The Chemistry of Paper Conservation

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1 Introduction

There are probably more collectable objects based on paper than any other material: books, prints, drawings, watercolours, stamps, banknotes, matchbox labels *etc*. Not surprisingly, owners of such objects want them to remain in good condition despite the fact that many of them were only intended to have a lifetime of as little as a few hours, *e.g.* tickets. However, some papers and the images upon them are inherently unstable and others deteriorate quickly when stored under the wrong conditions.

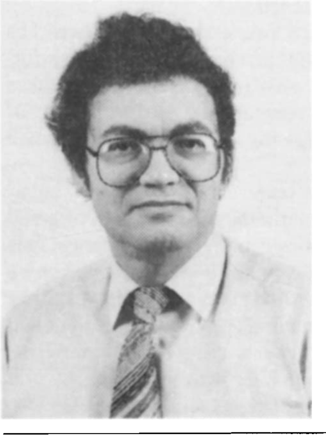
The study of paper conservation can be split into four areas: (*i*) the chemistry of the deterioration of paper and the writing or images thereupon, (*ii*) the physics and chemistry of processes that can be performed to enhance stability and appearance, (*iii*) the practical skills needed to carry out active conservation processes, *e.g.* bleaching and washing, and (*iv*) the management and storage of a collection. This review will concentrate on the first two of these areas as these will be of more interest to chemists.

There are two ways in which paper objects can be prevented from deteriorating; these are sometimes known as passive and active methods. Passive methods are those which involve creating good storage and climatic control so that damage by handling, incident light, thermal degradation, air pollution and excessively high or low relative humidity is minimised. Active methods involve treating objects to clean and stabilise them; examples of this are washing, deacidification and repair.

2 The Components of Paper

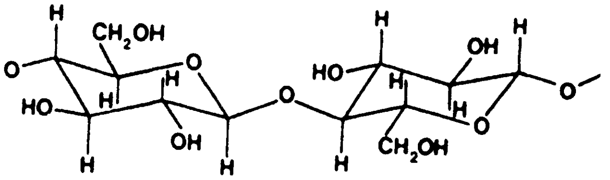
Paper is essentially a mat of cellulose fibres formed into a sheet by draining a suspension of fibres in water through a mesh. On drying, hydrogen bonds play a large part in bonding the fibres together. Many other materials can be added to sheets of paper: *e.g.* fillers, water repellents, wet strength additives, pigments, dyes and adhesives but often the main interest of a paper object is writing or surface decoration in the form of pencil, chalk, pastel, watercolour paint or printing and writing inks. With the huge variety of materials involved the study of the conservation of paper artefacts becomes wide ranging.

Cellulose occurs as a component of many plant cell walls. The amount of cellulose present varies between individual plants. Wood is 40—70% cellulose, while the purest source, cotton seed heads, contain up to 96%. These cellulose sources generally receive some sort of purification before they are made into paper, thereby increasing the amount of cellulose present in the fibrous components.



Vincent Daniels obtained a BSc in chemistry at University College, Cardiff (1970) and subsequently obtained a PhD studying the reactions of thermally degraded PVC (1973). He joined the British Museum in 1974 to work on the conservation science of paper. Since then he has worked on a wide range of conservation problems and is currently working on the deterioration and conservation of barkcloth and black-dyed New Zealand flax.

The cellulose molecule can be considered to be a linear polymer of *β*-D-glucose. The average number of glucose molecules in the cellulose chain is indicated by the degree of polymerisation (DP) which varies with the plant source and the severity of any purification method and indeed the method of measurement. Measured by the ultracentrifuge method, flax (*Linum utasitissimum*) cellulose has a DP of 3500, cotton 1000—3000 and sulfite wood pulp 600—1000.[1] When two glucose molecules condense to form part of a cellulose chain one of them has to rotate by 180° forming what many regard as the real repeat unit of cellulose, cellobiose:



The cellulose molecule possesses a very high concentration of hydroxy groups and thus interacts strongly with water.

Cellulose might be a water-soluble polymer if it did not have a strong tendency to associate to form crystalline regions. Natural wood, cotton and flax cellulose all show a strong X-ray diffraction pattern from a structure called cellulose I. The amorphous areas of a cellulose fibre are more hygroscopic and generally reactive than the crystalline areas because of their better accessibility to small molecules.

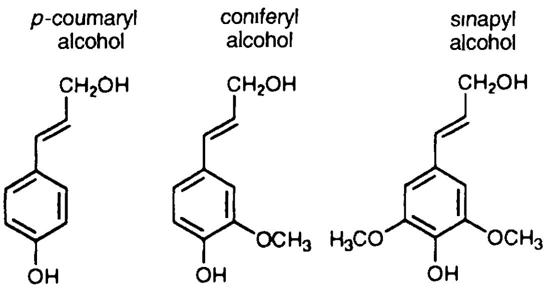
The cellulose used for paper making is present as fibres which retain some of the shape of the cells from which they were derived and thus occur in a variety of shapes and sizes depending on the plant source. Mechanical treatments for paper making, such as beating, enhance properties for paper-making but can destroy much of the natural structure and drastically decrease the crystallinity of the cellulose.

