17. Sizing/Resizing

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17. SIZING/RESIZING

Sizing is the application of a material, generally an adhesive, to paper to impart certain desirable qualities. Internal sizing refers to the addition of this substance to the pulp during manufacture principally in order to decrease wettability. Surface sizing is the application of a film-forming material to the surface of the sheet, subsequent to sheet formation. Resizing (or retrospective sizing), specifically indicates a conservation treatment, a special instance of surface sizing.

17.1 Purpose.

To impart strength to the sheet; improve the hand or "feel" of the sheet; improve abrasion resistance and dimensional stability; control absorptive qualities; protect against chemical, environmental or mechanical degradation; modify surface, texture, character and appearance; improve soil, grease, stain, and liquid resistance; alter reflectance properties. The purpose of resizing, a conservation treatment, is to reintroduce characteristics lost through degradative influences or conservation treatment. Resizing is rarely an isolated treatment; resizing may also serve to stabilize media. (See 23. Consolidation/Fixing/Facing.)

17.2 Factors to consider in resizing.

17.2.1 Future use of artifact.

A. Object will be handled or exposed to dust.

Resizing imparts strength to the sheet and can improve the soil, grease, tear and abrasion resistance of paper, thereby protecting it from effects of handling and fingerprints. These factors will be particularly important in the case of book leaves, archival or art objects in study or reference collections, and other materials subject to handling. For an item not otherwise protected in handling, resizing may impart strength as an alternative to lining, or resistance to grime as an alternative to encapsulation.

B. If the object will not be handled, the need for resizing is less critical; however it still may be desirable.

17.2.2. Aesthetic and ethical considerations.

A. Changes in the reflectance and refraction characteristics of the paper media.

When an object is resized overall, the sizing agent may sit on the surface of the design layer and alter its visual character. Such changes may become more evident as the object ages and the media and/or sizing agent deteriorate.

B. Loss of evidentiary value.

If resizing treatment is being considered, it usually follows washing and/or other conservation treatments which have already changed fundamentally the artifactual nature of the object, and have removed a large portion of the original size.

However, resizing papers represents an additional change in the artifactual nature of the object and may interfere with future attempts to extract physical or chemical information concerning sheet production, history and codicology by covering, replacing, or merging with the original size. Many bibliographers do not currently concern themselves with "ancillary" technical details of paper manufacture. Thus librarians, curators and archivists may not be sympathetic to the conservator's desire to retain the artifact in its unaltered form. Overall, resizing should be considered a definite alteration to the original artifact, and should be thoroughly documented.

C. Reversibility.

Although many of the resizing materials in use are expected to remain soluble upon aging, the nature of the interactions between the resizing agent and the cellulose surface structure makes complete removal of the resizing material unlikely. As a practical matter, resizing should be considered as largely irreversible.

D. Surface character.

Resizing may dramatically alter the surface nature of sheets. This is especially true for papers that originally were finished by burnishing, pressing (especially heated pressing), rolling, etc. By swelling the fibers, resizing can disrupt and "open up" a previously compacted, dense and smooth surface. On the other hand, by filling the fiber interstices and holding fibers in place upon burnishing or pressing, resizing can facilitate the recreation of such glazed surfaces or the recreation of a well-compacted surface.

Non-aqueous liquids may also disrupt surface sheen (TJV).

E. Color changes due to earlier treatment.

In some cases, when the sheet has become unnaturally and starkly white, perhaps as the result of past treatment, resizing by immersion in certain agents can reduce the starkness of tone. The effect is extremely subtle. Conservators have found methyl cellulose and sodium carboxymethyl cellulose to be effective. Although the mechanisms involved have not been explained, three plausible hypotheses have been suggested: 1) the size brings about a change in refractive index [i.e., the amount of light scattering from the air/fiber surface interfaces changes, making the sheet appear less white (bright) and allowing the true color of the fibers to mainfest themselves (TJV)]; the size itself may have a slight cast; the size moves colored material from within the sheet itself.

17.2.3. Characteristics of the paper.

The character, feel and sound of a paper sheet are major factors in deciding to resize. Surface softness, lack of abrasion resistance, absorbency, open texture, limpness, fluffiness, tendency to pill, and fragility indicate a need for resizing. The amount of size to be deposited should be determined by the degree to which these qualities are present. A sheet which shows strength, toughness at the surface, rattle and lack of absorbency suggests that resizing is not required. The presence of a surface coating may interfere with the possibility of resizing. As a result of sizing absorbency will be reduced. Thickness and density will usually decrease when sizing a waterleaf sheet (a paper made without size) or resizing a size-deficient sheet. The texture (surface quality) of the sheet will be affected by the size material and pressing procedure. The interaction of a resizing agent, original size, and the cellulose substrate is clearly a complex one. To date, no research has been carried out on this subject. In practice, beyond a general tendency to resize gelatin-sized papers with gelatin, starch with starch, etc., treatment decisions have usually been based on the properties of the resizing agent independent of any possible interactions with the original size. These interactions should be considered.

Waterleaf papers tend to be very absorbent. If a lot of size is used the sheet is called hard-sized whereas the opposite condition is called soft or slack-sized.

17.2.4. Character and extent of original sizing in paper.

The ability to determine accurately the original sizing and/or measure its presence can be critically important. Historical information is vital for determining the original size, although qualitative and quantitative tests make this less speculative. The lack of sufficient and unambiguous data concerning sizing history compounds the problem.

There are not enough good studies of the history of the use of sizing to construct an accurate picture of what was done when and where. (RE)

- A. Original sizing agents. (See 46. Adhesives.)
 - 1. Gelatin.

Gelatin is derived from collagen, the connective tissue in skin, cartilage, sinews and ossein, the protein matrix of bone. (JM)

- a. Gelatin was used in Europe at least as early as 1276 (at the Fabriano mill) and continuously thereafter. Until the last century some form of gelatin or glue sizing was the most common form of surface sizing. It generally appears to have aged without causing significant damage to substrate.
- b. Early printing inks, being substantially heavier than later inks, were capable of leaving a clean impression on waterleaf stock. Sizing was not required for this purpose. Consider Dard Hunter's remarks: "In an examination of more than a hundred different volumes of incunabula I have found that the papermakers of the fifteenth century followed no definite formula as to the sizing of their papers; many of the sheets are heavily sized, others contain a limited amount of sizing and a small amount with no sizing at all. [Hunter, Dard. Papermaking: History and Technique of an Ancient Craft. NY: Dover, 1978 reprint.]
- c. Experimental use of gelatin as internal size began in the eighteenth century.
- d. From the sixteenth century on, gelatin was frequently used in concert with additives or preservatives, especially alum (historically, potash alum; modern-day, aluminum sulfate). Used in concentrations as high as 20%, it stabilized the viscosity of the size, improved ink resistance, and prevented spoilage of the gelatin solution.

- e. Contemporary industrial practice follows similar lines as that done historically. Alum is sometimes added in small quantities as a thickener; larger quantities added to the gelatin result in reduced viscosity. Alum is a preservative and defoaming agent. Alkalis are occasionally added and starch is sometimes added as an extender. Various crosslinking agents (hardeners), principally formaldehyde, have been used to render the gelatin film hard and insoluble, i.e. for blueprint papers. Plasticizers such as glycerine, hygroscopic salts, sulfonated oils and emulsions of oils, fats and waxes are common additives. [Cushing, 1981]
- d. Contemporary cotton bond paper, onion skin and ledger papers are produced by surface sizing with gelatin or starch and winding into a roll. The roll is left for some time and the moist size is distributed throughout the sheet. The paper is fed through an air drier without tension to yield the strength, hardness and characteristic surface.

