NBSIR 74-499

An Analysis of the Aging of Paper: Possible Reactions and Their Effects on Measurable Properties

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Interim Report

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

CONTENTS

1. INTRODUCTION

At the request of the National Archives and Records Service, this laboratory is examining the variables associated with the accelerated aging of paper in an attempt to arrive at reasonable conditions for an aging method. Emphasis has been on (1) the preparation of laboratory handsheets under carefully controlled conditions, (2) precisely defined and controlled aging conditions, and (3) measures of change that reflect what actually occurs during the aging of paper, including the effects of oxygen and moisture.

The permanence of paper and laboratory aging have been discussed extensively in the literature. Pertinent articles, including reviews, have been authored by Spinner [1], Stubchen-Kirchner [2], Neimo [3], Browning and Wink [4], Luner [5], Millett [6], Kleinert [7], Smith [8], Barrow [9], Graminski [10], Byrne and Weiner [11], Kantrowitz [12], Venter [13], Cardwell [14], and Gray [15]. Much of this work was directed toward color reversion.

The permanence of paper can be studied from the standpoint of (1) composition, (2) environment, and (3) significance of test data with respect to changes that occur during aging. These three approaches are interdependent. Under composition one might list:

(a) aldehyde
(b) ketone
(c) carboxyl
(d) salt of carboxyl
(e) hemicelluloses
(f) lignin
(g) fiber, fiber length and degree of polymerization
(h) crystallinity, or order
(i) acid incorporated during manufacture
(j) other additives.

Under environment one might list:

(a) oxygen and ozone
(b) moisture
(c) smog and other impurities in the atmosphere
(d) light
(e) heat.

Reactions that might occur during the natural aging of paper include:

- (a) hydrolysis
- (b) oxidation
- (c) crosslinking
- (d) changes in order, or crystallinity, due to reported changes in moisture content
- (e) photolysis
- (f) photosensitization
- (g) photo-oxidation

Thermal decomposition must also be considered during accelerated aging, but it probably does not occur during natural aging unless the storage temperature is excessively high.

This report reviews the structure and basic reactions of cellulose in relation to the aging of paper and the effects these reactions might have on the measurable properties of paper. Also included is a discussion of some special reactions that normally occur due to environmental conditions, but are greatly influenced by composition of the paper.

2. POTENTIAL CHEMICAL AND PHYSICAL CHANGES IN CELLULOSE AND PAPER

2.1 Overview

Hundreds of articles have been written describing reactions of cellulose dispersed in aqueous solutions of various reagents. The actual reactions that occur during the aging of paper have received little attention in the literature. This is no surprise for "solid state" reactions of this type are not easy to follow. The effects of these reactions are evident from changes in physical and chemical tests, but these tests seldom describe what happens. Functional group analysis (aldehyde, carboxyl, ketone) is elusive, and Browning and Wink [4] found little change in functional group content during aging. However, the metal on the carboxyls greatly influences the course of decomposition during differential thermal analysis [16].

Moisture relationships in the degradation of cellulose have not been properly identified. Supposedly, at low moisture contents, water exists on cellulose as a monomolecular layer [17]. The differential heat of swelling (ΔH) and the free energy changes (ΔF) vary greatly with moisture content and with temperature. The relative humidity necessary to maintain a given moisture content increases somewhat with temperature. At constant relative humidity, the absolute vapor pressure of water increases dramatically with increase in temperature. This, in turn, decreases the partial pressure of oxygen. At accelerated aging temperatures, near 90°C, the rate of exchange of moisture with cellulose in equilibrium with a given vapor pressure of water would be orders of magnitude higher than at room temperature. Whether this higher rate of exchange of moisture and the differences in ΔH and ΔF would simply speed up reactions that occur at room temperature or cause other reactions to occur, is a matter for speculation.

Hydrolysis, oxidation, crosslinking, and changes in lateral order, or crystallinity, are possible reactions during the natural aging of paper. In addition, thermal decomposition must be considered during accelerated aging. The basic reactions that can occur during natural aging are fairly limited, but the conditions that make these reactions possible and their effects on paper properties are more extensive.

Degradation reactions may occur in the fiber and in the bonding areas between the fibers. As some physical tests are affected by changes in bonding (e.g., crosslinking as measured by wet strength) more than by changes in the fiber (depolymerization and its effect on tensile strength) or vice versa, this must be taken into consideration in the evaluation of data. Hydrolysis, oxidation, and crosslinking would occur in both the fiber and in the fiber bonding areas. In order to separate the effects of crosslinking in the fiber and in the bonding areas, it would be an interesting experiment to achieve crosslinking in fibers and then make paper from them. As there would be little crosslinking in the bonding area, one could separate the effects of crosslinking in the fiber and in the bonded area.

The effect of additives introduced during the papermaking process may have a profound effect on the behavior of paper during aging. For example, an additive may perform well as a bonding agent but degrade with time. Some wet strength resins are in this category. Another additive might perform well as a bonding agent, and be more stable than the cellulose.

2.2 Hydrolysis

The acetal linkages in cellulose are fairly stable in neutral and alkaline media, but are easily hydrolyzed in acid (rate increasing with hydrogen ion activity) [18, p. 991-1006]. Although the homogeneous (cellulose in solution) hydrolysis of cellulose is a random process [19, p. 122], heterogeneous (cellulose fiber dispersed in acid) hydrolysis is more complex. The bonds are not equally accessible in the crystalline and less well ordered areas. Peeling reactions occur in hot alkali [20, p. 596].

