

**Recycled Paper Research
at the
Library of Congress**

**Preservation Research and Testing Division
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Executive Summary

- The aim of this research is to determine if copy papers composed of recycled paper fibers can be considered permanent
- Permanence is defined in terms of chemical stability and physical strength, per national and international standards
- A literature review of previously published research on recycled paper processes is included as background
- Physical, optical, and chemical analyses are performed to determine the relative rates of degradation of experimental papers
- Results indicate that papers consisting of 30% and 50% recycled fiber performed mechanically similar to a general use copy paper that was not specified as to how much, if any, recycled fiber content was included in its furnish
- A paper consisting of 100% recycled paper performed significantly worse in all testing than the other copy papers
- Color change observed in the copy papers is not shown to be indicative of loss of strength, contrary to previous research
- pH values indicate high levels of alkaline reserve in all experimental copy papers; the high pH values are due to the addition of calcium carbonate as a filler material
- All experimental copy papers in this report showed significant loss of strength as a function of accelerated aging; however, based on the definitions of permanence outlined in this study, all of the copy papers can be considered permanent
- Recommendations for further exploration include:
 - Test papers from additional manufacturers
 - Examine the role of optical brighteners in the color change of papers
 - Additional chemical analyses such as the determination of molecular weight and the degree of polymerization of the recycled fibers

This report outlines and presents results obtained from research conducted in the laboratories of the Preservation Research and Testing Division (PRTD) at the Library of Congress (LC). The research is concerned with the permanence of copy papers made from postconsumer recycled fibers. The focus of this research is to gauge the relative stability of the recycled papers through physical, chemical, and optical testing. The subjects of this report are the type of copy papers or business printer papers used to document the day to day operations at LC and other federal agencies. For the sake of consistency the test papers will be referred to as copy papers in this report.

I. Introduction

The Library's mission is to support the Congress in fulfilling its constitutional duties and to further the progress of knowledge and creativity for the benefit of the American people.¹

The mission of the Preservation Directorate at the Library of Congress is to assure long-term, uninterrupted access to the intellectual content of the Library's collections, either in original or reformatted form. This mission is accomplished directly through the provision of conservation, binding and repair, reformatting, materials testing, and staff and user education; and indirectly through coordinating and overseeing all Library-wide activities relating to the preservation and physical protection of Library material.²

Whenever possible, publications and other material of lasting value shall be reproduced on permanent/durable paper. Material is considered to be of lasting value if it is intended to be retained as a permanent record, or as part of the collections of the Library or other institutions. Other materials which are likely to be retained for 50 or more years also shall be reproduced on permanent/durable paper. The originating office shall recommend the use of permanent/durable paper on Form 28, Publication Proposal, when publication is proposed.³

The Role of the LC in the Production and Retention of Federal Records

LC is one of many federal libraries, archives, and museums that are responsible for retaining our nation's cultural heritage and official records for posterity. The array of formats available for record keeping will provide many opportunities for the future researcher to access our collective history. However, numerous challenges confront LC and its fellow cultural institutions, especially as media evolve and technological obsolescence render formats unreadable.

LC is unique in that it functions dually in the roles of producer and repository of federal records, maintaining its own Records Management Section as part of its Office of

¹ <http://www.loc.gov>

² <http://www.loc.gov/preservation/about/mission.html>

³ *Library of Congress Regulation (LCR) 1316, Section 2: Policy and Procedure*

Support Operations. Records Management staff identify LC generated documents that are designated for retirement (storage) or for final disposition. LC's Printing Officer explains:

All federal records have a specific, corresponding lifecycle according to whichever records series they fall under in the Library of Congress records schedule (LRS). The LRS prescribes retention and disposition dates depending on the type of record. Because NARA [National Archives and Records Administration] charges us to process and store federal records created by the Library—and because we are required to transfer most permanent Library records to them after a specific time period—we generally keep any temporary records in Library custody until their destruction date arrives. With the exception of personnel medical files, most records that are transferred to NARA are intended to be kept in perpetuity. Once transferred to NARA's custody, they may be recalled with a records request but they are owned and maintained permanently by NARA at that point.⁴

Institutional records that are categorized for permanent storage are eventually transferred to NARA for custody; however LC serves as the permanent storage location for other documentation of national importance. For example, the Manuscript Division at LC serves as a repository for portions of the accumulated office records and paperwork of former members of Congress. LC's Head of Reference and Reader Services in the Manuscript Division, notes:

Although the Manuscript Division at LC serves as the repository for the personal papers of many former members of Congress (a 1980 published checklist lists almost 900 references), most of these collections date from the 19th and early 20th centuries. In recent years, the increasingly large volume of contemporary congressional collections precludes the Library from collecting comprehensively in this area.⁵

Paper: The Standard Medium for Recordkeeping

Emerging technologies continuously replace and render obsolete previous modes of data management. However, the ancient standard medium for recordkeeping, paper, can remain usable hundreds of years after its production. In a world of ubiquitous electronic media, the need for paper has been reduced but not eliminated. At the time of the writing of this report (2014), LC divisional offices on Capitol Hill use approximately 50 cartons of copy paper per month.⁶

⁴ Email correspondence June 18, 2014. For more information on LC Records Management visit: <http://staff.loc/sites/iss/records-management-unit/>

⁵ Email correspondence June 18, 2014. For more information on LC's Manuscript Division visit: <http://www.loc.gov/rr/mss/>

⁶ Conversation with Head of LC Printing and Duplication Services, May 22, 2014. Visit: <http://staff.loc.gov/sites/iss/about-iss/printing-and-grapics-services/printing-management/>

Preservation efforts have aided institutions in their mission to successfully manage the long-term custody of paper. Environmentally controlled storage, deacidification, and the creation of standards for permanence of paper, are a few of the critical developments that ensure paper records will remain usable generations after they are written.

Challenges to the longevity of records because of 19th and 20th century paper manufacturing techniques compelled lawmakers to address the issues of paper quality and stability. In 1990, a joint resolution of the U.S. Congress to encourage the use of “acid free permanent papers” was signed into law by President G.H.W. Bush. *Public Law 101-423, A Joint Resolution to Establish a National Policy on Permanent Papers (Section 3)* mandated the following:

The Librarian of Congress, the Archivist of the United States, and the Public Printer [Government Printing Office] shall jointly monitor the Federal Government’s progress in implementing the national policy [...] regarding acid free permanent papers and shall report to Congress regarding such progress on December 31, 1991, December 31, 1993, and December 31, 1995.⁷

Commensurate with the issues of paper permanence winning lawmaker attention, public awareness of environmental challenges increased; concerns such as landfill scarcity, climate change, and natural resource depletion found their way into public policy. An early example of such a law is the 1993 issuance of *Executive Order 12873, Federal Acquisition, Recycling, and Waste Prevention*. The mandate required that all federal agencies (LC, NARA, and the Government Printing Office (GPO) included) gradually implement the purchase and use of printing and writing papers that include at least 30% postconsumer recycled material. More recently, *Executive Order 12873* was superseded by *Executive Order 13514*, signed by President Barack Obama in 2009, which “promote[s] pollution prevention and eliminate[s] waste by [...] reducing printing paper use and acquiring uncoated printing and writing paper containing at least 30% postconsumer fiber.”⁸ The new mandate effectively left agency responsibility unchanged but it reinforced the use of recycled paper a critical component in government efforts for better environmental management.

Research Objective

The dichotomy of these two concerns-- paper permanence and the required inclusion of recycled content-- led to the need for this research. It was undertaken to better understand the impact of recycled content on permanence and the longevity of federal records. The goal was to assess whether recycled paper records can be considered truly “permanent” and meet required specifications for permanence. Additionally, this report includes reviews of federal standards for paper permanence, the technical challenges that recycling processes introduce to the paper matrix, and an overview of historical and recent research studies about recycled paper composition and strength.

⁷ *Public Law 101-423* can be viewed at:

<http://www.gpo.gov/fdsys/pkg/STATUTE-104/pdf/STATUTE-104-Pg912.pdf>

⁸ *Federal Leadership in Environmental, Energy and Economic Performance—Executive Order 13514*

The ultimate aim of the research was to determine whether papers comprised of recycled paper fiber can fulfill requirements of permanence, given the mandate to include 30% recycled component for all government agencies.

II. Defining Permanence

Before *Public Law 101-423*, various commercial definitions of paper quality had been used somewhat interchangeably. Specifically, the terms *acid free*, *alkaline*, *permanent*, and *archival-quality* were used in various combinations to describe paper that, purportedly, would not yellow or become brittle—undesirable qualities associated with many 19th and 20th century papers. *The Final Report to Congress on the Joint Resolution to Establish a National Policy on Permanent Papers* uses the more technically precise term ***alkaline***, rather than *acid-free* and uses the term ***permanent paper*** rather than *archival-quality* because it focuses on the required outcome—the longevity of the product.⁹ Under *The Final Report*... an alkaline, permanent paper was defined as:

- a fully bleached sheet with a pH of 7.5 or above
- an alkaline reserve of two percent or more
- a minimum folding endurance in either direction 30 double folds (tested with a MIT folding endurance tester)
- a minimum tearing strength in either direction of 25 grams for a 30 lb paper and proportionately higher tearing strengths for heavier papers¹⁰

The Final Report... definition of alkaline permanent paper aligns with the first specification for permanent paper, the American National Standards Institute (ANSI) Z39.48-1984, *Permanence of Paper for Publications and Documents in Libraries and Archives*. This specification was developed by National Information Standards Organization (NISO) and gained strong support in the archival and library communities. NISO works closely with the International Organization for Standardization (ISO) and the requirements of the standard, *ISO 9706, Information and Documentation – Paper for Documents – Requirements for Permanence*, are commensurate with *ANSI standard Z39.48- 1992 (R2009)*. *ISO 9706* differs slightly from *ANSI Z39.48-1992 (R2009)* in allowable fiber content (lignin, ground wood pulp, and unbleached pulp) and tear resistance measurement but otherwise serves as the requirements for paper permanence. One flaw to the Public Law definition is that a neutral paper such as 100% cotton rag paper – long known for its high permanence value - cannot qualify as permanent since it does not contain the required minimum of two percent alkaline reserve.¹¹

A 2009 revision of *ANSI Z39.48-1992 (R2009)* included the following preface:

*Publishers and paper manufacturers, take note! This standard sets the basic criteria for coated and uncoated papers that will last several hundred years under normal use. It covers pH value, tear resistance, alkaline reserve and lignin threshold. **Recycled papers will meet the criteria specified.***¹² *This revision to the original 1984 standard is based on testing conducted by the Institute of Paper*

⁹ Author's emphasis

¹⁰ *Final Report to Congress on the Joint Resolution to Establish a National Policy on Permanent Papers*, December 31, 1995

¹¹ Shahani, et al., *Accelerated Aging of Paper* (2000)

¹² Author's emphasis

*Science and Technology and contributions from paper makers, publishers, printers, and the preservation community.*¹³

The statement above addresses one of the original questions posed in this report-- that “recycled papers will meet the criteria specified.” However, other concerns immediately follow. One question would be can *all* recycled copy papers meet the requirements for permanence? The array of papers available commercially often includes options to purchase copy papers that have different amounts of postconsumer recycled fibers. This raises the question of whether the papers will age at a similar rate or whether the various amounts and type of recycled fiber influence the rates of degradation. Finally, how do we test for the permanence of papers now and how do we to predict if the paper will maintain its permanence in two hundred years’ time?

It is important to consider *how* permanence is measured as much as how it is defined. In their 1988 discussion *Paper Testing and Strength Characteristics*, Caulfield and Gunderson wrote that the “mechanical and strength properties of paper reflect the intrinsic chemistry, morphology and structure” of the material itself, and that those properties “reflect the chemical changes that cause paper to lose its permanence with time.”¹⁴ This suggests that the chemical composition of the paper matrix itself will be responsible for the quality and usability of the material in the distant future. This report will show that different test methods can reveal contradictory implications of measured properties relating to how long the copy papers may be usable.

Caulfield and Gunderson built upon a concept first formulated in 1926,¹⁵ the earliest found distinction between the terms *permanence* and *durability*; that *permanence* is a measure of **chemical stability** and that *durability* is a measure of **physical and mechanical properties**.¹⁶ Often, the color of a paper suggests to users that chemical changes have taken place, but color may not be the truest measure of chemical stability. The authors’ logic followed that the leading indicator of chemical permanence is the paper’s physical durability and that only by testing the physical properties of the material can information about the chemical makeup of the paper be discovered. They described various test methods for the determination of physical strength, what the tests revealed about paper fiber structure and bonding, and the role of accelerated aging tests in determination of permanence. The authors concluded that the ultimate aim of laboratory testing was to meet the desired end-use requirements.

¹³ ANSI Z39.48- 1992 (R2009), *Permanence of Paper for Publications and Documents in Libraries and Archives*

¹⁴ Caulfield and Gunderson, *Paper Testing and Strength Characteristics* (1988)

¹⁵ *Ibid.*

¹⁶ Author’s emphasis

III. Accelerated Aging and Permanence

It has long been recognized that in order to predict lifetime and longevity of library and archive materials, researchers need to be able to simulate natural aging through the use of known environmental parameters that can accelerate and increase the rate of degradation. Studies as far back as 1934 suggest that artificial aging of paper can be a good indicator of the real effects of time.¹⁷ To effectively execute this process, there need to be established links between the results of accelerated aging in relation to how materials age naturally. Increased temperature, light and relative humidity (and pollutants) are commonly used to accelerate aging of materials. While traditionally temperature has been commonly used for aging studies, more recent research has shown that the results may induce degradation mechanisms that are not common to natural aging. Most studies use reasonable temperature and relative humidity to induce degradation without introducing new degradation mechanisms, rather than the often extreme conditions used in earlier studies.¹⁸

In his 2000 examination of the subject, *Rate of Paper Degradation: The Predictive Value of Artificial Aging Tests*, Porck explains that accelerated or artificial aging is an experimental technique in which a “material is subjected to extreme conditions in a climate-chamber to try to speed up the natural aging process.”¹⁹ The report summarized the various techniques available and benefits of specific temperatures and humidity used at that time for artificial aging experiments. The writer concluded that there were widely diverging opinions amongst conservation scientists to the exact conditions under which artificial aging takes place and that there was no single generally accepted standard method. His analysis also stated that “artificial aging tests currently available do not allow for a reliable determination of paper degradation in absolute terms.”²⁰ This led to the conclusion that findings from artificial aging were qualitative and relative to the specific papers being studied.

Accelerated aging is also the most viable experimental method for analysis of recycled papers. Doshi, Technical Editor of *Progress in Paper Recycling*, noted in 1994:

*A satisfactory method for the quick simulation of the natural aging process lasting for several hundred years has not yet been developed. Some work is continuing in this area. In the meantime, the best way to test for permanence that we know of today is the moist accelerated aging test. The test involves exposing the paper to a specified temperature and relative humidity.*²¹

Doshi conceded that accelerated aging was a far from perfect model for prediction of paper longevity but that it was the best method to make some relative conclusions about recycled papers.

¹⁷ Shahani, et al., *Accelerated Aging of Paper* (2000)

¹⁸ Porck, *Rate of Paper Degradation: The Predictive Value of Artificial Aging Tests* (2000)

¹⁹ Ibid.

²⁰ Ibid.

²¹ Doshi, *Recycled Paper Technology: An Anthology of Published Papers* (1994)

A collaborative effort between the LC and the Canadian Conservation Institute (CCI) was “undertaken to develop an accelerated aging test for paper that could be unequivocally demonstrated to approximate the natural aging process.”²² The 2000 study examined the Arrhenius relationship between increased heat and increased rate of degradation of organic materials. The work investigated the degradation products of paper formed by natural and accelerated aging.²³ Additionally, a comparison between specific accelerated aging methods (free hanging sheets, stacks, and sealed tubes) was undertaken. Initial findings suggested that the tube method created degradation products similar to natural aging. One benefit to the tube method was the control of water content in the tube; appealing because only a dry oven is required, not a climate chamber. However, doubts about the efficacy of the seals of the tubes raised concern that water loss could result in different degradation mechanisms than those found in natural aging. For this research, the free hanging method was used because it allowed known and consistent environmental conditions to surround the samples, ensuring that the papers being aged and tested were all equally exposed and aged.

In 1992 Van der Reyden reviewed specific chemical, physical, and optical properties found with paper in *Recent Scientific Research in Paper Conservation*. Van der Reyden attested to the interdependency of those properties—that measuring one set of parameter can yield information about the others. The author noted that “optical properties are physical properties which conservators often monitor as indications of chemical changes.”²⁴ Van der Reyden also emphasized that the “properties are in turn affected individually and collectively by environmental parameters such as temperature, humidity, and light; by aging; and by conservation treatments.”

Aging studies highlight the relationships between internal paper properties and the effects of external environmental factors. This report used correlations of test results from disparate parameters (i.e. physical, optical, and chemical testing) to measure paper degradation. These properties change as a function of the effect of environment (i.e. artificial aging) and allow for comparisons of strength between papers but are not used to predict with any precision an exact life span of the papers.

