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Interactions Between Adhesives From Natural Sources and Paper Substrates

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Abstract

Traditionally, adhesives of natural origin have been used to repair and adhere paper-based material — most particularly, starch paste, gum arabic, and animal glue or gelatine. These adhesives are expected to remain relatively reversible over time. However, adhesives based on natural substances may react with the paper and related media to become less treatable than expected. Similarly, components within the adhesive may affect the degradation of the cellulose.

In this paper, three reaction pathways are investigated:
- Multivalent metal ions such as copper and iron are known to degrade cellulose, gum arabic, and other polysaccharide substances. There is evidence to suggest that they may also react with protein adhesives to form insoluble complexes.
- Aldehydes formed during the oxidation of cellulose may react with natural polymers, resulting in hardening.
- Adhesives containing both proteins and carbohydrates may undergo condensation reactions, resulting in discolouration and loss of solubility. These reactions may also occur with the cellulose or with a sizing layer on the paper sheet.

The paper provides an overview of these mechanisms and calls for further studies specific to the paper–adhesive bond. A better understanding of the reactions occurring between adhesive and paper would assist with the assessment of deterioration patterns and the evaluation of treatment options for adhesives that resist solubilization.

Titre et Résumé

Interactions entre les adhésifs de sources naturelles et les substrats de papier

Ce sont les adhésifs d’origine naturelle qui ont traditionnellement servi à réparer les matériaux à base de papier et à assurer leur adhérence. Ces adhésifs comprennent notamment la colle d’amidon, la gomme arabique et la colle animale (ou gélatine). Les adhésifs de ce type devraient conserver leur capacité de réversibilité au fil du temps. Toutefois, les adhésifs de sources naturelles peuvent réagir avec le papier et des médiums connexes, ce qui rend plus complexe le traitement prévu à l’origine. De même, les composants de l’adhésif peuvent aussi influer sur la dégradation de la cellulose.

Le présent article traite de l’étude de trois voies de réactions distinctes, soit :
- Il est reconnu que des ions métalliques polyvalents comme ceux du cuivre et du fer provoquent la dégradation de la cellulose, de la gomme arabique et d’autres

substances polysaccharidiques. Certains résultats semblent indiquer que ces ions peuvent aussi réagir avec des adhésifs protéiques et former des complexes insolubles;

- Les aldéhydes formés par oxydation de la cellulose peuvent réagir avec des polymères naturels et entraîner leur durcissement;
- Les adhésifs comprenant à la fois des protéines et des glucides peuvent subir des réactions de condensation, lesquelles entraînent une altération de la couleur et une perte de solubilité. Ce type de réactions peut aussi se produire dans le cas de la cellulose ou celui d'une couche de l'encollage de la feuille de papier.

L'article offre aussi un aperçu de ces divers mécanismes et des raisons qui demandent l'exécution d'autres études particulières sur l'adhérence papier-adhésif. En ayant une meilleure compréhension des réactions auxquelles participent l'adhésif et le papier, il sera plus facile d'établir des profils de détérioration et d'évaluer la pertinence de traitements au moyen d'adhésifs résistants à la solubilisation.

Introduction

Adhesives of natural origin are often found on paper-based collection material. Though adhesives like animal glue and starch paste were less widely used after the development of new synthetic polymers in the 1920s-1930s, they are still commonly encountered by paper conservators.

The exact composition of such adhesives is rarely of concern, as many remain treatable using standard aqueous methods. Similarly, the reactions that may have taken place between adhesive and paper over time are not often considered, unless the adhesive proves to be unresponsive to traditional treatment methods or when unusual degradation is observed.

This paper examines the types of reactions that may occur between adhesives of natural origin and paper, focusing primarily on reactions involving proteins and carbohydrates. To begin, the nature of the paper-adhesive bond and a brief overview of cellulose deterioration are presented. This is followed by a summary of natural binders used with paper. Three reaction pathways are then examined: reactions with metallic ions (particularly multivalent ions), the effect of aldehydes on natural binders, and condensation reactions. These reactions may occur within either the paper or the adhesive alone, creating new functional groups which may then react with other layers in the assembly. Alternatively, these reactions may occur across the bondline.

