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OXIDATIVE DAMAGE AND THE PRESERVATION OF ORGANIC ARTEFACTS

VINCENT DANIELS

Department of Conservation, The British Museum, London WC1B 3DG

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Organic artefacts degrade by a number of mechanisms. Autoxidation is one of the most important and involves free radicals. The importance of free radical reactions in the degradation of paper and other cellulosic materials, rubber and other organics is described. In the case of paper, treatment with calcium and magnesium compounds can inhibit oxidation, while transition metals increase the rate. Antioxidants have not been used a great deal due to unwanted side effects. The Russell effect, a technique for detecting oxidation using photographic materials, is described.

KEY WORDS: Oxidation, russell effect, cellulose, conservation, museum, rubber, paper.

INTRODUCTION

Most museums possess collections made of a very wide range of materials. There are not only the materials of which the objects themselves are made, feathers, skin, wood, paper, pigments, binding media, stone, ceramics, metals etc, but also the materials used for repair, consolidation and storage of the objects, eg textiles, wood, synthetic polymers etc. The materials deteriorate by different mechanisms, many of which have not been investigated through lack of commercial or academic interest. It would obviously be wrong to suggest that all mechanisms for deterioration of organic museum objects involves free radicals, but a number of them definitely do, and many more probably do. Some mechanisms of degradation are purely physical, eg migration and loss of pasticiser, absorbtion of contaminant, crystallisation of polymers, salt migration and subsequent crystallisation; some are mainly biological, eg damage by moths, beetles and their larvae; others are ionic, eg acid hydrolysis of cellulose and proteins.

OXIDATION OF PAPER

For several decades the main mechanism for degradation of paper has been assumed to be acid hydrolysis of cellulose, and for paper a good linear relationship exists between hydrogen ion concentration and the decrease of folding endurance strength on aging.[1] Now, there is a growing awareness of the importance of oxidation mechanisms especially in papers made from wood cellulose containing lignin.

The direct oxidation of cellulose by molecular oxygen is believed to be a chain reaction involving free radicals. The reaction is catalysed by some metal ions while

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others inhibit it, strongly alkaline conditions also increase the rate of oxidation. Classical initiation – propagation – termination schemes may include several possible types of reactants and products, including aldehydes, carboxylic acids, alcohols, organic peroxides and hydrogen.[2] The consequences of oxidation are loss of tensile strength by chain scission, cross linking inducing brittleness, and formation of oxygen containing functional groups; carbonyl groups are of particular importance. Lewin[3] has shown that yellowing of cellulose on aging is maximised when the cellulose aldehyde content is highest; neither a high ketone nor carboxyl content contributed to yellowing. The same trends are assumed to be true for the low molecular weight cellulose-like polymers grouped together under the heading of hemicellulose.

Lignin is a major component of inexpensive papers made from wood, this type of paper is often used for newsprint and paperback books. Photochemical oxidation is a major reaction in the degradation of lignin. The phenolic groups form radicals that are transformed into coloured end products[4] with quininoid structures. Dark aging of lignin procedures similar yellowing. Metals, especially iron, can form coloured complexes with decomposition products of lignin. Examination of books shows that the edges are most yellowed (oxidised); the reason for this may be that atmospheric sulphur dioxide has been absorbed there and that the observed increased acidity may be causing faster oxidation/hydrolysis of the paper. An alternative explanation, of oxygen starvation at the centre of the book, seems unlikely in view of the time scales involved. Photochemical darkening of lignin may produce amusing results. If a piece of poor quality board is placed behind a black and white print in a glazed frame and hung in strong light, a negative image of the print may sometimes be formed on the board.

METAL CATALYSIS OF PAPER OXIDATION

Metals may find their way into paper as impurities. In papermaking machinery particles of brass or iron may be released and eventually incorporated into the paper. These particles corrode forming discoloured spots, sometimes called foxing. The colour is formed by oxidation products of the paper as well as corrosion products. Small amounts of iron and copper can accelerate free radical oxidation reactions. The metal must be present as ions to participate in such reactions[2] eg

$$RO_2H + M^n \longrightarrow RO^{\cdot} + OH^- + M^{n+1}$$

$$RO_2H + M^{n+1} \longrightarrow RO_2^{\cdot} + M^+ + M^n$$

Most inorganic pigments contain transition metals but these are not generally available for catalysis of oxidation. One unfortunate example where this is not the case is the use of green pigment verdigris. Verdigris is a name given to basic and normal copper acetates; these pigments were often used for the preparation of illuminated manuscripts. Severe degradation of the paper substrate can occur with possible total loss of the painted area. The mechanism for this change is possibly a combination of acid attack from acetic acid and of copper catalysed oxidation.[5] Another example of copper catalysed degradation of artefacts is beeswax/rosin seals becoming brittle due to verdigris or copper resinate pigmentation. Gold leaf and paints may produce discolouration of paper due to the copper in the alloy corroding preferentially and catalysing degradation in adjacent areas.