Most European papers used to be made from recycled cellulose from cotton and linen (flax) rags. However, as the demand for paper grew, new sources of supply were looked for. Despite the use of some unusual sources for cellulose, *e.g.* mummy wrappings, a new plant source was needed; wood had the correct properties and from about 1870 until the present day most paper has been made from wood. Now, cotton and linen papers are only used for speciality uses such as banknotes, filters and artists' papers.[2]

Wood contains cellulose and two other main components: other carbohydrates and lignin. The most permanent papers are usually those with a high proportion of cellulose but for economic reasons the amount of purification used on wood pulps is often minimal; the process can sometimes be little more than grinding the wood followed by bleaching. Papers from this type of pulp, often known as ground wood papers, are often used for cheap books and newspapers. The permanence of these papers is much better than when they were first produced at the turn of the century but still present a challenge to conservators as these papers progressively discolour and become acidic and brittle. Indeed, the main conservation challenge to large libraries is the preservation of huge quantities of this paper, sometimes in the form of uninteresting, low value books. Faced with the high cost of conservation and storage some libraries may choose to discard this type of material; however, copyright libraries are obliged to keep it.

Besides the polymerised glucose in cellulose, papers contain other polymerised five- and six-membered ring sugars, polymers made from these are collectively known as hemicelluloses As they are not usually homopolymers, crystallinity is low and their reactivity is high compared to cellulose Hemicelluloses are thought to contribute to the flexibility of the cellulose fibre by having an effect on internal stress redistribution [3] Compared with cellulose the natural degradation of hemicelluloses (and lignin) has not been examined in detail but the accelerating factors for cellulose probably apply

Lignin is present at a proportion of 17—32% in wood Its chemistry is very complex and the structure of lignin varies between plant sources Essentially lignin is a three-dimensional polymer composed of building blocks similar to those shown The units are linked together in an almost random manner by a variety of links



Monomer units which make up lignin

These links may also be made to polysaccharides such as cellulose and hemicellulose [4] Full or partial extraction occurs as part of the paper-making process and this further complicates the chemistry of the residual lignin For the paper conservator, the presence of lignin in a paper is usually regarded as bad news as the initial strength of the paper is relatively low and it will be susceptible to development of acidity and discolouration However, the bad reputation that lignin has is partly due to the associated acid pulping processes that leave aluminium sulfate and other acidic resides Modern processes can now make alkaline mechanical wood papers which are predicted to have good permanence and the paper industry is now anxious to prove that this is so

Paper made only from plant fibres may have poor strength, be extensively absorbent and have poor surface smoothness or optical properties A variety of mechanical operations can change these properties, but additives such as fillers and surface coatings can be applied A common addition to most papers is that of a size, traditionally this was made from gelatin applied as a hot solution, sometimes with the addition of paper makers' alum (aluminium sulfate) In the 19th century resin and alum were found to be cheap and effective substitutes Sizes can be mixed into the vat of fibres or applied to the formed paper sheet

3 The Principal Chemical Mechanisms of Paper Degradation

When the DP of weak, brittle paper is measured, it is found to be considerably lower than that of the new paper Thus, the principal degradation mechanism is considered to be chain scission There are two principal routes for this acid-catalysed hydrolysis of the glycosidic bond and oxidation of the glucose ring, and of these the first is the most important

Absorbed air pollutants sulfur dioxide and nitrogen dioxide are important sources of acidity, but acidity may also be introduced into the paper-making process by use of acidic components, *e g* aluminium sulfate and resin Carboxylic acid groups on the cellulose chain are another source of acidity and these can be produced by oxidation of the cellulose during the paper making process by the use of oxidising bleaches or subsequently in storage by oxidation with ozone or oxygen The rate of oxidation both during bleaching and on subsequent ageing is dramatically accelerated by the presence of transition metals such as iron and copper as they enhance the decomposition of peroxides formed during oxidation [5] Light, especially ultraviolet, also increases the rate of oxidative degradation Oxidised celluloses are considered to be unstable when the carboxy groups are in their free form

Storage of paper in relative humidities of greater than about 70% encourages the growth of microorganisms which can rapidly cause destruction of paper

4 Acidity and deacidification

For paper not exposed to excessively high levels of relative humidity, heat or light, the effects of acid hydrolysis are regarded as being the most serious degradative factor The obvious remedy for excessive acidity is deacidification

Deacidification of paper can be as simple as immersing a sheet of paper in a bath of water or a dilute alkali However, the hazards of such an aqueous process can be considerable, possibly resulting in loss of image materials, delamination or disintegration of the paper Thus any processes described are best carried out by a paper conservator Readers interested in the practical skills of paper conservation can find more information in the paper conservation journals

The study of naturally old and artificially aged paper has shown that the introduction of calcium and magnesium carbonates is a good stabilising process However there are several other methods which can be used to give paper a neutral or alkaline pH We specify the pH of a water extract of a piece of paper to be in the range 6 0—8 5 for permanence Depending on the method adopted, the pH is defined as the pH of an aqueous extract of 1 g of paper in 50 or 70 ml of cold or hot water [6]

