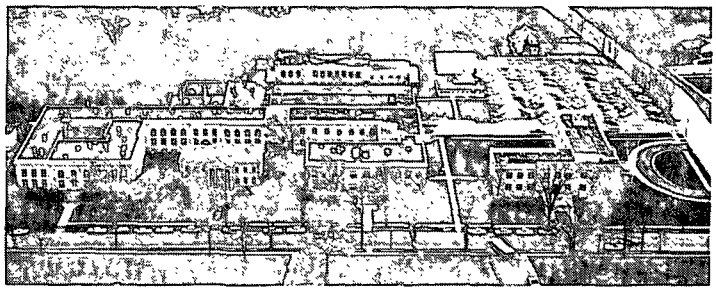

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MONITORING THE AGING OF PAPER

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MONITORING THE AGING OF PAPER

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ABSTRACT

This paper briefly reviews the degradation mechanisms and environmental factors affecting the aging of paper, as well as methods for measuring its progress. Prospects for employing nondestructive procedures such as ultrasonic wave propagation techniques for monitoring the extent of aging are also discussed.

INTRODUCTION

Most materials will undergo some form of breakdown or degradation during their lifetime. The extent of degradation will depend on the material, its environment, and the mechanisms involved. This is an important, and often neglected area of research, particularly so in the case of paper. The magnitude and seriousness of this problem was the subject of recent hearings on information storage at the National Archives by the Committee on *Preservation of Historical Records* (1) in which this author participated. Paper as an archival material and its deterioration was a major concern of this committee. Presently 3 billion pieces of paper are resident in the National Archives, 530 million of which are considered to be at a high risk of loss.

We certainly need to learn more about deterioration, its amelioration and simulation. There is also a concomitant need to be able to effectively monitor the process of deterioration, which is the main subject of this paper.

A number of terms have been used to describe the deterioration of paper including aging, loss of permanence, and durability. Browning (2) defines permanence and durability as follows:

> "Permanence refers to the retention of properties such as strength and color over extended periods. It is influenced by both internal factors (e.g., chemical composition) and external conditions (the effect of light, atmospheric contaminants, etc.)."

> "Durability refers primarily to the ability of the paper to fulfill its intended function during intensive usage without reference to long periods of storage."

Browning also states, "A paper may be permanent (in retaining its original characteristics) but nondurable (e.g., because of low initial strength), or durable (in resisting intensive usage over a short period) but nonpermanent (e.g., because of the presence of acids).

Although the emphasis would probably be on permanence for archival usage, a minimum level of durability would be required to access stored information. In library usage circulating books will require an even higher level of durability but nowhere near as high as might be demanded by currency. It is also interesting to note that one of the main measurements of permanence is the fold test - *also a measurement of durability!* The general term aging is used in what follows to embrace both permanence and durability.

The degradation of paper is complicated by the mechanisms involved and their dependence on raw materials and the papermaking process. In what follows we will briefly consider how some of the mechanisms and environmental factors affect aging and its measurement and the prospects for monitoring it nondestructively.

DEGRADATION MECHANISMS AND ENVIRONMENTAL FACTORS AFFECTING THE AGING OF PAPER

The mechanisms which may occur under natural and simulated aging conditions listed below have been investigated and reviewed by a number of researchers (3-7):

* HYDROLYSIS
* OXIDATION
* CROSSLINKING
* THERMAL DEGRADATION
* PHOTOCHEMICAL

These reactions can also be affected by the following environmental factors:

* Temperature and Moisture
* Radiation
* Pollutants
* Biological and Chemical
* Mechanical

The above mechanisms and environmental factors will usually result in changes at the molecular level: however, they may be more conveniently monitored at other levels of organization, i.e., changes in fiber or bond strength, optical properties, or viscoelastic behavior.

Wilson and Parks (6) specifically discuss these mechanisms in relation to their effect on measurable changes in the physical, chemical, and mechanical properties of paper. Table 1 of their paper, reproduced below, summarizes these effects and their direction.