2. Alum-rosin.

- a. The first sizing process used beyond experimental scale in the West, alumrosin size was introduced in Germany (1807) and later adopted elsewhere in Europe (1835). Originally the purpose of this size was to prevent inkfeathering on writing papers, but its use spread to many types of papers and has become all but universal. It is primarily an internal size.
- b. In general, the system depends upon the precipitation of a large aluminum rosinate aggregate (typically mono-rosinates, di-rosinates and free rosin acid), held together by hydrogen bonds between cationic alumina groups and anchored to the fiber by interactions between the alumina and the hydroxyl groups on the cellulose. Rosin is obtained from wood or exudates of pines and most often used in paste form. A saponified rosin, it is partially neutralized, but contains up to 30% of the rosin as a free acid. Fortified rosins, in which the rosin is reacted with dienophile dicarboxylic acids yielding improved size distribution and improved bonding with alumina, were introduced in the 1940's and remain popular today. Rosin may be delivered in modified forms such as wax rosin and rosin soaps.
- c. This size is highly acidic and causes deterioration of cellulose.

3. Synthetic (cellulose-reactive) sizes.

Developed since 1949, materials in this class consist of a hydrophobic end, composed of a chain of 16 or more carbons, connected to one of several cellulose-reactive functional groups which form covalent bonds with the hydroxyls on the cellulose. The ketene dimers and the anhydrides have been used commercially much more widely than other cellulose-reactive sizes, such as acid chlorides, isocyanates and masked isocyanates. The cellulose-reactive sizes are finding increased application in contemporary paper mills. Because they do not depend on alum (a degradative material when used in large quantity); because they allow use of calcium carbonate as a filler; and because

of improvement of sizing effect, strength and papermaking productivity, cellulose reactive sizes are finding increased application in contemporary mills.

A low melting point substance (40-50° C) with low reactivity to water, Aquapel, the first of the alkyl ketene dimers, is available in several forms: Aquapel 364 is a hard resinous flake that must be emulsified; Aquapel 380 is a hard emulsion; Aquapel 360 is a dispersion in cationic starch. Generally the paper inducstry uses these materials in concentrations of 0.1-2.0% applied at 60° C. In recent years, Aquapel has been largely superseded by Hercon 40, a similar material but with retention aid incorporated. All are products of Hercules, Inc.

a. Alkyl ketene dimer (Aquapel, Hercon 40).

Derived from long-chain fatty acids (such as hydrogenated tallow acids), the alkyl ketene dimers, such as Aquapel and Hercon 40 are composed of two 16-carbon chains joined via a lactone ringing. Until recently, it has been believed that this molecule will bond covalently to the cellulose substrate in a neutral or mildly alkaline environment, by opening the dimer's lactone ring and forming a beta-ketoester of cellulose. This covalent bond is expected to be highly stable because of its resistance to hydrolysis. Recently however this model has been called into question. Rohr, et al [Rohr, 1985] determined, by frustrated multiple internal reflection and other means, that in practice, no beta-ketoester bonds could be identified. Moreover, the sizing agent itself could be extracted by High Performance Liquid Chromatography and that the dialkylketene could migrate througout the paper, neither of which conditions would obtain if a ketoester of cellulose had been formed. The study suggests that hydrolysis products of dialkyl ketene, formed by reaction with other components of the furnish than cellulose, always believed to have no influence on sizing, may promote the development of sizing effect.

Under neutral pH or slightly alkaline conditions the alkyl ketene dimer molecules bond to the cellulose, and then orient long hydrocarbon chains outward to provide the very good water repellency characteristic of this size. The reaction of the size with cellulose forms, in essence, a new compound. Its attachment is considered to be relatively chemically inert and permanent. These sizes were a significant component in the development of durable/permanent papers (Permalife).

b. Stearic anhydride.

A cellulose-reactive size suitable for writing and printing papers, this material is more reactive (that is, more effective at covalently bonding with the cellulose substrate) than ketene dimer or alkenyl succinic anhydride. Tolerant of alum, it can be used in both alkaline and acid (to pH 5) systems though it is more efficiently employed in alkaline systems. As an highly reactive liquid mixture of isomers, its shelf life as an emulsion is a matter of hours and it must be prepared in the paper mill.

c. Alkenyl succinic anhydride.

Petroleum derivatives used in fine papers and secondary grades, the most familiar of these is Fibran. They are highly reactive with cellulose and also water.

4. Starch.

Starches can be obtained from a variety of natural sources, and are polysaccharides consisting of chains of glucose units arranged in combinations of two different forms: amylose (linear chain) and amylopectin (a highly branched polymer in which the repeat unit is an alpha-D-glucose in its pyranose or 6-membered ring form). Most starches are mixtures of these two forms. Contemporary commercial papermaking sources for starch size include corn, potato, sorghum and tapioca. (JM)

- a. Starch was used as a Chinese papers as early as the mid-ninth century.
- b. Early Arabic papers were surface sized with wheat starch, wheat flour or mixtures of starch and chalk, and glazed to produce a shiny, burnished surface. Early Spanish papers, which were developed under Arabic influence were coated with thick starch.
- c. A seventeenth century painting manual recommends starch sizing for paintings on paper that are to be varnished.
- d. Eighteenth and nineteenth century heavy papers made for steel engravings sometimes exhibit white tidelines after exposure to moisture. This may result from the movement of starch in the sheet.
- e. Contemporary cotton bond, onion skin and ledger papers are produced by surface sizing with starch. (See 17.2.4.A 1d Gelatin.)
- f. Contemporary starch sizing is employed in three ways:
 - 1) as an internal size, cooked first and usually added to the pulp prior to sheet formation;
 - as an external or surface size, applied to the formed sheet either at the size press on the paper machine; at a size tub through which the sheet passes; and/or at a calender stack at the paper machine (often for better grades of modern papers, especially writing, ledger and tablet papers.);
 - 3) as the adhesive in pigment coating. (JM)

As an internal size, the starch is usually unmodified, while for the external sizing and coating processes, the starch is commonly modified using hydrolysis methods, heat dextrinization, enzyme treatment, or oxidation. (JM)

g. Higher viscosity starches (4-10% concentration by weight) such as hydroxyethyl ether starches, are chosen to impart strength because they

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tend to form a film on the surface of the sheet. In order to improve printability (resistance to ink penetration) lower viscosity starches (6-18% concentration by weight) are used because they penetrate the sheet deeply. Both types of material yield increases in burst strength, tensile strength and fold endurance, but may be associated with decline in tear strength.

5. Other original sizing agents.

a. Gypsum.

Early Chinese paper (ca. eighth century) was coated with gypsum and burnished.

b. Lichen.

A substance derived from lichen replaced gypsum in later Chinese paper.

c. Alum.

Historically, alum referred to potash alum, while today it refers to aluminum sulfate. As early as the late seventeenth century a bath of alum water was used to act as a mordant for fixing colors, e.g. hand-colored prints. This has been noted for prints that were to be hand colored. After use of a steel eraser, alum or sugar water was sometimes used with writing and drawing papers to restore the surface of the sheet and provide thereby a workable writing surface. Paper so treated may have substantially different character than the untreated area around it [Sugarman, 1986].

- d. Albumen (eggwhite) has been used as a coating for Islamic manuscript papers.
- e. Alginates.

These water soluble carbohydrates are derived from alginic acid, a polymer of anhydro-beta-D-mannuronic acid, which is extracted from seaweed. Producing clear and strong but brittle films, they are currently used for surface sizing, either alone or with vegetable gums, starches, etc.

- f. Gum tragacanth or a rice preparation was sometimes used to size early Arabic papers.
- g. Acrylic resins.

Paper squeezes of ancient inscriptions, inkless intaglios made by pressing moistened filter paper into the stone, may be waterleaf but, at least since 1940, may have been sized with acrylic polymers. [Caley and Merit, 1940] Examples of materials treated this way in the 1960's have been seen to retain a firm hand and resistance to wetting and show no obvious signs of discoloration.

h. Natural waxes and oils have been used historically for waxed and oiled papers. Today petroleum products (paraffin wax and oil, microcrystalline wax and oil) have replaced them.

