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# 46. ADHESIVES

This outline considers adhesives used by the conservator and some of those encountered by the conservator during treatment. The advantages and disadvantages of a particular adhesive, and its preparation for use in conservation, are also discussed. Consideration is given to the suitability of the adhesive for the following uses: hinging, mending, filling, lining, fixing, consolidation, and sizing. Also considered is the unsuitability of specific stable adhesives for particular applications. Unsuitability of other adhesives for use on art and artifacts on paper is also discussed. Adhesive source and production, chemical and physical properties, and aging characteristics are discussed in section 46.3 Materials and Equipment. Section 46.4 Treatment Variations contains an overview of adhesives in current use, with information on preparation and application.

#### 46.1 Purpose

In paper conservation, adhesives are used to adhere reinforcing materials to damaged areas or readhere separated components of an object; to consolidate, fix, size, or provide binders, glazes, and varnishes. Adhesives are also used to construct archival housings for paper objects. (See 23. Consolidation/Fixing/Facing; 25. Mending; 26. Filling of Losses; 29. Lining; and 40. Matting and Framing.)

# 46.2 Factors to Consider

# 46.2.1 Possible Use of Non-Adhesive Treatments

- A. Because of adhesive-substrate interaction, the application of adhesive to a paper object cannot always be considered fully reversible. Also, limitations to practical reversibility of an adhesive can be imposed by the materials of an artwork and/or its condition. In these cases a nonadhesive alternative may be considered, for example placing an object with friable or water sensitive media in a special housing (e.g., rigid support) rather than lining it.
- B. When temporary housing is required (e.g., for display) non-adhesive methods such as photo corners or sling mats may be preferable to traditional hinging. These methods may also be used in cases when acceptable adhesives prove ineffective in bonding to the object. For example, wheat starch paste will not adhere to resin-coated photographic papers.

# 46.2.2 Suitability of Potential Adhesive for Conservation Use

- A. The adhesive selected should demonstrate long term stability and aging characteristics considered acceptable for conservation use.
  - 1. Stability may be judged by natural aging for time-tested, traditional materials and by analysis and accelerated aging for newer materials. Current testing and analysis in the conservation or related technical fields should be consulted when possible.

Data from accelerated aging tests should be carefully evaluated to determine validity and appropriateness in governing the choice of a specific adhesive. Whenever possible, aging of materials for use in paper conservation should be evaluated on a paper/adhesive testing system. Although testing programs carried out in another field of conservation (i.e., paintings conservation) may provide valuable information, accurate information for the assessment of adhesives applied to paper should be carried out on paper substrates.(PV)

- 2. Commercial preparations are recommended with caution because formulations can change without notice. Product literature may not fully disclose chemical composition or aging properties.
- 3. An adhesive may be available in several grades, with only the highest purity grades suitable for conservation use.
- Additives in commercially-prepared adhesives may affect long term stability. For example, synthetic resin dispersions with added
   plasticizers can be unstable since the plasticizers can migrate to adjacent materials causing staining and leaving the adhesive inflexible. Dispersions which are internally plasticized through copolymerization are generally more stable.
- B. The selection of the potential adhesive should be guided by the principle of reversibility. Materials whose later removal may endanger the physical safety of the object should be avoided. Consideration should be given to whether the adhesive might prevent future treatments.

The different levels of reversibility in conservation should be considered when applying adhesives to porous paper substrates. Reversibility may range from complete removeability of the adhesive to only swelling it in order to separate attached parts. Complete solubility of an adhesive layer, with potential penetration of the paper, may or may not be desirable.

# 46.2.3 Suitability of the Potential Adhesive to the Object

- A. The adhesive should bond well to the object's surface, yet not be so strong as to cause further damage to the object or so weak as to endanger the object. Shrinkage of the adhesive layer on drying should not cause planar distortions in the paper.
- B. Ideally, the adhesive and its method of application should not alter the appearance of the media or support. Whether aqueous or solvent-based the adhesive should not solubilize media, cause staining in paper, or alter media or paper color. Certain media cannot tolerate the pressure (i.e., pastel or charcoal) or heat (i.e., acrylics or colored pencil) required to attach some adhesives.
- C. The proximity of the adhesive to the object influences selection. Many adhesives are inappropriate for direct application to an object but are acceptable for constructing a housing (e.g., sink mat).

# 46.2.4 Suitability of Potential Adhesive and its Working Characteristics to Proposed Treatment

- A. The adhesive chosen should be appropriately modified considering treatment methods and materials. For example, an adhesive may require dilution for a particular lining process or modification to compensate a fill or size paper.
- B. The adhesive and its method of attachment should produce a bond whose strength is appropriate to the particular treatment. For example, a cellulose ether may be adequate for hinging a small object while wheat starch paste would generally be better for larger, heavier objects.
- C. The working and setting times should be appropriate for the proposed treatment.
- D. Chemical and physical properties of adhesives within a group (e.g., the PVAs) can vary and should be considered for a particular application. For example, higher viscosity materials will form stronger bonds but may require dilution or other methods to enhance penetration. Lower viscosity materials form weaker bonds but may be effective with several applications.

#### 46.3 Materials and Equipment

#### 46.3.1 Vegetable Adhesives

## A. Starches

## **1.** General Information

The adhesive qualities of vegetable starches were recognized in early history. The first recorded use of a starch adhesive dates from the first century A.D. in a description of papyrus manufacture by Pliny the Elder using a paste made from wheat flour. Starch adhesives are now used throughout the world in numerous industrial applications such as papermaking and textile manufacture. Western paper conservation use has been influenced by the Oriental scroll mounting tradition.

#### a. Source

Starch adhesives are derived from the roots and seeds of plants such as corn, potatoes, rice, and wheat. The last two are commonly used in conservation. The plant material is processed by a variety of means including treatment with acids, bases, enzymes, and oxidizers. These processes modify a starch's viscosity and "retrogradation" (i.e., stiffening). Depending on the starch type, and the processing method, a vast range of viscosities and adhesive strengths can be produced.

## b. Chemical and Physical Properties

Starches are naturally occurring polymers of glucose. With the empirical formula of  $(C_6H_{10}O_5)n$ , where the exact value of n is unknown. Starch has a more intricate structure than cellulose because its molecules have two distinct areas: 75% has a branched amylopectin molecular structure and 25% has a linear amylose molecular structure. The exact percentages of amylose and amylopectin for each starch is largely responsible for its working properties. "Amylose and amylopectin have different properties, both as dry films and in solution. The highly regular linear structure of amylose allows it to dry from solution to form strong films...Amylopectin, being more amorphous, forms weak films" (Horie 1987, 135-136). Wheat starch contains 18-27% amylose while rice starch contains approximately 17-19% amylose. An AYTEX-P wheat starch representative stated that their wheat starch consistently has an amylose fraction of 25% and that American wheat starches have a consistent range from 23-25%. The 18-27% amylose range reflects world-wide variation. European or Japanese amylose ranges may be different from American wheat percentages.(KN) Vincent Daniels measured the percentage of amylose in aged Japanese

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paste, reporting that at two years of aging the amylose is approximately 19%, at four years it is approximately 22%, and at fifteen years it is approximately 24% (Daniels 1988).

During paste-making the amylose and amylopectin areas of the molecule behave very differently. The amylose fraction is responsible for the internal strength of a starch, many of its working properties, and for its degree of stiffening upon cooling. Thus, the amylose is responsible for gelatinization (Skeist 1973, 170).

**Identification:** Amylose stains intensely blue in the presence of iodine. Amylopectin stains red to purple (Browning 1977). Wheat starch pastes stain blue/purple with iodine.

**Physical Form:** Vegetable starches are white powders consisting of tiny granules that vary among starch types in form, size, range of size, and marking. Granule sizes range from less than 0.001 mm to 0.15 mm of diameter. The granules are crystalline.

**Preparation:** Pastes for use in conservation are generally prepared by first soaking the starch in water and then cooking it in additional water. Longer cooking time, higher temperatures, and agitation promote the necessary bursting of the granules. Each starch has its characteristic gelatinization range which extends from approximately 55-80°C (131-176°F) (Horie 1987, 136). Cooking technique, as well as origin of the starch, affect the characteristics of the resulting adhesive. (See 46.4.1 A. Treatment Variations.)

**Solubility:** Starches do not form true solutions, but rather colloidal dispersions. Cooked starch paste is a mixture of greatly swollen granules, fragments of granules that have burst open, and dissolved starch. Starches swell in cold water and are partially dispersed in hot water. Starches are broken down with starch specific enzymes and are soluble in 2,1 n methyl pyrrolidone.

pH: The pH of starches and starch products is not reliably measured by indicator papers, but should be tested with the pH meter. During commercial manufacture, pH is usually kept between 4.0 and 7.5. In the lab, the pH of either the starchwater slurry or the cooked paste can be adjusted easily (Clapp 1987, 145-149; TAPPI 1957, 26). Some conservators use alkaline water to prepare pastes that can serve a dual purpose of adhesion and assistance in alkalization/neutralization (e.g., lining). High pH (above 7.5) favors ready dispersal and slow settling of the granules. However, above pH 7.5 discoloration may result when the paste film dries (TAPPI 1957, 26). Variations of pH among starch granules or uneven dispersion of any pH adjustor can negatively affect a paste's appearance and performance.

# Possible Additives: None.

Health Hazards: No health hazards. However, as with all fine powders, a dust mask should be worn by those sensitive to airborne irritants.

Storage/Shelf Life: Starch powder can be stored indefinitely if kept in an air-tight container in a cool place. Starch pastes are subject to fairly rapid biological attack within a few days of preparation. The deterioration can be slowed somewhat by the addition of a fungicide, but it is recommended that paste be made fresh on a weekly basis to avoid adhesive failure. Because fungicides can cause yellowing of paper over time some conservators avoid mixing a fungicide into their paste by attaching a fungicide-soaked cotton ball or blotter onto the storage container lid. Some conservators do not use any fungicide, but make fresh paste frequently. Others prefer to store their paste in a refrigerator; however, paste "should not be kept at the low temperature of a domestic refrigerator  $(4^{\circ}C/39.2^{\circ}F)$  as it will become granular and lose adhesive qualities" (Paper Conservation News 1989). Oriental and some Western conservators store their paste under water which is changed daily.(KN) Any blending, stirring, or straining of a starch paste before storage may result in more mold spores being introduced into the paste, making it spoil faster.

### c. Aging Characteristics

**Reversibility:** Pure starch adhesives remain indefinitely swellable in water and exhibit good reversibility. Starch adhesives of unknown quality found on objects being treated might require starch specific enzymes for their removal. Reversibility may be difficult with thick paste layers; enzymes or mechanical removal may be necessary.

"Amylose has been shown to degrade by photo-oxidation and hydrolysis reactions on exposure to ultraviolet, resulting in breaking of the chain and production of organic acids" (Horie 1987, 137).

pH:

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Appearance: Good quality starch adhesives should not undergo any color change after aging. As encountered by conservators on previously treated objects, appearances can range from invisible to continuous coatings of slightly gray or yellow translucence to crumbly, opaque surfaces in tones ranging from white to gray to yellow/tan.

**Relative Strength:** Some conservators feel that dried starch paste films gradually become brittle.

**Biological Attack:** Starch adhesives are also subject to attack by insects, rodents, and enzymes.

2. Wheat Starch Paste From Precipitated Starch - Western Style This is the primary adhesive for Western paper conservators and the standard against which other adhesives are judged. It is used in numerous applications such as hinging, mending, lining, facing, reinforcement, and consolidation or fixing of media. Wheat starch paste can be very strong, yet at the same time it can be modified and manipulated for very delicate applications. When diluted for delicate work, a well-made paste will not undergo a sudden loss of viscosity, but a gradual and continuous change. This allows a great number of adhesive strengths from one material.

#### a. Source

Starches are separated from flour in a wet partitioning step and then dried in the following manner. Wheat flour is kneaded with water producing a stiff mass in which the starch is trapped. After slight aging to allow the gluten and starch to separate from each other, the starch granules are washed out with water. Extraneous fibrous material is caught by a sieve as the starchwater slurry passes through. The starch is concentrated from the slurry by centrifuge and dried.

The most commonly used wheat starch in America is Aytex-P which is manufactured by Henkel (formerly by General Mills). It is distributed by several companies. Sources for precipitated starches from Japan include; Harada (Kisa & Co., Ltd.) and Nakamura Co. (available from Conservation Materials, Reno, NV, called Zin Shofu).

#### b. Chemical and Physical Properties

**Identification:** Wheat starch has more small granules than large, with 70% less than 50 microns in diameter. The granules are spherical and saucer-shaped.

**Physical Form:** Wheat starch is available as a fine, white powder.

pH: Varies with method of manufacture (TAPPI 1957).

**Possible Additives:** 

c. Aging Characteristics (See 46.3.1 A. General Information.)

**Reversibility:** Wheat starch has a higher linear fraction than rice starch and therefore exhibits greater retrogration than rice starch paste (TAPPI 1957, 65-70; Whistler 1965, 350-353, Vol. 2).

# 3. Wheat Starch Paste From Fresh Starch - Japanese Style (Shinnori)

This is the primary adhesive for Japanese conservators. In addition to the functions which parallel those in which Western conservators use wheat starch paste, this adhesive is used for wood to wood bonds in scroll mounting. This paste is felt by its advocates to have a degree of viscosity not matched by paste made from dried starch. (See Wills 1984.)

## a. Source

Japanese-style paste is made from a starch which has been freshly separated from flour in the process of gluten manufacture. This separation process is essentially like that used in the West, except that the starch is not concentrated by centrifuge and dried after separation. Instead, the starch-water slurry is poured into a vat where it is allowed to settle into three distinct layers. The bottom layer is nearly pure wheat starch. Freshly produced starch may be difficult to find in the U.S.

## b. Chemical and Physical Properties

Physical Form: Maintained as a starch-water slurry.

**Preparation:** Paste-making from wet starch is similar to the process used in the West, with individual preferences for, and modifications of, cooking temperature time and degree of agitation. The following modifications sometimes made in traditional Japanese methods are noted but not necessarily

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recommended. To reduce viscosity the paste is mixed with aged paste; seaweed gelatin is added to increase elasticity; persimmon extract is added to increase strength and water resistance, and presumably, resistance to bacterial, fungicidal, and vermin attack.

Storage/Shelf Life: The undried starch is stored in a cool, dark place with regular changes of its protective cap of water until needed for paste-making. If properly kept, the paste may be stored indefinitely.

c. Aging Characteristics

## 4. Wheat Starch Paste - Japanese-Style, Aged (Furu-nori)

Compared to freshly-made paste, this adhesive is reputed to be weaker and more flexible. It is less prone to cause planar distortions in paper supports. Typically used at least eight years after its preparation, it imparts flexibility in multiple lining layers where it is used for secondary and tertiary backings, as well as in scroll linings. This paste is not generally used in the U.S.

## a. Source

The paste is prepared from fresh wheat starch and is made in the coldest months of the year in order that it mature successfully.

#### b. Chemical and Physical Properties

**Physical Form:** Some authors describe properly made aged paste as snow-white, others as pale-beige. The paste is an opaque solid with a crumbly, almost dry texture. It is less viscous than its freshly-made equivalent.

**Preparation:** Specific methods of cooking and aging vary from workshop to workshop. One method is as follows. Several batches of freshly prepared, then cooled, paste are put into a thick-walled ceramic jar. A layer of water is added to cover the paste, an air space is left, and finally the jar is covered to prevent evaporation of the water layer. The jar is stored in a cool, dark place for eight to ten years or longer. Once a year, on an extremely cold winter day, the water layer is poured off and any mold is removed. Fresh water is added and the jar is resealed. For the paste to age properly, various organisms (a tick and several types of fungi) must develop and die in a certain sequence within the top layer of the paste. A method for making "artificially aged paste" is described by G. Van Steene and L. Masschelein Kleiner 1980, 64-70.

# Storage/Shelf Life: See Preparation, above.

## c. Aging Characteristics

Vincent Daniels studied the strength of adhesion between new and aged pastes and found no differences (Daniels 1988, 9). However, in Japanese traditional practice, aged paste is considered weaker and more flexible.

# 5. Rice Starch Paste

This is generally considered to be a weaker adhesive than wheat starch paste. However, it is uncertain what the amylose content is for American and European rice starches. Differing amylose percentages and individual working habits of conservators may contribute to contradictory statements regarding properties of rice versus wheat starches. Possible uses are in situations where wheat starch paste would be too strong. Some conservators believe that rice starch paste is not as likely to cause a grayish haze or stain when it dries.

# a. Source

The starch granules are separated from flour or kernels by chemical softening and steeping and then further processed by dewatering and drying, similar to wheat starch processing.

## b. Chemical and Physical Properties

Rice starch has less retrogradation than wheat starch paste (TAPPI 1957, 79).

**Identification:** The granules are polygonal in shape and are the smallest of any common starch, between 4 and 8 microns in diameter. Some conservators believe that this property makes rice starch paste smoother than wheat starch paste.

Physical Form: Available as a white powder.

**Preparation**: Generally prepared by soaking the dry powder in water, followed by cooking in additional water. The gelatinization temperature is usually somewhat higher than that of other starches, (about 68-78°C) (154-172°F).

**pH**: Usually about 8 since most commercial preparations use alkaline steeping.

**Solubility:** Some conservators feel rice starch adhesives swell and release sooner than wheat starch. This property can be utilized in mending with wheat starch paste followed by lining with rice starch. This could allow the lining to be applied and possibly removed without disturbing the tear repairs.

Storage/Shelf Life: Waxy or glutenous rice starch has great stability against water separation from the paste when stored cold.

## c. Aging Characteristics

#### 6. Modified Starches (To be expanded.)

(The following is from Kirby 1965.) Dextrins are modified starches whose molecular structure has been changed through the use of heat, acid, alkali, or other catalytic conversions. Dextrins have been widely used for stamps, labels, and paper tapes, where the adhesive is moistened for application.

#### a. Source

Depending on the manufacturing process used, hydrolytic scission at either the 1-4 or 1-6 glucosidic links is responsible for the molecular modifications of the parent starch. Dextrins have been used as adhesives since the early nineteenth century. The earliest patent was issued in 1867. Starch was spread on iron pans and moistened with a dilute hydrochloric-nitric acid solution. After heating it was dried and used as a gum. Dextrins are often mixed with animal glue, gum arabic, or gum tragacanth. Frequently, blends of different dextrins are used and borax is a common additive to increase tack. There are three major types of dextrins: white, yellow, and British gums.

- 1) White dextrins are prepared by roasting at 107.2°C (225°F) in the presence of acid. These dextrins are then neutralized with some alkaline material such as ammonia. They are used in 50% concentrations. The color is white.
- 2) Yellow (or canary) dextrins are prepared by roasting starch with acidic catalysts at high temperature. Colors vary from light yellow to dark brown. Suitable concentrations are between 50-60%.
- 3) British gums are prepared by roasting starch up to 148.8°C (300°F) without using acid. These dextrins are usually dark colored and exhibit high solubility in warm water. They are used in concentrations of 10-35%.

# b. Chemical and Physical Properties

Generally, dextrins are much more soluble in water than the source starch because processing has lowered the molecular weight. Dextrins also have a lower viscosity for an equal concentration as compared to starch. Dextrin properties are based on their method of preparation and the parent starch.

**Possible Additives:** Borax can be added to increase tack, rate of bonding, and to minimize wetting. Urea formaldehyde resin is used 5-15% for water resistance coatings.

#### c. Aging Characteristics

## 7. Flour Pastes (To be expanded.)

These are encountered in former linings as historical adhesives. Contain brown chaff and particles. Not currently recommended for use.

# B. Vegetable Gums

## 1. General Information

Gums are relatively weak adhesives; however, they function well as protective colloids, preventing agglomeration and settling of finelydivided particles. Because of this property, they have been used, probably since ancient times, as binders in painting media. Gums have been used by watercolorists and miniaturists to saturate and intensify colors, especially to create modelling. Gums were also used to saturate dark areas in prints, particularly lithographs. Gums have a wide variety of commercial uses, particularly in the food and drug industries. Some gums (e.g., gum arabic) are used in adhesive formulations for postage stamps, labels, and envelopes. Gums from fruit trees (e.g., cherry, apricot, and plum) have been used as binding media, glazes, and varnishes on ancient, traditional, and folk objects.

Mucilages, related to gums, are plant materials extracted from seeds, roots, and other parts of plants. The term "mucilage" is broadly used, however, to describe general-purpose paper adhesives prepared by cooking gums in water with odorants and preservatives (Davidson 1980, 8-13). Gums have not been widely used in conservation treatments.

#### a. Source

Gums occur either as the natural exudants of particular trees and shrubs or as algae. In trees they are produced in response to a "wound" in an effort to seal that wound from microorganism attack. The actual mechanism of gum production within a tree is not fully understood. In cultivated trees, the bark is incised to stimulate gum production and then it is periodically "tapped." The chief uses of gums are as protective colloids and emulsifying agents in the food industry.

## b. Chemical and Physical Properties

Gums are complex polysaccharides. Polysaccharides are carbohydrates made of chains of monosaccharide units. A monosaccharide is a sugar unit classed by the number of carbon molecules it contains. Gums are non-crystalline, amorphous colloids. They are readily distinguishable from proteins because they do not have the nitrogen-containing peptide linkages which characterize the latter. In historical literature, gums have often been erroneously referred to as resins. They are readily distinguished from natural resins by their solubility characteristics: resins are typically soluble in organic solvents while gums are typically water soluble. It is worth noting that aqueous solutions made from different gums are not always miscible due to their different chemistries.

**Identification:** Identification tests applicable to individual gums are of limited value in examining paper or media because the small amount of gum present makes obtaining a sample difficult. For qualitative tests to differentiate gums see Glicksman 1969, 530 and Browning 1969, 252. When heated, a gum decomposes completely without melting and is usually charred.

**Physical Form:** Gums are available as "tears" (rounded lumps), flakes, or powders. Finer grades of gum (often collected from cultivated trees) are colorless, partially due to bleaching by the sun. The colors of crude grades range from yellow to brown. Gums are odorless.

**Preparation:** There are various methods of gum solution preparation, all of which involve dissolution of the gum in water. Some preparations recommend initial swelling of the gum in cold water or in alcohol/water.

Solubility: Gums appear to dissolve in water, but actually swell and disperse. They are insoluble in organic solvents. There are three solubility types: soluble in water, forming a transparent solution; partially soluble in water; and insoluble in water, forming a gel and possibly a very thick, transparent solution. Good grades leave no residue when dispersed in water. Once dried, they generally disperse again in water.

Health Hazards: Gums are non-toxic and non-flammable.

Storage/Shelf Life: Solutions are subject to microbial attack.

c. Aging Characteristics

**Reversibility:** Conservators have found that gums used as binders or glazes often remain water-soluble. Some dried gumbased paint films have been observed to become embrittled and cracked.

**Relative Strength:** Gums are considered weak adhesives. Gum films can, however, be more flexible than starch films.

**Biological Attack:** Gums are subject to microbial attack.

# 2. Gum Arabic

a. Source

Gum arabic, traditionally the most highly recommended binder in watercolor paints, is the natural exudate of the acacia tree. There are over five hundred species of acacia trees. The exudations are collected, graded by color and size, cleaned, sifted, and often bleached. Gum arabic's adhesive properties and its ability to prevent settling of finely ground pigments make it ideal as a watercolor medium. Its shiny, glassy appearance in thick films has been used for modelling by miniature painters. The best gum is said to come from Acacia senegal. It should be noted that the gum from Acacia arabia is of inferior quality and is rarely used for artist's materials. Gum arabic's name seems to be related to early traders rather than its source.

#### b. Chemical and Physical Properties

Gum arabic is the slightly acidic salt of a complex polysaccharide. It is the calcium salt of arabic acid. Structurally, gum arabic can be conceived of as a long chain incorporating short, stiff spirals with numerous side branches. The structural features of the gum are: a fairly hydrolysis resistant core and various groups on the periphery of the molecule which are unstable to acids (Whistler 1973). The molecular weight ranges from about 240,000-580,000. Gum arabic's moisture content is usually 13-15% (Gettens and Stout 1966, 29). Gum arabic lowers the surface tension of water.

