NEUTRALIZATION AND ALKALIZATION

20. Neutralization

Application of an alkaline agent which reacts with acids in paper to form a salt.

Alkalization

Application of an alkaline agent which reacts with acids in the paper and leaves in paper an alkaline reserve capable of reacting with acids in the future.

(Because it enables paper to resist changes in pH, an alkaline reserve is sometimes called a buffer, and the treatment buffering.)

Note: 'Deacidification,' a less precise term, includes the concepts of neutralization, alkalization, and sometimes the removal of soluble acidity by washing.

20.1. Purpose: The purpose of both neutralization and alkalization is to stop acid hydrolysis of the cellulose and associated discoloration, weakening and embrittlement of the paper. Alkalization is also intended to stabilize the paper against further acid attack.

20.2. Factors to consider.

20.2.1. Chemical and mechanical quality of the paper.

A. Degree of inherent instability or expected degradation.

B. Sources of acidity.

1. Local (inks, pigments, etc.)

2. General (fiber finish, sizing, environment, etc.)

C. Effectiveness of prior washing (See 18. Washing.)

20.2.2. Housing and storage conditions after treatment.

A. Likelihood of reintroduction of acid due to poor environment.

B. Effectiveness of buffered housing material in protecting against environmental acidity.

20.2.3. Wet-strength of paper (ability to maintain physical integrity in aqueous/non aqueous alkaline solutions) including areas damaged by acidic media.

20.2.4. Permeability of object to aqueous/non-aqueous solutions.

A. Sizing and thickness of object; probable evenness of wetting.
1. Laminar structure including mounts and adhesives.

2. Possible development of uneven discoloration due to uneven deposition of alkali.

20.2.5. Possibility of changes in aesthetic/optical qualities of paper (color, luster, texture, opacity/ translucence).

A. Problems with solubility of fillers, coatings, sizes, etc. in alkaline solutions (e.g. gelatine, natural gums).

B. Problems of powdery or crystalline deposits on paper surface after drying.

1. Such deposits can sometimes be removed by treatment with a weak volatile acid (carbonated water, dilute acetic acid). Alkaline reserve may be affected.

C. Problems of color movement/discoloration in paper.

1. Presence of groundwood which darkens at alkaline pH.

2. Presence of soluble or pH-sensitive material (decomposition products, sizes, dyes, etc.) not previously washed out.

20.2.6. Problems with media. (See 3. Media Problems)

A. Solubility in aqueous/non-aqueous solutions.

B. Possible color change or increased solubility due to pH sensitivity of media.

20.2.7. Possibility/desirability of protecting against oxidation of cellulose.

20.2.8. Possibility of alkaline degradation of paper during treatment.

20.2.9. Size and number of objects to be treated.

A. Possible need for bulk treatment apparatus, oversized work area, etc.

20.2.10. Safety factors.

A. Toxicity.

B. Flammability, explosiveness.

20.3. Materials and Equipment.

20.3.1. Aqueous neutralizing/alkalizing agents.

A. Calcium hydroxide. Formula: $Ca(OH)_2$. Preparation: An excess (2g/L or more) of high-grade calcium oxide or hydroxide powder is dispersed in purified water, stirred thoroughly, and allowed to settle. This forms a saturated solution with a pH around 12.4. The solution left on its solids remains saturated, but becomes cloudy as insoluble carbonate forms, beginning at the solution/air interface. Any precipitate should be skimmed or filtered before use. For use in treatment the saturated solution is diluted with purified water; the dilute solution forms carbonate much more slowly than the saturated solution and may be stored longer. Commonly employed mixtures range from very dilute (pH @8) up to a 1:1 mixture (about 0.018 N, pH 10-11).

B. Calcium bicarbonate. Formula: $Ca(HCO_3)_2$. Preparation: High-grade calcium oxide or hydroxide powder is dispersed in purified water and carbon dioxide is bubbled through this liquid until it becomes clear. About 7.3 g/L of hydroxide powder are required to form a 0.1 M solution. (In practice not all will go into solution because of low solubility.) Use of a large excess of powder will cause difficulty in determining when the reaction is complete. Calcium bicarbonate solutions do not have a long shelf life and should not be used after a visible precipitate begins to form.