B. Original sizing technique.

1. Internal sizing (engine sizing, beater sizing).

Internal sizing is the addition of substances to the pulp stock which have the potential to develop hydrophobicity (low surface energy) and thereby increase the paper's resistance to penetration by aqueous liquids. Alum rosin, wax rosins and more recently alkyl ketene dimers have been used for internal sizing. The decrease of "wettability" in a sheet is known as "sizing effect," "degree of sizing" or, "sizing." The result should be a sheet that resists wetting, ink feathering and excessive absorbence. Although many theories about internal sizing have been propounded, the contact angle theory has gained favor. This theory suggests that a material with a high specific surface free energy, such as cellulose fiber, will be wet by a liquid if the contact angle is less than 90°. Sizing deposits functionally hydrophobic (low surface free energy) materials on the surface, effectively changing the surface free energy surface of the fiber, and thus increasing the contact angle, surface tension and viscosity of the liquid itself. [It is suggested that sizing imparts a contact angle between approximately 36-90°. (TJV)] In other words, sizing alters not only the fiber, but the entire surface-liquid system.

Internal sizing does not provide resistance to penetration by water vapor and does not create true water repellency; liquids will penetrate over time. Moreover sizing offers little increase in wet strength, but since it prevents the sorption of water, it may give the appearance of enhancing wet strength.

In principle, the ideal internal size would be one that would develop and maintain a strongly hydrophobic character; be well retained by the fibers; be distributed evenly in a monomolecular layer over the entire surface; and be strongly anchored to the substrate. In practice all of these factors are difficult to achieve, a fact that may account in part for the continuing popularity of alumrosin systems which provide reasonable success with moderate effort.

Since the anchoring of alum-rosin size depends upon the bonding interactions between the aluminum in the size and the hydroxyl groups on the cellulose, many of the charged sites on the cellulose may no longer be available for interaction with the resizing agent. This is also pertinent if using a resizing agent which must bond with the cellulose such as an alkyl ketene dimer. While papermakers aim for an evenly distributed, semi-continuous film, in practice, internally sized papers do not have the fibers totally enclosed in the sizing agent. Rather, small areas hold the hydrophobic materials in clusters of particles, which are distributed over the surface and which selectively prevent, or slow the adsorption/absorption of liquid. Thus, sufficient active surface sites are probably available for interaction with the liquid.

2. Surface sizing is done after the sheet has been made, by coating the waterleaf sheet, usually with gelatin or starch. A more or less continuous film is formed on the paper surface.

Surface sizing alters the character of the fiber surface and the way it interacts with what is put on the surface (i.e., liquids). Surface sizing affects the printing process by altering paper absorbency, flatness, density, fiber, consolidation. (RE)

a. Tub or vat sizing.

The principal sizing method used throughout the papermaking history, this surface size technique has become rare today except in a few mills where high grade rag papers are produced. The formed, dried waterleaf sheet is dipped into a vat containing the size and then redried.

b. Size Press.

This has become the primary method of surface sizing in the modern paper mill. The size is applied to both sides of the paper web as it passes through rollers that press the size into the sheet and remove excess size. The paper does not remain in contact with the size puddle very long, it does not pick up a large quantity of size.

c. Spray.

This technique is used primarily when one-sided sizing is desired, i.e. for specialty papers.

d. Smoothing Press.

The size is added at a point in the machine papermaking process when sheet formation and consolidation of the paper web is still incomplete. The result is complete penetration of the size through the sheet.

e. Gate Roll Size Press.

The sheet never passes through a size bath, but rather the size is formed into an independent film on rollers and then transferred to the surface of the sheet. The size film sits almost completely on the surface of the paper; there is no penetration. This technique allows one sided sizing or the use of a different size on each side of the sheet.

f. Calender sizing.

Only used for thicker papers; the paper is passed between hardenedsurface rolls with an application of an emulsified wax size or solution of a starch, alginate, or other film-forming adhesive. The paper may be sized on one or both sides.

g. **Blade coating** utilizes a blade set at an adjustable angle against the paper web supported by a soft backing roll.

C. Condition of original sizing.

In most cases, the original sizing, whether internal or surface, was intended to provide a specific effect such as improving printability, smoothness, and/or strength. If the sizing has already served its purpose, the mere loss or degradation

of the original sizing may not justify resizing. The needs of each sheet must be assessed.

Uneven sizing may require local resizing.

1. Microbiological attack.

Especially in the cases of starch and gelatin sizing, fungal or other microbiological attack can result in actual loss of sizing material. Even in cases where the microbiological agent does not directly consume the size, loss of effective sizing can result from damage to the underlying fibers, fillers, etc. Local resizing may be indicated. (See 17.2.7)

2. Insect attack (i.e., by silverfish or roaches) may have left uneven sizing in sheet.

3. Discoloration and embrittlement.

Rosin sizing is damaged by high alkalinity and exposure to light. Discoloration and embrittlement are noted over time in papers which have been sized with alum-rosin.

4. **Distinctive localized, irregular hardening** or stiffening in a paper sheet may be observed, especially where there is evidence of water damage. This may be a result of degradation of the original size. Sometimes local resizing can be used to reduce the stiffness.

Although the mechanisms involved are not well understood, this localized effect probably is due to an accumulation and reformation of the size where there has been an exposure to water. (CB)

5. Effect of conservation treatments on original sizing.

While resizing may be required before any conservation treatment takes place, resizing generally follows other treatment.

a. Washing.

Especially at elevated temperatures or with significant pH adjustments, washing will remove a certain amount of water soluble size.Considered choice of temperature and pH in washing can influence degree to which original size is lost.

Change in absorption of a drop of water by the sheet before and after washing will give an indication of the effect of washing. (BMJ)

b. Enzyme treatments.

Using an enzyme for removal of a starch and/or protein adhesive will also cause removal of a size of the same material. Selection of the enzyme should be as specific to the problem as possible to avoid unnecessary size removal.

c. Alkalization may destroy rosin sizing, and may remove protein sizing. If strongly alkaline, alkalization will affect gelatin. (CB)

d. Bleaching.

Chlorine dioxide bleach will cause discoloration of proteins, (i.e. gelatin).

D. Identification of original sizing.

1. Determination by observation.

Often determinations are based on visual, historical, experiential or even intuitive factors. The most common "tests" are listening to the rattle of the sheet, a method that dates at least from the end of the seventeenth century, and observing the rate and manner of wetting.

- a. Rosin. If ink has been applied to a creased rosin sized paper, the ink will have feathered.
- b. Protein. If ink has been applied to a creased gelatin sized paper, the ink will not have feathered.
- c. Synthetic sizes. If the sheet is neutral or slightly alkaline and is somewhat resistant to wetting, this may be an indication of cellulose reactive sizing.

2. Microchemical tests. (See 10. Spot Tests.)

Working with a microscope, fibers may be teased from the sheet and tested with microchemical tests. In cases where the size has been subjected to some form of extraction (washing, solvent treatment, enzyme treatment, etc.) the extract may provide an adequate sample for further testing with spot tests or analytical equipment.

- a. Rosin: Liebermann-Storch test; Raspail test; Halphen-Hicks test.
- b. Protein: Biuret Test; Ninhydrin Test; Amido Black.
- c. Starch: lodine in potassium iodide. Test results will vary according to type of starch present.

3. Non-destructive analytical techniques.

- a. Chromato scanner for ultraviolet light detection of protein-based coatings and binders in machine-made papers. (TB)
- b. Fourier Transform Infrared (FTIR) microscope: infrared spectroscopy on object itself [Van Zelst *et.al.*] (TJV)

17.2.5. Media condition and characteristics.

Solubility characteristics of media or paper additives will influence choice of aqueous or non-aqueous sizing material. Presence of highly soluble media may preclude resizing. Resizing may be chosen as the method to consolidate media which is friable, particularly in cases of broad areas of printing ink. (See 23. Consolidation Facing Fixing.)

17.2.6. Interaction with other conservation treatments.

Resizing is most often the last aqueous treatment. The sequence of conservation steps will be affected by the interaction of treatments.

A. Alkalization.

When following gelatin resizing alkalization may remove some of the gelatin. Resizing may interfere with penetration of alkalinization agent.

B. Fixing and consolidation.

Surface sizing may enhance or hinder efforts at fixing and consolidation of media, or may affect fixing as a side-effect. Resizing may also serve to fix undesirable elements, such as residual grime.