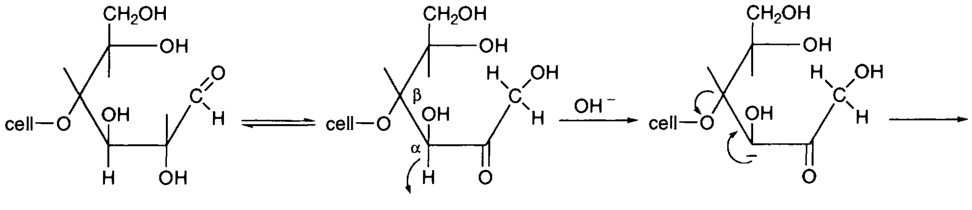
Water based deacidification treatments have the advantage that water-soluble acids and degradation products can be washed out The swelling of the cellulose fibre and the subsequent remaking of some hydrogen bonds in the drying process can change the properties of the sheet, usually for the better On air drying, the deacidifying agents calcium and magnesium hydrogencarbonates and calcium hydroxide form carbonates in the fibres leaving an 'alkaline reserve' to deal with subsequent formation of acids The Ca^{2+} and Mg^{2+} ions can also exchange with H^+ on carbonyl groups enhancing the stability of the cellulose against further deterioration [5]

Acidity may be neutralised with sodium carbonate or hydrogencarbonate but sodium ions have acquired a reputation for destabilising paper Unless carefully controlled, sodium carbonate can produce an excessively high pH in paper, alkalizing to over pH 10 eventually causes discolouration and oxidation, and so alkaline earth compounds which do not cause these side effects are preferred Novel deacidification agents are slow to be accepted, for example, French workers have reported that borax (sodium borate) can produce good results in accelerated ageing tests, but conservators prefer to use tried and tested methods [7]

The bad effect that sodium hydrogencarbonate has on paper can be explained by the mechanism of alkaline hydrolysis In conditions of mild alkalinity the principal degradation mechanism is β-alkoxy elimination In this reaction, a glucoside is eliminated which is in a position β to a carbon atom with an electron withdrawing group and an acidic hydrogen When the elimination occurs at the end of a cellulose chain it is called a 'peeling' reaction [8]

All straight cellulose chains have two ends, one of these has reducing properties as it is a potential aldehyde and electron withdrawing group If this is attacked by a hydroxy ion elimination takes place (Scheme 1) Other reaction mechanisms can be drawn for elimination due to electron withdrawing groups on other carbon atoms

This degradation mechanism has received a great deal of attention from the paper and textile industries as the bleaching of wood and textile fibres in alkaline conditions is of major importance One way of preventing this degradation is to remove metal ions known to catalyse it, particularly cobalt, iron and manganese However, the addition of magnesium carbonate minimises the oxidative degradation by either stabilising peroxides, deactivating transition metals, chelating with oxycellulose or complexing with hydroxy groups at C 2 and C 3 of the cellulose ring[9] [10] thereby stabilising the cellulose against β-alkoxy elimination



I glucose end II fructose end β-elimination

Scheme 1

While some single sheets of paper may sometimes be amenable to aqueous immersion treatments others are not and conservators have devised floatation and mist techniques enabling them to continue to use aqueous methods. However, some objects cannot be exposed to water in any form and non-aqueous deacidification is necessary. In particular, wet books distort badly when wetted and even more so in redrying.

A great deal of ingenuity has gone into devising non-aqueous deacidification treatments. One of the first was the use of barium hydroxide in methanol, but this has now dropped out of use because of the toxicity of barium carbonate residues in the paper. Magnesium methoxide in methanol is useful but the solution is particularly unstable to moisture. A great improvement in working properties is effected by saturating the solution with carbon dioxide, the resulting product is called methylmagnesium carbonate and may be purchased from some of the conservation supply houses as an aerosol or solution. Until recently, CFCs were added to the methanol to dilute the solution.[11]

For mass treatments of the vast amounts of paper in libraries a vapour phase method has many attractions. Ammonia is not suitable as the reaction product of the neutralisation of sulfuric acid (the essential reaction product of sulfur dioxide pollution) is ammonium sulfate which is still acidic (weak base + strong acid). Chemists in the USA have devised a treatment using diethylzinc gas (DEZ). The process has met with some success, however, under the wrong conditions DEZ reacts explosively with oxygen and water. The process has to be performed in a vacuum chamber with heat-dried books.[12]

Recently two new processes have been devised using magnesium butoxy glycolate in a non-aqueous solvent[13] and a micro-dispersion of magnesium oxide particles (unpublished). The search continues for new methods which are inexpensive and easy to use.

5 Discolouration of Paper

Discolouration is a natural consequence of ageing as oxidation, acid and alkaline degradation of the components take place and the chromophores formed start to absorb blue/violet light.

Discoloured products can be obtained from any of the ingredients which make up paper and the range of chromophores that can be expected is correspondingly large. Hon[14] has reviewed the types of chromophore expected and his list includes furans, quinones, quinone methides and stilbenes. He suggested that condensed furan derivatives produce most of the discolouration in paper and that cellulose containing aldehyde groups discolours most readily. Aldehydes can result from several of the paper degradation mechanisms, *i e* acid hydrolysis, alkaline hydrolysis, oxidation and pyrolytic chain scission. When paper is sized, as old papers often were, with gelatin, then there are possibilities for Maillard reactions to take place, producing brown products by reactions between proteins and reducing sugars.

The occurrence of brown spots on paper is known as foxing. This type of discolouration is associated with storage of paper in high relative humidity. Two mechanisms have been identified: one is the growth of fungi or bacteria in the paper, the other is the corrosion of metal, usually iron, inclusions in the paper, and both are caused by storage in excesively high relative humidity. Often these mechanisms can be distinguished by the fluorescence caused by an ultraviolet lamp (UVA). Microbial spots fluoresce showing various colours while iron salts quench the fluorescence and appear black against the fluorescence of the paper around the spot. In some papers, copper alloy particles may corrode with the aid of chloride residues from bleaching eventually producing black dendritic spots composed of copper sulfide by reaction with hydrogen sulfide in the air.