C. Magnesium bicarbonate. Formula: $Mg(HCO_3)_2$. Preparation: High-grade magnesium hydroxide powder is dispersed in purified water, and carbon dioxide is bubbled through this liquid until it becomes clear. About 5.8 g/L of powder are required to form a 0.1 M solution. Magnesium carbonate (light) may also be used but it is slower to dissolve. (8.4 g/L yield a 0.1M solution). Constant stirring, low temperatures, and maintenance of a pressurized CO_2 atmosphere may be employed to speed up the formation of bicarbonate. Use of a large excess of powder will cause difficulty in determining when the reaction is complete. Settling may be required to eliminate cloudiness. The pH of the solution as applied ranges from 6.5 to 8 depending on age and concentration. Magnesium bicarbonate solutions should not be used after a visible precipitate begins to form (2-5 days in closed container at room temperature). Shelf life may be prolonged by refrigerating the carbonated solution, preferably under a pressurized CO_2 atmosphere.

Testing solution strength: The concentration of finished solution is tested by titration for magnesium with EDTA. Equipment and chemicals for this procedure can be purchased from chemical supply houses, or from Taylor Chemical Co. as the Taylor Total Hardness Set, cat. no. 1123. This set indicates a 0.1 M solution by 18 ml. of titrant. A simpler, less expensive test is available as the Taylor Magnesium Carbonate Drop Test Kit, cat. no. 1597. Both sets may also be used to test calcium carbonate solutions, with suitable modification to the calculations.

D. Barium hydroxide. Formula: $Ba(OH)_2$. NOTE: Barium compounds are highly poisonous. One gram of barium carbonate (the residual alkali in this process) ingested is fatal to an adult. Sublethal doses are also toxic. Barium hydroxide-treated material should be so marked and handled with extreme care. Preparation: The solution may be made up in purified water as for calcium hydroxide, although barium hydroxide is slightly more soluble. The pH of the stock solution is around 12.

E. Magnesium acetate. Formula: $Mg(OOCCH_3)_2$. Preparation: The solution may be made up in purified water. A 5% (w/v) solution has been described for use alone. A 3% solution may be mixed with 3% calcium acetate in the first bath of a double decomposition treatment. Magnesium acetate has a good shelf life. Both the neutralization reaction and the conversion to the carbonate produce volatile acetic acid, which continues to be generated in treated paper. This may adversely affect lead seals, metalpoint drawings, silver-based photographic images, and lead-basccd pigments in the presence of sulphur.

F. Calcium acetate. Formula: $Ca(CH_3COO)_2$. Preparation: The solution may be made up in purified water. A 6% solution, or a mixture of 3% calcium acetate and 3% magnesium acetate, may be used as the first bath of a double decomposition treatment. Acetic acid is produced in treated paper (see 20.3.1E above).

G. Calcium chloride. Formula: $CaCl_2$. Preparation: The solution may be made up in purified water. A 6% (w/v) solution may be used as the first bath of a double decomposition treatment.

H. Ammonium carbonate (hartshorn). Mixture of ammonium bicarbonate (NH_4HCO_3) and ammonium carbamate (NH_2COONH_4). Preparation: Solution may be made up in purified cool water. A 6% (w/v) solution may be used as the second bath in a double decomposition treatment.

I. Borax (sodium borate, sodium tetraborate). Formula: $Na_2B_4O_7$. Preparation: The solution may be made up in purified water. The saturated solution (6.25% w/v) has a pH of 9.5; a 0.01M solution has a pH of 9.2. A 4% (w/v) solution has been employed for alkalizing.

J. Ammonia water (ammonium hydroxide). Formula: NH_4OH. Preparation: Commercially available as concentrated solution (28-30% NH_3 by weight). Concentrated solution is pH 12. For use in neutralization it is diluted to desired pH with purified water. Ammonia water leaves no residual alkaline reserve.