The hemicelluloses are much more readily accessible and occur in the amorphous state in wood [20, p. 164], but may precipitate out in the crystalline state on cellulose fibers during lignin removal [20, p. 510, 608]. Model compounds related to the hemicelluloses are hydrolyzed at a much higher rate than cellulose [20, p. 119; 21]. As long as the hemicelluloses are in the amorphous state, their rates of hydrolysis will be much greater than that of cellulose. When crystallized onto cellulose, some hemicelluloses probably do not hydrolyze appreciably faster than cellulose [20, p. 510]. As a large fraction of the bonding material in wood pulp papers may consist of hemicelluloses, their chemistry is germane to the stability of paper, especially with respect to the stability of interfiber bonding.

The hydrolysis of carbohydrate structures is enhanced by the presence of oxidized groups [20, p. 123, 124]. This probably explains the synergistic effect of oxygen and moisture in the degradation of cellulose [22] and cellulose acetate [23].

The most significant work on the effect of chemical structure on hydrolysis that is germane to the aging of cellulose has been compiled by Sharples [18, p. 993-996]. Oxidation and cleavage at the No. 2 and No. 3 carbon atoms in the anhydroglucose ring (Figure 1) leads to the formation of aldehydes or carboxyls. These structures cause an increase in the rate of hydrolysis, even when reduced to the dialcohol. Most dramatic is the discovery of evidence that an aldehyde group on the No. 6 carbon atom may increase the rate of acid hydrolysis as much as 70 times [24]. This effect can be eliminated by reduction of the aldehyde back to hydroxyl with sodium borohydride. Wood cellulose is hydrolyzed at a higher rate than cotton cellulose, and it has been suggested that the reason for this is oxidation during pulping to give an aldehyde on the No. 6 carbon. When this is coupled with the higher rate of hydrolysis of the hemicelluloses, it is obvious that cotton fiber is likely to be more resistant to hydrolysis than wood pulp fiber.

It has been demonstrated that glycolic acid, a product of cellulose oxidation and hydrolysis, can react with glucose under certain conditions to give reversion products [25]. Thus, the aging of paper may involve a multitude of reactions between decomposition products and between decomposition products and cellulose. Rapson has shown that color reversion is caused by degradation products of oxidized cellulose [26].

2.3 Oxidation

Little definitive work has been done on oxidation of carbohydrate structures during the aging of paper. Using the generally accepted formula for cellulose in Figure 1, one can review the possibilities [19, p. 140-183].

(1) The primary alcohol group on No. 6 carbon can be oxidized to aldehyde or carboxyl.

(2) The secondary alcohol groups on carbons in the No. 2 and 3 position can be oxidized to ketone, either separately or simultaneously.

(3) These same groups can be oxidized to aldehyde with cleavage of the ring, and then to carboxyl.

(4) Although not an oxidative reaction, the sensitivity of the 2,3 dialdehyde to alkali is worth noting. The aldehyde in the No. 3 position is two carbon atoms removed from the ring oxygen. This is an example of the general case where alkaline cleavage can occur if an ether linkage is separated by two carbon atoms from an electronegative group, i.e., aldehyde. A similar instability would occur with an aldehyde group in the No. 6 position, or a keto group in the No. 2 or No. 3 position. Further oxidation of the 2,3 aldehydes to carboxyls stabilizes the structure.

The above oxidation reactions normally take place with cellulose dispersed in an aqueous solution of oxidant. Oxidation reactions that occur during the natural aging of paper would be expected to proceed with oxygen or ozone as oxidant. A subtle example of oxidation that is devastating to paper (but does not directly involve paper in the oxidation process) is the oxidation, catalyzed by manganese and iron impurities in the paper [27], of sorbed sulfur dioxide to sulfur trioxide.

Kleinert [28] has shown that peroxide formation occurs during the accelerated aging of wood pulps at just under 100°C. Aging at high humidity produced much more peroxide than aging at low humidity. Strangely enough, aging at high humidity in nitrogen produced more peroxide than aging in air. Although much of the peroxide could be removed by washing with water, most remained with the pulp. While it is possible to follow aging by peroxide formation, peroxide also is destroyed during the process [29]. Kleinert [29] also showed that peroxide formation was several times greater in the fines than in the longer fibers in the pulp, and that peroxide was formed during air drying of pulp at 35°C.

Peroxide as an intermediate in the aging of paper should receive more attention, for cellulose basically is an ether. Ethers undergo oxidative degradation through peroxide formation [30, p. 77]. The transition metals, including iron which occurs as a common impurity in cellulose, catalyze the decomposition of hydroperoxides [30, p. 42] and could be a factor in the degradation of paper.

The above oxidation reactions of cellulose also occur in the hemicelluloses. Some monomer units that occur in the hemicelluloses are shown in Figure 2, and it is obvious that the units are very similar to anhydroglucose, the monomer unit of cellulose. The hemicelluloses normally are more accessible than cellulose and the building units may react much more rapidly with some reagents [20, p. 119; 31]. Therefore, this fraction of wood pulp paper should be more important to oxidative stability than the cellulosic fraction, especially as it is responsible for much of the interfiber bonding.

The fines probably represent the most vulnerable fraction of paper with respect to degradation. This is indicated by the much greater generation of peroxide in fines, as mentioned above. Fiber fraction studies show no real differences in chemical composition among the various fractions of chemical pulps except for the fines [32, p. 642]. The fines in a bleached sulfite pulp contained most of the ash and hemicellulosic material, which was reflected in greater alkali solubility, higher copper number, and lower viscosity.

2.4 Crosslinking

Although crosslinking of cellulose has been known for years, it has been recognized only recently as a reaction that occurs during the aging of paper [10].

Crosslinking in paper occurs at elevated temperature and is a consequence of conditions that could be described as accelerated aging, both in moist and in dry gases [33, 34, 35]. Back [33] has postulated that wet strength can develop as a result of a reaction between an aldehyde group on one chain with a hydroxyl group on a neighboring chain to form a hemiacetal. Presumably, a ketone on carbons 2 or 3 could form a hemiketal. Unless steric considerations prevent it, an aldehyde or ketone could form an acetal or ketal by reacting with adjacent hydroxyls with the elimination of water.