²² Shahani, et al., *Accelerated Aging of Paper* (2000)

²³ Ibid.

²⁴ Van der Reyden, *Recent Scientific Research in paper Conservation* (1992)

IV. Recycling Process Literature

Howard noted in his 1990 paper, *The Effects of Recycling on Paper Quality*, that some investigations into the effects of recycling began in the late 1960s.²⁵ That research focused on establishing the cause and effect relationships that lead to negative impacts of recycling papers. The study posited that the major cause of the change in properties was the reduced bonding ability of the fibers in the paper composite after recycling of the pulp. While loss of intrinsic fiber strength had been expected, a range of results were observed-- some indicating loss, no change, or even an initial increase in fiber strength.

The loss of flexibility in recycled papers was linked to the reduced swelling capacity of the fiber in the paper assembly, and McKee (1971) measured this trend using the Water Retention Value (WRV). In *Effect of Repulping on Sheet Properties and Fiber Characteristics* it was noted that the first two cycles showed the most rapid decrease in fiber swelling.²⁶ However other researchers suggest that the loss of bonding ability could be the result of two effects – changes occurring to the surface of the fibers and changes mainly occurring in the bulk of the fiber. These effects may relate to the accessibility of the fiber surface to enzyme attack and the rate of degradation of the bulk of the fiber.

Factors that control the recycle potential of pulp depend on the manufacturing history. There seems to be general agreement that a greater initial degree of beating of virgin pulp led to a greater loss of pulp quality in the corresponding recycled paper manufactured, and that this was probably due to a loss of internal swelling in the fibers. The effect of drying has an impact, where both high temperature and restrained drying can reduce the swelling potential of recycled papers. Multiple recycling tends to lead to an increase in cellulose crystallinity and decreased flexibility along with a reduced capacity for swelling and inter-fiber bonding. Yamagishi and Oye (2007) observed a small increase in cellulose crystallinity with recycling of commercial hardwood and softwood pulps.²⁷

The effects of chemical additives impact recycling since virtually all commercial papermaking utilizes additives. The presence of rosin/alum sizing in the original paper causes a large increase in the loss of quality of recycled paper, possibly due to inhibited bonding. Deinking of paper generally requires a range of processes, and research into the impact of these processes on recycled paper still needs to be investigated further. Sodium hydroxide has been used in recycling since 1800 for ink removal or to aid the breakdown of heavily sized papers. More recently sodium hydroxide has been investigated as an additive to recycled pulp since the inclusion of less than 1% led to improvements in breaking length. Blending recycled with virgin pulp has been shown to improve recycled paper properties, particularly if the added pulp was beaten. However further research is needed in this area.

Nazhad (1994) demonstrated that the degradative effects of recycling result in the loss of potential bonding of recycled fibers, a loss that translates into “hornification” – a series of

²⁵ Howard, *The Effects of Recycling on Paper* (1990)

²⁶ McKee, *Effect of Repulping on Sheet Properties & Fiber Characteristics* (1971)

²⁷ Yamagishi and Oye, *Influence of Recycling on Wood Pulp Fibers—Changes in Properties* (2007)

irreversible changes that cellulose fibers undergo when exposed to cycles of wetting and drying, and loss of fiber wet flexibility.²⁸ The term hornification is a technical term used in wood pulp and paper research literature that refers to the stiffening of the polymer structure that takes place in ligno-cellulosic materials upon drying or water removal.²⁹ When wood pulp fibers are dried, the internal fiber volume shrinks because of structural changes in the fibers. If fibers are then again suspended in water, the original water-swollen state is not regained.³⁰ The effect of hornification can be identified seen in the results from physically testing the paper such as burst or tensile testing. Nazhad's research showed that the overall result of drying and rewetting is a reduced swelling ability of the fibers, with most of the change taking place in the first cycle. Repeated cycling then further reduces the plasticity and therefore flexibility of the fibers.

Recycling should not be considered a modern phenomenon. A program for recycling was established in Southern Africa in 1826.³¹ Research in this country noted increases in strength properties after the first and or second cycles and then a sharp decrease in mechanical performance. It was suggested that this reduction was due to the increase in deformation of fibers in the paper assembly with these degraded fibers having reduced surface accessibility for bonding. They found that the rate of tensile strength loss from chemical (beaten) pulp was twice as high as that of unbeaten pulp with the recycled process indicating a similar trend between bending stiffness and tear strength.

In his 2008 thesis, *Effect of Progressive Recycling on Cellulose Fiber Surface Properties*, Brancato employed atomic force microscopy to assess the effects of hornification – the irreversible changes in cellulose fibers exposed to cycles of wetting and drying.³² These changes in the cellulose fiber surfaces indicated two separate effects; a) a decrease in the water absorption and retention capacity of recycled pulp, and b) a change in surface roughness of the recycled paper, resulting in a smoother surface. It was proposed that the free microfibrils of the fiber surface formed intrafiber hydrogen bonds, essentially laminating and presenting a more homogeneous surface on the recycled paper. The reduced swelling capacity of recycled fibers is caused by irreversible hornification and is the accepted morphological reason for strength loss in recycled papers.

Brancato also describes Jayme's introduction of the water retention value (WRV) measurement by centrifugation. The definition of irreversible hornification is described in terms of decrease in WRV and expressed as a percentage of the original value. The decrease in WRV was found to correlate well with fiber thickness measured in electron microscopic images; though no change in fiber width was detected after multiple fiber dryings.³² Repeated recyclings showed progressive variations in these properties.³³

²⁸ Nazhad, *Fundamentals of Strength Loss in Recycled Paper* (1994)

²⁹ Diniz, *Hornification—Its Origin and Interpretation in Wood Pulps* (2004)

³⁰ Ibid.

³¹ Sutjipto et al., *Effect of Recycling on Paper Properties* (2007)

³² Brancato, *Effect of Progressive Recycling on Cellulose Fiber Surface Properties* (2008)

³³ Ibid.

Improvements to the quality of recycled papers have been in the interest of consumers, producers, and scientists alike. McKee's concern in 1955 for significant physical property difference shown between "repulped or regenerated fibers (and papers made therefrom)" and virgin fibers predate the term 'recycled paper' by years.³⁴ At LC, efforts by McComb and Williams (1981) suggested that recycled fiber from alkaline paper was more akin to the properties of virgin fiber, and would produce recycled paper with better long-term properties.³⁵ Doshi compiled and edited *Recycled Paper Technology: An Anthology of Published Papers* in 1994. The text includes a comprehensive examination of all aspects of the paper recycling. The essays range from discussions of public policy, equipment technology, paper chemistry, paper strength, quality control, and permanence and should be referenced by any reader wishing to pursue this topic.³⁶

McKinney, editor of *Technology of Paper Recycling* and another expert on the subject wrote that "recycled pulp potential can be maximized by blending with virgin pulp... [virgin pulp] had a disproportionately large effect in improving recycled pulp properties." It is important also to note that the "softwood to hardwood fibre mixture is within the 20/80% range normally utilized in the manufacture of printing and writing grades of paper."³⁷ That is to say the type of virgin pulp also has an effect on the end product. Additional fillers in the furnish of the paper have tremendous implications for chemical stability as well. The addition of calcium carbonate as a filler, economically advantageous to the paper producer also adds pigment for enhanced brightness and an alkaline reserve which will be shown in this report to provide the chemical stability required of permanent papers.³⁸

³⁴ McKee, *Effect of Repulping on Sheet Properties & Fiber Characteristics* (1971)

³⁵ McComb et al., *The Value of Alkaline Papers for Recycling* (1981)

³⁶ Doshi, M. (editor): *Recycled Paper Technology: An Anthology of Published Papers* (1994)

³⁷ McKinney, *Technology of Paper Recycling* (1995)

³⁸ McComb et al., *The Value of Alkaline Papers for Recycling* (1981)

V. Characterizing Paper Degradation through Physical and Optical Testing

Physical Testing

Tumosa, Erhardt, Hufford, and Quasney (2008) investigated the permanence and durability of “ephemera”-- the magazines, newspapers, and paperback novels printed on acidic papers that make it into our libraries and archives. The research was conducted to better understand the mechanisms of degradation of these papers and to “provide information to make more informed decisions regarding the necessity or urgency of replicating or discarding acidic wood pulp based paper materials.”³⁹ Clearly, the acidic papers cannot be considered permanent by ANSI standards. The authors suggested that the parameters measured offer the difference in interpretation of permanence (chemical properties) and durability (physical properties). The investigation relied on the stress-strain data collected from tensile testing to adequately provide results that are relevant to the physical and mechanical effects of routine handling.

As suggested by Caulfield and Gunderson, Tumosa et al. also supported the notion that defining what is being measured would yield the best information for evaluation of permanence. For example, while traditional paper longevity studies have based predictive models on fold endurance testing, this test was developed by industry for measurement of durability, not permanence. Durability is the ability to resist change during use, while permanence is the ability to resist change when not in use. In this report we will see from tensile testing results that copy papers hold up after long term exposure to accelerated aging. Conversely, we will also find that the degree of discoloration of the sheets does not correlate well with the tensile testing results. Though at first glance this may suggest a contradiction in results, when viewed from the perspective that the physical test is a better evaluation of permanence, we can make some valid points about the nature of the paper’s degradation.

Early research into paper tensile characteristics was thoroughly reviewed in 1970 by Van Den Akker.⁴⁰ Key concepts of the review include research into stress-strain relationships, fiber orientation, polymer mechanics, and bond strength. Graminski (1970) investigated the stress-strain behavior of aged papers and found an increase in stiffness (decrease of flexibility) due to an increase in the degree of crystallinity or the formation of inter-molecular cross-links.⁴¹ More recently, in 2006 Bonham and Rolniczac studied a range (from 10% to 100%) of recycled fiber containing papers and examined how well they conform to standards for permanence and longevity. Loss of strength and discoloration were explored and longevity was ultimately attributed to the presence of sufficient alkaline reserve.⁴² Correlation found between loss of brightness and loss of fluorescence. Okayama et al. (2010) attempted to estimate degradation behavior of papers containing recycled fibers by artificial aging and testing for fold endurance and brightness

³⁹ Tumosa et al., *The Deterioration of Newsprint and Implications for Its Preservation* (2008)

⁴⁰ Van den Akker, J.A. *Structure and Tensile Characteristics of Paper* (1970)

⁴¹ Graminski, *Stress-Strain Behavior of accelerated and Naturally Aged Papers* (1970)

⁴² Bonham and Rolniczac, *Accelerated Ageing of Copy Papers Containing Recycled fiber* (2006)

measurements. Research concluded that papers with recycled fibers perform less well than virgin pulp papers on tests.⁴³

Wu et al. (1999) assessed the permanence of paper in regards to fold endurance and color (brightness) and found that the content of recycled fiber had a significant influence on paper permanence since it reduced fold endurance by 50% with a recycled content of 25%.⁴⁴ The initial fold endurance of 25% recycled paper was only 30% of the value of virgin fiber (12 versus 42 folds respectively for an assessment of physical properties). After 28 days accelerated aging (TAPPI test method T453: heating at 105°C for increasing periods of time) both showed a reduction in fold endurance of one-third from their original. The fold endurance decreased with increasing recycled fiber content but with a similar percent loss to that of virgin fiber. Brightness measurements indicated a minimal reduction after 28 days accelerated (heat) aging. For increasing fiber recycled fiber content from 0% to 100% the crystallinity of the papers after 28 days of heating remained relatively constant while that of virgin fiber increased about 1.5%.

Zhang et al. (2003) investigated the mechanisms of paper strength loss that occurs in recycled paper made from chemical pulps.⁴⁵ It was noted that tensile strength and compression strength both decrease with recycling. Drying reduced water retention values, flexibility and accessible fiber surface resulting in lower strength and lower density, with large effects for recycled papers made from virgin fibers that had been dried in temperatures higher than 150°C. An assessment of the efficacy of adding certain chemicals to virgin fibers before drying showed that some strength loss of the corresponding recycled papers could be prevented.

In *Physical Properties of Textile Fibres* (1975), Morton and Hearle offer comprehensive discussions concerning the chemical structure; physical, electrical, and optical properties; and test methods for experimentation on natural and synthetic fibers.⁴⁶ This book was an invaluable tool for the design of this experiment, a reference for defining and describing the technical fundamentals observable in the tensile testing of paper. Because various test methods call for specific tensile testing properties to be measured, many considerations were accounted for in the design. For example, the Technical Association of the Pulp and Paper Industry (TAPPI) method 494 states that “TEA [Tensile Energy Absorption] is a measure of the ability of a paper to absorb energy... and indicates the **durability**⁴⁷ of a paper... it expresses the toughness of a sheet’.”⁴⁸ Similarly, “Tensile Strength” is indicative of fiber strength, fiber length, and bonding.” Other considerations in tensile testing, specifically the information that can be gleaned from stress/strain curves, illustrate the test’s effect on the material itself. The plots show strain (deformation of paper as a ratio) as a function of stress (the force or load per area). To relate changing

⁴³ Okayama, T., Goto, T., Higashiyama, H., and Matsida, T.: *Estimating Degradation Behavior of Recycled Pulp-Containing Papers by Accelerated Aging Tests* (2010)

⁴⁴ Wu, et al., *Effects of Recycled fiber on Paper Permanence* (1999)

⁴⁵ Zhang, et al., *Preventing Strength Loss of Unbleached Kraft Fibers* (2003)

⁴⁶ Morton and Heale, *Physical Properties of Textile Fibres* (1975)

⁴⁷ Author’s emphasis

⁴⁸ TAPPI 494, *Tensile Properties of Paper and Paperboard*

terminology, the initial slope of the stress/strain curve is often referred to as Young's Modulus, modulus of elasticity, and "stiffness" in older literature. This parameter relates to how much stress the material can take before permanent deformation occurs. For this experiment multiple stress/strain curves were generated for each paper specimen tested. Rather than presenting the collected data in the form of these plots, tensile testing results are reported as "max load", a single number taken from the moment the sample broke.

In the *Handbook of Fiber Chemistry*, edited by Lewin (2007), strength is defined as "the power to resist force, [that] can best be stated as a breaking strength or the force or the load necessary to break a fiber under certain conditions of strength."⁴⁹ Max load can be used alone but to fall in line with the ISO standard for tensile testing of paper, the report should include results reported as tensile strength. Tensile strength is defined as max load divided by width of the sample. The graphs for these two parameters look the same but the units that define the graph comprise the difference. Max load is a measurement of force, defined in Newtons (N). Tensile strength is a measure of force per load area, defined in Pascals (Pa). For this report, max load will be used as the parameter for analysis.

In addition to the tensile testing presented in this report, fold endurance testing is used as a second measure of physical strength characterization. PRTD uses fold endurance as a measure of Quality Control in its specifications for materials used to rehouse collection items at LC. Fold endurance has been used in past research at LC to measure paper degradation as a function of accelerated aging and, noted above; several examinations of recycled paper have used fold endurance as the primary indication of physical strength.

Optical Testing

Billmeyer and Saltzman's *Principles of Color Technology* (2000) outlines technical specifics of color science and was used as a guide in the development of the experimental plan described in this report. The CIE 1976 ($L^*a^*b^*$) color system, also known as CIELAB-- defined by the Commission Internationale de l'Éclairage-- was used to describe the results of the color change of the copy papers, measured by a spectrophotometer. Ruth Johnston-Feller's *Color Science in the Examination of Museum Objects* was used as a guide in the selection of the specific geometry used for testing and as to whether the effects of specular light was to be included or excluded.⁵⁰ Johnston-Feller found and suggested that diffuse measurements using sphere geometry mostly agree with TAPPI brightness meter, the traditional method for measuring optical changes in paper. The spectrophotometer was calibrated in the Reflective Specular Excluded (RSEX) mode.

