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Comparison of Accelerated Aging of Book Papers in 1937 with 36 Years Natural Aging *

by WILLIAM K. WILSON & E. J. PARKS

CONTENTS

1. INTRODUCTION

The development of an accelerated aging procedure requires information on the correlation between accelerated aging and natural aging. Few successful studies of this type have been made as, 1) planning and executing an experiment over a period of 20–50 years is very difficult, 2) test methods and their significance change with time, and 3) materials of manufacture change so that one may be evaluating the stability of materials that are no longer manufactured. However, the development of information on a continuing basis, with emphasis on, 1) the examination of characteristics of old papers and, 2) the determination of what actually happens – chemically and physically – during accelerated aging of paper under various conditions, can be very useful.

A group of commercial papers was tested at the National Bureau of Standards (NBS) before and after accelerated aging in 1929, and these papers were retested after 4, 8, 22, and 26 years of natural aging.[1] Although these data were useful, manufacturing data on the papers were not available and, unfortunately, the papers were accidentally discarded several years ago. Data on these

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49968

papers showed that an empirical correlation existed between accelerated aging and natural aging. In general, rag papers stood up better than wood pulp papers. Although the acidity values did not vary sufficiently to enable much of a correlation between acidity and stability, it was obvious that some sort of correlation did exist. The soda-sulfite papers were especially vulnerable to acid. This is consistent with recent work at NBS[2,3,4] which indicated that aluminum on the carboxyls in cellulose contribute to the degradation of paper. These soda-sulfite papers probably had a high carboxyl content, but they are no longer available for examination.

Most accelerated aging has been carried out in dry atmospheres, except that which has been directed towards evaluation of brightness reversion. Work at NBS has shown that significant differences exist between moist accelerated aging and dry accelerated aging.[2,3,4] Therefore, it is desirable to obtain as much test data as possible on papers that are still available that were subjected to accelerated aging several years ago.

Graminski[5] has made an important contribution to the aging of paper through his extensive study of accelerated aging at various temperatures and relative humidities.

A comprehensive literature survey of the aging of paper with a discussion of the factors involved in aging was included in an earlier report.[6] Some of the more outstanding reports in the past several years on the aging of paper have been authored by Graminski,[5] Browning and Wink,[7] Luner,[8] Cardwell,[9] and Gray.[10]

Publications dealing with comparisons of accelerated aging with natural aging, or of the characteristics of naturally aged papers have been authored by Barrow,[11] Wilson,[1] Hanson,[12] Richter and Wells,[13] Royen,[14] and Lewis.[15]

In 1937 a group of book papers made in the NBS experimental paper mill was tested before and after accelerated aging for 72 hours at 100°C in a circulating oven. This work was reported in a paper by Shaw and O'Leary entitled, *Effect of Filling and Sizing Materials on Stability of Book Papers.*[16] Although there was no plan to test these papers after a period, or periods, of natural aging, a collection of some of these papers had been kept in an office for several years for occasional evaluation, as the manufacturing history was known and the physical and chemical properties of the papers had been extensively evaluated for that time. Out of a total of 72 papers, 18 were found that could be assembled to form a reasonably coherent set of samples.

This probably is one of the most valuable collections of papers ever assembled for comparison of natural aging with accelerated aging. Having the manufacturing details at hand, one can make observations that otherwise would be impossible. In addition, extensive studies on the differences between moist and

Table 1. Papermaking details on book papers made in NBS mill in 1937.[1]
Table 1. Détails de fabrication des papiers de librairie à la papeterie NBS en 1937.
Tabelle 1. Details über die Zusammensetzung der Buchpapiersorten, die 1937 in der NBS-Fabrik hergestellt worden sind.

Machine Run No.	Fiber	Kind	Filler Added %	Filler Retained %	Alum Added %	Rosin[2] Added %	Rosin[2] Retained %	pH at Headbox
1129	sulfite 50%, soda 50%	clay	15	11.2	2.1	0	0.2	4.2
1130	″	clay	15	10.1	1.5	0	0.2	4.6
1133	″	none	–	–	0	0	0.3	7.3
1158	″	calcium carbonate	15	7.2	0	0	–	8.2
1172	″	″	15	11.2	1.1	2	1.6	8.0
1175	″	″	15	9.9	1.0	2	1.3	7.7
1161	purified wood pulp	clay	15	11.5	0.8	2	1.6	5.9
1162	″	″	15	11.9	1.1	2	1.7	4.8
1163	″	″	15	11.1	2.3	2	1.9	4.2
1164	″	″	15	12.1	0.6	1	1.1	5.6
1165	″	″	15	11.9	0.8	1	1.1	4.7
1166	″	″	15	11.2	2.1	1	1.0	4.2
1191	old rag	″	15	13.9	0.7	0	0.2	6.7
1192	″	″	15	13.8	1.3	0	0.2	4.9
1193	″	″	15	13.8	2.1	0	0.3	4.2
1203	″	″	15	13.4	4.0	2	1.5	4.0
1207	″	titanium pigment	5	4.6	1.4	1	0.8	4.9
1208	″	″ ″	15	12.3	1.3	1	0.9	4.9

[1] Data taken from NBS Research Paper RP1149.
[2] Analytical values include natural resins in pulps.

dry accelerated aging[2,3,4,5] enabled certain tentative conclusions to be drawn concerning moisture in an accelerated aging method.

2. Samples

The fiber compositions fall into three categories (Table 1):

(1) 50–50 soda-sulfite
(2) purified wood pulp
(3) old rag

Table 2. Chemical test data obtained in 1937 on book papers made in NBS mill in 1937.[1]
Table 2. Donnée d'analyse chimique obtenues en 1937 sur des papiers de librairie fabriqués à la papeterie NBS en 1937.
Tabelle 2. Daten der chemischen Tests, die man 1937 von den Buchpapiersorten erhalten hat, die 1937 in der NBS-Fabrik hergestellt worden sind.

Machine Run No.	pH cold	pH hot	Alpha Cellulose	Copper No.	Pentosans
			%		%
1129	4.9	4.3	76.0	3.6	
1130	5.3	4.8	75.7	3.6	
1133	6.9	6.4	75.8	3.2	about 11
1158	9.6	–	75.5	3.3	
1172	8.9	–	75.6	3.4	
1175	8.5	–	74.2	3.3	
1161	6.1	5.7	90.2	0.8	
1162	5.6	5.3	90.2	0.9	
1163	5.2	4.5	90.0	0.9	about 4
1164	6.0	5.7	89.8	0.9	
1165	5.6	5.0	89.9	0.8	
1166	5.0	4.4	89.6	0.9	
1191	6.8	–	92.3	0.3	
1192	5.8	–	91.1	0.4	
1193	5.1	–	91.6	0.5	none
1203	5.3	4.5	89.2	0.7	
1207	5.2	–	90.2	0.5	
1208	5.7	–	90.5	0.4	

[1] Data taken from NBS Research Paper RP1149.

With respect to fiber and chemical treatment, these compositions are very different. The soda-sulfite papers contain a high percentage of pentosans (hemi-celluloses) (Table 2). The purified wood pulp papers are fairly low in pentosans, and rag papers contain no pentosans. As the pentosans usually contain more functional groups than the cellulose fraction, one would expect these papers, in general, to be more vulnerable to degradation. Most of the papers contain fillers. Number 1133 is very interesting and useful as it contains no filler, alum, or rosin. Three papers contain calcium carbonate. Most of the papers contain clay and two are filled with titanium pigments, one of which is a mixture of titanium dioxide and barium sulfate.

Varying amounts of alum were added to the papers during manufacture. Greater variation in amounts of alum and rosin would have been desirable, as

Table 3. Physical test data obtained in 1937 on book papers made in NBS mill in 1937.[1]
Table 3. Résultats de tests physiques obtenus en 1937 sur des papiers de librairie fabriqués à la papeterie NBS en 1937.
Tabelle 3. Daten der physikalischen Tests, die man 1937 von den Buchpapiersorten erhalten hat, die 1937 in der NBS-Fabrik hergestellt worden sind.

Machine Run No.	Thickness µm	Thickness mils	Weight g/m²	Weight 25 × 40,500 lb	Burst points	Breaking Load kg[2] MD	Breaking Load kg[2] CD	Elongation % MD	Elongation % CD	Fold, MIT 0.5 kg[2] tension MD	Fold, MIT 0.5 kg[2] tension CD	Tear g MD	Tear g CD
1129	89	3.5	77.2	54.9	23	5.7	3.3	1.7	4.6	599	140	46	51
1130	89	3.5	78.0	55.5	24	5.5	3.7	1.8	5.0	548	423	48	49
1133	89	3.5	81.0	57.6	31	7.6	4.6	2.0	5.5	2828	1228	55	54
1158	94	3.7	78.7	56.0	20	5.3	3.1	3.0	5.0	644	150	51	55
1172	99	3.9	80.1	56.9	19	4.2	2.6	1.5	3.0	251	122	50	52
1175	94	3.7	79.3	56.4	23	5.0	3.3	1.0	4.5	445	135	45	47
1161	86	3.4	77.3	55.0	21	5.0	2.5	2.5	5.5	2270	474	82	96
1162	91	3.6	80.7	57.4	21	4.8	2.6	2.0	5.5	1734	428	79	84
1163	91	3.6	80.2	57.0	22	5.3	2.7	2.5	6.0	2328	556	77	87
1164	84	3.3	79.4	56.5	23	5.2	2.6	2.5	6.0	3506	487	79	86
1165	91	3.6	81.7	58.1	23	5.1	2.6	3.0	5.5	2480	592	83	91
1166	94	3.7	78.7	56.0	23	5.3	2.5	3.0	6.0	2646	696	75	85
1191	91	3.6	79.3	56.4	15	3.3	2.2	2.5	4.0	71	55	55	60
1192	97	3.8	80.3	57.1	14	3.2	2.2	2.0	4.0	66	48	57	61
1193	91	3.6	78.7	56.0	15	3.4	2.2	2.5	4.5	76	53	56	59
1203	94	3.7	78.9	56.1	14	3.0	2.2	2.5	4.5	64	37	54	57
1207	97	3.8	80.7	57.4	19	3.7	2.7	2.5	5.0	217	113	60	64
1208	89	3.5	78.7	56.0	15	3.1	2.2	2.5	5.0	94	47	54	56

[1] Data taken from NBS Research Paper RP1149.
[2] 1 kilogram force = 9.80665 newton.

