



***PRESERVATION PRINCIPLES FOR PAPER-BASED
COLLECTIONS:***

**FUNDAMENTALS AND FUTURE DIRECTIONS
IN A DIGITAL WORLD**

**INTRODUCTION TO PAPERMAKING
FURNISH & FORMATION**

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PAPER PROPERTIES AND DEGRADATION

(Modified from the article "Recent Scientific Research in Paper Conservation" by Dianne van der Reyden, in The Journal of the American Institute for Conservation, Vol. 31, pp. 117-138, 1992)

BACKGROUND: WHAT IS PAPER AND HOW IS IT MADE?

FACTORS OF FURNISH AND FORMATION

A paper sheet is a composite material. Each component of its composition affects its appearance and stability. The structure of paper depends on two things:

- its **furnish** (the materials used to make the paper), and
- its **formation** (the processes used to make the paper).



Some examples of **furnish materials** used to make paper include those seen in Photo 1:

- **fibers** (derived from cellulosic plant materials such as cotton or wood);
- **water** (used to carry and bond the fiber slurry or pulp stock in a vat); &
- **additives** (applied to the pulp stock in the vat or on the cast sheet) such as fillers & sizes (e.g. gelatin, starch or methylcellulose w high control water permeability), or colorants & coatings (e.g. pigments or dyes).

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Some examples of **formation processes** used to make paper include those seen in Photo 2:

- **beating** to separate & fibrillate the fibers to enhance physical interlocking & chemical bonding;
- **casting** of the fiber slurry in water onto a paper-making mold;
- **couching** to remove the wet sheet from the mold; and
- **drying & flattening** to consolidate bonding & strength.

PAPER COMPOSITE

FURNISH

FORMATION

| FIBER TYPE | STOCK | REFINING | OTHER ADDITIVES | HANDMADE/ MACHINE VARIABLE | CALENDARING | COATING | DRYING |
|--|--|--|--|--|---|---|--|
| BAST FIBERS SEED FIBERS (COTTON) GROUND WOOD HARDWOOD SOFTWOOD | RATIO OF FIBERS WATER SIZES - Starch - Gelatin - Methylcellulose FILLERS | CHEMISTRY - Soda - Sulfite - Sulfate BLEACHING | COLORANTS COATINGS* | BEATING CASTING (SPEED, DIRECTION) DRAINING COUCHING PARTING WET PRESSING | BURNISHING HAMMER GLAZING COLD/HOT PRESSING FLINT CALENDARING FRICTION CALENDAR SUPER CALENDARING | BRUSH ROLLER AIR KNIFE BLADE EXTRUSION | AIR PRESS HEAT DRUM STRETCH FESTOON |
| Dispersers | | | Pigments | Binders** | Anti-foamers & Defoamers | Eveners | |
| -fluidifiers & viscosity stabilizers (anionic & nonionic surfactants, urea, dicyandiamide polyoxyethylene stearate, polyethylene glycol laurate, sulfated oleic acid) | -softeners (invert sugar, sorbitol, urea, glycerine, corn syrup) | *plasticizers or lubricants (calcium stearate, resin latexes, ethanola mine soaps, alkyd resins, fatty acid esters, polyglycols) | -clay -calcium carbonate -titanium dioxide -diatomaceous silica -polystyrene -fluorescent pigments (zinc or cadmium sulfide strontium or calcium sulfide) | -starch (rice, wheat, corn, tapioca, potato, sorghum) -protein (glue, casein, soy) -resins, latexes & emulsions (wax, shellac, styrene-butadiene, polyacrylate, polyvinyl acetate) | -skim milk -animal fats -vegetable oils -sulfonated oils -pine oils -amyl alcohol -ether -kerosene -tributyl phosphates -silicones | -levelers -smoothers (pine oil, sulfonated oil, carboxy methylcellulose paraffin & microcrystalline wax) | |

THE STRUCTURE OF PAPER AND CELLULOSE

A paper sheet is a felted-web composed primarily of fibers, which are made up of fibrils, which in turn are formed of chains of cellulose polymers, all held together by different types of bonds having various strengths. An exploded, schematic view of paper would look something like the following (Fig. 1):

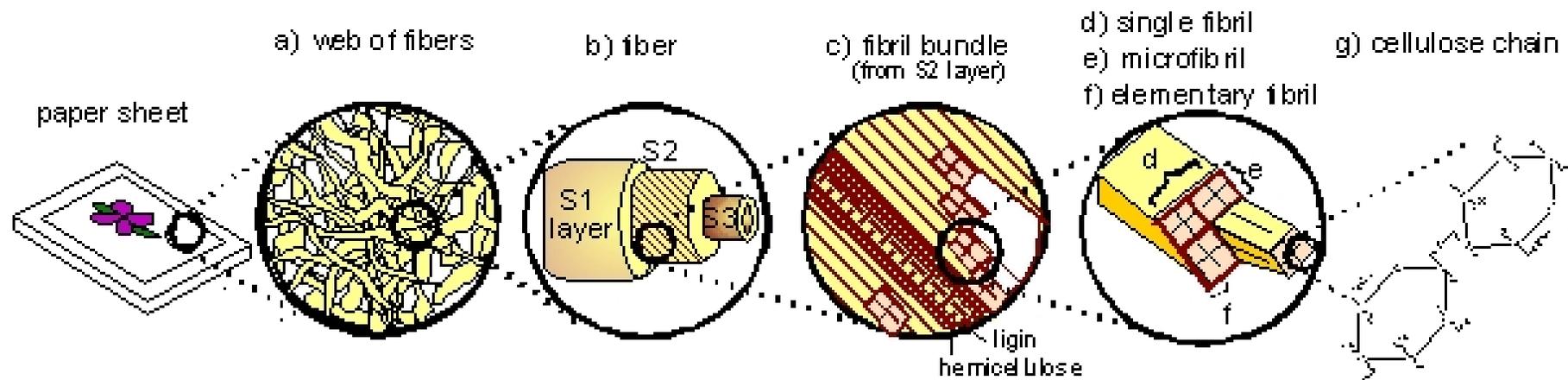


FIG. 1: PAPER STRUCTURE AND BONDING:

a) web of fibers from paper sheet;

b) fiber;

c) fibril bundle, held by weak Van der Waals forces with a bond strength of 2-10;

d) fibril, composed of microfibrils;

e) microfibril, composed of elementary fibrils of layers of cellulose chains;

f) one elemental fibril layer, composed of cellulose chains held side by side with hydrogen bonds having bond strengths of 3-6;

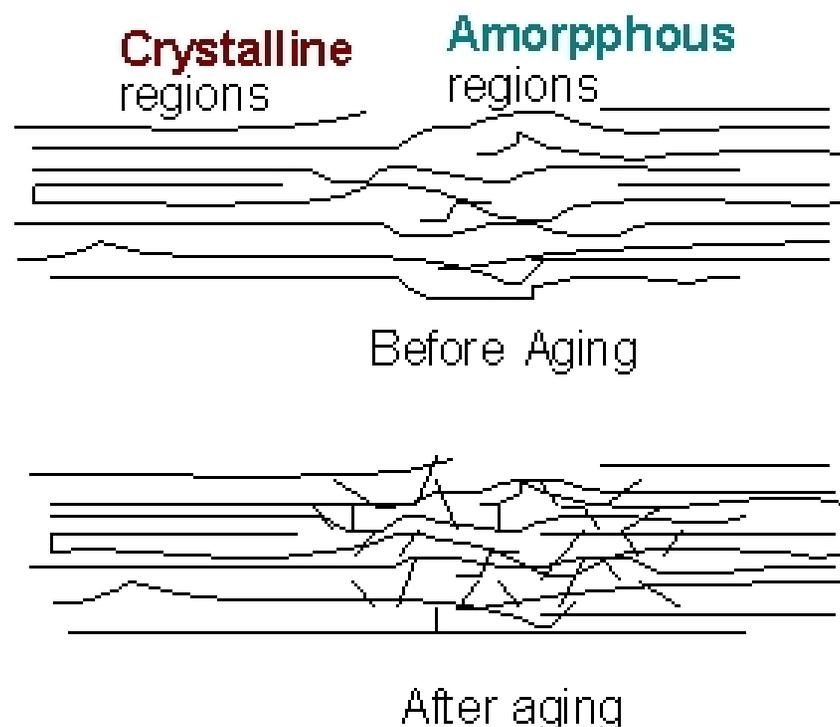
g) cellulose chain, composed of glucose units held by strong covalent bonds having bond strengths of c.86.

(Modified from Waterhouse 1982, Dwan 1987)

On a molecular level, cellulose (Fig. 1), has properties imposed by its structure of **crystalline** and **amorphous** regions (Fig. 2).

FIG. 2: **CRYSTALLINE** & **AMORPHOUS** AREAS OF CELLULOSE (BEFORE & AFTER AGING)

(Modified from Koura, A. and T. Krause, 1987)



"In polymers, crystallization implies an intramolecular ordering...."

(From: Alfrey, R. H. "The Crystallinity of Cellulosic Fibers," *Presentation of Paper and Textiles II*, American Chemical Society, 1951, pp. 166-170) (Modified from Figs 1-3)

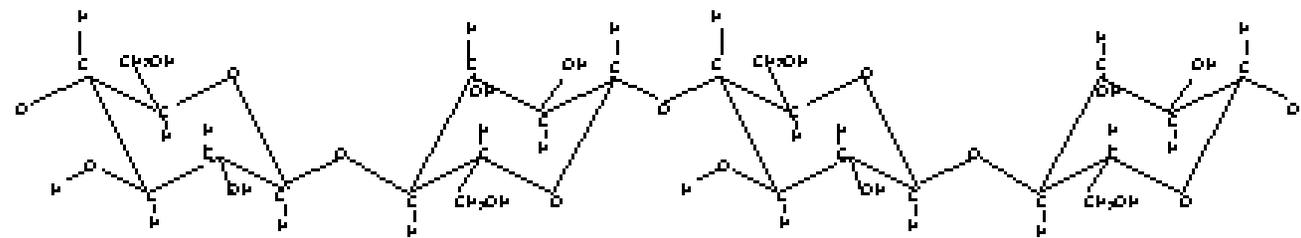
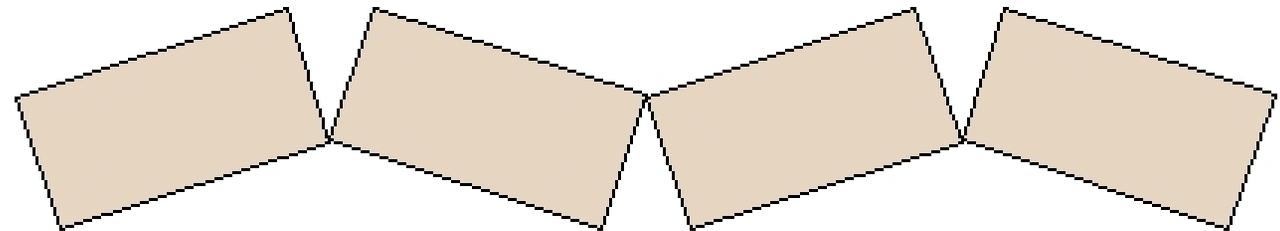
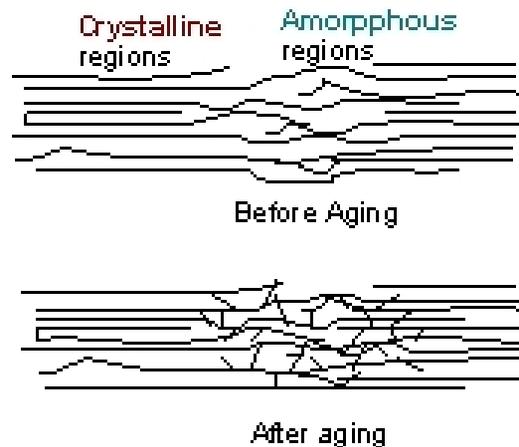
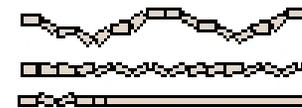