20.3.2. Non-aqueous neutralizing /alkalizing agents.

Note: The use of magnesium compounds in organic solvents for deacidification is protected by patents (Langwell, Smith). The following information is given in good faith and offers no exemption from proprietary rights.

A. Magnesium methoxide in methanol. Formula: $Mg(OCH_3)_2$. Preparation: Commercially available from Wei T'o Associates (on special order) as an 8% solution in methanol. It can also be prepared in the laboratory by adding magnesium to methanol with iodine crystals to act as a catalyst. The iodine evaporates to leave a colorless solution. For use in alkalizing magnesium methoxide is commonly diluted to 1% (about 0.116M) with methanol or other organic solvents. Trichlorotrifluoroethane (Freon) is often used as a diluent because it is a poorer solvent for many media than is methanol. The pH of the solution as used for alkalizing is between 10-11. Magnesium methoxide solutions are extremely sensitive to moisture and should be stored under airtight, moisture-free conditions. They should not be used after a visible precipitate begins to form.

B. Methylmagnesium carbonate (methoxy magnesium methyl carbonate, or MMMC). Formula (proposed): $CH_3OMgOCO_2CH_3 \cdot XCO_2$ (X varies with solvent and temperature). Preparation: This solution is available commercially from Wei T'o Associates. It can be prepared in the laboratory as follows: Carbon dioxide is bubbled through a 1% solution of magnesium methoxide in organic solvents (described above). If pure methanol is employed, the solution will remain clear; the reaction is complete when the solution pH remains steady below 8.5. If a mixture of methanol and Freon is employed, the solution will become cloudy, and the reaction is complete when it becomes completely clear again (pH @ 7.5). Methylmagnesium carbonate solutions are less sensitive to moisture than are magnesium methoxide solutions, to a degree depending upon the solvents used. They should nevertheless be stored under airtight, moisture-free conditions; they should not be used for treatment after a visible precipitate begins to form.

C. Ethylmagnesium carbonate (ethoxy magnesium ethyl carbonate, or EMEC). This alkalizing agent is available commercially from Wei T'o Associates in two different ethanol/trichlorotrifluoroethane blends. Except for differences in solvent properties (evaporation rate, effect on inks, etc.) its use is similar to MMMC.

D. Magnesium acetate in methanol. Preparation: Magnesium acetate may be made up as a solution in methanol. Concentrations of 4% (w/v) have been described for alkalization. Acetic acid is formed in treated paper (see 20.3.1E above.)

E. Calcium acetate. Formula: $Ca(CH_3COO)_2$. Preparation: 2g of high-grade powder are dissolved in 20 ml purified water. 95% ethanol (in water) is slowly added to make 1 liter of solution. If precipitate forms, a few drops of water are added until it clears. Acetic acid is formed in treated paper (see 20.3.1E above).

F. Barium hydroxide in methanol. NOTE: Barium compounds are highly poisonous. See 20.3.1. above. Preparation: A common formula (1% w/v) is prepared by dissolving 19g of barium hydroxide (octahydrate) per liter of high-grade methyl alcohol. The solution has a pH around 12.

20.3.3. Vapor phase neutralizing/alkalizing agents.

A. Ammonia vapor. Ammonia (NH_3) has been used for deacidification. (Kathpalia) It neutralizes incompletely and volatilizes from treated objects in a few months, leaving no alkaline reserve. Observe proper health precautions against vapors.

B. Cyclohexylamine carbonate (CHC). (Langwell) NOTE: CHC is suspected of being a carcinogen; it may also cause liver/kidney damage. CHC has been used in the form of impregnated sachets and interleaving tissues. It neutralizes effectively but leaves no alkaline reserve. It has an unpleasant odor. Commercially available from Interleaf Inc.