Table 4. Effect of accelerated aging for 72 hours at 100°C in 1937 on book papers made in NBS mill in 1937.
Table 4. Effet du vieillissement accéléré pendant 72 heures à 100°C en 1937 sur des papiers de librairie fabriqués à la papeterie NBS en 1937.
Tabelle 4. Auswirkung der beschleunigten Alterung von 72 Stunden bei 100°C im Jahre 1937 auf die Buchpapiersorten, die 1937 in der NBS-Fabrik hergestellt worden sind.

Machine Run No.	Alpha[1] Cellulose	Copper Number	Fold Retention	Tear Retention
	change	change[2]	%	%
1129	−7.6	+0.6	19	58
1130	−3.3	+0.4	56	80
1133	+0.1	−0.1	69	80
1158	−0.4	0	77	92
1172	−2.1	+0.4	55	91
1175	−3.3	+0.3	75	93
1161	−0.8	+0.3	108	90
1162	−3.6	+0.5	97	90
1163	−4.6	+0.7	81	80
1164	−1.8	+0.2	93	91
1165	−2.9	+0.4	95	80
1166	−5.0	+0.5	62	74
1191	−3.1	+0.1	114	97
1192	−3.0	+0.1	114	92
1193	−8.1	+0.2	95	90
1203	−9.6	+0.9	100	91
1207	−4.4	+0.5	96	91
1208	−3.7	+0.4	107	94

[1] Alpha cellulose value based on total cellulose; change is decrease in analytical value.
[2] Change in analytical value.

well as information on the natural mineral content of the pulps before they were processed into paper. For the time, however, the amount of information available is considerable.

3. Methods of Test

3.1 *Methods Used in 1937*

Filler was determined from the ash content and by use of an empirical formula. In addition, titanium dioxide and barium sulfate were determined on the papers containing titanium pigment, and calcium carbonate filler was determined by a titration procedure. Rosin, acidity, and alpha, beta, and gamma cellulose

Table 5. Effect of 36 years of natural aging on the alpha cellulose content of book papers made in NBS mill in 1937 compared with accelerated aging in 1937.
Table 5. Effet de 36 années de vieillissement naturel sur la teneur en alfacellulose de papiers de librairie fabriqués à la papeterie NBS en 1937 comparé au vieillissement accéléré en 1937.
Tabelle 5. Auswirkung der 36 Jahre langen natürlichen Alterung auf den Alpha-Zellulose-Gehalt der Buchpapiersorten, die 1937 in der NBS-Fabrik hergestellt worden sind, im Vergleich zu der beschleunigten Alterung von 1937.

Machine Run No.	Alpha Cellulose, % 1937	Alpha Cellulose, % 1973	S[1], % 1973 data	Change[2], %, After: 36 Years Natural Aging	Change[2], %, After: Accelerated Aging
1129	76.0	59.3	1.0	16.7	7.6
1130	75.7	62.3	0.8	13.4	3.3
1133	75.8	73.6	0.5	2.2	+0.1
1158	75.5	68.6	0.3	6.9	0.4
1172	75.6	70.2	0.6	5.4	2.1
1175	74.2	67.8	1.4	6.4	3.3
1161	90.2	86.3	0.4	3.9	0.8
1162	90.2	84.4	0.4	5.8	3.6
1163	90.0	77.1	0.7	12.9	4.6
1164	89.8	85.8	0.7	4.0	1.8
1165	89.9	77.8	1.9	12.1	2.9
1166	89.6	76.0	0.7	13.6	5.0
1191	92.3	85.3	1.0	7.0	3.1
1192	91.1	83.1	1.1	8.0	3.0
1193	91.6	76.5	1.5	15.1	8.1
1203	89.2	72.7	1.3	16.5	9.6
1207	90.2	81.1	0.4	9.1	4.4
1208	90.5	79.8	0.8	10.7	3.7

[1] Standard deviation. Three specimens for 1158; 4 for all others.
[2] Decrease in analytical value.

were determined by methods developed by Launer.[17,18,19] pH at the headbox was determined by the Quinhydrone method except for the runs containing calcium carbonate for which a glass electrode system was used. Ash and copper number were determined by TAPPI methods that have not changed appreciably since that time. Physical test data including weight, bursting strength, tensile properties (pendulum tester), thickness, sizing value, opacity (contrast ratio), Schopper fold, MIT fold, and tearing strength were obtained using TAPPI methods. These methods have not changed substantially since 1937. MIT fold was performed at 0.5 kg tension. All physical tests were made at 65% relative humidity and 21°C.

The papers were aged for 72 hours in a circulating oven maintained at 100°C.

Figure 1. Decrease in alpha cellulose: natural aging for 36 6ears vs. accelerated aging in 1937.
Figure 1. Baisse du taux d'alfacellulose: vieillissement naturel pendant 36 années contre vieillissement accéléré en 1937.
Abb. 1. Abnahme der Alpha-Zellulose: natürliche Alterung von 36 Jahren gegenüber beschleunigter Alterung im Jahre 1937.

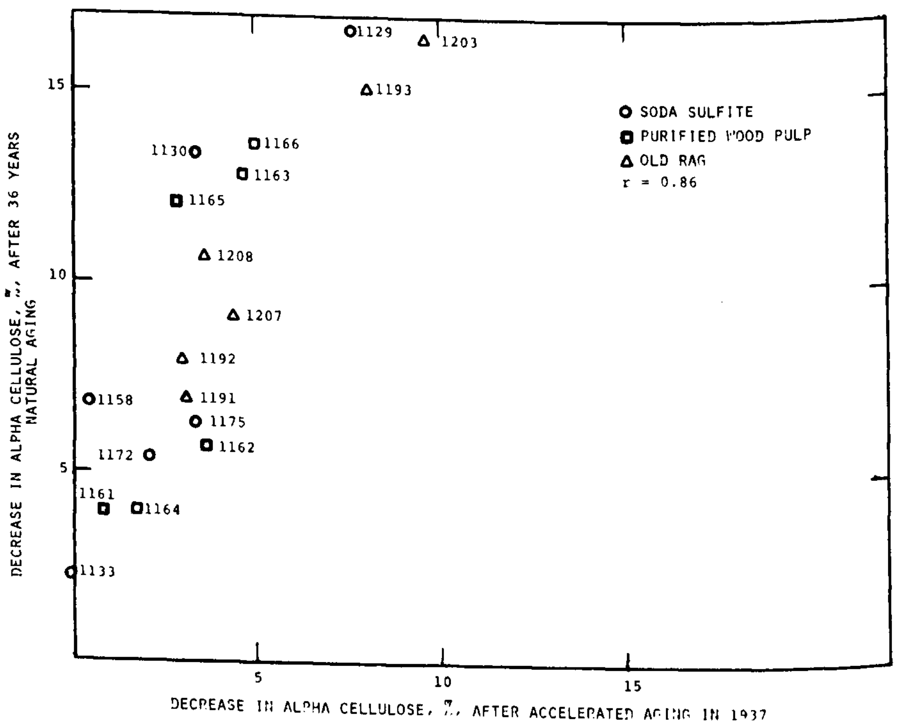


Figure 2. Increase in copper number: natural aging for 36 years vs. accelerated aging in 1937.
Figure 2. Accroissement du taux de cuivre: vieillissement naturel pendant 36 années contre vieillissement accéléré en 1937.
Abb. 2. Ansteigen der Kupferzahl: natürliche Alterung von 36 Jahren gegenüber beschleunigter Alterung im Jahre 1937.

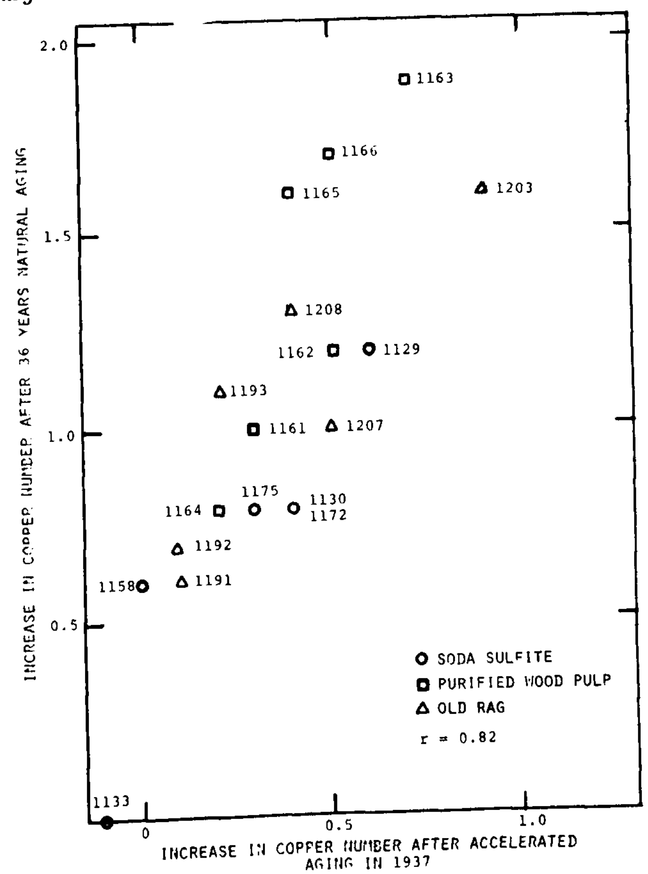


Table 6. Effect of 36 years of natural aging on the copper number of book papers made in NBS mill in 1937 compared with accelerated aging in 1937.
Table 6. Effet de 36 années de vieillissement naturel sur le taux de cuivre de papiers de librairie fabriqués à la papeterie NBS en 1937 comparé au vieillissement accéléré en 1937.
Tabelle 6. Auswirkung der 36 Jahre langen natürlichen Alterung auf die Kupferzahl der Buchpapiersorten, die 1937 von der NBS-Fabrik hergestellt worden sind, im Vergleich zu der beschleunigten Alterung von 1937.