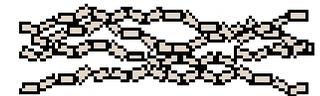
FIG. 2: CRYSTALLINE & AMORPHOUS AREAS OF CELLULOSE (BEFORE & AFTER AGING)
(Modified from Hauer, A. and T. Krause, 1987)



Example of cellulose molecule ("chain" structure) and schematic model of cellulose structure



Example of degrees of order in a cellulose chain



Example of increasing order of cellulose structures

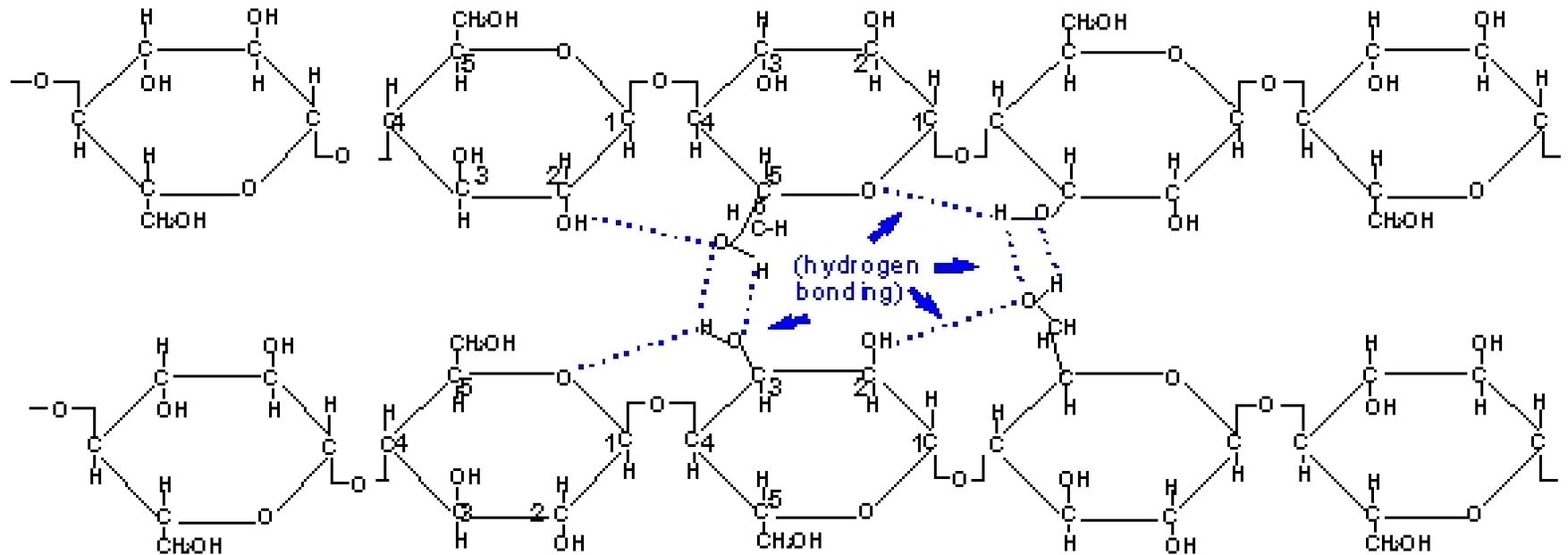
The **crystalline** regions are

- ordered,
- rigid,
- inert, and
- relatively impermeable to water

The **amorphous** regions are

- random,
- flexible and
- water accessible (Fig. 3)