Identification: See 46.3.1 B. General Information.

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**Physical Form:** Gum arabic comes in "tears", thin flakes, granules, or powder. It is white to amber in color. The color of the dry form cannot be used to predict the color of the resulting solution.

**Preparation:** Gum arabic is not widely used in conservation. Throughout history, artist's manuals describe a variety of gum solution recipes for use as a painting medium. They involve dissolution of gum "tears" in water by agitation at room temperature, agitation at slightly elevated temperatures, and immersion in rapidly boiling water. Humectants such as ox-gall, honey, sugar, and glycerine were often added to retain moisture in the dried films. One ounce of gum to one quart of water will yield a gum solution appropriate for use as a binder (Dossie 1764).

Solubility: Gum arabic is insoluble in oils and most organic solvents. It slowly disperses in glycerine and dissolves in water. It is one of the most water soluble of gums, able to form solutions of greater than 50% concentration. Solubility characteristics of a particular gum will depend on the age of the tree, the amount of rainfall in the region where it is collected, time of exudation, and conditions of storage. Gum arabic is incompatible with gelatin and trivalent metal ions.

**pH:** The pH of aqueous gum arabic is generally acidic with wide variations among samples. Variations can be attributed to the source of the gum and the method of solution preparation. Viscosity is pH dependent with a maximum at pH 7, although high viscosity can be retained over a wide pH range.

**Possible Additives:** See Preparation, above. Added dextrins can be detected with iodine (Gettens and Stout 1966, 28).

Health Hazards: Gum arabic is non-toxic and non-flammable.

Storage/Shelf Life: In commercial use, the gum is often packed in polyethylene-lined bags or drums. A cool, dry environment is recommended to avoid lumping. Solutions are subject to microbial attack.

#### c. Aging Characteristics

**Reversibility:** Gum arabic films become most readily waterinsoluble under conditions of dry heat aging. Extensive exposure to light alone does not appear to induce such insolubility. The cross-linking believed to cause the water-insolubility is favored under acidic conditions and is likely related to the amount of heat applied during the gum solution preparation.(JS) Gum arabic solutions dried at temperatures of 110°C (230°F) have been observed to yield insoluble gum (Whistler 1973).

Appearance: Water-insoluble gum arabic films discolor to amber or light brown. They often become embrittled.

#### **Relative Strength:**

#### 3. Gum Tragacanth

This gum has been primarily used as a binder for pastels.

#### a. Source

Gum tragacanth is extracted from any of the thousands of species of leguminous shrubs belonging to the genus, Astragalus. The exudations are collected from incisions made at the roots or in the bark of the shrub, those from the roots being of higher quality. These exudations seem to result from a transformation of pith cells and not from a plant secretion (as with other gums). The binding strength of gum tragacanth is about eight to ten times that of gum arabic; gum tragacanth is also less brittle.

#### b. Chemical and Physical Properties

Gum tragacanth is the slightly acidic salt of a complex mixture of polysaccharides. It is generally believed that it is composed of a water-soluble component called tragacanthin and a waterswellable major component called bassorin (60-70%) along with small amounts of starch and cellulose (Davidson 1980, 11-3). It forms more viscous solutions at lower concentrations than gum arabic. This may be explained by its larger molecular weight (840,000) and its more elongated shape (Masschelein-Kleiner 1985, 59). The moisture content ranges from 12-15%. Specific gravity varies from 1.25-1.384.

Identification: Under the microscope, gum tragacanth in water exhibits angular fragments with circular or irregular lamellae and no fragments of lignified vegetable tissue. Under infrared analysis, gum tragacanth exhibits a strong carbonyl absorption at  $5.75 \ \mu$ m. An 0.5% gum tragacanth solution forms a yellow, stringy precipitate in 10% potassium hydroxide (Davidson 1980, 11-29).

**Physical Form:** Gum tragacanth comes in the form of coarse crystals, powder, ribbons, flakes, and in solution. Color ranges from white to yellow. Gum tragacanth is more opaque than gum arabic; it has less luster and it is not as glassy or brittle.

**Preparation:** The gum is first wet with alcohol and then with water. After several hours of swelling, the gelled gum may be shaken with more water. A 2-3% solution will be thick, but can then strained through cheesecloth (Gettens and Stout 1966, 28). Other methods involve mixing a dry blend of the gum into the vortex of an aqueous system. Because gum tragacanth is hydrophilic, care must be taken in mixing solutions to avoid lumping (Davidson 1980, 11-5).

Solubility: The gum disperses in water and is insoluble in alcohol. Solutions of uniform consistency are difficult to obtain. Solutions of greater than 0.5% in water form gels. Solution viscosity is pH-dependent with a maximum initial viscosity at pH 8. Gum tragacanth solutions become thin at elevated temperatures. Upon cooling, however, viscosity is regained indicating that heat does not seem to degrade the polymeric structure (Davidson 1980, 11-9).

**pH**: Gum tragacanth is slightly acidic. Decreasing the solution pH has less effect on gum tragacanth's initial viscosity than on other gum solutions. Gum tragacanth is noted for its stability in acids. It has a maximum stable viscosity at pH 5.

**Possible Additives:** Because the pure product is very expensive, it is sometimes adulterated with lesser quality gums and whitened with lead carbonate.

Health Hazards: Gum tragacanth is non-toxic and non-flammable.

Storage/Shelf Life: Solutions of gum tragacanth have longer shelf lives than other gums. There is virtually no loss of viscosity or microbial growth (Davidson 1980, 11-13).

## c. Aging Characteristics

#### 4. Agar

Agar or agar-bearing algae can be purified to isolate the hydrocolloid agarose, which has been popularized by Richard Wolbers as a gel medium in which enzymes can be suspended for poulticing procedures. Agar is widely used as a microbiological medium and commercially in the food and pharmaceutical industries.

# a. Source

Agar, a seaweed colloid, is extracted from marine algae of the class Rhodophyceae from one of two species: gelidium or gracilaria. It is typically manufactured by hot water extraction followed by freezing and filtration. One brand used by conservators for poulticing is Sigma Type VII (Sigma).

## b. Chemical and Physical Properties

This polysaccharide (a hydrophilic colloid containing sulfur, sodium, and calcium) can absorb up to twenty times its weight in cold water with swelling (Hawley 1977, 20; Horie 1987, 142). It is a mixture of at least two polysaccharides, agarose being one. The viscosity of a given percentage concentration of agar and agaroid dispersions will be dependent on the raw materials and processing conditions. A 1.5% weight solution congeals between 32-39°C (89.6-102.2°F) to a firm, resilient gel which will not melt again below 85°C (185°F); this behavior distinguishes it from other seaweed colloids (Davidson 1980, 7-2).

#### Identification: See 46.3.1 B. General Information.

**Physical Form:** Agar is available in thin membranous pieces or granulated and powdered forms. Its color is white to light yellow. It is either odorless or slightly mucilaginous in smell.

**Preparation:** Agar is usually prepared in boiling water. It is recommended that the agar be allowed to swell in cool water first to prevent scorching.

Solubility: Many agars are insoluble in cold water and yet readily dissolve in boiling water. They are insoluble in alcohol.

#### pH:

Softening Point/Glass Transition Temperature  $(T_g)$ : Agar and agaroid gels melt in the range of 60-97°C (140-206.6°F) when there is 1.5% solids. Gelation can occur at concentrations as low as 0.4% (Davidson 1980, 7-5).

#### **Possible Additives:**

Health Hazards: Agar is non-toxic and non-flammable.

Storage/Shelf Life: In industry it is stored in polyethylene-lined fiber drums, between 20-25°C (68-77°F). Gel strength decreases with time in warm temperatures.

#### c. Aging Characteristics

#### 5. Algin or Sodium Alginate

#### a. Source

Alginates are extracted from several species of kelp: Macrocystis pyrifera, L. digitata, or L. saccharina (Windholz 1976, 228). They are used industrially as surface sizings and coatings for paper and as food additives. In conservation, they are added to paste or used as suspension media for colorants.

#### b. Chemical and Physical Properties

The alginates, usually the sodium salt of alginic acid, are a carbohydrate polymer of anhydromannuronic acid (Browning 1977, 277).

**Identification:** Alginates are extracted from paper in alkaline solution, neutralized with 1% hydrochloric acid, and precipitated as alginic acid by adding one drop of sulfuric acid. An alginate reagent solution of saturated  $Fe_2(SO_4)_3$  will cause a purple-red to brown-black color (Browning 1977, 277).

**Physical Form:** Sodium alginate is a colorless to yellow filamentous or granular powder or solid.

**Preparation:** The sodium salt is dissolved in water.

**Solubility:** The sodium salt dissolves in water to form a viscous colloidal sol (a liquid colloidal dispersion). It is not soluble in alcohol, chloroform, or ether, nor in water/alcohol mixtures of greater than 30% wt./wt. alcohol (Sax 1984, 2407; Windholz 1976, 34). Acidic solutions of less than pH 3 or divalent metal ions produce a precipitate or a gel (Windholz 1976, 34; Browning 1977, 277).

Health Hazards: While sodium alginate is used as a food additive, it is also listed on the EPA TSCA (Toxic Substance Control Act) Inventory of 1980. It is a hazard taken intravenously or intraperitoneally, though these routes seem unlikely in conservation use!

**Storage/Shelf Life:** Keep sodium alginate solutions cool to prolong shelf life.(FP)

c. Aging Characteristics

## 6. Funori (Japanese Seaweed Adhesive)

Funori has been used in Japan since 1673 as an adhesive and sizing material (Chapman 1970, 146). Japanese scroll mounters use funori to attach facing papers to paintings and to consolidate flaking paints.

## a. Source

Extracted from marine algae, red seaweed species of the Gloiopeltis family: Gloiopeltis tenax, G. complanata, and G. furcata (Winter 1984, 119; Masuda 1984, 128). Seaweed is gathered, rinsed, and cleaned, then pressed and dried into sheets composed of interlocking yellow-brown strands. This seaweed is gathered in Japan and China, where it is called "Halio" (Chapman 1970, 147). One U.S. source is Aiko's Art Materials (714 N. Wabash Ave., Chicago, IL 60611), which will special order the seaweed from Japan.

#### b. Chemical and Physical Properties

The mucilage extract is called funoran. It is a polysaccharide based on galactose units with a high proportion of sulfate groups, distinguishing it from agar (Winter 1984, 120). Unlike agar, it does not gel on cooling (Horie 1987, 142).

Physical Form: See Source, above.

**Preparation:** The mucilage is extracted by cooking sheets in water and straining (Koyano 1979, 31).

Solubility: Soluble in water.

Storage/Shelf Life: Funori in solution keeps under refrigeration for two to three months. Eventually it grows mold. Dried funori keeps indefinitely in a dry place.(FM) Funori solutions spoil rapidly in the summer (Masuda 1984, 128).

## c. Aging Characteristics

### **Reversibility**:

**Relative Strength:** Funori adhesive is less contractile than paste and adheres better to tea ceremony walls (Masuda 1984, 128).

## C. Cellulose Derivatives

# 1. Cellulose Ethers - General Information

In 1912, a process was patented in Germany for reacting cellulose with dimethyl-sulfate in the presence of bases to produce a water soluble cellulose. In 1927, the first industrial production of methyl cellulose began in Germany using gaseous methyl chloride to etherify cellulose. Several years later, commercial production of sodium carboxymethyl cellulose began world-wide (Kennedy et al. 1985, 274). Since then, the processes have been modified and production of a variety of cellulose ethers has expanded to millions of pounds yearly. Commercially, cellulose ethers are used as thickeners, anti-redeposition agents, and protective colloids for liquids in the food, paint, adhesive, and oil-well drilling industries.

In paper conservation, cellulose ethers have been used alone or with starch pastes for lining, hinging, and mending. Their moisture holding, surfactant, and anti-redeposition properties may be used to advantage as poultices for removing stains, old adhesives, and other accretions. Dilute solutions have been used for sizing or resizing paper. Cellulose ethers have also been used for consolidating flaking or friable media and as a binder for cellulose powder fills. Because some cellulose ethers become less soluble as water temperature increases, they have been used as facing materials during warm aqueous treatments.

#### a. Source

Cellulose ethers are made using glucose from wood pulp or cotton linters that have been prepared by swelling and decrystallizing with sodium hydroxide. The "alkali" cellulose then undergoes methylation or etherification to partially substitute the hydroxyl groups on the anhydroglucose ring with alkyl or hydroxyalkyl groups, such as methyl, ethyl, sodium carboxymethyl, hydroxyethyl, or hydroxypropyl. The product is neutralized with acids and the cellulose ether is isolated and purified by extraction of salts and byproducts. The cellulose ether may be varied further by compounding and surface crosslinking to facilitate dispersion. The product is then dried, milled, and sifted (Kennedy et al. 1985, 276).

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Degree of Substitution on Anhydroglucose Units.



Molecular Substitution and Degree of Substitution on Anhydroglucose Units.

#### b. Chemical and Physical Properties

Each anhydroglucose ring has three hydroxyl groups which may be substituted. The degree of substitution (DS) is therefore three or less. During synthesis, reagent concentration, temperature and duration are factors which control DS. In general, low degrees of substitution produce rather brittle materials while increasing the amount of substitution increases the plasticity of the cellulose ether (Horie 1987, 126). Increasing molecular weight and thixotropy can be achieved when alkyl oxides are used as reactants and side-branching on the hydroxyl group of the new alkyl substituent occurs. The total amount of ether functions substituted by side-branching is referred to as the Molar Degree of Substitution (MS). The basic structures for DS and MS are diagrammed above, with R representing the alkyl or hydroxyalkyl substitution (Kennedy et al. 1985, 275). Viscosity of the final product is determined by the extent of pretreatment of the cellulose raw material and by subsequent oxidation of the finished product to the desired molecular weight. Pretreatment may include chemical additives, grinding, heating, or oxidizing. These decrystallization processes improve accessibility of the cellulose to the reactant and therefore yield a higher DS but result in a reduced end product viscosity (Nicholson 1985, 364). Properties such as pH, refractive index, and gel temperature vary depending on DS, concentration, and the distribution of substituents. Recent analysis conducted by

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Gelman for Hercules Incorporated suggests that materials of the same molecular weight and DS/MS can have vastly different performance and that there was no analytical method to ascertain the exact distribution of substituents or predict behavior. Moreover, distribution cannot be controlled during synthesis (Gelman 1985, 296, 299-300).

**Identification**: "A small portion of solid sample is placed in a test tube with benzene (0.5 ml) and 93% sulfuric acid (1 ml), and the tube is warmed carefully in a water bath until an intense yellow color develops and then rapidly turns reddish. The tube is cooled and a layer of alcohol (0.5% ml) is added without stirring. A blue or green ring between the two phases indicates hydroxyethyl or carboxymethyl cellulose; ethylcellulose gives a violet ring" (Browning 1969, 254). Also see individual ethers.

**Physical Form:** Cellulose ethers are available as fine to granular powders which range in color from white to yellow. Each cellulose ether is available in several grades of purity and in a range of types, varying in viscosity, particle size, and thixotropy.

**Preparation:** Most cellulose ethers used in conservation are prepared by first dispersing the granules in cold or hot water, stirring continuously for a required amount of time, and then allowing the solution to gel.

**Solubility**: The DS and the uniformity of distribution of substituents along the chain influence the extent to which polar solvents may be added to a cellulose ether initially solubilized in water (Nicholson 1985, 364). Increasing substitution increases the solubility of the cellulose ether in organic solvents (Horie 1987, 126). Cellulose ethers are generally soluble in cold water. Sodium carboxymethyl cellulose and hydroxyethyl cellulose are also soluble in hot water. Only hydroxypropyl, ethylhydroxy ethyl cellulose, and ethyl cellulose are initially soluble in polar organic solvents.

**Possible Additives:** Anti-oxidants or plasticizers (e.g., glycerine) are possible additives. See various product literature under headings such as: Chemical Degradation, Plasticity, and Compatibilities.

Health Hazards: Cellulose ethers are non-toxic and nonsensitizing (see product literature). However, breathing the powder should be avoided. Storage/Shelf Life: Protect from oxygen, light, heat, microorganisms, moisture, and extremes of pH. All cellulose ethers are susceptible to oxidative chain breaking, both in storage and in situ, especially with light exposure (Horie 1987, 126-127). Sodium CMC and hydroxalkyl ethers degrade faster than the alkyl celluloses (Horie 1987, 126). Because they are strongly hydrophilic, they should be stored tightly sealed in a dry environment. Empirically, Cellofas B3500 has been found to degrade in solution through acid hydrolysis; however, Cellulose Gum 7H or 7HSP, a more pure product, will not degrade when prepared with deionized water.(CB) Microbiological deterioration reduces viscosity (Hercules, Inc.). It is not advisable to add preservatives known to cause discoloration of paper to cellulose ethers which are intended for permanent contact with works of art.

## c. Aging Characteristics

Like cellulose, all cellulose ethers will suffer from chain breaking through oxidation. This oxidation is enhanced by light exposure. The extent to which degradation occurs varies widely among the many types of cellulose ethers.

Wilt and Feller determined that different types of cellulose ethers underwent dramatically different rates of degradation in heat aging. Sodium carboxymethyl cellulose and methyl cellulose proved to be the most stable followed by ethylhydroxy ethyl cellulose. Hydroxypropyl cellulose was found to have intermediate stability. Generally, cellulose ethers soluble in organic solvents were found to be less stable than those not soluble in organic solvents (Wilt and Feller in press).

**Reversibility**: Unlike the nonionic cellulose ethers, sodium CMC can form irreversible insoluble complexes in the presence of metal ions. All the cellulose ethers can be cross-linked at the hydroxyls under acidic conditions (Horie 1987, 126-127). Long-term resolubility after natural aging is unknown. Indictor, Baer, and Phelan tested two types of methyl cellulose and a sodium carboxymethyl cellulose using dry oven accelerated aging and found them easily reversible <u>after</u> aging. A third type of methyl cellulose they tested was found to be less soluble, but comparable to accelerated aged rice and wheat starch paste (Indictor, Baer, and Phelan 1975, 145). It should be noted that dry oven aging favors the cross-linking reaction.(TJV)

Appearance: Wilt and Feller's testing (cited above) showed that dry powder samples yellowed and demonstrated greater color changes than films formed from 2% solutions.

# Relative Strength:

Biological Attack: The alkyl ethers, methyl, and ethylhydroxyethyl cellulose, are resistent to biodeterioration in solution while hydroxyalkyl ethers such as hydroxyethyl and hydroxypropyl cellulose and sodium carboxymethyl cellulose are susceptible to biological attack (Horie 1987, 128-129).

- 2. Methyl Cellulose
  - a. Source

Methocel A4M, A15C, A4C, A15 (Dow Chemical Co., USA); Culminal (Henkel, Germany, was available through Talas in 1982 and from Process Materials as Process Materials or Archivart Methyl Cellulose, also available in the U.S. from Aqualon); Methofas (Imperial Chemical Industries, England); other brands from unspecified manufacturers are available; Light Impressions Methyl Cellulose. Synthesized by reacting methyl chloride with alkali cellulose.



## b. Chemical and Physical Properties

Non-ionic. Average DS ranges from 1.3-2.6. (See product literature for additional information.) Dow-Methocel A is available in the following viscosities (at 20°C/68°F and 2%), 4C (400 cps), 15C (1500cps) and 4M (4000 cps).

Identification: "A 1% aqueous solution of methyl cellulose gives no precipitate upon addition of five volumes of 95% ethanol plus three drops of saturated NaCl solution, whereas most other gums do. Methyl cellulose is soluble in ethylene glycol and insoluble in ethyl ether. When heated it chars without melting and produces a smell of burning paper. It is characterized by its. content of methoxyl groups, which can be determined by the Zeisel method" (Browning 1969, 255).

Physical Form: See 46.3.1 C. General Information.

**Preparation**: Disperse powder in water and agitate.

Solubility: Soluble in cold water. Forms a reversible gel on heating to 50-90°C (122-194°F) (Horie 1987, 127). Aqueous solutions can be diluted somewhat with water miscible organic solvents such as ethanol and acetone. Addition of too much solvent will cause methyl cellulose to precipitate out of solution. Neither powder, nor film are soluble in hot water greater than 80°C (176°F).(CB)

**pH**: The pH measurements of various methyl celluloses in solution range from approximately 6.5-7.5.

**Refractive Index:**  $n_{D} = 1.49$  (Horie 1987, 125).

## c. Aging Characteristics

In accelerated aging tests methyl cellulose was found to be nondamaging to silk (Masschelein-Kleiner and Bergiers 1984, 73).

Appearance: Methocel A4M on Whatman chromatography paper was tested using artificial aging at 90°C (210.2°F) and 55% RH for sixteen days and found increased strength of papers tested without dramatic decrease in pH or color whiteness (Baker 1984, 59).

**Relative Strength:** Methyl cellulose is a relatively weak adhesive that may not be strong enough in some applications.

#### 3. Sodium Carboxymethyl Cellulose (CMC)

#### a. Source

(Often referred to as carboxymethyl cellulose.) Cellulose Gum CMC 7HSP (Hercules, Inc., USA now available through Aqualon); Cellofas B3500 (ICI, England, no longer manufactured but was listed in a Conservation Materials catalog in 1984). Manufactured by reacting chloracetic acid with alkali cellulose in a slurry with an organic solvent, generally a short chain alcohol (Nicholson 1985, 366).



b. Chemical and Physical Properties Ionic, DS ranges from 0.4-1.2 (Gelman 1985, 263). Hercules Cellulose Gum CMC 7HSP is 1500-2500 cps (1% solids at 25°C/77°F). Contains metal salts, such as sodium, as part of the molecular chain. The approximate sodium content of CMC 7 is 7.0-8.5% (Baker 1984, 55).

Identification: "A method for determination of CMC in paper is based on extraction with NaOH solution and treatment of the extract with sulfuric acid to produce glycolic acid which is determined calorimetrically with 2,7-dihydroxynaphthalene" (Browning 1969, 256).

Physical Form: An off-white powder.

**Preparation:** Disperse powder in water and agitate.

Solubility: Soluble in hot or cold water with maximum hydration under alkaline conditions. In solution, it is compatible with most anionic and non-ionic polymers and gums. Compatibility with salts depends on whether added cations can form soluble salts of carboxymethyl cellulose. Cations forming insoluble salts are aluminum ion, silver, chromium, and zinc (Hercules, Inc.). Limited dilution of an aqueous solution is possible with ethanol, acetone, and other organic solvents. Increasing DS makes the ether more hydrophilic, increasing electrolytic concentration makes it more hydrophobic.

pH: The pH of a 2% solution is about 7.5.(CS) The pH of Aqualon cellulose gums in various concentrations range from 4.6-6.3 (Aqualon).

**Refractive Index**:  $n_p = 1.515$  (Hercules, Inc.).

**Possible Additives:** Less pure products, such as Cellofas B3500, contain sodium chloride and sodium glycolate and appear off white to light brown in color.

# c. Aging Characteristics

In 1984, Baker reported that Cellofas B3500 had been used in England as an adhesive and size for over twelve years with no adverse effects having been observed. There is considerable documentation in the literature to predict that sodium CMC is unstable at low pH (Whistler 1973, 704-5). However, because sodium carbonate is formed in small amounts after drying, the pH of the dry film will probably remain quite stable.(CB) Oxidative degradation can occur to films at pH > 9.0 (Hercules, Inc. 1976, 20). In some accelerated aging tests, sodium carboxymethyl cellulose had no discernible damaging effects on silk (Masschelein-Kleiner and Bergiers 1984, 73).

**Reversibility:** Treating a film with cations such as  $Fe^{3+}$  or  $CU^{2+}$  will lead to water resistance or insolubility (Hercules, Inc. 1976, 21).

Appearance: Some yellowing of Cellofas B3500 and Cellulose Gum CMC 7HSP was found after humid oven accelerated aging and dark storage aging. NaCMC films are non-staining and do not become brittle with age (Baker 1984).