Back [33] has mentioned the possibility of formation of ether linkages between hydroxyls of adjacent chains by elimination of water. This certainly is a possibility, for this reaction takes place in an acidic solution of alcohol at around 110-130°C [36]. At higher temperatures an alkene is formed.

Ruffini [34] has presented evidence showing that cross-linking occurs by the formation of an ester linkage between a carboxyl in one chain and a hydroxyl in a neighboring chain. He postulates that uronic acid groups in the hemicellulose fraction and, in unbleached sulfite pulps, sulfonic acid groups in the lignin, are responsible for the high strength level of paper made from certain pulps. The sheets Ruffini made from the experimental pulps were dried for three minutes at 130°C. As it should be possible for esters to be formed at this temperature, it would be interesting to prepare sheets by air drying without heat to determine the effect of the drying process on ester formation.

Regardless of the mechanism, wet strength development is catalyzed by aluminum sulfate, zinc chloride, ferric chloride, acids, and cupric nitrate [33, 35]. Back [33] has reported that the generation of wet strength is catalyzed by low pH and by metal ions with a high redox potential. He also found that salts that produce wet strength at a high rate also cause a rapid decrease in wet strength. This is especially true of those salts that release acids at elevated temperatures.

Improved bonding of cellulose fibers occurs after exposure to oxygen and ozone in a corona discharge. The bonding is further improved by soaking in 0.1 M sodium hydroxide after exposure to the corona discharge. These effects have been attributed to surface oxidation of the cellulose [37].

2.5 Changes in Lateral Order

Changes in lateral order of cellulose in paper would be expected to affect most physical properties of paper. The discussion here will be confined to change in order that may occur in the bonding areas of paper. Recrystallization has been reported to occur during heterogeneous hydrolysis [18, p. 996; 38]. It has been reported that partially decrystallized cellulose recovered most of its crystallinity when exposed to moist air [39]. Extensive changes in physical properties of paper over a period of 36 years, apparently without changes in fiber strength [40], are difficult to explain without assuming some change in the order of the system. Cellulose fibers change dimensions with changes in moisture content, and this is reflected in hygroscopic dimensional instability in paper. When pulp is dried and rewetted, the physical properties (wetting, strength, moisture regain) are never quite the same [18, p. 724; 41]. The properties of paper made from "broke," the waste paper from the paper machine, are significantly different from those of the paper from which it was made [42]. Luner [5] found that cycling of temperature and, therefore, relative humidity and moisture content, had an effect on physical properties of paper during accelerated aging.

From the above, it appears that, if conditions are favorable, crystallinity in the fiber may increase in water suspension or in a moist atmosphere. At the same time, the "order" that exists in the bonding regions of paper may decrease with time. This could seriously affect some physical properties without damaging the fiber. A possible explanation for this is that crystallization occurs with the exclusion of water, but requires the presence of water for the necessary mobility, whereas fiber to fiber bonding occurs through water bridges. With cycling of relative humidity, these water bridges probably can relax with time and affect the properties of paper that depend most on interfiber bonding. If some agent, such as rosin size, is present to enhance these bridges, they are less likely to relax with time. Chemical degradation with time in a sizing-bonded paper would affect those properties dependent on fiber integrity.

It has been reported [43] that dialdehyde cellulose (carbons 2 and 3) and monocarboxyl cellulose (carbon 6) exhibit higher moisture regains than the unoxidized control. On the other hand, the moisture regain of dialcohol cellulose (reduced dialdehyde cellulose) was less than the unoxidized control. The heat of interaction of the samples with water showed the same trend. However, the levels of oxidation necessary to achieve these changes in moisture regain and heat of wetting were far higher than those which occur in the aging of paper. Therefore, oxidation is not likely to affect "order" or moisture regain in the bonding areas of paper as a primary effect.

The effects of destruction of bonding depend, in part, on the fiber length. In a long-fibered paper, fold, for example, might be affected hardly at all; but in a short-fibered paper, fold would be drastically reduced.

2.6 Thermal Decomposition

A property that often is overlooked in the accelerated aging of paper is the purely thermal instability of cellulosic and noncellulosic carbohydrate structures. This thermal instability should be more pronounced with increasing amounts of oxidized cellulose and with increasing amounts of hemicelluloses. Thermal decomposition at various temperatures has been discussed by Schwenker [44], who showed that thermal degradation occurs even below 100°C.

3. PROBABLE EFFECTS OF CHEMICAL AND PHYSICAL CHANGES ON MEASURABLE PROPERTIES OF PAPER

3.1 Overview

The changes that might be expected to occur during the accelerated aging of paper are given in Table 1 along with anticipated effects on various laboratory tests. Many of the reactions must occur concurrently or consecutively. Some may be isolated by excluding oxygen or moisture (or oxygen and moisture) from the aging atmosphere. This also may confuse the situation by preventing synergistic reactions from occurring.

The effects of various changes are listed as primary or secondary. A decrease in degree of polymerization (DP) is a primary effect of hydrolysis. Decrease in wet strength probably would be a secondary effect resulting from a general weakening of the structure.

3.2 Hydrolysis

During accelerated aging, hydrolysis could be expected to affect test properties as indicated in Table 1.

(a) Degree of polymerization (DP) would be reduced by random attack in accessible areas.

(b) Organic acids could be generated from carbohydrate structures, and protonic acid from aluminum complexes (if present).

(c) Aldehyde content would be increased, as one aldehyde group is formed with each hydrolytic chain break.

(d) Carboxyl, ketone, and peroxide should not be affected.

(e) Moisture regain should be relatively unaffected by chain scission, as the latter occurs in the accessible areas and none of the material is lost. This is in contrast to heterogeneous hydrolysis in acid solution where the hydrolyzed material becomes soluble and is lost. The remaining cellulose is highly crystalline and has a low moisture regain [18, p. 736].