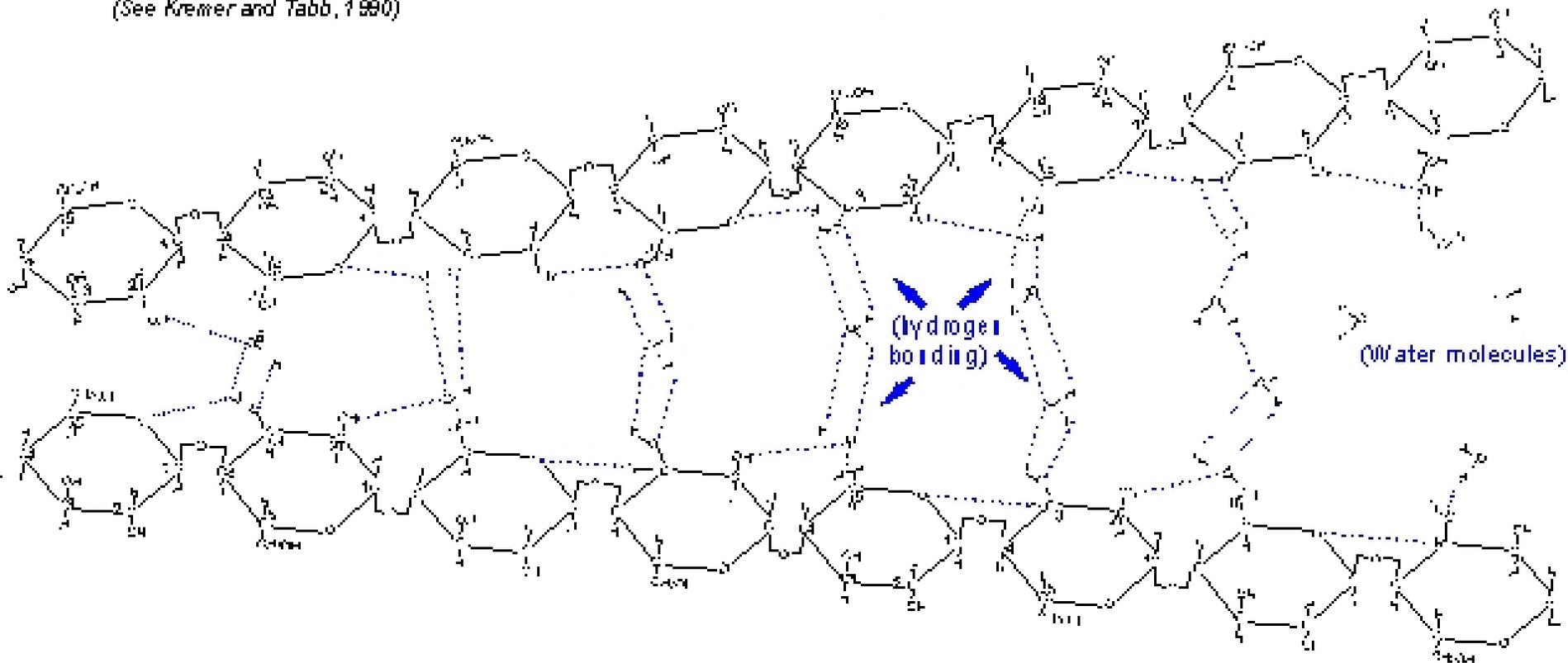
FIG. 3 Hydrogen Bonding in Cellulose



For more on hydrogen bonding in cellulose, see Gardner, K.H. and J. Blackwell, "The Hydrogen Bonding in Native Cellulose," biochimica et Biophysica Acta 343, 234, 1974; modified from Fig. 8)

FIG. 3 Hydrogen Bonding in Cellulose: Affect of Water

Example of dislocation of crystalline structure because of water adsorption in an amorphous region of a cellulosic microfibril
(See Kremer and Tabb, 1990)



1. WHAT DIFFERENCE DO FURNISH AND FORMATION MAKE TO PAPER?

PAPER PROPERTIES AND DETERIORATION

Each of the furnish and formation factors used to make paper has specific properties that affect the appearance and stability of the paper.

Three types of properties are:

1. **optical properties**, such as color (of the fiber, additives, or final sheet);
2. **physical properties**, such as strength (of the fiber or final sheet); and
3. **chemical properties**, such as acidity (of the fiber, additives, water, etc.).

Unfortunately, these properties can change over time, depending on furnish, formation and environmental factors. The color of paper can darken; its strength can weaken; and its acidity can cause the paper to become brittle and torn.

The mechanism for these changes appear in Table 1.

Fortunately, these changes can be minimized if good, stable materials, processes and environments are used.

Poor environments, which cause changes to properties, include those with excessive

1. **temperature** (which can cause thermal oxidation, leading to discoloration and stiffening of paper)
2. **light** (which can cause thermal and photo oxidation, leading to discoloration and stiffening)
3. **humidity** (which can cause acid hydrolysis, leading to embrittlement of paper)
4. **pollution** (which can cause acid hydrolysis, leading to embrittlement)
5. **pests** (which can cause acid hydrolysis and physical loss of paper)