**Relative Strength:** Accelerated aging tests revealed a drop in strength after humid oven aging and dark storage aging. Cellulose Gum CMC 7HSP was found to respond similarly although a smaller degree of loss of strength was noted compared to Cellofas B3500 (Baker 1984).

# 4. Hydroxypropyl Cellulose (HPC)

#### a. Source

Manufactured under the tradename Klucel (Hercules, Inc., USA). Manufactured from alkali cellulose reacted with propylene oxide at elevated temperatures and pressure.



# b. Chemical and Physical Properties

Hydroxypropyl cellulose is non-ionic. Higher molecular weight increases tensile strength and elasticity. (See product literature.) The viscosity is unchanged over a pH range of 2-11, with the most stable viscosity at pH 6-8. Viscosity is lowered by heating the solution and increases rapidly with increasing concentration. It is possible to mix two viscosity types to achieve an intermediate. Klucel is described as having unexpected viscosity effects when combined with anionic or nonionic polymers in aqueous solution. Combined with anionic polymers such as sodium CMC and sodium alginate, it has higher than expected viscosity. Combined with nonionic polymers, such as MC or HEC, it has lower than expected viscosity (Hercules, Inc.).

Physical Form: An off-white powder.

**Preparation:** Prepare a slurry in hot water, allow to sit, add cold water and agitate.

Solubility: Klucel is soluble in water up to 40°C (104°F) and in polar organic solvents. Heat accelerates dissolution with organic solvents. By first dissolving the cellulose ether in a solvent, it is sometimes possible to add an otherwise incompatible solvent. Once dried, the film is soluble in water, ethanol, and acetone (Hercules, Inc.). The propyl groups cause it to be more hydrophobic than methyl cellulose, therefore giving it good solubility in polar organics; insoluble in water 40-45°C (104113°F) and will precipitate out of solution on heating (Horie 1987, 127). Will precipitate at increasingly higher temperatures when water is replaced by other solvents such as ethanol (Hercules, Inc.).

**pH:** 5.0-8.5.

Softening Point/Glass Transition Temperature  $(T_{\mu})$ : Softening temperature is 130°C (266°F).

**Refractive Index:**  $n_{D} = 1.56$  (Horie 1987, 125).

**Storage/Shelf Life:** Solutions are susceptible to both chemical and biological degradation, generally resulting in decreased viscosity. Greatest stability is at pH 6-8 and in absence of oxidizing agents (Hercules, Inc.).

c. Aging Characteristics

See Wilt and Feller, in press.

# 5. Ethyl Hydroxyethyl Cellulose (EHEC)

# a. Source

Manufactured under the tradenames Ethulose (Chemaster Corporation, Long Island City, NY. No longer available at this address) and Bermocoll (Berol was formerly Modocoll); EHEC is also available from Hercules, Inc, USA and Conservation Materials, USA. Formed by reacting alkali cellulose with ethylene oxide or ethylene chlorhydrin.



## b. Chemical and Physical Properties

The product is substituted with ethylhydroxyethyl groups. With DS of ethyl groups about 0.9 and MS of hydroxyethyl groups about 0.8. According to product literature, Ethulose is non-ionic, stable in the presence of dilute acids or alkaline salts. Ethulose 100 is available in viscosities ranging from 50-1200 centipoises.

**Preparation:** Add to cold water at a uniform rate, stirring vigorously.

Solubility: Soluble in cold or warm water. Insoluble in hot water, hydrocarbons, alcohols, toluene, and xylene. Precipitates out of solution on heating to 40-45°C (104-113°F) (Horie 1987, 127). An aqueous solution can be diluted many times with alcohol, acetone, and other solvents without precipitating.

pH: The pH of a 2% solution is 6 (Chemaster Corporation).

Storage/Shelf Life: Solutions are resistant to mold and bacteria (Horie 1987, 128).

## c. Aging Characteristics

In Wilt and Feller's testing, HPC was found to have intermediate stability, being less stable than methyl cellulose and sodium carboxymethyl cellulose. (See Wilt and Feller, in press.)

# 6. Hydroxyethyl Cellulose (HEC)

## a. Source

Natrasol 250 GR and 250 HHR (Hercules, Inc.). Prepared by reacting alkali cellulose with ethylene oxide.



# b. Chemical and Physical Properties Hydroxyethyl cellulose is non-ionic, unaffected by cations.

**Identification**: "Hydroxyethyl cellulose is soluble in ethylene glycol and insoluble in ethyl ether; it chars without melting and gives an odor of burning paper" (Browning 1969, 255).

Preparation: Add powder to vigorously agitated water.

Solubility: The water soluble range of DS is about 0.8-2.5, with greater DS giving increased solubility. HEC is initially soluble in hot or cold water. Essentially insoluble in organic solvents. Polar or water miscible solvents sometimes affect the solubility; effects vary from swelling to solubility. Its nonionic character allows dissolution in many salt solutions that will not dissolve other water-soluble polymers. It is compatible with more foreign materials than most other water-soluble polymers. Once dried, it is resoluble in water (Hercules, Inc.).

pH: 6.5-8.5.

**Softening Point/Glass Transition Temperature (T<sub>1</sub>)**: Softening range is 135-140°C (275-284°F) (Hercules, Inc.).

**Refractive Index:**  $n_p = 1.51$  (Hercules, Inc.).

c. Aging Characteristics

Also see Wilt and Feller, in press. Based on their findings and those of Howells et al. 1984 and Masschelein-Kleiner and Bergiers 1984, hydroxyethyl cellulose is not recommended for prolonged contact with paper.

Appearance: Howells et al., found acrylic dispersions with Natrasol (hydroyethyl cellulose) added as thickener aged poorly and yellowed (Howells et al. 1984).

**Relative Strength:** Masschelein-Kleiner and Bergiers found HEC caused further weakening of impregnated silk after accelerated aging (Masschelein-Kleiner and Bergiers 1984).

# 7. Methyl Hydroxyethyl Cellulose (MHC)

a. Source

Manufactured under the tradename of Tylose MH 2000, MH 300 (Kalle Hoechst, West Germany).


# b. Chemical and Physical Properties

The Tylose products are methyl celluloses that contain a small amount of hydroxyethyl substitution which raises the thermal gel point from about 55 °C (131°F) to about 70°C (158°F). The more polar nature of the hydroxyethyl group allows for the formation of a slightly stiffer gel than is possible with hydroxypropylmethyl cellulose of comparable gelation temperature (Davidson 1980, 3-4).

**Preparation**: Disperse powder in hot water, then add cold water with agitation.

Solubility: Soluble in cold water; insoluble in hot water 70°C (158°F) and above. Solutions can be further diluted with alcohol.

# c. Aging Characteristics

Appearance: Yellowed only slightly under accelerated aging conditions (Verdu et al. 1984, 67).

**Relative Strength:** Tylose MH2000 was found to be nondamaging to silk in accelerated aging tests (Masschelein-Kleiner and Bergiers 1984, 73).

# 8. Cellulose Esters - General Information

#### a. Source

In the cellulose molecule, like all adhesives derived from it, the -OH groups on the ring are partially substituted. Esterification is completed (triester) and then hydrolyzed back to the desired free radical content. Some free radical substitution improves solubility and adhesive qualities.

Cellulose, an alcohol, is reacted with one of a variety of acids to produce an ester and water. The water is removed to drive the reaction to completion.

# b. Chemical and Physical Properties

**Identification:** Esters can be readily distinguished from cellulose ethers by the easy saponification of the esters: an unknown material is boiled with methanolic KOH, the alcohol evaporated to a small volume, and the residue warmed with an excess of dilute  $H_2SO_4$  The odor of acetic, propionic, or butyric acid will be detected easily. See specific entries for indicator tests. Many infrared spectra are available. Molecular Weight: Esters made from cotton, about 700,000-800,000. Esters from wood pulp, about 80,000-400,000. Low MW gives low viscosity. High MW gives high viscosity.

**Physical Form**: Method of film formation is by solvent evaporation. See specific ester entries also.

Viscosity: Dependent on MW. Lower viscosity means easier solubility, greater compatibility with other resins and plasticizers, lower MP/Softening Point. Higher viscosity/higher MW means more strength and toughness.

Solubility: Soluble in various organic solvents.

**Possible Additives:** Stabilizers against discoloration, degradation, thermal decomposition.

# 9. Cellulose Acetate - General Information

Cellulose acetate was first developed in France in 1869 by the acetylation of cellulose. Industrial production of cellulose acetate began to replace the highly flammable cellulose nitrate as a coating for airplane wings and fuselage fabrics during World War I. It was not manufactured as a film on a large scale until 1930. The properties of cellulose acetate are varied by the degree of acetylation. In the plastics industry it is suitable for both injection molding and continuous extrusion. In paper conservation cellulose acetate has been used in sheet form for the lamination of documents, or in dilute solution as a consolidant for flaking or friable media. Laminating film meeting the National Bureau of Standards (NBS - now called the National Institute Standards and Technology - NIST) specifications is no longer commercially available. However, this film formerly qualified as appropriate archival laminating film.

#### a. Source

Cotton linters and purified wood pulps are the two major sources of cellulose for the manufacture of acetate. Acetate from cotton linters is of better color and solution clarity. Cellulose acetate is produced by the acetylation of cellulose with acetic acid in the presence of a catalyst - usually sulfuric acid because it creates the most uniform product. The reaction produces a triacetate. To prepare a product of a low degree of substitution (DS) (with a lowered softening temperature), the triacetate is hydrolyzed to remove some of the acetyl groups, usually to a final acetal value of 52-56% (Windolz 1976). The reaction is carried out via the controlled reversal of the esterification reaction, by the addition of water and dilute acetic acid. Hydrolysis is stopped by diluting the mixture even further with water. The acetate is subsequently purified by washing with water, and the cellulose acetate flakes are centrifuged and dried (Odian 1981, 672-674) modifying the cellulose-liquid ratio, temperature, catalyst concentration, and solvent produce acetates of varying character. Kodak #4655 and Celanese P911 are two brands which are used in conservation. The basic structure is:





Cellulose Acetate Repeating Unit.

# b. Chemical and Physical Properties

Each anhydroglucose unit has three hydroxyl groups which may be substituted. DS is therefore equal to or less than three. The properties of cellulose acetates are dictated by their molecular weight and acetyl content, which is expressed as DS or percent acetyl content. Due to decreased hydrogen bonding and crystallinity relative to cellulose, the cellulose acetates, are thermoplastic. Most are not sufficiently thermoplastic to permit easy processing without the addition of plasticizers. To further lower the softening point these esters are fused with plasticizer under heat and pressure, and then the acetate flake can be processed into products by extrusion and molding. Grades range according to percent acetyl content: plastic, 52-54%; lacquer, 54-56%; film 55.5-56.5%; water-resisting, 56.5-59.0%; triacetate, 60.6-62.5%. The relationship between percent acetyl content and DS is as follows:

51% acetic acid = 2.2 DS; 53% acetic acid = 2.3 DS; 55% acetic acid = 2.4 DS; 56% acetic acid = 2.4 DS; 56% acetic acid = 2.5 DS; 59% acetic acid = 2.7 DS; 62% acetic acid = 2.9 DS (Faith et al. 1975, 241).

**Identification**: Cellulose acetate burns slowly, with melting, dripping, and the odors of acetic acid and burning paper. When removed from the flame, it burns slowly with beading at burnt edges.

**Physical Form:** White, odorless, granular flakes, or powder. Clear solution.

**Preparation**: Cellulose acetates used as consolidants are prepared by dispersing the flakes in acetone, ethyl acetate or methyl ethyl ketone (MEK).

Solubility: Soluble in acetone, MEK, ethyl acetate, chloroform, and other chlorinated solvents, and various mixtures of organic solvents, depending on the degree of acetylation. Soluble in glacial acetic acid. Insoluble in water and ethanol. Resistant to weak acids, oils, greases, and fats (Faith et al. 1975, 241). Cellulose acetate is less resistant to moisture or water than cellulose nitrate.

pH:

Softening Point/Glass Transition Temperature  $(T_g)$ : Laminating film 114.5 ± 2.5°C (238.1 ± 36.5°F); flake 60-97°C (140-206°F). Commercial products do not have sharp melting points.

**Refractive Index:**  $n_D = 1.48-1.50$ .

**Possible Additives:** Instability in cellulose acetate is caused by the presence of residues of bound sulfuric acid which are very difficult to eliminate during manufacture. Alkaline earth metal salts such as magnesium and calcium may be used to neutralize bound sulphate at the end of hydrolysis. Further addition of an acid acceptor, such as magnesium acetate, ensures that the bound sulphate remains in the salt form. Plasticizers are necessary to lower the melting range and increase tensile strength. A cellulose acetate film should contain an antioxidant and ultraviolet absorber for maximum stability (McBurney 1954; Wilson and Forshee 1959a). Cellulose acetate does not readily accept additives to modify viscosity or clarity.(CS)

**Health Hazards:** Cellulose acetates are non-toxic (Hawley 1977, 175-176). However, breathing of powders should be avoided. They are flammable and not self-extinguishing, and therefore present a moderate fire risk.

Storage/Shelf Life: Protect from extreme heat and excess oxygen, ultraviolet light, moisture, and extremes of pH. Resistant to biodeterioration.

# c. Aging Characteristics

Films of plasticized cellulose acetate may be considered reasonably stable if they meet the NBS specifications (Wilson and Forshee 1959b).

Reversibility: Chemical breakdown of cellulose acetate film or flake involving changes in the acetyl content may cause corresponding changes in resolubility. Hydrolytic degradation is due to acid cleavage of the glucosidic links in the polymer molecule. Chain cleavage is accompanied by deacetylation. Oxidative degradation appears to produce the volatile products of carbon monoxide, water, carbon dioxide, and acetic acid. In turn, these products can accumulate and catalyze degradation of the cellulose acetate in the form of chain breaking (McBurney 1954, 1019-1055). The greater the DS, the greater the stability of the polymer molecule. For laminating film, a DS of 2.4  $\pm$  0.1 is recommended (Wilson and Forshee, 1959b, 17). Plasticizers, which may comprise as much as 20-30% of the laminating film, are often the chief contributors to cellulose acetate instability. Some are volatile and many are more easily oxidized than the acetate itself. Plasticizers most resistant to oxidation, including dimethyl phthalate or triphenyl phosphate, extend the stability of cellulose acetate (Wilson and Forshee 1959a).

Delamination of a document is performed by immersion in a solvent bath, generally acetone. However, experience gained from performing delamination treatments has shown that degraded cellulose acetate films that will no longer dissolve inacetone, will often dissolve in acetone/water mixtures, in proportions ranging from 10:1 to 4:1. Dimethyl formamide (DMF) or ethyl acetate may also dissolve deteriorated film. **pH**: Acidity is increased considerably by traces of acid catalysts remaining from manufacture. Incorporation of an acid acceptor (i.e., magnesium acetate) retards the process of degradation. Some early cellulose acetate film employed for lamination may degrade, releasing acetic acid and having an acidic, vinegar-like odor.

Appearance: For cellulose acetate film or flake, oxidation is accompanied by progressive orange-yellow discoloration (DeCroes and Tamblyn 1952). Cellulose acetate film meeting NBS specifications is resistant to oxidation and discoloration. Degraded cellulose acetate film may exhibit a moderate to severe amount of contraction.

**Relative Strength:** See Wilson and Forshee 1959b for data on tensile strength, edge tear, internal tear, and elongation at break for cellulose acetate laminating film prior to, and following lamination.

Biological Attack: Resistant to biological attack.

### 10. Cellulose Nitrate - General Information

Cellulose nitrate was the first major plastic in commercial use, having been formulated in 1832 by Braconnot and produced industrially as early as 1845 in England. Cellulose nitrate was used initially for military explosives (gun cotton) and later plasticized with camphor to produce the first successful synthetic plastic. It was widely used in still negative film and motion picture film until the 1950s. The plastic was patented in England in 1864, and developed independently in America in 1869 where it was marketed as "Celluloid." Industrial lacquer finishes constitute the largest market for cellulose nitrates; explosives and propellants are the second largest market (Kirk and Othmer 1979, 118-143).

In paper conservation cellulose nitrate has been encountered as a surface coating and consolidant, as well as a solander box and book cloth coating (known as pyroxylin). Conservators have encountered it on paper substrates used as a general purpose adhesive. (See Skeist 1977, 214 for general purpose nitrocellulose cement recipe.) In the printing industry it has also been used as a binder for inks, especially aniline types because it is tough and pliable. In Dresden, Germany in 1890, a cellulose nitrate product called Zapon was experimentally applied to military maps as a paper strengthener (Marwick 1964). Cellulose nitrate is not currently recommended for use on paper objects.

# a. Source

Cellulose nitrate is formed by reaction of cellulose from cotton linters or wood pulp with mixtures of nitric and sulfuric acids. By varying strength of acids, temperature, time of reaction, and acid/cellulose ratio, products showing a wide range of chemical characteristics are obtained. Duco Cement (Dupont), UHU Hart (Lingner and Fischer GmbH), Durofix (Rawlplug), Duco (Decon), Randolph's Universal Cement (Randolph), and H.M.G (H. Marcel Guest, Ltd.) are commercially available cellulose nitrate-based adhesives (Horie 1987, 133; Koob 1982, 31-34).

#### b. Chemical and Physical Properties

Molecular weight approximately 25,000 for adhesives; 120,000 for plastics (Hawley 1977, 614-615). Theoretically it should be possible to replace each of the three hydroxyl groups on the anhydroglucose unit with nitrate groups, producing a calculated 14.14% nitrogen content. Complete nitration is not feasible, however, since the resulting product, cellulose trinitrate, is unstable. In practice, the upper limit of nitration is about 2.9% or 13.8%. Most commercial cellulose nitrates range between 10.9% to 12.2% nitrogen content. The characteristic properties of cellulose nitrate in sheet form depend on molecular weight, degree of nitration, stabilization, film thickness, and plasticizer content. Cellulose nitrate is an inherently unstable substance. (See Aging Characteristics.)

Cellulose nitrate in which the nitrogen content is relatively low (10% or less) is a useful lacquer base because of its fast drying properties. Collodion and pyroxylin are plastic forms of lownitrogen cellulose nitrate which are variable mixtures consisting chiefly of cellulose tetranitrate. Other names for this form are colloxylin, xyloidin, celloidin, and Parloidion (Windholz 1983, 7914). If the nitrogen content is allowed to rise to almost 14% (i.e., cellulose hexanitrate) the product is a high explosive (gun cotton) (Hampel and Hawley 1976, 189).

**Identification:** Cellulose nitrate will give an immediate deep blue color when tested with one drop of diphenylamine solution (6% in concentrated sulfuric acid). On an infrared spectrum it shows prominent bands at  $6.1\mu$ m and  $11.9\mu$ m. It burns rapidly with an intense white flame and the odor of camphor.

**Physical Form:** Yellowish-white matted mass of filaments, having the appearance of raw cotton; colorless liquid to semisolid (solution). It can be safely shipped only when wet with 25-30% water or alcohol.

**Preparation:** Cellulose nitrate, dissolved in a 50/50 solution of acetone and amyl acetate was recommended in the conservation literature since 1926 as a consolidant and adhesive (Koob 1982, 31-34). Cellulose nitrate film is formed by solvent evaporation.

Solubility: Solubility depends on degree of nitration. Low nitrogen form (pyroxylin) is soluble in ether-alcohol mixtures, acetone, methanol, and amyl acetate.

**pH**: Low pH indicates the presence of acid impurities remaining from nitration process of manufacture. Traces of acid will accelerate the hydrolysis of the cellulose nitrate and contribute to instability.

Softening Point/Glass Transition Temperature  $(T_g)$ :  $T_g$  is 100°C (212°F); flash point is 13°C (55°F); autoignition point 170°C (338°F).

**Refractive Index:**  $n_D = 1.49-1.51$ .

**Possible Additives:** Plasticizers such as camphor, tricresyl phosphate, dibutyl phthalate, diocyl phthalate, dibutyl adipate, and castor oil may be present. Eventual volatization of plasticizers contributes to shrinkage and brittleness.

Various stabilizers such as light absorbers, peroxide decomposers, inhibitor regenerators, or chain-terminating agents have been tested on cellulose nitrate, but have shown little success in arresting its decomposition (Koob 1982, 31).

**Health Hazards:** According to the literature, cellulose nitrates are non-toxic (Hawley 1977, 615). Breathing of powders, however, should be avoided. Highly flammable. High fire and explosion risk. Degraded cellulose nitrate releases acidic gases of nitrous oxides which are hazardous to humans and objects.

**Storage/Shelf Life:** Exposure to strong light causes cellulose nitrate to become acidic, forming nitric, formic, and oxalic acids, cyanogen and glucose. Will also decompose rapidly when exposed to moderate heat, air, and moisture. Volatile at less than 50% RH; more stable at over 70% RH. Store loosely packed, under refrigeration, away from light and moisture. Resistance to microbial deterioration is excellent.

### c. Aging Characteristics

In general, cellulose nitrate adhesive is strong and flexible when new, but after aging shows brittleness, shrinkage, and adhesive failure. Cellulose nitrate is primarily subject to thermal degradation. The reactivity brings about carbon-carbon bond cleavage and the production of aldehydes and ketones. The cleavage reaction results in lowering of chain length, and the addition reaction can result in cross-linking with subsequent insolubility in some formulations. The breakdown of cellulose nitrate in film form by ultraviolet irradiation is greatly accelerated by the presence of oxygen. The denitration reaction produces nitrogen dioxide to nitrogen oxide. These reaction products instigate an autocatalytic process. Cellulose nitrate may undergo hydrolysis by acids or by alkaline reagents, resulting in denitration and reduction in chain length (McBurney 1954). Paper objects stored in unstabilized cellulose nitrate envelopes have been destroyed by the products of decomposition, principally nitric acid. Upon aging, cellulose nitrate adhesive becomes very discolored and brittle, with loss of adhesion. Cellulose nitrate film is capable of spontaneous combustion under certain high temperature conditions, but concern is more reasonably directed toward motion picture film, where there is a high concentration of film packed together in a reel, rather than toward individual sheet negatives, which are generally separated from one another by paper envelopes (Ritzenthaler et al. 1984, 116-117).

Reversibility: Dissolves in ketones.

Appearance: Discoloration occurs when exposed to light and inflammability increases with exposure. In addition, degradation continues after removal from light. The color changes from clear to yellow to brown. The loss in strength and toughness can be almost complete before any change in hardness is detected (Koob 1982, 31).

Biological Attack: Excellent resistance to microbial deterioration.

# 46.3.2 Proteinaceous Adhesives

# A. Collagens

1. General Information

Adhesives such as gelatin, parchment size, hide glue, bone glue, and fish glue are collagen-based. Adhesives of animal origin have been used since ancient times. Fish glues have been in use since the eighteenth century. North American paper conservators generally use the purest forms, gelatin and parchment size, as consolidants, fixatives, and sizes and in the treatment of parchment. Other bone or hide glues are used by Japanese conservators. Russian isinglass, a pure fish collagen, is used extensively in Eastern Europe.

### a. Source

Collagen is the structural protein of connective tissue, bone, and skin in animals and fish. When these materials are heated in water a partially degraded protein, gelatin, is leached from them. Prolonged boiling also extracts impurities and forms darkly-colored compounds (Mills 1987, 75). Gelatin and parchment size are the result of shorter heating times. Longer heating times produce the less pure adhesives known as hide glue and bone glue. Fish collagen can be processed into either a more pure gelatin product or a fish glue (Skeist 1977, 153). "Photographic quality" gelatin for use in conservation is available through Kodak and Fisher Scientific. Food and pharmaceutical grades of gelatin are also available.

Animal collagen primarily contains the amino acids glycine, proline, and hydroxyproline. The amino acid sequences form three separate protein strands which are coiled together and bound by hydrogen bonding interaction. Upon boiling, scission of the hydrogen bonds occurs, the three strands separate and are bound to solvent water (Mills 1987, 75). Upon cooling, the strands will partially reform at a few sites, producing a network of strands linked together like a fishnet.(MB) The hydrolysis of collagen to gelatin may be represented by:

 $C_{102} H_{149} O_{38} N_{31} + H_2 O \stackrel{\sim}{\leftarrow} C_{102} H_{151} O_{39} N_{31}$ 

(Skeist 1977, 139).