Table 1 illustrates the complexity of the relationship between measurable properties and possible reactions. Clearly no single measurement would be a satisfactory indicator of the type of reaction which had taken place during aging. Furthermore the monitoring of properties which are enhanced by certain reactions, e.g., modulus and wet strength, might be misleading indicators of the actual state of degradation.

Not included in Table 1, although discussed by Wilson and Parks (6), are changes in crystallinity. Atalla (8) has also discussed changes in crystallinity and polymorphic form in cellulose as a result of pulping and environmental variables, and their implications for paper conservation.

1

Table 1. Reactions, or changes that might occur during natural and accelerated aging of paper and their effects on various tests. [Taken from Wilson and Parks (6) courtesy of the Restaurator.]

Reaction or Change; P = Primary, S = Secondary

Test	Hydrolysis P	Hydrolysis S	Oxidation P	Oxidation S	Crosslinking P	Crosslinking S	Bonding "Order"[a] Decrease P	Bonding "Order"[a] Decrease S	Thermal[b] Decomposition P	Thermal[b] Decomposition S
DP[c]	↓		↓	↓	↑		—	--	↓	
Acid, H+		↑	↑		--	--	--	--	↑	
Carboxyl		↑	↑			↓	--	--		
Aldehyde	↑		↑↓			↓	--	--	↑	
Ketone	--	--	↑			↓	--	--	↑	
Peroxide	--	--	↑		--	--	--	--	↓	
Moisture regain	--	--	↑↓		↓		↑		--	--
Alkali solubility	↑		↑		↓		—	--	↑	
Fold	↓		↓		↓			↓	↓	
Tear	↓		↓		↓			↑	↓	
Burst	↓		↓		↓		↓		↓	
Tensile	↓		↓		--	--		↓	↓	
Elongation	↓		↓		↓		↓		↓	
Modulus	↓		↓		↑		↓		↓	
TEA[d]	↓		↓		↓		↓		↓	
Zero span	↓		↓			↓	--	--	↓	
Wet tensile		↓		↑	↑		--	--	--	--
Blue reflectance		↓	↓	↓	--	--	--	--	↓	

[a]Includes degradation of bonds formed by sizing agents.
[b]Probably occurs only during accelerated aging.
[c]Degree of polymerization.
[d]Tensile energy absorption.

METHODS FOR MONITORING THE PROGRESS OF AGING

The properties listed in Table 1 for monitoring the progress of aging might be updated to include other endurance tests such as fatigue, creep failure, and flex testing. In the area of nondestructive testing, ultrasonic, electrical, and even subjective testing might be added. Next we will briefly discuss endurance and tensile testing before considering nondestructive testing using ultrasonic techniques as a possible means of monitoring the state and progress of aging.

Destructive Testing

Fold endurance is one of the most sensitive indicators of both permanence and durability, although it is not particularly well understood. The test is highly variable, and only a small area of the sample is tested. Special precautions are necessary to ensure constant temperature and moisture in the fold area. The sample is subjected to a complex stress situation as shown in Fig. 1.

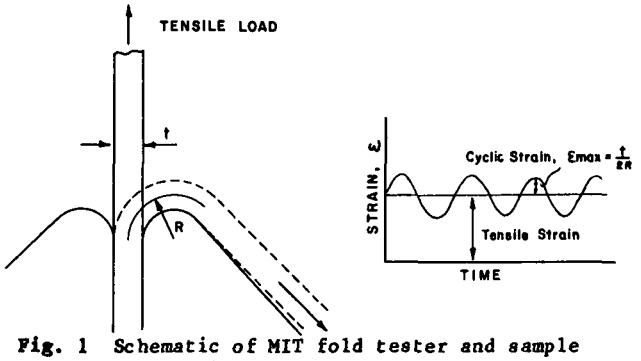

Fig. 1 Schematic of MIT fold tester and sample strain history.

Superimposed on a constant tensile stress is a cyclic bending stress, and in some cases a significant shear component is developed. The magnitude of these stresses will depend on the deformation behavior of the paper.