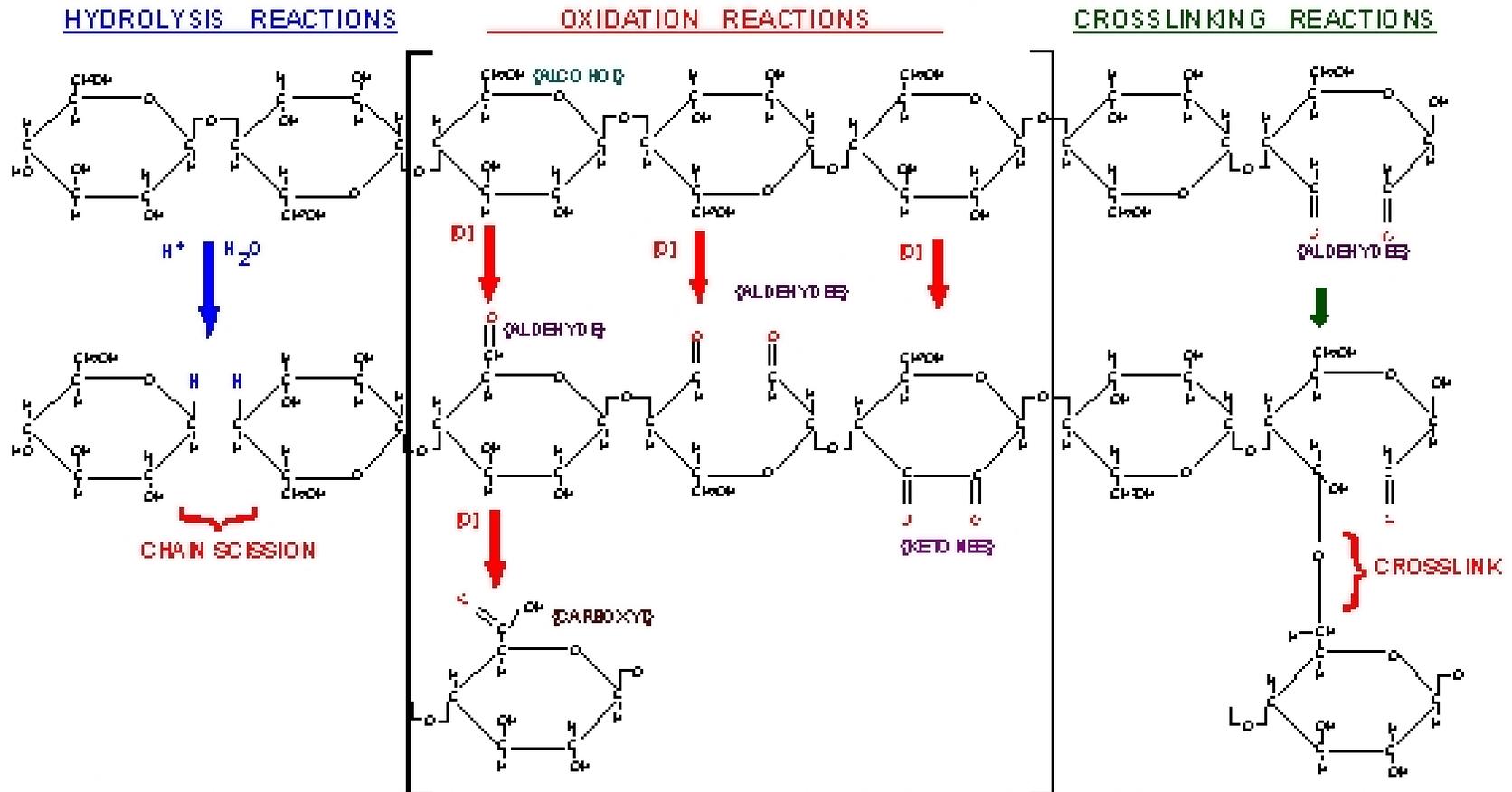
Put another way, changes in properties are caused by the following three chemical reactions, which occur in the cellulose chain:

1. **hydrolysis** (which leads to chain scission that eventually makes paper brittle)
2. **oxidation** (which leads to the formation of double bonds that absorb light and make paper look darker)
3. **crosslinking** (which increases the crystalline order of cellulose chains and makes paper stiffer)

EXAMPLES OF HOW CELLULOSE DEGRADATION REACTIONS OCCUR AT THE MOLECULAR LEVEL

Below is a schematic diagram of a cellulose polymer chain (Table 1). The diagram shows how the cellulose chain (top row) can be attacked at vulnerable sites by hydrolytic and oxidative agents (first row of arrows) resulting in a damaged chain (second row). These hydrolysis and oxidation reactions lead to chain scission and formation of double-bonded compounds at vulnerable sites. Double bonds absorb light, making the paper look darker. Double-bonded compounds include **carboxylic acids**, **aldehydes**, and **ketones**.

TABLE 1: SOME EXAMPLES OF COMMON CELLULOSE DEGRADATION REACTIONS



HYDROLYSIS REACTIONS (FROM HUMIDITY AND ACID; CAUSE **CHAIN SCISSION** LEADING TO INCREASED REACTION SITES AND WEAKENING)

OXIDATION REACTIONS (FROM HIGH TEMPERATURE OR LIGHT; CAUSE DOUBLE-BOND FORMATION LEADING TO LIGHT ABSORPTION, MAKING PAPER LOOK DARKER)

CROSSLINKING (FROM OXIDATION; CAUSES STIFFENING OF PAPER)

2. HOW DO DEGRADATION MECHANISMS AFFECT PAPER PROPERTIES?

TESTS AND MEASUREMENTS

Paper has many **chemical**, **physical** and **optical** properties. Some of these are listed below (Table 2) and defined in the next section on examples of paper properties. These properties change through **hydrolysis**, **oxidation**, and **crosslinking**.

These changes can be measured numerically.

| PROPERTY TEST | HYDROLYSIS | | OXIDATION | | CROSSLINKING | | THERMAL DECOMPOSITION | |
|--------------------------------------|------------|---|-----------|---|--------------|---|-----------------------|---|
| | P | B | P | B | P | B | P | B |
| 2.1 CHEMICAL PROPERTIES | | | | | | | | |
| Degree of polymerization | ▼ | | ▼ | ▼ | ▲ | | ▼ | |
| Acid hydrogen ions (H ⁺) | | ▲ | ▲ | | | | ▲ | |
| Carbonyl | | ▲ | ▲ | | | ▼ | | |
| Aldehyde | ▲ | | ▲▼ | | | ▼ | ▲ | |
| Ketone | | | ▲ | | | ▼ | ▲ | |
| Peroxide | | | ▲ | | | | ▼ | |
| Molecular weight | | | ▲▼ | | ▼ | | | |
| Alkali solubility | ▲ | | ▲ | | ▼ | | ▲ | |
| 2.2 PHYSICAL PROPERTIES | | | | | | | | |
| Fold | ▼ | | ▼ | | ▼ | | ▼ | |
| Tear | ▼ | | ▼ | | ▼ | | ▼ | |
| Elongation | ▼ | | ▼ | | ▼ | | ▼ | |
| Tensile | ▼ | | ▼ | | | | ▼ | |
| Elongation | ▼ | | ▼ | | ▼ | | ▼ | |
| Modulus | ▼ | | ▼ | | ▲ | | ▼ | |
| Tensile energy absorption | ▼ | | ▼ | | ▼ | | ▼ | |
| Creep | ▼ | | ▼ | | | ▼ | ▼ | |
| Wet tensile | | ▼ | | ▲ | ▲ | | | |
| 2.3 OPTICAL PROPERTIES | | | | | | | | |
| Bleed resistance | | ▼ | ▼ | ▼ | | | ▼ | |