Machine Run No.	Copper No. 1937	Copper No. 1973	S[1], Cu No. 1973 data	Change[2] After: 36 Years Natural Aging	Change[2] After: Accelerated Aging
1129	3.6	4.8	0.14	1.2	0.6
1130	3.6	4.4	0.05	0.8	0.4
1133	3.2	3.2	0.14	0.0	-0.1
1158	3.3	3.9	0.14	0.6	0.0
1172	3.4	4.2	0.17	0.8	0.4
1175	3.3	4.1	0.22	0.8	0.3
1161	0.8	1.8	0.05	1.0	0.3
1162	0.9	2.1	0.10	1.2	0.5
1163	0.9	2.8	0.07	1.9	0.7
1164	0.9	1.7	0.06	0.8	0.2
1165	0.8	2.4	0.07	1.6	0.4
1166	0.9	2.6	0.07	1.7	0.5
1191	0.3	0.9	0.04	0.6	0.1
1192	0.4	1.1	0.02	0.7	0.1
1193	0.5	1.6	0.12	1.1	0.2
1203	0.7	2.3	0.07	1.6	0.9
1207	0.5	1.5	0.07	1.0	0.5
1208	0.4	1.7	0.04	1.3	0.4

[1] Standard deviation. Five specimens for 1129, 1130, and 1133; 2 specimens for 1158; 4 for all others.
[2] Increase in analytical value.

3.2 *Methods Used in 1973*

Tests that were repeated in 1973 were made under the same conditions, as well as could be determined, as the tests in 1937. Wet tensile properties (paper thoroughly wetted before testing) were measured by TAPPI Method T 456.[20] Zero span tensile was measured using a commercial testing made especially for the purpose. In this test the jaws of the tensile tester actually touch at the beginning of the test, and the values are considered to be a function of fiber strength. Moisture regain (moisture content based on the dry weight of the

Table 7. Acidity (pH) and hydrogen ion concentration $[H^+]$ of TAPPI extract in 1937 and again in 1973 of book papers made in NBS mill in 1937.
Table 7. Acidité (pH) et concentration en ions hydrogène (H^+) d'extraits TAPPI effectués en 1937 et renouvelés en 1973 de papiers de librairie fabriqués à la papeterie NBS en 1937.
Tabelle 7. Azidität (pH) und Wasserstoffionenkonzentration (H^+) des TAPPI Extrakts im Jahre 1937 und im Jahre 1973 von Buchpapiersorten, die 1937 in der NBS-Fabrik hergestellt worden sind.

Machine Run No.	pH Cold Extract 1937	pH Cold Extract 1973	pH Hot Extract 1937	pH Hot Extract 1973	$[H^+] \times 10^{-7}$ calculated from extract pH, Cold Extract 1937	Cold Extract 1973	Cold Extract Change	Hot Extract 1937	Hot Extract 1973	Hot Extract Change
1129	4.9	4.5	4.3	4.1	126	316	190	501	794	293
1130	5.3	4.8	4.8	4.4	50	158	108	158	398	240
1133	6.9	5.3	6.4	5.1	1	50	49	4	79	75
1158	9.6	–	–	–	–	–	–	–	–	–
1172	8.9	8.4	–	9.0	–	–	–	–	–	–
1175	8.5	8.2	–	8.7	–	–	–	–	–	–
1161	6.1	5.0	5.7	4.8	8	100	92	20	158	138
1162	5.6	4.7	5.3	4.4	25	200	175	50	398	348
1163	5.2	4.6	4.5	4.1	63	251	188	316	794	478
1164	6.0	5.0	5.7	4.7	10	100	90	20	200	180
1165	5.6	4.6	5.0	4.2	25	251	226	100	631	531
1166	5.0	4.6	4.4	4.2	100	251	151	398	631	233
1191	6.8	6.3	–	6.2	2	5	3	–	6	–
1192	5.8	5.1	–	4.7	16	79	63	–	200	–
1193	5.1	4.9	–	4.4	79	126	47	–	398	–
1203	5.3	4.8	4.5	4.3	50	158	108	316	501	185
1207	5.2	4.9	–	4.5	63	126	63	–	316	–
1208	5.7	4.9	–	4.6	20	126	106	–	251	–

specimen) was determined at 50% relative humidity and 23°C.[21] Brightness (reflectance using a blue filter with peak transmittance at 457 nm) was determined by TAPPI Method T 452.[22]

3.3 *Statistical Treatment of Data*

The standard deviation, s, is a measure of dispersion of the data obtained for n measurements $(x_1, x_2, \ldots x_n)$ of the sample, and is estimated by means of the expression:

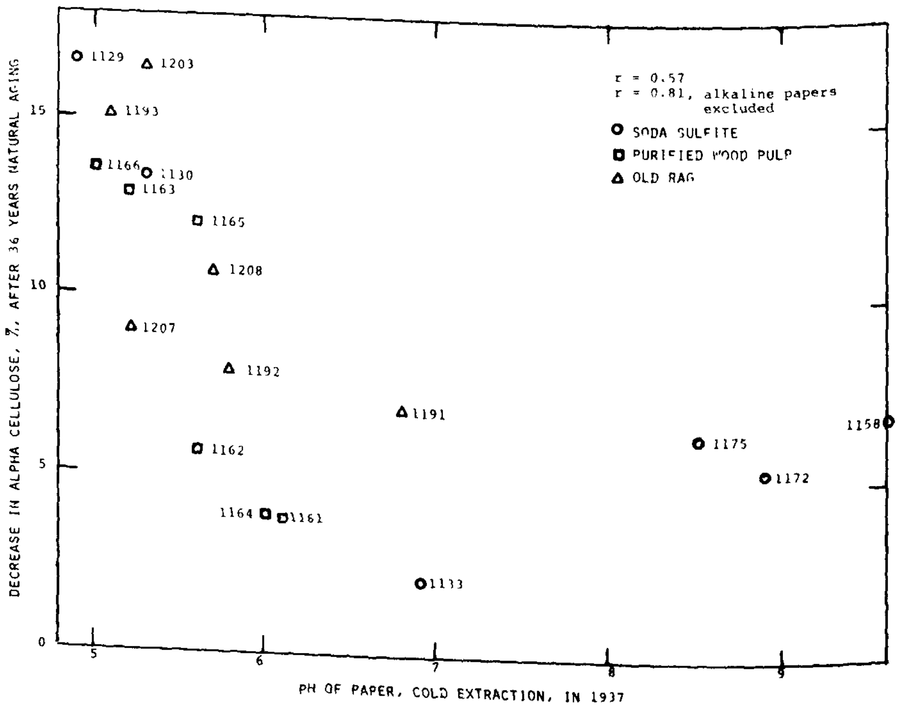
$$s = \sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}$$

Where $\bar{x}$ is the arithmetic mean of n measurements.

Figure 3. Decrease in alpha cellulose after 36 years natural aging as a function of pH, cold extraction, in 1937.

Figure 3. Baisse du taux d'alfacellulose après 36 années de vieillissement naturel en fonction du pH de l'extrait à froid en 1937.

Abb. 3. Absinken der Alpha-Zellulose nach 36 Jahren natürlicher Altarung als eine Funktion von pH, Kaltextraktion, im Jahre 1937.



Correlation coefficients were calculated according to the following formula:

$$r = \frac{\Sigma xy - \frac{\Sigma x \Sigma y}{N}}{\sqrt{\left(\Sigma x^2 - \frac{(\Sigma x)^2}{N}\right)\left(\Sigma y^2 - \frac{(\Sigma y)^2}{N}\right)}}$$

Where x and y are measurements from two sets of data, and $N = n_x + n_y$.