- C. Dry cleaning after resizing will be more difficult than beforehand.
- D. Alcohol may cause precipitate aluminum hydroxide in association with gelatin size. (CB)

17.2.7. Future storage environment for artifact.

In high relative humidity environments, it is desirable to resize with a material which will not support mold growth easily. (See 17.2.4.C1 Microbiological attack; 17.3.1A Aqueous resizing agents.) The presence of insects such as silverfish and roaches suggests not using starch or protein materials which will be food source for insects. For items not otherwise protected from dust and pollutants, (i.e. lining or encapsulation) resizing may help resist penetration of these harmful materials into the sheet.

The mold-resistance of resizing materials is always a concern, especially for objects which already have been mold-damaged. Gallo tested the mold resistance of a variety of papers treated with several resizing agents including hydroxyethyl methyl cellulose (Glutofix 600), gelatin, and polyvinyl alcohol. The results indicate that hydroxyethyl methyl cellulose and to a lesser extent poly(vinyl alcohol) impart a degree of resistance to microbial growth in paper, but they will support mold growth if the growing conditions are appropriate. [Gallo, F. "Ricerche sperimentali sulla resistenza agli agenti biologici di materiali impiegati nel restauro de libri: VI Saggi su coll-anti puri o addizionati di fungicidi" *Bol. Istit. Pat. Libro* 28: Nr 1/2 (1969), 9-47] Other research, by T. Barrett, indicates a tendency for gelatin and gelatin/alum size to minimize mold growth. [Barrett, T., "Early European Papers/ Contemporary Conservation Papers." *A Report on Research Undertaken Fall 1984 through Fall 1987*; pre-publication report.] Beljakova found that sodium carboxymethyl cellulose increased the mold-resistance of paper. [Beljakova, L. A. and O. V. Kozulina, "Book Preservation in USSR Libraries." *UNESCO Bulletin for Libraries* 15, No. 4 (1961), 198-202.]

17.3. Materials and Equipment.

17.3.1. Resizing agents. (See 46. Adhesives.)

A. Aqueous resizing agents.

1. Cellulose ethers.

It is important to note that the purity of materials, especially methyl cellulose and sodium carboxymethyl cellulose, greatly influence their properties. The most pure substances are preferred. (CB)

a. Methyl cellulose.

This sizing material is relatively resistant to fungal attack, which may be a factor in deciding to use it under housing conditions of high relative humidity. One study, however, finds no mold resistance with methyl cellulose. Since methyl cellulose is hygroscopic, mold growth may be possible. [Florian, Mary-Lou, and David Dudley, "The Inherent Fungicidal Features of Some Conservation Processes." *AIC Preprints-Dearborn*, 1976.]

The lower molecular weight solutions will penetrate paper more easily (evaluated in terms of centipoise -cps). Low to mid-range cps methyl celluloses ranging 400 (4C) -1500 (15C) are generally used as a size while 4000 (4M) cps methyl cellulose is more frequently used for adhesive purposes. (CB) Lower molecular weight cellulose ethers are more brittle and less permanent than those of higher molecular weight. The letter "A" indicates the appropriate grade for use in conservation (i.e. Methocel A1500.) The most pure materials are recommended.

Although methyl cellulose has been used in very dilute solutions (as low as 0.02%), it is more commonly used in the range 0.25-0.75%). The choice of concencentration will be related in part to the molecular weight of the cellulose ether. During resizing, the material makes the surface of the sheet extremely slippery and manipulation can be difficult.

<u>Preparation</u>: Follow manufacturers' recommendations for various types of methyl cellulose.

- 1. Surface-treated: mix with cold water for immediate water solubility.
- 2. Non-surface treated: stir the powder into approximately one third of the water that has been heated to 80°C-90°C and continue stirring until the powder has been thoroughly wetted. Stir in the remaining water, which has been chilled, or iced, and allow to cool quickly to 0°C-5°C. Temperature should be held for 20-40 minutes. Rapid cooling will promote a clear solution. To avoid excess foam, do not whip solution.

b. Sodium carboxymethyl cellulose.

Cellofas B (Hercules, Inc; Imperial Chemical Industries) is a technical grade material often used by conservators but "probably should not be used if permanence is required" as it is impure, according to Baker and Barrett [Baker, 1985].

Sodium carboxymethyl cellulose is generally effective even in very dilute solutions (0.02-0.05%) and can be used in concentrations up to 1% or so. During resizing, the material makes the surface of the sheet extremely slippery, and manipulation can be difficult.

- c. Hydroxypropyl cellulose (Klucel) Generally used in solution with organic solvents, it is occasionally used in water. Desirability particularly is due to solvent solubility.
- e. Methyl hydroxyethyl cellulose (Tylose MH 300) is used in a 0.25-0.5% solution.
- 2. Proteins.
 - a. Gelatin.

Background The raw material is insoluble in water, so it is first put in an acid or alkaline "cure" to become soluble in water and to remove the noncollagen impurities. For the "cure", the raw material is first washed, then soaked in either saturated lime water or cold dilute mineral acid. The "cured" protein is then washed and neutralized. The iso-electric point of a given gelatin is 4.8-5.1 or 7.8-9.0 depending on whether it is derived from acid or alkaline cured material. The iso-electric point is that in which there is no net charge in the gelatin molecule. The extraction process is the conversion of collagen to gelatin by hydrolysis in heated water. A series of extractions may be made - each being somewhat hotter than the preceding one. The extractions give higher and higher molecular weight gelatin, [but they also contain more non-collagen proteins (TJV)]. The highest quality gelatin is from the first extraction at the lowest temperature. Gelatins are made from blending the different extractions to obtain the desired qualities. (JM)

Gelatin is evaluated on the basis of two colloidal properties: viscosity of solution and stiffness of gel (Bloom strength). Gelatin is insoluble in cold water, but will absorb moisture with swelling. The swollen gel will go into solution when warmed to about 120°F (49°C), forming a gel again when cooled. The swollen gel will dissolve in hot water, hot aqueous glycerin, hot acids, alkalis and salts. It is insoluble in most organic solvents except materials such as water-soluble phenols and carboxylic acids. Concentrated mineral acids or alkalis dissolve gelatin with considerable hydrolysis taking place. (JM)

Advantages Commercially prepared food or photographic grade gelatins tend to be used in conservation. [These contain large amounts of calcium, whereas in the purest grade (pharmaceutical) all metals have been removed. (TB)] It should be possible to select among gelatins of varying properties (flexibility, color, gel, strength, film strength etc.) to fit the unique needs of individual artifacts, although it is not known if this is done in conservation. Acidic solutions are associated with gelatin of increased viscosity, whereas more alkaline solutions are less viscous. Because gelatin generally has not, been associated with significant damage to the paper substrate upon natural aging, gelatin is popular among conservators. It may be favored by conservators who prefer an historically validated material to a modern synthetic.

<u>Disadvantages</u>. Gelatin has been thought to be vulnerable to fungal attack which would contraindicate its use under housing conditions of high relative humidity. A recent study however suggests a tendency for gelatin and gelatin/alum to minimize microbiological growth. (See 17.2.7 Future storage environment.) In any case many conservators feel comfortable using the material on mold damaged papers.

In general gelatin tends to become brittle, especially if it has been heated for a long time. As a thin film well distributed over the fiber surface, it is unlikely that this brittleness poses any serious problems; the resulting system can be expected to be at least as flexible, and usually significantly more so, than the sheet alone. (The brittleness of gelatin can be reduced with a plasticizer, such as sorbitol or glycerine. However, the humectant qualities of glycerine make it inappropriate for use in treatment.)

It has been noted that aged gelatin tends to discolor to a light gold or brown tone. This effect may result from the use of impure materials or excessive heating and reheating of the size during preparation. Gelatin sometimes becomes rather insoluble with age. Whether this is the result of impurities, additives, etc., of intentional crosslinking (hardening), or unintentional crosslinking associated with degradation is unclear.