For example, one thing that affects a paper's **chemical properties** are the length of the cellulose polymer chain, referred to as the degree of polymerization (DP). The shorter the cellulose chain, the lower its DP. When a long chain undergoes **chain scission** and therefore becomes two or more shorter chains, more chain ends are created. The chain ends are unstable, because they provide sites vulnerable to chemical reactions when exposed to harmful conditions, such as those causing **hydrolysis**.

Consequently, when paper undergoes **hydrolysis**, the **chemical property** of DP decreases, thereby increasing reactivity and instability of the paper. Likewise, **hydrolysis** leading to **chain scission** can result in a reduction in the **physical property** of fold endurance.

| PROPERTY TEST | HYDROLYSIS | | OXIDATION | | CROSSLINKING | | THERMAL DECOMPOSITION |
|--------------------------------------|------------|---|-----------|---|--------------|---|-----------------------|
| | P | B | P | B | P | B | P |
| 2.1 CHEMICAL PROPERTIES | | | | | | | |
| Degree of polymerization | ▼ | | ▼ | ▼ | ▲ | | ▼ |
| Acid hydrogen ions (H ⁺) | | ▲ | ▲ | | | | ▲ |
| Carbonyl | | ▲ | ▲ | | | ▼ | |
| Aldehyde | ▲ | | ▲▼ | | | ▼ | ▲ |
| Ketone | | | ▲ | | | ▼ | ▲ |
| Peroxide | | | ▲ | | | | ▼ |
| Molecular weight | | | ▲▼ | | ▼ | | |
| Alkali solubility | ▲ | | ▲ | | ▼ | | ▲ |
| 2.2 PHYSICAL PROPERTIES | | | | | | | |
| Fold | ▼ | | ▼ | | ▼ | | ▼ |
| Tear | ▼ | | ▼ | | ▼ | | ▼ |
| Burst | ▼ | | ▼ | | ▼ | | ▼ |
| Tensile | ▼ | | ▼ | | | | ▼ |
| Belongation | ▼ | | ▼ | | ▼ | | ▼ |
| Modulus | ▼ | | ▼ | | ▲ | | ▼ |
| Tensile energy absorption | ▼ | | ▼ | | ▼ | | ▼ |
| Creep | ▼ | | ▼ | | | ▼ | ▼ |
| Wet tensile | | ▼ | | ▲ | ▲ | | |
| 2.3 OPTICAL PROPERTIES | | | | | | | |
| Bulk reflectance | | ▼ | ▼ | ▼ | | | ▼ |

Finally, the **optical property** of reflection relates to how bright a paper appears. This brightness or reflection decreases if a paper darkens because of **hydrolysis** and/or **oxidation** (i.e. arrow points down). On the other hand, **crosslinking** causes no change in reflectance.

EXAMPLES OF PAPER PROPERTIES

2.1 CHEMICAL PROPERTIES

Chemical properties of a paper sheet are determined primarily by variables of **furnish** (pulp components) and **formation** (manufacturing processes), such as those listed in Diagram 1.

Each variable in turn has distinct properties. For example, the furnish of pulp stock has specific properties which affect the nature of the final sheet, including

- crystallinity and
- fiber bonding.

Formation processes such as beating affect

- fibrillation,
- swelling, and
- water retention.

Examples of **chemical properties** of paper and their respective test methods are listed in Table 2 and below.

Degree of polymerization (DP) of the cellulose chain, decreased by hydrolysis, oxidation, and chain scission, and increased by crosslinking (Table I), can be determined by viscosity measurements or gel permeation chromatography, which also indicates molecular weight distribution.

Acid content can be measured by alkaline reserve titration, odometric total acid, and surface and cold extraction pH (Burgess and Binie 1960).

Production of functional groups such as carboxyls and carbonyls, including aldehydes and ketones (Table I), due to hydrolysis and oxidation, alters the molecular structure. Content can be measured by several methods including titration and iodometric techniques.

Peroxide formation, which could result from oxidation, can be measured by the Russell Effect (Daniels 1963).

Moisture content and regain can be measured by gravimetric and thermodynamic methods.

Alkali solubility includes measurements of carbonyl content by hd-1% alkali solubility test, copper number, and the borohydride reducing method. Ester and ether content may be measured by Raman Spectroscopy, nuclear magnetic resonance, and ultrasound.

2.2 PHYSICAL PROPERTIES

Physical properties of a paper sheet are determined by variables of

- smoothness/roughness,
- thickness,
- density,
- two-sidedness,
- rigidity and
- porosity.

These in turn affect sheet properties of

- softness/hardness,
- compressibility,
- dimensional stability,
- curl, and
- strength (*Casey 1981; Bolam 1962*).

Attention tends to focus on strength measurements since "strength properties can...serve as indications of the permanence of paper, even when the nature of the chemical changes responsible for the deterioration remains unknown...[and] can also be used for evaluating the effectiveness of treatments for aging" (Caufield and Gunderson 1988, p. 31). The following are some strength, or mechanical, properties and examples of respective test methods.

