

Paper Conservation Research 1974-2004

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I have been asked to provide a reflection on the way paper conservation research has changed over the time I have been involved as a researcher. This is a purely personal view and as such is certain not to be representative of the field. The time span corresponds to the thirty years following my first employment in conservation research until a year after I started working for the Royal College of Art.

I started as a conservation scientist at the British Museum in April 1974 working with A. D. Baynes-Cope or “BC” to his friends and co-workers (Figure 1, Photograph of Baynes-Cope, died 2002). I soon made the acquaintance of many conservators who worked on the British Museum site. These were not only the BM’s own staff but those in the then recently split off British Library, including binders and conservators of manuscripts, both European and Oriental. I was welcomed in all the conservation areas making the British Museum site an excellent place to learn about paper and book conservation. The state of conservation training had not reached the sophisticated heights that we are used to nowadays and some conservators, particularly those from craft backgrounds were not at-home with technical concepts. The only paper conservation scientists in the UK were those at the British Museum which made us a magnet for telephone calls from paper conservators and members of the public wanting information.



Figure 1. Photograph of Baynes-Cope a couple of years before his death in 2002

It is important to realise the dearth of printed information about conservation at that time. The only conservation textbook was *Conservation of Antiquities and Works of Art* by Harold Plenderleith updated by Tony Werner (Plenderleith and Werner 1971); both heads of the Research Laboratory at the BM.. The Institute of Paper Conservation was not yet formed so there was no *Paper Conservator*. *Restaurator*, nowadays a prominent journal for paper conservation research articles, did not come out until 1969 and at that time was a slim volume. The 4th triennial meeting of ICOM -Conservation Committee was in 1975 and these are the first proceedings I am aware of. At that time the Graphic Documents group was headed by François Flieder. Over the last 30 years, paper conservation

scientists have been reluctant to publish books. While we have seen books on the conservation science of a wide variety of materials, it is only recently that the first books on paper conservation science have started to come out.

Nowadays a good quantity of sophisticated research on paper properties is generated by the conservation research community. I particularly remember the high quality of work coming from the Library of Congress Laboratory and William K. Wilson. However in 1974, much of the experimental work on which we based our assumptions about paper came from research in the paper industry in Scandinavia and North America. .

At that time, the research done by the W. J. Barrow Research Laboratory in the 1950s and 60s (it closed in 1977) was the bed rock of the theory of paper deterioration and the majority of paper deterioration was explained by “acid”. Paradoxically they also pioneered a laminating process which used cellulose acetate. The subsequent deterioration and release of acetic acid led to the deterioration of laminated paper which was not sufficiently buffered with alkaline material. Having recently completed a PhD on PVC degradation with a heavy emphasis on free radical reactions, I was only too aware of the lack of emphasis on free radical oxidation reactions, a fault which was gradually remedied by subsequent work internationally. Robert Feller and co-workers at the Mellon Institute were interested in oxidation of museum materials but they did not work on paper until 1978.

In the BM’s Department of Prints and Drawing’s conservation studio, I gained practice in the conservation of the very large Italian print collection which were then routinely bleached, usually with chlorine dioxide in solution and then deacidified. Bleaching is out of fashion now as curators and the public seem to be able to accept a higher degree of discolouration than they did then and seem content with the results of water washing. However, we now know that there is no water washing technique which will restore the paper to the colour it probably was when new and there is still a place for bleaching -which may become popular again. During my career, one of my favourite paper conservation scientists was Helen Burgess (Figure 2) who worked at the Canadian Conservation Institute. She published a large amount of work on hydrogen peroxide as a bleach just as bleaches were falling out of favour (Burgess 1988). Chlorine dioxide also fell out of favour and I don’t think anyone uses it now. A lot of conservators used chloramineT a powder which when dissolved in water releases hypochlorite ions. In my first years at the BM, I published a paper (Daniels 1976) saying that some papers, particularly those which contained aluminium ions would retain chloramineT when being washed. Conservators seem to take any criticism of a conservation material very



Figure 2. Helen Burgess

seriously and it was not long before chloramineT entered the word-of-mouth list of substances of which it was whispered “it’s been banned” and joined the ranks of barium hydroxide in methanol (deacidification) and chloroform (for sticking Perpex). “Banning” of conservation materials has been either due sometimes to the toxic hazards or a realisation that there were better products, e.g. methanol solutions of soluble nylon sometimes used by paper conservators to protect water fugitive inks was banned when it was realised that it became insoluble on ageing. ChloramineT is still used in private conservation sector.