In 1976 Baer et al noted that there has been little investigation of the interaction of the adhesive-artifact system in conservation literature. This would still seem to be the case. The information in this paper is largely drawn from studies of related effects, such as the deterioration of cellulose by iron or copper-containing inks or the degradation of sizing layers on paper. Further studies specific to adhesive-substrate interactions would be of benefit to the conservation profession, both to understand observed degradation and to assist with the development of treatment methodologies for insoluble adhesives.

The Adhesive Bond

To understand what reactions may take place between adhesives and paper, it is first necessary to understand the nature of the adhesive bond. An adhesive bond typically contains three distinct parts — two adherends (e.g. the two pieces of paper to be joined) and the adhesive in between. Petrie (2006, pp. 8-9) defines two additional ‘interphase’ regions. These are thin volumes of material between the adhesive and each adherend. The interphase regions may contain many layers, such as adsorbed water, corrosion products, oxidation products or contaminants and plasticisers that have migrated out of either adhesive or adherend. The weak boundary layer theory of adhesion even proposes that adhesives bind with these layers, rather than to the substrate itself (Petrie 2006, pp. 50-66).

Size layers are also significant in a paper-adhesive assembly. Size is added to decrease the porosity of the paper surface and may be added to the pulp itself, before the sheet is formed, and/or to the surface of the paper after sheet formation. Traditionally, starch and gelatin were used to size paper. From the early nineteenth century, alum and rosin were often added to gelatin size, to improve its water resistance (Gess 1996). On old papers, the adhesive and the size may be very similar materials.

The surfaces of materials are highly energetic compared to the bulk of the material within or beneath. As they have fewer neighbouring molecules, the surface molecules are less closely bound and have more energy available for other reactions. These atoms can interact with each other, with atoms from the ‘bulk’ (below the surface or within the material) or with other materials in the environment (Schneberger 1983, pp. 21-22).

Much of the adhesion between an adhesive and paper is due to simple mechanical interlocking — paper is a fibrous, porous surface; adhesive molecules can penetrate the surface and become mechanically intertwined. However, adsorption is also thought to play a role in adhesive bonding to cellulose. Hydrogen bonding is likely to play an especially important role, due to the large number of hydroxyl groups (OH) available for bonding on the cellulose molecule (Petrie 2006, pp. 50–66). Many natural binders also contain side groups capable of forming hydrogen bonds. (See *Table 1*). For example, proteins contain amino groups (NH_2) and carboxyl groups (COOH); polysaccharides contain hydroxyl groups (OH). Hydrogen bonds are therefore likely to form between various natural binders and cellulose (or a sizing layer), across or encompassing molecules in the interphase regions.

Cellulose Deterioration

Paper is primarily composed of cellulose, a straight-chain polysaccharide, consisting of long chains of D-glucose units joined by 1-4-β-glycosidic bonds. Hydrogen bonds form within and between molecules, contributing to the strength of the material. Though relatively stable to degradation, acid hydrolysis can occur as cellulose is oxidised to form acidic carboxyl groups. Oxidation can also occur, particularly on exposure to light. Here, primary hydroxyl groups are oxidised to carboxyl groups (Mills & White 1999, p. 73). Cellulose can also oxidise to form peroxy radicals. These radicals then cause chain scission or cross-linking of nearby materials. Metallic ions are powerful oxidizing agents and may be present as residues of the papermaking process or as components of various media applied to the paper substrate.

Of course, paper is rarely (if ever) just cellulose. Hemicellulose, lignin, pectin and other materials may also be present within the fibre matrix, adding to its already complex chemistry. In addition, paper may have had size, dyes, bleaches, bluing agents and various other substances added during or after manufacture.

Natural Binders used as Adhesives for Paper

A study of published adhesives recipes from the period 1870-1920 found a wide variety of natural substances in use as adhesives for paper (Cannon 2009, pp. 45-74). The most commonly used materials were animal glue (and its purer form, gelatin) and starch or flour pastes. Sugar, dextrin and gum arabic were also very common organic binding agents. Less common materials included shellac, linseed oil, gum tragacanth, rubber, gutta percha, casein, fish glue, egg, cellulose nitrate and plant resins such as dammar and mastic. *Table 1* contains a summary of these materials and *Table 2* a description of their common functional groups. In terms of broad chemical categories, natural binders include proteins, polysaccharides, polyisoprenes, terpenes or triglycerides. Many are naturally-occurring polymers, or biopolymers.