Results from the spectrophotometer were reported in several ways. A spectral curve showing the percent reflectance of the specimen at each wavelength illustrates the changes each paper exhibited as it was aged; the plotted curve can be used to assess the relative color change of a paper compared with a known standard. It is a graph of the relative percent of electromagnetic measured at each wavelength. For this report results

⁴⁹ Nissan, *Retrospect and Prospect of Physical and Mechanical Testing of Paper and Paperboard* (1983)

⁵⁰ Johnston-Feller, *Color Science in the Examination of Museum Objects: Nondestructive Procedures* (2001)

were reported using the CIELAB color coordinates as a matter of convenience for analysis. The CIELAB color space is a:

*... three-dimensional approximately uniform color space, produced by plotting... $L^*a^*b^*$ quantities defined as... L^* a measure of lightness of a piece, where $L^*= 0$ corresponds to black and $L^*= 100$ is defined by a perfect reflecting diffuser... $+a^*$ a measure of redness... $-a^*$ a measure of greenness... $+b^*$ a measure of yellowness... $-b^*$ a measure of blueness...⁵¹*

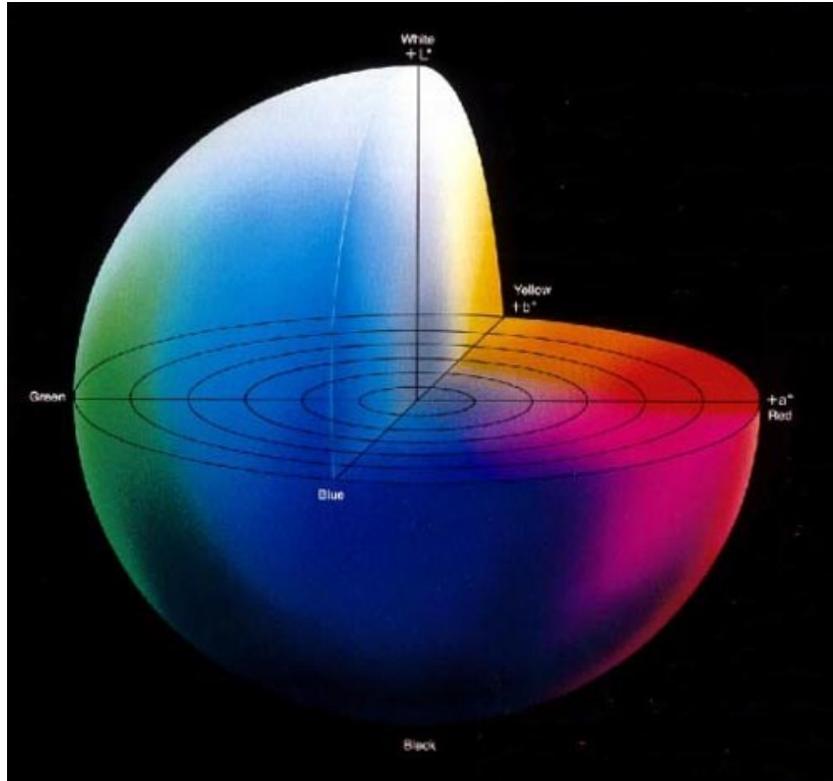


Figure 1. CIELAB 1976 Color Space (Sphere Representation)⁵²

⁵¹ ISO 5631-2: 2008(E), *Paper and Board—Determination of Color by Diffuse Reflectance, Outdoor Daylight Conditions (D65/ 10°)*

⁵² Image courtesy of <http://www.rpdms.com/cielch/>

VI. Experimental

The ultimate aim of this study is to determine whether papers composed of recycled paper fiber can fulfill requirements for permanence, given the mandate to purchase 30% recycled component papers for all government agencies. The characterization of physical, chemical and optical properties of known archival and recycled content papers is undertaken to assess the interactions between these properties and to assess the ability of optical measurements to predict paper permanence.

Materials

Given the immensity of the market for 8 ½" x 11" copy papers that are available for purchase, materials for this examination were limited to a single manufacturer that offered a variety of papers with various percentages of postconsumer recycled content. Three multi-purpose copy papers available from the manufacturer were sold as to including 30%, 50%, or 100% postconsumer recycled content. Information about a fourth paper, the "general use" copy paper, did not specify whether or not recycled fibers were included. These four papers, aside from percentage recycled content, were otherwise featured as having identical physical characteristics. Specific qualities noted on the ream wrappers included basis weight (20 lb.) and brightness values (92). The copy papers are all lignin-free.

In addition to the four commercially available papers, two additional papers from the Library of Congress Center for Library Analytical Scientific Samples (CLASS) were chosen for comparison. The first was a bleached kraft wood pulp waterleaf (WPWL) (50 lb. basis weight) from a stock comprised of northern softwoods (60%) and Lake States hard woods (40%). This paper was made from mechanically ground wood pulp, has no additional fillers or sizing, is lignin-free, and served as an acidic reference paper. The second reference paper is a 25% CC (cotton fiber content) copy paper that is often used as a "permanent" paper for official LC administrative records. This permanent paper has a high alkaline reserve, has a basis weight of 20 lb., and is lignin-free.

Single pages in one ream of each of the six papers were numbered from 1 to 500. An Excel random number generator function was then used to create an experimental sample set consisting of 120 sheets from each ream. Accelerated aging of the papers were designated into twelve time intervals, ten sample sheets for each interval, making a total of 720 sample sheets of paper comprising the test sample set.

Accelerated aging was used to assess the papers for changes in optical, physical, and chemical characteristics. If a link between physical and optical testing could be established the feasibility of non-destructive optical testing to reliably estimate the condition of papers would be entirely possible.

The ASTM standard for moist accelerated aging of paper was used as the basis for this experiment, *ASTM D4714: Standard Test Method for Determination of Effect of Moist Heat (50 % Relative Humidity and 90°C) on Properties of Paper and Board*.

A Parameter Generation & Control (PGC) aging chamber (Model Number 1362-04) held steady conditions of 90° +/- 0.1°C and 50% +/- 1% relative humidity (RH). The paper samples were aged as loose sheets hung vertically on a rack which permitted the free flow of the conditioned air around them. One set of ten papers was set aside in a ‘TAPPI’ chamber (23°C, 50% RH) to act as a “Day 0” control. The interval batches of ten sample papers for each paper type were removed from the aging chamber after days 1, 3, 7, 10, 14, 21, 28, 35, 42, 49, and 56. Although many factors contribute to the degradation of paper, for context in this study a perfect Arrhenius relationship will be assumed for the accelerated aging. For each 10° C increase in temperature, a doubling of reaction rate will be assumed. A rise in temperature from ambient (20° C) to experimental (90° C) calculates to be 128 days of natural aging for each day of accelerated aging. Table 1 spells out the number of days of accelerated aging and the natural aging equivalents.

Days of Accelerated Aging	Day 0	Day 1	Day 3	Day 7	Day 10	Day 14	Day 21	Day 28	Day 35	Day 42	Day 49	Day 56
Natural Aging Equivalent	0 Days	128 Days	384 Days	2.5 Year	3.5 Year	4.9 Year	7.4 Year	9.8 Year	12.3 Year	14.7 Year	17.2 Year	19.6 Year

Table 1. Accelerated aging and approximate natural aging equivalents

Physical Testing

Tensile Testing

For tensile testing, ISO 1924-2:2008(E), *Paper and Board—Determination of Tensile Properties—Part 2: Constant Rate of Elongation Method* was used. The test method specifies directions for sample preparation, testing, and reporting results “for measuring the Tensile Strength, Strain at Break, and Tensile Energy Absorption of paper...”⁵³ Samples were cut to the specified width (15+/- 0.1 mm) using a parallel blade sample cutter. To ensure an adequate number of test strips, six strips of paper were cut in the machine direction from five different sheets per time interval for each paper. Cotton gloves were worn when preparing the samples. The samples were all conditioned at 23°C/ 50% RH for at least 24 hours before testing.

The strips were individually loaded into the clamps of an Instron 5564 tensile tester. The clamps were spaced 180+/- 1 mm apart, per the test method. Slack was removed from the paper by alternating alignment of the strip and opening and closing the clamps. Ten specimens of each time interval of each paper were tested; bad breaks and poor stress/strain curves were discarded and retested.

⁵³ ISO 1924-2:2008(E), *Paper and Board—Determination of Tensile Properties—Part 2: Constant Rate of Elongation Method*

The strips were pulled apart at a constant rate of elongation (20 mm/min). The Bluehill software used for analysis reported results in terms stress/ strain curves that additionally show the maximum slope of the curve. The stress applied, on the Y-axis of the graph, is the amount of force used to pull the material apart, expressed in Newtons (N). The strain reported on the X-axis describes the amount of deformity of the material as a function of the stress. The maximum slope is also referred to as the modulus of elasticity and indicates how elastic a material is prior to breaking.

The conclusion drawn from each stress/ strain curve was recorded as the breaking point of the material. The data collected and analyzed for this experiment used the maximum “max load”, expressed in Newtons (N), to describe the physical strength of each paper sample. Traditional reporting for tensile strength evaluates the force divided by initial width of the sample (15+/- 0.1 mm), expressed in megaPascals (MPa). Data from ten specimen strips were reported for each sample paper and used to calculate the mean and standard deviation of each set.

Fold Endurance Testing

The traditional method for physical testing of paper was its fold endurance. This is a practice common in the paper industry and has been used for paper testing in LC laboratories since the inception of the Preservation Research and Testing Division.⁵⁴ The test is being included in this report to compare the two physical test methods. TAPPI Test Method T 511 om-06: *Folding Endurance of Paper (MIT Tester)* uses the same sample preparation method as noted above for the tensile test. The machine direction samples are cut from the sheets using the parallel cutter and the samples are conditioned at 23° C/ 50% RH.

Double-fold testing was performed using a Tinius Olsen Massachusetts Institute of Technology (MIT) fold endurance tester. The fold endurance tester holds the specimen under a constant tension load of 500 or 1000 grams. The paper is then folded to an angle of 135° in either direction, at the rate of 175 double folds per minute until the specimen is severed at the crease.⁵⁵ For this study, the 500 gram load was used because it is a more sensitive measure. The results are reported as log rhythmic (base 10) values of the number of double folds each paper endured before breaking.

Optical Testing

Colorimetry

For measurement of color change, the standard test method ISO 5631-2: 2008(E), *Paper and Board—Determination of Color by Diffuse Reflectance—Part 2: Outdoor Daylight Conditions (D65/ 10°)* was used. The method calls for use of “an abridged spectrophotometer, and the color coordinates are then calculated for D65 (daylight) and

⁵⁴ Shahani, et al., *Accelerated Aging of Paper* (2000)

⁵⁵ <http://www.testingmachines.com/31-23-mit-folding-endurance-tester.html>

10° (illumination incidence) conditions.”⁵⁶ The instrument used to make the measurement was a HunterLab UltraScan PRO. The UltraScan PRO is a dual beam xenon flash spectrometer with a wavelength range from 350 nm to 1050 nm, wavelength intervals reported at 5 nm. The diffuse/ 8° (d/8) viewing geometry of the instrument uses an integrating sphere that is six inches in diameter.⁵⁷

Ten specimens of each paper at each aging interval were conditioned for at least 24 hours at TAPPI conditions and were handled with cotton gloves during testing. The specimens were randomized and measured against a white tile standard provided with the instrument. One reading from the “front” side of each leaf of paper was taken. Areas chosen for measurement had no flaws to influence the measurements. The stack of ten specimens served as its own “backing material,” ensuring methodical reproduction of results.

For this experiment, the specular excluded (RSEX) setting was chosen to negate the effects of sheen created by optical brighteners present in some of the papers and to more closely measure diffuse light interaction with the paper samples. In a HunterLab Application Note, *Reflectance Measurements: Specular Included versus Specular Excluded*, “to describe color in CIE terms, diffuse reflectance [RSEX] must be used.”⁵⁸

Results of color testing for this project are reported in two forms: CIELAB *Delta E** values and CIELAB *b** values. CIELAB color coordinates are represented by quantities of:

- Lightness (*L**); on a scale that runs from perfect black (value 0) to perfect reflecting diffuser (value 100)
- *+a** is a measure of the degree of redness
- *-a** is a measure of the degree of greenness
- *+b** is a measure of the degree of yellowness
- *-b** is a measure of the degree of blueness
- *Delta E* is a simplified calculation used to give the Mean Color Difference representative of the overall change of color of an object as a single value. It is calculated by adding together the sums of *Delta L** squared, *Delta a** squared, and *Delta b** squared and then taking the square root of that sum. Mathematically, *Delta E* is represented by the following equation:

$$\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

As stated, the primary focus of optical properties testing for this research is color change measurements, reported as CIELAB coordinates. However, traditional optical testing in the PRTD laboratory included brightness measurements. Brightness measurements were completed and will be reported and compared with the results from the color change measurements.

⁵⁶ ISO 5631-2: 2008(E), *Paper and Board—Determination of Color by Diffuse Reflectance—Part 2: Outdoor Daylight Conditions (D65/ 10°)*

⁵⁷ HunterLab UltraScan Pro *User’s Manual* (2006)

⁵⁸ *Ibid.*

Brightness Measurements

In the previous description of physical testing, it was noted that fold endurance testing was the traditional method of assessment. The traditional methodology for measuring optical changes in paper was known as the brightness measurement. Brightness testing is a paper industry standard that has also been used for paper testing in LC laboratories since the inception of the Preservation Research and Testing Division.⁵⁹ The test was included in this report to compare the two optical measurement methods. TAPPI Test Method T 452 om-08: *Brightness of Pulp, Paper, and Paperboard (Directional Reflectance at 457 nm)* uses the same sample preparation method as noted above in the color measurements section.

TAPPI brightness was measured using a Technidine Brightmeter S-5. The Brightmeter instrument uses a 45° illumination and a 0° viewing geometry (45/0). The instrument is calibrated with a standard white tile and each specimen is measured for the directional reflectance at 457 nm of light.⁶⁰ Brightness values are expressed as unitless numbers ranging from 0 (darkest) to 100 (brightest).

Chemical Testing

The LC method for pH determination (cold-extraction) was used to test the pH of each paper at three different stages of accelerated aging. The method calls for 2.5 grams of each specimen to test. Specimens from days 0, 28, and 56 were macerated into slurries using 250 mL of deionized water each. End-point determinations of pH was recorded after allowing five minutes for the electrode meter to stabilize. A phloroglucinol indicator was used to test for the presence of lignin.

Environmental Scanning Electron Microscopy

A survey of paper surface morphology was conducted using an FEI Quanta 600 environmental scanning electron microscope (ESEM) and elemental analysis was performed using Oxford X-max energy dispersive spectroscopy (EDS). Two samples were prepared from each paper—a day 0 (control) sample and a day 56 (aged) sample. The specimens were sputter coated with palladium to reduce the effects of charging. It was hoped that some visible difference in the fibers would be apparent between the before and after accelerated aging samples. Quantitative analysis with EDS was not conducted because of a requirement for a polished sample. However, EDS was used effectively as a semi-quantitative evaluation of these rough, fibrous materials.⁶¹ EDS limitations for analysis of paper also include:

the spatial resolution of the paper additives [being] somewhat diffuse due to the size of the interaction volume... the x-rays of a particular element are not generated at the surface of the specimen but originate at various depths....

⁵⁹ Shahani, et al., *Accelerated Aging of Paper* (2000)

⁶⁰ TAPPI Test Method T 452 om-08: *Brightness of Pulp, Paper, and Paperboard (Directional Reflectance at 457 nm)*

⁶¹ Conners, et al.: *Surface Analysis of Paper* (1995)

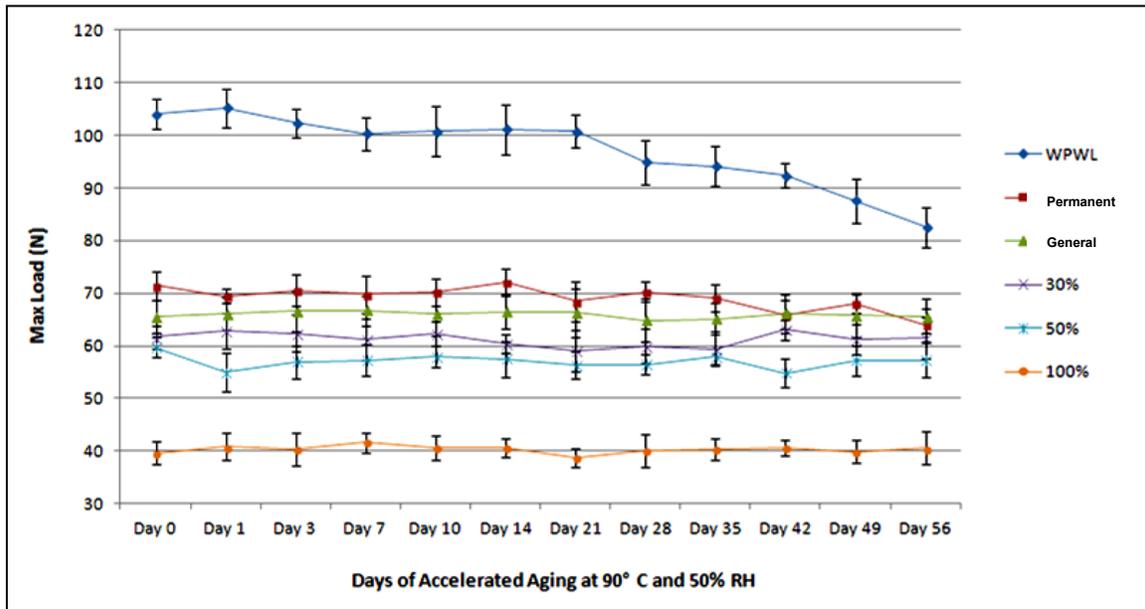
Secondary x-rays generated by BSE interacting w/ various particles closer to the surface will also contribute to the mapping of these elements, giving them a diffuse outline, further decreasing resolution.⁶²

⁶² Ibid.