Preparation. It has been suggested that excessive cooking, resulting in thermal degradation, may be blamed for poor behavior of some historic animal glue products. The problems are no doubt exacerbated by the historic practice of repeatedly cooling and reheating the glue or size and leaving the material in heated solution for extended periods. In any case, excessive heating will result in hydrolysis and loss of viscosity and gel strength. To avoid degradation of the gelatin, the gelatin should be allowed to swell in pure, cold water for thirty minutes or until fully swollen. (Some forms may require as much as two hours). Then it is cooked in a double boiler at the lowest possible temperature (industrial practice suggests 45°C-60°C) and for the shortest possible time necessary to allow the material to "dissolve" (actually, to form a uniform colloidal dispersion). The size should be used as soon as solution is achieved (subject to temperature considerations) and should not be reused. A final solution temperature of 32°C-54°C is usually effective. Working concentrations of as low as 0.02% have been reported, but concentrations of 0.5-1.0% are more commonly encountered. Some conservators prefer to prepare a stock gel of 10-15% from which working solutions can be prepared.

In the papermaking industry, research indicates that the temperature at which gelatin size is prepared has a significant effect on the nature the resulting films. If the size solution is prepared at a very high temperature (60°C-96°C) and applied to the paper while hot, the molecular chains of the gelatin will be in a disordered and contracted state, as they are in the solution. The film formed will be of low strength. On the other hand, forming the film from a solution at lower temperature by slow drying creates a situation in which dehydration is preceded by gelling, which tends to extend the molecules and orient them in the plane of the film. Such a film is stronger than the hot-formed film, although a continuous film is generally not formed. These effects may be of some indirect application in resizing, as the nature of the film formation may be subject to rather subtle control. [Ward, A. G. and Courts, A., *The Science and Technology of Gelatin* (London: Academic Press, 1977) 445-447.]

Weaker sizing films may actually be better; upon contraction they may cause less damage to the surface of the fiber. (TJV)

b. Parchment/Vellum size.

Since this material is simply a special form of gelatin, the factors that pertain to gelatin generally will apply here also.

Advantages. The vellum size can be produced in the conservation lab and thereby be subject to close quality controls. The pH of the size is slightly alkaline. The material is considered to be similar both in chemical composition and method of manufacture to the original sizing agents in many historical papers, without the possible contamination by additives, degradation products and other impurities found in early glue sizes. It is, however, difficult to ascertain if the modern parchment or vellum scraps have contaminants such as formaldehyde, now used by some parchmentmakers. The handling characteristics of the sized paper sheet are thought to be different from those of sheets sized with other materials. Some book conservators find the rather soft, fluid drape of vellum sized sheets appropriate to the flow of the textblock.

<u>Disadvantages</u>. With high concentration solutions or with prolonged immersion, the sheet can develop a slightly rubbery or an excessively rattly feeling that indicates a sheet too stiff for proper textblock opening. Because the size is made up from a stock solution of inexact concentration, it is difficult to quantify accurately the final solution concentration. The stock is prone to spoilage.

<u>Preparation</u>. To prepare a stock solution, scraps of parchment or vellum, which can be purchased in quantity from binders' supply houses, are cut into small pieces (approximately 5-10 mm square). The pieces are soaked in cold water (21 grams of scrap to 2.5 liters of water is a workable quantity) and cooked in a double boiler at low heat for about 45 minutes. It may be wise not to let the mixture boil since impurities may be drawn from the skin. When the solution is cooled overnight, the resulting stock will be a thick gel, the quantity and stiffness of which will depend on cooking time and parchment:water ratio. Traditional recipes call for the addition of a vinegar

as a preservative, but the gel alone will keep at least for several days in the refrigerator and can be frozen for longer-term storage. For use, enough stock is stirred into warm water (35°C-50°C) to create a solution that is slightly tacky. (Dip thumb and forefinger into solution, press together and let cool; the film should offer minimal resistance to separating fingers).

Another similar procedure, (as handed down by English conservators through the Library of Congress) is to soak 100 grams of parchment chips (finely chopped, 5 mm x 5 mm) in one liter pure water overnight, and then to cook in a double boiler over low to moderate heat for three to six hours. The solution is then strained through cheesecloth and cooled. This produces a stock gel which can be stored in a refrigerator or a freezer until use. For use, approximately one part stock gel (by volume) is dissolved in 15 parts pure water and warmed to approximately 40°C. This produces a solution of fairly low concentration, in range of 0.25%-1% by weight (RE) (See 23. Consolidation/Fixing/Facing for another recipe.)

In the commercial preparation of gelatin, the first extractions and the purest quality gelatin come from the lowest cooking temperatures, and successive extractions from gradually elevated cooking temperatures yield lower quality stock. This can also be done in a lab situation, cooking for two to three hours for each extraction, and increasing the temperature five to ten degrees Centigrade for each extraction, beginning at 55-60°C and continuing to about 90°C. This process can also be combined with an alkaline pre-soak of several days, to improve yields of high grade gelatin at lower extraction temperatures, which is also an industrial practice. (RE)

- c. Rabbit Skin Glue.
- Fish Glue (Russian Isinglas, derived from Sturgeon).
 This has been regarded as the clearest, most desirable gelatin material since the early days of western papermaking.

3. Starches and other vegetable materials.

Rice or wheat starch paste, diluted with water to a thin consistency and applied with a brush to roughened or fractured surfaces can restore a smooth and slightly shiny surface to paper which has been overly handled. This may be useful for paper laminate works such as Near Eastern calligraphy sheets. A starch solution can be lightly applied, blotted and burnished gently with a bone folder, then lightly weighted starch can also be used to set down lifting layers, edges and small edge tears. Starch applied too thickly or dryly can stiffen the paper too much, causing cockling or giving a gray appearance to lightly colored papers. For use in conservation, the most common sources are wheat and rice. (SA)

4. Other sizing/resizing materials.

a. Poly(vinyl alcohol) (PVOH).

Films have high tensile strength, are very transparent and oil resistant. In addition they impart air resistance and at least some water-resistance. PVOH may be combined with starches to improve film formation. The paper industry uses 20% by weight. Poly(vinyl alcohol) has been found to be relatively resistant to fungal attack which may indicate their use under housing conditions of high relative humidity. (See 17.2.4.C1.) Solubility of poly(vinyl alcohol) is thought to become irreversible over time [Horie, 1987].

It is not clear if the insolubiility is associated with degradation of cellulose and/or yellowing. (DH)

b. Cellulose-reactive sizes.

(Aquapel, Hercon 40) The paper industry uses concentrations of 0.1-2.0%, applied at 60°C as internal size. These sizes require a curing period. Belenkaja *et. al.* found that sizing sulfite paper with Aquapel did not bring about change in the firmness of the sheet. [Belenkaja, 1965]

c. Polyamide-epichlorihydrin (Kymene 557).

A retention aid manufactured by Hercules, Inc. (similar to Reten 763) normally associated with Aquapel and with the production of wet-strength papers,Kymene 557 has been used in small quantities as an additive to cellulose ethers for resizing. One conservator recommended adding 6 drops of Kymene (which is provided by the manufacturers in a 10% solution) per liter of .02% sodium carboxymethyl cellulose. Raff, Ziegler and Adams experimented with a more drastic resizing scheme (which they characterized as "impregnation") in which Kymene 557 was added to sodium carboxymethyl cellulose for resizing. In addition to improving the wet strength, a feature that increased upon artificial aging, it is claimed that the cellulose ether-kymene combination improved folding endurance and reduced blocking (pages sticking together.) However the technique required heated drying and thus may be of extremely limited utility [Raff, Ziegler and Adams, 1967].

d. Funori.

An extract of *Gloiopeltis furcata* seaweed which does not gel on cooling. Susceptible to mold growth. (See 23. Consolidation/Fixing/Facing)

e. Texicryl.

Acrylic/methacrylic copolymer emulsion, used in a 20% solution in calcium bicarbonate.

f. Soluble nylon.

Calaton CB or CA. Its use has been discouraged [Horie, 1987]

- B. Non-aqueous resizing agents can be used in situations where simple water solutions are inappropriate.
 - 1. Hydroxyethyl cellulose (Klucel). (See 17.3.1.A1c.)
 - 2. Ethyl hydroxyethyl cellulose (Ethulose).

Generally diluted with organic solvents, but also effective in water.