Often an overall brown discolouration is acceptable on an old piece of paper. If such a piece of paper is washed in water, a lot of the discolouration can be removed as soluble products. However, intentional or accidental local wetting will cause migration and concentration of the stains, and on drying an unsightly brown line is caused at the wet–dry boundary. However, localised wetting and subsequent drying can produce a line of brown or UV-fluorescing material even on a sheet of paper which is new or has recently been washed. Such lines may be familiar to readers who have performed paper chromatography and are an indication of the position of the solvent front. Such lines may be removed by washing, but if left untreated may produce discolouration on ageing. The chemistry of this phenomenon is still unclear[15] but is associated with areas of enhanced oxidation.

Some types of paper discolouration may be caused by storage of an object next to an unsuitable material, *e g* a piece of wood or acidic cardboard. In dismantled picture frames and inside the covers of books are good places to look for these effects. Often the grain pattern of wood transfers itself to paper. This type of discolouration is usually attributed to the migration of acids which accelerate degradation and subsequent yellowing. Acids are thought to migrate through the fibres by liquid diffusion or may be transferred through the vapour phase. There has been very little research on the migration of chemical species, but work in the paper industry has demonstrated that several components from resins in wood can migrate through air to deposit on adjacent objects causing water repellency. Another possibility is that species from the degradation of paper can migrate from one sheet to another. In particular, during oxidation of paper, hydrogen peroxide and oxygen-containing free radicals may be formed. The production of hydrogen peroxide from autoxidation of paper and other cellulosic materials can be visualised on a photographic plate using the Russell effect. In this process, H_2O_2 reduces the alkaline photographic emulsion which is then developed to form an image such as the one shown in Figs 1 and 2.[16] Reactive oxygen-containing intermediates such as these may have been responsible for the image on the Turin shroud.

Other types of discolouration are produced by simpler mechanisms. Traditionally, printing inks were made from pigment (usually carbon black) mixed with a drying oil. Sometimes the oil does not fully dry and it may transfer to an opposite page producing an offset image (Fig 3).

On exposure to light, most pigments and dyes eventually fade. Paper also bleaches in these conditions but may instead discolour. Lignified papers, *e g* mechanical wood pulp, are prone to discolouration as anyone who has left a newspaper in the sun for several weeks will know. When a framed print is disassembled, the area protected from illumination by the inner frame of card (matt) is sometimes seen to be a different hue. In some cases, the print itself will act as a type of photographic negative. The paper behind the print will discolour in the areas where the light penetrates, while areas behind black printing remain unaffected (Fig 4).

Such phenomena are hopefully not produced in the museum or gallery environment in which both the illuminance (the amount of visible light) and the proportion of ultraviolet light in that light are usually controlled (passive conservation). Illuminance is usually

Figure 1 Discoloured end papers in a book (J Black s Experiments upon Magnesia Alba Quicklime *etc* Publ 1910)

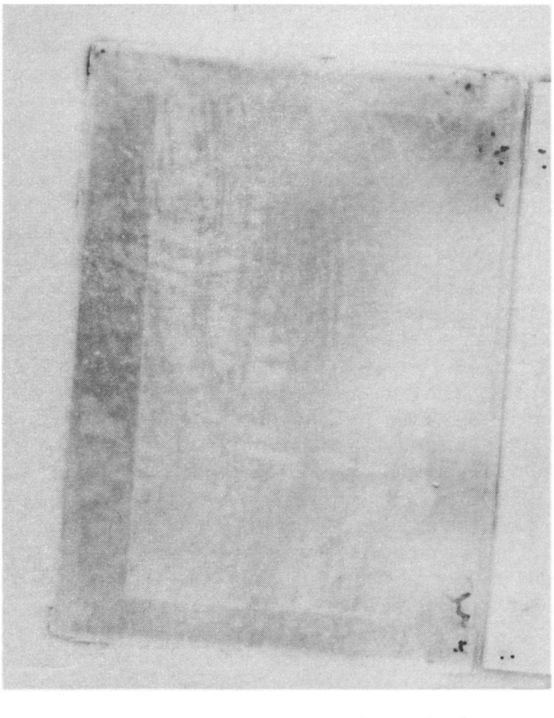


Figure 2 Russell effect image from the book cover in Fig 1

specified to be below 50—80 lux and the ultraviolet level to be below 75 μW/lumen Ultraviolet light is more energetic than visible light and is more effective in promoting most photochemical degradation mechanisms The use of flash lights for photography is prohibited in many exhibitions but calculations will easily show that photochemical changes are not the reason behind this ruling as the amount of light produced by the flash is equivalent to only a few seconds of exposure to normal museum lighting A strange discolouration produced by light is that associated with zinc oxide pigment Zinc oxide (Chinese white) has been used as a white pigment since the 1830s In the presence of light and water a photochemical reaction takes place which produces hydrogen peroxide [17]