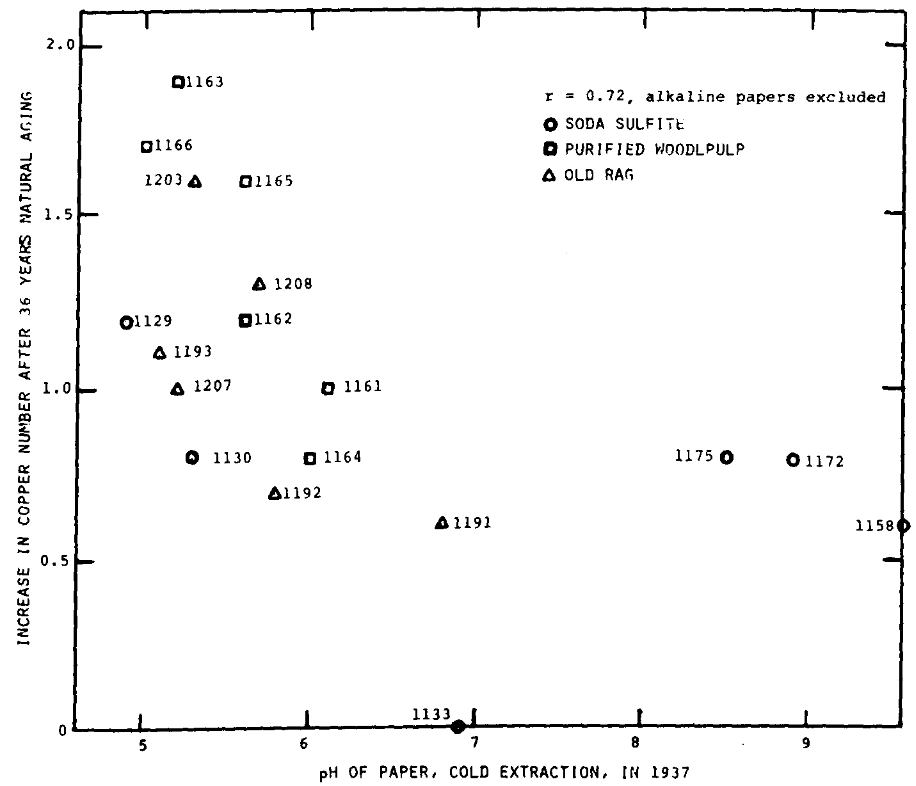
The slope m of the regression line was calculated from the formula:

$${}^{t}m = \frac{\Sigma xy - \frac{\Sigma x \Sigma y}{N}}{\Sigma x^2 - \frac{(\Sigma x)^2}{N}}$$

Figure 4. Increase in copper number after 36 years natural aging as a function of pH, cold extraction, in 1937.

Figure 4. Accroissement du taux de cuivre après 36 années de vieillissement naturel en fonction du pH de l'extrait à froid en 1937.

Abb. 4. Ansteigen der Kupferzahl nach 36 Jahren natürlicher Alterung als Funktion von pH, Kaltextraktion, im Jahre 1937.



A correlation coefficient is valid only if the data come from the same statistical population. The latter varies according to the test. For example, if thickness were the only important variable pertaining to a group of samples of paper, the thickness would determine statistical populations. Reflectance might vary enormously, but as long as thickness is maintained within allowable limits, the sample would be from a given statistical population. On the other hand, if the group of papers contained newsprint and a bond paper, introduction of this second variable would mean that there would be at least two statistical populations with respect to reflectance. In the set of 18 papers discussed in this report, there are three subsets with respect to fiber composition. Each subset usually

Table 8. Effect of 36 years of natural aging on the tensile strength of book papers made in NBS mill in 1937.
Table 8. Effet de 36 années de vieillissement naturel sur la résistance à la traction de papiers de librairie fabriqués à la papeterie NBS en 1937.
Tabelle 8. Auswirkung der 36 Jahre langen natürlichen Alterung auf die Zugfestigkeit von Buchpapiersorten, die 1937 in der NBS-Fabrik hergestellt worden sind.

Machine Run No.	Tensile Strength kg 1937		Tensile Strength kg 1973		Standard Deviation, kg[1] 1973 data		Retention of Tensile After Natural Aging, %			No. of Specimens
	MD	CD	MD	CD	MD	CD	MD	CD	Ave.	
1129	5.7	3.3	4.4	2.5	0.28	0.18	77	76	76	10
1130	5.5	3.7	4.7	2.9	0.29	0.09	85	78	82	10
1133	7.6	4.6	5.4	3.2	0.49	0.35	71	70	70	9
1158	5.3	3.1	5.1	2.9	0.49	0.00	96	93	95	4
1172	4.2	2.6	4.5	2.5	0.20	0.06	107	96	102	10
1175	5.0	3.3	5.1	3.1	0.33	0.23	102	94	98	10
1161	5.0	2.5	4.8	2.5	0.43	0.25	96	100	98	10
1162	4.8	2.6	4.9	2.6	0.47	0.14	102	100	101	10
1163	5.3	2.7	5.0	2.6	0.23	0.10	94	96	95	10
1164	5.2	2.6	5.0	2.8	0.47	0.10	96	108	102	10
1165	5.1	2.6	4.5	2.7	0.49	0.14	88	104	96	10
1166	5.3	2.5	4.2	2.4	0.23	0.17	79	96	88	10
1191	3.3	2.2	3.3	2.1	0.23	0.08	100	95	98	9
1192	3.2	2.2	3.2	2.1	0.31	0.07	100	95	98	10
1193	3.4	2.2	3.2	2.1	0.28	0.06	94	95	94	10
1203	3.0	2.2	3.2	2.1	0.16	0.09	107	95	101	10
1207	3.7	2.7	3.9	2.5	0.16	0.12	105	93	99	10
1208	3.1	2.2	3.2	2.1	0.19	0.12	103	96	100	10

[1] 1 kilogram force = 9.80665 newton.

can be treated as belonging to the same statistical population. In order to maintain a given statistical population, one or more papers must be eliminated with some tests, before the subset can be treated as a separate statistical entity. There is considerable scatter in most of the plots, possibly because several concurrent relationships result in deviation from a net straight-line relationship; without complete identification of all variables, straight-line relationships must be assumed in calculating correlation coefficients.

A complex situation undeniably exists with respect to interactions among the various physical and chemical properties of paper. Correlation coefficients are useful as a rough guide in identifying unusual situations, and indicating trends in the data.

Table 9. Effect of 36 years of natural aging on the elongation of book papers made in NBS mill in 1937.
Table 9. Effet de 36 années de vieillissement naturel sur l'élongation de papiers de librairie fabriqués à la papeterie NBS en 1937.
Tabelle 9. Auswirkung der 36 Jahre langen natürlichen Alterung auf die Dehnung von Buchpapiersorten, die 1937 in der NBS-Fabrik hergestellt worden sind.

Machine Run No.	Elongation, % 1937		Elongation, % 1973		Standard Deviation, % 1973 data		Retention of Elongation After Natural Aging, %			No. of Specimens
	MD	CD	MD	CD	MD	CD	MD	CD	Ave.	
1129	1.7	4.6	1.0	2.6	0.07	0.29	59	57	58	10
1130	1.8	5.0	1.2	3.2	0.08	0.32	67	64	66	10
1133	2.0	5.5	1.3	2.6	0.19	0.63	65	47	56	9
1158	3.0	5.0	1.5	5.0	0.25	0.29	50	100	75	4
1172	1.5	3.0	1.4	3.9	0.08	0.37	93	130	112	10
1175	1.0	4.5	1.4	4.7	0.11	0.66	140	104	122	10
1161	2.5	5.5	1.8	5.4	0.22	1.02	72	98	85	10
1162	2.0	5.5	1.5	5.1	0.25	0.56	75	93	84	10
1163	2.5	6.0	1.5	5.0	0.14	0.44	60	83	72	10
1164	2.5	6.0	1.7	5.8	0.22	0.50	68	97	83	10
1165	3.0	5.5	1.4	4.8	0.24	0.64	47	87	67	10
1166	3.0	6.0	1.4	4.7	0.12	0.69	47	78	62	10
1191	2.5	4.0	2.0	4.6	0.32	0.71	80	115	98	9
1192	2.0	4.0	1.9	3.8	0.16	0.42	95	95	95	10
1193	2.5	4.5	1.9	3.8	0.27	0.28	76	84	80	10
1203	2.5	4.5	1.9	3.6	0.13	0.32	76	80	78	10
1207	2.5	5.0	2.1	4.2	0.18	0.53	84	84	84	10
1208	2.5	5.0	2.1	4.2	0.22	0.26	84	84	84	10

3.4 *Sampling*

Sheets were selected at random from the supply of paper at hand to create the sample. Unfortunately, sample size frequently was limited and most of the available paper constituted the sample.

4. Results and Discussion

For convenience, original data are given in appropriate tables. Papermaking details on the papers, made in the NBS mill in 1937, that are included in this report, are given in Table 1. Chemical and physical test data obtained in 1937 are given in Tables 2 and 3, respectively. Data obtained in 1937 after accelerated aging for 72 hours at 100°C are given in Table 4.

Table 10. Folding endurance (MIT, 0.5 kg at 65% relative humidity), measured in 1937 and in 1973, of book papers made in NBS mill in 1937, and retention of fold after accelerated aging in 1937 for 72 hours at 100°C and after 36 years of natural aging.
Table 10. Résistance au pliage (MIT, 0,5 kg à 65% d'humidité relative) mesurée en 1937 et en 1973 de papiers de librairie fabriqués à la papeterie NBS en 1937 et rémanence du pli après un test de vieillissement accéléré effectué en 1937 pendant 72 heures à 100°C et après 36 années de vieillissement naturel.
Tabelle 10. Falzfestigkeit (MIT, 0,5 kg bei 65% relativer Feuchtigkeit), gemessen im Jahre 1937 und 1973, von Buchpapiersorten, die 1937 in der NBS-Fabrik hergestellt worden sind, und Beibehaltung des Falzes nach beschleunigter Alterung von 72 Stunden bei 100°C im Jahre 1937 und nach 36 Jahre langer natürlicher Alterung.