(f) Alkali solubility should increase depending on the extent of hydrolysis. If hydrolysis is known to be the only reaction taking place, alkali solubility is an excellent diagnostic test.

(g) Fold, tear, burst, tensile, elongation, and tensile energy absorption (TEA) would decrease. Modulus should decrease somewhat, but not extensively. Tensile, elongation, and TEA are increasingly sensitive, in that order, to a decrease in DP. This is illustrated in Figure 3 [10], which shows typical load-elongation curves for an unaged specimen and an aged specimen of the same paper, whose retention of tensile strength, elongation, and tensile energy absorption are approximately 65 percent, 35 percent, and 25 percent, respectively. In this particular sample, modulus has increased due to crosslinking.

(h) Zero span would be decreased by fiber degradation, due to decrease in DP.

(i) Wet strength would decrease as a secondary effect due to general weakening of the structure, or to hydrolysis of crosslinks as a primary effect.

(j) Blue reflectance would not be expected to change if the cellulose is unaltered. However, this is never the case, and humic substances may be formed during hydrolysis [19, p. 23]. These may be dark in color and, therefore, would reduce the blue reflectance.

3.3 Oxidation

Oxidation of carbohydrate structures during aging of paper could be expected to affect test properties as indicated in Table 1.

(a) A direct decrease in DP could be expected, partly as a result of increased sensitivity of oxidized structures to hydrolysis. Although viscosity measurements are a function of DP, viscosity solvents for cellulose usually are alkaline and are likely to cause chain scission [19, p. 147]. An alternate approach is to nitrate the cellulose and dissolve in acetone for measurement of viscosity [45], but this procedure has its own set of problems, especially with wood pulps [46].

(b) Carboxyl, aldehyde, ketone, and peroxide would be expected to increase, although aldehyde might also decrease, depending on the specific reaction. Low molecular weight oxidation products with an appreciable vapor pressure would be lost. Peroxides would be expected to form and decompose, so for a given set of experimental conditions, peroxide concentration should stabilize at a steady state value.

(c) Moisture regain should decrease as a secondary effect due to crosslinking reactions [18, p. 857].

(d) Alkali solubility should increase with oxidation and should be a sensitive test, but not a diagnostic one.

(e) All of the physical properties, except wet strength, should decrease with oxidation, especially with the synergistic action of oxidation and hydrolysis.

(f) Blue reflectance should decrease with oxidation. Saturated organic compounds (no double bonds) absorb in the ultraviolet, and the absorption moves up to the blue end of the visible spectrum only after the formation of a conjugated system of double bonds [47]. As it is not possible to form a conjugated system between anhydroglucose units in cellulose, because of the presence of an oxygen bridge, a conjugated system can exist only on carbons 1, 2, and 3 in the anhydroglucose ring, and on 1 only when it is terminal. Therefore, absorption in the visible due to oxidation of cellulose and hemicellulose is likely to occur only in the blue. Oxidation of hemicelluloses in wood pulp is far more probable than oxidation of cellulose.

3.4 Crosslinking

Crosslinking could be expected to affect the tests listed in Table 1 as follows:

(a) Some crosslinking should increase the molecular mass, and eventually crosslinking may render the material insoluble [48]. This may or may not show up in a viscosity determination, as some viscosity solvents may destroy the crosslinks.

(b) Carboxyl [34] could be consumed in ester formation, and aldehyde and ketone [33] could be consumed in acetal and ketal formation, respectively.

(c) Moisture regain should be decreased by crosslinking [18, p. 857]. The structure would become more rigid and less accessible to moisture.

(d) Alkali solubility should decrease unless the crosslinks are decomposed in alkali [48].

(e) Fold, tear, and burst deteriorate with crosslinking [49]. Changes in tensile strength will depend on the extent of crosslinking. Elongation decreases with crosslinking [50], modulus increases [10], and TEA should decrease as a function of decrease in elongation. Zero span should not be affected except as a secondary effect of fiber degradation if crosslinking occurs due to the presence of an acid catalyst.

(f) Wet tensile increases significantly with crosslinking [33].

(g) Blue reflectance should not be affected.

3.5 Changes in Bonding

A discussion of decrease in order in the bonding area will be confined to (1) decrease in bonding due to decrease in "order" of the cellulose in the bonding area (conjecture at the moment), and (2) degradation of bonds formed by sizing agents. Concepts of the nature of fiber bonding and of sheet formation are changing rapidly but a good introduction to the subject is given by Casey [32]. Graminski [51] has shown that the film-like material created by the "fines" in paper affects properties, especially durability, in a way not previously anticipated. Apparently, failure occurs first in the "fines" area and not in the fiber to fiber bonding.

The bonding in paper depends on a host of variables such as type of fiber, extent of beating, wet pressing, sizing agents, carboxyl groups, zeta potential, and many others. McKee [42] has shown that repulping degrades those properties that are a direct function of fiber strength and fiber bonding, but those properties such as tearing strength, that are inversely related to bond strength, increase with the number of repulpings. This is not the same situation as degradation of bonding in a sheet of paper, but it may indicate that tearing strength would increase, or decrease more slowly, if degradation of bonding were the dominant reaction during aging.

As so little is known about selective degradation reactions in the bonding area of paper, the indications in Table 1 are conjecture only. Bonding is discussed because degradation of bonding and its effect on the properties of aged paper have been largely overlooked.

3.6 Thermal Decomposition

As a result of thermal decomposition, one would expect DP, all physical properties, and blue reflectance to decrease. Carboxylic acid content probably would decrease due to decarboxylation.

4. SOME SPECIAL SITUATIONS

4.1 Overview

The above discussion is basic to an understanding of the natural aging of paper and the effects of aging on paper properties. Several specific situations related to the aging of pulp and paper deserve special attention, such as catalytic action of metals, generation of acid from unsuspected sources, and the potential of air pollutants for causing damage to paper. Although these examples of degradation are generated mostly by environmental factors, papers that are damaged most extensively have the seeds of their own destruction built into them.