Advantages. Can be used in situations where simple water solutions are inappropriate. Although it is usually diluted with no more than equal volume of ethanol, the manufacturer states that "a water solution of Ethulose may be diluted many times with alcohol without precipitation of the gum." Ethulose will penetrate the sheet very quickly and will dry very quickly. The resulting film may have a very slightly rubbery feel to it, but not overly so.

<u>Disadvantages</u>. May be made insoluble under "relatively mild conditions" by various crosslinking agents.

<u>Preparation</u>. Stir 1% (weight/volume) Ethulose in very cold water at a regular rate. (Cold water will improve solution clarity.) Adding the powder either too slowly or too quickly may result in lumps. If a blender is used, use slow speed to avoid foaming. Let stand for 30 minutes and mix again. Dilute with equal volume of ethanol or other organic solvent for 0.5% (w/v) solution and mix in blender. Some indications from initial research (Feller) suggest that solvent-soluble cellulose ethers are not as stable as wholly water-soluble cellulose ethers (CB).

17.3.2 Equipment

A. Trays.

Generally a tray only slightly larger than the object is desirable as the weight of the sizing material can make manipulation difficult. The tray need not be deep as the size solution will generally need only cover the object or gather it up. It is useful to have one or two very shallow trays, such as cafeteria trays, for use in pressing; the tray catches the size runoff.

B. Brushes.

Large Japanese water brushes for overall sizing. Stiff fan blending brushes for local sizing.

C. Press and pressing boards.

Thick Plexiglas sheets function well, but ordinary wooden pressing boards can be lined with polyester film. The boards will get wet during use, so to prevent warping it is wise to rotate them and allow them to dry.

D. Heating equipment.

- E. Spray equipment. (See 22. Humidification.)
- F. Support materials include blotters, polyester film, polyester web, (i.e., Hollytex).
- G. Solvents.

17.4 Treatment variations.

17.4.1 General considerations for resizing.

When paper is wet with a sizing material, it often has less strength than it would when wet with water alone. As such it is especially prone to tearing, deformation and disruption.

A. Size deposition.

In principle, size tends to behave in two ways: film-formation and penetration; in practice both processes occur simultaneously. Although an overgeneralization, the first form, in which the sizing material tends toward the formation of a more or less continuous film on the surface of the sheet, is associated with increased protection from attack by external agents (gases, liquids, oils) and protection from abrasion, while the second results in increased interfiber bonding and concomitant increases in strength (burst, tensile, folding).

- 1. Factors that influence the depth of penetration.
 - a. Viscosity.

"Penetration varies inversely as the square root of the viscosity of the solution." (Cushing, 1981). Anything that will decrease the viscosity of the size solution, such as increases in temperature, decreases in concentration or selection of lower viscosity grades (cps), will favor penetration and minimize film formation (and vice versa).

- b. Surface tension of the polymer/solvent system (i.e., size liquid) is a factor in the relative wettability of the paper-polymer/solvent system. The lower the surface tension, the better the wetting
- c. Length of exposure to sizing agent.
- d. Solids content/concentration will influence viscosity primarily, but also has an independent effect on penetration.
- e. Temperature primarily will influence viscosity, but also has an independent effect on penetration.

2. Measurement of the depth of penetration.

The depth of penetration of the resizing agent sometimes may be determined by examining sample papers treated with the proposed technique. The test paper is successively delaminated using pressure sensitive tape and the tape spot tested for the sizing agent. If the experience of commercial surface sizing can be applied to resizing, it is useful to note that heavier sheets may be expected to pickup less size than lighter sheets and high density papers. This suggests that longer immersions, higher solution concentrations and/or lower molecular weight materials may be indicated for such papers. The moisture content of the sheet also affects the quality of surface sizing. In the papermaking industry, it has been found that sizing at the optimal moisture content 5-12%, a condition which represents a sheet that is fully dry to the touch, results in maximum deposition of size; sheets wetter or drier will pick up less size. Slow drying, as obtained by air drying, leads to the formation of good films and greatest strength, though slow drying allows cockling to develop. Whether these observation may be extended to the context of resizing is uncertain.

3. Barrier effect.

It has been suggested by some conservators that size may physically block access to the fibers and may protect somewhat against attack by oxygen and other, principally gaseous, substances. There is some support for this notion in the surface sizing literature, but the hypothesis has yet to be verified in a treatment context.

17.4.2 Local sizing and resizing.

A. Original support.

1. Brush.

Size can be feathered (using stiff fan blenders), to create a gradual transition from unsized to sized areas. There is some concern that the irregularity of deposition caused by brush application will age differently over time.

2. Squeegee.

When applying size with a squeegee, conservators protect the surface of the paper with polyester web or Japanese tissue.

B. Pulp fills. (See 26. Filling of Losses.)

1. Internal sizing.

The addition of a very small quantity of adhesive (typically a cellulose ether) to pulp serves to prevent floculation of fibers or to aid in keeping the fibers in suspension in the pulp. Although the practice of incorporating an adhesive material into pulp used for fills or leafcasting bears a superficial resemblance to internal sizing, the processes are fundamentally different. Nevertheless, the literature of internal sizing may provide a valuable resource for individuals concerned with pulp fills.

Probably the most common reason for incorporating adhesives in the pulp is to provide adequate fiber-to-fiber bonding in compensation for inadequate

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beating, especially in the case of recycled pulp prepared in a blender. If the concentration of adhesive is too high, the adhesive may actually interfere with sheet formation and result in a paper web that is integrated by adhesive bonds. Such webs may lose their integrity when wet.

2. Surface sizing.

Pulp fills and insert papers may be brushed or sprayed with any of the resizing agents in order to prepare the filled area for toning or inpainting or to impart to the filled area handling characteristics similar to those in the remainder of the sheet.

17.4.3 Overall resizing techniques.

A. Brush.

- 1. Makes possible resizing of oversized objects.
- 2. Brushing is appropriate when only one side of the sheet needs to be resized. It can also be used when the media, existing surface coatings, other conservation procedures (fixing, etc.) make immersion unwise. If only one side is to be treated, it is often desirable to maximize penetration (by using material of low viscosity, higher temperature and increased "soak" time), so that the sheet is sized all the way through, with the sizing material stopping just below the upper surface of the sheet. If a thick film is allowed to sit on the surface of the reverse of the sheet, it will have something of the character of a lining. One sided resizing is likely to carry with it the problems associated with differential hygroexpansivity (i.e., curl).
- 3. Brushing tends to result in a less even deposition of size than immersion. This effect will be more pronounced with a thicker size. If brushing is repeated, the size may sit on top of previous size layers, increasing the gloss and stiffness, a feature that can be exploited for desirable ends.
- 4. Fairly soft brushes and a delicate touch are essential due to weakness of sheet while wet with size. Size can be brushed on through tissue paper, polyester web, silk screen, etc. This will help protect the object from the action of the brush, and may facilitate even deposition, while helping to avoid depositing excess material. Removing the interleaving support can place the object under serious strain, thus the nature and condition of the media must be considered. Polyester web and similar materials can be left in place through the drying process.

B. Immersion.

1. Risks.

When saturated with size, especially with the cellulose ethers, the paper will have less wet strength than when simply wet with water. The sheet will be heavy and swollen; in this state the paper is vulnerable to damage and must be well supported. With some sizes, such as the cellulose ethers, the wet sheet may be very slippery and manipulation can be difficult.

2. Variations.

- a. Procedure (RE)
 - A tray slightly larger than the material to be sized should be used, with enough size in the tray to cover the material to be sized. If the size is gelatin, provision should be made to keep the size warm in use, about 40°C.
 - A support sheet, such as a polyester web material, should be placed in the tray first, to aid removal of material.
 - 3) Single items can be immersed with support sheets on top and bottom. Book gatherings are unfolded for immersion and each sheet immersed one at a time, forming a stack of leaves; about 75 to 100 leaves can be sized in a stack. Enough size must be in the tray to cover the stack.
 - Single items may be removed once they are saturated, and excess size blotted off.
 - 5) For multiple items, the whole stack is removed with support sheets top and bottom, the stack is drained, placed between blotters and pressing boards (laminate pressing-boards or other moisture resistant surface), and nipped in a press for about one minute.
 - For single items, the support material should be changed by flipping the item from wet material to dry material, and placed on drying racks for air drying.
 - 7) For a stack of book leaves, each leaf is "peeled" off the stack with care and transferred to drying racks which have been covered with a polyester support material. A spatula is useful for lifting the initial corner.
 - The sheet is left to air dry until it begins to curl, i.e. dry to the touch but with considerable humidity still present.
 - 9) The sheet is placed between blotters or felts and under light pressure, depending on the texture and surface characteristics, for final drying. In the case of book leaves, final alignment of the folded leaves into gatherings can be done as they are removed from the drying racks, and then the leaves pressed in groups of gatherings with blotters inserted every two to three gatherings. An alternative is to rehumidify the leaves after complete drying, and realign the leaves gathering for final pressing. The latter provides more working time and may be necessary for large groups of leaves. Great care must be exercised in order to avoid loss of surface characteristics in the final drying under pressure.