Cardwell, Lyon, and Luner (9) have suggested that it is more meaningful to compare fold results at the same ratio of applied load to failure load. The present author (10) also used a similar idea and calculated the ratio of applied stress to failure stress to account for differences in sample grammage and polymer content when measuring the fold endurance of polymer impregnated paper as shown in Fig. 2.

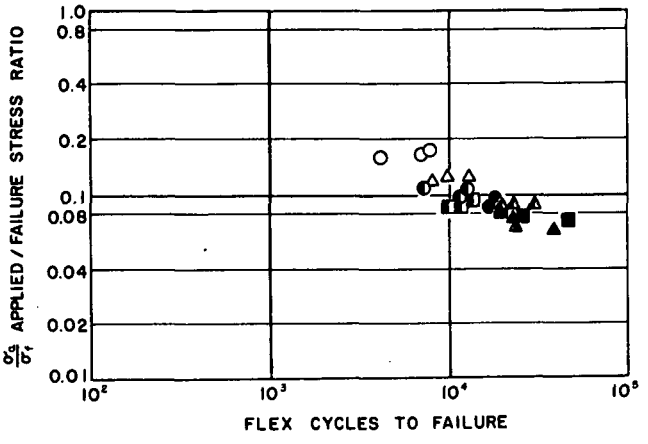

Fig. 2 Flex cycles to failure as a function of applied stress for neoprene impregnated handsheets of varying grammage.

Creep failure (duration of load) is another form of endurance test which involves measuring the times to failure at various levels of applied load. It has been suggested by Coleman (11), Fulmer and Guthrie (12), and Caulfield (13), that creep failure and fold can be modeled by applying the theory of absolute reaction rates. This modeling suggests that there is no essential difference in the mechanism leading to failure in a creep or fatigue test of certain materials.

In comparing the creep and fatigue behavior of polymethylmethacrylate, Penn and McKenna (14) reported that fatigue measurements fell between two boundaries comprising creep and fatigue predictions. In metal fatigue, fracture mechanics is the main approach, where failure is controlled by the rate of crack growth per cycle.

The flex tester developed by Graminski (15) is probably closer to simulating end use performance where durability is important, i.e., the handling of currency. One important difference in the flex test is that a larger area of the sample is tested. The applied stresses are similar to those of the fold tester, although the bend radius is larger. Graminski investigated how the tensile load elongation curve is affected by flexing. For a high grade rag paper there appears to be a loss in modulus with flexing, and after about ten thousand flexes there is a reduction in both tensile and elongation. It would be interesting to determine how aged samples perform on the flex test.

2

The tensile load/elongation curve may be modified in a number of ways by aging. In an accelerated aging test (Fig. 3) Graminski (16) has shown that modulus increases, whereas maximum load and elongation both decrease. TEA is also significantly reduced.

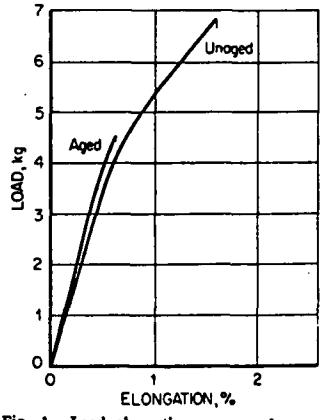

Fig. 1. Load-elongation curves of paper unaged and aged 15 days at 90°C and 50% RH.

Fig. 3 Effect of aging on the load elongation behavior of paper [taken from Graminski (16) courtesy TAPPI.]

Graminski suggested that the increase in initial modulus may be due to an increase in crosslinking or crystallinity. Page (17) found, using accelerated heat aging, a slight increase in normal span tensile strength before it decreased at the highest level of beating. This is explained by a loss in fiber strength being offset by an increase in bond strength.

It would seem reasonable, in view of Graminski's results, that fold endurance should correlate with TEA. Using the data of Wilson and Hebert (18), Fig. 4 illustrates that there is indeed a reasonable correlation.