### b. Chemical and Physical Properties

The chemical and physical properties of all collagen-based adhesives are basically consistent and thus are described together in this section. Identification: The hydroxyproline test is specific for animal-based adhesives. The ninhydrin test is sensitive to all proteins and is commonly used by paper conservators to detect proteinaceous adhesives. The biuret test is also used (Browning 1977, 103-104).

Molecular Weight: Animal-based adhesives have molecular weights reported to range from 20,000-250,000. Fish-based adhesives have an estimated molecular weight of 30,000-60,000 (Skeist 1977, 140, 153).

**Physical Form:** Animal and fish-based adhesives are available dry in granulated, sheet, or cake form, as cold liquid glues, or in jelly form. They are graded by viscosity in millipoises and jelly value in Bloom grams (Skeist 1977, 142). The lower the Bloom number, the weaker the gel. For example, Fisher Silver Label Sheet Gelatin has a Bloom number of 130. Fisher G-8 lab grade granular gelatin has a Bloom number of 275. Percent concentration cannot be compared between different sources. The collagen-based adhesives most commonly used in North American paper conservation are gelatin, in granulated or sheet form, and parchment size, which is prepared from parchment scraps. Color ranges from white to pale yellow for gelatin, to darker shades for less pure forms.

**Preparation:** Gelatin is prepared by dissolving the dry adhesive in warm water, or by swelling in cold water, then heating. Parchment size is made by cooking parchment scraps in water and straining. Upon cooling it forms a gel which can be sliced and dried for later use.

**Solubility:** Animal-based adhesives swell in cold water and pass into solution upon heating to 43.3°C (110°F). They are insoluble in organic solvents (Skeist 1977, 142, 153). Gelatin is soluble in glycerol and acetic acid (Windholz 1976, 564). Fish glue is miscible with alcohol and acetone. Gelatin solutions and parchment size can be diluted with ethanol or isopropyl alcohol.

**pH**: Hide glues are generally neutral (pH 6.5 - 7.4). Bone glues are generally slightly acidic, pH 5.8 - 6.3. The pH of fish glues ranges from 5.0 to 8.0 (Skeist 1977, 141, 153). The pH of gelatin and parchment size varies according to grade and/or preparation.

**Refractive Index:**  $n_D = 1.516-1.534$  for gelatin (Weast 1978, E-220).

**Possible Additives:** There are a number of additives which may be present in commercial formulations or may have been added traditionally for use (Skeist 1977). Commercial additives may include preservatives, defoaming agents, wetting agents, dispersing agents, plasticizers, and tannages. Formaldehyde was sometimes added to gelatin as a cross-linking (hardening) agent. Alum was added to alter viscosity and prevent spoilage.

Health Hazards: As proteinaceous, natural materials, collagen-based adhesives should pose no health hazards.

Storage/Shelf Life: Dry forms of collagen-based adhesives may be stored indefinitely. Liquid or gel forms are susceptible to microbial attack. Refrigeration delays this decay.

#### c. Aging Characteristics

Certain aging characteristics of animal-based adhesives have been studied by Deborah Ann Dyer and Margaret Ann Haupt of the Conservation Programme, Queens University. Their study "An Examination of Animal Glues" was presented as a student paper at the AIC Seventeenth Annual Meeting in May of 1989.

**Reversibility**: In theory, collagen-based adhesives should remain water soluble, especially in warm or hot water and alkaline water solutions.(CB) In practice, however, they may not. Decreased solubility may be caused by cross-linking, impurities, or additives. Proteolytic enzymes may be used to digest an otherwise insoluble collagen-based adhesive.

**pH**: Alum added to some gelatins in very small percentages (based on the dry weight of the gelatin) is likely to result in a neutral pH due to the buffering capabilities of the gelatin itself. (CB and Tim Barrett)

Appearance: Impure collagen-based adhesives may become brittle, shrink, or darken over time. Aged films can show cracking and flaking. Gelatin will darken slightly over time, although the effect is barely noticeable if dilute solutions are used. Prolonged storage of gelatin-sized paper in conditions of high humidity causes breakdown of size with discoloration and weakening of the paper.(SRA)

**Relative Strength**: Collagen-based adhesives may lose strength over time as a result of impurity or microbial attack.

**Biological Attack:** Collagen-based adhesives are susceptible to microbial attack. Manufacturers caution that alkaline gelatins are more susceptible to microbial attack.

# **B.** Caseins

# 1. General Information

Casein is a traditional adhesive which has been used since ancient times. It varies from the collagen adhesives in source, solubility, permanence, and strength. Casein has been used as a binder for pigments and painting grounds, as well as for paper coatings. It has been recommended in contemporary artist handbooks as a matte fixative for pastel (Wehlte 1975, 466).

### a. Source

Casein is the principal protein in milk. It is precipitated from skim milk by acidification to the isoelectric point, pH 4.5-4.8. Acidification may be achieved by the addition of an acid, the formation of lactic acid during fermentation, or the addition of rennet. A technical grade casein is available from Fisher Scientific.

Casein is a phosphoprotein, consisting of amino acids and containing 1% phosphorous (Mills 1987, 76). Unlike collagen, casein does not form any kind of network. It is this linear structure that causes it to be stiff and brittle.(MB)

# b. Chemical and Physical Properties

Identification: The Millon test and tryptophan test are specific for casein (Browning 1977, 105).

Molecular Weight: Alpha-casein, the protein which constitutes 75% of the casein proteins, has a molecular weight of 27,600 (Mills 1987, 77).

**Physical Form:** Casein is available as a white, amorphous powder or in granule form (Windholz 1976, 240).

**Preparation**: Casein adhesives may be prepared in one of two ways. The addition of lime to casein results in a water-resistant glue containing calcium caseinate. If lime is not added, but rather sodium salts provide the alkalinity, a non- water-resistant adhesive results. It is the second of these two methods of preparation that provides the paper adhesive. This casein adhesive is prepared by soaking dry casein in water, adding the alkali, then bringing the mixture to 71.1-82.2°C (160-180°F) (Skeist 1977, 168).

**Solubility:** Casein is insoluble in water, but forms a colloidal suspension in alkaline solutions. Organic amines, including alkyl amines, ethanolamine, and morpholine are solvents (Skeist 1977, 160).

pH:

### **Refractive Index:**

**Possible Additives:** Preservatives and plasticizers are often added to casein adhesives. Hardening agents, such as formaldehyde, are added to promote water-resistance. Additives may also be used to affect viscosity. Commercial formulations may be combinations of adhesives with casein as the major component (Skeist 1977, 160-162).

Health Hazards: Casein is generally regarded as safe by the Food and Drug Administration (FDA) (Skeist 1977, 159).

Storage/Shelf Life: Liquid casein adhesives are susceptible to microbial attack within a few days of preparation. Proteolytic enzymes naturally present in casein may also cause deterioration (Skeist 1977, 161).

#### c. Aging Characteristics

**Reversibility:** Casein adhesives may either be initially insoluble by nature of their preparation (see above) or may become insoluble due to cross-linking.

pH:

Appearance: Casein adhesives yellow over time.

**Relative Strength:** Casein adhesives are quite strong. This is mostly due to the high hydrogen bonding which promotes both cohesive and adhesive strength.(MB) They may lose strength due to microbial or enzymatic attack.

**Biological Attack:** Casein adhesives are subject to microbial and enzymatic attack.

# 46.3.3 Synthetic Polymer Adhesives

# A. Poly Vinyl Acetate Solutions (PVA)

# 1. General Information

PVA resins have been commercially available since the 1930s with dispersions available since the 1940s. They are used in conservation primarily as varnishes for paintings, media for inpainting, consolidants for insecure media, adhesives for facings, and as heat or solvent-activated adhesive films. PVA is a thermoplastic, odorless, non-toxic, essentially clear and colorless resin. It has a noncrystalline structure which is relatively branched rather than linear (Skeist 1973, 349, 352). PVA polymers are "among the limited number of polymers adapted by conservators since 1930 which have a common characteristic, they possess 'reasonable' flexibility without the need of added plasticizers" (Stolow, Feller, and Jones 1971, 130). Viscosity grade, solubility, and hardness vary with the MW of the polymer. Methods of adhesion include solvent evaporation, pressure activation, and heat sealing.

# a. Source

Vinyl acetate is synthesized from acetylene and acetic acid (Gettens and Stout 1966, 74). In the past, vinyl acetate has been polymerized in a free radical addition reaction (for description see Skeist 1973, 344-351). It is likely that industrial processes currently use the ionic reaction more than the free radical reaction since the former is more easily controlled.(MB) In the U.S. the principal supplier is the Union Carbide Company, makers of the Vinylite AYA series. Elsewhere other sources include: Gelva (Shawnigan Products Corporation, Canada); Mowilith (Farberwerke Hoechst AG, Federal Republic of Germany); Vinalak (Vinyl Products, Ltd., England); Vinavil (Societá Rhodiatoce, Italy); Rhodopas (Société des Usines Chimiques Rhône-Poulenc, France); Vinnapas (Wacker-Chemie GmbH, Federal Republic of Germany); Lamatec, unsupported adhesive film (Ademco, England) (see 46.3.3 F. Proprietary Formulations) (Feller, Stolow, and Jones 1985, 227).



## b. Chemical and Physical Properties

Identification: Dried PVA resin films can be identified using infrared spectrophotometry. However, the MW of the resin cannot be determined using this technique; thus, resin grades cannot be distinguished. Small amounts of additives are not detected by IR, because the strong PVA absorption peak in the spectra can mask others (Williams 1988, ARS No. 2313).

Molecular Weight: Poly vinyl acetate solid resins come in a range of molecular weights. Those made by the Union Carbide company are known as the AYA series: AYAA, AYAB, AYAC, AYAF, and AYAT. Physical properties vary considerably among poly vinyl acetate resins due primarily to differences in molecular weight (Skeist 1973, 352). These properties include solubility, viscosity, softening point, heat-seal temperature, tensile strength, and glass transition temperature. (See individual resins below.) The monomer vinyl acetate MW is 46. Molecular weight of AYA series is listed below:

AYAA	83,000
AYAB	No MW found
AYAC	12,500
AYAF	113,000
AYAT	167,000

Viscosity Grade: Viscosity grade is defined as the viscosity in centipoise of a resin solution in toluene at 21°C (70°F) at a concentration of 20% by weight (Feller, Stolow, and Jones 1985, 126).

AYAA	40 cps
AYAB	9 cps
AYAC	Not given
AYAF	80 cps
AYAT	167 cps

Water Absorption: Percent of water absorbed after sixteen hours at 25°C (77°F) (Union Carbide and Cargon Corp. n.d.).

AYAA	1.6%
AYAB	2.0%
AYAC	2.4%
AYAF	1.4%
AYAT	1.6%

Percent of water absorbed after 144 hours at 25°C (77°F).

AYAA	4.%
AYAB	7.3%
AYAC	8.3%
AYAF	3.6%
AYAT	3.6%

PVA films are permeable to water vapor and should not be chosen where protection from moisture is first consideration (Gettens 1935, 19).

**Physical Form:** Resins come in beads or dissolved in solvent as concentrated solutions. Resins and their solutions are colorless.

**Preparation:** Suspend resin beads in a cheesecloth bag inside a solvent container. Depending upon the solvent, the beads may need overnight or longer to dissolve at room temperature with occasional stirring.

Solubility: At room temperature resins are soluble in acetone, 95% ethanol, isopropanol, cyclohexanone, diacetone alcohol, MEK, methanol, ethyl acetate, trichloro-ethane, benzene, and 1:9 toluene. A small amount of water aids solubility in many solvents. (Partial list only. See Skeist 1973 for complete information.)

Softening Point/Glass Transition Temperature  $(T_{g})$ :

PVA-AYAA T<sub>g</sub>: 21°C (70°F); Softening point is 66°C (150.8°F) PVA-AYAB T<sub>g</sub>: 17°C (158°F); Softening point is 45°C (111.2°F) PVA-AYAC T<sub>g</sub>: 16°C (60.8°F); Softening point is 32°C (89.6°F) PVA-AYAF T<sub>g</sub>: 24°C (75.2°F); Softening point is 77°C (170.6°F) PVA-AYAT T<sub>g</sub>: 26°C (78.8°F); Softening point is 86.5°C (187°F)

**Refractive Index:**  $n_D = 1.4665$ .

**Possible Additives:** Proprietary formulations may contain additives such as, plasticizers, extenders, fillers, pigments, dyes, thickeners, solvents, and wetting agents. Common plasticizers are dibutyl phthalate and PVOH. Non-solvent diluents are used to modify viscosity and evaporation rate. Resins and gums are sometimes added to modify temperature sensitivity, tack, and water resistance (e.g., rosin and its derivatives, chlorinated diphenyl) (Union Carbide and Cargon Corp. n.d.).

Health Hazards: Polymers are non-toxic, but organic solvents present their associated hazards.

Storage/Shelf Life: Resins are not measurably affected by sunlight, air, or ultraviolet light, according to Skeist and early conservation literature. However, see Aging Characteristics, below for a more recent appraisal. PVA resins absorb a small amount of moisture (Skeist 1973, 352).

#### c. Aging Characteristics

PVA is a stable resin showing excellent aging properties. These have been reported thoroughly in the conservation literature (see Feller, Stolow, and Jones 1985). The resin has been shown to be highly resistant to deterioration at normal temperatures and to be resistant to reaction with dilute acids and alkalis. The resin does not hydrolyse and has an acid number of 0 (Gettens 1935, 18). If there are additives in the PVA, volatilization or migration of external plasticizer may lead to embrittlement of bond, staining of substrate, insolubility, or darkened color.

**Reversibility:** The branched polymer structure of PVA with additives can continue to bond over time and cross-link making resolubility difficult. The purity of the product directly affects its aging characteristics. Heat or aromatic solvents should reverse a pure PVA film which has been used in a conservation application (e.g., to adhere a lining or to consolidate a paint film). To reverse a known PVA applied as a consolidant, see AIC/BPG/PCC 1988 23. Consolidation/Fixing/Facing, 9. PVA has been shown to be dissolvable from objects after more than thirty to forty years (Cronyn and Horie 1985, 92). The greater challenge to the conservator is reversing an unknown PVA adhesive which has been applied to paper: the adhesive is often no longer soluble in the complete range of solvents mentioned above. Application of heat, ethyl acetate, or acetone and sometimes water can be successful in these instances. Appearance: PVA resin is not appreciably affected by UV light and does not measurably break down and discolor when exposed to strong sunlight (see Feller, Stolow, and Jones 1985).

Newer information shows that PVA is not totally transparent to UV light, according to its spectrum. Since everything is affected by air and light eventually, it may be that some early tests are overly optimistic about the aging properties of PVA. For example, what Skeist considers "unaffected" is probably unacceptable to those in the conservation field.(MB)

**Relative Strength:** PVA resins are flexible and strong (Stolow, Feller, and Jones 1985, 130-133).

**Biological Attack:** Not subject to biological attack.

# **B.** Poly Vinyl Acetate Dispersions (PVA)

# 1. General Information

PVA dispersions were developed in the 1940s, although major technical developments did not occur until the 1950s and 1960s (Skeist 1977, 465). Dispersions consist of minute particles of PVA polymer suspended in water. Polymer dispersions are frequently referred to as emulsions, which is a misnomer. Emulsions are liquid/liquid suspensions, while dispersions are solid/liquid suspensions (DeWitte, Floroquin, and Goessens-Landrie 1984, 32; Feller, Stolow, and Jones 1985, 218; Howells et al. 1984, 36).

Unlike PVA solutions, PVA dispersions have low viscosities even at high concentration of solids and at high molecular weights. PVA dispersions form strong, flexible bonds to many materials, although complete film formation may take several months at the proper temperature (Feller, Stolow, and Jones 1985, 221). The minimum film formation temperature (MFFT) varies slightly with different manufacturers' formulations, but in general the MFFT and Glass Transition Temperature (T<sub>g</sub>) fall in the range of 0-20°C (32-68°F). Homopolymers of PVA (e.g., CM-1,-3) have a higher MFFT and T<sub>g</sub> of 20-30°C (68-86°F) (Horie 1987, 95, 183). Copolymers of PVA, such as ethylene vinyl acetate, tend to have a lower T<sub>g</sub> of -10-10°C (14-50°F). PVA dispersion polymers can be either homopolymers or copolymers. Homopolymers require the addition of an external plasticizer, which make them susceptible to those usual aging problems typically associated with externally plasticized materials: embrittlement, discoloration, insolubility, staining. Copolymers were developed to overcome these problems with the comonomer acting as an internal, and therefore, stable plasticizer.

Dispersions have many industrial applications as adhesives, sizing/coating agents, ink binders, etc. In conservation, PVA dispersions have been used as adhesives in book binding and box making; a lining adhesive for paintings; an additive to paste for mending, mounting, hinging; a heat-activated adhesive; and a consolidant.

a. Source

The monomer vinyl acetate is synthesized from acetylene and acetic acid (see 46.3.3 A Poly Vinyl Acetate Solutions). Poly vinyl acetate dispersions are made by emulsion polymerization. Many commercial grades are available, made by forty to fifty manufacturers (Skeist 1977, 466). Major U.S. suppliers of dispersions commonly used in conservation include: Jade, Archivart, Conservation Materials, Reichhold Chemicals, and Talas.



Poly Vinyl Acetate Repeating Unit Poly Vinyl Acetate Ethylene Comonomer Unit

(Copolymers have blocks of PVA and polyethylene joined together, or random patterns of vinyl acetate and ethylene. The above diagram at right represents one possible combination of the ethylene and vinyl acetate groups.)

# b. Chemical and Physical Properties

Identification: The PVA dispersion or dried film swollen with water, stains orange-red with KI/I<sub>2</sub>; additives such as dextrin and other starches may stain blue, the characteristic positive reaction for starch. The dried film may swell in water or organic solvent.

Molecular Weight: PVA dispersions come in a range of molecular weights and viscosities.

Physical Form: PVA dispersions are viscous white liquids.

**Preparation:** Dispersions can be used directly from the supplied stock. Some can be diluted with water, although over-dilution can interfere with proper film formation and adhesive tack. Some dispersions can be further diluted with organic solvents.

Solubility: See Preparation, above.

**pH**: In general, the pH of commercially available dispersions is 4-7 in the liquid state, near neutral in the dried state, and 4.5-6 after artificial oven aging (Baer et al. 1975, 20; Baer, Indictor, and Phelan 1975, 127; De Witte, Florquin, Goessens-Landrie 1984, 32; Horie 1987, 95).

**Possible Additives:** Commercially available dispersions contain: 30-50% polymer solids, 1-3% surface active agent, 0-3% protective colloid, 1-3% initiator, 0-1% modifier, 0-5% plasticizer, 0-1% buffer, and 50-70% water (DeWitte, Florquin, and Goessens-Landrie 1984, 32). Poly vinyl alcohol is the usual protective colloid. Solvents (usually toluene), natural gums and starches, as well as synthetic colloids (various cellulose ethers) are used as thickeners. Buffers, if included, might be calcium carbonate or calcium acetate (Horie 1987, 94). Fungicides are added to many formulations to reduce the chance of mold growth. Additives may affect aging characteristics radically and may be subject to change in industry due to changes in supply, economics, etc. (DeWitte, Florquin, and Goessens-Landrie 1984).

The most common external plasticizer used is dibutyl phthalate. PVA dispersions can be internally plasticized by copolymerization with ethylene (e.g., Elvace dispersion) or poly vinyl alcohol. Internally plasticized PVA dispersions made by co-polymerization are considered more stable than formulations containing plasticizers added to the dispersion. Vinyl acetateethylene copolymer dispersions became available commercially in 1966 (Skeist 1977, 484).

Storage/Shelf Life: In general, the shelf life for most PVA dispersions is nine to twelve months at  $4.44-49^{\circ}$ C ( $40-120^{\circ}$ F) (Baer, Indictor, and Phelan 1971, 37). PVA dispersions have limited shelf life because they react to slowly release acetic acid (Horie 1987, 94). Dispersions are susceptible to damage by temperatures less than  $4.44^{\circ}$ C ( $40^{\circ}$ F). Product literature must be consulted as shelf life, storage temperatures, and shelf life of opened stocks varies with formulation. PVA dispersions can support mold growth.

#### c. Aging Characteristics

Films become tacky at high temperatures and are subject to cold flow due to the low  $T_g$  of the polymer. Volatilization or migration of external plasticizer leads to embrittlement, staining, insolubility, and yellowing. At longer aging times, the color changes and mechanical strength tests indicate that poly vinyl acetate dispersions are not, in general, recommended adhesives for paper objects. The range of behavior is quite marked from product to product and may arise from differences in MW, in the quantity and kind of additives, or in the initial ratio of acetate and alcohol groups (Phelan, Baer, and Indictor 1975).

**Reversibility:** Reversibility is a function of mode of application. Dispersions applied directly to paper substrates may be very difficult to remove. Dispersions which are dried as films and applied with heat to a paper substrate are more easily reversible. Recently formed films from PVA dispersions may be swollen in water and solvents (e.g., ethanol, acetone, toluene, etc.). Swelling decreases with the age of the film and varies somewhat with formulation (Baer, Indictor, and Phelen 1975, 134; Howells et al. 1984, 39-40). Aged films may be difficult to swell with solvents and difficult to remove from paper substrates without damage. Some workers have found that methylene chloride was needed just to swell an aged PVA dispersion prior to mechanical removal.(TJV) PVA dispersions are susceptible to thermal degradation and the production of acetic acid.(PV)

One source suggests that the insolubility of films formed from PVA dispersions stabilized with PVOH is caused by the tendency of PVOH to cross-link (Horie 1987, 99).

Appearance: Certain formulations yellow with age, according to accelerated aging tests (Baer, Indictor, and Phelan 1975, 130). Additives may make some formulations more susceptible to yellowing (Howells et al. 1984, 38, 42). In general, dispersions with no additives, and those that are internally plasticized, are less likely to discolor.

In unpublished tests at L.A. County Museum of Art, the shelf life appeared to influence yellowing upon aging dramatically. Newer batches of adhesive exhibited less discoloration upon artificial aging.(PV)

**Relative Strength:** Dried films of PVA dispersions can be flexible and strong. However, the loss of external plasticizer, when present can lead to embrittlement. When applied to a paper substrate, a PVA dispersion may penetrate moderately or remain on the surface. The degree of penetration depends on the size of the dispersed polymer particle and the polymer's molecular weight.

# 2. Jade 403

# a. Source

Composed of 80/20 vinyl acetate/ethylene copolymer; 50% solids, 6000-7000 cps, internally plasticized. Composed of 75/25 vinyl alcohol/vinyl acetate copolymer.(PV) Available from Jade Adhesives, 2929 Campbell Ave., Chicago, IL 60618. (Comparable formulation is Mowolith DM5 made by Hoechst.)

# b. Chemical and Physical Properties

Physical Form: A viscous white liquid.

**pH**: Neutral; 5.8 aqueous (PV) 6.6 as dry, unaged film (Baer, Indictor, and Phelan 1975, 127).

**Possible Additives:** Possible additives include poly vinyl alcohol/poly vinyl acetate, poly acrylate, possibly polyamide (Down and Williams 1988).

Health Hazards: Residual monomer is considered toxic.

Storage/Shelf Life: One year at 4.44-49°C (40-120°F).

#### c. Aging Characteristics

(The information below is from Baer, Indictor, and Phelan 1975, 121-138.)

**Reversibility**: Becomes less soluble, but swells in water, ethanol, and toluene.

pH: pH drops to 5.7 after accelerated aging.

Appearance: Becomes slightly yellow.

# 3. Jade 454

# a. Source

Composed of 80/20 vinyl acetate/ethylene copolymer.(PV) Composed of 38% solids, 40000-45000 cps, internally plasticized. Available from Jade Adhesives, 2929 Campbell Ave., Chicago, IL 60618.