If bleaching is done at all today, it is often done using light. Bleaching by sunlight has been used for centuries for bleaching cotton and linen and the principle was adapted by Keiko Keyes (Keyes 1980) for use by paper conservators. This is seen as a very “green” process and indeed has a great deal going for it in that the laws of photochemistry predict that only discoloured areas are bleached as these are the only areas that should absorb visible light. The bleaching is performed in alkaline conditions, often magnesium bicarbonate or calcium hydroxide solution.

The development of suction tables and ultrasonic mist methods are extra tools which conservators use when washing paper and these allegedly obviated the need for some bleaching methods. I have been interested in the basics of paper washing for many years (Daniels and Kosek 2003) and we are gradually learning more about the interaction of water with paper. Indeed a summary of the most useful information on this will soon be published (Banik and Bruckle forthcoming). Hot water washing is a traditional Chinese practice and Western conservators have used water up to 100°C has been used to wash iron gall ink documents occasionally. Despite comprehensive research (Tse *et al* 2005) which showed very positive results, the practice is shunned by most practicing conservators.

The discoloration of paper on ageing is a large area and presents several mechanisms which could take place. Although development of colour is an undesirable consequence of ageing it has probably rightly been neglected in favour of the study of strength change or chemical change. However, colour is easily and cheaply measured non-destructively. It is also a pity that the types of chromophore present in discoloured paper are so poorly characterised. When washing discoloured paper, conservators talk about washing out discoloured size and Maillard products but this has never been proved. The mysteries of what happens at the wet/dry boundary to promote the formation of fluorescent and eventually brown compounds are still promising research areas (Pedersoli Junior and Ligterink 2001)

Deacidification is a field which is full of interest for the paper conservation scientist with imagination. In my early days there were two aqueous treatments, calcium hydroxide and bicarbonate and magnesium bicarbonate. On the non-aqueous side, there was barium hydroxide in methanol (invented by BC and thus well known at the British Museum). A later entrant was magnesium ethoxide which reacts with water on storage but can be stabilised by reacting it with carbon dioxide. Barium hydroxide fell out of use as toxicity issues came into focus due to a greater emphasis on health and safety issues. Plenderleith

and Werner mention a vapour phase treatment invented by Langwell based on cyclohexylamine carbonate which was sold as an interleaving tissue for insertion in books. This was not very effective and made the paper go yellow. In the last few decades, a whole load of interesting and chemically sophisticated methods have been invented. A paper by Cedzová et al (2006) lists 70 patents for deacidification processes.

Good mass deacidification processes are much in demand as libraries and archives are full of acid paper in need of deacidification and in some cases subsequent strengthening. One of the most exciting was diethyl zinc, a vapour phase process developed by the Library of Congress using vessels left over from the space program for the reaction chambers. However several novel treatments have achieved commercial success including one with particles of magnesium oxide. I remember we used to pour scorn on the idea that particles of solid could cause deacidification because there was no mechanism for chemical reaction to take place. Maybe we were reckoning without the mechanism of acid migration.

Whatever the process to be tested, the efficacy could only be tested with accelerated ageing tests. In 1974, 100°C for 3 days in a dry oven was a popular ageing regime. Nowadays temperatures tend to be lower and maybe include an elevated relative humidity if the laboratory has access to a climate chamber. There cannot be any doubt that the lower the test temperature the more the degradation mechanisms during the test reflect those in natural ageing. I recall testing a sample of PVC laminating film which I tested at 100°C. At the end of the test the PVC had turned purple due to dehydrochlorination and the formation of polyenes. I knew all about that just having studied PVC degradation for my PhD. This deserved greater study and I performed ageing at several temperatures from 80 to 120°C and plotted an Arrhenius graph to calculate the activation energy. This is a similar methodology to that used by paper conservation scientists studying paper degradation. Extrapolation of the graph revealed that the new tape would turn purple in 22 years. I kept the samples and 29 years later the samples had not changed at all including some which were exposed to accelerated ageing and already starting to go purple.