About one third of all recipes identified by Cannon (2009, pp. 75-116) contained more than one binder. For example, animal glue mixed with starch or flour paste was a common recipe. Plant resins were sometimes added to starch and protein adhesives to increase tack. Linseed oil was added to animal glue to make a more waterproof adhesive. It may not be unusual, therefore, to encounter an aged adhesive that contains both protein and starch, or starch and terpene, and so on.

The insolubility of an adhesive based on natural substances may, of course, be a characteristic entirely independent of the paper substrate. The adhesive may have been formulated to be water-resistant, utilizing either non-water soluble binders (e.g. rubber, linseed oil, plant resins) or chemical hardeners (e.g. alum, formaldehyde, potassium permanganate, tannic acid).

All of these substances are complex on an individual level; in combination even more so. The chemical makeup of an adhesive based on natural binders may be further complicated by the presence of various additives, including metal salts, essential oils, solvents and diluents, which were often added to alter the working properties of the adhesive or the qualities of the dried film. This complexity makes it hard to predict what chemical degradation may occur within the adhesive itself, as well as what effects it may have on an adjacent paper substrate.

Table 1: Common binding agents of natural origin

Binder	**Description**	**Reactive groups**
Animal glue, gelatin, fish glue	Fibrous protein. Consists primarily of partially degraded collagen. Collagen contains frequently repeating glycine-proline-hydroxyproline sequences.	Amine (NH_2) Carboxyl (COOH) Peptide links (-C(=O)NH-) Double bonds

Casein	The principal protein in milk; composed of α, β, γ, and κ-caseins (differing molecular weights). Contains about 1% phosphorous, mostly in the form of phosphoric acid.	Amine (NH_2) Carboxyl (COOH) Peptide links (-C(=O)NH-) Double bonds
Egg albumen	A globular protein, though on denaturing adopts an open chain-like structure. Egg white contains ovalbumin, conalbumin (both glycoproteins) and lysozyme proteins. Egg yolk contains phosphorous and lipids, amongst other materials.	Amine (NH_2) Carboxyl (COOH) Peptide links (-C(=O)NH-) Double bonds
Starch	Polysaccharide. Comprised of glucose units joined by α-glycosidic bonds. Composed of varying amounts of amylase (linear chain) and amylopectin (branched chain).	Hydroxyl (OH) Acetal (R(RO-C-OR)H)
Flour	Polysaccharide containing protein component (prolamins and glutelins). Cereal grains generally contain about 10% by weight of protein, seeds or beans as much as 50% of dry, de-fatted materials.	Hydroxyl (OH) Acetal (R(RO-C-OR)H) Functional groups related to protein component (e.g. amine, carboxyl)
Dextrin	Polysaccharide. More highly branched than starch. Made from starch that has been hydrolysed and then re-polymerized with heat and/or acid.	Hydroxyl (OH) Acetal (R(RO-C-OR)H)
Plant gums (gum arabic, gum tragacanth etc)	Mixtures of polysaccharides ($C_6H_{12}O_6$) and glycoproteins. Contain different sugars and acid salts – e.g. arabinose, galactose, galacturonic acid. Gum arabic also contains calcium, magnesium and potassium.	Aldehyde (H(C=O)) Hydroxyl (OH)
Sugar	Disaccharide (contains sucrose, which is composed of glucose and fructose).	Carbonyl (C=O) Hydroxyl (OH) Hemiacetal and/or hemiketal (R(RO-C-OH)H, R(RO-C-OH)R)
Cellulose nitrate	Modified polysaccharide – hydroxyl groups on glucosidic rings substituted with nitrate groups.	Hydroxyl (OH) Nitrate ($R\text{-}ONO_2$)