C. Morpholine. In an automated commercial system designed for mass treatment, paper and books to be treated are exposed to a mixture of morpholine vapor and water vapor in an evacuated chamber for ten minutes, after which the excess vapor is flushed and the material removed from the chamber. Morpholine is sufficiently toxic to require special handling equipment, but treated objects are not believed to pose a health hazard. The process neutralizes effectively and imparts some residual alkalinity, but this may diffuse out of the object under even moderately humid conditions. A small percentage of treated materials exhibit color changes, particularly leather and pyroxylin book covers and groundwood papers.

D. Diethyl Zinc (DEZ). In a very large-scale commercial process now under development by the Library of Congress, paper and books to be treated are placed in a chamber and partially dried under vacuum and mild heat. Gaseous diethyl zinc is admitted to the evacuated chamber at low pressure

to neutralize the acid in the paper fibers and concurrently deposits an alkaline reserve compound. The books are allowed to be treated by the gas for twelve to fifteen hours. After this step the small excess of diethyl zinc is pumped from the chamber and recovered. At this point the treated books are exposed to moist carbon dioxide, which partially converts the zinc oxide left in the paper from the first stage of treatment to zinc carbonate. This leaves an alkaline reserve of about 1.5-2% zinc carbonate/zinc oxide in the treated paper. The treatment also acts as a fungistat to retard mold growth.
NOTE: Diethyl zinc decomposes into ethane and zinc oxide on contact with air and excess water and the ethane ignites burning away rapidly. This process requires special engineering facilities with chemical and vacuum equipment and is not recommended for in-house conservation lab operation. (PGS)

20.3.4. <u>Combined alkalizing/strengthening agents</u>.

A. <u>CMC (sodium carboxymethyl cellulose)</u>. Description: Film-forming sodium salt of a polymeric cellulose derivative; high buffering capacity, moderate alkalinity. An aqueous solution, 1% by weight of CMC-12HP and 0.1% of Hercules Kymene, a wet-strength resin, has been used to impregnate paper using a modified mimeograph machine. The effectiveness of any such reinforcing resin depends on the strength remaining in the deteriorated paper (see 23 Consolidation/Fixing/Facing/Sizing).

B. <u>Magnesium acetate and polyvinyl acetal, polyvinyl butyral, etc. (Regnal process)</u>. Paper to be treated is brushed with or immersed in 4-6% magnesium acetate (alkalizing agent) in an organic solvent solution of polyvinyl acetal, polyvinyl butyral, etc. (strengthening resin). Book pages must be separated while drying. Strenghthening achieved is variable.

C. <u>Magnesium acetate in heat-set adhesive (Postlip lamination tissue)</u>. A commercially produced tissue coated on one side with an acrylic or vinylacetate polymer containing magnesium acetate. The tissue is heat-laminated to paper to strengthen it and provide some alkaline protection in one operation.