Machine Run No.	Folding Endurance 1937		Folding Endurance 1973		Standard Deviation 1973 data		Retention of Fold After Natural Aging, %			Retention of Fold After Accelerated Aging in 1937, %
	MD	CD	MD	CD	MD	CD	MD	CD	Ave.	Ave.
1129	599	140	26	23	9	7	4	16	10	19
1130	548	423	92	56	34	18	17	13	15	56
1133	2828	1228	2446	1158	911	380	94	87	90	69
1158	644	150	387	104	134	26	60	69	64	77
1172	251	122	121	75	39	25	48	61	55	55
1175	445	135	311	135	163	52	70	100	85	75
1161	2270	474	2720	526	967	299	120	111	115	108
1162	1734	428	1130	291	794	212	65	68	66	97
1163	2328	536	570	154	201	45	24	28	26	81
1164	3506	487	2490	315	1410	160	71	65	68	93
1165	2480	592	347	305	159	105	14	51	33	95
1166	2646	696	306	151	135	42	12	22	17	62
1191	71	55	62	44	20	8	87	80	84	114
1192	66	48	55	35	16	4	83	73	78	114
1193	76	53	45	27	10	5	59	51	55	95
1203	64	37	35	21	7	3	55	57	56	100
1207	217	113	148	68	28	14	68	60	64	96
1208	94	47	62	36	18	4	66	77	72	107

Data on the effect of natural aging on alpha cellulose, copper number, acidity, tensile strength, elongation, folding endurance, and internal tearing resistance are given in Tables 5, 6, 7, 8, 9, 10 and 11, respectively. Summaries of retention of various chemical and physical properties after 36 years of natural aging and after accelerated aging are given in Tables 12 and 13, respectively.

Table 11. Internal tearing resistance, measured in 1937 and again in 1973, of book papers made in NBS mill in 1937, and retention of tear after accelerated aging for 72 hours at 100°C in 1937 and after 36 years of natural aging.
Table 11. Résistance interne au déchirement mesurée en 1937 et en 1973 de papiers de librairie fabriqués à la papeterie NBS en 1937 et rémanence au déchirement après un test de vieillissement accéléré de 72 heures à 100°C en 1937 et après 36 années de vieillissement naturel.
Tabelle 11. Innere Reissfestigkeit, gemessen im Jahre 1937 und 1973, von Buchpapiersorten, die 1937 in der NBS-Fabrik hergestellt worden sind, und Beibehaltung der Reissfestigkeit nach beschleunigter Alterung im Jahre 1937 (72 Stunden bei 100°C) und nach 36 Jahre langer natürlicher Alterung.

Machine Run No.	Tearing Resistance 1937	Tearing Resistance 1973[1]	Retention of Tearing Resistance, %, after 36 Years Natural Aging	Retention of Tearing Resistance, %, after Accelerated Aging
	MD	MD	MD	Ave. MD & CD
1129	46	20	43	58
1130	48	25	52	80
1133	55	29	53	80
1158	51	–	–	92
1172	50	38	76	91
1175	45	34	76	93
1161	82	49	60	90
1162	79	44	56	90
1163	77	35	45	80
1164	79	45	57	91
1165	83	33	40	80
1166	75	29	39	74
1191	55	–	–	97
1192	57	38	67	92
1193	56	32	57	90
1203	54	31	57	91
1207	60	41	68	91
1208	54	35	65	94

[1] No standard deviation is reported because all available plies of a given paper were torn together in a single test.

Zero span tensile and moisture regain are given in Table 14, and data on wet tensile properties in Table 15. Brightness data are given in Table 16.

As the original data on individual specimens are no longer available, it is not possible to calculate standard deviations for the data obtained in 1937. However, some data are available showing that standard deviations for aged and unaged papers are not appreciably different.[23,24] Correlations among various properties are given in Tables 17–21.

Table 12. Summary of changes in various chemical properties of book papers made in NBS mill in 1937 after 36 years natural aging and after accelerated aging for 72 hours at 100°C in 1937.
Table 12. Résumé des changements intervenus dans diverses propriétés chimiques de papiers de librairie fabriqués à la papeterie NBS en 1937 après 36 années de vieillissement naturel et après un test de vieillissement accéléré de 72 heures à 100°C effectué en 1937.
Tabelle 12. Zusammenfassung der Veränderungen der verschiedenen chemischen Eigenschaften von den Buchpapiersorten, die 1937 von der NBS-Fabrik hergestellt worden sind, nach 36 Jahren natürlicher Alterung und nach beschleunigter Alterung von 72 Stunden bei 100°C im Jahre 1937.

Machine Run No.	Natural Aging, 36 Years				Accelerated Aging in 1937	
	Increase in [H$^+$] Cold	Increase in [H$^+$] Hot	Alpha Cellulose, Decrease	Copper Number, Increase	Alpha Cellulose, Decrease	Copper Number, Increase
1129	190	293	16.7	1.2	7.6	0.6
1130	108	240	13.4	0.8	3.3	0.4
1133	49	75	2.2	0.0	+0.1	-0.1
1158	–	–	6.9	0.6	0.4	0.0
1172	–	–	5.4	0.8	2.1	0.4
1175	–	–	6.4	0.8	3.3	0.3
1161	92	138	3.9	1.0	0.8	0.3
1162	175	348	5.8	1.2	3.6	0.5
1163	188	478	12.9	1.9	4.6	0.7
1164	90	180	4.0	0.8	1.8	0.2
1165	226	531	12.1	1.6	2.9	0.4
1166	151	233	13.6	1.7	5.0	0.5
1191	3	–	7.0	0.6	3.1	0.1
1192	63	–	8.0	0.7	3.0	0.1
1193	47	–	15.1	1.1	8.1	0.2
1203	108	185	16.5	1.6	9.6	0.9
1207	63	–	9.1	1.0	4.4	0.5
1208	106	–	10.7	1.3	3.7	0.4

Data in Tables 4–6 are plotted in Figures 1 and 2. Few of the correlations given in Table 17 show a close and direct relationship between the extent of changes in alpha cellulose and copper number after accelerated aging and natural aging. The correlations are calculated for the collection of 18 papers and also for subsets of papers. The subsets usually show higher correlations than the correlations for the complete set of 18 papers. This suggests that either the number of samples is less than adequate to provide a valid statistical population or the accelerated aging method used in 1937 does not fully simulate natural aging, or both. However, the fact that changes in alpha cellulose and in

Table 13. Summary of retention, %, of various properties of book papers made in NBS mill in 1937 after 36 years of natural aging and after accelerated aging in 1937.
Table 13. Résumé de la rémanence en % des diverses propriétés de papiers de librairie fabriqués à la papeterie NBS en 1937 après 36 années de vieillissement naturel et après un test de vieillissement accéléré effectué en 1937.
Tabelle 13. Zusammenfassung der Beibehaltung in % von verschiedenen Eigenschaften der Buchpapiersorten, die 1937 in der NBS-Fabrik hergestellt worden sind, nach 36 Jahre langer natürlicher Alterung und nach beschleunigter Alterung im Jahre 1937.

Machine Run No.	Natural Aging Fold	Natural Aging Tear	Natural Aging Tensile	Elongation	Accelerated Aging Fold	Accelerated Aging Tear
	Ave.	MD	Ave.	Ave.	Ave.	MD
1129	10	43	76	58	19	58
1130	15	52	82	66	56	80
1133	90	53	70	56	69	80
1158	64	–	95	75	77	92
1172	55	76	102	111	55	91
1175	85	76	98	122	75	93
1161	115	60	98	85	108	90
1162	66	56	101	84	97	90
1163	26	45	95	72	81	80
1164	68	57	102	83	93	91
1165	33	40	96	67	95	80
1166	17	39	88	62	62	74
1191	84	–	98	98	114	97
1192	78	67	98	95	114	92
1193	55	57	94	80	95	90
1203	56	57	101	78	100	91
1207	64	68	99	84	96	91
1208	72	65	100	84	107	94

copper number follow the same trends is reasonable evidence that these are suitable chemical tests for aging.

Figures 1 and 2 show that the decreases in alpha cellulose and increases in copper number are much greater during 36 years of natural aging than during three days of aging at 100°C. It is undesirable to calculate the number of years of natural aging that is equivalent to three days of oven aging at 100°C. These values inevitably would be quoted out of context, and they differ with different tests.

The slopes of the subsets of papers in Table 17 show considerable variation. From this it is obvious that these subsets do not belong to the same statistical population. The slope of the straight line from regression analysis is a result of

Figure 5. Retention of fold: natural aging for 36 years vs. accelerated aging in 1937.
Figure 5. Rémanence du pliage: vieillissement naturel pendant 36 années contre vieillissement accéléré en 1937.
Abb. 5. Bewahrung der Falzfestigkeit: natürliche Alterung von 36 Jahren gegenüber beschleunigter Alterung im Jahre 1937.

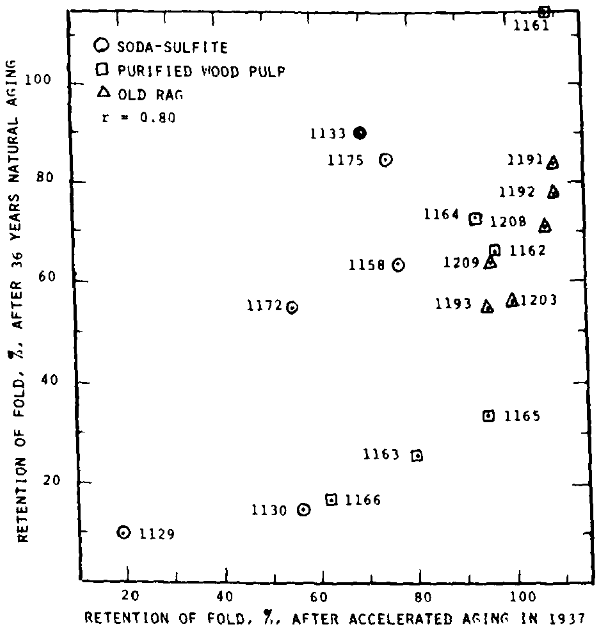


Figure 6. Retention of fold after 36 years natural aging as a function of pH, cold extraction, in 1937.
Figure 6. Rémanence du pliage après 36 années de vieillissement naturel en fonction du pH de l'extrait à froid en 1937.
Abb. 6. Bewahrung der Falzfestigkeit nach 36 Jahren natürlicher Alterung als funktion von pH, Kaltextraktion, im Jahre 1937.