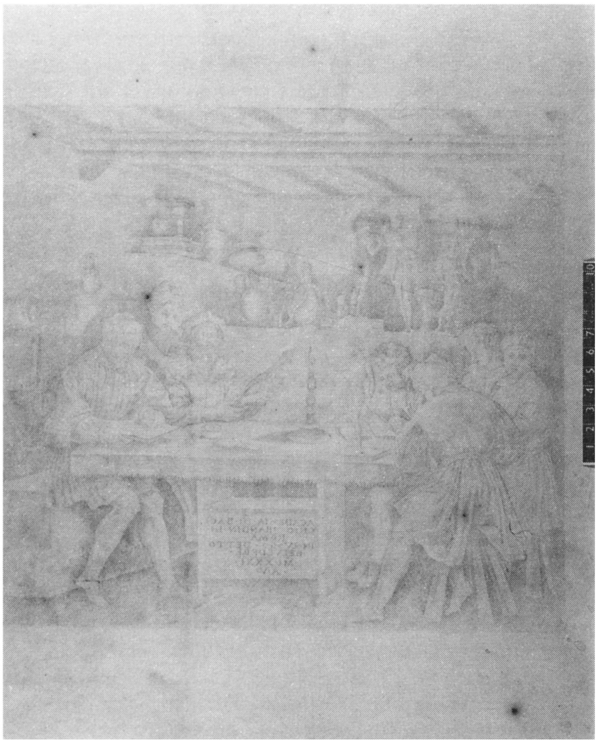


Figure 3 The image is offset from a print on the facing page and caused by non drying oils in the ink The spots are caused by corrosion of iron particles

$$ZnO + O \xrightarrow{h\nu} (ZnO) \quad + O$$

$$O \quad + H\ O \rightarrow HO \quad + HO$$

$$2HO \rightarrow H\ O \quad + O$$

$$H\ O\ \ (ZnO) \xrightarrow{h\nu} 2HO$$

Some or all of these reactive species can then react with the paper producing oxidation products At the time of illuminance no visible effect is produced but maybe a year later a yellow/brown discolouration can be seen around the area of zinc oxide Figs 5 and 6 show

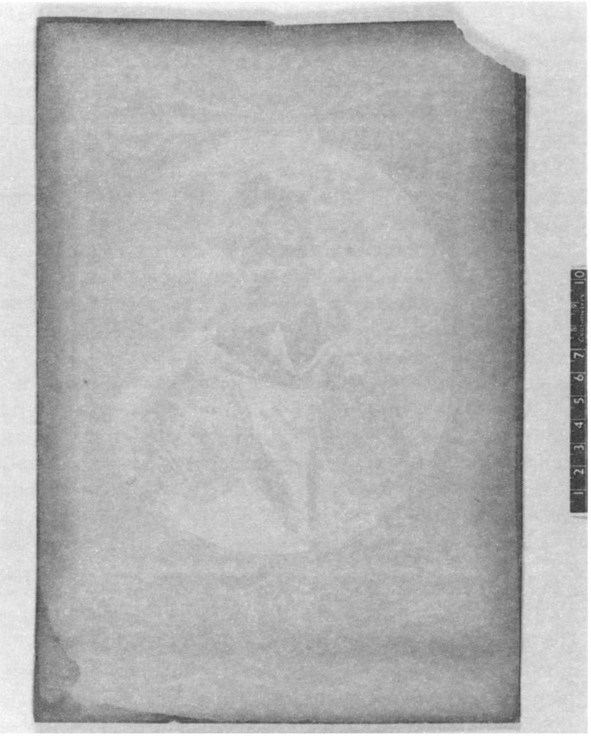


Figure 4 A negative image of a print caused by light induced discolouration of the backing board

a backing board from a Japanese print the areas of discolouration correspond to areas of zinc oxide on the print in front This and many other discolouration reactions on paper have been reviewed by Daniels[18]

6 Elimination of Discolouration

Many types of uniformly distributed or localised discolouration in paper can be removed by washing in water Often a few drops of a non ionic surfactant or ethanol are added to the water to aid wetting Immersion of a piece of paper in a dish of water is often used but flotation of a sheet on the surface of the water or placement on wet blotting paper are favoured when the image materials might be mobile or the paper s wet strength is low Two recent advances have aided washing and have eliminated the necessity of using more chemically exotic techniques One of these techniques is the use of a suction table The paper is placed on a perforated table and solvent usually water based is drawn through by a low vacuum The other is the use of ultrasonically generated water mist in which objects are bathed for several hours without becoming too wet

Stains which do not yield to treatment with cold water may be dissolved in warm water or water made alkaline with ammonia solution Proteinaceous or starch based stains may be removed with the aid of enzymes but oils may be removed by solvents such as morpholine

Metallic stains *e g* iron stains caused by rusting paper clips or staples can be eliminated by dissolving the iron with a complexing agent Some of the solutions that have been used include oxalic acid hydroxylamine hydrochloride the disodium salt of ethylene diaminetetraacetic acid ascorbic acid and mercaptoacetic acid

Insoluble organic stains may be bleached out and there is a wide variety of treatments for this process The ideal bleach is one that does not harm the paper but most oxidising bleaches do damage the paper to some extent Although widely used up to ten years ago chemical bleaching agents are now out of favour however one green technique has achieved a degree of popularity that is light bleaching Conservators place paper in solutions of a dilute alkali *e g* magnesium hydrogencarbonate and expose it to sunlight or a

