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Development of Specifications for Archival Record Materials

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Paper Evaluation Section
Institute for Materials Research
National Bureau of Standards

May 23, 1974

Annual Report Covering the Period
July 1, 1973–June 30, 1974

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

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

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

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1. SUMMARY

Effort on a long range program on the Development of Specifications for Archival Record Materials has included:

(1) Reappraisal of research needs.

(2) A study of 18 papers made in 1937, tested before and after dry accelerated aging in 1937, and tested again in 1973.

(3) Evaluation of 19 commercial papers, evaluated before and after moist accelerated aging in 1963, and tested again in 1973.

(4) Development of specifications for copies from office copying machines.

A review of the literature on stability of paper and data obtained in this laboratory over the past several years indicate that a fresh approach is needed to a study of the stability of paper. The following tasks are suggested:

(1) Continue to use handsheets of known composition.

(2) Study old papers to determine changes that probably have occurred during natural aging.

(3) Confine testing to methods that give some clues concerning <u>what</u> happens during aging such as zero span tensile, wet strength, peroxide formation, functional group content, and molecular chain length distribution.

(4) Study the effect of cycling of relative humidity on the properties of paper.

2. BACKGROUND

In response to a request by the National Archives and Records Service, the National Bureau of Standards is developing information on the variables associated with the stability of archival record materials, especially paper. Several U.S. Government agencies and the Society of American Archivists have joined in sponsorship of the project through National Archives and Records Service.

Many record materials of archival or long-term historical value in repositories in the Federal Government and throughout the United States are in bad physical condition. If proper specifications were available for materials that are designed to be used for permanent records, future problems concerned with the deterioration of record materials and the cost of repairing the mistakes of the past would be greatly minimized.

Much of the earlier work on this project was directed toward the development of an accelerated aging method. As this is a long-range effort, in terms of time and scope, and as archivists and librarians need specifications today for record materials, interim specifications based on pH requirements have been prepared for selected materials. Specifications for manifold papers, for bond and ledger papers, and for file folders have been cleared through the American Society for Testing and Materials (ASTM). In response to an urgent need to establish permanence criteria for papers that can be used in office copying machines, interim specifications have been written. An accelerated aging method is required for this specification. Other materials that merit attention are inks, typewriter ribbons, carbon paper, laminating film, mending tape, binding materials, and manuscript boxes.

3. OBJECTIVES

The objectives of this program are as follows:

(1) The development of information on the stability of paper and other record materials.

(2) The development of test methods for the evaluation of the stability of paper and other record materials.

(3) The development of specifications for materials suited for permanent records.

4. COMPLETED SPECIFICATIONS

The following specifications have been cleared through the American Society for Testing and Materials (ASTM):

D-3208, Standard Specification for Manifold Papers for Permanent Records. This specification was completed about a year ago and appears in Part 20 of the 1974 ASTM Book of Standards. It also is available from ASTM as a single reprint.

D-3290, Standard Specification for Bond and Ledger Papers for Permanent Records. This specification has been printed and is available as a single reprint. It does not appear in the 1974 ASTM Book of Standards.

D-3301, Standard Specification for File Folders for Storage of Permanent Records. This specification has been printed and is available as a single reprint. It does not appear in the 1974 ASTM Book of Standards.

These specifications are now ready to use for procurement purposes.

These specifications are being submitted through channels to Committee P3, Paper, of the American National Standards Institute (ANSI) for consideration as ANSI standards.

5. EVALUATION OF STABILITY OF COPIES FROM OFFICE COPYING MACHINES

Technology has provided over the past 20 years a plethora of machines for making copies of originals by pressing a button. As some of these copies have not proven to be particularly stable, and as these copies have found their way into permanent record files in various organizations, specifications for this type of copy are urgently needed. Paper must be capable of being transported through the copying machine for which it is intended. The paper may be plain, coated, or impregnated, and supplies may be purchased from sources other than the suppliers of the copying machines. As pH can be used as a sole criterion of probable longevity only for plain uncoated paper, an accelerated aging method is required. The only official accelerated aging method for paper involves oven aging for 72 hours at 105°C. In addition, stability of the image must be evaluated.