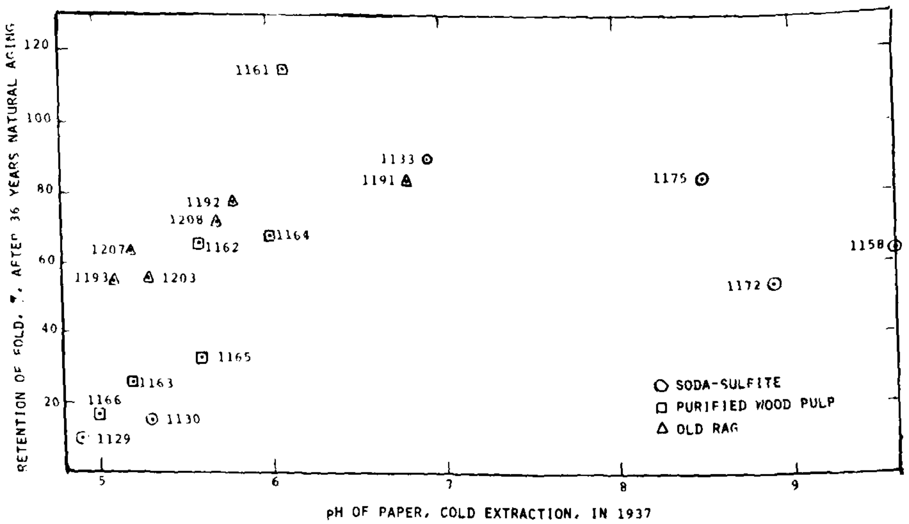


Table 14. Zero span breaking length and moisture regain of book papers made in NBS mill in 1937 after 36 years of natural aging.
Table 14. Allongement à la rupture à tension nulle et réhumidification de papiers de librarie fabriqués à la papeterie NBS en 1937 après 36 années de vieillissement naturel.
Tabelle 14. Null-Spannung-Reisslänge und Feuchtigkeitswiedergewinnung von Buchpapiersorten, die 1937 in der NBS-Fabrik hergestellt worden sind, nach 36 Jahre langer natürlicher Alterung.

Machine Run No.	Measured Zero Span Breaking Length		Standard Deviation		Fiber Component of Paper	Zero Span Breaking Length Corrected to 100% Fiber Component		Moisture Regain Corrected to 100% Fiber Component
	km		km		%	km		%
	MD	CD	MD	CD		MD	CD	
1129	8.36	6.00	0.39	0.23	88.3	9.47	6.80	6.22
1130	8.97	6.98	0.58	0.27	89.5	10.02	7.80	6.30
1133	11.61	8.81	0.72	0.27	99.7	11.64	8.84	6.89
1158	10.84	7.24	0.49	0.34	91.2	11.89	7.94	6.36
1172	10.56	7.71	0.66	0.40	87.7	12.04	8.79	6.45
1175	11.02	8.28	0.73	0.34	88.7	12.42	9.33	6.45
1161	11.33	7.71	1.13	0.43	87.8	12.90	8.78	6.26
1162	11.55	7.60	0.55	0.61	87.6	13.18	8.68	6.26
1163	10.34	6.79	0.64	0.42	88.4	11.70	7.68	6.09
1164	11.39	7.98	0.85	0.42	88.5	12.87	9.02	5.91
1165	10.22	7.36	0.68	0.43	87.6	11.67	8.40	5.90
1166	8.44	6.54	0.51	0.36	88.3	9.56	7.41	6.00
1191	10.10	7.77	0.66	0.35	85.5	11.81	9.09	5.27
1192	9.12	7.56	0.44	0.32	85.7	10.64	8.82	5.33
1193	8.76	6.43	0.47	0.28	85.7	10.22	7.50	5.26
1203	8.50	6.49	0.60	0.33	86.0	9.88	7.55	5.23
1207	14.62	10.93	0.68	0.68	95.0	15.39	11.51	5.29
1208	13.30	10.22	0.42	0.39	86.7	13.34	11.79	5.27

finding the best linear fit for a set of points that may not be on a straight line. Consequently, cold pH is poorly correlated with changes in alpha cellulose and copper number, after either accelerated aging or natural aging. Again, correlations are observed in the subsets with the exception of the correlation between pH and copper number for the soda-sulfite subset. The pH of paper has been used for years as a rough guide to stability.

The relationship between cold extract pH and changes in alpha cellulose and copper number after 36 years natural aging are plotted in Figures 3 and 4. It is obvious that a good straight line relationship does not exist but an overall trend is evident.

Table 15. Wet tensile properties of book papers made in NBS mill 1937.
Table 15. Propriétés élastiques de papiers de librairie fabriqués à la papeterie NBS en 1937.
Tabelle 15. Dehnungseigenschaften von Buchpapiersorten im nassen Zustand, die 1937 von der NBS-Fabrik hergestellt worden sind.

Machine Run No.	Breaking Load g		Std. Deviation of Break g		Elongation at Break %		Std. Deviation of Elongation %		Energy at Break g-cm		Std. Deviation of Energy g-cm		Extensional Stiffness kg		Std. Deviation of Stiffness kg		Wet Breaking Load as % of Dry Breaking Load		No. of Specimens
	MD	CD	MD	CD	MD	CD	MD	CD	MD	CD	MD	CD	MD	CD	MD	CD	MD	CD	
1129	460	258	53	18	0.6	2.4	0.07	0.44	17	44	3.4	9.9	132	35	24	4	10.5	10.3	10
1130	465	270	54	11	0.7	2.4	0.04	0.47	22	52	3.8	7.2	123	36	18	8	9.9	9.3	10
1133	311	192	31	13	0.8	1.7	0.10	0.23	14	20	3.8	4.5	73	24	9	3	5.8	6.0	8
1158	341	179	17	11	0.8	2.3	0.08	0.18	16	31	2.7	4.2	93	23	17	4	6.7	6.2	9
1172	274	162	32	15	0.7	2.2	0.10	0.40	20	27	4.5	6.9	77	21	13	2	6.1	6.5	10
1175	439	198	44	16	0.8	2.4	0.11	0.33	22	36	5.2	6.8	120	28	18	3	8.6	6.4	10
1161	475	214	64	23	1.1	3.2	0.08	0.37	32	49	6.3	9.9	98	23	16	5	9.9	8.6	10
1162	656	287	61	13	1.1	3.6	0.11	0.41	49	77	7.1	12.3	130	34	15	4	13.4	11.0	10
1163	745	330	93	32	1.2	3.9	0.17	0.39	59	91	16.9	14.9	138	31	14	7	14.9	12.7	10
1164	503	241	34	27	1.0	3.5	0.11	0.33	33	60	3.1	9.3	103	22	10	5	10.0	8.6	10
1165	590	278	47	15	1.0	3.6	0.11	0.27	40	73	6.5	7.4	131	31	17	3	13.1	10.3	10
1166	623	273	32	15	1.1	3.7	0.10	0.45	45	69	4.9	11.2	127	27	16	3	14.8	11.4	10
1191	261	161	29	14	0.9	1.9	0.16	0.27	17	23	4.1	4.5	61	24	6	5	7.9	7.7	9
1192	317	203	15	17	1.1	2.3	0.10	0.28	25	34	3.5	7.0	60	24	7	3	9.9	9.7	10
1193	377	234	27	8	1.2	2.6	0.12	0.17	32	43	4.1	4.7	77	29	7	4	11.8	11.1	10
1203	404	249	32	12	1.3	2.9	0.14	0.14	38	53	5.8	3.1	84	32	10	4	12.6	11.9	10
1207	414	244	17	9	1.2	2.7	0.14	0.18	35	50	4.9	5.9	86	34	9	3	10.6	9.8	10
1208	332	199	24	14	1.2	2.4	0.11	0.42	29	35	4.1	8.2	70	26	9	5	10.4	9.5	10

Table 16. Brightness of NBS mill papers after 36 years of natural aging.
Table 16. Brillance de papiers NBS après 36 années de vieillissement naturel.
Tabelle 16. Helligkeit der Papiersorten, die von der NBS-Fabrik hergestellt worden sind, nach 36 Jahre langer natürlicher Alterung.

Machine Run No.	Brightness %	Standard Deviation[1]
1129	60.9	1.6
1130	61.0	2.9
1133	60.0	0.9
1158	67.1	1.7
1172	67.1	0.42
1175	60.8	0.85
1161	72.4	2.8
1162	73.7	2.0
1163	71.2	1.3
1164	75.6	1.0
1165	74.3	2.5
1166	74.1	1.4
1191	79.7	0.49
1192	80.2	1.9
1193	80.2	0.6
1203	73.5	0.9
1207	78.6	0.5
1208	78.9	0.7

[1] Ten specimens.

It is not surprising that an alkali solubility test appears to be useful in evaluating the stability of paper. Alkali solubility is a measure of the short-chain material that goes into solution during the test. The amount of carbohydrate material dissolving depends, among other things, on the strength of alkali and on whether the chain break occurs near enough to the end of a chain for the fragment to become soluble. Any alkali solubility test is largely empirical.

By today's standards, these tests are considered to be archaic. Alpha cellulose[25] has been supplanted by other more convenient and supposedly more meaningful alkali solubility tests. The copper number test[26] is not widely used. Copper numbers are proportional to aldehyde content for specific types of oxidation, but the slopes of the lines relating copper number to oxidation level varies with the location of the aldehyde group in the anhydroglucose ring.[27] In addition, the copper number reagent causes further degradation of alkali sensitive cellulose during the copper number test.