Nondestructive Testing

Although a number of nondestructive test methods are possible for determining the aging of paper, we will limit our consideration to ultrasonic techniques. There has been a significant development in these techniques as applied to paper over the last ten years. Procedures have been developed by Baum, Habeger, and Wink for determining both in-plane and out-of-plane elastic constants of paper (19-20), as well as relating these measurements to the end use performance of paper (21). Ultrasonic techniques have also been developed by Baum and Habeger (22) for the on-line measurement of mechanical properties; and in more recent work Pankonin and Habeger (23) have developed techniques for measuring the ultrasonic viscoelastic parameters of paper.

Ultrasonic measurements were one of a number of techniques employed by Smith (24) to monitor changes in sonic modulus with years since publication of identical books kept in libraries in Appleton, Chicago, and New York. Smith's results are shown in Fig. 5. Although the sonic modulus differences are not statistically significant, other measurements he made support the trend shown in Fig. 5 that the books in the New York library became embrittled with age due to air pollution.

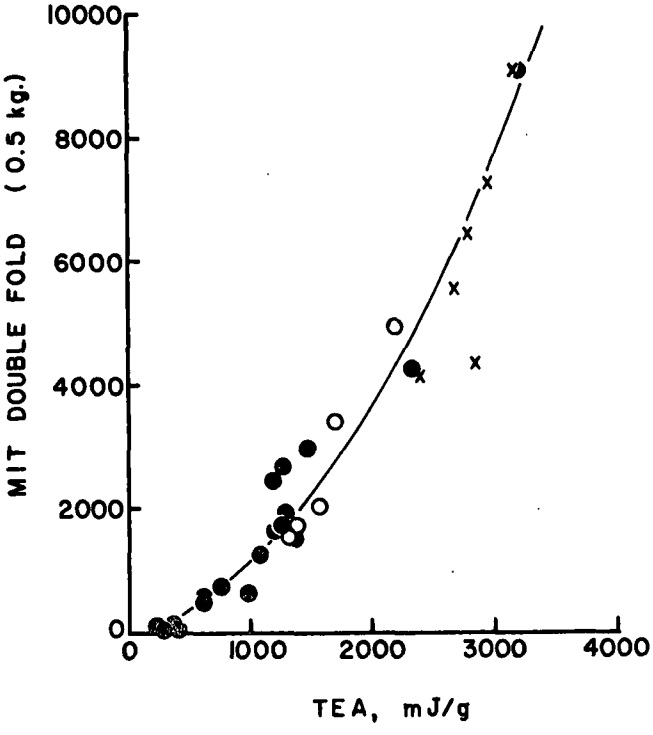

Fig. 4 Variation of MIT double fold with TEA using data of Wilson and Hebert (18).

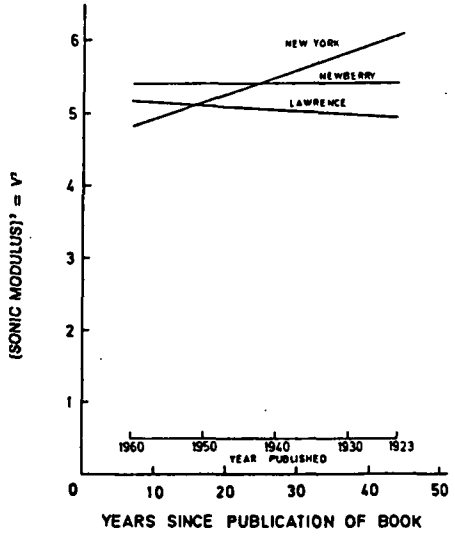

Fig. 5 Sonic modulus measurements of aging. [Taken from Smith (24) courtesy of the Restaurator.]

Some in-plane and out-of-plane ultrasonic measurements of heat aged samples made by Waterhouse and Brennan (25) are shown in Table 2.

3

Table 2. Ultrasonic testing of heat-aged paper samples.