 Additional considerations: Normally about five minutes is sufficient for the size to penetrate the paper. However the nature of the object, previous treatment and intended sizing effect may warrant longer immersion. Exposures of 30-45 minutes have been reported.

It is essential that before a stack of leaves is placed in the press, all excess size is removed, (as by blotting). Failure to do so can lead to sheet rupture or uneven concentration of size.

C. Spraying.

Makes possible the resizing of oversized objects. Spraying tends to favor the deposition of a layer on the surface of the sheet rather than deep penetration of the size into the sheet. It may be useful in cases where the surface of the sheet or the design layer is especially delicate; where minimal wetting or size deposition is desired; in conjunction with humidification and flattening.

D. Suction table.

Size can be applied to the paper on the suction table either locally or overall with a brush or by spray. If a brush is used, the tendency toward irregular local deposition, which is a concern with any brush application, may be exaggerated because of the increased downward movement and accelerated drying associated with suction table treatments. The same concerns pertain as with spray application but to a lesser extent. Spraying tends to favor the deposition of a film on the surface of the sheet rather than deep penetration of the size into the sheet.

With either technique on the suction table, the nature of the movement of the sizing agent through the paper fiber web is likely to be different than it is with immersion. The nature of that difference has not yet been examined. One might hypothesize that because the sheet is usually dampened before it is placed on the suction table, and the fibers are at least partially swollen, the movement of the viscous size through the paper web is less free than it would be through a dry sheet. Conversely, if the suction is very strong and if the sheet is allowed to become sufficiently wet so that the size can remain fully solvated as it moves completely through the paper mesh, one might expect an increased solids concentration at the layer near the table surface. This situation corresponds to conditions observed on the papermaking machine where size deposition is found to be concentrated at the wire side.

Another hypothesis is that on the suction table the size will become distributed within the sheet due to the tendency of the suction to pull materials into the sheet and its pores. (TJV).

Moreover, because the film-forming materials will alter the draw of the suction table, the free movement of air and liquids will be restricted through the web after initial deposition of size. Therefore additional size may tend to form a film on the uppermost layers. As such, the size itself can interfere with the expansion and contraction of the sheet while on the table. In addition to altering the ultimate effect of the sizing with respect to gloss, flexibility etc., this factor demands special efforts to avoid planar distortion during treatment.

E. Floating.

One of the fundamental differences between original sizing and resizing is that in resizing the sizing agent sits on top of the design layer rather than beneath. When this situation is likely to bring about an undesirable change in the visual quality of the image, the sheet can be sized from the verso by floating it on a size bath. This technique can also be called into play when the nature of the media, existing surface coatings, other conservation procedures (fixing, etc.) obviate immersion. (See 16. Washing.) The procedure is identical to float washing in water but because the surface tension of the bath will be dramatically altered by the size, the behavior of the sheet may vary considerably.

Floating will also favor uneven local distribution because the fluid moves into the largest pores. The large pores are distributed throughout the sheet more or less evenly, but not close enought to each, to make distribution even, except in the most porous sheets. The size agent will be deposited primarily around the large pores and on the reverse. (TJV)

Overall deposition should probably be rated as less deep than with the suction table method because the driving force is not as great as on the suction table. Deposition will be deeper, however, than spray or brush method because the reservoir of size solution is larger water with dissolved sizing is larger. (TJV)

F. Other resizing techniques.

Size can be deposited using a brayer. This may serve to drive the size into the paper and form an even film on the surface. Protection of the surface is required.

17.4.4 Regeneration of original sizing.

Marjorie Cohn [Cohn, 1982] demonstrated that in some instances, when a sheet is repeatedly float washed and dried between the washings, the paper develops a resistance to wetting (sizing effect). This effect may be uneven and thus interfere with the proper washing of the sheet, resulting in tide lines and other undesirable sideeffects. The irregular wetting is influenced by incipient mold, creases, abrasion, tears, deckel edges and other elements that affect the morphological character of the sheet. Such deformed or disturbed areas will continue to wet out even when the sheet as a whole resists wetting.

Cohn speculates that development of sizing effect stems from the regeneration of existing sizing agents in those areas where the size has not been damaged or otherwise disrupted and suggests that the phenomenon may account for the improvement in luster and hand in washed papers. She points out that among papers she examined, those sheets that had never been sized failed to develop sizing effect.

Two factors are shown to interfere with the tendency of a sheet to develop resistance to wetting after repeated float washing: light aging and pre-floating on a bath of ethanol and water.

<u>Compiler's comment</u>. This study, which clearly has significant implications for treatment, has been proffered by several conservators as evidence in favor of a blanket rejection of resizing as a treatment modality. It is argued that if float washing (and perhaps, by extension, simple washing) is capable of regenerating the sizing," resizing must be at best unnecessary.

However, this argument is rather unconvincing. In the first place, decreasing the wettability of the sheet, while a principal function of the original sizing (especially internal sizing), is only rarely an issue in resizing. While resizing may indeed be unnecessary because some of the desired ends of resizing, such as the improvement of hand and certain mechanical properties will be effected by water washing alone, Cohn's study was not intended to examine this area. Indeed, Cohn's only claim on this subject is that her hypothesis "goes far to explain the subjective opinion held by practically all paper conservators...that washing old paper greatly restores its luster and 'hand' " Clearly, any information we can bring to bear on the issue of water/paper interactions will bring us closer to understanding the ways in which the mechanical behavior of the sheet can be improved and as such this study may serve effectively to condition our thinking in the area of washing and resizing.

Moreover, the argument ignores the study's finding that the development of sizing effect was not always regular and could result in irregular wetting or mottling.

Additional note (RE): Industrial references to the phenomena of self-sizing which have a direct bearing on this issue underscore need for better understanding of the whole process. See Aspler, J. S.; Davis, S; and Lyne, M. B. "The Dynamic Wettability of Paper, Parts 1 and 2." *Tappi Journal 67* (September 1984) 128-31; 67 (October 1984) 96-99.

17.4.5 Special effects.

Mylar. It is possible to create an especially smooth, hard-surfaced, and "sealed" effect in a sheet by resizing and allowing the sheet to dry on a sheet of polyester film. A dilute starch paste seems particularly effective in this regard, as it tends not to build up thick glossy film on the paper surface.

The sheet is sized overall, by immersion or by brush, if it is desirable to restrict the size to one side of the sheet. After blotting away any size standing on the surface of the sheet, the sheet is smoothed down gently onto the film, being careful to avoid air pockets, and allowed to dry in the air, without weight. Sometimes it is useful to weight the corners of the film to hold the sheet flat during drying.

Since the paste adheres the paper to the polyester film and restricts its motion during drying and since the surface of the sheet moves in contact with the smooth film, the

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technique has much in common with friction drying (See 28.4.28.4.17. Friction Drying). Assuming that the sheet is left exposed on one side (and not under weight), as it dries it will lift from the surface of the film partially (and irregularly) relieving the drying stresses. Normally the sheet will need further flattening. If only one side of the sheet is sized in this manner, flattening may be complicated.

This technique can subject the support and perhaps the image layer to vigorous stress. Type impressions, plate marks, and the like can be destroyed by the severe surface flattening. The technique is suitable only for the most robust papers and images. Nevertheless, despite the apparent severity of the technique, the end result can be quite subtle, if it is sensitively performed.