VII. Results and Discussion

Physical Testing

Results of tensile testing are reported first as the maximum stress of force exerted upon a test strip at the moment the specimen broke-- also known as the max load at break or simply max load. Graph 1 is a plot of the data collected for all six experimental papers. Each point on a colored line represents a mean value for ten test specimens at a single time interval and the error bars represent one standard deviation from that mean. Results were analyzed to determine if differences within each paper set (and between the six paper samples) were statistically significant.



Graph 1. Max Load Results

ISO standard 1924-2:2008(E) specifies that reports conforming to it shall report the tensile strength of the papers. Tensile strength is calculated by dividing the max load by the width of the specimen (15mm). For all data points illustrated in Graph 1, a corresponding table (Table 2) with max load values divided by 15 mm (force per unit area) is included below. As noted previously, the graph of these values would look exactly identical to Graph 1 but with different units of measurement (megaPascals, MPa).

	Day 0	Day 1	Day 3	Day 7	Day 10	Day 14	Day 21	Day 28	Day 35	Day 42	Day 49	Day 56
WPWL	46	47	46	45	45	45	45	42	42	41	39	37
Permanent	48	46	47	47	47	47	46	47	46	44	45	43
General	44	44	44	44	44	44	44	43	43	44	44	44
30%	41	42	42	41	42	40	39	40	40	42	41	41
50%	40	37	38	38	39	38	38	38	39	37	38	38
100%	26	27	27	28	27	27	26	27	27	27	27	27

Table 2. Tensile Strength (MPa)

WPWL is a heavier paper (50 lb. basis weight) than the copy papers (20 lb. basis weight) analyzed in this study and is composed of longer fibers (See ESEM photomicrograph, Image 1). These two factors contribute to the overall higher max load the WPWL paper samples were able to withstand. The max load decreases significantly for WPWL over the course of accelerated aging (day 0 - day 56). However, as observed in the Graph 1, there is no significant difference from original strength until day 28 of aging.

The measure of max load for the commercially manufactured copy papers tested indicate that they can be ranked in terms of decreasing strength in the following order: the permanent paper, the general use paper, the 30% recycled fiber paper, the 50% recycled fiber paper, and finally the 100% recycled fiber paper. The max load does not decrease significantly for any of these papers over the 56 days of accelerated aging. While it is difficult to show any significant difference between the data sets of the permanent paper and the 30 % recycled fiber paper, and similarly between the 30 % recycled fiber and 50% recycled fiber papers, the difference between max load for the permanent paper and the 50% recycled fiber paper is significant.

The copy paper composed of 100% recycled fiber had the lowest mean max load of all papers. The difference in mean max load for 100% recycled fiber is significantly different than the mean max loads for all other papers. However, like the other copy papers, the mean max load for 100% recycled fiber does not decrease significantly from day 0 to day 56 of accelerated aging.

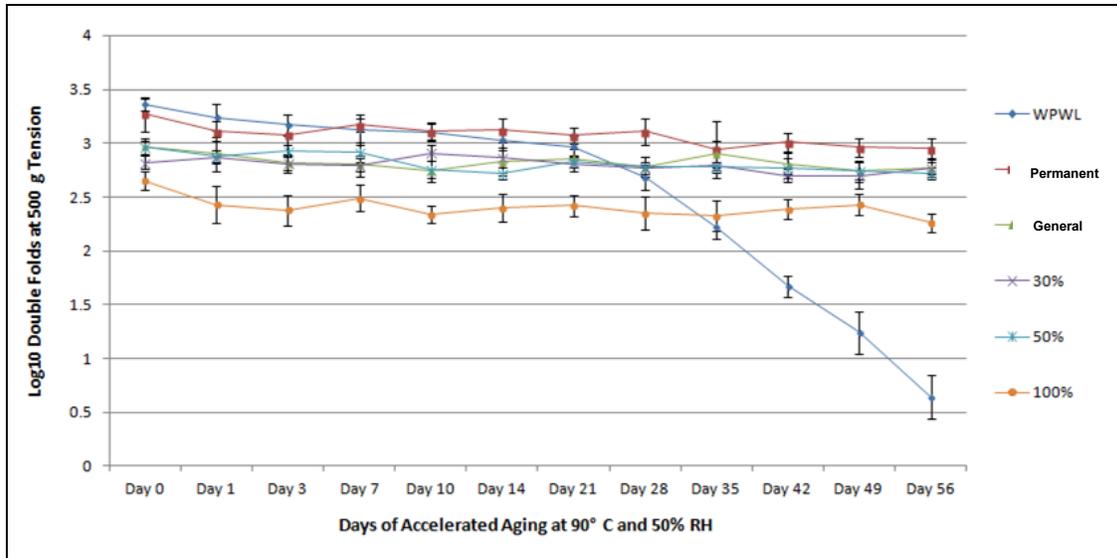
To place the tensile testing results of this experiment in the context of other recycled paper research presented in this report, it should be noted that other researchers relied solely on fold endurance data to evaluate paper performance.^{63, 64, 65} It will be remembered, though, that tensile testing is perhaps the best indicator of fiber strength, fiber length, and bonding. To determine if the tensile testing data collected in this report more accurately describe a sample's material properties and permanence, it is necessary to review the results of fold endurance testing.

Fold endurance results for this report are plotted as the logarithm (base 10) values of the number of double folds that each paper withstood before breaking. The logarithmic reporting follows TAPPI Test Method T 511 om-06 and allows more immediate visual interpretation of the data, compared with graphing of the raw number of double folds. A table of the actual number of double fold is reported below (Table 3). Graph 2 illustrates fold endurance data for all six experimental papers, where each point on the colored line represents a mean value for ten test specimens at a single time interval and the error bars represent one standard deviation from that mean.

⁶³ Okayama, T., Goto, T., Higashiyama, H., and Matsida, T.: *Estimating Degradation Behavior of Recycled Pulp-Containing Papers by Accelerated Aging Tests* (2010)

⁶⁴ Wu, *Effects of Recycled fiber on Paper Permanence* (1999)

⁶⁵ Zhang, *Preventing Strength Loss of Unbleached Kraft Fibers* (2003)



Graph 2. Log10 Double Fold Endurance

	Day 0	Day 1	Day 3	Day 7	Day 10	Day 14	Day 21	Day 28	Day 35	Day 42	Day 49	Day 56
WPWL	2302	1810	1527	1396	1286	1107	966	493	173	48	19	5
Permanent	1967	1300	1280	1476	1310	1360	1177	1323	1004	1038	941	906
General	956	848	673	631	567	705	732	620	827	663	563	594
30%	673	739	660	624	814	784	652	599	620	509	517	601
50%	922	768	856	842	581	534	674	620	608	605	564	524
100%	457	288	252	322	251	258	271	238	221	252	276	187

Table 3. Average Number of Double Folds (Raw Data)

As stated above in the tensile test results, WPWL is a heavier paper with longer fibers than the copy papers used in this study. These two factors contribute to the initial higher number of double folds WPWL was able to withstand. In Graph 2, WPWL shows the most dramatic decrease in fold endurance between day 0 and day 56 of accelerated aging. Significant decreases in WPWL values are seen between each interval after 21 days of accelerated aging, suggesting initial stability and resistance to accelerated aging but a steady decline in strength thereafter.

The permanent paper shows significant decreases in fold endurance between day 0 and day 56 of accelerated aging. However, the error bars overlap between sequential intervals (i.e. between day 0 and day 1, day 14 and day 21, etc.) suggesting there is not a significant decrease in fold endurance from interval to interval.

The general use copy paper, 30% recycled fiber paper, and 50% recycled fiber paper do not show a significant decline in fold endurance between day 0 and day 56 of accelerated aging. The mean double folds of these papers alternate the relative ranking of each paper between intervals. The graph illustrates no significant difference in fold endurance between these general, 30%, and 50% recycled papers. This data is in contrast to the results obtained from tensile testing, which indicate that significant differences exist between mean max load for general use and 50% recycled fiber.

The 100% recycled fiber paper has the lowest mean fold endurance of all of the copy papers. There is no significant decrease in fold endurance between day 0 and day 56 of accelerated aging. However, one interesting observation made was that by day 35 the fold endurance of 100% recycled fiber was better than that of WPWL.

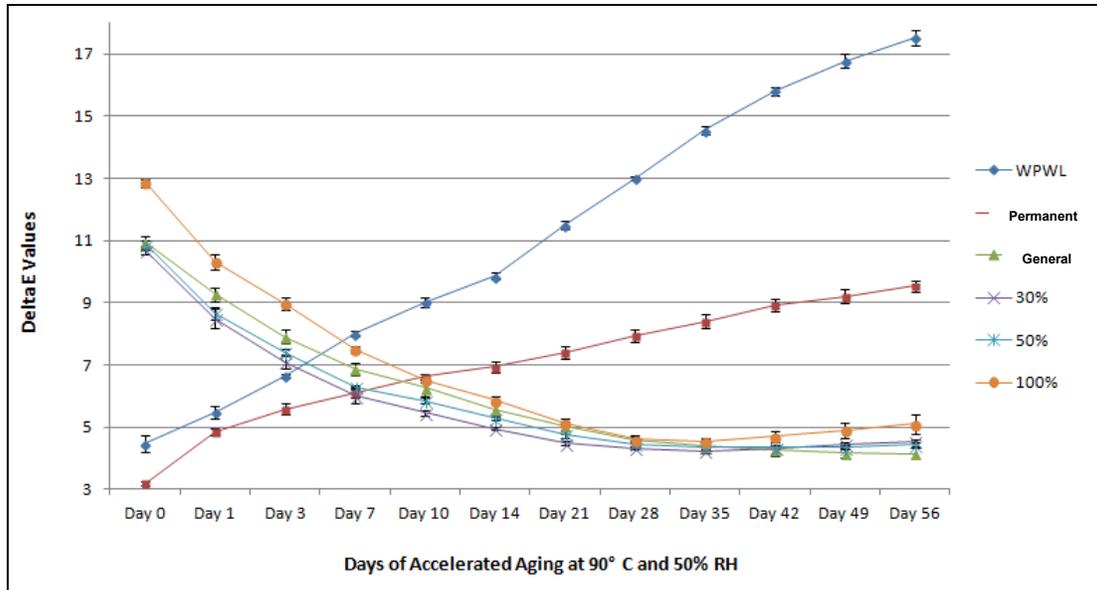
It is not possible at this time to determine which method of physical testing is more accurate concerning the permanence of these papers. However, the similarities and differences between tensile testing and fold endurance can lead to at least two general conclusions. First, both methods reveal very clear differences in the physical properties between a) WPWL, b) the permanent paper, c) 100% recycled fiber paper, and d) all of the other copy papers tested. Tensile testing may be the most sensitive measure, though, because of the significant differences seen between the general use paper and the 50% recycled fiber paper. The difference is not seen in the fold endurance results and should be a consideration in evaluating of the success of the tests. Secondly, both methods reveal how very stable the copy papers are in their resistance to the effects of accelerated aging. As noted above, no significant differences could be measured by tensile testing between day 0 and day 56 for any of the copy papers. WPWL, lacking the alkaline reserve present in the other samples, showed significant difference in the results of both methods after 21 days of accelerated aging. For fold endurance results, the 100% recycled fiber paper, WPWL, and the permanent paper show significant differences between day 0 and day 56.

Optical Testing

Graph 3 represents the *Delta E** color change (L^* , a^* , b^*) data collected for all six experimental papers, with each point on the colored line representing a mean value for ten test specimens at a single time interval and the error bars represent one standard deviation from that mean.

The standard deviations for the optical test means are less than those reported for the physical tests. This could be attributed to either a) the inhomogeneous nature of the physical structure of paper giving less than consistent physical testing results or b) that consistent color and finish of the papers are due to optical enhancing additives. The color and brightness of the papers are key features used by the manufacturers to promote their products.

WPWL shows the greatest change in *Delta E** values, each consecutive time interval significantly differing from the previous. WPWL and the permanent paper both show an increase in *Delta E** values while all four of the copy papers show decreasing values as a function of days of accelerated aging. The greater losses in L^* values (darkening) of the two reference papers and the change in b^* values (yellowing) of the copy papers can account for the differing trends of the *Delta E** values.



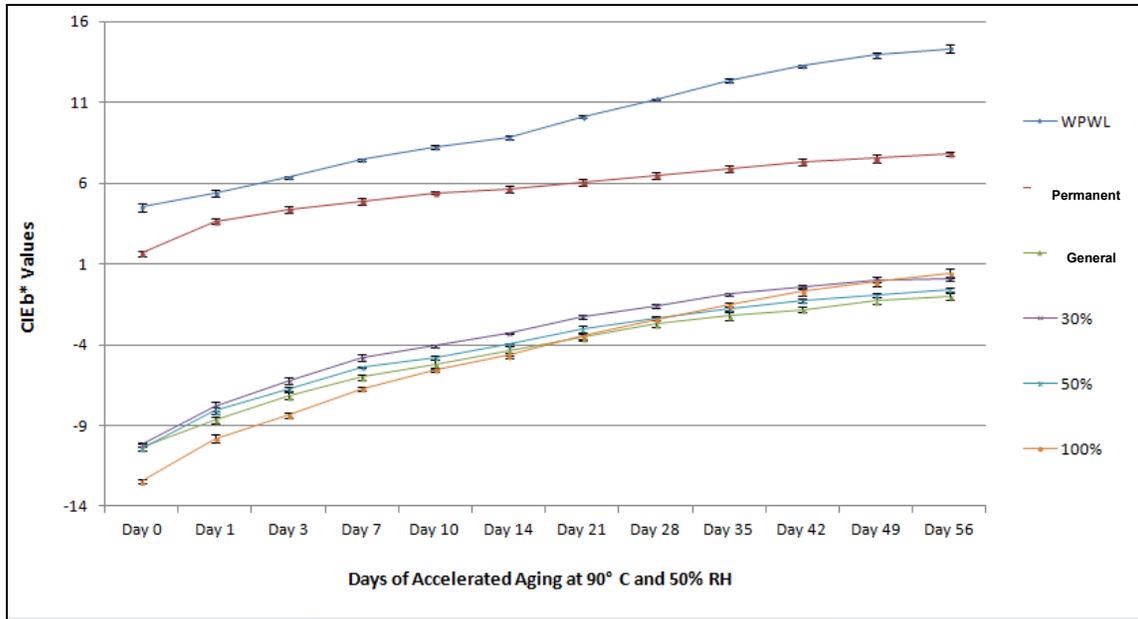
Graph 3. CIELAB ΔE^* Values

ΔE^* values show an overall decrease for all of the copy papers until about Day 28 when significant change in values do not occur for the remaining intervals of aging. The ΔE^* values can be used to rank the greatest change in optical properties between the copy papers in the following order (from most change to least): 100%, general use, 50%, and 30% papers. There doesn't appear to be a significant difference in values between the general, 30%, and 50% papers although they do significantly differ from the values of the 100% paper. This could be related to the fact that 100% recycled papers has no virgin pulp and therefore the optical properties are determined more by its homogeneous composition of all recycled fibers and filler materials.

To further separate and analyze the optical data, a second graph was created to examine the changes in CIELAB b^* values. Graph 4 plots the data for all changes in the yellow-blue axis of the CIELAB color space. Each plotted point on the graph represents a mean value for ten test specimens and the error bars represent one standard deviation.

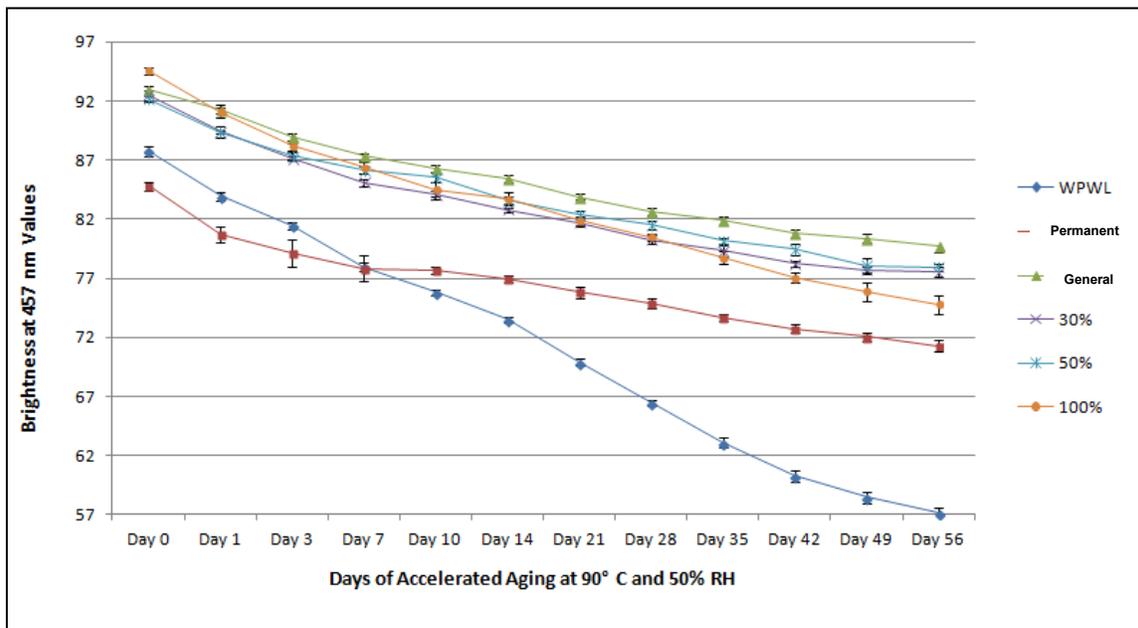
CIELAB b^* values increase for all six papers, showing a trend from the blue region of the spectrum, resulting in an increasing yellowness of the paper. All four of the copy papers start with very blue (-9 or lower) b^* values and with accelerated aging increase and finally cross the yellow threshold at 0 only toward the end of the experiment. The yellowing levels off for a number of the papers towards the latter part of the accelerated aging. This could be suggested to relate to the addition of optical brighteners or whitening agents to papers with recycled content to make them appear whiter. A separate study to measure the specific effect of accelerated aging of optical brighteners leading to increased yellowing of the substrates, could be a useful addition to this area of research. Only the WPWL paper samples illustrate significant increases in yellowness between increments at the end of aging.