Sample Scratch Pad Paper	Basis Wt., g/m^2	Density, g/cm^3	$\bar{E}/\rho$, $(km/sec)^2$	E_z/ρ, $(km/sec)^2$
Control	59.3	0.791	7.23	0.102
Heat aged[a] 30 min	58.5	0.797	7.85	0.102
Heat aged[a] 60 min	57.5	0.783	7.64	0.102
Heat aged[a] 120 min	58.0	0.802	7.73	0.0995
Heat aged[a] 180 min	56.2	0.776	7.59	0.0989

[a]Air circulating oven 400°F.

These results were somewhat disappointing in view of the fact that the 120 and 180 min heat aged samples were extremely delicate.

Further work is therefore required to determine if more meaningful measurements of the aging process can be made. In addition to exploring other frequencies we would also like to determine the extent of changes in viscoelastic behavior.

An interesting study has recently been conducted by Barrett (26) to determine why certain European handmade papers have such excellent permanence and durability compared with papers made in the same time period (1400-1800) which are in very poor condition. As part of this investigation ultrasonic and other measurements were made at IPC on good and poor samples supplied by Barrett and are summarized in Table 3.

Table 3. Characterization of handmade papers made between 1400 and 1800. [Taken from Barrett (24)].

Sample #/year	Grammage, g/m^2	IPC Density, g/m^3	E_z/ρ $(km/sec)^2$	E/ρ $(km/sec)^2$	G/ρ $(km/sec)^2$	Grain Ratio	Zero Span Nm/g	% Gelatin Predicted	pH
GOOD CONDITION									
G12/1483	91.8	0.869	0.419	6.07	2.47	1.13	84	10.8	7.3
	96.4	0.742	0.455	5.83	2.27	1.41	--	--	--
G17/1400	85.4	0.638	0.389	6.16	1.84	1.56	74	--	7.5
G1/1685	78.7	0.819	0.275	6.07	2.19	1.23	111	9.7	--
G2/1701	74.6	0.823	0.334	6.13	2.23	1.39	108	12.1	7.9
G3/1704	84.6	0.793	0.317	6.43	2.51	1.27	107	--	8.4
POOR CONDITION									
P39/1590	61.5	0.797	0.042	3.16	1.07	1.36	87	7.12	4.4
P32/1685	89.1	0.907	0.064	2.86	1.12	1.34	74	--	6.4
P35/1695	62.5	0.769	0.068	2.84	1.12	1.47	66	2.71	5.0
P46/1710	75.8	0.720	0.137	3.60	1.33	1.21	77	--	6.4
P44/1711	70.6	0.847	0.058	2.99	1.39	1.32	81	6.07	6.5
	71.6	0.840	0.062	3.20	1.39	1.65			

It is interesting to note that the in-plane and out-of-plane elastic constants of the good papers are much higher than those of the poor papers. In fact the out-of-plane constants of the good papers are considered to be very high compared with present day printing and writing papers. It later became clear that gelatin was the main factor responsible for the high elastic constants. The poor samples contained a lower percentage of gelatin, and FTIR measurements indicated that it was in a degraded state and that pH values were on the acid side. There were also strong indications that fiber strength (zero-span strength) of the poor papers was also reduced.

In Barrett's study ultrasonic measurements served two main purposes: first they provided data on the magnitude of elastic constants to be expected for European papers made in this time period, and secondly they identified which were the poor papers. Further work will be required to determine if these and other nondestructive measurements can identify the reason for the difference in performance between the the good and poor papers, i.e., were the good papers stored in a more favorable environment or were there vital composition and manufacturing differences?

PROSPECTS FOR NONDESTRUCTIVE TESTING

The complexities of the aging process, both chemical and mechanical, make it difficult at the moment to envisage a single test which might be used to predict unambiguously the overall mechanical condition of an aged sample of paper. There is obviously a need to investigate the effects of raw materials, papermaking process variables and different aging mechanisms on the viscoelastic properties of paper using ultrasonic and other nondestructive techniques. There is also an associated need of increasing our understanding of how aging mechanisms affect property measurements at different structural levels of organization within paper.

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4

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5