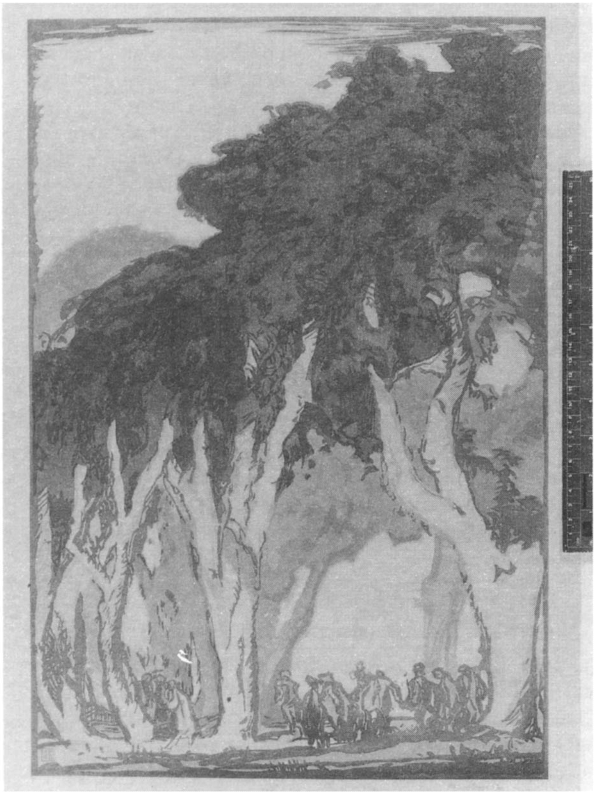


Figure 5 A modern Japanese print recently purchased by the British Museum The area on the top left hand corner has a high concentration of zinc oxide

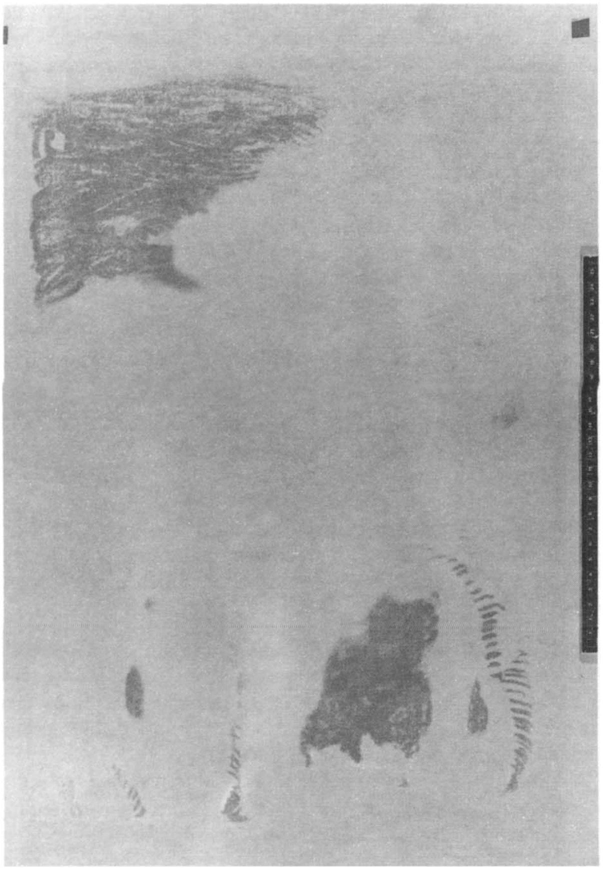


Figure 6 Discolouration of the backing board of the print in Fig 5 caused by light

bank of fluorescent tubes, ultraviolet light being filtered out The discoloured areas are, theoretically, the only ones which absorb light and the only ones to be oxidised Fluidity measurements have shown that there is no degradation of the unstained paper and conservators feel that the paper has been generally improved by the process [19]

Other bleaching methods owe much to the paper industry Only a few years ago the most popular bleaches were chlorine dioxide (in solution) and alkaline hydrogen peroxide Chlorine dioxide solution can be made by mixing sodium chlorite in water with formaldehyde, owing to its toxicity it must be used in a fume cupboard For the home based conservator hydrogen peroxide or a hypochlorite bleach, *e g* Chloramine T, used to be popular Colour reversion after bleaching has been extensively studied by Burgess[20] who found that some yellowing may return but that retention of Chloramine T by paper sometimes resulted in further bleaching on ageing

Reducing bleaches have never achieved any degree of popularity, but chemically they are attractive as reduction of carbonyl groups to C—OH results in enhanced stability to ageing Evolution of hydrogen bubbles by the reagents used, *e g* sodium borohydride, unfortunately enhances the removal of unstable image pigments and loose fibres

7 Methods for studying the Ageing of Paper

The degradation of paper is slow under ambient conditions and measurable changes in chemical or physical properties often cannot be detected until after several decades of storage Two methods currently exist which may be used to study oxidation of paper under ambient conditions One of them, the Russell effect, uses specially prepared photographic film which develops a latent image by reaction of the silver halide emulsion with hydrogen peroxide liberated during free radical oxidation processes such as

$$HO_2 + RH \rightarrow R + H_2O_2$$

The technique may be used to compare samples when the rate of hydrogen peroxide evolution varies [16] The other technique, chemiluminescence, may also be used to monitor the rate of oxidation Cycling relative humidity has been found to produce an increase in the apparent rate of oxidation In this case, chemiluminescence is produced by reaction between peroxide radicals