Table 17. Correlation of changes in alpha cellulose and copper number due to natural aging with (1) changes due to accelerated aging and (2) pH, cold extraction, of papers in 1937.
Table 17. Coefficients de corrélation des changements du taux d'alfacellulose et des taux de de cuivre dus au vieillissement naturel et 1) des changements dus au vieillissement accéléré, 2) du pH de l'extrait à froid de papiers mesurés en 1937.
Tabelle 17. Korrelation der Veränderungen in der Alpha-Zellulose und der Kupferzahl auf Grund der natürlichen Alterung mit (1) Veränderungen auf Grund der beschleunigten Alterung und (2) pH, Kaltextraktion, von Papier im Jahre 1937.

Correlation Variables	Papers Included in Calculations	r, Correlation Coefficients	m, Slope
X alpha-natural aging	all	0.86	0.49
Y alpha-accelerated aging	soda-sulfite	.88	.45
	purified sulfite	.82	.29
	rag	.97	.70
X alpha-natural aging	all	−0.57	−0.18
Y pH, cold, 1937	all except alkaline	−0.81	−0.10
	soda-sulfite	−0.70	−0.26
	soda-sulfite: 1129, 1130, 1133	−0.99	−0.14
	purified sulfite	−0.89	−0.08
	rag	−0.69	−0.11
X copper no.-natural	all	0.82	0.44
Y copper no.-accelerated	soda-sulfite	0.91	0.62
	purified sulfite	0.86	0.35
	rag	0.87	0.72
X copper no.-natural	all	−0.55	−1.67
Y pH, cold, 1937	all except alkaline	−0.72	−0.90
	soda-sulfite	−0.28	−1.37
	purified sulfite	−0.88	−0.88
	rag	−0.64	−1.07

Tensile strength

Tensile strength is not a particularly sensitive method for detecting changes in paper after natural aging. This is what one would expect from an examination of load elongation curves for unaged and aged papers. Until the reduction in elongation reaches the yield point, most of the deterioration shows up as a reduction in elongation. An examination of the data in Tables 8 and 9 shows that the retention of elongation with natural aging is appreciably lower than the

Table 18. Correlation of retention of folding endurance after 36 years natural aging with (1) retention of folding endurance after accelerated aging, (2) pH, cold extraction, of papers in 1937, (3) retention of folding endurance as a function of alum added, percent, minus rosin retained, percent, and (4) retention of elongation after natural aging.
Table 18. Coefficients de corrélation de la rémanence de la résistance au pliage après 36 années de vieillissement naturel et de 1) la rémanence de résistance au pliage après un test de vieillissement accéléré, 2) pH de l'extrait à froid de papiers en 1937, 3) rémanence de la résistance du pliage en fonction de l'alun ajouté, du pourcentage déduction faite de la collophane retenue, du pourcentage et 4) de l'élongation après vieillissement naturel.
Tabelle 18. Korrelation der Bewahrung der Falzfestigkeit nach 36 Jahre langer natürlicher Alterung mit (1) Bewahrung der Falzfestigkeit nach beschleunigter Alterung, (2) pH, Kaltextraktion, der Papiersorten von 1937, (3) Bewahrung der Falzfestigkeit als eine Funktion des zugesetzten Alauns in Prozent, minus verbliebenes Harz in Prozent und (4) Bewahrung der Dehnung nach natürlicher Alterung.

Correlation Variables	Papers Included in Calculations	r, Correlation Coefficients	m, Slope
X fold retention after natural aging	all	0.63	0.54
Y fold retention after accelerated aging	all except alkaline	0.71	0.60
	all except 1129 and alkaline	0.65	0.41
	soda-sulfite	0.79	0.50
	purified sulfite	0.83	0.36
	rag	0.92	0.67
X fold retention after natural aging	all	0.41	0.02
Y pH, cold, 1937	all except alkaline	0.75	0.01
	soda sulfite	0.69	0.04
	purified sulfite	0.88	0.01
	rag	0.89	0.05
X fold retention after natural aging	all	−0.50	−0.02
Y alum added, %, minus rosin retained, %	soda sulfite: 1129, 1130, 1133	−0.98	−0.02
	purified sulfite	−0.82	−0.02
	rag	−0.73	−0.05
X retention of fold after natural aging	all	0.52	0.31
Y retention of elongation after natural aging	soda sulfite	0.40	0.33
	purified sulfite	0.87	0.23
	rag	0.95	0.65

retention of tensile strength. This is generally true of polymers, and cellulose acetate is a specific example.[28]

The three alkaline soda-sulfite papers, 1158, 1172, and 1175, show good, but

Figure 7. Retention of fold after 36 years natural aging as a function of alum and rosin added during manufacture.

Figure 7. Rémanence du pliage après 36 années de vieillissement naturel en fonction du taux d'alun et de collophane ajouté durant la fabrication.

Abb. 7. Bewahrung der Falzfestigkeit nach 36 Jahren natürlicher Alterung als Funktion des während der Produktion zugesetzten Alauns und Harzes.

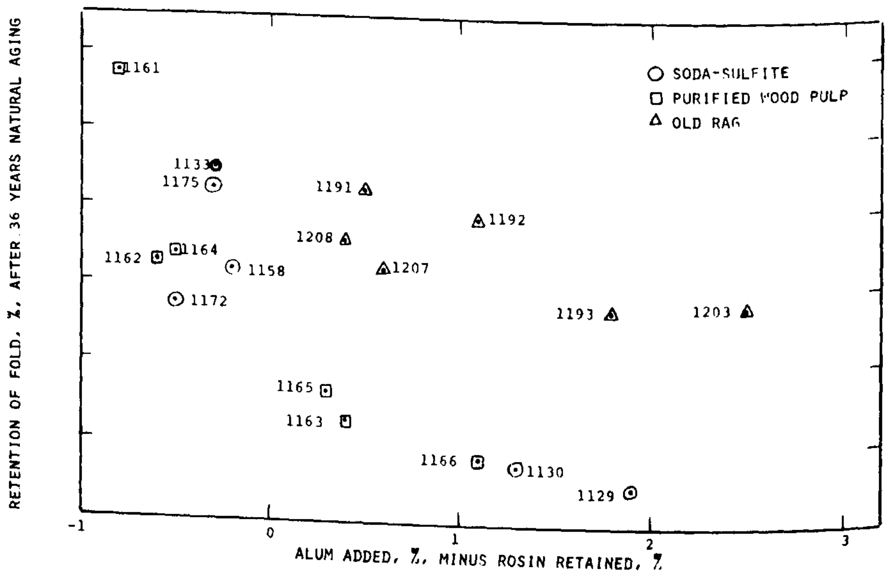


Figure 8. Retention of internal tear: natural aging for 36 years vs. accelerated aging.

Figure 8. Rémanence du déchirement interne: vieillissement naturel pendant 36 ans contre vieillissement accéléré.

Abb. 8. Bewahrung der inneren Reissfestigkeit: natürliche Alterung von 36 Jahren gegenüber beschleunigter Alterung.

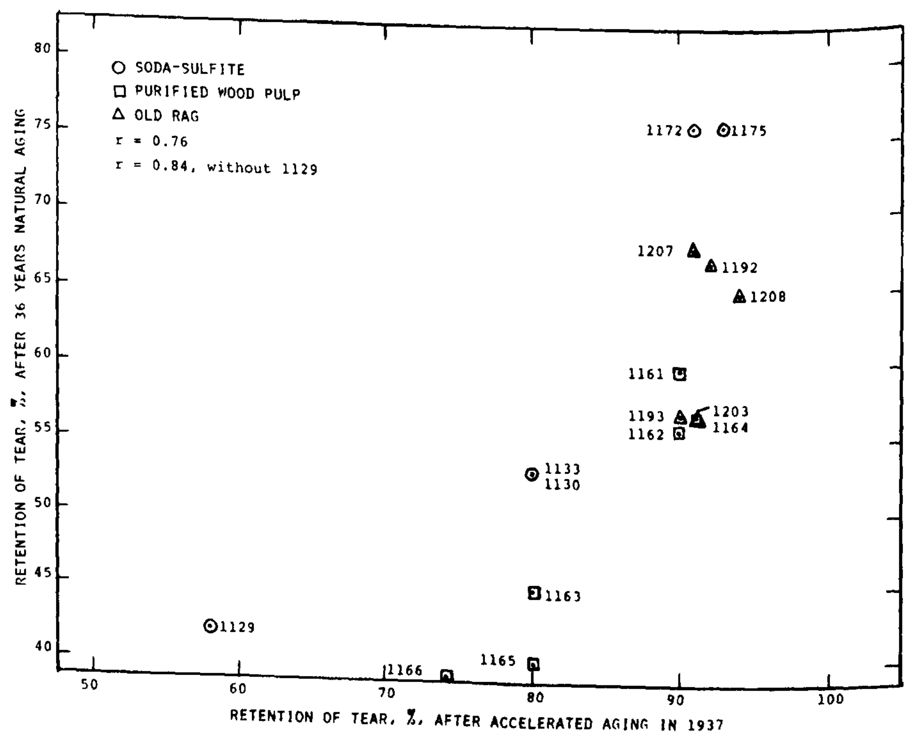


Table 19. Correlation of retention of internal tear after 36 years natural aging with (1) retention of internal tear after accelerated aging and (2) pH, cold extraction, of papers in 1937.

Table 19. Coefficients de corrélation de la rémanence au déchirement interne après 36 années de vieillissement naturel intervenant avec 1) la rémanence du déchirement interne après un test de vieillissement accéléré et 2) le pH de l'extrait à froid de papiers en 1937.