Linseed oil	Triglyceride. Main components linolenic, linoleic, oleic, palmitic and stearic acids. Contains high number of unsaturated esters.	Alkyl group (-O-) Ester bonds formed from hydroxyl (OH) and carboxyl (COOH): RCO_2H
Rubber, gutta percha	Polyisoprenes (rubber is the cis isomer, gutta percha the trans). Composed of isoprene units (C_5H_8). Contains a small percentage of other materials, such as proteins, fatty acids, resins and inorganic materials (salts).	Methyl (CH_3) High proportion of double bonds
Plant resins (dammar, elemi, mastic, sandarac etc)	Terpenes (diterpenes and triterpenes). Composed of isoprene units (C_5H_8), which may be arranged in chains and/or rings.	Aldehyde (H(C=O)) Carboxyl (COOH) Hydroxyl (OH) Double bonds
Shellac	Terpene (sesquiterpenes) combined with colouring matter and waxes.	Aldehyde (H(C=O)) Carboxyl (COOH) Hydroxyl (OH) Double bonds

Table 2: Common organic functional groups

Functional group	**Description**	**Formula**
Acetal	Two single bonded oxygen atoms attached to the same carbon atom. A component of glycosidic bonds in cyclic glucose molecules.	R(RO-C-OR)H
Alkoxy	An alkyl (carbon and hydrogen chain) group single-bonded to oxygen.	-O-
Aldehyde	Carbon double-bonded to oxygen, on the end of polymer chain.	RCHO
Amino	Contains a basic nitrogen group with a lone pair.	$-NH_2$, -R(NH) or –R(N)R
Carbonyl	Carbon double-bonded to oxygen. A characteristic of aldehydes, ketones, carboxylic acids and esters. If found on the end of a chain it forms an aldehyde H(C=O). If found between two carbon atoms, it denotes a ketone.	C=O
Carboxyl	Consists of a carbonyl group and a hydroxyl groups. Characteristic of carboxylic acids, the most common type of organic acid.	-COOH
Hemiacetal	Formed by the addition of an alcohol to a carbonyl group. Derived from aldehydes. Less stable than acetal groups, but glucose and other aldoses exist as cyclic hemiacetals.	R(RO-C-OH)H

Hemiketal	Formed by the addition of an alcohol to a carbonyl group. Derived from ketones. Less stable than acetal groups, but fructose and other ketoses exist as cyclic hemiketals.	R(RO-C-OH)R
Hydroxyl	Characteristic of alcohols; especially predominant in carbohydrates.	-OH
Imine	Contains a carbon-nitrogen double bond. May be found on primary or secondary carbons and attached to either a hydrogen ion or another molecule.	C=N
Ketone	Carbon double-bonded to oxygen, between two carbon atoms.	RCOR’
Methyl	The simplest alkyl group, which consist only of single-bonded carbon and hydrogen atoms.	$-CH_3$

Possible Reaction Pathways between Paper and Adhesives

The paper-adhesive assembly is clearly a complex structure. A multitude of reactions may be expected to occur within and between components of the assembly. The following reactions may occur within the adhesive or the paper alone, or they may occur across the bondline. These reactions result in crosslinking, manifested by increased insolubility of the adhesive, or in chain scission, which weakens paper and adhesive binders alike. Oxidation (the reaction of oxygen with radicals formed within a substance) may result in oxygen and other molecules becoming embedded in the structure. Yellowing generally indicates the formation of double bonds within the structure (Horie 1992, pp. 37-38).

Metallic ions

Metallic ions often act as oxidizing agents for cellulose and adhesive materials. Multivalent (or polyvalent) metal ions are particularly reactive, as they can participate in ionic reactions in two or more oxidation states. Common multivalent ions are iron, copper, lead, chromium, aluminium, mercury and manganese. The alternation between charged states for multivalent metal ions (e.g. between Cu^{+2} and Cu^{+3}) requires a partner in the oxidation/reduction process. Cellulose and other polysaccharides (e.g. gum arabic) can act as the reaction partner and thus will undergo oxidative degradation, creating radicals that further contribute to the deterioration process (Daniels 2002; Hagadorn 2004). Kireyeva (1995) additionally found that aged samples of fruit tree gums, gum arabic and egg white plasticised with honey were decomposed to various organic acids (e.g. formic, lactic, oxalic and acetic) on exposure to copper acetate. Such acids may contribute further to the deterioration of the adjacent paper substrate.