17.5. Bibliography.

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17.6 Special Considerations.

17.6.1 Essay by Walter Henry.

In 1982, Garlick and Henry conducted a survey of practicing book and paper conservators to determine whether there was an established set of theoretical assumptions and rationales underlying the practice of resizing or whether, on the other hand, resizing was a more casual marginal practice. Making no attempt to ascertain the value or lack thereof of any of the practices under consideration, the study examined five principal areas 1) how frequently conservators resize objects after aqueous treatment; 2) why conservators resize; 3) what criteria are brought to bear on the decision to resize; 4) what sizing agents are employed both for resizing was "a mature praxis," the authors reasoned, it ought to be possible by statistical means to discern clear sets of associations between the stated aim of resizing, the criteria for the treatment decision and the materials and procedures employed. Moreover, it was hypothesized that book conservators and paper conservators might approach resizing differently, and that one group or the other might tend to resize more frequently.

<u>Conclusions</u>. Resizing was found to be a procedure seldom performed, with half the respondents reporting they were resizing 5% or fewer of the objects they treated aqueously and three quarters of the group resizing 20% or less.

For all practical purposes no meaningful distinctions between book conservators and paper conservators could be discerned. However, the group of conservators that worked on both books and paper resized somewhat more frequently than either of the other groups. Although approximately 40 statistically significant associations between variables were discovered, such as the tendency of paper conservators to cite improvement of hand as a function of resizing, all of these were very weak associations, so weak as to be essentially trivial.

The stated functions for which sizing is carried out were, in the order of popularity, strength improvement, general protection, hand improvement, and texture or appearance improvement.

When deciding whether or not to resize, conservators were likely to consider, again in order of popularity, the hand of the sheet, its condition, or miscellaneous other criteria. In addition, the use to which the item is to be put, the presence of mold and the appearance of the sheet were also common criteria.

For both resizing and sizing of fills, the cellulose ethers were by far the most popular sizing agents, followed by proteins, starches and other materials. Within the cellulose ethers methyl cellulose, sodium carboxymethyl cellulose, hydroxypropyl cellulose, and methyl hydroxy ethyl cellulose were the most popular choice. Poly(vinyl alcohol) and Aguapel were the most popular among the "Other materials" category.

The most common techniques were, in order, brushing, immersion, spray and other techniques.

In general the study found an overall amorphous character in the survey responses. It found that "resizing artifacts following aqueous treatment is an infrequently performed procedure about whose value or function there is little consensus." Beyond a clear preference for the cellulose ethers and an agreement upon hand as an important diagnostic variable, the study did not find "the well developed network of correlations that would indicate that the practice is, to any significant degree, systematic."

17.6.2 Essay by Robert Espinosa.

The subject of the sizing of paper for conservation purposes is laden with questions and there are many holes in the technical and historical information we do have. The washing and sizing of papers by conservators must date early in the history of the treatment of paper artifacts by restorers, and certainly has been practiced for several centuries. See job tickets of the eighteenth century English bookbinder Roger Payne. [Cyril Davenport, Roger Payne: English Bookbinder of the Eighteenth Century (Chicago: The Caxton Club, 1929), 69-71] The practice seems to have evolved quite naturally from the processes used by hand papermakers, and perhaps has been historically more common in book restoration than in other related paper treatment areas. It has been largely an empirical practice handed on from one practitioner to another, and therefore one should not be surprised at the lack of a theoretical framework. Perhaps this is why the practice is not particularly standardized. The fact that the practice of resizing has persisted indicates at least a perceived benefit to paper which has been wet processed, especially in restoring the handle and feel of the paper, in improving its resistance to handling, and in giving back a certain crispness (the rattle) lost in washing.

Developing a theoretical framework today is an intriguing and engrossing task, one that leads the investigator to a diverse and uneven body of historical and technical literature. Naturally most of the literature is centered around the sizing of paper as an integral part of the manufacturing process.

In sizing, one is usually concerned with the reaction of paper to what will be placed upon it, and attempts to alter or affect in some manner the interaction between the media and the paper. As has been pointed out in an important article on the nature of paper by Dwan (Antoinette Dwan, "Paper Complexity and the Interpretation of Conservation Research,": *Journal of the American Institute for Conservation*, Vol. 26, No. 1 (Spring, 1987) pp. 1-17.) paper may be characterized as a composite material with many simultaneously active variables, among which is the sizing material, when present. Historically the application of a sizing material was a finishing operation, designed to prepare the surface for printing or writing. How and why the various sizing agents produce their desired effect is the subject of many articles in the technical literature, which discuss the complex interaction of the fiber network, sizing, and media - as well as the dynamic wettability of paper. An understanding of the effect of sizing naturally begins with study of the practice in papermaking, and this outline reveals this bias. The purposes of sizing stated in this outline combine the purposes intended by the papermaker - control of absorptive capacity; modification of surface, texture, character, and appearance; improvement of soil, grease, and stain resistance; alteration of reflectance properties - with the purposes desired by the conservator - improvement in the hand or "feel" of the sheet; imparting strength to the sheet; protection against chemical and mechanical degradation. In addition, the purpose of sizing or resizing by the conservator is corollary to the papermaker's intent, i.e. to reintroduce sizing characteristics previously lost.

This underscores certain inherent problems in the current level of understanding of sizing as a conservation treatment. The relationship between sizing by the papermaker and resizing by the paper conservator is ambiguous and has yet to be defined. In fact, what separates the two processes may be greater than what they have in common. They are performed under very different circumstances - in completely different contexts - and this should be strongly emphasized and borne in mind when examining the actual techniques and methods employed. Knowledge of the papermakers' sizing practices has its own raison d'etre in conservation practice: the understanding of how and with what materials the paper in question was produced. The value of knowing the practical techniques of sizing, if it can be shown that sizing can or should be utilized for conservation purposes, is incidental to this historical understanding (although the historical information is of immeasurable help to the practical knowledge.)

In either case, one is dealing with virtually the same very large body of literature. What becomes intriguing in the literature is the interrelation of the parts, both in the process of papermaking and in the finished product, and the inevitable implications of this interrelation for conservation treatments of paper. For example, sizing is almost always concerned with the absorbency of paper, its reaction to water and aqueous media. The technical literature on this subject in the paper industry attempts characterize the complex interaction of paper and water, and potentially has useful information concerning the wet processing of paper by the conservator.

However there are distinct limitations to this line of investigation, principally the concentration of the technical literature on modern papermaking practice, and quite frequently on internal sizing methods. From a practical point of view, the discrepancy between this literature and the sizing practice handed on to conservators is as large as the gap between the hand papermaker and the modern papermill - correlation frequently require acute powers of interpolation and an active imagination.

Surface sizing in the paper trade/industry is most closely related to hand sizing by the conservator, and for the purposes of gaining practical insight into the sizing process, is of the most interest. This does not lessen the importance of understanding all sizing processes for documentation and descriptive purposes, or for characterizing the condition of the paper based on its component materials. In point of fact, consideration of the sizing of a sheet of paper, as a mitigating factor in treatment decisions is hardly at a refined stage. The understanding of the effect of treatments, especially wet treatments, on the variety of original sizing agents present in historical papers is superficial, at best. This is an area of research requiring a great deal more study and

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experimentation. The further refinement of treatment techniques that include sizing as a finishing operation also deserve considerable study and research, to understand the effects of sizing on the physical character of a particular sheet, not to mention its longevity. So, both as an integral component of papers under investigation, and as a tool for the conservator in preserving treated paper, sizing has been much neglected and deserves considerable attention.

There is no question that wet processing of paper affects the surface characteristics of the sheet: such dynamic qualities as the hand or "feel" of the sheet, its pliancy and drape. The practice of resizing book leaves which have been washed imparts desirable physical qualities to the sheet which "restore" the handling characteristics of the sheet. Also of considerable interest is the potential protection of the sheet at the chemical level by resizing, through the protection of the fiber from chemical interactions. But it must be pointed out that the occasion for resizing is in the majority of instances the previous wet treatment of paper, and the effects of resizing and its desirability need to be studies and considered in this context.

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