Fold endurance, more sensitive to changes than other strength tests but hampered by a wide standard deviation owing to the limited area tested, can be measured with the MIT folding endurance tester (produces results most consistent with the handling of books).

Tear resistance, including edge tear resistance or internal tear resistance (similar to the kind of tearing occurring to a nicked book page), can be measured using the Elmendorf tear test.

Burst strength, one of the most common tests in the paper industry but not much used in paper conservation, is measured by the Mullen test.

Tensile strength is often determined by standard span tensile strength testing, which measures interfiber bonding and total network strength, and is expressed by stress-strain plots, **tensile energy absorption**, and **Young's modulus** (Fig. 4). Fiber strength, internal bonding, or fiber orientation may be measured by zero-span, z-direction (through-the-thickness), and **wet tensile tests**.

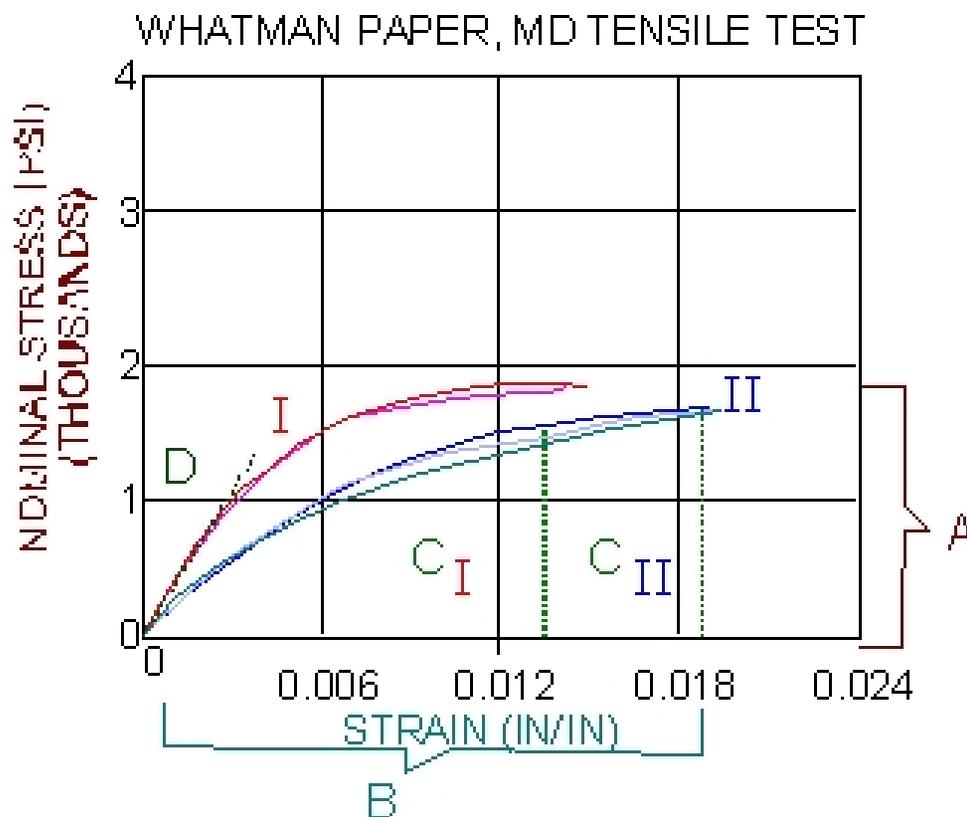


FIG. 4

Example of a stress-strain plot of the machine direction (MD) tensile strength of [I] unwashed and [II] washed Whatman paper (Ca(OH)_2 deionized water 1:1), showing **A)** stress or load to break; **B)** strain, elongation or stretch to break; **C)** **tensile energy absorption area (TEA)** or total area under the curve, representing work expended to break, and characteristic of durability (e.g. the washed paper [II] may be more durable than the unwashed paper [I] since its total area under the curve [C_{II}] encompasses most of and exceeds [C_I]); and **D)** **Young's modulus**, or initial straight line of the slope characteristic of elastic materials and indicative of stiffness. (Modified from van der Reyden et al. 1988)

2.3 OPTICAL PROPERTIES

As mentioned before, optical properties are a form of physical properties. Changes in optical properties may result from changes in chemical properties.

Optical properties of paper include

- color,
- reflectance,
- brightness,
- gloss,
- opacity/transparency or transmittance of light, and
- fluorescence (Mark 1983).

Measurements are made with reflectometers, spectrophotometers and gonimeters. Findings may be reported in various modes including percent reflectance, CIE L*a*b*, and Kubelka-Munk scattering and absorption coefficients (Berndt 1989; Burgess and Binnie 1991).

Paper properties are interdependent. Interpretation of test data is complicated by the fact that measurements represent "a combination of such factors as flexibility, bonding strength, and fiber strength...which are dependent on type of fibers, length and thickness of fibers, imperfections in fibers, flexibility, pattern of fiber network, number of bonds, strength of the individual bonds, the weight of the paper, the apparent density, the moisture content, and many other factors" (Casey 1961, p. 1779). Properties are in turn affected individually and collectively by environmental parameters such as temperature, humidity and light; and by aging and conservation treatments.

3. WHAT ARE THE LONG-TERM EFFECTS OF DEGRADATION MECHANISMS ON PAPER?

THE AGING OF PAPER

In order to determine the long-term effects of degradation on paper, there has been a great deal of research into the effects of aging on the properties of paper. The research has aimed at clarifying the following two issues:

- 1) What are the effects of natural aging on paper?
- 2) What are the parameters of accelerated aging (done to speed up the effects of aging, for research purposes) which most nearly match the effect upon paper of natural aging?