In addition to the tensile testing, fold endurance testing was conducted to add a link to the traditional measurements of physical strength. To compare traditional methods with more



Graph 4. CIELAB b^* Values

recent optical measurements, brightness was measured using the traditional industry standard test method for paper. Brightness measurements are read as the reflectance of a single wave length (457 nm) on a unit-less scale that ranges from 0 (darkest) to 100 (brightest). Figure 5 is a graph of the TAPPI brightness data collected for all six experimental papers; each plotted point on the graph represents a mean value for ten test specimens and the error bars represent one standard deviation.



Graph 5. Brightness at 457 nm Values

Similar to the observation made for CIE color space measurements; the standard deviations of brightness measurements were much less than those observed for the

physical testing. The greatest change in brightness values was exhibited by WPWL, with each time interval differing significantly from the previous. All papers show a nearly linear decline in brightness values as a function of days of accelerated aging. This contrasts with the results of *Delta E** values which showed no significant changes in values of the copy papers after 28 days of aging. The 100% recycled paper has the greatest brightness value of all the copy papers but also loses the most brightness over the course of aging. The general paper appears significantly brighter than the 30% and 50% recycled content papers and remains so throughout the entire aging period.

As noted by Johnston-Feller, the diffuse measurements offered by the sphere geometry of the spectrophotometer mostly agree with TAPPI brightness measurements. The data collected for this report indicate that CIELAB *b** values align well with brightness measurement trends of the copy papers but that some differences exist, most notably for WPWL.

Chemical Testing

Table 4 displays initial experimental results for pH determination of the test papers. All papers except WPWL have very high pH levels due to the addition of calcium carbonate as a filler material. All papers but WPWL remain chemically stable under accelerated aging conditions. All papers tested free of lignin using the phloroglucinol indicator. Though lignin-free, WPWL has no buffer additives to help stabilize the paper matrix. The pH results correlate well with the physical testing results that suggest all of the copy papers maintain strength and stability while WPWL is significantly affected by accelerated aging.

	Day 0	Day 28	Day 56
WPWL	7.38	6.90	5.10
Permanent	9.41	9.28	9.24
General	9.64	9.24	9.26
30%	9.61	9.08	9.46
50%	9.60	9.45	9.35
100%	9.46	9.33	9.20

Table 4. pH Results

As noted by McComb and Williams, recycled paper from alkaline paper were more akin to the properties of virgin fiber papers. The data collected for this report indicate that beyond just a furnish consisting of alkaline paper, an adequate alkaline reserve can equally add to the chemical stability, and therefore the permanence, of a paper.

Statistical Correlation Between Properties

Hsu and Peruggia reviewed Tukey's method for multiple comparisons used in statistical packages such as Statistical Analysis Software 9.2 (SAS). Mean-mean scatter plots and notched box-plots are described. This method was used to create Figure 2, which shows five of the measured parameters plotted against one another.⁶⁶ The clearest correlations between physical and optical testing are between the data of CIE b^* (blue-yellow) and load at break (maximum load). Four individual groups are designated in Figure 3. Each grouping includes a population of specimens that are not significantly different. WPWL (Group 1), the permanent paper (Group 2), and 100% recycled content paper (Group 4) are each very much their own species, defined by correlation of load at break with CIE b^* values. However, it is clear that the general paper, 30% recycled content, and 50% recycled content copy papers (Group 3) are very similar in strength and color and should not be read as being statistically separable given these parameters.

As previously stated, one of the goals of this research is to determine if a less invasive method of analysis such as optical testing can be used to determine physical characteristics. Although a strong correlation does exist between the CIE b^* values and the load at break values for the three copy papers of Group 3, optical testing results are not sufficient to determine physical characteristics.

⁶⁶ Hsu, J.C. and M. Perguggia, *Graphical Representations of Tukey's Multiple Comparison* (1994)

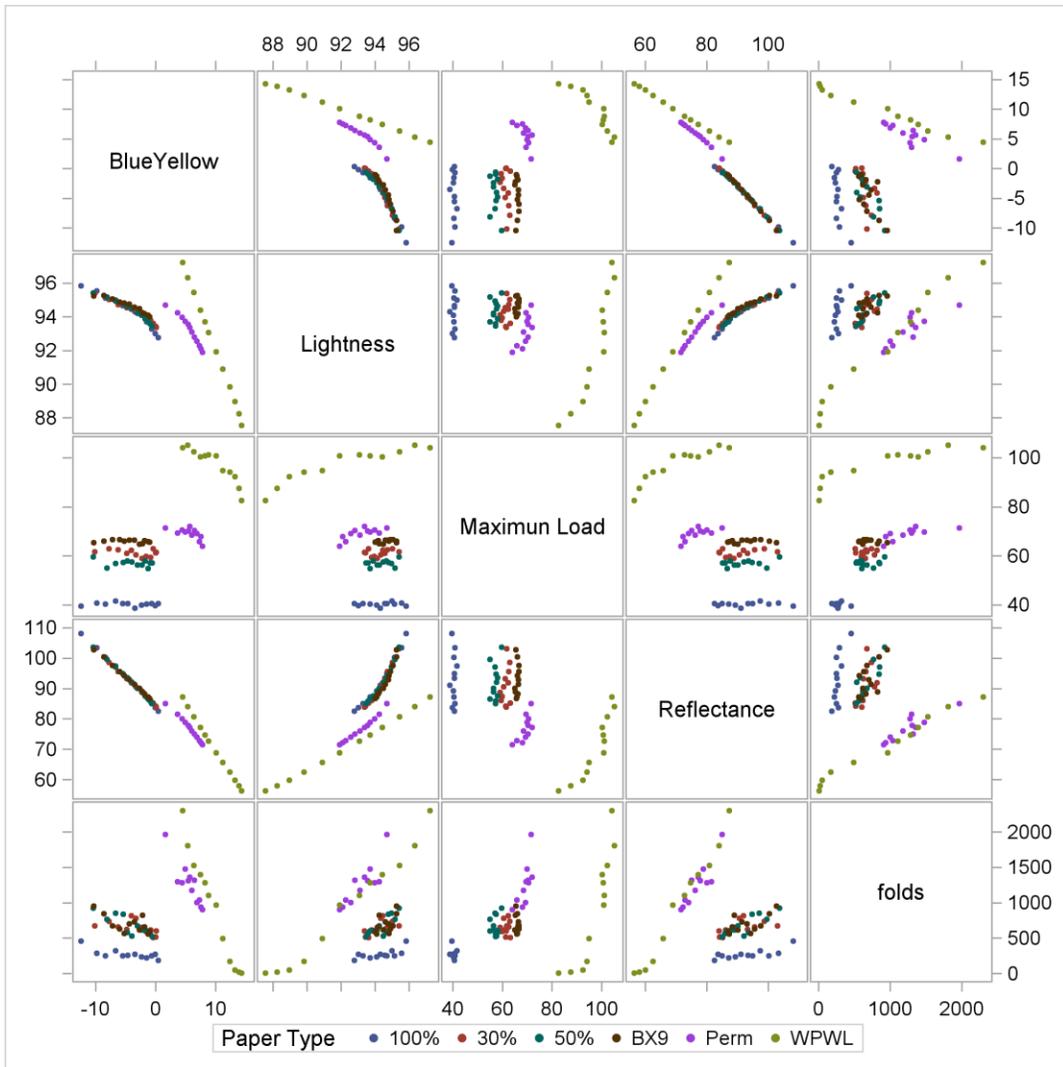


Figure 2. SAS Scatter Plot Matrix

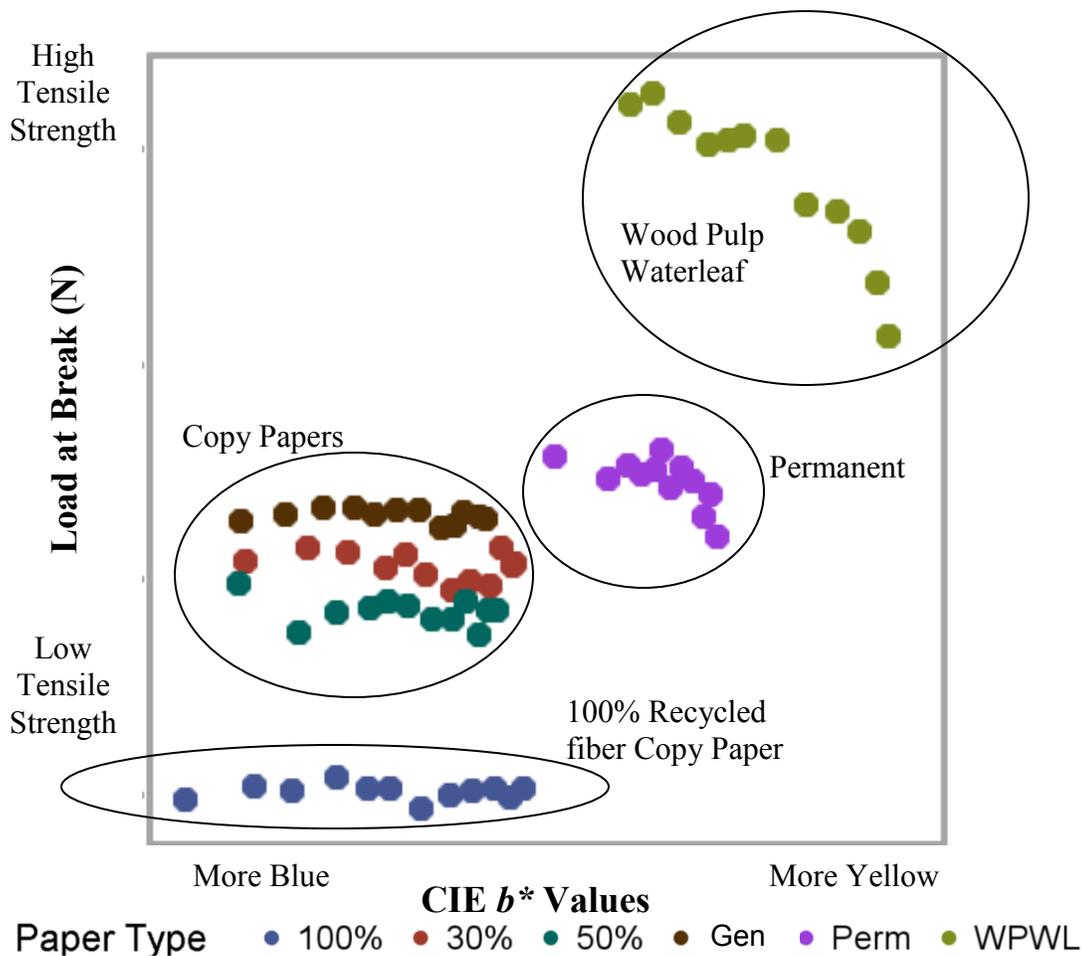


Figure 3. SAS Scatter Plot Correlating Data from Load at Break Values with CIE b^* Values

Figure 3 illustrates the correlation between b^* values and load at break values for the six papers. Four distinct groupings can be pulled from the data. Group 3 includes the general paper, the 30% recycled content, and the 50% recycled content copy papers. The results for optical and physical testing are not significantly different between the general paper and 30% recycled content papers, nor are the results between the 30% recycled content and 50% recycled content papers. The four groups are distinct from one another, and the results of the individual tests support the conclusion illustrated by Figure 3.

Paper Morphology and Elemental Analysis (ESEM-EDS)

An FEI Quanta 600 Environmental Scanning Electron Microscopy (ESEM) was used to image and observe paper morphology and structural differences for all six papers before (control) and after 56 days of accelerated aging. The following photomicrographs show the images of each paper before and after the experiment. Although the images offer a good contrast between the reference and copy papers, it is difficult to discern any visual change in the papers as a result of accelerated aging. In addition to the images, EDS spectra of the elemental composition and mapping of elemental distribution of the papers are included.

As noted by Conners, quantitative analysis of paper elemental composition using EDS is not ideal but semi-quantitative elemental mapping can illustrate the degree and relative distribution of filler materials among paper fibers. Map 1 of WPWL can easily be contrasted with any of the other papers, the lack of filler materials obvious in the paper's composition. All four of the test copy papers examined include the addition of 3% to 4% calcium content (likely CaCO_3) and trace levels of aluminum and magnesium (likely clay filler). There is no visibly discernible difference between the spectra of those four papers. The permanent paper is the only paper examined that contained titanium (probably titanium dioxide, used often as an optical brightener).

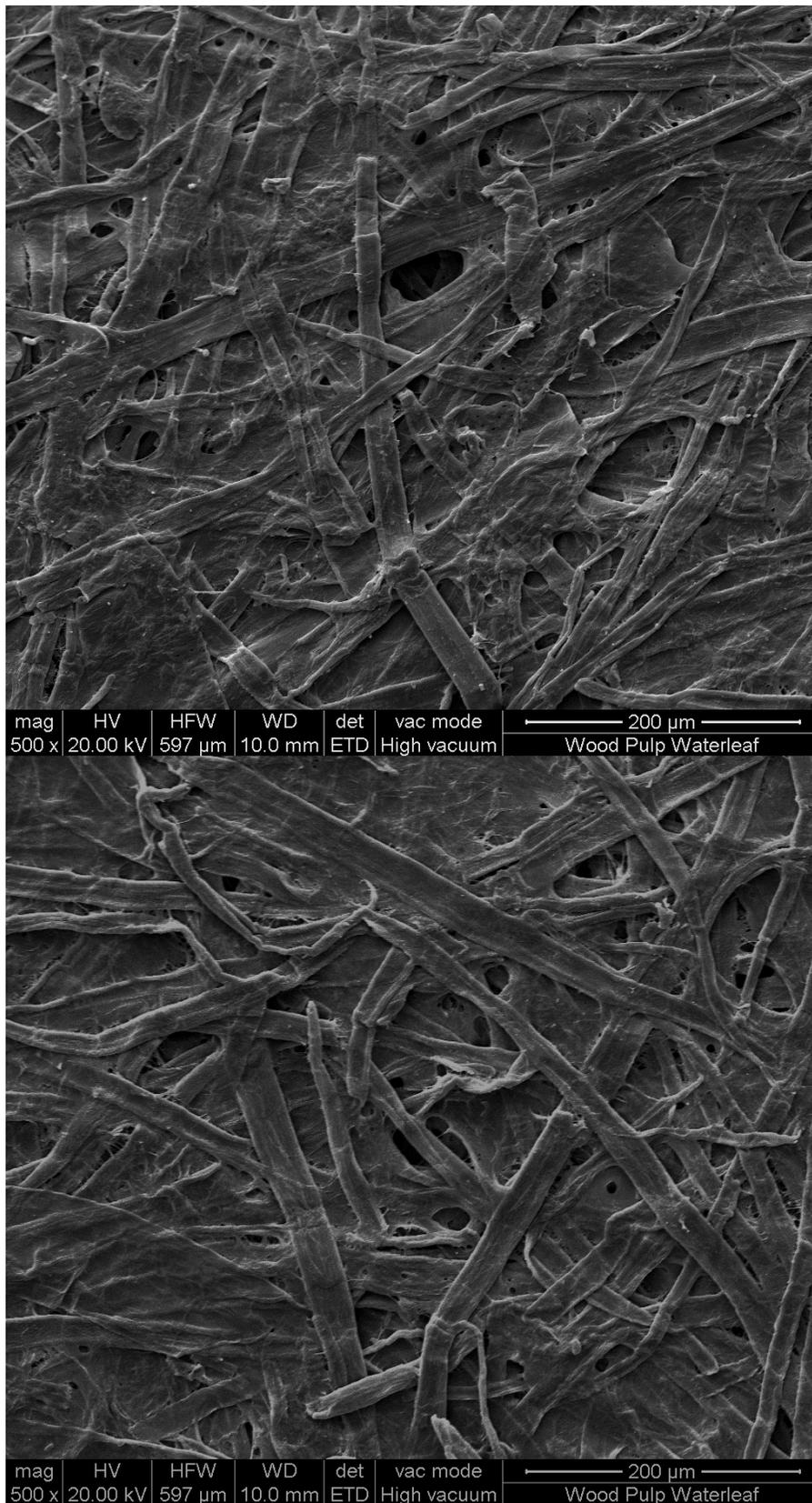


Image 1. ESEM micrographs of WPWL at 500x; unaged (top) and aged (bottom)