Representative samples were obtained from several manufacturers and tested in order to obtain the data necessary for preparing specifications for the paper and for stability of the image. This work has been completed, and a report is in the editorial process. The specification is based on: (1) minimum pH requirement, (2) minimum retention of tear and fold after accelerated aging, and (3) retention of reflectance of image after exposure to a xenon arc and after abrasion by a standard technique.

6. ACCELERATED AGING OF BOOK PAPERS AT 100°C COMPARED WITH 36 YEARS NATURAL AGING

In 1936 a group of book papers made in the NBS paper mill was tested before and after accelerated aging for 72 hours at 100°C. Although there was no plan to test these papers after natural aging, a collection of some of these papers had been kept in an office for several years. The manufacturing history was known and the physical and chemical properties had been extensively evaluated for that time. Out of a total of 72 papers, 18 were found that could be assembled to form a reasonably coherent set of samples.

The fiber furnishes fall into three categories: (1) 50-50 soda-sulfite, (2) purified wood pulp, and (3) old rag. Chemically, these papers are very different. The soda-sulfite papers contain a high percentage of hemicelluloses, the purified wood pulps are low in hemicelluloses, and the rag papers contain no hemicelluloses. The hemicelluloses are more vulnerable to degradation than cellulose.

The following conclusions may be drawn from data obtained on these papers:

(1) Elongation is fairly sensitive to natural aging.

(2) Folding endurance is very sensitive to natural aging, but the scatter of the data is very great.

(3) A plot of retention of folding endurance against acidity (pH measured in 1937) shows some correlation, if data on each set of six papers are viewed separately.

(4) A waterleaf paper containing neither rosin nor alum was very unstable with respect to folding endurance and tensile strength and was not outstanding with respect to retention of tearing strength. Fiber strength did not appear to deteriorate, but the fiber bonding deteriorated badly. Thus, the basic stability of the structural components is high, but the structure itself became weak. This is a new concept in the natural aging of paper.

(5) Three alkaline papers performed well after 36 years of natural aging, but retention of properties was not as great as expected.

(6) Data obtained in this laboratory show that much more acid is generated in moist accelerated aging than in dry accelerated aging. Some acid, as measured by differences in pH values, was generated in most of the papers during natural aging. It would appear that some moisture should be present in an accelerated aging atmosphere, but a relative humidity of 50 percent probably is too high.

(7) Bonding strength in short fibered papers appears to contribute heavily to folding endurance but not to zero span tensile strength.

(8) There is a recognizable relationship between cold extract pH measured in 1937 and wet strength measured in 1973.

(9) It is possible to specify stable papers using retention of folding endurance and retention of tearing strength after accelerated aging for 72 hours at 100°C, especially when coupled with a pH requirement. The specification can be as rigid as the use requirements dictate.

(10) There is some evidence that the cycling of relative humidity as a factor in the deterioration of some types of paper should receive attention.

Although a draft of the report on this work has been prepared and could be submitted essentially in its present form, data on alkali solubility and reducing power (a measure of oxidized structures) should be obtained. These data were obtained in 1937 before and after accelerated aging. This work will require approximately two months.

Evaluation of materials by methods that are almost 40 years old never is very satisfying, but a review of the reactions that may occur during the aging of paper and their effects on measurable properties (Section 8) has made this task more meaningful.

7. STUDY OF UNCOATED BOOK PAPERS AFTER 10 YEARS OF NATURAL AGING

Work on the retesting of these papers has been completed, but a report has not been started. Some preliminary conclusions were given in NBS Report 73-249. These data are not likely to be as valuable as the data from the papers made in 1937, as the manufacturing details are not known and the spectrum of composition is very broad.