4.2 Metals as Catalysts

Although the deleterious effect of sulfur dioxide on paper has been long recognized [52], Langwell apparently was the first to show that the oxidation of sulfur dioxide was catalyzed by metallic impurities such as manganese and iron in paper, to sulfur trioxide [27]. Hudson and Milner [53] were able to detect the pickup of sulfur dioxide within two hours using radioactive sulfur as a tracer. Hudson [54], Smith [55], and Scribner [56] have shown that books stored in libraries in urban areas are more acid than books stored in rural areas. Pickup of sulfur is especially noticeable at the edges of pages in books, and Langwell [27] showed that the sulfate content was higher at the edges. This was noted earlier by Jarrell [57].

The effect of certain metals that promote crosslinking already has been mentioned.

Several investigators [58, 59, 60] have shown that metals act as catalysts in brightness reversion.

4.3 Effect of Chlorinated Extractives

Bergman et al [61] have shown that removal of extractives can reduce color reversion. It also has been shown that chlorinated lignin [62] and chlorinated extractives [63] cause serious brightness reversion during accelerated aging. Chlorinated extractives release hydrochloric acid at comparatively low temperatures and cause brightness reversion of pulp during storage.

4.4 Migration of Impurities

Barrow [64] has reported on the migration of various impurities in paper. He showed that acid could migrate from one sheet to another and appreciably decrease the folding endurance. Examples of migration of impurities from sheets containing groundwood to fully bleached papers are quite common. It is not known whether the migration of colored impurities affects permanence.

4.5 Air Pollutants

The effect of air pollutants on the stability of paper has received little attention in the laboratory, with the exception of sulfur dioxide. The problem could be more serious than is suspected, for urban atmospheres contain several compounds that could be injurious to paper [65]. The possibility that certain metals may catalyze reactions of air pollutants with paper, or that some functional groups may cause paper to be more susceptible, cannot be overlooked. For various large cities in the U.S., mean values for 1964 for various gaseous pollutants in parts per million are as follows [66]:

	Range of Means	Maximum
Carbon monoxide	5 -12	60
Hydrocarbons	2 - 3	20
Sulfur dioxide	0.01- 0.18	1.62
Nitric oxide	0.03- 0.09	1.35
Nitrogen dioxide	0.03- 0.06	0.79
Total oxidants	0.02- 0.03	0.85

Aldehydes may run as high as 1.87, with a normal range of 0.05-0.60. Ozone may run as high as 0.90 with a normal range of 0.05-0.65.

Nitrogen dioxide has been found to degrade cotton, partially acetylated cotton [67], and cellulose acetate film [23]. From these examples, it is obvious that air pollutants other than sulfur dioxide can give trouble.

5. RESULTS OF SOME RECENT STUDIES ON ACCELERATED AGING OF PAPER

Venter [13] conducted an extensive investigation of the aging of paper. All of his conclusions are germane only to the samples he used and to his aging conditions, but the following of his conclusions appear generally pertinent:

(1) Alkali solubility is a very useful test, for changes in alkali solubility may show up, due to formation of alkali-sensitive linkages, before changes in physical properties.

(2) Degradation reactions that occur during the aging of paper are random and are not "peeling" or "unzipping."

(3) Chain length distribution provides very useful information, but the test is most time-consuming.

(4) Sharp changes in slopes of plots of degradation rates against temperature occur at about 70°C with tear, fold, and alkali solubility.

(5) Copper number (and, therefore, reducing power) increases with time of aging.

(6) The presence of rosin does not cause paper to be less stable during aging when change in alkali solubility is used as a criterion.

Cardwell [14] studied several variables associated with the aging of handsheets and commercial papers, and some of his conclusions are as follows:

(1) If a crosslinking reaction occurs during the aging of paper, paper with a high bonding volume should develop crosslinks more rapidly during aging. (This probably is the reason that papers made from highly beaten stock are considered to be less stable than papers made from mildly beaten stock.)

(2) ". . . more information is needed on the chemical and physical reactions contributing to loss in paper permanence over a temperature range before the Arrhenius relationship can be used with confidence to predict paper permanence."

(3) An increase in interfiber bonding--presumably cross-linking--occurs during aging. (Cardwell suggests that water bridges may be replaced by direct hydrogen bonding between cellulose chains. It is more likely that disappearance of water bridges would "relax" bonding, so crosslinks would be formed by some other mechanism.)

(4) The three tests for best predicting the stability of paper are tensile energy absorption, tensile breaking length, and force to give 300 folds. (On the basis of changes that occur in the force-elongation curve during aging, the sensitivity and usefulness of tensile breaking length might be questioned.)

(5) Cycling of temperature and relative humidity increased the rate of degradation over that which occurred under constant conditions of temperature and relative humidity.

Neither Browning and Wink [4] nor Venter [13] found an increase in carboxyl content during accelerated aging. As any increase in carboxyl probably would be small, and as oxidized structures may become alkali-sensitive or soluble due to chain scission, the analytical tools presently available are not likely to be capable of measuring, or detecting, changes in carboxyl due to natural or accelerated aging.

Several investigators [4, 13, 23, 15, 68] have used Arrhenius plots as a tool in the evaluation of accelerated aging data. This approach has merit only if properly used within the limitations of (1) knowledge of the reactions involved and (2) mathematical treatment of data [69, 70, 71]. A far more useful approach should be to probe the reactions that occur during natural aging and devise accelerated aging conditions that cause these same reactions to occur.

6. SUMMARY

(1) The predominant chemical reactions in accelerated aging are hydrolysis, oxidation, and crosslinking. In some cases, especially waterleaf papers, a decrease in bonding order may be predominant.

(2) Hydrolysis and oxidation are synergistic.