WPWL Map



Spectrum 1 (below). EDS Spectrum of WPWL at 20 keV.
Elements detected in significant quantities: C, O
Elements detected in trace quantities: Al



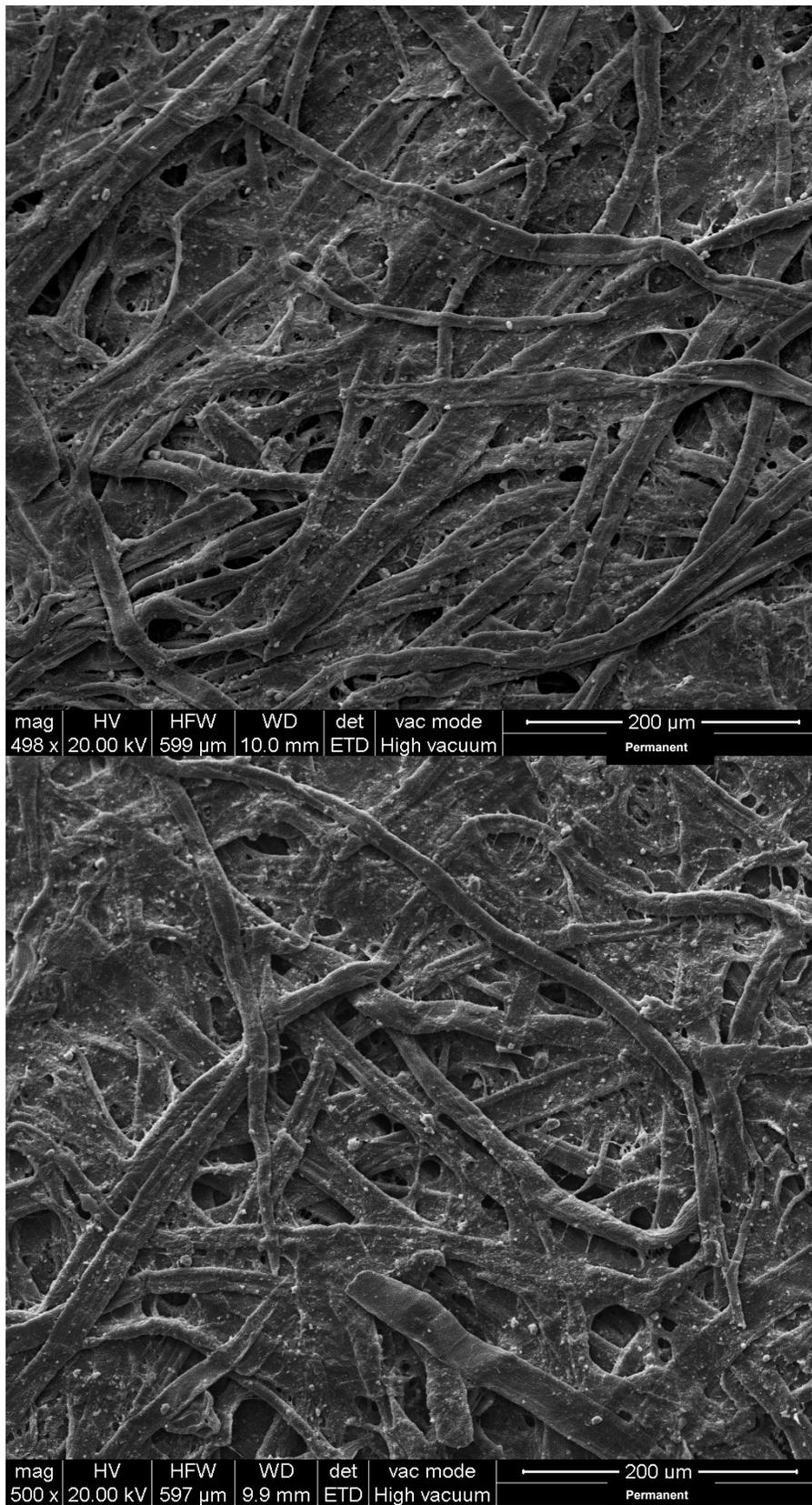
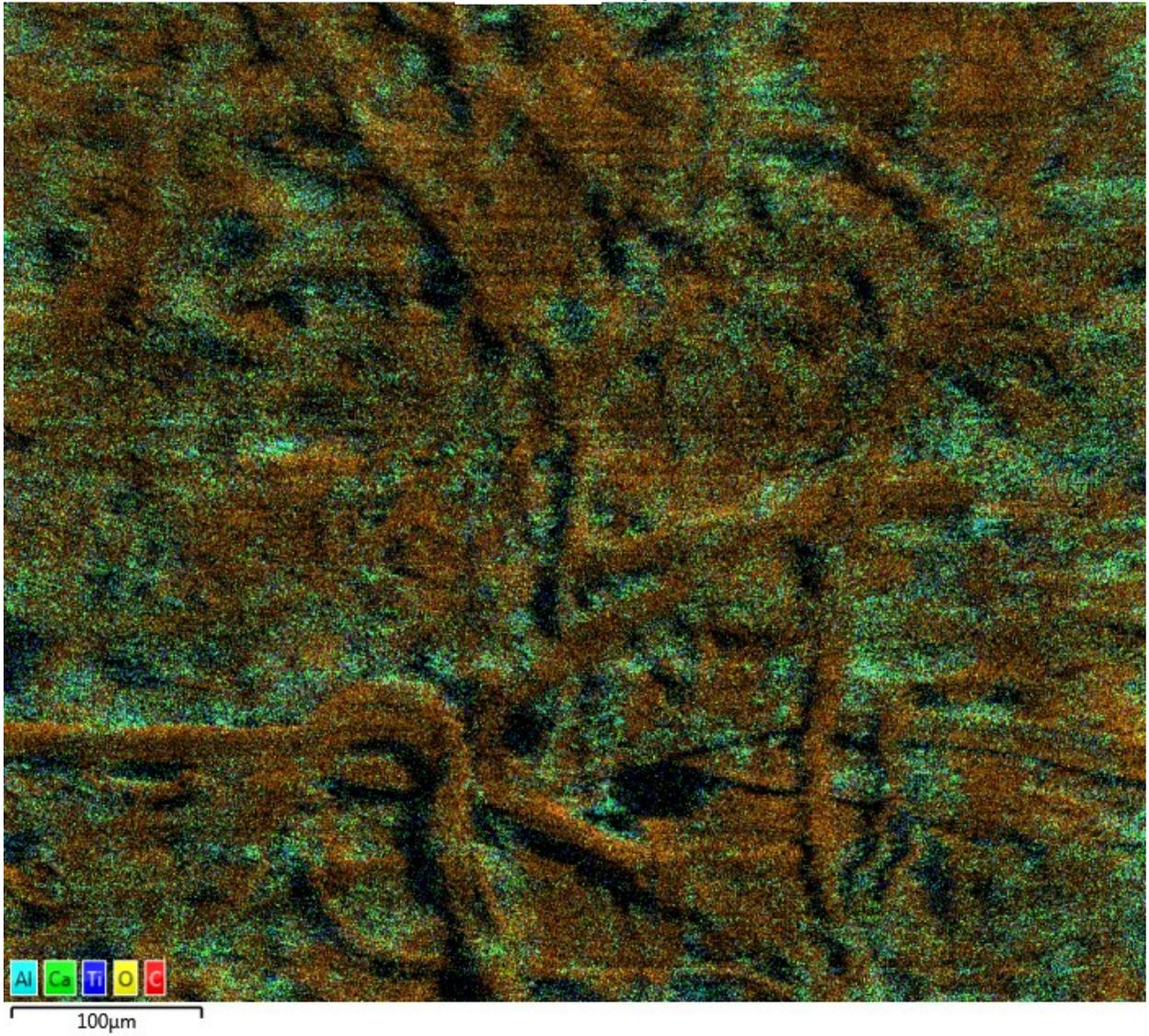


Image 2. ESEM micrographs of the permanent paper at 500x; unaged (top) and aged (bottom)

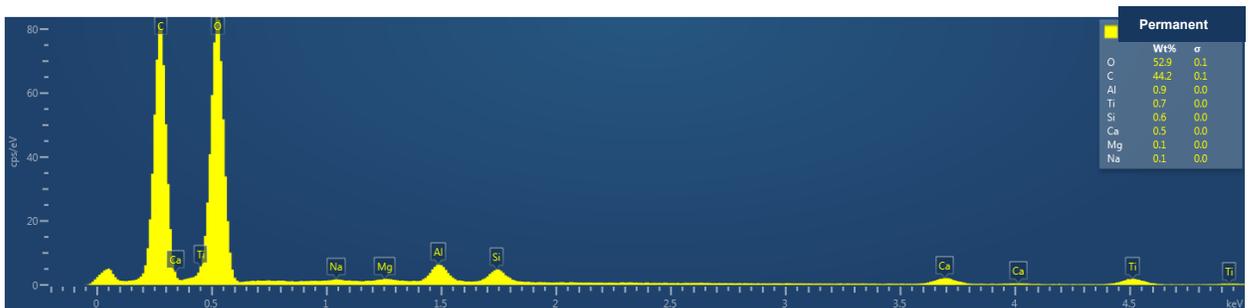
Permanent Map



Map 2 (above). EDS elemental map of the permanent paper at 500x. Elements detected: C, O, Al, Ca, Ti

Spectrum 2 (Below). EDS spectrum of the permanent paper at 20 keV.

Elements detected in significant quantities: O,C
 Elements detected in trace quantities: Al, Ti, Si, Ca, Mg, Na



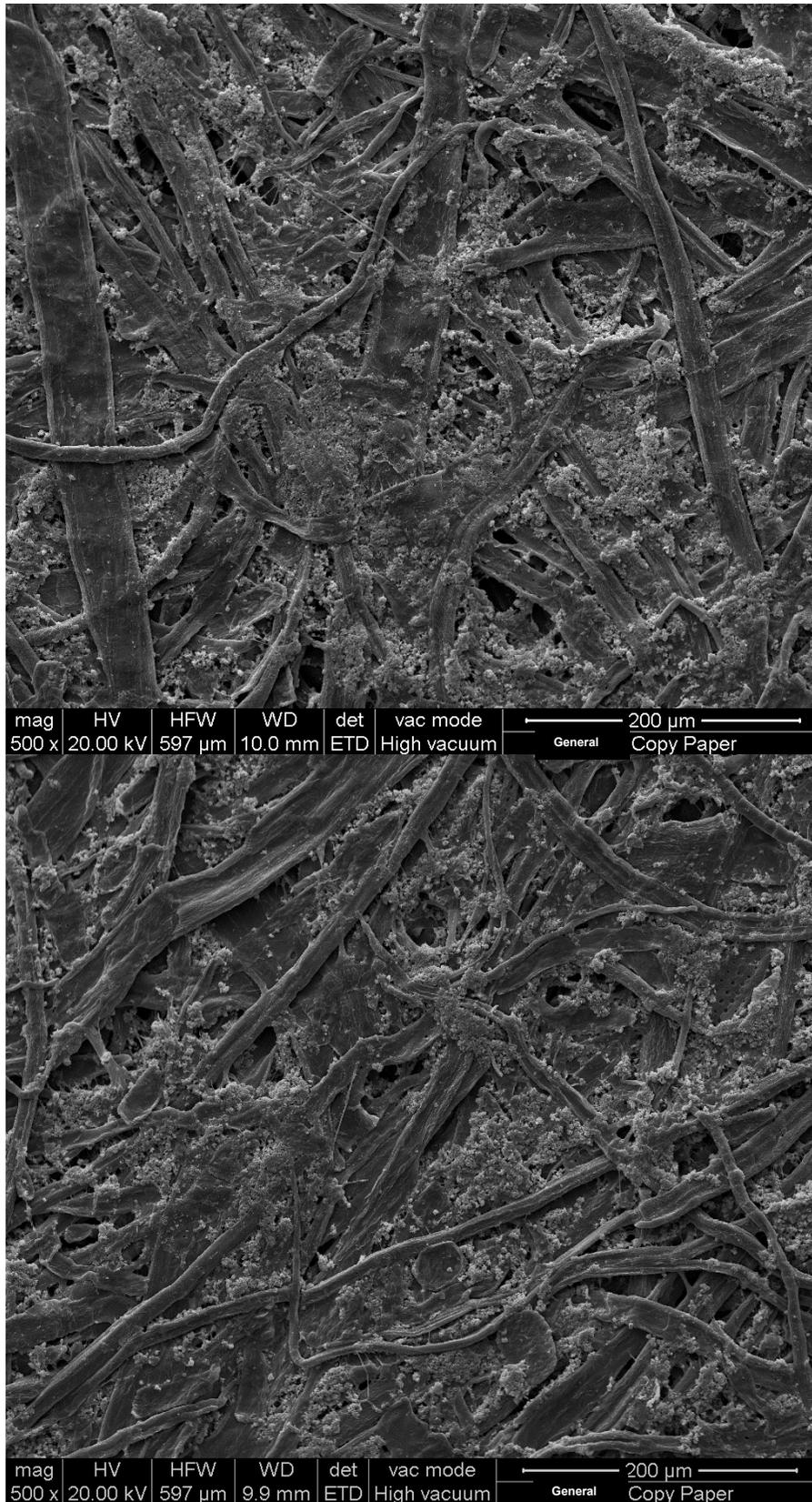
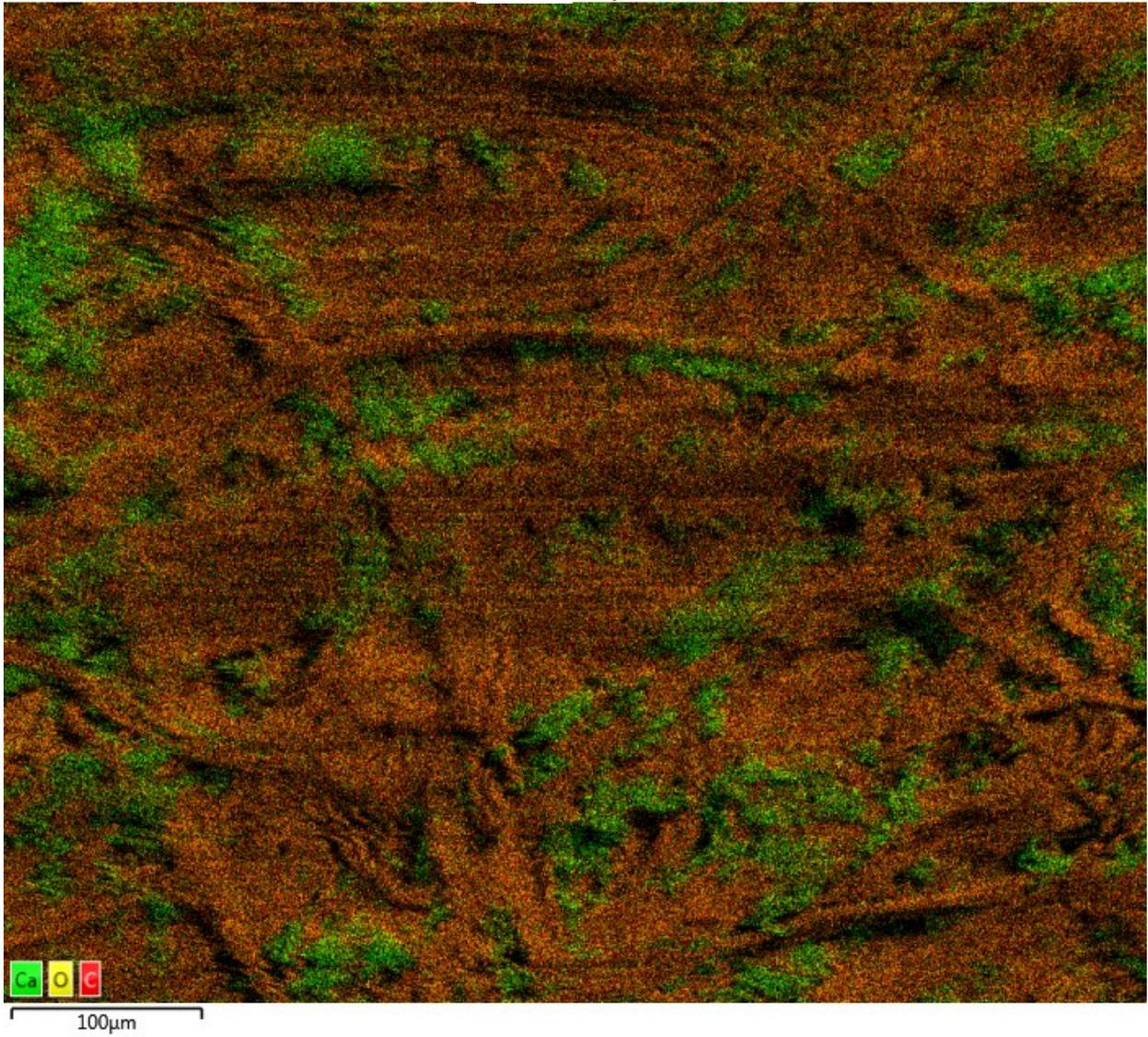


Image 3. ESEM micrographs of the general use copy paper at 500x; unaged (top) and aged (bottom)

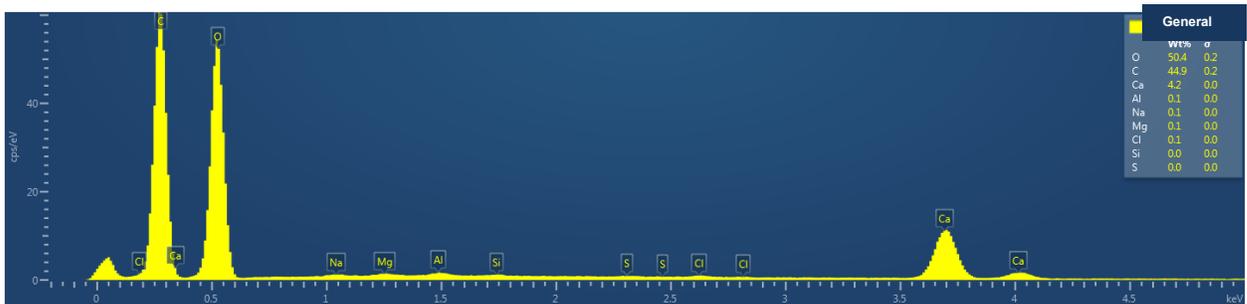
General Map



Map 3 (above). EDS elemental map of the general use copy paper at 500x. Elements detected: C, O, Ca

Spectrum 3 (below). EDS spectrum of the general use copy paper at 20 keV.