An interesting type oxidation produce discolouration may be seen in paintings which have zinc oxide as a white pigment. Zinc oxide catalyses the formation and decomposition of peroxides in UV light.[7]

$$ZnO + O_2 \longrightarrow (ZnO)^+ + O_2^{\cdot -}$$

interaction of $O_2^{\cdot -}$ with water or hydrogen ions leading to the formation of HO_2 radicals.

$$O_2^{\cdot +} + H_2O \longrightarrow HO_2^{\cdot} + OH^-$$

$$2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2$$

$$H_2O_2(ZnO) \xrightarrow{h\nu} 2HO_2$$

These reactions are better known as leading to the accelerated degradation of associated organic materials such as rubber and nylon.

On one water colour painting the presence of a highlight of zinc oxide had caused a halo of darkened paper surrounding it. A painting on silk has also caused discoloured areas to appear on a backing paper, the area os greater discolouration being behind areas of white pigment. The first example suggests that migration of oxidising species may be possible over the range of about 10 mm.

METAL INHIBITION OF PAPER OXIDATION

Early investigations on old, stable, pieces of paper showed the presence of calcium and magnesium in the form of alkaline carbonates. Unstable, brittle or weak papers were acidic. These observations supported the idea that acids were resonsible for degradation of paper and deacidification treatment for paper became popular; they are still the best stabilisation treatments availabe. Most aqueous deacidification techniques involve the use of calcium hydroxide or magnesium carbonate solutions to neutralise acidity and leave an alkaline reservoir in the paper to absorb future acid absorbed from the atmosphere or generated by oxidation. Non-aqueous deacidifying solutions containing magnesium and barium compounds also exist. It has been discovered that the presence of magnesium ions in bleaches eg hydrogen peroxide and hypochlorite protected cellulose from oxidation durign manufacture of pulps and the calcium, magnesium and barium inhibit the oxidation of cellulose.[6] There are four possible mechanisms to explain the stabilisation by magnesium (a) peroxides may complex with magnesium to explain the stabilisation by magnesium (a) peroxides may complex with magnesium (b) peroxides are indirectly are indirectly stabilised when magnesium deactivates transition metals present (c) oxycellulose may be stabilised by chelation with magnesium ions (d) magnesium may complex with the hydroxyls at C-2 and C-3 of the cellulose ring.

CELLULOSE CONTAINING NATURAL PRODUCTS

Ethnographic collections contain many types of vegetable fibre, such as leaves, grass. These items are of a complex composition but all become increasingly brittle with age. The mechanisms for these changes include loss of plasticising water, but by analogy with cellulose and lignin in paper, oxidation and acid hydrolysis should be included. As many natural products are of little commercial importance, their degradation mechanisms have not been studied, in contrast. The cultural and financial value of ethnographic material can be very high, this had lead to renewed interest in their degradation mechanisms.

INSECT PEST CONTROL

There is an increasing awareness of the health and safety hazards of using fumigants such as methyl bromide and ethylene oxide for the control of insects and microorganisms in museum objects. Attention has been turning recently, to the effects of gamma irradiation on objects. Gamma rays can cause free radical formation in many organic materials and there is concern that the longterm effects of irradiation sterilisation will cause unacceptable damage. Paper has been the attention of several such studies, experimentally, the problem has been to choose an acceptable accelerated aging test.[8] Conclusions are variable, the amount of degradation which is predicted to occur is often at the limits of detectability. Detectable degradation is usually unacceptable.

PICTURE VARNISHES

Easel paintings are often varnished to enhance the brilliancy of the colours and to provide a protective layer against moisture, gases, dust and physical damage. Many of the traditional varnishes, eg mastic, rosin or dammar discolour badly on aging due to oxidation. Recently, more durable resins, such as acrylics, polyvinyl acetate, cyclohexanones, etc, have almost entirely replaced the natural resins. Many artists still prefer natural resins and efforts have been made to stabilise a traditional triterpenoid resin, dammar, with antioxidants. This has had some success, of the range of antioxidants Irganox 565 exhibited the most promise.[9]

RUBBER AND NITROCELLULOSE

The preservation of rubber and the early synthetic plastics are problems which face military and technology museums. These materials are relatively unstable and not a great deal is known about halting their deterioration. Nitrocellulose illustrates this problem well. Its decomposition is a free radical one, involving nitrogen dioxide liberation. The nitrocellulose becomes brown and brittle. Nitrogen dioxide is autocatalytic for the decomposition of nitrocellulose and degrades adjacent organic materials and metal. Loss of plasticiser (camphor) by volatalisation is an additional problem as this causes shrinkage and embrittlement, this is a purely physical process.