# b. Chemical and Physical Properties

Physical Form: A viscous white liquid.

**pH:** 3.84 aqueous at 22°C (71.6°F).(PV) There is no data available on unaged film.

**Possible Additives:** Possible additives include plasticizers and solvents (toluene and cellosolve acetate). Other possible additives are dextrin and poly acrylate resin.(PV)

Storage/Shelf Life: One year at 4.44-49°C (40-120°F).

#### c. Aging Characteristics

(The information below is from Baer, Indictor, and Phelan 1975, 121-138.)

**Reversibility**: Becomes less soluble, but swells in water and toluene.

**pH**: Drops to 5.4 after accelerated aging.

Appearance: Becomes yellow-brown.

### 4. Archivart Reversible Adhesive A-1023

# a. Source

Poly vinyl acetate homopolymer (Process Materials 1983, Bull. No. CP-114-AD). Composed of 63% solids, 16000-18000 cps, homopolymer, medium MW (product literature). Archivart, 4226 Howard Ave., Kensington, MD 20895. Sold as Promacto A-1023 by Talas.

# b. Chemical and Physical Properties

Physical Form: A viscous white liquid.

**Preparation**: Dilute by 3-5% with water, can be diluted by 40% with cold water.

pH: 4-6 for liquid state and may be supplied neutralized; pH is 5.6 for dry film (Baer, Indictor, and Phelan 1975, 122, 127).

**Possible Additives:** Dibutyl phthalate plasticizer, protective colloid, stabilizers, detoxicants, and inhibitors (product literature).

Storage/Shelf Life: Shelf life is nine to twelve months stored at 4.44-49°C (40-120°F) (product literature).

### c. Aging Characteristics

(The information below is from Baer, Indictor, and Phelan 1975, 121-138.)

**Reversibility**: According to product literature, dried film is resoluble in cold water. Swells in water, less soluble in toluene.

pH: Drops to 4.5 after accelerated aging.

Appearance: Becomes yellow-brown.

# 5. CM Bond, CM-1

#### a. Source

Vinyl acetate homopolymer.(PV) Composed of 54-56% solids, 300-600 cps, 550,000-650,000 MW. Conservation Materials, 240 Freeport Blvd., Box 2884, Sparks, NV 89431. (Manufactured by W.R. Grace and Co.)

# b. Chemical and Physical Properties

Physical Form: A viscous white liquid.

pH: 5-7 according to product literature.

Possible Additives: No plasticizer.

Storage/Shelf Life: Nine to twelve months,  $4.44-49^{\circ}$ C (40-120°F).

c. Aging Characteristics Long term aging studies not available.

**Reversibility**:

pH:

**Appearance:** May yellow with age (Conservation Materials Catalog n.d.).

# 6. CM Bond, CM-2

a. Source

Homopolymer, 54-56% solids, 1500-2000 cps, 200,000-300,000 MW (product literature). Composed of 90/10 vinyl acetate/vinyl alcohol copolymer.(PV) Conservation Materials, 240 Freeport Blvd., Box 2884, Sparks, NV 89431. (Manufactured by W.R. Grace and Co.)

# b. Chemical and Physical Properties

Physical Form: A viscous white liquid.

**pH**: 4.5-6.

Possible Additives: No plasticizer

Storage/Shelf Life: Nine to twelve months, 4.44-49°C (40-120°F).

c. Aging Characteristics Long term aging studies not available.

**Reversibility**:

pH:

Appearance: Slight yellowing.(PV)

# 7. CM Bond, CM-3

a. Source

Composed of 75/25 vinyl alcohol/vinyl acetate copolymer.(PV) Homopolymer, 54-56% solids, 2300-2700 cps, 550,000-650,000 MW (product literature). Conservation Materials, 240 Freeport Blvd., Box 2884, Sparks, NV 89431. (Manufactured by W.R. Grace and Co.)

b. Chemical and Physical Properties

Physical Form: A viscous white liquid.

**pH:** 5-7.

Possible Additives: No plasticizer.

Storage/Shelf Life: Nine to twelve months, 4.44-49°C (40-120°F).

# c. Aging Characteristics

Long term aging studies not available.

Reversibility:

pH:

Appearance: Slight yellowing after 1.45 years, 1400 lux at 22- $25^{\circ}$ C (71.6-77°F) at 45% RH.(PV)

# 8. CM Bond, CM-4

# a. Source

Vinyl alcohol/vinyl acetate copolymer. Composed of 54-56% solids, 300-700 cps, 175,000-225,000 MW (product literature). Conservation Materials, 240 Freeport Blvd., Box 2884, Sparks, NV 89431. (Manufactured by W.R. Grace and Co.)

## b. Chemical and Physical Properties

Physical Form: A viscous white liquid.

**Preparation:** Can be heat-activated at  $93.3^{\circ}$ C (200°F), heat sealable.

**pH**: 4-6.5.

Possible Additives: No plasticizer.

Storage/Shelf Life: Nine to twelve months, 4.4-49°C (40-120°F).

c. Aging Characteristics

Long term aging studies not available.

**Reversibility:** Product literature says it is reversible in methanol.

# 9. Elvace 40-704

#### a. Source

Vinyl acetate-ethylene copolymer, less than 1% vinyl acetate monomer. Composed of 55% solids, 3500-4000 cps. Reichhold Chemicals Inc. Dover, DE. (Formerly Elvace 1874, distributed by DuPont; Vinamul 3252 in U.K.)

# b. Chemical and Physical Properties

Physical Form: A viscous white liquid.

**pH**: 4.5-5.5 (Baer et al. 1975, 15).

Softening Point/Glass Transition Temperature  $(T_g)$ :  $T_g$  is 5°C (41°F), MFFT is 3°C (37.4°F).

# **Possible Additives:**

Storage/Shelf Life: Use within five months of shipment. Store at 2-43°C (35-110°F). Ideal storage is at 22.2°C (72°F).(PV)

### c. Aging Characteristics

Long term aging studies not available. Studies on Vinamul 3252 done by Howells et al. 1984. Long term aging studies done on Elvace 1875 by Baer et al. 1975, 15). **Reversibility**: Heat activation, swells in ethanol.(PV) Slight reduction of solubility in accelerated aging studies of Vinamul 3252 (Howells et al. 1984, 40).

Appearance: Unpublished research conducted at the Los Angeles County Museum of Art showed little discoloration in artificial aging tests.(PV) Excellent color stability of Elvace 1874 (Baer et al. 1975, 15) and Vinamul 3252 (Howells et al. 1984, 38).

# 10. Texicote VJC 555

# a. Source

Composed of 54-56% solids. Trylon Ltd, Distributed by Talas, 213 W. 35 St., NY, NY 10001-7744. (No longer available through this supplier; may have been discontinued.)

# b. Chemical and Physical Properties

Physical Form: A viscous white liquid.

**pH**: Unaged film pH is 6.4 (Baer, Indictor, and Phelan 1975, 127).

**Possible Additives:** Fifteen percent ethylhexyl acrylate, plasticizer, inhibitor.

Storage/Shelf Life: One year at 4.44-32°C (40-90°F).

### c. Aging Characteristics

See Baer, Indictor, and Phelan 1975, 121-138 for more information.

**Reversibility**: Very insoluble. Some swelling in toluene (Baer, Indictor, and Phelan 1975, 133).

**pH:** Neutral, after accelerated aging pH is 7.0 (Baer, Indictor, and Phelan 1975, 127).

Appearance: Slight yellowing (Baer, Indictor, and Phelan 1975, 129).

#### C. Poly Vinyl Alcohol Solutions (PVOH)

#### 1. General Information

Poly vinyl alcohol thermoplastic resin solutions have been commercially available since the 1940s, but were not used in conservation until the 1950s. They have been used by conservators as adhesives, consolidants, coatings, sizes, and filling materials. In industry they have been used for these purposes and as emulsifiers, binders, barriers, and stabilizers. In adhesive formulations, they are often found in combination with poly vinyl acetate emulsions. The various grades of PVOH resins provide films that differ in water and solvent resistance, adhesion, flexibility, and elongation (Skeist 1977, 473).

#### a. Source

Poly vinyl alcohol is produced by replacing ester groups on a PVA resin with hydroxyl groups involving alcoholysis in methanol or ethanol using an acid or alkaline catalyst. The resins are described by percent hydrolysis. Some grades are fully hydrolyzed while others contain residual acetate groups (4-40% acetate groups). Characteristics of the solutions vary due to the percent hydrolysis and the molecular weight of the PVA resin used in manufacture (Skeist 1977, 472). Brand names and manufacturers include: Alcotex (Revertex); Elvanol (DuPont); Lemol (Borden); Gelvatol (Shawinigan); Gohsenol (Nippon Synthetic Chemicals, Tokyo); Mowiol (Hoechst), Polyviol (Wacker); Poval (Kurashiki); Rhodoviol (Rhone-Poulenc); and Vinavilol (Montecatini) (UNESCO 1968, 312).

> -CH-CH<sub>2</sub> | OH

Repeating Unit of PVOH.

# b. Chemical and Physical Properties

Identification: When stained with iodine solution PVOH produces a green color (Horie 1983, 50). If borates are present, as found in some paper coatings, or if added at the time of the test, PVOH forms a blue lake with iodine solution. (In contrast, starch gives a dull blue color) (Browning 1977, 279, 280).

Molecular Weight: Numerous grades ranging in weight from 2000-130,000 (Masschelein-Kleiner 1984, 72).

**Physical Form:** Available as a white powder.

**Preparation:** PVOH is generally prepared by dispersing powder in cold water and heating solution if necessary. Necessity for heating depends upon the resin grade.

**Solubility:** PVOH powder is soluble in water, but not in organic solvents. Low molecular weight, low (ca. 70-80) % hydrolyzed grades dissolve in water at room temperature; medium molecular weight, medium (ca. 80-95) % hydrolyzed grades dissolve in warm water (60-80°C/140-176°F); and high molecular weight, high (ca. 95-100) % hydrolyzed grades dissolve only in hot water (80-90°C/176-194°F) and on cooling and standing will either gel or precipitate (Skeist 1977, 473; Horie 1987, 97). PVOH softens or dissolves in acids or bases (Argana 1962, 92).

Molecular weight and percent hydrolysis are not the same. For example, Gelvatol 20-30 and 1-30 have similar MWs (about 90000) but different percent hydrolyzed (about 88 and 99 respectively). The lower the MW and the higher the percent hydrolysis, the more water soluble the polymer will be. A medium MW, 100% hydrolyzed PVOH will be soluble in cold water.(MB)

pH: 6-8 for all grades (Argana 1962, 91). 4.5-7 (Horie 1987, 97).

Softening Point/Glass Transition Temperature  $(T_g)$ :  $T_g$  is approximately 85°C (185°F) for high viscosity grades and 75°C (167°F) or less for lower viscosity grades. Softening point is 120-150°C (248-302°F) (UNESCO 1968, 311, 320). Heat-activated bonds can be made between 160-180°C (320-356°F) (Modern Packaging 1927).

**Refractive Index**:  $n_D = 1.49-1.53$ .

**Possible Additives:** PVA resin. Commercial products used as coating binders may contain boric acid or borax.(CS)

Health Hazards: None cited in literature.

Storage/Shelf Life: No deterioration over several years (Argana 1962, 92). Solutions are vulnerable to mold (Torraca 1968, 311; Windholz 1976).

# c. Aging Characteristics

**Reversibility:** In the short term, some PVOH resin films are soluble in water or hot water. As they age, they cross-link and their solubility decreases to insolubility. Reversibility is limited when applied to paper and textiles because permanent bonding between the resin and these substrates occurs. PVOH can react with inorganic salts, polyaldehydes, polyacids, and some dyes to become insoluble, especially with exposure to light. In slightly acidic or alkaline conditions, the chains will cross-link and become insoluble (Horie 1987, 77, 97). Horie suggests that the insolubility of films formed from PVA dispersions stabilized with PVOH is caused by this tendency of PVOH to cross-link (Horie 1987, 97).

#### pH:

Appearance: Good stability to ultraviolet, but may cross-link on light aging (Horie 1987, 97). Will yellow and become insoluble from heat above 100°C (212°F) (UNESCO 1968, 311). Grades with greater than 93% hydrolysis shrink upon drying (Horie 1987, 97).

**Relative Strength:** Strength varies depending upon percent hydrolysis and molecular weight. Tensile strength is greatest for grades fully hydrolysed. Prolonged exposure to light results in loss of strength due to chain breakage. Strength depends upon humidity (UNESCO 1968, 311-312).

**Biological Attack:** Dried films exhibit strong resistance to mold (Skeist 1977, 472).

#### **D.** Acrylic Resin Solutions

#### **1. General Information**

Acrylic polymers were developed for industrial use in 1931. The Fogg Art Museum began experimental use of the methacrylate polymers Lucite 44 and 45 (now Elvacite 2044 and 2045) in the early 1930s. These n-butyl and isobutyl methacrylates are the acrylic polymers in longest use in conservation. In 1963, Robert Feller brought attention to the outstanding characteristics of Acryloid B-72, an ethyl methacrylate methyl acrylate copolymer (Feller, Stolow, and Jones 1985, 124). Internal plasticization gives these resins excellent flexibility, especially for softer polymers. Typical uses of acrylic resins are as consolidants, fixatives, facing adhesives, and surface coatings. Acrylic resin solutions are strong, durable adhesives.

### a. Source

Acrylic resins are addition polymers of acrylic and methacrylic acid and their esters. Rohm and Haas, Philadelphia, manufactures a number of acrylic resins under the tradename Acryloid (called Paraloid in Europe). DuPont manufactures acrylic resins under the name Elvacite and previously also used the tradenames Hypalon and Lucite. Certain resins are also sold as proprietary aerosol sprays: Krylon sprays (Borden Company) and Lascaux-Fix (A.K. Diethelm AG). The Borden Company has marketed several proprietary resin aerosol sprays under the brandname Krylon, see 46.3.3 F. Proprietary Formulations. Assorted European tradenames for acrylic resins include Plexisol and Plexigum (Röhm and Haas, GmbH); Synacryl, formerly called Bedacryl (Cray Valley); Pliantex (Frank W. Joel, Ltd.); and Lascaux (A.K. Diethelm AG, Bruettisellen, Switzerland).



Methacrylate and Acrylate Repeating Units

Poly (methyl methacrylate)  $R = CH_3$ -Poly (ethyl methacrylate)  $R = CH_3CH_2$ -Poly (n-butyl methacrylate)  $R = CH_3CH_2CH_2CH_2$ -Poly (isobutyl methacrylate)

$$R = CH_{3}$$

$$|$$

$$CH_{2}$$

$$|$$

$$CH_{2}$$

$$|$$

$$CH_{3}$$

b. Chemical and Physical Properties

Identification: No simple spot tests are known. Browning 1977, 241, describes analytic methods to distinguish methacrylate from acrylate resins. Starch is added to some proprietary brands.(CS) Its presence is detected by the  $KI/I_2$  test.

**Physical Form:** Available as colorless, transparent resin beads or dissolved in solvents in concentrated solutions.

**Preparation**: Suspend beads in cheesecloth inside a container of solvent for twenty-four hours or more.

Solubility: Initially soluble in toluene, xylene, acetone, MEK, ethyl acetate, and amyl acetate. For comparative viscosities of different resins see UNESCO 1968, 314; Feller, Stolow, and Jones 1985, 124.

pH: 4-6.5 (Down and Williams 1988, 4).

Softening Point/Glass Transition Temperature  $(T_g)$ :  $T_g$  depends on molecular weight. Approximate temperatures are n-Butyl 22°C (71.6°F), ethyl 65°C (149°F), methyl 105°C (221°F) (UNESCO 1968, 313). Resin hardness can be correlated to pencil hardness: B-72 and B-82=H, B-67=HB, F-10=B (Rohm and Haas 1975, 17; see Feller, Stolow, and Jones 1985, 130).

**Refractive Index:**  $n_D$  = approximately 1.48-1.49 (de la Rie 1987, 3; Tennent 1984, 206).

Health Hazards: Resins are not known to be hazardous, but solvents require appropriate safety measures.

Storage/Shelf Life: Isoamyl and n-butyl resins develop a butyric odor and cross-link more readily when old (Feller 1972, 205).

### c. Aging Characteristics

**Reversibility:** Acryloid B-72 remains soluble and does not measurably cross-link. Other acrylic resins tend to cross-link through heat, ultraviolet and visible light exposure; particularly isoamyl, n-butyl, and isobutyl methacrylate (Feller, Stolow, and Jones 1985, 156-165). Horie states that methacrylates are more likely to cross-link if exposed above or near their glass transition temperatures (Horie 1987, 104).

**pH**: Changes in pH after 2.4 years dark aging and 1.9 years light aging are given below.

Appearance: Resins remain colorless and transparent. Acrylic glazing exposed to concentrated thymol has been observed to yellow (Daniels and Boyd 1986, 156).

**Relative Strength:** 

**Biological Attack:** 

2. Poly (ethyl methacrylate) poly (methyl acrylate) copolymer (PEMA/PMA) (Acryloid B-72)

# a. Source

Sold under the tradename Acryloid B-72, currently is a 70% ethyl methacrylate, 30% methyl acrylate copolymer made by Rohm and Haas, Philadelphia. A previous formulation was 68:32 and soluble in slightly less polar solvents (Horie 1987, 106).



Methyl Acrylate and Ethyl Methacrylate Repeating Units

# b. Chemical and Physical Properties

Identification:

**Physical Form:** Resin beads or 50% solids in toluene.

Preparation: See 46.3.3 D. General Information.

Solubility: B-72 is unique among acrylic resins in having a high tolerance for ethanol, though resin is insoluble in isopropanol. Ethanol dispersions will be cloudy, but will dry to clear, coherent films (Rohm and Haas 1975, 15).

pH: 6.41 (Down and Williams 1988, 5).

Softening Point/Glass Transition Temperature (T<sub>g</sub>):  $T_g$  is 40°C (104°F).

**Refractive Index:**  $n_D = 1.487$  (Rene de la Rie 1987, 3). B-72 cast from solution nD = 1.481 (Tennent 1984, 206).

Health Hazards: See 46.3.3 D. General Information.

Storage/Shelf Life: Indefinite shelf life.

c. Aging Characteristics

**Reversibility:** Remains soluble upon aging according to extensive studies by Robert Feller (see 46.5 Bibliography).

pH: Unchanged in dark aging, dropped to 5.93 after light aging (Down and Williams 1988, 5).

Appearance: The resin remains clear and colorless.

- 3. Poly (isobutyl methacrylate) (PiBMA) (Acryloid B-67)
  - a. Source

Sold under tradenames of Acryloid B-67 (Rohm and Haas) and Elvacite 2045 and 2046 (DuPont; formerly Lucite 45 and Lucite 46).



Isobutyl Methacrylate Repeating Unit

b. Chemical and Physical Properties

Identification:

**Physical Form:** B-67 is available in beads or dissolved in VMP naphtha or mineral thinner (45% solids).

Preparation: See 46.3.3 D. General Information.

**Solubility:** Soluble in less polar solvents than Acryloid B-72. Soluble in most solvents except ethanol, ethylene glycol, and dimethyl formamide (DMF). Insoluble in isopropanol.

pH: 6.68 (Down and Williams 1988, 5).

**Softening Point/Glass Transition Temperature (T<sub>a</sub>):** T<sub>g</sub> for B-67 is 50°C (122°F).
**Refractive Index:**  $n_{D} = 1.477$  (Rene de la Rie 1987, 3), for B-67  $n_{D} = 1.486$  (Tennent 1984, 206).

Health Hazards: See 46.3.3 D. General Information.

Storage/Shelf Life

Some conservators have found that solutions of B-67 yellow.(SRA)

c. Aging Characteristics

**Reversibility:** Solubility decreases with accelerated light aging and with natural light aging (Feller, Stolow, and Jones 1985, 157, 159). Feller speculated that B-67 may contain an inhibitor to give it resistance to cross-linking (Feller 1972, 205).

**pH**: Dropped to 6.42 in dark aging, increased to 7.41 in light aging (Down and Williams 1988, 5).

## Appearance:

- 4. Poly (n-butyl methacrylate) (PBMA) (Acryloid F-10)
  - a. Source

Sold under the tradenames of Acryloid F-10 (Rohm and Haas) and Elvacite 2044 (DuPont; formerly Lucite 44). A proprietary aerosol spray called Krylon 1301 (Borden Co.) contains a resin resembling n-butyl methacrylate. European tradenames include Synocryl 9122x (Cray Valley Products Ltd.) (formerly called Bedacryl 122x, Imperial Chemical Industries Ltd.); Plexisol P550 (Röhm and Haas GmbH); and Lascaux P550-40 TB (A.K. Diethelm AG). It is not known whether resin is used by paper conservators, though its properties have been documented.



n-Butyl Methacrylate Repeating Unit

# b. Chemical and Physical Properties

Identification:

**Physical Form:** A colorless and transparent resin, F-10 is available at 40% solids in mineral thinner/Amsco F at solvent ratio 9:1.

## Preparation: See 46.3.3 D. General Information.

Solubility: Soluble in petroleum hydrocarbons. Solubility parallels that of B-67.

pH: 6.73 for F-10 (Down and Williams 1988, 5).

Softening Point/Glass Transition Temperature  $(T_g)$ :  $T_g$  is 20°C (68°F) for F-10, 15°C (59°F) for Lucite 2044.

**Refractive Index:**  $n_D = 1.483$  (de la Rie 1987, 3),  $n_D = 1.476$  for F-10 (Tennent 1984, 206).

Health Hazards: See 46.3.3 D. General Information.

Storage/Shelf Life: On long standing in the container, "old" polymer develops butyric odor and cross-links more readily (Feller 1972, 205).

c. Aging Characteristics

**Reversibility**: Solubility decreases with accelerated light aging (Feller, Stolow, and Jones 1985, 157).

**pH**: Dropped to 6.57 in dark aging, 6.01 in light aging (F-10) (Down and Williams 1988, 5).

Appearance: Film softness makes it prone to collect dirt (Feller 1972, 201; Welsh 1980, 142).

# 5. Poly (ethyl acrylate) Poly (methyl methacrylate) copolymer (PEA/PMMA) (Acryloid B-82)

# a. Source

Sold under the tradename of Acryloid B-82 (Rohm and Haas) (50% ethyl acrylate), Elvacite 2008, 2009, 2010, and 2041, (DuPont) and Pliantex (Frank W. Joel, Ltd.) (more than 66% ethyl acrylate). (Values for ethyl acrylate percentages from Down and Williams 1988, 2.) Rohm and Haas describe B-82 as a low cost acrylic with films similar in properties to B-72. It is not known whether this resin is used by paper conservators, though its properties are documented.

Η	CH <sub>3</sub>
C-CH2	$C-CH_2$
COOCH <sub>2</sub> CH <sub>3</sub>	COOCH <sub>3</sub>

Ethyl Acrylate and Methyl Methacrylate Repeating Units

b. Chemical and Physical Properties

Identification:

**Physical Form:** B-82 is available as resin beads and 40% and 50% solids in toluene.

Preparation: See 46.3.3 D. General Information.

Solubility: Parallels that of B-72.

**pH**: 6.41 for B-82 (Down and Williams 1988, 5).

Softening Point/Glass Transition Temperature  $(T_g)$ :  $T_g 35^{\circ}C$  (95°F) for B-82.

**Refractive Index:**  $n_D = 1.482$  for B-82 (Tennent 1984, 206).

Health Hazards: See 46.3.3 D. General Information.

Storage/Shelf Life:

#### c. Aging Characteristics

**Reversibility:** Solubility decreases and requires a strong, more polar solvent for removal (Feller, Stolow, and Jones 1985, 161).