Elements detected in significant quantities: O, C, Ca
 Elements detected in trace quantities: Al, Na, Mg, Cl, Si, S



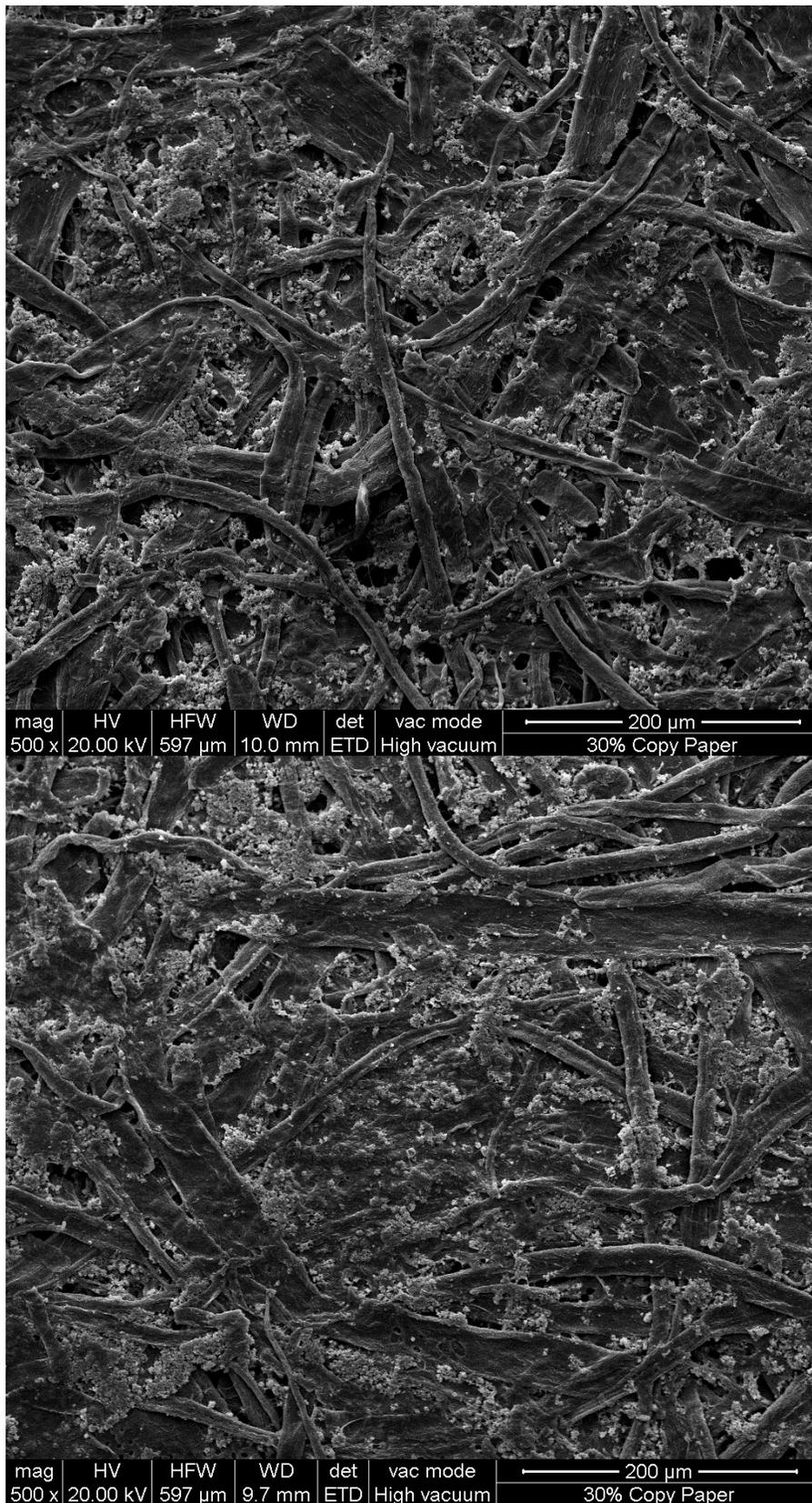
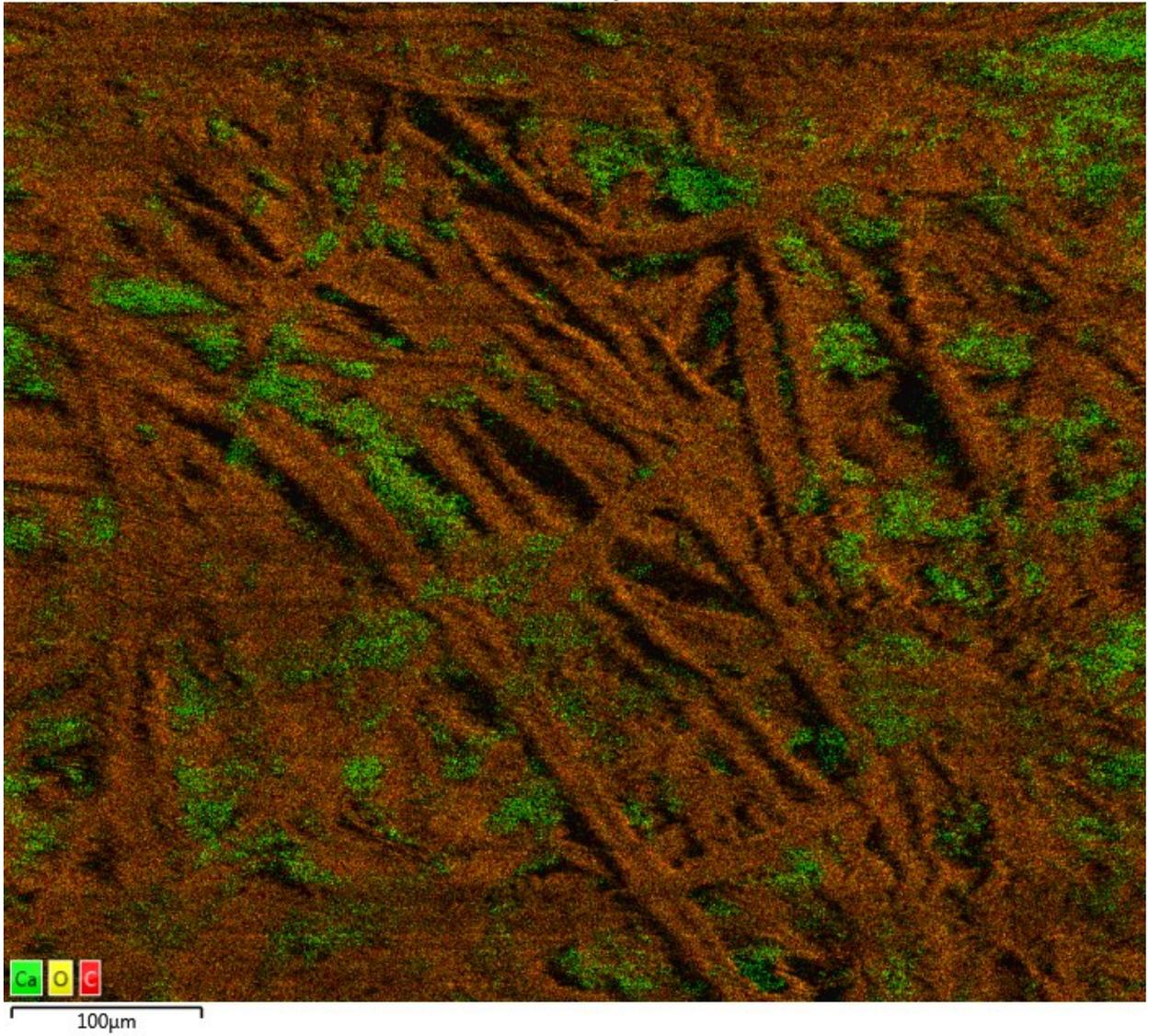


Image 4. ESEM micrographs of 30% recycled paper at 500x; unaged (top) and aged (bottom)

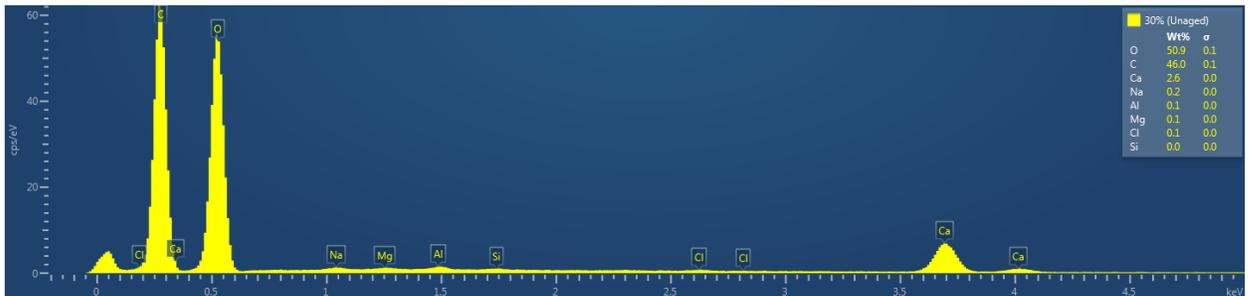
30% Map



Map 4 (above). EDS elemental map of 30% recycled paper at 500x. Elements detected: C, O, Ca

Spectrum 4 (below). EDS spectrum of 30% recycled paper at 20 keV.

Elements detected in significant quantities: O, C, Ca
Elements detected in trace quantities: Na, Al, Mg, Cl, Si



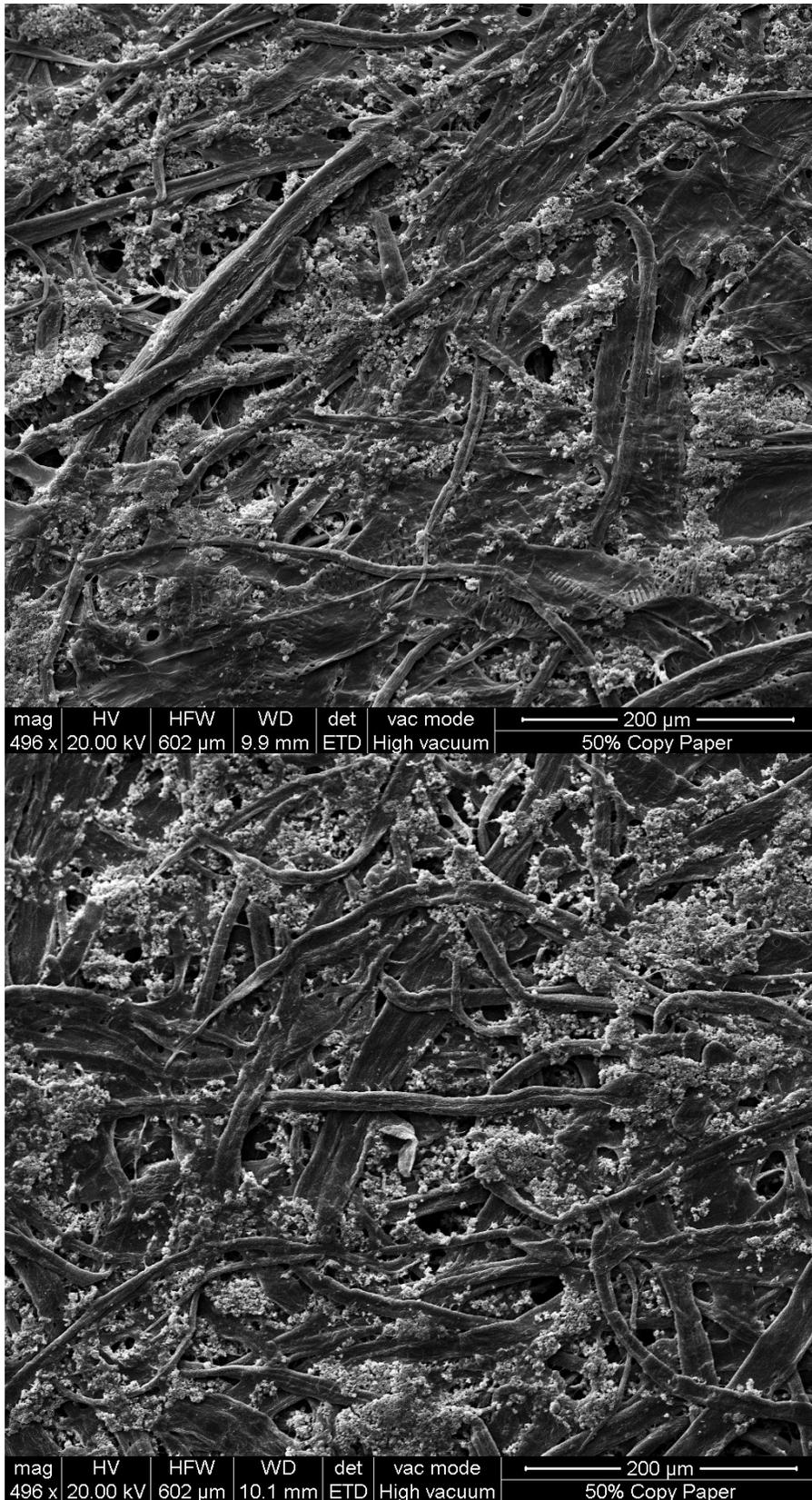
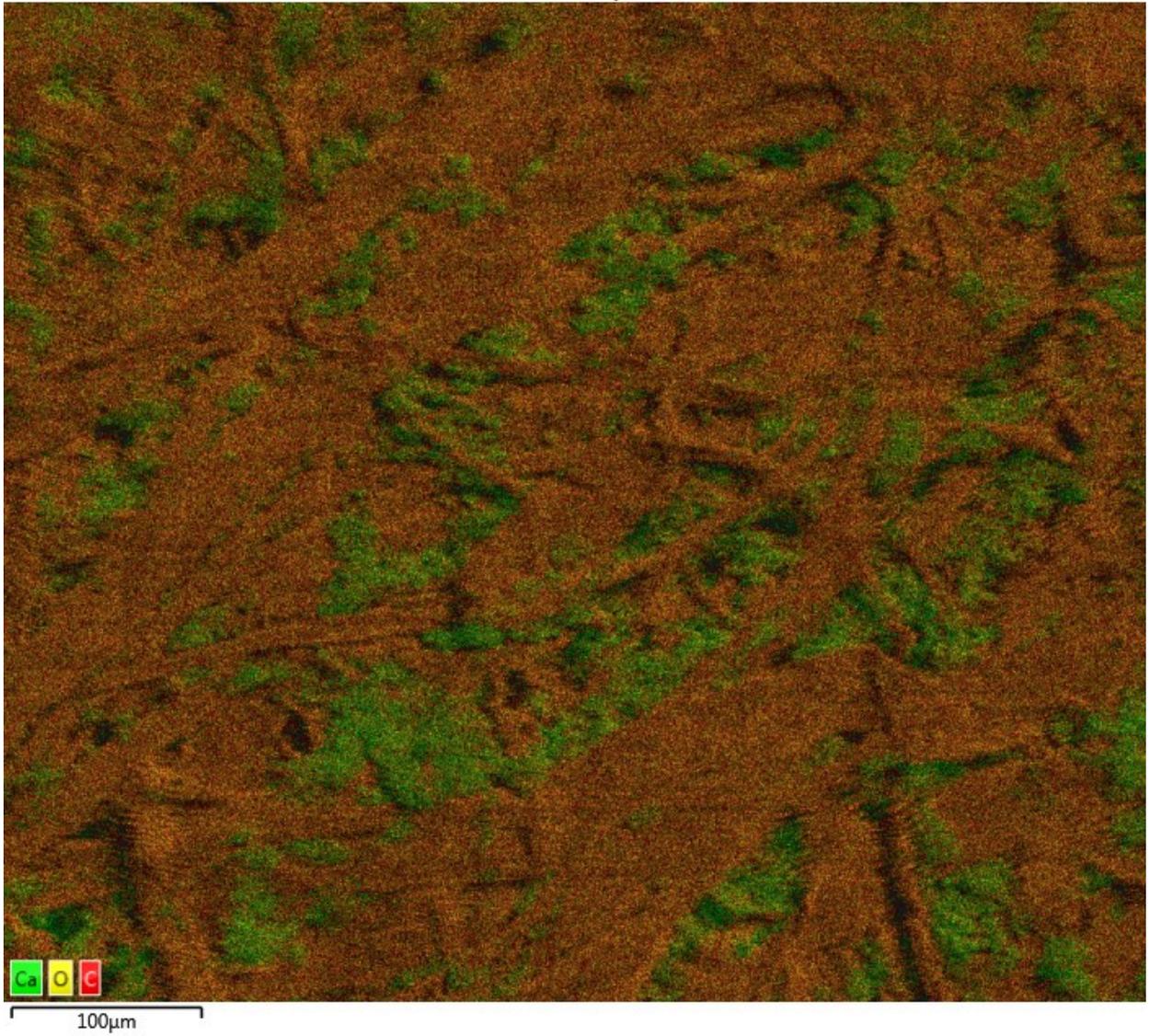