The oxidation of rubber has long been recognised as a free radical process and one which is of considerable commercial importance. Cured natural rubber and gutta percha, (cis and trans 1, 4^- polyisoprene respectively) have double bonds in them, one per monomer unit, which makes them particularly susceptible to oxidation. Five activation mechanisms have been listed for the oxidation process namely: metallic, heat, light, flexing and atmospheric (ozones or peroxides).[10] Once the reaction is initiated the degradation is free radical autoxidation. It can be argued that there is no point in conserving some types of materials, eg modern rubber ballons and rubber bands, and that these could be replaced with substitutes wiout any significant loss of evidence about the past. However, for other types of objects were rubber is the principal component it would not be ethical to replace the rubber with modern, more stable materials. Degradation produces cracking, softening and embrittlement.

Three main approaches have been adopted for the permanent storage of rubber, one is to apply a treatment which both forms a barrier against oxygen and contains an antioxidant, another is to store in an oxygen free atmosphere and the last is to house at low temperatures to slow down chemical decomposition. So far, the last two approaches seem to have most success, but are expensive and inconvenient. Surface treatments are popular but have difficulty in penetrating the bulk of the rubber and barriers are never perfect especially on flexible materials. Most surface treatments are also designed to consolidate weak and brittle materials.

LONG TERM STORAGE OF ARTEFACTS

On aging, organic substances evolve volatile materials which migrate through the air and react with other substrates. Proteins and other sulphur containing materials evolve hydrogen sulphide, woods and synthetic polymers evolve formic, acetic and higher acids all of which cause corrosion of metals. Drying oil based paints and other oxidising organic materials evolve peroxides and aldehydes.[11] A combination of acetic acid and hydrogen peroxide causes rapid corrosion of copper and its alloys. Peroxides are capable of oxidising the silver in a black and white photographic image and has caused consternation amongst those responsible for the archival storage of microfilm.[12] Peroxides were found to be evolved from cardboard, wood, resins and many other oixidisable materials.[12]

It is possible that peroxides evolved from one material can migrate to another and initiate oxidation there, (induced oxidation). Ericsson[13] has been shown that in solutions hydrogen peroxide will be released by the oxiation of lignin and migrate to cellulose where it will initiate oxidation. Hydrogen peroxide and other organic compounds and radicals are capable of aerial migration and may possibly cause deterioration at a distance, producing oxidation and subsequent discolouration and loss of strength. There are, of course, other neutral materials capable of migrating in a similar way, but the evidence offered by the Russell effect described in the next section offers supporting evidence for migration of oxidising materials. Discolouration of paper adjacent to illuminated zinc oxide may also be due to initiation of oxidation by aerial migration from oxidising species, in this case, hydrogen peroxide or HO_2^0, as described previously.

THE RUSSELL EFFECT

Becquerel discovered the effects of radioactive substances on photographic film in 1896. A year later, W J Russell found that certain non-radioactive materials in direct contact with unexposed film could also form images.[14] Moser in 1842 and de Saint Victor in 1857[15] had previously made similar observations, but, today, the phenomenon bears Russell's name, a reflection of the quantity of work he carried out.

Russell found that certain freshly abraded metals could fog a photographic plate. These metals included zinc, magnesium, cadmium, nickel, aluminium, lead, bismuth and tin. Later he found that certain organic materials would also act in a similar manner. Especially active in this respect were air-drying oils (eg linseed oil) woods, leaves, most essential oils and natural resins.[16,17]

Russell found that the active substances were evolving a chemical species that affected the film. He discovered that hydrogen peroxide was able to produce strong images in very low concentrations and therefore concluded that it was produced by oxidation of materials.

Today, this view is alsmost unchanged but we are now able to reinterpret this phenomenon. It has been established that hydrogen peroixde is evolved from oxidizing metal surfaces in air[18] and that autooxidation proceeds by a free radical mechanism producing an abundance of peroxides, including some hydrogen peroxide.