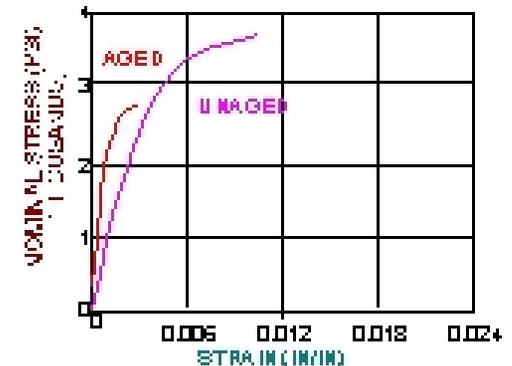


Fig. 5 Stress-strain curve of paper before and after aging 15 days at 50 degrees C, 50% RH. (Modified from Waterhouse, 1989)

NATURAL AGING

Natural aging may cause paper to become discolored, and cellulose to become more crystalline and stiff, as has been shown for accelerated aging (Fig. 5). Crystallinity can be measured by

- x-ray diffraction,
- acid hydrolysis, or
- moisture content (Daniels 1986).

Discoloration of a paper's sheet may be caused by the formation of chromophores upon aging as a result of exposure to, among other things,

- light (Lee et al. TBP 1991) and
- volatile gases (Daniels 1988).

Some researchers have hypothesized that **oxidation** could be induced in paper by

- hydrogen sulfide from proteins and other sulphur-containing materials;
- formaldehyde and acetic acid from wood and paints; and
- hydrogen peroxides from oxidation of lignin, leading to a **utoxidation** of paper (Daniels 1988).

Recent studies have focused on the effects of pollution upon aging of papers, particularly deacidified papers, which appear to have a greater capacity to absorb sulfur dioxide and nitrogen dioxide (Williams and Grosjean 1990).

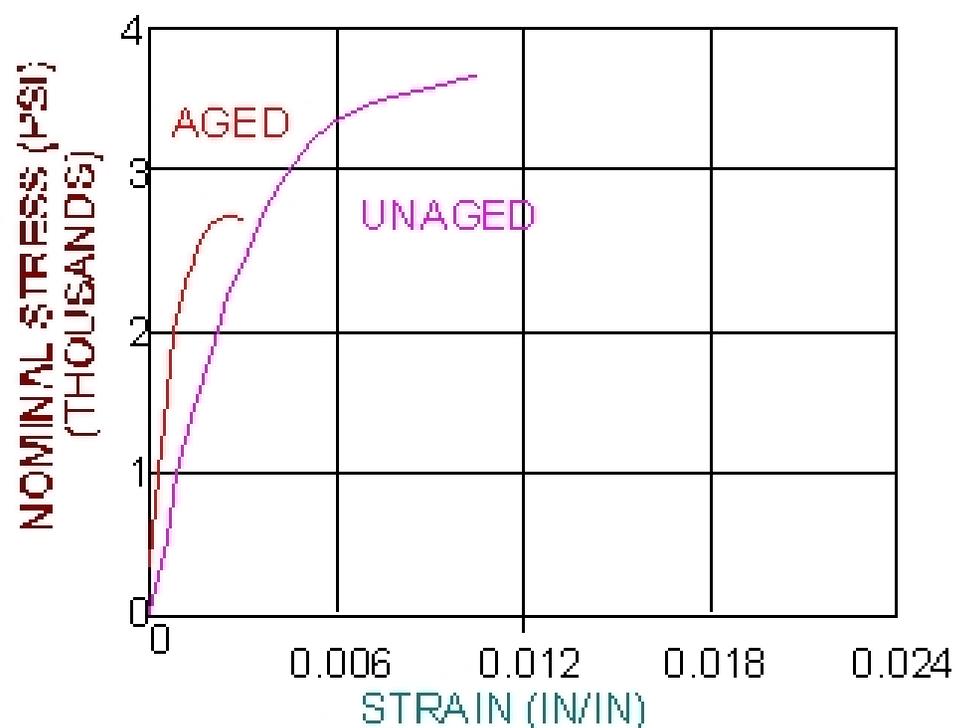


Fig. 5 Stress-strain curve of paper before and after aging 15 days at 90 degrees C, 50%RH (Modified from Waterhouse, 1988)

ACCELERATED AGING

Accelerated aging, done at elevated temperatures and humidities, may initiate reactions resulting from thermal degradation which could, depending on conditions and length of exposure, produce products different from those of natural aging. Gas chromatography mass spectrometry to analyze extracts of papers aged at different temperatures and relative humidities. It was found that humid oven aging of Whatman 1 filter paper (at 90°C and 100% RH) hydrolyzed cellulose and xylan, producing mostly **glucose** and **xylose**, found also in naturally aged papers. Dry oven aging at 90°C and above produced very little glucose. Aging at 150°C produced a different set of products (Erhardt 1987, 1988; Feller 1987).

Other researchers have focused on the effects of **cycling** aging conditions, finding that cycling relative humidity increases the degradation of single sheets of paper (Shahani et al. 1989). However, the effects of cycling appear to be less pronounced for books, the format of which may slow down changes. On the other hand, simulated book materials tend to age faster in comparable accelerated aging conditions than single sheets, perhaps owing to the trapped concentration of degraded materials forming what amounts to an adverse microclimate. In general, a wide variety of aging conditions continues to be used in current research.