20.3.5. Apparatus for mixing chemicals.

20.3.6. Apparatus for testing solution strength.

A. pH measuring device.

B. "Drop test" or titration for Mg or Ca with EDTA (see 20.3.1.C above).

20.3.7. Trays.

20.3.8. Drying equipment (see 28. Drying and flattening).

20.3.9. Brushes.

20.3.10. Washing supports/moisture barriers.

A. Non-woven polyester web.

B. Wet-strength paper.

C. Polyester film.

20.3.11. Spray equipment.

A. Aerosol can.

B. Pump spray.

C. Pressurized commerical cylinder and airless spray gun.

D. Air compressor, pressure pot and spray gun/airbrush.

E. Pressurized inert gas tank and spray apparatus.

F. Cleaning materials for spray equipment.

G. Ventilation system.

1. Fume hood.

2. Spray booth.

3. Custom-designed system.

H. Respirator, goggles and gloves for protection against toxic solvents/vapors.

20.4. Treatment variations.

20.4.1. Aqueous treatment techniques. General procedures: Paper and media should be tested for solubility and color changes in both water and alkaline solution. Good penetration of alkaline solution is essential. One way to achieve penetration is to wash first in water and treat while still wet. Water in the paper will dilute the alkaline solution and may reduce the alkaline reserve. Wetting agents such as alcohols may be employed to achieve thorough wetting. Powdery or crystalline deposits may form on the paper surface during drying, especially when using concentrated solutions, if solution is left standing on the surface, or conditions favor the movement of salts with the evaporating liquid and their concentration at the evaporation surface. This problem may be ameliorated by a) using a less concentrated solution, perhaps repeating the treatment (drying between) to achieve adequate alkaline reserve; b) drying slowly in a humid atmosphere; c) drying between blotters; d) drying the object face down with only the verso directly exposed to the atmosphere; e) redissolving the deposits in a solution of a weak volatile acid such as carbonated water or dilute acetic acid. Alkaline reserve may be reduced by a, c, or e.

A. Barrow two-bath process (calcium hydroxide & calcium bicarbonate). Barrow originally employed twenty-minute immersions: saturated calcium hydroxide for neutralization followed by saturated calcium bicarbonate to precipitate the calcium carbonate buffer. The second bath was later deemed superfluous because the hydroxide was converted to carbonate by atmospheric CO_2 during drying.

B. Calcium hydroxide.

1. Immersion. Calcium hydroxide is now used in single bath treatments at widely varying concentrations (see 20.6). During removal from the bath, treated paper should be protected from any insoluble carbonate "skin" floating on the liquid surface.

2. Brush application. Calcium hydroxide may be applied with a soft wide brush, usually to control or limit penetration (e.g., application from one side only). This method is not usually advantageous for aqueous solutions, since washing is desirable prior to their application. Any alkalizing method which does not completely saturate the paper creates the possibility of uneven distribution. This may result in uneven discoloration of the paper upon subsequent aging.

3. Spray. Spray application may be useful to economize on materials, to facilitate rapid treatment of large numbers of items, and to control penetration. Evenness of application is a concern. Spray application can be less efficient than other methods due to premature precipitation of carbonate. This can leave a powdery surface deposit, as well as reducing alkaline reserve.

C. Barrow/Gear one-step process (magnesium bicarbonate).

1. Immersion. Barrow recommended a saturated solution of magnesium bicarbonate for spray treatments (see below) and Gear in 1957 introduced a treatment consisting of a thirty-minute immersion in a 0.025M solution of the same agent. The Library of Congress has recommended a minimum concentration of 0.1M to achieve an alkaline reserve of 2-3%.

2. Brush application. Magnesium bicarbonate may be applied by brush (see 20.4.1. B 2 above).

3. Spray. Magnesium bicarbonate may be applied by spraying (see 20.4.1.B 3 above).

   Modification. A. Clapp (1973) has described a treatment in which the paper, supported by a piece of tissue, is placed face down on a sheet of polyethylene and sprayed with a mixture of 90% magnesium bicarbonate solution and 10% alcohol. The damp surface is brushed with a broad soft brush to more evenly distribute the solution. Excess liquid is blotted from the plastic sheet and the paper is covered with tissue and a second sheet of polyethylene. The envelope is closed with "snake" weights and the paper allowed to "marinate" for three to four hours. The envelope is opened and the paper allowed to dry face down.

D. Barium hydroxide.

1. Immersion. NOTE: Barium compounds are highly poisonous (see 20.3.1 D above) Aqueous barium hydroxide was one of the agents employed by O. Schierholtz, whose 1936 patent formed the basis for modern neutralization and alkalization treatments. His immersion times ranged from five seconds to two minutes. Somewhat longer immersion may be necessary for maximum penetration. Extensive premature carbonation of aqueous barium hydroxide solutions may be a problem.

2. Brush application. Barium hydroxide solutions may be applied by brush (see 20.4.1 B 2 above).

3. Spray. Spray application of barium hydroxide poses a serious health hazard.

E. Borax.

1. Immersion. Borax has been employed in a single bath treatment by F. Flieder and others. M. Hey has reported adverse effects on iron-gall inks and limited improvement in paper strength after moist aging.