(3) Hydrolysis in a heterogeneous system is especially enhanced by an aldehyde on the No. 6 carbon of anhydroglucose.

(4) Hydrolysis is catalyzed by acid.

(5) Aluminum catalyzes degradation.

(6) Aluminum, other metals, and acids enhance and also destroy crosslinking.

(7) Under proper experimental conditions, aldehydes and carboxyls enhance crosslinking.

(8) Cycling of moisture content degrades physical properties of paper.

(9) Some degradation reactions decrease moisture regain.

(10) Moisture greatly enhances some types of degradation.

(11) The "fines" in paper contribute significantly to the degradation of paper.

(12) It is obvious from a review of the literature on accelerated aging of paper that:

(a) Accelerated aging conditions that would satisfy all possibilities are impossible to define.

(b) An accelerated aging test does not tell what a paper will be like after 25 or 50 years of storage. It only provides information concerning the ranking of different samples with respect to storage properties.

(c) Some conclusions can be drawn concerning aging conditions.

(d) Some conclusions can be drawn concerning useful tests for evaluation of aging.

(e) Published data do not give a coherent picture of the aging of paper.

(f) Most of the data are of limited utility because the samples were not adequately defined.

(g) Arrhenius plots must be used with caution in the evaluation of stability.

(h) The correlation of natural aging with accelerated aging is never likely to be perfect, or even high, as different natural aging conditions produce different results [55, 72].

(i) Extensive mathematical treatment of data, and predictions of stability based on these treatments, are not likely to be very fruitful.

7. RECOMMENDATIONS

(1) The following tests should be useful in determining <u>what</u> happens during the aging of paper:

(a) Zero-span tensile (fiber strength)

(b) Wet tensile (crosslinking)

(c) pH (generation of acid)

(d) Alkali solubility (some chain scission and alkali sensitivity)

(e) Functional group content (oxidation)

(f) Molecular chain length distribution (chain scission and randomness of chain scission)

(g) Peroxide formation (probably oxidation, but peroxides apparently can be formed in cellulose in the absence of air)

(h) Oxygen sorption (oxidation)

(2) The following tests should be useful for <u>detecting</u> changes during the aging of paper, but are not particularly useful for identifying the nature of the change:

(a) Folding endurance

(b) Tearing strength

(c) Elongation

(d) Tensile energy absorption

(e) Alkali solubility

(f) Copper number

(g) Viscosity

Alkali solubility appears under both (1) and (2). Without additional information, it belongs under (2); with information on functional group content, change in zero-span tensile, viscosity, and peroxide content, it can be evaluated properly and belongs under (1).

(3) Other tests that may be somewhat less useful are:

(a) Tensile strength

(b) Burst

(4) The following general conditions for accelerated aging should be evaluated:

(a) Low temperature (50°-70°C)

(b) Cycling of relative humidity, probably between 0 percent and 70 percent on hourly cycles.

(c) Oxygen atmosphere

(5) General guidelines for the composition of permanent record paper (not for specification purposes) are as follows:

(a) Low functional group content (aldehyde, carboxyl, ketone)

(b) Alkaline filler, or pH in the neutral range

(c) Stable sizing material

(d) Large percentage of long fibers (2-3 mm)

(e) Low percentage of fines

(f) No lignin

(g) No aluminum salts during manufacture

(6) Recommendations for future work:

(a) Examine papers that have been in storage for some time and attempt to identify the changes that have taken place during storage.

(b) Devise one or more accelerated aging methods that cause these same changes to occur.

Work is in progress on both of these tasks.

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Table 1. Reactions, or changes, that might occur during natural and accelerated aging of paper, and their expected effects on various tests.

Test	Reaction or Change; P = Primary, S = Secondary									
	Hydrolysis		Oxidation		Crosslinking		Bonding "Order"[1] decrease		Thermal[2] Decomposition	
	P	S	P	S	P	S	P	S	P	S
DP[3]	↓		↓	↓	↑			--	↓	
Acid, H^+		↑	↑		--			--	↑	
Carboxyl		↑	↑			↓		--		
Aldehyde	↑		↑↓			↓		--	↑	
Ketone	--		↑			↓		--	↑	
Peroxide	--		↑		--			--	↓	
Moisture regain	--		↑↓		↓		↑			--
Alkali solubility	↑		↑		↓			--	↑	
Fold	↓		↓		↓			↓	↓	
Tear	↓		↓		↓			↑	↓	
Burst	↓		↓		↓		↓		↓	
Tensile	↓		↓		--			↓	↓	
Elongation	↓		↓		↓		↓		↓	
Modulus	↓		↓		↑		↓		↓	
TEA[4]	↓		↓		↓		↓		↓	
Zero span	↓		↓			↓		--	↓	
Wet tensile		↓		↑	↑			--		--
Blue reflectance		↓	↓	↓	--			--	↓	

[1] Includes degradation of bonds formed by sizing agents.
[2] Probably occurs only during accelerated aging.
[3] Degree of polymerization.
[4] Tensile energy absorption.