Such apparent failures in extrapolation of the Arrhenius equation to predict the future performance of materials make me admire workers who have the foresight, time and patience to perform ageing at low temperatures and for long times. The alternative is to devise a method for studying degradation at ambient temperature. Long-term trials have been set up by scientists and some experiments are underway. One other approach is to look back at the experiments have been unintentionally set up for us in libraries and museums. The British Library's project on looking at identical books in different libraries is one example. However those scientists who work in museums and libraries should realise that whole collections are different experiments of different degrees of interest. If we only could know what the objects were like before they started to age and their storage history! Another approach is to monitor ageing at ambient temperature. One example has been my own work on the Russell effect (Daniels 1984) which studied a process which produces a latent photographic image produced (probably) by hydrogen peroxide from objects due to their oxidation. Unfortunately the process is difficult to

quantify and the amount of hydrogen peroxide evolved probably differs from one material to another. The phenomenon of chemiluminescence can be used to monitor oxidation of paper. Modern equipment has made it possible to detect the very low levels of light produced with reliable and inexpensive equipment. The PAPYLUM project (Strilic 2004) had this as its core subject. Again the mechanism which caused chemiluminescence is oxidation.

Methods for measuring acid-catalysed hydrolysis, the other principal mechanism for paper deterioration are not sensitive enough to follow degradation at room temperature. However it may be that methods for the detection of evolved volatile organic compounds may be developed to do this. Mass spectrometers are now highly sensitive, reliable and robust instruments and are capable of detecting the low levels of the organic acids which may accelerate ageing of paper. (Buchbauer et al 1995) detected over 70 compounds in the head space above old books. The British Museum has pioneered the use of accelerated corrosion tests for the effect of materials on metals (Thickett 2004). Lead is extremely sensitive to the effects of organic acids which are catalysts for the reaction of lead with carbon dioxide and water to form basic lead carbonate. However I will not comment further as I do not wish to second guess the conclusions of this meeting.

Several papers have been published on the differences between the ageing of single sheets of paper and stacks of paper (for example Carter *et al* 2000). Invariably, there is more degradation when the paper occurs in bulk which tempts the interpretation that volatile materials, either oxidants or acids may be being released from one sheet of the paper and are influencing the adjacent sheet.

Hydrolysis produced non-volatile organic compounds too and work has been done on simple sugars such as glucose produced during degradation with very interesting results. One recent experiment has studied the effect of fluctuating RH on paper with an amazingly high acceleration in degradation rate as indicated by the release of sugars (Bogaard & Whitmore 2002).

As a scientist who has worked on organic materials in general, I often find that it is a shame that there is not more connection made between research done on cellulosic textiles and plant fibres and paper. The smells in stores of plant material may owe something to other associated materials but amongst these must be volatile organic compounds from cellulose-based products. Black-dyed New Zealand flax is dyed with a similar dye to that in iron gall ink. An accelerated lead corrosion test on the black New Zealand flax showed a prodigious outpouring of organic acids possibly due to acetyl groups in the hemicellulose. Hemicelluloses are also found in paper but I don't know of any recent work on the acetyl content of papers.

Much paper conservation research involves accelerated ageing and the paper then has to be tested to see if there is loss of desirable mechanical properties or chemical change. There are a large number of tests to choose from but many laboratories opt for tensile testing as the machines can be used to test a wide variety of different materials e.g. stone crushing or the strength of adhesive joints. The folding endurance test or a tensile test

after one fold as suggested by Bansa and Hofer (1980) more accurately reflects the usability of the paper. Methods for non-destructive testing of paper are much to be desired and mention must be made of the valuable work done by Derek Priest and colleagues at Manchester University's Department of Paper Science in the 1980-90s. Research topics included cockling, non-destructive testing of paper and the effects of alum on paper deterioration. The close liaison between this department and the paper conservation community lead to Dr Priest serving a term as chairman of the Institute of Paper Conservation.