2. Brush application. Borax solutions may be applied by brush (see 20.4.1 B 2)

3. Spray. Borax solutions may be applied by spray (see 20.4.1B 3)

F. Magnesium acetate. Aqueous solutions of magnesium acetate may be employed in immersion, brush and spray treatments.

G. Double decomposition treatments. These methods, proposed and patented about 1973 by the Library of Congress, were tested but not used for actual treatment.

1. Calcium chloride/ammonium carbonate. Paper to be treated is soaked for 10-15 minutes in 6% calcium chloride solution, drained well, and immersed for 15 minutes in 6% ammonium carbonate solution. The second bath should be covered to prevent loss of CO_2 and NH_3. The paper is then washed thoroughly (e.g., 20 minutes in running water followed by four changes of distilled water). The last 10 ml of liquid (roughly) draining from the sheet should be saved in a beaker. 5 drops of 0.025N silver nitrate solution are added to the beaker. If this mixture yields more cloudiness than the same volume of pure water treated with 5 drops of silver nitrate, then residual chloride is present in the paper and it should be washed until the test is negative.

2. Magnesium acetate+calcium acetate/ammonium carbonate. Paper to be treated is soaked for 20-30 minutes in a mixture of 3% magnesium acetate and 3% calcium acetate solutions, drained well (perhaps allowed to dry to dampness), and immersed for 20-30 minutes in 6% ammonium carbonate solution. The paper is then rinsed for two hours to remove any excess ammonium carbonate solution.

H. Ammonia water. Ammonia water in various concentrations may be employed for immersion, brush and spray neutralizing treatments. No alkaline reserve is deposited. Adequate ventilation should be provided to dissipate irritating vapors.

I. Other Procedures.

1. Two-bath treatment (calcium hydroxide & magnesium bicarbonate). When labor costs permit, immersion in calcium hydroxide solution to effect neutralization and swell the paper fiber may be followed by immersion in concentrated magnesium bicarbonate solution to deposit a large alkaline reserve.

2. Double treatment (immersion in aqueous alkali followed by non-aqueous treatment). After washing and alkalizing with calcium hydroxide or other aqueous agent, a non-aqueous agent such as MMMC may be applied overall or locally in heavily acidic areas (e.g. iron-gall ink). This procedure can be used to produce an extremely high alkaline reserve, and the non-aqueous solvent is less likely to cause movement of salts deposited in the first bath than is a second aqueous treatment.

20.4.2. Non-aqueous treatment techniques. General procedures: Paper and media should be tested for solubility and color change in the alkalizing solution.

Adequate ventilation and safety equipment should be employed. Solvent carriers may be chosen to manipulate penetration rate, toxicity and effects on media.

A. Magnesium methoxide in methanol, methanol/Freon.

1. Immersion. Thorough penetration is essential. Use of poor solvents such as Freon may increase the time necessary to achieve this. Several seconds to a few minutes is usually adequate. Drying (or conducting any portion of this treatment) in a humid environment will encourage undesirable precipitation at the paper surface. Drying between thoroughly dry blotters may help avoid this. Alkaline reserve may be affected.

2. Application by brush. This agent may be applied by brush to economize on materials, to minimize vapor exposure and to limit penetration (e.g. application from one side only.) Any alkalizing method which does not completely saturate the paper creates the possibility of uneven distribution. This may result in uneven discoloration of the paper upon subsequent aging.

3. Spray application. Spray application may be employed to facilitate the treatment of large numbers of items or paper in bound format, to economize on materials, and to control penetration. All spray equipment should be kept scrupulously clean; clogged nozzles can cause uneven spray patterns and premature precipitation of hydroxide/carbonate. Moisture in the air or in the paper can cause serious problems of precipitation. Several spray systems are available (see 20.3.11 above); these are often designed for use with specific alkalizing chemicals and can be tailored to the space and production requirements of the conservator or institution.

B. Methoxy magnesium methyl carbonate in methanol, methanol/Freon. MMMC may be used in immersion, brush and spray treatments (see 20.4.2A). It is less sensitive to moisture than is magnesium methoxide, but caution with regard to humidity and water contact is still advisable.