The formation of radicals via this path can occur in both acidic and alkaline environments. Bicchieri & Pepa (1996) found that in low-acid environments, iron ions acted as a catalyst for the cleavage of cellulose at the 1-4-β-glycosidic bond, whereas copper catalysed the oxidation of the anhydroglucose ring. If conditions were acid or neutral, the new end groups formed on the chain were aldehydes; if alkaline, the groups became carboxyl groups. An increased concentration of metal ions within the paper appears to accelerate the rate of reaction and thus subsequent damage. More soluble form of these ions — for example, copper acetate, found in the pigment verdigris — are more likely to be diffused through the paper (Banik 1989).

Multivalent ions are also known to cause protein chains to crosslink, hence the use of aluminium, iron and chromium in leather tanning. Metal ion-induced crosslinking between protein chains is thought to include hydrogen, ionic and covalent bonds. For example, copper may form metal mercaptides with sulphur groups in proteins (Walsh 1962; Gettens & Stout 1966, pp. 24-25; Hubbard 1977; Norland 1977). Lead ions have been found to complex with proteinaceous material on the surface of paintings, making them insoluble to normal aqueous treatment methods (Wolbers 2000, pp. 119-120).

There are many potential sources of metal ions within the adhesive-adherend structure. Metal ions may have been present in the original binding materials — for example, gum arabic naturally contains calcium and magnesium salts of arabic acid. Old adhesive recipes based on natural binders often included metal salts as additives, in order to alter the physical properties of the adhesive. Some recipes contained chemical hardeners, such as alum (as aluminum sulphate or aluminium potassium sulphate), potassium dichromate or tannic acid. Copper sulphate was used occasionally, most likely as a preservative. Lead salts, such as lead acetate, lead carbonate, lead (II) sulphate and lead oxide (litharge), when added, were probably intended as driers or fillers, though on occasion it seems they were intended to increase the water-resistance of the adhesive. Mercury salts were added to prevent insect attack (Cannon 2009, pp. 81-91). Paper itself often contains iron and copper impurities from papermaking equipment. Alum sizing was common from the seventeenth century (Kolbe 2004) and so aluminium is likely to be present in many historic papers. Inks and paints may contain iron, copper, zinc, calcium, lead, chromium and a host of other metallic ions.

It seems likely that the diffusion of metallic ions from one layer to another could bring about adhesive insolubility and/or paper degradation. For example, *Figure 1* shows a printed label adhered to a scrapbook page. The adhesive was easily soluble in water except for the portions directly below the gold-coloured ink. This ink was found to contain copper, by using x-ray fluorescence (XRF). The machine used was a Bruker AXS TRACeR III-V hand-held instrument loaned by KeyMaster Technologies. The item in question is a printed label from the Victorian Patent Office Copyright Collection belonging to the State Library of Victoria. Diffusion of copper ions through the paper and into the adhesive, causing crosslinking, could explain this difference in solubility.

Figure 1: Printed label adhered to scrapbook page. Adhesive is water-soluble except in areas immediately adjacent to gold-coloured ink.

Many authors have examined the role of size layers and media binding agents in the degradation of cellulose by copper and iron. Though not directly concerned with any adhesive layer, these studies nevertheless indicate what may occur when metal ions react with natural adhesives.