Most laboratories use accelerated ageing tests to predict the effects of dark and light ageing and each has its own preferred conditions For dark ageing, various ageing regimes exist, all are based on the principals encapsulated in the Arrhenius equation Dry oven ageing at 100 °C for three days was once widely used, however, humid conditions and lower temperatures are now more popular Heat ageing in sealed containers keeps the water content reasonably constant but produces different results as the rates of degradation can be up to eleven times faster than expected Light ageing is usually performed by exposing samples to greatly increased illuminance, sometimes with an enhanced ultraviolet content The light sources range from sunlight to mercury and xenon lamps but in most experiments heating is an unwanted side effect

The aged paper can be characterised chemically by the methods used in the paper industry, *e g* reducing power (copper number), DP (fluidity), pH, FTIR *etc* Physical methods can distinguish between the strength of the fibres and the strength of the fibre to fibre bonds by the use of both standard tensile testing and zero span tensile testing A test which involves both bending and tensile strength is the folding endurance test All these methods reveal something different about the paper but it is impractical to perform them all Most workers use one or two of these

A complicating factor in paper conservation research is the enormous variety of paper types encountered A conservation treatment found to be ideal for one type can be damaging for another Ideally any conservation study should include over ten different papers, however, the scale of such projects can soon become overwhelming and the choice of papers has to be restricted

8 Ideal Storage Conditions, do they exist?

The deterioration of the components of paper requires photochemical or thermal energy and reactants in the form of water and oxygen and air pollutants

Storage in an oxygen free environment is not usually considered worth the effort as oxidation is not the principal degradation mechanism Storage under dry conditions enhances stability considerably but there is associated shrinkage and embrittlement Two pieces of paper joined together have different hygroexpansivities and storage at low relative humidity will produce a stress which may produce creep in the paper and subsequent loss of flatness on a return to ambient conditions [21] Storage at low temperatures is also effective in prolonging the life of paper but bears a high energy cost Both low relative humidity and low temperature storage present problems of acclimatisation to ambient conditions when objects need to be removed from the store for examination

The storage conditions generally accepted are within the range 14—20 °C with a tolerance of ±2 °C within the range and a relative humidity within the range 45—55% these are a compromise between cost human comfort and practicability It is recommended that colour prints should be stored at 30—50% relative humidity preferably below 40% and at less than 2 °C [22]

9 Effect of some Image Materials

9.1 Iron-gall ink

Prior to this century many writing inks were either based on carbon or iron gallotannate black pigments Inks made from iron gallotannates now present the conservator with challenges as they can cause so much damage to the paper that the degraded paper falls out of the page Preparation of these inks usually involved the use of iron sulfate and oak galls rich in tannins Reaction of these ingredients produced a blue/black iron–tannin complex and sulfuric acid Ageing of these inks produces fading as the tannin component degrades and the complex is destroyed with subsequent loss of colour intensity The degradation of the ink pigment may release the iron in a form which can catalyse the oxidative degradation of paper The sulfuric acid accelerates hydrolysis of the cellulose

The standard treatment for stabilisation of these inks is deacidification Recently Neevel has shown that deacidification using magnesium hydrogencarbonate coupled with complexation of free iron(II) ions with phytic acid is particularly effective [23] in this way both acid hydrolysis and oxidative degradation are slowed down An example of iron gall ink damage is shown in Fig 7 where the ink has completely degraded the paper in parts of a Guercino drawing

9.2 Verdigris

Artists throughout the world have used a great variety of pigments Most have no accelerating effect on the ageing of the paper substrate but the one that has proved most troublesome to the paper conservator is that known as verdigris, a blue/green pigment of variable composition but which contains copper and acetate ions When painted onto paper, usually in a gum binder the copper ions cause catalysed oxidation of the paper, the simultaneous release of acetic acid also accelerates deterioration by stimulating acid catalysed hydrolysis As with iron gall inks the paint can cause destruction of the paper

This pigment was often used in Indian and Persian miniature paintings and was often applied as a rectangular border round a painting The interesting, but unfortunate, separation of the painting from its border often results

Magnesium hydrogencarbonate solution as a deacidifying agent and stabiliser for oxidative degradation has been shown to prove effective in accelerated ageing tests If the paper has not deteriorated too much, a strengthening consolidant of water soluble hydroxypropylcellulose has been recommended [24] Fig 8 shows one of the finest of all Moghul miniature paintings Princes of the House of Timur The roof of the pavilion has been almost entirely destroyed by verdigris, only a cotton backing applied to strengthen the painting remains

Figure 7 Iron-gall ink burn on a Guercino (1599—1666) drawing. The holes are the result of iron-catalysed degradation and acid-catalysed hydrolysis.

