of oxidation, pollution, environmental fluctuations and handling.

When LC published its pamphlet in 1980 on polyester film encapsulation, it stressed the desirability of deacidification of paper objects before their encapsulation. This recommendation was based on laboratory data which showed that some paper samples aged faster after encapsulation if they did not contain an alkaline reserve. Based on this research, conservators hoped that when encapsulating an unbuffered item, that if the envelope was left open along an edge or not completely sealed, that acid degradation products could escape. Alternatively, by enclosing another sheet of paper containing an alkaline reserve in the envelope, it was thought that acidic compounds could be neutralized.

Chandru Shahani at the Library of Congress recently tested some of these ideas and although he feels that further testing is required due to some possible flaws in the experimental set-up, some of his conclusions include the following for materials which are not deacidified:

1. air holes do not slow degradation, although the degradation is slightly less if the envelope is open along two edges.
2. enclosing a buffering sheet does slow deterioration on neutral sheets and actually benefits acidic papers.
3. polypropylene can be used as a less costly alternative to mylar although it lacks the rigidity and therefore the support characteristics of mylar.
4. The best solution for the long term preservation of the object still is deacidification.

However, Shahani cautioned that these experimental observations should not be misinterpreted as a general and uncompromising recommendation against encapsulation without a prior deacidification treatment. After all, polyester film encapsulation does offer physical support and may be the last step before format transfer.

In part as a result of mylar research, I think that more consideration is being given to partial encapsulation. For example: Instead of envelopes where the entire enclosure is made of mylar, we are seeing mylar overlays on ragboard backings that are not completely sealed. Consistent with the research, we are also seeing greater use of open envelopes particularly where the storage environment is carefully monitored and relatively clean.

The whole question of acidic volatile components being trapped around an object because of encapsulation is quite interesting. It comes up not only when we look at polyester encapsulation, but also when we consider the effects of parylene on paper and books. As far as I know, the parylene process is still experimental and not currently being used on books because there are serious technical difficulties involved in distributing parylene evenly through a bound volume. But the parylene process simulates encapsulation and one can expect similar benefits and concerns <u>without</u> the reassurance of reversibility.

Susan Lee-Bechtold at the National Archives has been looking into the chemical consequences of another type of encapsulation: the shrink wrapping of books. While there are aesthetic disadvantages, shrink wrapping offers the advantages of saving space and containment of decomposing bindings in cases when treatment is not immediately available. It is easily reversible if the volume is needed for research, and it is a relatively inexpensive and quick solution for libraries and archives. The concerns, as you might expect, are the same as they are for any of the closed systems, with the further complication of enclosing binding materials such as acidic leather or pyroxylene coated cloth.

Perhaps the Chinese solution to mold in archives is also the best compromise vis-a-vie the holding-something-in-verses-keeping something-out dichotomy. I have been told that one day a year, some Chinese archivists take their books out and fan them in the breeze.

FUMIGATION

Speaking of mold, I want to conclude my talk this morning with a few words about fumigation.

Ideas about fumigation to kill or inhibit mold growth on paper have changed a great deal in recent years. It used to be that every lab had a thymol chamber where screen racks sat over a low wattage light bulb which heated a dish of thymol. The accepted treatment was to put the mold damaged article in the chamber for a few weeks and then, when you removed it, to brush off the dead mold. Presto, your artifact was protected -- or at least the mold was dead. Well, apparently not.

Research has found that in addition to being hazardous to your health, thymol is not effective in killing the broad spectrum of mold that we thought it would kill. Mary Wood Lee gave an inkling of this when she mentioned at the Baltimore AIC meeting that placing mold infested articles into a thymol chamber just gave the mold more time to grow and spread!

In recent years various researchers and conservators have shared with us their favorite fumigants. Some like thymol. Some favor orthopenophenol. Ethylene oxide will sterilize anything (including the staff). Biblio-cryobionics has been suggested, as have vacuum treatments, radiation, and carbon dioxide. I am sure

I have missed some.

While it has always been known that the way to control mold growth is to control the environment, the current thinking is that controlling the environment is also the most effective way to stop mold. According to Tom Parker's (of Pest Control Services, Inc.) research, what stimulates a spore to germinate is not the moisture content of the substrate, but the relative humidity in the immediately surrounding area. If the RH is less that 65%, a spore cannot germinate and more importantly, for treatment, cannot continue to survive. That means that if an object with an active mold growth is subjected to a RH below 65% it will be killed. The spores may not be killed, but the feeling among many researchers is that we live in a spore-filled world anyway, and killing a few will not eliminate the problem -- regulating the environment will.

Certainly if the intrepid conservator is still intent on killing spores, there seem to be much less toxic agents available than thymol and ethylene oxide. For example, Richard Smith has suggested the use of the vaccuum chamber which will cause mold spores to burst.

It may seem strange to think that a non-treatment may be the best treatment for a problem like mold, but research into fumigation has increasingly rendered the fumigation chamber a thing of the past.

I would like to thank all of the individuals listed in this article for doing the research that they do in conservation -- it is much needed. In addition, I would like to thank those who so generously gave of their time to help me clarify the scientific data and the issues which are being debated in our specialty. Helen Burgess, Diane Van der Reyden, Robert Feller, Tom Parker, Keiko Keyes, Tim Vitale, Chandru Shahani, Susan Lee-Bechtold, Tom Albro and the paper conservators at LC were of invaluable assistance to me.

In conclusion I would like to urge all of my fellow paper conservators to take a conservation scientist to lunch -- or vice versa.

I welcome comments and discussion at:
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