8. AN ANALYSIS OF THE AGING OF PAPER: POSSIBLE REACTIONS AND THEIR EFFECTS ON MEASURABLE PROPERTIES

About two years ago three reports on the accelerated aging of laboratory handsheets were submitted to NARS, NBS Reports 10 627, 10 628, and 10 687. These reports are based on data obtained from the evaluation of carefully prepared laboratory handsheets. Although the significance of the data was discussed in each report, there has been a need to bring the data in these three reports into a coherent picture and to draw some conclusions about the significance of accelerated aging. An attempt was made to do this, but it soon was realized that this would be useless without an analysis of the possible reactions that might occur during the aging of paper and their effects on measurable properties. This was intended to be an introduction to an analysis of the data in the three reports mentioned above, but the effort developed into a report that stands by itself.

This report includes a review of the literature and draws to some extent on data obtained on the papers made in 1937. The preparation of this report has been extremely valuable in reviewing the status of our knowledge on the stability of paper and in preparing plans for future work. Section 6, Summary, and Section 7, Recommendations, of this report are included here because they sum up our current thinking on stability and aging of paper and in what directions further research should go.

Summary of Draft Report, An Analysis of the Aging of Paper

(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 in a heterogeneous system is enhanced by oxidized structures, especially by aldehyde on the No. 6 carbon of anhydroglucose.

(3) Hydrolysis and oxidation are synergistic.

(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 are not likely to be a particularly useful tool 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.

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

Recommendations of Draft Report, An Analysis of the Aging of Paper

(1) The following tests should be useful in determining what 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 <u>general</u> 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.

The tests that should be most useful in determining what happens during the aging of paper and should give the most information for the least investment of time:

(a) Zero span tensile (fiber strength)

(b) Wet tensile (crosslinking)

(c) pH (generation of acid)

(d) Peroxide formation

If time and resources are plentiful, alkali solubility, functional group content, oxygen sorption, and molecular chain length distribution should be valuable.

For detecting changes during aging of paper, folding endurance, elongation, tensile energy absorption, and alkali solubility should be most useful for time expended. It is clear that folding endurance is not a good test for defining what happens during the aging of paper. Inasmuch as the folding endurance of a stable paper can deteriorate very badly, folding endurance can be misleading.

9. STATUS OF REPORTS AND MANUSCRIPTS

(1) An Analysis of the Aging of Paper: Possible Reactions and Their Effects on Measurable Properties. In NBS editorial process.

(2) Evaluation of Archival Stability of Copies From Representative Office Copying Machines. In NBS editorial process. This includes a draft specification that will be started through the ASTM standardizing process as soon as it clears the NBS editorial committee.

(3) Accelerated Aging of Book Papers for 72 Hours at 100°C Compared with 36 Years Natural Aging. Most of the work is finished and a draft of a report has been prepared. A review of the data showed that alkali solubility and reducing power, both of which were measured in 1937 before and after accelerated aging, should be run. This should require about two months.

(4) Accelerated Aging of Commercial Book Papers at 90°C and 50 Percent Relative Humidity Compared with 10 Years Natural Aging. The testing of these papers is completed but no progress has been made toward writing a report.

(5) A Review of Accelerated Aging of Laboratory Handsheets. This will be a review of three earlier NBS reports, 10 627, 10 628, and 10 687. It is hoped that a review of the data in these reports coupled with data obtained on the naturally aged papers will enable some conclusions to be drawn concerning an accelerated aging test. This report is in the incubation stage.

10. PLANS FOR THE PERIOD JULY 1, 1974-JUNE 30, 1975

(1) Complete alkali solubility and reducing power measurements on the 36 year papers.

(2) Complete the reports mentioned in Section 9.

(3) Measure oxygen sorption at 50°C on representative pulps.

(4) Determine the effect of cycling of moisture content on properties of paper.

(5) Explore the possibility of aging paper in oxygen at 50°C.

(6) Examine old papers as time permits to determine what changes have occurred during aging.

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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)*

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