C. Ethoxy magnesium ethyl carbonate in ethanol, ethanol/Freon. EMEC may be used in immersion, brush and spray treatments (see 20.4.2A). It is less sensitive to moisture than is magnesium methoxide but caution with regard to humidity and water contact is still advisable.

D. Magnesium acetate in methanol. Methanolic magnesium acetate may be used in immersion, brush and spray treatments (see 20.4.2A).

E. Calcium acetate in ethanol/water. Paper to be treated is immersed for about 30 minutes in 0.2% (w/v) calcium acetate in ethanol/water (see 20.3.2E above); then allowed to dry in a ventilated area until the smell of acetic acid has disappeared (2 days or longer). The relative proportion of water in the liquid will increase as the paper dries. Areas of water-soluble media should be protected (e.g., blotted). Precipitation of calcium sulphate may be a problem in papers containing high levels of sulphuric acid. If the solution becomes cloudy, the paper should be immersed in a fresh bath of the solution to prevent surface deposition of sulphate.

F. Barium hydroxide in methanol. NOTE: Barium compounds are highly poisonous (See 20.3.1D). Methanolic barium hydroxide may be used in

immersion and brush treatments. Spray treatment is possible but poses serious health hazard.

20.4.3. Vapor-phase treatment techniques. Currently effective vapor-phase treatments are commercial systems designed for large-scale use. They are not suitable for application by the conservator in the laboratory. (See 20.3.3 for description).

20.4.4. Combined alkalizing/strenghthening treatment techniques.

A. Heat-set lamination/lining tissues. These may be obtained commercially (Langwell's Postlip) or prepared by thoroughly mixing a suitable alkalizing agent into a heat-set adhesive solution prior to applying it to the tissue.

B. Lining adhesives. A suitable alkalizing agent may be dissolved in the solvent for aqueous or non-aqueous adhesives (e.g. magnesium bicarbonate solution in water for wheat starch paste; methoxy magnesium methyl carbonate diluted with toluene for PVA resin).

C. Lining supports. Japanese papers with naturally occurring alkaline fillers have been suggested by A. King for linings using aqueous adhesives. Western or Japanese papers may also be alkalized prior to use as lining supports (they should be allowed to dry thoroughly before beginning the lining process).

D. Sizings/consolidants. These may be applied as auxiliary consolidants or to replace degraded sizes removed during treatment. Non-aqueous commercial versions are available (Regnal) and both aqeuous and non-aqueous types may be prepared in the laboratory. The alkalizing agent may be the strengthening agent (parchment size, PVA) or an alkalizing agent may be included in the solvent for the strengthening agent (e.g. methoxy magnesium methyl carbonate in methanol for hydroxy propyl cellulose).

20.4.5. Other treatment techniques.

A. Mild alkaline wash. This technique, which has been called "calcium replenishment," employs a wash water that has been made mildly alkaline by passing it through marble chips or by the addition of an agent such as magnesium carbonate. It is not intended to introduce a large new alkaline reserve, but rather to prevent removal of any extant alkaline salts from a paper due to solvent action of the wash water. In this process water pH is typically 8.5 or below.

20.5. Bibliography.

See Next page

In process of compilation.

20.6. Special Considerations.

20.6.1. Criteria for decision to alkalize.

* See next pages

20.6.2. Criteria for selecting alkalizing method.

* See next pages

In process of compilation.

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20.7 . Special Considerations

20.7.1. Criteria for decision to alkalize.

A. Reasonable evidence of potential damage to the work from acid should exist. This may be provided by pH measurement, fiber analysis, environmental testing, etc. Visual recognition of such inherently acidic paper types as newsprint, or observation of symptoms such as browning and embrittlement, may be adequate given confidence that the work has not been previously alkalized. Environmental conditions to which the work will be returned should be considered.

In deciding whether to alkalize, one must weigh the potential benefit to the specific paper versus its vulnerability to the treatment step itself. Some conservators feel that the beneficial effect of alkalization will be slight for a paper which has already degraded to extreme brittleness, while it may be vulnerable to alkaline degradation such as the peeling reaction during alkaline treatment.