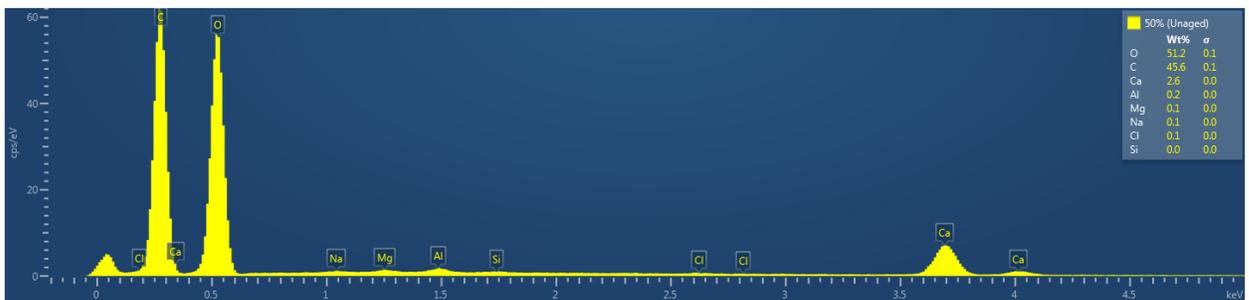
Image 5. ESEM micrographs of 50% recycled paper at 500x; unaged (top) and aged (bottom)

50% Map



Map 5 (above). EDS elemental map of 50% recycled paper at 500x. Elements detected: C, O, Ca

Spectrum 5 (below). EDS spectrum of 50% recycled paper at 20 keV.
Elements detected in significant quantities: O, C, Ca
Elements detected in trace quantities: Al, Mg, Na, Cl, Si



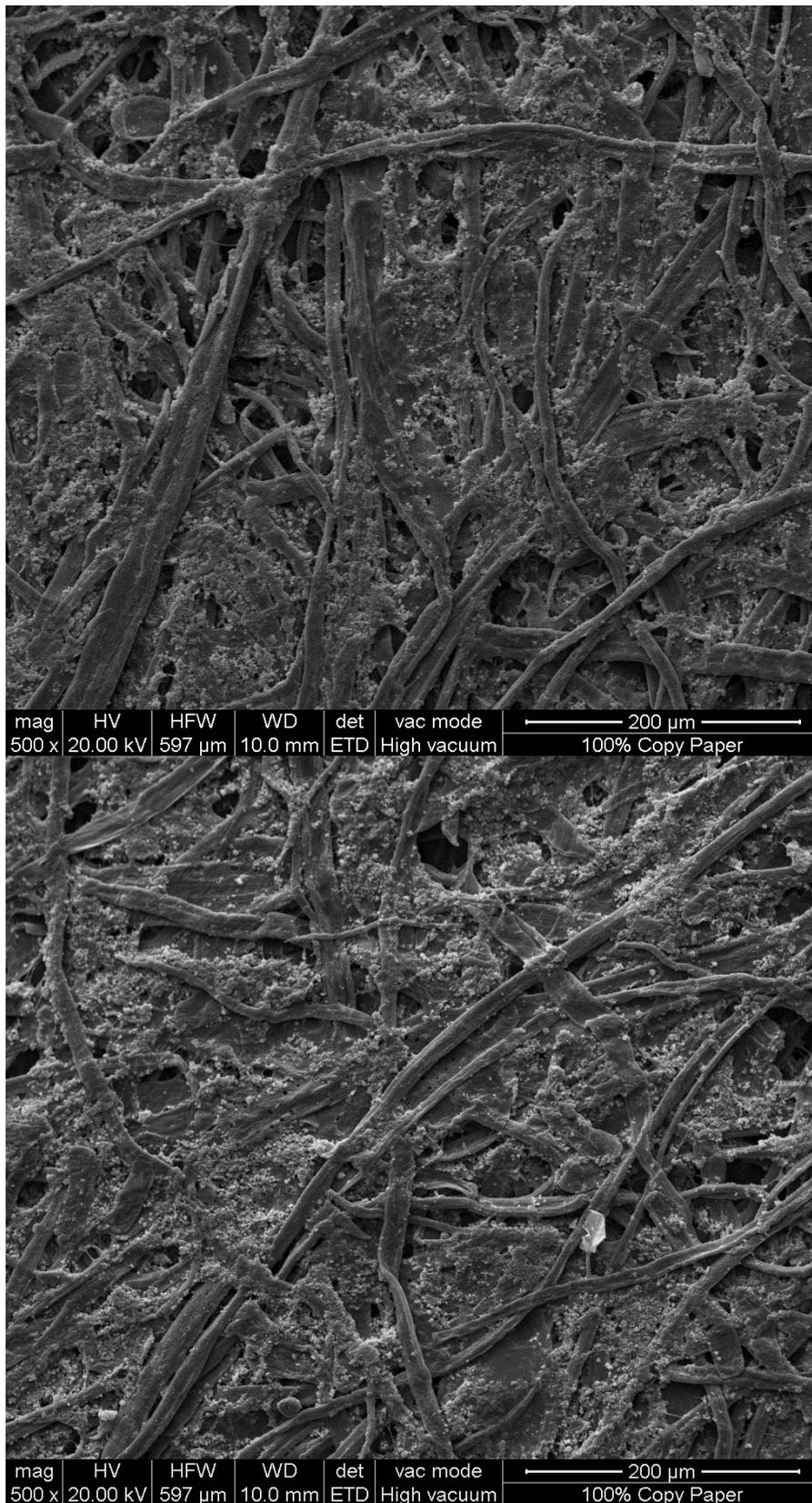
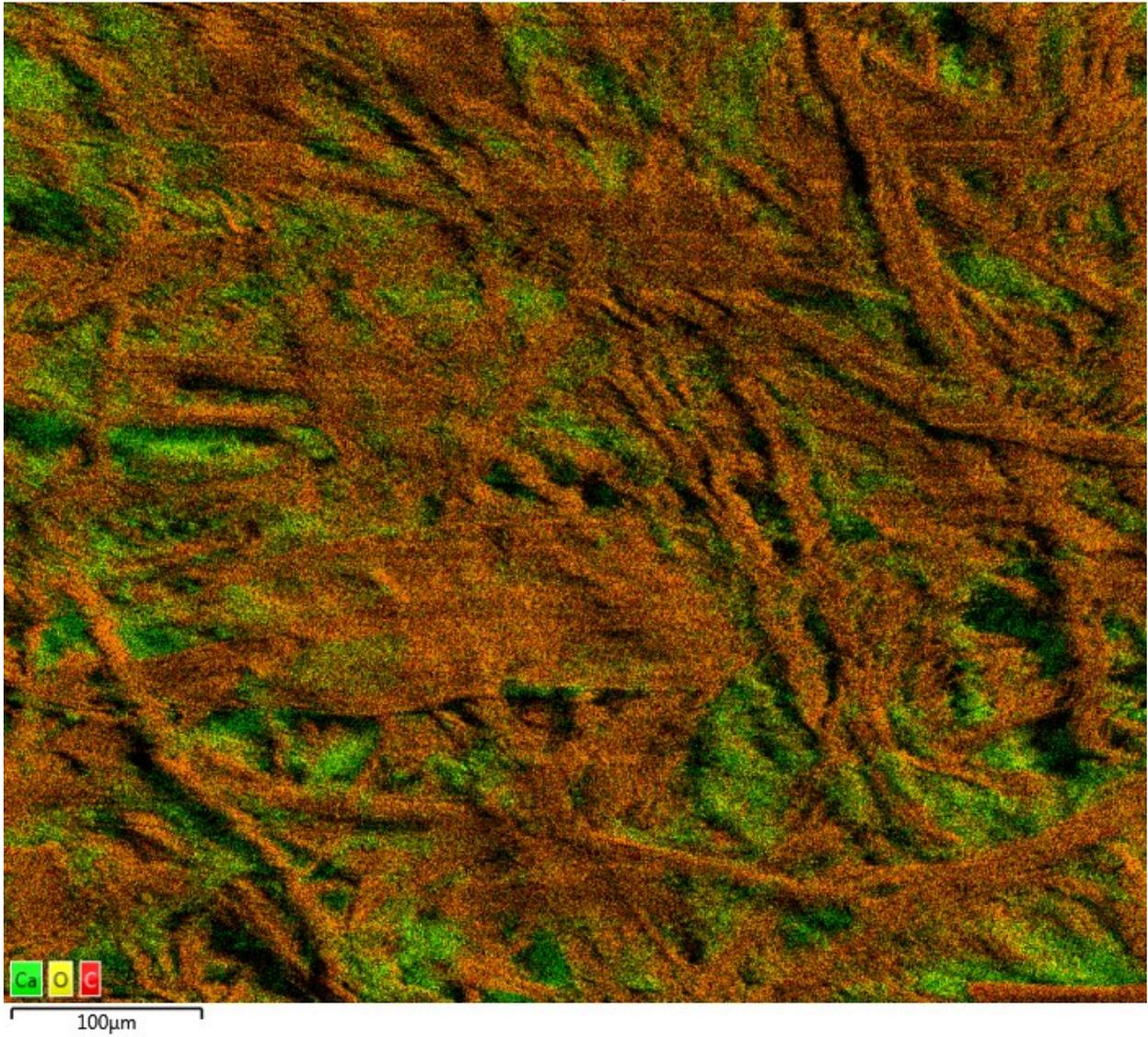


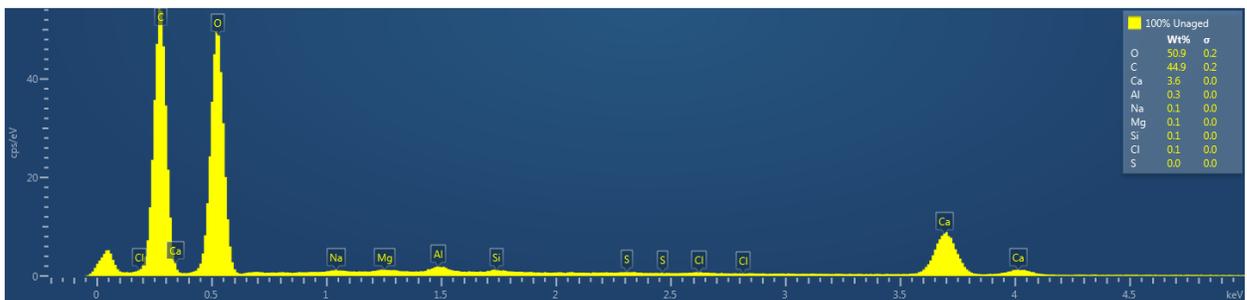
Image 6. ESEM micrographs of 100% recycled paper at 500x; unaged (top) and aged (bottom)

100% Map



Map 6 (above). EDS elemental map of 100% recycled paper at 500x. Elements Detected: C, O, Ca

Spectrum 6 (below). EDS spectrum of 100% at 20 keV.
Elements detected in significant quantities: O, C, Ca
Elements detected in trace quantities: Al, Na, Mg, Si, Cl, S



VIII. Conclusions

The primary requirements for paper permanence, as specified by ANSI/NISO, were evaluated by PRTD staff using a number of laboratory techniques. As stated in the review characterizing degradation in this report, durability is the ability to resist change during use while permanence is focused on the required outcome. Accelerated aging was used in the experimental design to rate the performance of four test papers and two reference papers in terms of observable physical, optical, and chemical changes. Several observed phenomena support the notion that papers made with recycled fibers can and should be considered permanent. All copy papers in this report passed the criteria outlined by ANSI/NISO. Only the reference paper WPWL failed the double fold test, and failed only after 49 days of accelerated aging. WPWL was the only test paper in this report that contained no additives or fillers, suggesting that the addition of fillers such as calcium carbonate increased pH levels (reducing acidity) and aided the strengthening of the chemical stability of the paper matrix.

There was no statistically significant difference between the test results for the general use paper and 30% recycled content papers, nor was there a significant difference between the results for 30% recycled content and 50% recycled content papers in terms of the physical, optical, or chemical parameters. There was a statistically significant difference between 100% recycled content paper and all other copy papers looked at in this study for all parameters. Similarly, there was a statistically significant difference between the permanent paper and WPWL. A correlation plot of the data from CIELAB **b* values versus load at break values clearly illustrated that the papers fell into four distinct groups: WPWL (Group 1), permanent (Group 2), and 100% recycled content paper (Group 4), all being distinctly different from the other three copy papers tested (Group 3).

Accelerated aging caused significant difference in all properties of these papers between day 0 and day 56 but did not result in significant difference between each interim interval for the copy papers. Changes in paper performance over the course of 56 days of accelerated aging, was not as significant as color change results may suggest. All papers in this report showed a tendency to increase in the yellow direction of CIELAB color space as a result of accelerated aging. The data from both color testing and brightness measurements showed initial changes in optical properties but exhibited a “leveling off” trend as the aging proceeded. This could be contrasted with tensile testing results that suggested the papers were somewhat chemically stable and maintained tensile strength throughout the course of the aging period tested.

Testing for pH of the papers in this study over the period tested, indicated that the copy papers did not change chemically, despite the optical changes. This showed that for these papers tested, paper yellowing was not necessarily an indication of chemical change and did not result in increased brittleness for these papers. Surface examination of the papers showed very little change to the physical composition of the fibers and fillers that comprise the samples.

	Alkaline?	Lignin?	Tensile Strength Loss?	Color Change?	Morphology Change?	Permanent?
WPWL	No	No	Yes	Yes	No	No
Permanent	Yes	No	No	Yes	No	Yes
General	Yes	No	No	Yes	No	Yes
30%	Yes	No	No	Yes	No	Yes
50%	Yes	No	No	Yes	No	Yes
100%	Yes	No	No	Yes	No	Yes

Table 5. Summary of results after 49 days of accelerated aging

IX. Recommendations

The research was restricted to papers of various recycled fiber content from one manufacturer. Results can only be implied across the spectrum of recycled papers that are commercially available. It is recommended that future research on this topic include the examination of papers available from multiple manufacturers. Measurements of optical properties revealed some interesting results and the role of the degradation rates of optical brighteners should be studied to determine if that is the cause of the observed color change. Additional pH testing and chemical analyses of molecular weight and degree of polymerization will be useful in describing the differences among recycled papers at the molecular level, providing a more direct measure of physical degradation to the cellulose structure.

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