The formation of hydrogen peroxide during the slow oxidation of phosphorus, oil of turpentine and metals by gaseous oxygen in the presence of water was studied by Schoenbein[19] as early as 1858. Since then hydrogen peroxide has been shown to be evolved by a wide range of oxidation processes including oxidation of monosaccharides,[20] phenols, lignin and xylan,[13] cellulose and primayr alcohols[21] and propan-2-ol.[22] In the last study HO_2 was shown to be the chain carrier, this species easily producing hydrogen peroxide by hydrogen abstraction. Indeed, hydrogen peroxide has been prepared industrially by autooxidation of substances such as 2-ethyl anthraquinone.[23] Other chemicals can produce images on a photographic plate in the same way as hydrogen peroxide, however, it is difficult to ascertain whether the image is produced by the chemical itself or by its oxidation products.

Because hydrogen peroxide is detectable by a photographic plate and because it is evolved by a wide range of objects, the technique has potential as a method of non-destructive testing. Early workers in this subject were able to use commerially available photographic films, but modern types are not suitable as they are made to be stable to the chemicals evolved by storage materials. A method for studying the Russell effect with modern materials is described elsewhere.[24]

Image production by hydrogen peroxide is probably brought about by oxidation or reduction of the siulver halide in the emulsion, these sites are subsequently developed in the normal way.

Weak chemiluminescence is known to be produced by oxidation of paper and other organic materials and this method has been used to follow rates of autooxidation.[25] However, chemiluminescence and phosphorescence can be ruled out as mechanism for formation of images because a piece of silica glass placed between an object and the film blocks all activity.

Paper deteriorates by oxidative processes and can give a Russel image. If the paper has been locally treated with an aqueous solution, this invariably produces a change in the activity of the paper by redistributing soluble oxidizing components in the paper, or altering the rate of evolution of hydrogen peroxide. The latter process can be changed by either altering the rate of oxidation or trapping or destroying hydrogen peroxide before it can leave the paper.

Iron (II), iron (III) and copper (I) salts can destroy hydrogen peroxide by the Fenton reaction and decrease the image produced by the Russell effect, e.g.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\cdot} + OH^-$$

and

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + O_2^{-} + H^+$$

The overall rate of oxidation can be increased but the image produced by the Russell effect is decreased.

Migration of the species responsible for the Russell effect can be illustrated by the image obtained from two overlapping circles of filter paper. In the region of overlap the image density is doubled. This shows that migration of the image forming species has taken place from one sheet of filter paper and through another to the photographic film.

Readers wishing to find more on the Russell effect should first consult the present author's work.[24,26,27]

ANTIOXIDANTS

So far, antioxidants have found little use in the conservation of museum objects. As stated previously antioxidant stabilised picture varnishes are available, and conservators are probably using commercial products for restroation which contain antioxidants, but may be unaware of the fact, the same may be said of materials for the construction of storage for antiquities. The basic problem with antioxidants is that they are themselves reactive materials and will often oxidise faster than the substrate they are put into. When deterioration of the antioxidant damages the arteface eg by discolouration, then the antioxidant is not suitable. Two examples of discolouration have come to the author's attention. Firstly, there is concern in the textile industry about the discolouration of textiles store in polyethylene sheeting, the butylated hydroxy toluene (BHT) often present is capable of aerial migration and oxidation by oxygen, or nitrogen oxides, to form coloured products on stored textiles.[28] This phenomenon has, so far, only been seen in the textile industry. There is no reason to suppose that the reactions are not equally likely in museums, the discoloured nature of many old textiles makes detection of slight extra discolouration difficult. Secondly, we have observed that porcelain restorations carried out with one type of epoxy putty in combination with varnishes have severely yellowed. Inspection of the unused epoxy putty revealed a yellow outer layer. The manufacturers suggested that an antioxidant could be responsible. The putty had been used for repair of white porcelain, the yellowing occurred about a year after the repair was done and had to be replaced using more stable materials.

PREVENTION OF OXIDATIVE DEGRADATION

Almost all museum objects are stored at ambient temperature, and in air, oxidation can be inhibited by storage in an oxygen free environment or at low temperature. So far, in museums, only photographic film and prints are stored at low temperatures, the number of objects sotred in inert atmospheresis very few, a notable exception is the US declaration of independence which was sealed in a helium atmosphere.

Light is an important initiator of free radical oxidation and, in the conservation world, its importance in the deterioration of organic materials has been fully appreciated. Organic dyes and pigments are faded by photoxidation and damage will occur to many organic materials including synthetic, animal and vegetable fibres. For this reason light levels are kept low in museusm when organic materials are displayed. Ultraviolet light is excluded using appropriate lighting sources and filters, less than 75 microwatts per lumen is the rule. The illuminance should be maintained at 50 lux for light sensitive materials eg dyed textile and 150 lux for less sensitive materials eg black on white printed paper.

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