When used as a binder for iron and copper-containing inks, gum arabic binders have provided a temporary barrier between the metallic ions and the cellulose, though the binder itself eventually suffers copper-induced decomposition (Hagadorn 2004). Gelatin has a similar buffering effect but appears more effective than gum arabic, with less deterioration of the cellulose observed. Barret and Mosier (1995) proposed that gelatin acts as an acid acceptor, buffering the paper from acidic environmental pollutants and degradation products. Daniels and Leese (1995) theorised that gelatin may act simply as a physically protective layer, preventing metal ions from passing into the substrate. Kolbe (2004) proposed that gelatin may complex transition metals, making them unavailable for oxidative decomposition of the cellulose beneath. Kolbe additionally noted that iron-gall ink brings about local “tanning” on the surface of vellum and of gelatin-sized paper. When investigating the effects of copper on gelatin binders, Meyer and Neumann (2009) found that copper-gelatin complexes were relatively unstable and that the presence of moisture may cause them to dissolve. Short-chain gelatin was more effective at forming complexes than longer chain molecules. Alum also has a crosslinking effect on gelatin size, forming bridges between gelatin and cellulose and making the size more resistant to water (Dupont 2002). It is presumably also possible for these reactions to occur with an adhesive layer.

Though acidic polymers such as proteins and degraded cellulose may not strictly be called chelating agents, polymers that form complexes with metal essentially act as such. In doing so, they may become very difficult to resolubilise in aqueous systems (Wolbers 2000, p. 121). It seems clear that metal ions can diffuse through the adherend-adhesive layers, regardless of the layer in which they originate. Metal ions will thereby accelerate the degradation of proteins and polysaccharides and/or cause crosslinking of proteins.

Aldehydes

Aldehydes (e.g. formaldehyde) have been observed to harden proteins, with vapours of formaldehyde reportedly enough to cause films of fish glue to become insoluble (Walsh 1962). Aldehydes are also used to tan animal skins. The reaction between aldehyde and protein occurs primarily at amino groups, resulting in intra and intermolecular crosslinking (Hopwood 1968). In undegraded collagen, an N-hydroxymethyl group (collagen-NH-CH_2OH) is formed from the initial reaction with an aldehyde. This group is highly reactive, combining with further amino groups to form crosslinks between collagen molecules (Covington 2006).

In a study on the degradation of gelatin size on paper, Dupont (2002) found evidence to suggest that crosslinking of gelatin occurred during ageing, through links other than hydrogen bonds. On ageing an alkali-prepared gelatin, Dupont found that there was an increase in low molecular weight fractions as well as formation of high molecular weight proteins, the latter probably formed through crosslinking or aggregation of chains. Crosslinking occurs in proteins when bound water within the gelatin molecule is progressively removed. However, as mentioned previously, the degradation products of cellulose contain aldehyde groups and thus can react with free amino groups on the protein molecule. Amino glycosides are formed, which can react with other gelatin amino groups. The result is a crosslinked, less soluble structure.

Starch is also reported to form insoluble complexes with aldehydes. The chemical pathways are not thoroughly understood, but it is likely that aldehydes react with hydroxyl groups on the starch chain. Crosslinking of chains may occur through the formation of bonds between methylene groups on the aldehyde and hydroxyl groups on the starch. Borax (sodium tetraborate) is thought to have a similar effect and has been used widely for tackifying starch and dextrin adhesives. It is possible that any ‘polyhydroxy’ acid groups (those having three or more hydroxyl functional groups) could have similar crosslinking mechanism with starch (Kerr 1950, pp. 466-470; Kruger & Lacourse 1990).

Maillard (browning) reactions

In these reactions, amino groups (NH_2) from a protein react with carbonyl groups (C=O) from carbohydrates, or from oils undergoing auto-oxidation. Derivatives of these substances or their acid-catalyzed degradation intermediates may also participate. The subsequent reactions are complex and varied, comprising a number of reactions occurring in series or in parallel. The results are cross-linked products, thought to be polymeric carbonyl-amine compounds containing free carboxyl groups (COOH) and phenols — substances containing a six-membered ring structure bonded to a hydroxyl group. The resulting brown or yellow colouration is due to the presence of conjugated double bonds. The resulting compounds are also insoluble (Palladino 1992; Cortesi et al 1998; Mills & White 1999).

Maillard reactions are known to occur within glycoproteins (substances that contain both protein and sugars, such as egg albumen and gum arabic). Such reactions are thought to be responsible for the yellowing and browning of albumen photographic prints (Reilly 1982). It is likely that similar reactions occur in adhesives containing both protein and carbohydrate binders (e.g. animal glue or gelatin mixed with starch, sugar, dextrin or gum arabic). Certainly, sugars have been used to cross-link gelatin for pharmaceutical purposes (Cortesi et al 1998).