9.3 Mercury Scarlet

An unusual pigment, sometimes found in the Victorian watercolour box, is based on the scarlet mercury(II) iodide, Hg_2I_2. It was used to paint flowers. Unfortunately, the pigment has a significant vapour pressure and unless painted thickly or sealed into a binder has evaporated from many pictures leaving nothing behind.[25]

9.4 Vermilion

This pigment, mercury(II) sulfide, HgS, is found in nature as cinnabar but is also synthesised. Sometimes the pigment blackens, particularly on wall paintings. Recent research has shown that the blackening is accelerated by the presence of halide anions and that the reaction responsible is probably solubilisation and reprecipitation as the amorphous HgS or a black crystalline form metacinnabarite. The solubilisation is aided by the halide ions forming an HgX_4^{2-} ion and by increased relative humidity.[26]

9.5 Arsenic sulfides

The pigment orpiment, As_2S_3 was widely used in oriental and Egyptian paintings. It is, however, unstable to light and heat. In some instances the pigment bleaches to form the corresponding oxide and causes flaking of the pigment possibly due to destruction of the binder. The liberated sulfur may combine with other inorganic pigments containing lead and copper, *e.g.* basic lead carbonate, lead oxide, lead chromate, copper carbonate, *etc.* to form black sulfides. Fig. 9 shows two adjacent sheets of papyrus bearing stripes of initially yellow orpiment. The stripes on the right-hand sheet have completely faded because of exposure to light.

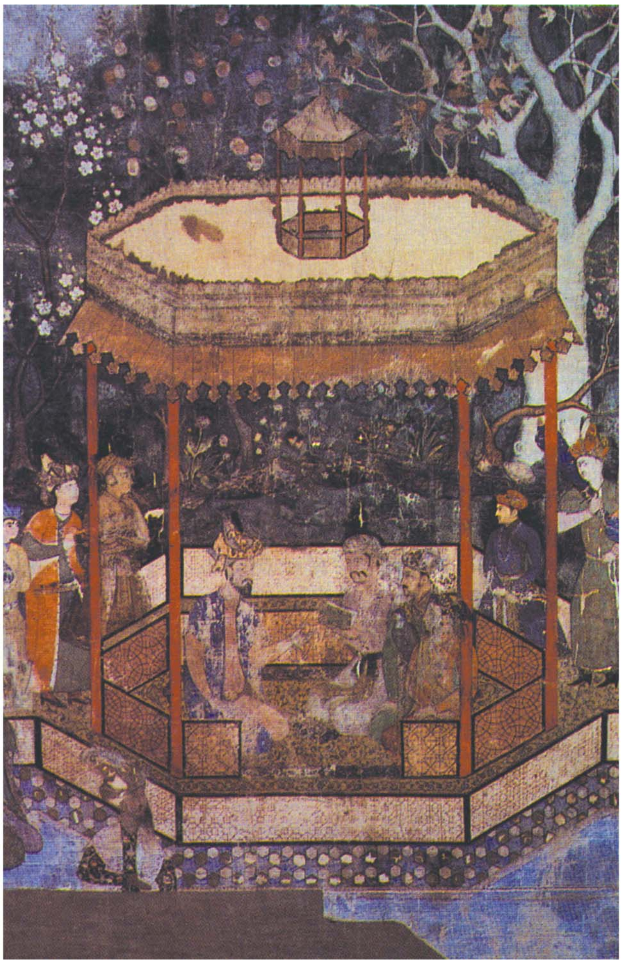


Figure 8 Detail of the Moghul miniature painting Princes of the House of Timur. The combined effects of copper-catalysed oxidation and acid-catalysed hydrolysis have destroyed the roof of the pavilion

9.6 Lead White

A white pigment made by the corrosion of lead metal is basic lead carbonate, $2PbCO_3{\cdot}Pb(OH)_2$. It was widely used as a pigment before being replaced by zinc oxide and later by titanium oxide. It has one great drawback: it reacts with atmospheric hydrogen sulfide to form black lead sulfide. In paintings affected, white areas appear grey or black and in drawings the once white highlights become shadows giving a peculiar photographic 'negative' appearance to a picture. The cure for this affliction is the use of an ethereal solution of hydrogen peroxide. Diethyl ether and 20 volume hydrogen peroxide are shaken together and some of the peroxide dissolves in the ether. The ether layer is brushed onto the blackened areas and the sulfide is oxidised to white sulfate restoring the original appearance.[27] Fig. 10 shows a drawing in which white highlights have been blackened.

9.7 Metals

Some manuscripts carry metal foils; one particular problem is silver foil which tarnishes, forming a layer of silver sulfide It is rare that the silver is sufficiently thick to polish so the change is permanent. In the case of finely divided silver in a paint medium, blackening is similarly permanent. The conservation of photographs on paper has not been covered in this review but the black and white image is made of silver particles which are likewise sulfided resulting in fading of the image or silvering of the surface; a good review has been published by Kodak.[28]

Figure 9 Orpiment (As_2S_3) on adjacent papyrus sheets of a book of the dead. The sheet on the right has been exposed to a lot of light.

Figure 10 Blackened lead white highlights on a drawing from the Dal Pozzo Collection (*ca.* 17th century).

10 Conclusions

The many types of paper that have been made and the variety of images on the paper ensure that the study of the deterioration and conservation of paper is a vast subject. The principal deterioration mechanisms for papers and associated materials have been scientifically studied and many useful conservation methods have been produced. However, many objects will remain untreated because of a lack of resources. Despite all the efforts of conservators and chemists deterioration can only be slowed down not halted.

11 Bibliography

At present there is no text exclusively or even partly devoted to paper conservation science. Interested readers are directed to the two principal paper conservation journals: *Restaurator* and *The Paper Conservator*. General conservation journals such as *Studies in Conservation* and *The Conservator* have articles related to paper conservation. Conference proceedings carry a large proportion of the published material; the American Chemistry Society's *Advances in Chemistry Series* No. 164, 193, 212 and 410 are a good introduction.

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