**pH**: Rises to 6.61 on dark aging, 6.65 on light aging (B-82) (Down and Williams 1988, 5).

## Appearance:

#### E. Acrylic Resin Dispersions

# 1. General Information

Acrylic acid was first synthesized in 1843, developed through the early twentieth century, and produced commercially in 1930 (Skeist 1977, 528). Acrylics have been used since the 1950s in the paper industry as coatings and adhesives. In 1953, acrylic dispersions were formulated for use as painting media both for artists and industry. Acrylic dispersions used in conservation have been investigated by Margaret Hey and Peter Waters for heat-set tissue for paper and by V.R. Mehra and B. Hacke for nap-bond linings for paintings where heat, pressure, and moisture could be selectively chosen during treatments. Many of the formulations suggested under **Treatment Variations** originally were proposed for lining paintings, but have been adapted to solving paper conservation problems where more traditional methods were inappropriate for a particular treatment problem. An advantage of these adhesives is that they can be tailored for specific uses.

Detailed information on conservation adhesives has been obtained from a computer database and is cited as (Getty/CCI n.d., MCIN No.).

# a. Source

Acrylic dispersions are manufactured by many companies, but only a few are currently used by conservators. Rohm and Haas (Philadelphia) manufactures the Rhoplex series which is the American product and not a direct substitute for the German Röhm GmbH Plextol series. Lascaux products are modified adhesives based on Plextol dispersions, but manufactured by Alois K. Deithelm and distributed by Lascaux Conservation Materials. Texicryl acrylic adhesives are manufactured by Scott Bader Ltd. in England. For other manufacturers and their products see Skeist 1977, pp. 534-539. Acrylic dispersions are prepared by emulsion polymerization. This process allows a high concentration of high molecular weight resins to be prepared in dissolved form; high molecular weight resins have improved characteristics of tensile strength, melting temperature, and elasticity as opposed to low molecular weight resins.(PV)

Acrylic dispersions currently used for conservation treatments are copolymers of acrylic resins: blends of ethyl acrylate and methyl methacrylate made from monomers of methyl, butyl, and other longer chain esters of acrylic or methacrylic acids. They are derived from acrylic acid esters:

 $CH_2 = CH - C = O$ 

Methyl Acrylate $CH_2 = CH-COO-CH_3$ Ethyl Acrylate $CH_2 = CH-COO-C_2H_5$ n-Butyl Acrylate $CH_2 = CH-COO-C_4H_9$ 

# b. Chemical and Physical Properties

**Physical Form:** Dispersions are resin solids dispersed in water that appear as milky white liquids that become white to transparent upon drying. Viscosity ranges from 80-4500 cps.

**Preparation:** Dispersions can be used as supplied, diluted with water, or thickened with cellulose derivatives, ammonia, solvents, or inert materials. (See 46.4.3 E. Treatment Variations.)

Solubility: Dispersions can be initially diluted in water. Product information states that dispersion films swell in water after drying and are reversible in acetone and other solvents (see specific entries). However, it can be difficult to remove even solubilized products from a paper support. This difficulty should be considered when evaluating treatment options. Heat or peeling off mechanically the adhered layer could be useful in reversing adhesive.

**pH**: Range for dispersions is 3.5-10 depending on specific dispersion and additives. Initial high pH's may be associated with ammonia added as a fungicide. On drying, the pH may drop as ammonia volatizes.

Softening Point/Glass Transition Temperature  $(T_g)$ :  $T_g$  varies with each acrylic adhesive. Horie states "polymers with a glass transition temperature above 65°C (149°F) should not be used" (Horie 1987, 76). Some dispersions do not have  $T_g$  listed by the manufacturer or in product literature and it is presumed that they are intended only for contact (pressure sensitive) applications. Temperatures cited are from sources that are often contradictory.

## **Refractive Index:**

**Possible Additives:** Can vary tremendously depending on the intended use of the acrylic and how it was manufactured. It is possible to have few or no additives, or to incorporate initiators (organic peroxide or azo compounds) thickeners (ammonia or solvents), or cross-linking agents (polyisocyanates etc.) (Skeist 1977, 531, 533), formaldehyde, brightening agents, surfactants, or optical brighteners (Down and Williams 1988). However, conclusions from tests at CCI indicated "very few harmful volatiles are emitted from acrylic adhesives" (Down and Williams 1989, 9).

Health Hazards: Slight, can cause chemical sensitivities; headache, nausea, irritations to nose, eyes, lungs, and skin. Formaldehyde, sometimes used as an additive, is a carcinogen in animals. Use in a ventilated area.

Storage/Shelf Life: Generally one year if the dispersions are kept from freezing and are stored in closed containers.

c. Aging Characteristics

**Reversibility:** Jane Down and Scott Williams of The Canadian Conservation Institute, Environment and Deterioration Research Department, are involved in a long term evaluation of acrylic emulsions along with other adhesives. Their investigation covers changes in pH, color, presence of additives or volatile substances, and long term stability, but is not complete and all the results not yet available. For those tests completed, resulting information is included under specific entries.

Feller made an earlier observation that elevated temperatures may play an important role in causing cross-linking reactions (Thomson 1963, 173). Horie states that "The methacrylate polymers are more likely to cross-link if they are exposed above or near their glass transition temperature" (Horie 1987, 104).

**pH**: Changes in pH after aging dried films were measured as part of the CCI adhesive study. The pH value of wet dispersions were higher than the dried films (possibly due to volatile ammonia in dispersions). Films were aged in both dark and light aging tests. The results are given under specific entries.

Appearance: According to product literature and Skeist: "All acrylics are characterized by excellent resistance to aging. They are stable to light, resistant to high temperature and oxidation, and have no tendency to yellow." This aspect is currently being tested in the CCI study.

Some preliminary tests have indicated that acrylic dispersions yellow with ultraviolet exposure during accelerated aging.(KS) Horie remarks that testing these dispersions is difficult: "Unfortunately the properties of the films formed from these dispersions are extremely variable, presumably from batch to batch" (Horie 1987, 110). He reports that test results for the same dispersions are often contradictory.

# 2. Rhoplex AC-33

# a. Source

Ethyl acrylate 66%, methyl methacrylate 34% Formaldehyde .05%, ammonia 0.2%, monomer 0.1% (CCI/Getty, n.d., MCIN Nos. 179, 181, 186, 187). Composed of 46-47% solids. Manufactured by Rohm and Haas, Philadelphia. Previously used by conservators, but is no longer available. Similar to European "Primal AC 33."(PV)

# b. Chemical and Physical Properties

Solubility: Dilute with water (see 46.4.3 E. Treatment Variations). After drying, soluble in acetone and removable with heat 70-72°C (158-161°F).

pH: 9.6 as supplied. New dried film pH 5.9.

Softening Point/Glass Transition Temperature ( $T_g$ ): Various temperatures cited for  $T_g$ ; 61-93.3 °C (140-200 °F). Slightly tacky at 22-24 °C (71.6-75.2 °F) (CCI/Getty n.d., MCIN No. 179ff).

Viscosity: 1500 cps.

# c. Aging Characteristics

**Reversibility:** Non cross-linking.

**pH**: Light aged film 4.4, dark aged film 5.2 (Down and Williams 1988).

## 3. Rhoplex AC-73

 a. Source: Ethyl acrylate 50%, methyl acrylate copolymer 50%. Residual ammonia .2%, residual monomer .2% (CCI/Getty n.d., MCIN No. 197). Composed of 46-47% solids. Manufactured by Rohm and Haas, Philadelphia.

# b. Chemical and Physical Properties

Solubility: Dilute with water (see 46.4.3 E. Treatment Variations). After drying, soluble in ethanol and acetone; removable mechanically or with heat 70-73°C (158-163.4°F).

**pH**: 9-10 as supplied. New dried film pH 6.5.

Softening Point/Glass Transition Temperature  $(T_g)$ : Activation temperature 70-73°C (158-163.4°F) (CCI/Getty n.d., MCIN No. 199).

Viscosity: 250 cps.

## c. Aging Characteristics

No volatile emissions or potentially dangerous compounds after two years of dark aging (Down and Williams 1988).

**Reversibility**: Non cross-linking.

pH: Light aged film 3.6 (Down and Williams 1988). Dark aged film 4.5.

# 4. Rhoplex AC-234

#### a. Source

Ethyl acrylate 66%, methyl acrylate 34%. Additives data not available. Composed of 46-47% solids (CCI/Getty n.d., MCIN No. 201-206). Manufactured by Rohm and Haas, Philadelphia.

## b. Chemical and Physical Properties

Solubility: To dilute in water (see 46.4.3 E. Treatment Variations). After drying, soluble in ethanol and acetone; removable mechanically or with heat 70-72°C (158-161.6°F).

**pH**: 9-10 as supplied. Due to high pH, CCI does not recommend direct application to cellulosic materials. New dried film pH 6.5.

**Softening Point/Glass Transition Temperature** (T<sub>g</sub>): Various temperatures cited for T<sub>g</sub>, 82.2-96.1°C (180-205°F); slightly tacky at 22-24°C (71.6-75.2°F) (Getty/CCI n.d., MCIN No. 201).

Viscosity: 1200 cps.

c. Aging Characteristics

**Reversibility**:

**pH**: Light aged film 5.2, dark aged film 5.8 (Down and Williams 1988).

## 5. **Rhoplex 495**

a. Source

Unknown acrylic copolymer. Additives data not available. Composed of 57-59% solids. Manufactured by Rohm and Haas, Philadelphia.

## b. Chemical and Physical Properties

Solubility: Dilute with water (see 46.4.3 E. Treatment Variations).

pH: 3.5-5.0 as supplied.

Softening Point/Glass Transition Temperature  $(T_g)$ : No  $T_g$  information available. Minimum Film Forming Temperature is 0°C (32°F) (used for pressure sensitive applications).

Viscosity: 1500 cps.

### c. Aging Characteristics

#### 6. Rhoplex N580

## a. Source

Butyl acrylate homopolymer, ammonia .02%, formaldehyde .095%, monomer .4% (CCI/Getty n.d., MCIN No. 211). Contains anionic surfactants.(PV) Composed of 55% solids. Manufactured by Rohm and Haas, Philadelphia.

## b. Chemical and Physical Properties

Solubility: Dilute with water (see 46.4.3 E. Treatment Variations). After drying, soluble in acetone, methanol, hexane.(PV)

pH: 7.5-8.5 as supplied. Dried film 7.

Softening Point/Glass Transition Temperature  $(T_g)$ : No  $T_g$  information available, MFFT is 0°C (32°F) (used for pressure sensitive applications).

Viscosity: 80 cps.

c. Aging Characteristics

**Reversibility:** 

**pH**: Light aged film 6.4, dark aged film 6.5 (Down and Williams 1988).

- 7. Rhoplex N619
  - a. Source

N-butyl acrylate/iso-butyl acrylate copolymer, ammonia .2%, monomer .2%, (CCI/Getty n.d., MCIN No. 212). Contains anionic surfactants.(PV) Composed of 57% solids. Manufactured by Rohm and Haas, Philadelphia.

b. Chemical and Physical Properties

Solubility: Dilute with water (see 46.4.3 E. Treatment Variations). After drying, soluble in acetone, methanol, hexane.(PV)

pH: 7.7 as supplied. New dried film 6.9.

**Preparation**: Add solvent to BEVA 371 and warm in a double boiler until the solution is clear, stirring occasionally. Use extreme caution when heating BEVA solutions due to flammability.

Solubility: BEVA 371 is soluble in benzine, naphtha, xylene, toluene, mineral spirits, and Amsco Solv. B. It becomes swollen in acetone and is insoluble in water, alcohol, dimethyl formamide, and cellosolve. It can be reactivated with heat (product literature).

## **pH:** 7.(PV)

Softening Point/Glass Transition Temperature  $(T_g)$ : The softening temperature is 68°C (154.4°F).(PV) Application temperature of approximately 66°C (150°F) is used in the lining of paintings (product literature).

# **Refractive Index:**

## **Possible Additives:**

**Health Hazards:** Solvents are present. Solvent hazards are cited for discontinuation of the gel product from Adams Chemical. Fire and explosion hazards (flash point 45°C [113°F]).(PV)

Storage/Shelf Life:

## c. Aging Characteristics

Ethylene vinyl acetate and all copolymers of vinyl acetate are susceptible to thermal degradation with the production of acetic acid and other noxious products. Possibilities of cross-linking on aging (Williams 1984, ARS No. 2309).

**Reversibility**: Degree of reversibility is dependent upon the type of bond and the strength of adhesion. BEVA 371 is reversible in naphtha and xylene. Heat reversibility may depend upon the surface texture of the paper substrate as well as the initial activation temperature (Pavitt 1987, 4).

BEVA 371 film may be too thick to be used in paper applications, especially when the melting temperature  $(66^{\circ}C/150^{\circ}F)$  is exceeded. (Finer films can be produced by spray or silk screening applications.) In its molten state, BEVA may stain the material to which it is applied by effecting a change in the refractive index in the material and not by causing a chemical reaction (Berger 1989, 89). Some conservators are concerned about the reversibility of BEVA on paper substrates.

pH: A two year natural aging study at CCI showed that the pH is in acceptable range for cellulose and leather (Abbey Newsletter 1989, 21).

## **Appearance:**

**Relative Strength:** BEVA 371 appears to produce strong bonds which remain flexible after accelerated aging (Blackshaw and Ward 1983, 2-1-2-15; Pavitt 1987, 3). Bond strength depends upon film thickness, method of application, and temperature of application. Solvent-activated bonds are weaker than heatactivated bonds (Hawker 1987, 164-166).

**Biological Attack:** 

## 2. BEVA D-8

Beva D-8 was formulated by Gustav Berger to act as a nap-bond adhesive for the lining of a theater curtain by Picasso (Berger 1976).

### a. Source

BEVA D-8, an aqueous, non-ionic dispersion, consists mainly of an ethylene vinyl acetate emulsified by a volatile material which evaporates during drying. Contains 55% solid resins (Conservator's Products Company, n.d.). Available from Conservator's Products Company, P.O. Box 411, Chatham, NJ, 07928. Telephone 201-762-9335.

b. Chemical and Physical Properties

Identification:

Physical Form: Is a dispersion.

**Preparation:** Can be used as supplied or diluted with water.

Solubility: Can be diluted with water.

pH:

Softening Point/Glass Transition Temperature  $(T_g)$ : Activation temperature is 82-90°C (179.6-194°F).

**Refractive Index:** 

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Softening Point/Glass Transition Temperature  $(T_g)$ : No  $T_g$  information available, MFFT is less than 0°C (32°F) (used for pressure sensitive applications).

Viscosity: 185 cps.

c. Aging Characteristics

**Reversibility**:

**pH**: Light aged film 6.6, dark aged film 6.6 (Down and Williams 1988).

- 8. Rhoplex N1031
  - a. Source

Butyl acrylate acrylonitrile copolymer. Additives data is not available. Contains anionic surfactants. (PV) Composed of 54% solids. Manufactured by Rohm and Haas, Philadelphia.

# b. Chemical and Physical Properties

Solubility: Dilute with water (see 46.4.3 E. Treatment Variations).

pH: 7.5 as supplied. Dried film 7.2.

Softening Point/Glass Transition Temperature (T<sub>g</sub>):

Viscosity: 100 cps.

c. Aging Characteristics

**Reversibility**:

pH: Light aged film 6.5, dark aged film 6.4

- 9. Plextol 360
  - a. Source

Butyl acrylate/methyl methacrylate. Chemical composition not quantified, 59% solids (CCI/Getty n.d., MCIN No. 178). Manufactured by Röhm GmbH, Germany.

# b. Chemical and Physical Properties

**Solubility**: After drying, soluble in most organic solvents; insoluble in aliphatic hydrocarbons.

pH: 7-8 as supplied.

Softening Point/Glass Transition Temperature  $(T_g)$ :  $T_g 0^{\circ}C$  (32°F) or greater. (Used for pressure sensitive applications.)

Viscosity: 1000-3000 cps.

## c. Aging Characteristics

## 10. Plextol 500

a. Source

Ethyl acrylate/acrylic acid copolymer. Additives data not available. Composed of 50% solids (CCI/Getty n.d., MCIN Nos. 174, 175, 176, 177). Manufactured by Röhm GmbH, Germany.

# b. Chemical and Physical Properties

Solubility: Dilute with water (see 46.4.3 E. Treatment Variations). After drying, soluble in organic solvents, soluble or swells in isopropanol, acetone, ethanol, toluene; removable with heat  $22^{\circ}$ C (71.6°F).

**pH**: 9 as supplied.

Softening Point/Glass Transition Temperature  $(T_g)$ :  $T_g 82.2^{\circ}C$  (180°F). MFFT is 7°C (44.6°F).

Viscosity: 1100-4500 cps.

c. Aging Characteristics

## 11. Plextol 498

- a. Source Butyl acrylate. Additives data is not available. Manufactured by Röhm GmbH, Germany.
- b. Chemical and Physical Properties
- c. Aging Characteristics

# 12. Lascaux 360 HV (Plextol 360 Base)

# a. Source

Butyl acrylate/methyl methacrylate copolymer, 48% solids. Manufactured by Alois K. Diethelm AG/Farbenfabric CH-8306 Bruttisellen. U.S. distributor is Lascaux Conservation Materials, LTD, New York. Based on butyl acrylate thickened with methacrylic acid, 50% butyl acrylate.

# b. Chemical and Physical Properties

Solubility: Dilute with water (see 46.4.3 E. Treatment Variations). After drying, soluble in alcohols, aromatics, esters, ketones, glycol esters.

**pH**: 8-9 as supplied. Dried film 7. CCI recommends caution with applications to proteins since pH is alkaline.

Softening Point/Glass Transition Temperature  $(T_g)$ :  $T_g 44$  °C (111.2°F).

Viscosity:

c. Aging Characteristics

**Reversibility**:

**pH**: Light aged film 6.5, dark aged film 6.8 (Down and Williams 1988).

## 13. Lascaux 498 HV (Plextol 498 Base)

# a. Source

Butyl acrylate/butyl methacrylate copolymer, 40% solids. Manufactured by Lascaux Co. from Plextol 498 (Röhm GmbH, Germany).

# b. Chemical and Physical Properties

Solubility: Dilute with water (see 46.4.3 E. Treatment Variations). After drying, soluble in alcohol, aromatics, esters, ketones, glycol esters.

pH: 9-10 as supplied.

Softening Point/Glass Transition Temperature  $(T_g)$ :  $T_g 26^{\circ}C$  (78.8°F).

Viscosity:

# c. Aging Characteristics

**Reversibility**: After aging: as for dried films. Non cross-linking.

pH:

# 14. Texicryl See 46.3.3 F. Proprietary Formulations.

# F. Proprietary Formulations

# 1. BEVA 371 - General Information

BEVA 371 heat-activated adhesive was developed by Gustav Berger in 1970 as a lining adhesive and consolidant for the treatment of paintings.

# a. Source

Available from Conservator's Products Company. P.O. Box 411, Chatham, N.J. 07928. Telephone 201-762-9335. Adam Chemical Company (Spring Valley, NY 10977, telephone 914-356-9448) supplied a form of BEVA 371 now designated Adams EVA due to proprietary disputes. They currently supply only EVA film, recently discontinuing the EVA adhesive in gel form.(PV)

BEVA 371 is composed of 23% ethylene/vinyl acetate copolymer 80/20 [17% Elvax Resin grade 150 (DuPont) and 6% A-C copolymer 400 (Allied Chemical Corp.)]; 10% Ketone Resin N; 3% paraffin (oil-free, melting point 65°C (149°F), Essowax 4610); 3% Phthalate Ester of Technical Hydroabiethylalcohol (Cellolyn 21); 1% plasticizer; 34% toluene; and 27% Naphtha (benzine) (Williams 1988, ARS No. 2313).

## **b.** Chemical and Physical Properties

## Identification:

**Physical Form:** BEVA 371 is available as a gel (38% solids content) and as a film (3.5 mil thick) sandwiched between silicone release materials.(PV)

Possible Additives: No information available.

Health Hazards:

Storage/Shelf Life: Sensitive to freezing.

# c. Aging Characteristics

**Reversibility:** Film is soluble in toluene, petroleum benzine, naphtha, and xylene.(CB) Requires more aromatic mixtures for removal than BEVA 371. After prolonged accelerated aging, becomes soluble in alcohol, indicating that during aging the breakage of cross-links exceeds their formation. Mixtures of toluene, alcohol, and mineral spirits will remove the adhesive from porous materials without leaving a residue (Conservator's Products Company n.d.).

## Appearance:

# **Relative Strength:**

## 3. Lamatec

Adhesive film composed of vinyl acetate homopolymer. Developed by Ademco and other British institutions for conservation purposes as a heat seal adhesive film. Also called Texicryl by the Conservation Materials Catalog and others. NOTE: There is confusion between the names Lamatec and Texicryl in some supply catalogs. Lamatec, manufactured by the Archival Aids Branch of Ademco, is a PVA film whereas Texicryl, made by Scott Bader, USA, is an acrylic copolymer (Skeist 1977, 539; Down and Williams 1988).

# a. Source

Lamatec comes as a poly vinyl acetate cast film. One source identifies Lamatec as a PVOH/PVAC copolymer (Horie 1983, 99). It has also been identified as a vinyl acetate homopolymer with no additives (Williams 1988, ARS No. 2313). Thus, it is unclear whether the product is pure PVA or PVA with an additive.

## b. Chemical and Physical Properties

Identification: FTIR identifies strong PVA peak (Williams 1988, ARS No. 2313).

**Physical Form**: Unsupported adhesive film deposited on silicone-coated backing paper, which peels away. Lamatec is also available coated onto cloth, Crompton Tissue, or other repair tissues from Ademco.

**Preparation:** Comes ready for use. Can be attached onto any support desired by heat seal in a press or with a tacking iron.

**Solubility:** Is soluble in ethyl alcohol or industrial methylated spirits according to Archival Aids of Ademco.

pH: Manufacturer claims a neutral pH.

Softening Point/Glass Transition Temperature  $(T_g)$ : Activation temperature is 80-90°C (176-194°F) (Ademco specifications).

**Possible Additives:** CCI tests did not pick up anything other than vinyl acetate homopolymer in FTIR analysis.

Health Hazards: No volatilization of solvent.

Storage/Shelf Life:

## c. Aging Characteristics

**Reversibility**: Described as reversible in ethyl alcohol bath (Conservation Materials 1988, 102) or methylated spirits (Ademco).

pH:

Appearance: According to manufacturer, Lamatec Repair Tissue has successfully passed tear and fold strength tests after artificial aging and has withstood artificial aging of up to approximately 170 years without causing embrittlement or discoloration of the laminated document.

# 4. Texicryl

Texicryl is an unsupported adhesive film which is made from an acrylic copolymer. One source identifies Texicryl as a poly (methyl methacrylate-co-ethyl-acrylate) adhesive (Down and Williams 1988). Another source identifies Texicryl as an ethyl acrylate-methyl methacrylate-ethylmethyl-acrylate copolymer (Bromelle et al. 1984, 32). Skeist lists eight different varieties of Texicryl which vary according to percent solids, viscosity, and application. The applications include pressure sensitive, cross-linkable, flocking, heat seal, and laminating adhesives (Skeist 1977, 538).

## a. Source

Manufactured by Scott Bader Co., USA (Skeist 1977, 538).

## b. Chemical and Physical Properties

**Identification:** CCI FTIR analysis does not detect components which make up less than 5% of the adhesive. Small amounts of unidentified additives may be present.

**Physical Form:** Supplied as an unsupported adhesive film. May also be available as a dispersion.

**Preparation**:

Solubility:

pH: 4.18 (Down and Lafontaine 1988).

Softening Point/Glass Transition Temperature  $(T_g)$ :

**Possible Additives:** 

Health Hazards:

Storage/Shelf Life:

c. Aging Characteristics

**Reversibility**: Remains soluble in aromatic hydrocarbons after thermal aging (Bromelle et al. 1984, 40).

**pH:** After thermal aging 4.7.

Appearance: Yellowed under various light aging tests, together with thermal aging of 59°C (138.2°F) or above. Therefore, additives may be present (Bromelle et al. 1984, 38).