Chemical tests for paper were developed industrially and were available as British Standards or American TAPPI (Technical Association of the Pulp and Paper Industry) standards. Chemical tests can be used to test the relative amounts of α -, β - or γ -cellulose. Feller introduced the useful idea that alkali solubility was related to copper number which in turn is linked to the extent of oxidation of the paper or pulp. This test was useful as the lignin content of papers often made other tests invalid. Viscosity of cellulose solutions could be used to follow the changes in molecular weight of cellulose. The industry standard tests were those in which cellulose (either paper or textile) was dissolved in cuprammonium hydroxide or a copper ethylenediamine complex. Both these solutions were alkaline enough to cause alkaline degradation of badly degraded cellulose and the solutions had to be kept free of oxygen; no mean task. Helen Burgess introduced Cadoxen (cadmium ethylenediamine) solutions of cellulose to conservation. The problem was that, as time went on and health and safety data was getting more reliable, it was realised that Cadoxen was hazardous because of cadmium toxicity. A major advance in determining the molecular weight of cellulose is that simpler and safer solutions can be made, one popular method is to dissolve cellulose in lithium chloride and N,N-dimethyl acetamide (Strlič et al 2005). Further more the distribution of molecular weights in a single sample can be determined by passing the solution through a gel permeation chromatography apparatus (also known as size exclusion chromatography); the shape of the curve obtained reveals the molecular weight distribution. The calibration of the apparatus is done against a maltotriose carbohydrate (pullulan) solutions of known molecular weight so there may be some errors introduced because of the dissimilarity of the polymers. However this is a great leap forward for assessing the degradation of paper.

This probably a good point to reflect on the advances in computer technology that have taken place over the review period. In 1973/4 the electronic pocket calculator had recently fallen below the \$100 mark and the term "personal computer" was not yet coined. The concept of Fourier transform infra-red spectroscopy had been around for a long time but was awaiting cheap computing technology to enable apparatus to enter the chemical laboratory. The first instruments were built in 1969, but only started to appear in conservation laboratories in about 1981. FTIR microscopes were invented in 1982 but were not in conservation laboratories until several years later. Tensile testing machines became much more useful when attached to a computer. The first one at the BM had an x-y pen plotter and was difficult to set up having two sensitivity knobs which needed continuous adjustment. Computers enabled the stress/strain curve to be measured and a myriad of different parameters calculated including maximum stress, tensile energy absorption (TEA) and the Young's modulus. When sufficient results were obtained, the

statistical treatment to obtain mean and standard deviation were calculated in a trice. However, scientists probably lost a true feel for errors in experimental measurement.

Finally, I will mention collaboration between scientists. First the bad news, the British Museum was once a fully integrated part of that great national institution called the Civil Service, the civilian counterpart to the armed forces. Different areas of the Civil Service used to cooperate and share knowledge and expertise free of charge. Why not - for it was all paid for by the Government? As the Civil Service fragmented into smaller partly or fully privatised sections, all this stopped. Similarly in industry, individuals in large multi-national companies became afraid to speak freely about the fields they were working in case they were giving information that could be charged for.

The good news is that cooperation between conservation scientists has grown due to well-funded international interdisciplinary projects. Some of the more recent European projects have been summarised (Havermans 2002). Some of the recent projects were POPYLUM chemiluminescence for studying deterioration of paper, PARELA laser technology for laser cleaning of paper, MIP research on the effect and occurrence of metals in paper, deterioration of paper by iron gall ink, Very recently there has been the SurveNIR project which looked at the use of near infra-red spectroscopy for characterising paper. In Canada, there has been a project on the effect of lignin on the permanence of paper has been studied. The American Society for the Testing of Materials (ASTM) with a team of 25 researchers from all over the world, studied tests for the accelerated ageing of paper (Havermans 2002)

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Captions

Figure 1 A.D.Baynes Cope

Figure 2 Helen Burgess