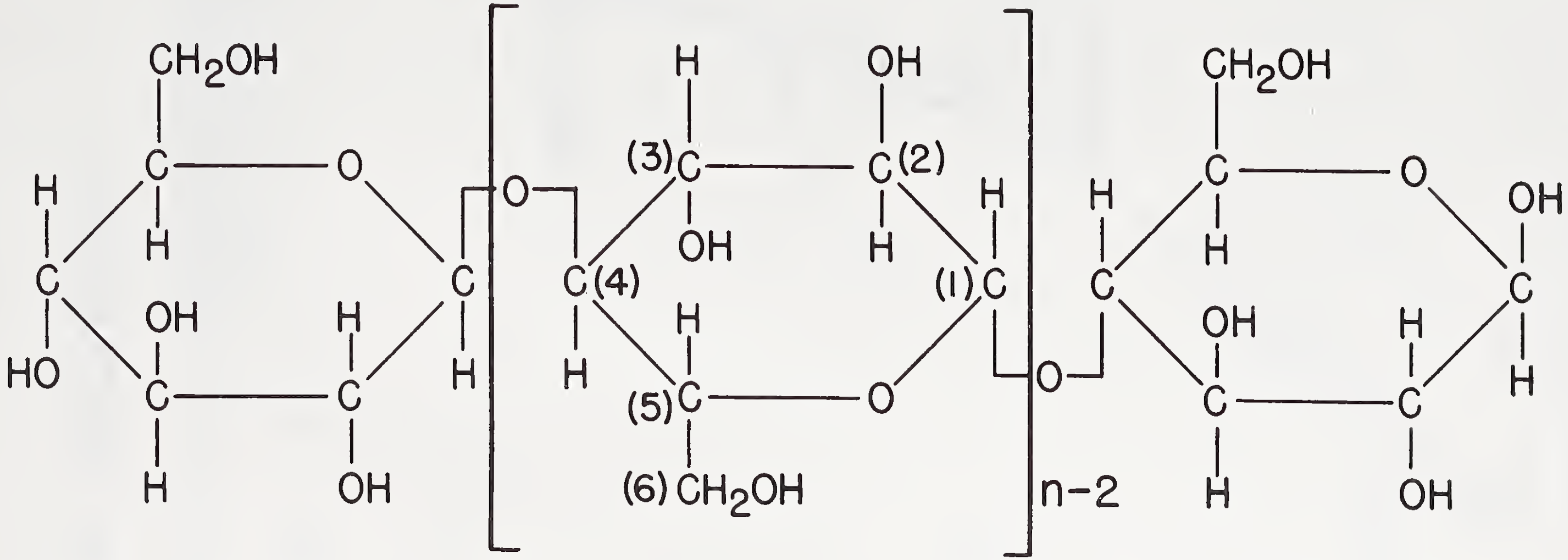
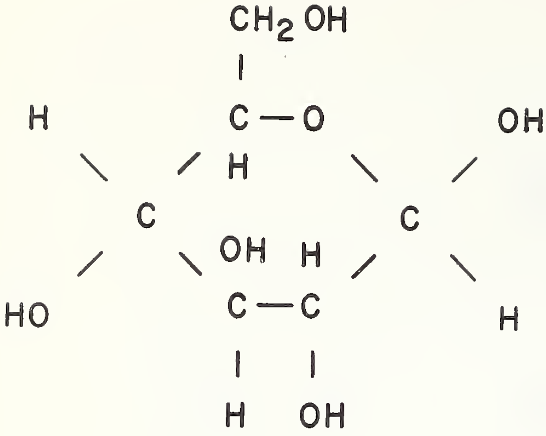


Figure 1. Generally accepted formula of cellulose chain. Brackets enclose one molecule of anhydroglucose.



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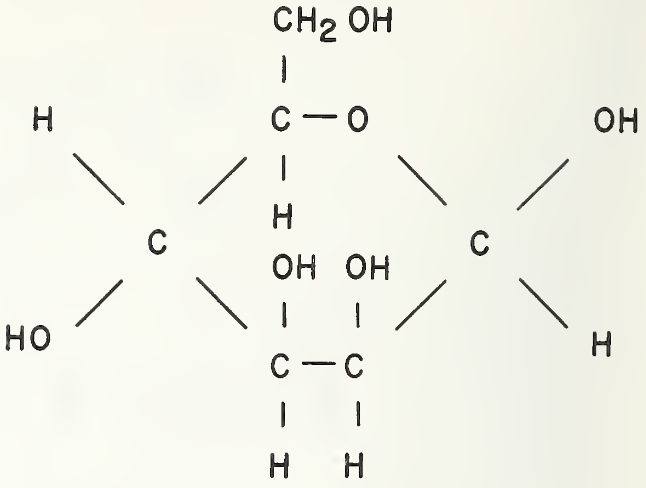

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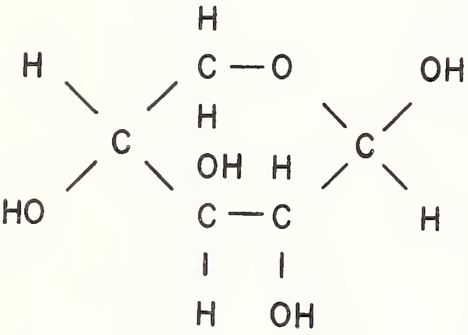

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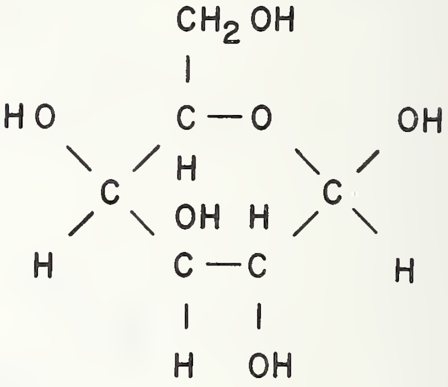
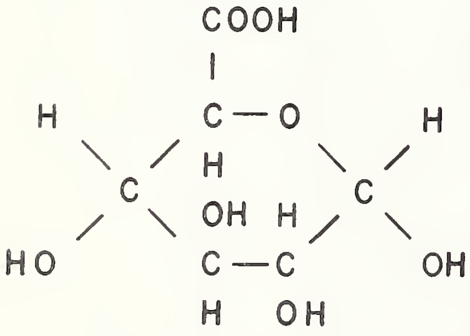