# 5. Fusion 4000 - General Information

Vinyl acetate ethylene copolymer, used as a dry mount tissue for photographs and other materials (Down and Williams 1988). Elizabeth Moffet, CCI states that 4000 is at least 80% ethylene.

# a. Source

Seal Co. Product, Shelton, CT 06418. Available through Light Impressions Catalogue.

# b. Chemical and Physical Properties

Identification: IR transmission spectroscopy will identify both components.

Physical Form: Dry-mount unsupported adhesive film.

**Preparation**: Supplied ready for use as an unsupported adhesive film which is activated at 71.1-87.7°C (160-190°F). Is liquified when applied at higher temperatures.

Solubility: According to Seal Company it is resoluble with heat.

pH: According to manufacturer, pH is neutral.

Softening Point/Glass Transition Temperature (Tg):

**Refractive Index:** 

**Possible Additives:** 

Health Hazards:

Storage/Shelf Life:

c. Aging Characteristics

Abstracts from the Photomaterials group meeting, 1984 in Louisville, KY contain a summary by Bob Lyon on commercially used dry-mount tissues including Fusion 4000, which discusses aging characteristics.

**Reversibility:** Reversible with heat.

pH:

Appearance:

**Relative Strength:** 

**Biological Attack:** 

# 6. Document Repair Tape - Filmoplast P

Pressure-sensitive, thin, transparent paper for repair of documents. Comes in tape form and is used by framers for hinging.

## a. Source

Filmoplast P (Hans Neschen GmbH & Co., KG, Germany) is a vinyl acetate/acrylic copolymer with dibutyl pthalate additive (Down and Williams 1988).

# b. Chemical and Physical Properties

Identification: FTIR Spectroscopy.

Solubility: Adhesive initially gels in water and organic solvents.

pH: Manufacturer claims Filmoplast P has a pH of 7.7.

Possible Additives: Dibutyl phthalate.

Health Hazards: Exposure to solvents is necessary to reverse material after aging.

# c. Aging Characteristics

**Reversibility**: Unpublished Library of Congress tests indicate adhesive is not reversible in water after dry aging. Aromatic solvents may be required to remove aged adhesive from paper.

pH: Manufacturer claims pH after aging is 6.9.

Appearance: The Library of Congress has observed yellowing upon aging. Substrate to which it is attached may also yellow. Humid and dry aging yellows the carrier alone. Tape has been observed to cause a bleaching effect in cyanotypes.

## 7. Archival Document Repair Tape

Pressure-sensitive tape used to repair documents and bindings.

# a. Source

Made by Archival Aids (formerly a division of Ademco). According to manufacturer, it is composed of an acid and sulfur free, bleached, wood-based tissue coated on one side with a butyl acrylate acrylic adhesive which contains a small amount of dibutyl phthalate plasticizer. (Horie 1987, 112 says it is made of DBA.)

# b. Chemical and Physical Properties

Identification:

Physical Form: A pressure-sensitive, coated tissue.

**Preparation:** Comes ready to apply on a roll.

**Solubility:** According to manufacturer, it is soluble in "spirit" solvents (alcohol based).

pH:

Softening Point/Glass Transition Temperature (T<sub>g</sub>):

**Refractive Index:** 

Possible Additives: Possible additives include dibutyl phthalate.

Health Hazards:

Storage/Shelf Life:

## c. Aging Characteristics

**Reversibility**: Manufacturer says to apply lightly moistened swab of cotton containing alcohol and gently dab tape carrier. After a minute or so the paper will lift off revealing the acrylic adhesive. Further application of solvent should remove this.

**Appearance**:

**Relative Strength:** 

# 8. Archival Framing Tape

Water-activated adhesive coated tape advertised by manufacturer for use in hinging works of art on paper.

# a. Source

Available from Archival Aids (formerly a division of Ademco). According to manufacturer, tape adhesive is composed of a PVA adhesive with 3% calcium carbonate buffer added.

# b. Chemical and Physical Properties

#### Identification:

**Physical Form:** Comes as tape on a roll which has been coated on one side with an adhesive.

**Preparation**: Activate with a slight amount of moisture.

Solubility: According to manufacturer, activated with water.

**pH**: According to manufacturer, adhesive has a pH of 7.0, base stock has a pH of 6.2.

Softening Point/Glass Transition Temperature  $(T_g)$ :

**Refractive Index:** 

**Possible Additives:** Possible additives include calcium carbonate 3%.

Health Hazards:

Storage/Shelf Life:

- c. Aging Characteristics
- 9. Proprietary Resin Aerosol Sprays

# a. Source

The Borden Company has sold several proprietary resin aerosol sprays as fixatives to be used by artists and others. During the 1970s three Krylon resin products were analyzed by a major conservation research lab. Analytic results were recorded in inhouse reports but not published. At that time, Krylon 1301 was found to resemble n-butyl methacrylate, while Krylon 1303 resembled polyethyl methacrylate. Krylon 1306, however, contained nitrocellulose and camphor! A recent note in the <u>AIC</u>

<u>Newsletter</u> indicated that one of the Krylon sprays contains Acryloid B-66 (<u>AIC Newsletter</u>, 13, no. 4 July 1988, 11). The Lascaux Company sells Lascaux-Fix, which is described as 4% B-72 in toluene and isopropanol (<u>AIC Newsletter</u>, 13, no. 6 November 1988, 11).(KN)

# 46.3.4 Heating Equipment

## A. Double Boiler

(For preparing starch pastes.) Should be an inert material such as glass or stainless steel.

# B. Electric Saucepan with Teflon Lining

Regular, thorough, stirring provided by the stirring mechanism, creates a strong, smoother paste than hand-stirring. The proportionately greater exposure to heated metal surfaces and the more thorough stirring causes greater water loss than with hand stirring in a double boiler and requires adjusting the starch/water ratio (e.g., from 1:6 to 1:8). Dry air in the workroom calls for a slight addition of water (e.g., to 1:8 1/2 or 1:9).

# C. Microwave Oven

Because the energy penetrates from the outset of cooking instead of being partially reflected as with conventional cooking, the starch granules heat, swell, and burst open much more quickly. Less water evaporates from the paste mixture because the cooking process occurs more rapidly and this gives the starch granules more opportunity to absorb water and burst.

# **D.** Hot Plate

For warming parchment size, cooking starch pastes, etc.

# 46.3.5 Diluents

- A. Deionized/distilled water
- B. Organic solvents

## 46.3.6 Miscellaneous Equipment

- A. Weighing balance
- B. Graduated glassware
- C. Thermometer

- D. Stirring rod or spoon glass, plastic or ceramic
- E. Cheesecloth for suspending resins in solvent within a glass container with lid

# 46.3.7 Mixing/Straining

- A. Electric food blender or food processor
- B. Japanese horsehair strainer; small plastic strainer for preparation of small batches of paste
- C. Stiff bristle brushes for kneading and working starch paste

# 46.3.8 Application Equipment

- A. Brushes
- B. Roller
- C. Sprayer or spray gun with variable pressure
- D. Suction table
- E. Equipment for heat activation tacking iron, heat-seal press
- F. Silicone release paper or polyester web
- G. Hypodermic syringe
- H. Spatulas
- I. Mylar (polyester film) strips

# 46.3.9 Storage

- A. Refrigeration
- B. Inert glassware with solvent resistant lids
- C. Air tight glass/ceramic storage jar for starch paste

## **46.4** Treatment Variations

## **46.4.1 Vegetable Adhesives**

# A. Starches

# 1. Preparation

All recipes under Treatment Variations use distilled or deionized water.

a. Wheat Starch Paste From Precipitated Starch - Western Style. Most recipes call for wetting the dry starch thoroughly before cooking. Using cold water can help avoid premature thickening and inadequate dispersion. Assuming reasonable mixing together of the dry starch and water, any lumps that form are precipitation of macro-particles that result from retrogradation. Too high a temperature and/or too long a cooking time can adversely affect viscosity, adhesive strength, and color of many starches. The gelatinization temperature range for wheat starches is 58-64°C (136.4-147.2°F). When using a new material, run tests to determine proportion of water to starch, cooking temperature, and time and amount of agitation that will give best results.

Wheat Starch Paste #1 (Library of Congress)

Weigh out 200 g of dry starch. Measure 400 ml water and stir into starch to make a slurry. Heat remaining 1000 ml of water in the top of a double boiler unit and place assembled unit on heat source. Heat water to at least 80°C (176°F). Slowly pour slurry into heated water, stirring vigorously. Stir until thoroughly blended. Cover and cook over water about 45 minutes, stirring every 10 minutes. The gel temperature range of Aytex-P wheat starch is between 65-90°C (149-194°F). Cool paste before use. (Quick cooling can be achieved by placing pan in a tray of ice.) Paste sets up in a semi-solid mass as it cools and will need to be strained through a strainer or blended in an electric blender. Stored in the refrigerator, paste keeps approximately one week.

<u>Wheat Starch Paste #2</u> (Winterthur Museum)

Soak 30 g (1.5 oz.) wheat starch in about 150 ml (5.1 fl. oz.) water for half an hour. Cook over high heat in a glass double boiler, stirring constantly with a glass rod until paste turns translucent. Turn down heat, but keep warm at a gentle simmer

for 20-30 minutes. Stir continuously. The adhesive should be thick and forming stiff peaks. Cover with a paper towel and allow to cool. Strain through a non-metallic strainer before storage in a sealed container which has been swabbed with thymol. Keep jar in a cool place.

# <u>Wheat Starch Paste #3</u> (Upper Midwest Conservation Association)

Cook 30 g of wheat starch and 150 ml of water, stirring constantly until the paste turns translucent. Cover with a damp towel and allow to cool. Strain and store in a sealed container in a dark location or store unstrained and covered with water in the refrigerator.

<u>Wheat Starch Paste #4</u> (Harvard University Museums) Place 5 g of wheat starch in small pot with several ml of the required 150 ml of water. Make a slurry. Boil the remaining water. Add the boiling water to the paste slurry. Mix quickly for 5-10 minutes. Place paste in a 5" x 7" tray and let cool. If paste is mixed correctly, a thin scum will form on the surface. Comb this off before using. If no scum forms, discard paste and try again. This will make enough lining paste for a 30" x 40" object. If you wish to thin the paste use 1 part paste to 30 parts water. For a mending paste use 1 part paste to 10 parts water.

# <u>Wheat Starch Paste #5</u> (Christine Smith)

(Starch paste made in an electric saucepan.) Three points are important in making wheat or rice starch paste in an electric saucepan with stirring mechanism: the total volume of starch and water used, the ratio of starch to water, and the heat level(s) used. With some experimentation, excellent results will be obtained with almost no effort expended.

Due to greater surface contact between the paste mixture and the doughnut-shaped metal pot, more paste will be lost as a hard skin than in a glass double-boiler; therefore measure a total volume of starch and water approximately 15-20% more than would be used for cooking in a double-boiler.

The large, open surface of the pot, the constant stirring, electric heat source, and metal container seem to contribute to more water being removed from the starch-water mixture than when using a double-boiler over a gas burner. The relative humidity in the workroom also has a noticeable effect on cooking. In our Washington, DC area lab, we generally use a starch:water ratio of 1:8 (wt./vol.). During times of dryness, we use ratios of 1:8.5 or 1:9. In times of high humidity, cooking requires noticeably more time.

Our pot is a Salton "Cook 'n' Stir," a brand which may be unavailable now. Conversation with colleagues who have the same product suggests that different pots may generate different amounts of heat. We have excellent results with our pot by cooking the starch/water mixture for approximately 25 minutes with the pot set at "5", which is the highest setting. Other conservators have said they cook their paste half-way at "5" and then reduce the heat to "3." Still others have said that at "5" they are unable to generate sufficient heat. After about 25 minutes, the sound of the stirrer changes as it moves through the nearly completed paste. At that point, we watch carefully until the outer edges of the paste batch show definite taffy-like pulling; we wait until just before we would lose the paste to dryness. At that point, we remove the paste and sieve it.

Our cooking is preceded by a three-hour period during which we periodically stir the starch-water mixture. The wheat starch we use is "Zin Shofu" from Conservation Materials in Sparks, NV. Our rice starch is "Belgium Rice Starch" from the same company.

## Wheat Starch Paste #6 (Microwave Oven)

Soak 100 g of starch in 500 ml of water in a Pyrex beaker. Cook for 3 minutes in a 500 watt microwave oven at a high setting, but since the starch must be kept in suspension agitation is required and the paste should be taken out of the oven and stirred 2-3 times. The result is a creamy, soft paste which may not need sieving. (From Anne Leane, IPC meeting London 1988 notes summarized in the Paper Conservation News No. 48, 1989.)

## b. Rice Starch Paste

Rice Starch mixed with PVOH can be refrigerated for long periods of time. It makes a very strong paste for mending and holds well in mending tears before an overall lining.(SRA)

For recipes using an electric saucepan or a microwave oven see wheat starch paste recipes #5 and #6.

<u>Rice Starch Paste #1</u> (Metropolitan Museum of Art) Combine 52 g of rice starch and 364 ml water in a closed container and shake. Allow to soak at least one hour. Cook starch and water in an enamel pot, with constant stirring, until it boils. (At this point, 5 g laboratory gelatine which has been heated in 50 ml water until dissolved may be stirred in until it boils again.) Continue stirring until paste becomes quite thick. One may, with good ventilation, stir in fungicide (5 ml of a saturated solution of thymol in methanol). Another option is the addition of 1 g of calcium carbonate in 5 ml of water. Remove from heat. Pour into a jar, allow to cool somewhat, and cap.

## <u>Rice Starch Paste #2</u> (Katherine Eirk)

Stir 3/4 tsp. of methyl cellulose into 25 ml of water and let stand 20 minutes. Add 25 ml water and stir and let stand another 20 minutes. Add another 25 ml water, stir.

Place 1 1/2 cup of rice-starch powder in top section of a double boiler. Add small amount of the 2 cups of required water, and stir to a smooth paste. Bring water in lower half of the double boiler to boil. Boil the remaining water in a separate glass plan. Assemble the double boiler. While constantly stirring the starch mixture, slowly add the boiling distilled water. Cook and stir the paste until it becomes translucent (25-40 minutes). Remove the top section of the double boiler and cover. Allow the paste to cool to room temperature. When the paste is cool, add the prepared methyl cellulose jelly.

Dissolve 1/3 tsp ortho-phenylphenol in 5 tsp. grain alcohol. Stir the solution into the paste. Store the paste in a dark jar, unrefrigerated, but in a cool, dark place.

Dilute with water to consistency of heavy cream before use. (If paste seems lumpy, force through a strainer several times.) Undiluted paste will keep about two months.

# c. Modified Starch Paste

<u>Sodium Alginate Paste</u> (Frances Prichett) Sprinkle 1 g sodium alginate in 100 ml water and stir until dissolved. Add 10 g (used for repairs) or 5 g (for lining) arrowroot and heat in water bath until mixture is transparent. Cook for a further 15 minutes.

Sodium alginate granules can be added dry (a pinch) to existing paste to modify it.

Methyl Cellulose and Starch Paste See 29. Lining.

# 2. Application

a. Wheat Starch Paste From Precipitated Starch - Western Style A well made paste can be diluted indefinitely and retain its proportionate strength. High water content of starch pastes may require methods to minimize overwetting and resulting cockling and staining. Such methods include dry linings or blotting the adhesive prior to use. Wheat starch paste does not adhere well to fatty grounds and is not recommended for use with oil media.

A disadvantage of wheat starch paste is that it sometimes causes a faint, grayish haze in paper, for example around mended tears. This is presumed to result from an altered refractive index of the paper surface. Assuming application of the thinnest, driest paste film possible, this situation can be remedied by using rice starch paste. If maximum strength is unimportant, or can otherwise be compensated for, an appropriate cellulose ether can be suitable. Starches are largely free of nitrogen and sulfur and have no negative effects on pigments.

## b. Rice Starch Paste

Rice starch paste is preferred when very flexible, smooth, and clean adhesion is essential. Rice paste is diluted and used to adhere tears from the front of an image through the media. After drying, the artifact is turned face down and reinforced on the back with wheat starch paste. It is also very successful for adhering fills or inserts.(AD)

# c. Modified Starch Paste

Sodium alginate paste is a very strong "dry" adhesive and therefore useful for water-sensitive objects or when cockling must be avoided.(JR) Can be used to increase the "slip" of starch pastes (i.e., rice and starch), for instance when added to a lining paste.(PV)

# **B.** Vegetable Gums

## 1. Preparation

## a. Agarose

The large number of agarose products available are characterized according to: sulphate content (an indicator of purity for non-conservation applications where less than 0.3%sulphate content is required); electroendosmosis (a type of liquid movement in the presence of electric voltage and not of concern in paper conservation); gel strength (the force in grams gms/cm<sup>2</sup> that must be applied to a 1.0 or 1.5% gel to fracture it); and gel point (the temperature at which an aqueous solution forms a gel). For paper conservators gel point is important: choose an agarose which will remain gelled at room temperature.

Sigma Type VII gels below 30°C (86°F) at a solution concentration of 1.0%, but experience has been that the water component wicks out of a 2.0% solution enough to make poulticing difficult on objects with water sensitive media.

# <u>Agarose</u> (Christine Smith)

(For use as an enzyme poultice.)

Heat water to the temperature at which selected agarose will melt and stir in the agarose. Cool down to just above gel point, stir in enzyme, pour into a flat bottomed tray to a thickness of about 1/8 inch, and allow to gel. Slice the gel to desired size(s) and place on object to be treated. Necessary working time will vary in the same ways as with liquid enzyme procedures.

Note: The gel cannot be stored in a freezer successfully. Although, agarose is inexpensive the cost of enzymes makes it advisable to prepare only enough gel for one days use.(CS)

# b. Algin or Sodium Alginate

<u>Sodium Alginate</u> (Jane McAusland) Dissolve 0.5 g in 100 ml water to form a 0.5% aqueous solution.

# English Arrowroot Paste With 1% Alginate Solution (Frances Prichett)

Sprinkle 1 g sodium alginate in 100 ml water and stir to dissolve. Add 10 g arrowroot and heat in a double boiler until mixture becomes translucent. Cook an additional 15 minutes. Already made paste can be modified by adding a pinch of the dry alginate powder.

# c. Funori (Japanese Seaweed Adhesive)

## Funori Recipe (Masako Koyano)

Dried seaweed (6 g) is soaked in 200 ml water overnight, then cooked over low heat until mucilage dissolves out. The liquid extract is strained through a medium-coarse cotton cloth (Koyano 1979, 31).

#### <u>Funori Recipe</u> (Katsuhiko Masuda)

Take a 10 cm<sup>2</sup> piece of dried seaweed and tear it into small pieces. After soaking the pieces in 200 ml water overnight, they are cooked just below the boiling point. The extract is diluted as needed (Masuda 1984, 128).

# Funori Recipe (Frank Mowery)

Take about 1 part dried funori and 4 parts water. Rinse the funori and soak for several hours, or better, overnight. Cook at just under simmering for about 20-30 minutes. When all that is going to melt into solution has done so, strain it through two layers of cheesecloth. This can take 15 minutes or more.

#### <u>Aiko's Art Funori Recipe</u> (Aiko Art Materials)

(Approximately 4% solution, based on dry seaweed weight.) Mix and cook a five inch square sheet of funori in one cup of water (approximately 9.7 g dry funori to 237 cc water) over a low flame until funori becomes very soft. Strain before using.

# Oriental Paintings Studio and Technical Laboratory (Freer Gallery of Art)

(Approximately 0.67% solution.)

Rinse 1 g seaweed, squeeze out excess water, and soak in 150 cc water, covered, for 6 hours at room temperature or overnight in a refrigerator. Cook over low heat  $(80^{\circ}C/176^{\circ}F)$  for 30-60 minutes, stirring frequently, until most of the seaweed has dissolved. Strain through 2-4 layers of cheesecloth. The resulting solution will be lighter in color if darker seaweed strands are removed before cooking. Boiling or simmering seems to reduce adhesive strength.

# 2. Application (See 23. Consolidation/Fixing/Facing.)

- a. A .05% sodium alginate solution is used as a suspension medium to create smooth washes of India ink and burnt sugar (McAusland 1978, 30). A .05% solution is added to paste in order to give it more slip (McAusland and Stevens 1979, 37).
- b. The funori seaweed adhesive can be applied without heating, because the extract is liquid at room temperature. It has been used by Japanese conservators as a consolidant, as a facing adhesive (Koyano 1979, 31), for applying cut gold leaf decoration called kirikane (Winter 1984, 120), for sizing paper, gilding paper and silk, or added to paste to give it viscosity and smoothness (Masuda 1984, 128). Used to consolidate Persian miniatures by some Western conservators. The Freer Gallery Technical Laboratory has used funori in solution to successfully attach flaking pigment to wood, cotton textile, and Near Eastern linen paper.(FM) Funori does not generally change the appearance of pigment or paper. It may take a few minutes for funori to be absorbed, which allows it to soften and flatten lifted flakes. Funori seems to be a relatively strong adhesive and somewhat viscous as a 0.6% solution, but it generally penetrates well. Addition of alcohol seems to reduce tack. A stronger bond can be achieved by mixing funori with paste, or simply by repeated application of funori alone.(MMS)

# C. Cellulose Derivatives

## 1. Preparation

Granular grades of cellulose ethers dissolve more easily in water than the finer powders. Granular or coarse types were formulated to be added to vigorously stirred water. Coarse types require longer solution time.

Powders should be sifted slowly into the vortex of vigorously agitated water, but not so slowly that solution thickens before all powder is in. Agitate 10-30 minutes until all swollen particles are dissolved.

Alternatively, powders can be pre-wet in a non-solvent to prevent lumping and added to the main volume of the solvent (Horie 1987, 126; Aqualon n.d., 1, Bulletin VC-524).

- a. Methyl Cellulose: Do not use a blender because mixture tends to foam. Disperse powder first in hot water (about 1/3 of full measure) to avoid lumping and gelling, then pour in remaining ice-cold water and agitate until mixture is smooth. Wait twenty minutes to one hour for mixture to thicken. Lowering temperature will hasten solution and increase viscosity.(CB) MC can also be prepared using a non-aqueous, pre-wetting slurry.
- b. Hydroxypropyl Cellulose: Prepare a slurry in hot water above 50°C (122°F) and allow to sit for several minutes, maintaining temperature to prevent lumping. Add main volume of cold water and stir until dissolved, approximately ten minutes. Alternatively, add HPC powder to a blender, run approximately ten minutes, or until gel free solution is obtained. Allow to stand for several minutes before use. HPC can also be prepared in non-aqueous solvents. A pre-slurry can be prepared using aliphatic, aromatic, etc. non-solvents. The main volume of an organic solvent may then be added as described for aqueous solutions above. Organic liquids are better solvents for HPC when hot rather than cold (Hercules, Inc.). A non-aqueous slurry may also be used.
- c. Ethylhydroxyethyl Cellulose: Add to cold water at a uniform rate, stirring vigorously. Continue stirring for thirty minutes or leave standing for thirty minutes. Stir again before using. For improved clarity, cool mixture by adding ice.
- d. Sodium Carboxymethyl Cellulose: Cellulose Gum CMC 7HSP or 7H is more easily made in a blender. Cellofas B3500 may be made by sifting powder into vigorously agitated hot or cold water.(CB) Never mix sodium carboxymethyl cellulose in organic solvent, add organic solvent to NaCMC already dissolved in water. Viscosity increases over a period of one hour. Cellofas B3500 will gradually lose viscosity over several weeks.(CB) The same solution can appear very different depending on how it is mixed. The molecules separate more quickly when mixed under conditions of high shear (i.e., not by hand) and/or when solvent is strongly polar.(CS) NaCMC can also be prepared using an alcohol or glycol as a non-aqueous, pre-wetting slurry.
- e. Methyl Hydroxyethyl Cellulose: Do not use blender because mixture tends to foam. Disperse powder first in 75°C (167°F) water (about 1/3 of full measure) to avoid lumping and gelling, then pour in remaining ice-cold water and agitate until mixture is smooth. Wait twenty minutes to an hour for mixture to thicken.

f. Two varieties of Cellulose Acetate flake used in conservation for consolidation are Kodak #4655 by Eastman Kodak and Celonese P911 by British Celanese. Dissolve cellulose acetate in acetone, MEK, or ethyl acetate to give a 2-3% solution.