Maillard reactions are very sensitive to temperature and may be initiated by a period of high heating — possibly, for adhesives, by the cooking required in their preparation. (The Maillard reactions are responsible for much of the browning and flavour of cooked food — see McGee 2004, pp. 778–779). After initiation, the reactions can continue at room temperature (Reilly 1982). Moisture also accelerates the reaction (Karpowicz 1981). The reactions would appear to occur in both alkaline and acid conditions — some authors have found that alkaline conditions accelerate browning (e.g. Reilly 1982); however, Daniel & Lohneis (1997) found that instead acid conditions promoted browning of sugar and egg white confectionery. It seems likely, therefore, that adhesives could react with a sizing layer or the paper itself via this mechanism. Maillard reactions may also explain excessive discolouration of adhesives containing both proteins and carbohydrates.

Conclusions

Adhesives of natural origin and cellulose contain reactive groups that can interact across the bondline. On ageing, degradation products (such as radicals, aldehydes or organic acids) from either material may migrate across the bondline and bring about crosslinking, chain scission and/or oxidation of the other materials present in the assembly.

The most likely reactions to occur are those involving multivalent metal ions, contained in either the adhesive or the paper, resulting in crosslinking of the adhesive and cellulose deterioration. There have already been studies on the effects of multivalent ions contained in pigments on cellulose degradation. Though these studies have examined the role of binders such as animal glue and gum arabic in the reaction, the deterioration of binders has not been the primary focus.

Other chemical reactions that take place within organic substances may also occur over the adhesive-substrate bond. These include condensation reactions (e.g. the browning or Maillard reactions), and reactions caused by the production of free radicals or other deterioration by-products, such as aldehydes. To date there is little specific information available about the reactions that may occur between adhesives of natural origin and a paper substrate, on ageing. Most information must be inferred from studies of similar systems, such as the ageing of sizing layers on paper or the degradation of cellulose by metallic ions. The reactions between paper and adhesives of natural origin have not been a major research concern, as the majority of such adhesives have remained treatable with aqueous solutions over time. However, some adhesives resist solubilisation or swelling. Others deteriorate in unexpected ways. Closer investigation of possible reaction pathways can only benefit the materials conservator.

References

Baer, N.S., N. Indictor and A. Joel. “An Evaluation of Glues for Use in Paper Conservation” pp. 182-190 in *Conservation and Restoration of Pictorial Art* (edited by N. Brommelle and P. Smith). London: Butterworths, 1976.

Banik, G. Discolouration of Green Copper Pigments in Manuscripts and Works of Graphic Art. *Restaurator* 10, 2 (1989), pp. 61–73.

Barrett, T. and C. Mosier. The Role of Gelatin in Paper Permanence. *Journal of the American Institute for Conservation* 34, 3 (1995), pp. 173-186.

Bicchieri, M. and S. Pepa. The Degradation of Cellulose with Ferric and Cupric Ions in a Low-Acid Medium. *Restaurator* 17 (1996), pp. 165-183.

Bordignon, F., P. Postorino, P. Dore and M.L. Tabasso. The Formation of Metal Oxalates in the Painted Layers of a Medieval Polychrome on Stone, as revealed by Micro-Raman Spectroscopy. *Studies in Conservation* 53 (2008), pp. 158-169.

Cannon, A. *Adhesives for Paper 1879-1920: Recipes and Proprietary Products*. Masters by Research thesis. Melbourne: Department of History, Centre for Cultural Materials Conservation, The University of Melbourne, 2009. Unpublished. Permanent URL: http://repository.unimelb.edu.au/10187/8554.

Cortesi, R., C. Nastruzzi and S.S. Davis. Sugar Cross-Linked Gelatin for Controlled Release: Microspheres and Disks. *Biomaterials* 19 (1998), pp. 1641-1649.

Covington, A.D. “The chemistry of tanning materials” pp. 22-35 in *Conservation of leather and related materials* (edited by M. Kite and R. Thomson). Oxford: Elsevier, 2006.