B. Reasons for the work's selection for preservation should be known and their relative priorities established. Owner or custodian should be consulted.

1. Works whose primary value is as historical evidence may suffer from any alteration of their chemical structure. Alkalization may not be appropriate for such works. Papers collected as examples of historic technologies or unusual papermaking materials are instances of this type.

2. The value of book leaves, some manuscripts and certain kinds of paper art may depend upon their ability to withstand flexing, handling or other movement. It may be important to preserve the physical strength of such items, sometimes even at the expense of visual alteration.

   Occasionally, studies have found an initial drop in paper folding endurance after alkalization, though in subsequent accelerated aging these papers have shown maximum retention of folding endurance. The short term drop in folding endurance may be caused by excess crystals disrupting or abrading the cellulose fibers. The conservator must weigh the trade-off in improved stability on aging versus possible short-term reduced durability.

3. Most works of art are valued primarily for their visual effect. This should be preserved in all its subtlety, sometimes even at the expense of loss of physical strength. Alkalizing treatments may be justified if they are not expected to produce visual alterations, or

if such alterations are judged to be less significant than those which would occur without treatment.

Possible alterations include various shifts in paper color depending on pH and the type of alkaline solution (calcium bicarbonate, magnesium bicarbonate or ammonia water), color shifts in pH-sensitive pigments and colorants (gamboge, turmeric, logwood, cochineal, iron gall inks), decolorization of Prussian blue, blueprints and other alkaline-sensitive colorants. (See 3.2.5. Media Problems.)

C. Subsequent planned treatment steps may call for a preliminary alkalization to ensure least damage to the paper.

1. The use of bleaches will be more or less damaging to paper depending on its pH. Paper industry research has found a few bleaches such as chlorine dioxide and potassium permanganate are less damaging to cellulose below pH 7. The hypochlorite bleaches, chloramine-T, hydrogen peroxide and sodium borohydride are less damaging above pH 7. Maximum damage occurs to cellulose which passes through neutral pH during bleaching. (See 19. Bleaching.)

2. Paper sealed in polyester encapsulations without alkalization has shown reduced permanence after accelerated aging. The deleterious effect can be minimized by adding a sheet with an alkaline reserve within the encapsulation. (See 41. Encapsulation.)

D. If alkalization is thought appropriate, the object should be tested for stability in specific alkalizing agents and their solvents.

1. Testing should demonstrate that the proposed alkalization is compatible with any earlier treatments or with prior steps in the current treatment sequence.

2. Testing should make explicit any risks to the paper support. These may include damage to the physical integrity of the sheet or changes in such qualities as texture, color, etc. (See 20.2.5.)

3. Testing should make explicit any risks to the ground, media or other image components. (See 20.2.6 and 3. Media Problems.)

20.7.2. Criteria for selecting alkalizing method.

A. Chemical objectives of the alkalization treatment.

1. Removal of soluble acidity.
2. Neutralization of strong acids.
3. Neutralization of weak acids.

4. Deposition of a moderate alkaline reserve.
5. Deposition of maximum alkaline reserve.
6. Protection against cellulose oxidation.

B. Constraints imposed by the materials of the object to be treated.

1. Sensitivity to aqueous/non-aqueous solvent.
   (Permeability, swelling, solubility, dessication, changes in optical properties. For bindings and other auxiliary supports, adhesives, paper support, fillers, sizings, coatings, image components.)

2. Range of pH safety.
   (Swelling, solubility, color changes, saponification of oily ink binders, alkaline hydrolysis and other chemical reactions. For adhesives, auxiliary supports, paper support, fillers, sizings, coatings, image components.)

3. Physical compatability with particles/crystals of alkaline salts.
   (Abrasion of fibers during flexing, disfiguring surface deposits, changes in optical properties of supports/media. For auxiliary supports, paper support, coatings, image components.)

C. Practical constraints.

1. Number and size of objects to be treated.
2. Toxic or hazardous nature of treatment process or chemical residue in treated objects.