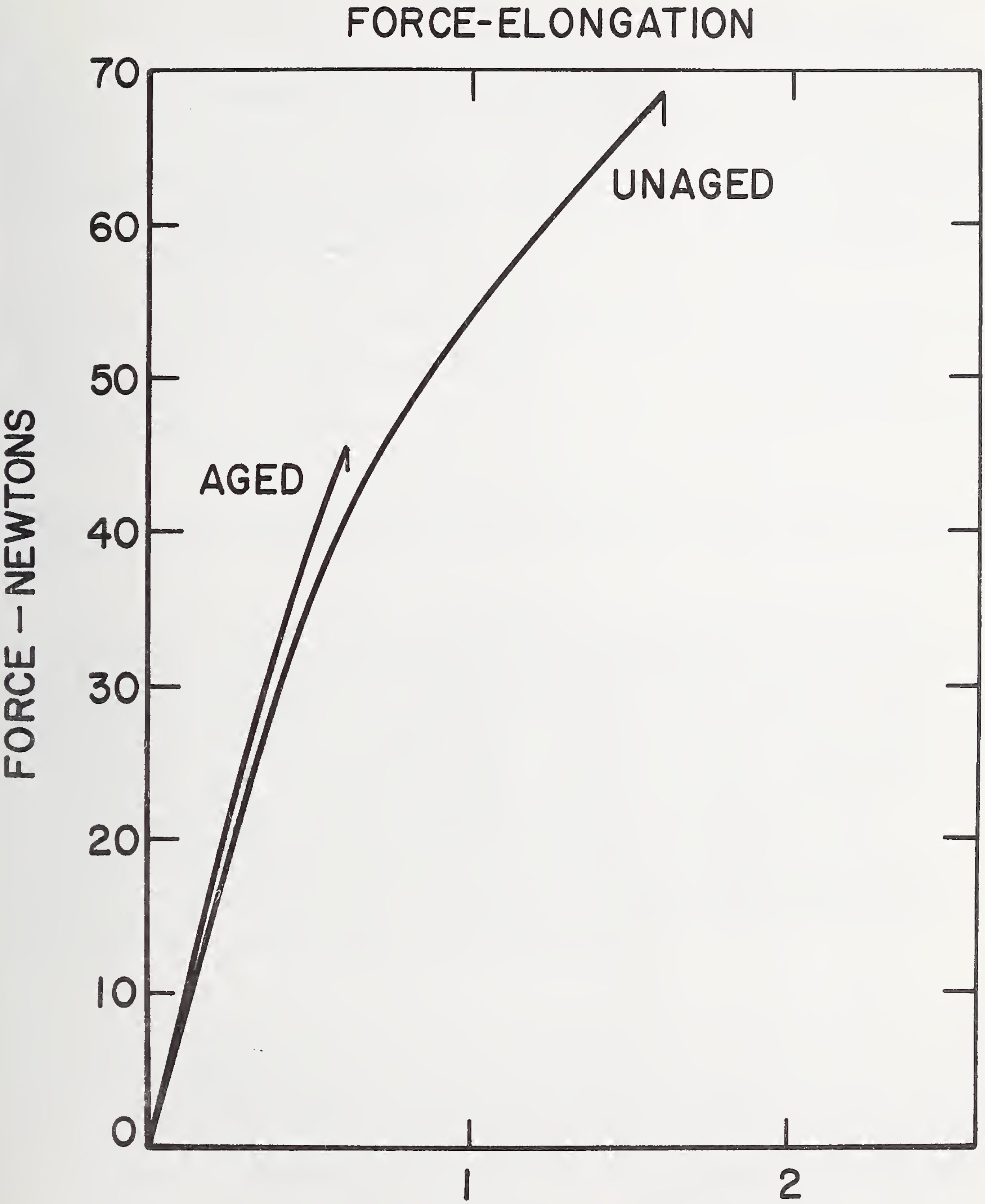
GALACTOSE



GLUCURONIC ACID

Figure 2. Some monomer units of the hemicelluloses. Polymers of mannose occur principally in softwoods and polymers of xylose principally occur in hardwoods. Galactose is a minor constituent. Glucuronic acid is an oxidation product of glucose and is a site for crosslinking (see text).

Figure 3. Typical force-elongation curves for aged and unaged paper. Except for elongation, the two curves are not radically different.



NBS-114A (REV. 7-73)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET**	1. PUBLICATION OR REPORT NO. NBSIR 74-499	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

An Analysis of the Aging of Paper: Possible Reactions and Their Effects on Measurable Properties

5. Publication Date
April 1974

6. Performing Organization Code

7. AUTHOR(S)
W. K. Wilson and E. J. Parks

8. Performing Organ. Report No.
NBSIR 74-499

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.
3000442

11. Contract/Grant No.

12. Sponsoring Organization Name and Complete Address *(Street, City, State, ZIP)*

National Archives and Records Service
Washington, D.C. 20408

13. Type of Report & Period Covered
Interim

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

Various reactions that cellulose can undergo are reviewed in relation to their bearing on the aging of paper. The principal reactions of cellulose are hydrolysis, oxidation, crosslinking, change in lateral order in the bonding area, and, during accelerated aging, thermal decomposition. The effects these various reactions might have on tests that are available for evaluating changes that occur during the aging of paper are reviewed. Some special examples of these reactions that occur during natural aging, because of special composition characteristics of the paper, are discussed. Suggestions are made concerning most sensitive tests for use in detecting changes in paper and tests, regardless of sensitivity, available for determining what happens during aging. Some general guidelines regarding specifications for permanent record papers are discussed.

17. KEY WORDS *(six to twelve entries; alphabetical order, capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Accelerated aging; aging; aging of cellulose; aging of paper; cellulose; cellulose aging; natural aging; paper; paper aging; tests for paper.

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Springfield, Virginia 22151

19. SECURITY CLASS (THIS REPORT)
UNCLASSIFIED

20. SECURITY CLASS (THIS PAGE)
UNCLASSIFIED

21. NO. OF PAGES
49

22. Price

USCOMM-DC 29042-P74