Daniels, V. and M. Leese. The Degradation of Silk by Verdigris. *Restaurator* 16, 1 (1995), pp. 45–63.

Daniels, V. and G. Lohneis. Deterioration of Sugar Artifacts. *Studies in Conservation*. 42, 1 (1997), pp. 17–26.

Daniels, V. “Aging of Paper and Pigments Containing Iron and Copper: A Review” pp. 116-121 in *The Broad Spectrum: Studies in the Materials, Techniques, and Conservation of Color on Paper*. London: Archetype Publications, 2002.

Dupont, A-L. Study of the Degradation of Gelatin in Paper Upon Aging Using Aqueous Size-Exclusion Chromatography. *Journal of Chromatography A*. 950 (2002), pp. 113-124.

Gess, J.M. “The sizing of paper with rosin and alum at high pH” pp. 120-139 in *Paper Chemistry*, 2nd edition. (edited by J C Roberts). Glasgow: Blackie, Glasgow, 1996.

Gettens, R.J. and G.L. Stout. *Painting Materials — A Short Encyclopaedia*. New York: Dover Publications, Inc, 1966.

Hagadorn, A. An Investigation into the Use of Blue Copper Pigments in European Early Printed Books. *The Book and Paper Group Annual* 23 (2004), pp. 41–55.

Horie, C.V. *Materials for Conservation*. Oxford: Butterworth-Heinemann Ltd, 1992.

Kerr, R.W. *Chemistry and Industry of Starch*. New York: Academic Press Inc., Publishers, 1950.

Karpowicz, A. Ageing and Deterioration of Proteinaceous Media*. Studies in Conservation* 26, 4 (1981), pp. 153–160.
Kireyeva, V. Destruction of the Binding Media of the Green Paint Layer in an Eleventh-Century Greek Manuscript. *Restaurator* 16, 2 (1995), pp. 86–92.

Kolbe, G. Gelatin in Historical Paper Production and as Inhibiting Agent for Iron-Gall Ink Corrosion on Paper. *Restaurator* 25, 1 (2004), pp. 26–39.

Kruger, L. and N. Lacourse. “Starch Based Adhesives” pp. 153-166 in *Handbook of Adhesives* (edited by I. Skeist). New York: Van Nostrand Reinhold Company, 1990.

McGee, H. *McGee on Food & Cooking: An Encyclopedia of Kitchen Science, History and Culture*. London: Hodder & Stoughton Ltd, 2004.

Meyer, F. and A. Neumann. Recombinant Proteins: A New Material for the Chemical Stabilization of Copper Pigment Corrosion on Paper? *Restaurator* 30 (2009), pp. 96-130.

Mills, J.S. and R. White. *The Organic Chemistry of Museum Objects*. Oxford: Butterworth-Heinemann, 1999.

Norland, R.E. "Fish Glue" pp. 152-157 in *Handbook of Adhesives* (edited by I. Skeist). New York: Van Nostrand Reinhold Company, 1977.

Palladino, D.E.H., R.M. House and K.A. Cohen. Measurement of Amino Acid Compositions of Glycoprotein Systems by Gas-Phase Hydrolysis and Reversed-Phase High Performance Liquid Chromatography. *Journal of Chromatography* 599 (1992), pp. 3-11.

Petrie, E.M. *Handbook of Adhesives and Sealants*. New York: McGraw-Hill Professional, 2006.

Reilly, J.M. "The Role of the Maillard, or Protein-Sugar Reaction in Highlight Yellowing of Albumen Photographic Prints" pp. 160-168 in *The 10th Annual Meeting of the American Institute for Conservation, Milwaukee*. Washington DC: The American Institute for Conservation of Historic & Artistic Works, 1982.

Schneberger, G.L. *Adhesives in Manufacturing*. New York; Basel: Marcel Dekker Inc, 1983.

Walsh, H.C. "Fish Glue" pp. 126-128 in *Handbook of Adhesives* (edited by I. Skeist). New York: Reinhold Publishing Corporation, 1962.

Wolbers, R. *Cleaning Painted Surfaces — Aqueous Methods*. London: Archetype Publications Ltd, 2000.

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