## 2. Application

- a. Klucel G has been used for lining as a 1-2% solution in methanol or a 5% solution of Klucel G has been combined with Mowilith DMCZ (poly vinyl acetate) to size paper and prepare a solvent-activated lining (Hofenk de Graaf 1981). It has been used for fixing a seventeenth century charcoal drawing on brittle paper during bleaching and washing (Hofenk de Graaf 1981). Klucel G (5%) has been used on Japanese tissue to prepare a facing in order to allow removal of an old backing in warm water (Klucel G is insoluble in warm water). Removed with ethanol (Hofenk de Graaf 1981). Klucel G applied to thin cast tissue has been used for solvent-activated lining/reinforcement or mends.(FM) Solutions of Klucel G in ethanol are used by book conservators at the Library of Congress to consolidate powdering leather.(SRA)
- b. Methyl Cellulose has been used to swell scratches and abrasions and for changing the saturation of blanched colors. It has been used as a consolidant for flaking inks and paints, and for waxresin seals on parchment documents.(CB) It has been used as a surfactant, stain remover (2-3%), or to remove layers of adhesive after backing removal (Baker 1984, 55). Solutions of 2.5-3% methyl cellulose can be used as a poultice to draw up water stains, water soluble adhesives, etc. It may also be used with Fuller's Earth (Baker 1984, 55). When used as poultice or in any function where controlling the degree of wetness is important, methyl cellulose is a more surface active cellulose ether compared to NaCMC (same dilution and viscosity grade). Therefore, methyl cellulose will penetrate into a surface faster and easier while NaCMC is "drier."(CB) Methyl cellulose has been used to bind Whatman Cellulose Powder CF11 to fill small losses (Baker 1984, 55). It is used for sizing in a 0.5%solution and may be brushed on through polyester web or applied by immersion. Lower MW is better (e.g., 15 cps or 400 cps) and the object may be immersed only if the paper is strong and not torn, since the solution's weight and viscosity may cause weak or damaged paper to tear. Sized objects may be dried on silicone-coated Mylar or on Pecap (a tightly woven, non-stick surface, polyester fabric).(CB) Methyl cellulose has been used to line degraded wood pulp papers where it acts as an easily

reversible adhesive which also resizes weak paper surfaces. Thin Japanese paper objects have also been lined using MC alone as the adhesive.(KN) Methyl Cellulose has been used successfully for hinging on supports which may be distorted by slower drying paste. It has been observed not to penetrate supports as deeply as paste. Must be applied quickly.(DT) MC may be used for mending where graving of an edge cannot be tolerated (e.g., repair of chamfered tears inside the tear).(KE) It has been used as a poulticing vehicle for enzymes (Hatton 1977, 9). Methyl cellulose and ethulose in an aqueous solution (with alcohol added to enhance penetration) has been used as a consolidant for powdered pigments without changing surface gloss (see 23. Consolidation/Fixing/Facing). MC may be mixed with wheat starch paste (e.g., 1:2 or 1:3 v/v) for linings. It improves slip and makes it possible to position fragments before adhesive sets (Baker 1984). It also increases reversibility after drying.(KE) MC may be mixed with rice starch paste to increase initial tack, water resistance, and strength/flexibility of the dried film.(KE) MC can be used as an isolating layer over paper losses prior to inpainting, which makes it possible to remove in paint by preventing penetration into paper fibers.(KN)

- c. Sodium Carboxymethyl Cellulose may be used on its own for linings or it may be mixed with a starch paste (Baker 1984, 55).
- d. Cellulose Acetate lamination is accomplished by sandwiching a document between two sheets of film and subsequently sandwiching these layers between two sheets of tissue. The thermoplastic cellulose acetate film in this sandwich softens with heat and is pressed into the fibers of the document and tissue. Lamination is conventionally carried out with a flat-bed hydraulic press or roller press. As a consolidant it is usually effective when applied by brush. For treatment variations see AIC/BPG/PCC 1988 23. Consolidation/Fixing/Facing, 7.
#### 46.4.2 Proteinaceous Adhesives

- A. Collagens
  - 1. Preparation
    - a. Gelatin is prepared by dissolving the dry adhesive in warm water (approximately 43.3°C/110°F) or by swelling in cold water, than heating. The temperature should not exceed 55°C (130°F). It is better to successively heat up small amounts then to keep a larger batch warm, due to loss of strength.(CB) Repeated heating causes yellowing and decreased viscosity and strength. Viscosity may be varied by altering grade, concentration, or temperature.(CS)
    - b. Parchment size is made by cooking parchment scraps in water and straining. Upon cooling it forms a gel which can be sliced and dried for later use. Heating prior to the addition of alcohol seems to allow more alcohol to be added. However, excess alcohol alters parchment size.(DH) (See 17. Sizing and 23. Consolidation/Fixing/Facing.)

## 2. Application

- a. Other collagen-based adhesives are used abroad, but perhaps not in the U.S. Certain bone or hide glues are used by Japanese conservators (e.g., bone glue used for surface sizing paper or rabbit skin glue used in 2% solution as consolidant or inpainting binder). Russian isinglass is a pure collagen prepared from the swim bladders of the sturgeon fish. It is used extensively in Eastern Europe. (See 23. Consolidation/Fixing/Facing.)
- b. Collagen-based adhesives may be applied by brush, spray, floating, or immersion. Gelatin is used as a consolidant for flaking media (see 23. Consolidation/Fixing/Facing). Gelatin is also used for resizing paper. Its use as such is described in Walter Henry's "Resizing Following Aqueous Treatment: Current American Practice." AIC Book and Paper Group Annual 1986, Vol. 5. It is used as an isolating layer before color compensation. Gelatin is used to reinforce creases or abrasions and to align tears, especially by conservators of photographic materials.
- c. **Parchment size** is used in the treatment of parchment and as a consolidant and fixative in the treatment of paper.

B. Casein

Casein adhesives are not known to be typically used by paper conservators.

# 46.4.3 Synthetic Polymer Adhesives

#### A. Poly Vinyl Acetate Solutions

#### 1. Preparation

Suspend the resin beads in a cheesecloth bag inside the solvent container. Depending upon the solvent, the beads may need overnight or longer to dissolve at room temperature. Heat and agitation encourage solution of the material. For brushing, a 10-30% solution is recommended. For spraying, a much lower concentration of solution is used (i.e., 3-10%). Adhesion is brought about by reactivation of the resin film with solvent or by heat seal methods. Different resins can be modified and mixed, for specific applications.

Thick, even coatings are created by brush, roller application (e.g., making heat-seal film). Web coatings are created by spray (e.g., light lining). Only the lowest viscosities can be sprayed.(CS) Selection of the solvent for the resin in solution varies the penetration of the resin into the adherent. Strength of the adhesive can be tailored to some extent for application through the mixture of various resin grades.(PV)

# 2. Application

PVAs can behave as penetrating or surface adhesives depending on the size of the resin molecule and the viscosity of the solution. They bond well to porous or non-porous surfaces.

- a. **PVA** solutions wet non-polar surfaces better than do emulsions, permit more controlled drying, and produce clearer films. Complete evaporation of solvent occurs slowly. As a result, there is some time before full bond strength is achieved, possible interaction of solvent, and eventually some shrinkage of film.(CS) As a consolidant or adhesive film, PVA can have a shiny appearance which may not be desirable for a particular application. Films are sensitive to heat and subject to cold flow at normal temperatures, resulting in a tackiness to the touch in some circumstances. Films can also pick up dirt because of their softness. Softness or problems with low glass transition temperature can be altered through the mixture of different resins grades.(PV)
- b. As a lining adhesive (AIC/BPG/PCC 1988 29. Lining, 39-41).

- c. A lining technique using **PVA-AYAF** sprayed onto nylon gossamer web for use in conserving fragile iron gall ink drawings on tracing paper (Jirat-Wasiutynski 1980, 96).
- d. AYAT for use as a hinge adhesive for albumen photographs. (See the article by Deborah Dyer in the <u>AIC Photomaterials</u> <u>Group Abstracts</u> from the 1983 Winter Meeting.)
- e. AYAC for use as a spray consolidant for historic wallpapers (AIC/BPG/PCC 1988 23. Consolidation/Fixing/Facing, 10, 17.) For use as a consolidant, see 23. Consolidation/Fixing/Facing).
- f. For use as an adhesive in mounting deteriorating textiles (Himmelstein and Applebaum 1976, 57-65).
- **B.** Poly Vinyl Acetate Dispersions

## 1. Preparation

Use straight from stock container, or dilute as necessary with water if recommended by product literature.

## 2. Application

As a consolidant or adhesive film, PVA may have a shiny appearance. When applied to a paper substrate, a PVA dispersion may penetrate moderately or remain on the surface. The degree of penetration depends on the size of the dispersed polymer particle and the polymer's molecular weight.

- a. PVA dispersions such as Jade 403 can be mixed with wheat starch paste or methyl cellulose to increase "strength" of these adhesives for mounting, hinging, bookbinding, and boxmaking applications (Baer, Indictor, and Phelan 1975, 123).
- b. Lining adhesive for painting (Horie 1987, 96; Werner 1952, 62; King 1976).
- c. As a heat-activated adhesive film Texicote (Baer, Indictor, and Phelan 1975, 123) Vinamul 6526 for textiles (Horie 1987, 96).
- d. Elvace 40-704 (Vinamul 3252) as a consolidant (AIC/BPG/PCC 1988 23. Consolidation/Fixing/Facing, 12).

## C. Poly Vinyl Alcohol Solutions

#### 1. Preparation

Disperse powder in cold water and warm if necessary, depending upon resin grade. Use agitation. (See 46.3.3 C. PVOH - Solubility for temperatures for specific grades.)

# 2. Application

- a. PVOH has excellent wet tack. Most grades produce dried films that remain tack-free up to approximately 90% RH. Films are strong, flexible, and resistant to oils and greases.(CS) Fully hydrolyzed grades have greater tensile strength (Horie 1987, 97).
- b. Consolidant for Japanese screen paintings (Higuchi 1984).
- c. Evenol 52-22 (15-20%) mixed with rice starch paste (80-85%) as a mending and binding adhesive (Library of Congress Adhesives File n.d.).
- d. Compatible with hydroxypropyl cellulose, and possibly with sodium carboxymethyl cellulose and gums (Horie 1987, 64).

# **D.** Acrylic Resin Solutions

#### 1. Preparation

Suspend resin beads in cheesecloth inside a jar of appropriate solvent for twenty-four hours or longer. Use of cheesecloth or netting improves solvent access to beads and speeds dissolution. Resin supplied in solvent can be diluted to desired concentration, 2.5% for brush and spray application.

#### 2. Application

Acryloid B-72 is the acrylic resin most widely used by paper conservators in the following ways.

a. Acryloid B-72 has been used as a fixative for soluble media during bathing or other aqueous treatments, such as steam or wet removal of Fraktur from wooden supports. Fixative is generally removed after treatment by immersion or by applying solvent on suction table. As a consolidant for flaking or friable media. With brush application (Weidner 1972, 977) of n-butyl methacrylate in xylene and petroleum benzine to fix friable Fraktur pigments. Acryloid B-72 as a spray application (in toluene and xylene or in diethylbenzene) (Welsh 1980, 146). Or spray application on suction table (approximately 2.5% in xylene

and diethylbenzene) (Couch 1985, 22-30). Acryloid B-72 has been used as an isolating layer prior to inpainting (approximately 10% solution) (Hamm 1981, 121). As a heat set adhesive (Zappala and Mendola 1978; Pavitt 1987, 3-5); an adhesive for facing tissue; and as a protective coating over exposed wallpaper or globes (approximately 4-10% in toluene) (Schulte 1981, 108; van der Reyden 1986, 27). Acryloid B-72 has been used to simulate original high gloss in loss areas of globes, wallpaper, etc., or to restore glossy appearance in intact areas which have suffered damage to surface (van der Reyden 1986, 27).

h. As a barrier coating for metal components in collages or other artifacts made of diverse materials. Acryloid B-48N (ethyl methacrylate copolymer from Rohm and Haas) has been useful because it adheres to bare and primed metals, including copper, bronze, and zinc.(CS) Other Acryloid resins, such as B-72, have also been used as barrier coatings on metal.

# E. Acrylic Resin Dispersions (See AIC/BPG/PCC 1988 29. Lining, 15-19.)

- 1. Pressure Sensitive Adhesives: The following acrylic dispersions are better suited for pressure sensitive applications.
  - a. Rhoplex N-1030, N-580, N-619
  - b. Lascaux 360 HV
  - c. Plextol 360

Depending on the desired solvents for application, the reversibility requirements, or the need for adhesion to an unusual support, additives including methyl cellulose, hydroxyethyl cellulose, or inerts may be added. **Methyl cellulose** as a powder or in a solution, reduces the moisture of the adhesive and can break up the acrylic film for better reversibility in the future. **Lascaux 360 HV** diluted with methyl cellulose solution was used on a lithograph/collage that had failed pressure sensitive tapes as part of the artifact holding the elements together. The yellowed tape adhesive was removed, and the Lascaux/methyl cellulose mixture coated on the tape carrier and elements reapplied.(AD) **Hydroxyethyl cellulose** can assure solubility in various solvents in the future and also acts to prevent penetration of the support due to its large molecular size. Adhesives can be diluted with water and retain their strength.  Solvent Reactivation: The following acrylic dispersions have been applied by coating secondary support with adhesive, drying, positioning on artifact, spraying adhesive with solvent to reactivate: Plextol B-500, Rhoplex AC-234, Lascaux 360 HV, Lascaux 498 HV, Library of Congress Heat-Set Tissue. The modifications listed under pressure sensitive applications may apply.

1% toluene can be whipped in as a thickener and is in low enough concentration to interact only with the acrylic dispersion and not the support. Toluene in 15% concentration will also interact with the support and is used for wax lined paintings but could be useful when a paper support has a material resistant to aqueous adhesives. One formulation is Plextol B-500 91 ml, toluene 9 ml; an alternate formulation is Plextol B-500 89 ml, toluene 9 ml, and water 2 ml. Either formulation thickens the adhesive to prevent penetration and eliminate moisture. Adhesive mixture is applied to the support, allowed to dry, reactivated with isopropanol (CCI/Getty n.d., MCIN No. 175).

Heat set tissues can be toned prior to applying adhesive. This tissue was used successfully to stabilize fire damaged documents.(LG)

Also the L.C. heat set tissue formulation b., can be applied by reactivating with ethanol or other solvents rather than with heat.

A preliminary study was carried out on acrylic resin coated lens tissue (formulation b., below) at the National Archives. The study compared heat activation (using a tacking iron) at 76.6-82.2°C (170-180°F) and solvent-activated (toluene) acrylic-coated lens tissues which were bonded to early twentieth century ledger sheets. The samples were exposed to light from a window for five months during the winter. The lens tissue was coated with Rhoplex AC-73, AC-234, and deionized water (1:1:1) and applied using the Library of Congress technique. Before aging, it was observed that the solvent-activated tissue strips had increased bond, greater transparency, and were easier to reverse (in toluene) than the heatactivated strips. Also, it is likely that the toluene carried the adhesive further into the paper than heat-activated adhesive. After aging, it was observed that both heat and solvent-activated strips were readily reversible in toluene while only slightly reversible with heat from a tacking iron. There was no staining evident from either heat or solvent-activated adhesives on the ledger sheets after five months, though considerable light bleaching had occurred.(LC)

3. Use as Heat-Activated Adhesive: The following acrylic emulsions are best suited for heat activation. The modifications listed under Pressure-Sensitive Application apply.

Horie states that dispersions should not be heated above their  $T_g$  temperature because cross-linking could occur (Horie 1987).

Formulations

- a. Rhoplex AC 234 50 ml + water 50 ml. Can be removed in solvent or heat of 68-70°C (154.4-158°F). Alternate formulation: Rhoplex 234 40 ml + Rhoplex AC-73 40 ml + water 20 ml. The addition of Rhoplex AC-73 creates a stiffer support. Support is coated with acrylic mixture and allowed to dry, then positioned with the artifact and attached with heat. Activation temperature 70-72°C (158-161.6°F) (CCI/Getty n.d., MCIN Nos. 202, 205).
- b. Library of Congress Heat Set tissue: Rhoplex AC-234 (or Plextol B 500) 29 ml, Rhoplex AC-73 42 ml, water 29 ml Alternate formulation AC-73 40 ml, AC-234 (or Plextol B 500) 40 ml, water 20 ml. Either formulation is applied with brush or spray to lens tissue and allowed to dry. Attached with tacking iron and overall heat. Activation temperature is 90°C (194°F). Reversible in ethanol, acetone, mechanically (CCI/Getty n.d., MCIN Nos. 177, 198).
- c. Rhoplex AC-33 50 ml, water 50 ml; alternate version Rhoplex AC-33 40 ml, Rhoplex AC-73 40 ml, water 20 ml (the latter version gives a more rigid lining). Sprayed onto support, allowed to dry and attached with heat (CCI/Getty n.d., MCIN Nos. 180, 186).
- d. Lascaux 360 HV applied to support and allowed to dry. Large, oversize drawing positioned and activated at 43.3°C (110°F) (Eckmann).

# F. Proprietary Formulations

- 1. Preparation
  - a. Add naphtha, toluene, or xylene to **BEVA 371** and warm in a double boiler until the solution is clear, stirring occasionally. Various percentages of BEVA 371 to solvent have been used in conservation depending upon application (8%-37%). Use extreme caution when heating BEVA solutions due to flammability.(PV) BEVA 371 dries to a matte, slightly waxy appearance before aging.

- b. **BEVA D-8** dries to a clear, relatively matte, colorless film. Can be diluted with water.
- 2. Application
  - BEVA 371 used as mending adhesive: Brush directly onto tissue, a. dry twenty-four hours or more, use as a heat-seal adhesive for water sensitive objects.(KE) Squeegee warmed undiluted adhesive through woven polyester screen (like Pecap) onto tissue, dry one week minimum, activate heat-seal tissue with 54.4°C (130°F), solvents or solvent vapors (weak bond).(CB) Diluted with naphtha (1:4), heated, sprayed onto tissue, applied with tacking iron (Stone 1987). Solution of 1:1 with toluene or naphtha sprayed under high pressure with opening on spray gun set at widest setting.(PV) Due to problems with penetration, flock application of adhesive (1:1 with toluene) with a spray gun is recommended. Flocking should be done on the lining or mending substrate rather than the primary artifact.(PV) BEVA 371 has been used in workable dilutions as both a consolidant and a fixative on soluble iron gall ink manuscripts.(CB)

Note: Silicone release materials must be used in contact with BEVA adhesive. It sticks <u>very well</u> to Mylar, Plexiglas, and glass.

- b. Lamatec coated repair tissue and Lamatec Coated Crompton tissue: Apply with heat, 20-25 seconds at 80-90°C (176-194°F), to document as mending tissue or lining tissue.
- c. Lamatec unsupported film: Laminate with hot press or tacking iron to chosen support paper or cloth at 80-90°C (176-194°F) for 20-25 seconds.
- d. **Texicryl 13-002** for use as a lining adhesive: Apply in the heat seal method. See Hackforth-Jones 1981, 23-26, using Texicryl 13-002 coated tissue.
- e. **Fusion 4000** unsupported film: Apply with heat to materials which are to be attached.
- f. **Filmoplast P:** Pressure-sensitive tape. Not advised for use in contact with artworks.
- g. Archival Aids Tape: Pressure-sensitive tape. Not advised for use in contact with artworks.

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## 46.6 Special Considerations

#### 46.6.1 Glossary of Selected Terms

Adhesive: "A substance capable of holding materials together by surface attachment" (Skeist 1977).

<u>Colloid, protective</u>: "Any surface-active substance that prevents the dispersed phase of a suspension from coalescing by forming a thin layer on the surface of each particle" (Hawley 1977).

<u>Gel</u>: "A semisolid system consisting of a network of solid aggregates in which liquid is held" (Skeist 1977).

<u>Glass Transition Temperature</u> ( $T_g$ ; "The temperature at which an amorphous material (such as glass or a high polymer) changes from a brittle, vitreous state to a plastic state. Many high polymers, such as the acrylics and their derivatives, have this transition point, which is related to the number of carbon atoms in the ester group" (Hawley 1977).

<u>Retrogradation</u>: "A change of starch pastes from low to high consistency (...comprised...of viscosity, plasticity, and other phenomena) on aging" (Skeist 1977).

<u>Thermoplastic</u>: "A high polymer that softens when exposed to heat and returns to its original condition when cooled to room temperature. Natural substances that exhibit this behavior are crude rubber and a number of waxes; however, the term is usually applied to synthetics such as polyvinyl chloride...linear polyethylene...and cellulosis and acrylic resins" (Hawley 1977).

<u>Thixotropy</u>: "The ability of certain colloidal gels to liquify when agitated (as by shaking or ultrasonic vibration) and to return to the gel form when at rest" (Hawley 1977).

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## 46.6.2 Adhesive Application Methods

Different adhesive application methods offer advantages and disadvantages. The use of brushes offers precise, local application. However, **brush application** can result in heavy penetration with staining and alteration of the paper's color or surface texture. Brushing adhesive over a large area, for example in lining or sizing treatments, may result in uneven coating with uneven adhesion and the eventual appearance of brush marks. Brush application of an adhesive generally requires subsequent application of pressure which the object must be able to withstand.

Floating or immersion (for example, in sizing with gelatin or cellulose ethers) theoretically produces an equal coating; thus, avoiding the problem of uneven adhesion. The sheet is then consistent in hygroscopicity, color, texture, etc. Disadvantages of floating or immersion are heavy penetration and possible change in surface texture. This process often requires application of pressure at a later stage in the object's treatment.

Application using **rollers** theoretically gives a more even distribution of adhesive, eliminating small lumps and air bubbles. Roller application enables quick coverage of large surface areas. The pressure can be altered either to prevent or to ensure penetration. Disadvantages of roller use are the potential for track marks due to adhesive being pushed to outer edges and the lack of precise and local application. One must consider possible adverse effects of pressure on the object from rolling action.

**Spraying** achieves an even coating whose quality can be adjusted from tiny, discrete beads sitting on the surface to a penetrating and continuous coating, without brush or roller mark problems. Disadvantages include the difficulty of spraying in precise, localized areas and the requirement for costly equipment. Spraying of organic solvents requires proper safety and ventilation equipment.

**Squeezing** through a woven screen material (of varying fineness) offers an even application of the adhesive onto or into the paper.(CB)

The use of the **suction table** has the advantage of not requiring application of pressure to the object's surface and therefore may be useful for objects which will not withstand direct pressure. Disadvantages include the potential to create wrinkles in the paper or to embed airborne dirt, as well as the longer drying time.

**Heat activation** of an adhesive avoids water- or solvent-related problems. There is generally less penetration of adhesive into the object, depending on a knowledgeable combination of object, thickness of adhesive, intensity of heat, and duration of exposure. The bond may be undone without applying water or solvent. However, the use of heat may be inappropriate for some papers and media and temperature must be carefully controlled.

Solvent activation avoids water related problems, both during application and later if the bond is undone. However, disadvantages include potential for solvent to cause bleeding of media or dyes and sizing in the paper. Proper safety and ventilation equipment are necessary. Liaison: Catherine I. Maynor, Diane van der Reyden.

Compilers: Christine Smith with Sarah Bertalan, Antoinette Dwan, Janet English, Catherine Nicholson, Sylvia Rodgers Albro, Kimberly Schenck, Linda Stiber, Sarah Wagner.

Contributors: Cathy Baker, Mary Baker, Lage Carlson, Dan Clement, Katherine Eirk, Lynne Gilliland, Doris Hamburg, John Krill, Debora Mayer, T.K. McClintock, Frank Mowery, Francis Prichett, Janet Ruggles, Martha M. Smith, Jill Sterrett, Denise Thomas, Tim Vitale, Paula Volent.