Tabelle 19. Korrelation der Bewahrung der inneren Reissfestigkeit nach 36 Jahre langer natürlicher Alterung mit (1) Bewahrung der inneren Reissfestigkeit nach beschleunigter Alterung und (2) pH, Kaltextraktion der Papiersorten im Jahre 1937.

Correlation Variables	Papers Included in Calculations	r, Correlation Coefficients	m, Slope
X tear retention after natural aging	all[1] except 1158 and 1191	0.76	0.62
Y tear retention after accelerated aging	all except 1158, 1191, and 1129	0.84	0.47
	soda-sulfite except 1158	0.90	0.83
	purified sulfite	0.96	0.73
	rag except 1191	0.51	0.14
X tear retention after natural aging	all except 1158 and 1191	0.68	0.07
Y pH, cold, 1937	soda-sulfite except 1158	0.95	0.11
	purified sulfite	0.82	0.04
	rag except 1191	0.54	0.03
X tear retention, MD, after natural aging	all except 1158	0.88	1.69
Y retention of elongation, MD, after natural aging	soda-sulfite except 1158	0.86	1.90
	purified sulfite	0.95	1.27
	rag except 1191	0.82	1.19

[1] No sample available for 1158 and 1191.

not outstanding, retention of tensile strength, when compared with the other 15 papers. The three acid soda-sulfite papers, 1129, 1130, and 1133, exhibit comparatively poor tensile retention (70–85%, MD). With the exception of 1166 (79%, MD) all of the other papers show retention values of 94% or above. Number 1133 is a very slightly acid, waterleaf, short-fibered paper. As the fiber strength did not deteriorate (shown later), the bonding must have deteriorated with time.

Elongation

The data on elongation after natural aging in Table 9 might be more valuable if data on retention of elongation after accelerated aging were available. Several correlations of changes in elongation with natural aging are discussed in con-

Table 20. Correlation of (1) zero span tensile, MD, and (2) retention of elongation, ave., with pH, cold extraction, of papers in 1937.
Table 20. Coefficients de corrélation de l'élasticité à tension nulle, MD et 2) rémanence de l'élongation, moyenne avec le pH de l'extrait à froid de papiers en 1937.
Tabelle 20. Korrelation der (1) Null-Spannung, MD und (2) Bewahrung der Dehnung, ave., mit pH, Kaltextraktion von Papiersorten im Jahre 1937.

Correlation Variables	Papers Included in Calculations	r, Correlation Coefficient	m, Slope
X zero span tensile, MD Y pH, cold, 1937	all	0.22	0.20
	all except 1207 and 1208	0.48	0.57
	soda-sulfite	0.91	1.48
	purified sulfite	0.82	0.26
	rag	–0.02	–0.01
	rag except 1207 and 1208	0.96	0.87
X elongation retention after natural aging Y pH, cold, 1937	all	0.53	0.04
	soda sulfite	0.65	0.04
	purified sulfite	0.81	0.04
	rag	0.86	0.07

nection with other tests. Correlations of retention of elongation with cold pH are given in Table 20. Although the correlation for all 18 papers is low, the correlation coefficients for the three subsets are somewhat higher. Elongation is a fairly sensitive measure of the degradation of polymeric materials, but this was not generally recognized when the original testing was done on these papers.

Folding endurance

Data on folding endurance in Table 10 are not as useful as they might be because of the high standard deviations. More specimens would have been desirable but sufficient samples were not available. Data on retention of folding endurance after natural aging against retention of fold after accelerated aging in 1937 are plotted in Figure 5. The correlation coefficients in Table 18 for the subsets are fairly good, but not for the group of 18 papers. Differences in slopes indicate that the subsets belong to different statistical populations.

Retention of fold after natural aging as a function of cold extract pH is plotted in Figure 6 and retention of fold after natural aging as a function of alum and rosin added during manufacture is plotted in Figure 7. Correlation coefficients in Table 18 show that correlations for the subsets are much higher

Table 21. Correlation of wet tensile properties with pH, cold extraction, in 1937.
Table 21. Coefficients de corrélation des propriétés élastiques à l'état humide et du pH de l'extrait à froid en 1937.
Tabelle 21. Korrelation von Dehnungseigenschaften im nassen Zustand mit pH, Kaltextraktion im Jahre 1937.

Correlation Variables	Papers Included in Calculations	r, Correlation Coefficient	m, Slope
X WBL as % of DBL, MD Y pH, cold, 1937	all	–0.75	–0.39
	all except alkaline	–0.74	–0.18
	soda-sulfite	–0.72	–0.70
	soda-sulfite: 1129, 1130, 1133	–0.99	–0.41
	purified sulfite	–0.96	–0.16
	rag	–0.90	–0.35
X wet energy at break, CD Y pH, cold, 1937	all	–0.56	–0.04
	all except alkaline	–0.56	–0.02
	soda sulfite	–0.62	–0.10
	purified sulfite	–0.72	–0.02
	rag	–0.89	–0.05
X wet extensional stiffness, MD Y pH, cold, 1937	all	–0.26	–0.01
	all except alkaline	–0.54	–0.01
	soda-sulfite	–0.57	–0.04
	1129, 1130, 1133	–0.99	–0.03
	purified sulfite	–0.82	–0.02
	rag	–0.79	–0.04

than correlations for the set of 18 papers. The fiber lengths and the chemistry of the three paper subsets are quite different, so the three subsets could be expected to react differently.

Correlations in the paper subsets of fold retention as function of alum added minus rosin retained are surprisingly good for the soda-sulfite papers, but not so good for purified sulfite and rag. During manufacture, rosin size was added first and alum was added later to precipitate the rosin size onto the fibers. One would expect that carboxyl groups in the cellulose would not have an opportunity to interact with aluminum until the rosin size had reacted and an excess of alum was available. The reactions of alum with rosin size and with carboxyl groups in cellulose are quite complex and probably nonstoichiometric. Subtracting the weight of rosin from the weight of alum is hardly a stoichiometric approach, but without information on the composition of the rosin size

Table 22. Arbitrary definitions of stable papers based on 1937 data compared with retention of properties in 1973.
Table 22. Définitions arbitraires de papiers stables basées sur des données de 1937 comparées au maintien de ces propriétés en 1973.

Arbitrary definitions of stable papers based on pH, cold extraction, and changes[1] in properties after *accelerated aging* in 1937

Machine Run No.	pH >5.5	pH >6.0	pH >5.5 Alpha <4.0 Fold >80	pH>6.0 Alpha <4.0 Fold >80	Retentions[2] Σ	Rank
1129					131	18
1130					258	14
1133	1133	1133	1133	1133	349	5
1158	1158	1158			365	2
1172	1172	1172			280	12
1175	1175	1175			301	8
1161	1161	1161	1161	1161	357	4
1162	1162		1162		294	10
1163					235	15
1164	1164	1164	1164	1164	343	6
1165	1165		1165		300	9
1166					229	16
1191	1191	1191	1191	1191	368	1
1192	1192		1192		364	3
1193					279	13
1203					191	17
1207					286	11
1208	1208		1208		318	7

[1] Decrease in alpha cellulose, increase in copper number, percent retention of tear, and percent retention of fold.

[2] Retentions for alpha cellulose, copper number, fold, and tear were totaled to obtain Σ of retentions. The correlation coefficient of the ranks of the summations is 0.79. Retentions for alpha cellulose and copper number were obtained by expressing maximum change as zero percent retention, no change as 100 percent retention, and normalizing the changes between these extremes.

precipitate (highly variable), metals on the carboxyls, composition of the natural resins in the pulp, and ratio of free rosin size to rosin sodium salt in the size solution, nothing more is warranted.

The pulps used in preparing the alkaline filled papers first were sized (except

Tabelle 22. Arbiträre Definitionen von stabilen Papiersorten auf der Grundlage von Daten von 1937 im Vergleich zur Beibehaltung der Eigenschaften im Jahre 1973.

Arbitrary definitions of stable papers based on changes[1] in properties after 36 years of *natural aging*

Tear >50% Fold >50%	Tear >50% Fold >70%	Tear >50% Fold >80%	Tear >50% Fold >50% Alpha <10%	Tear >50% Fold >50% Alpha <7.5	Retentions[2] Σ	Rank
					90	17
					145	13
1133	1133	1133	1133	1133	330	1
1158[3]			1158[3]	1158[3]	255	8
1172			1172	1172	262	5
1175	1175	1175	1175	1175	283	4
1161	1161	1161	1161	1161	299	2
1162			1162	1162	224	10
					94	16
1164			1164	1164	259	7
					117	15
					86	18
1191[3]	1191[3]	1191[3]	1191[3]	1191[3]	294	3
1192	1192		1192		260	6
1193					164	12
1203					130	14
1207			1207		225	9
1208					205	11

[3] Tear data not available in 1973, but retention *assumed* to be same as for fold: 1158, 64%, 1191, 84%.

1158, which has no sizing) with rosin and alum before calcium carbonate was added. None of the three alkaline papers shows outstanding retention of fold, either after natural aging (55–85%) or after accelerated aging (55–75%). Several papers showed much better retention of fold after accelerated aging in 1937 than the three alkaline papers. After natural aging the three alkaline papers, as a group, are good, but not outstanding. Number 1161 shows 115% retention of fold after natural aging. Number 1191 also shows up well in both accelerated and natural aging. Both of these papers are almost neutral, although small quantities of alum and rosin were used during manufacture.

Figure 9. Retention of internal tear after 36 years antural aging as a function of pH, cold extraction, in 1937.

Figure 9. Rémanence du déchirement interne après 36 années de vieillissement naturel en fonction du pH de l'extrait à froid en 1937.

Abb. 9. Bewahrung der inneren Reissfestigkeit nach 36 Jahren natürlicher Alterung als Funktion von pH, Kaltextraktion, im Jahre 1937.

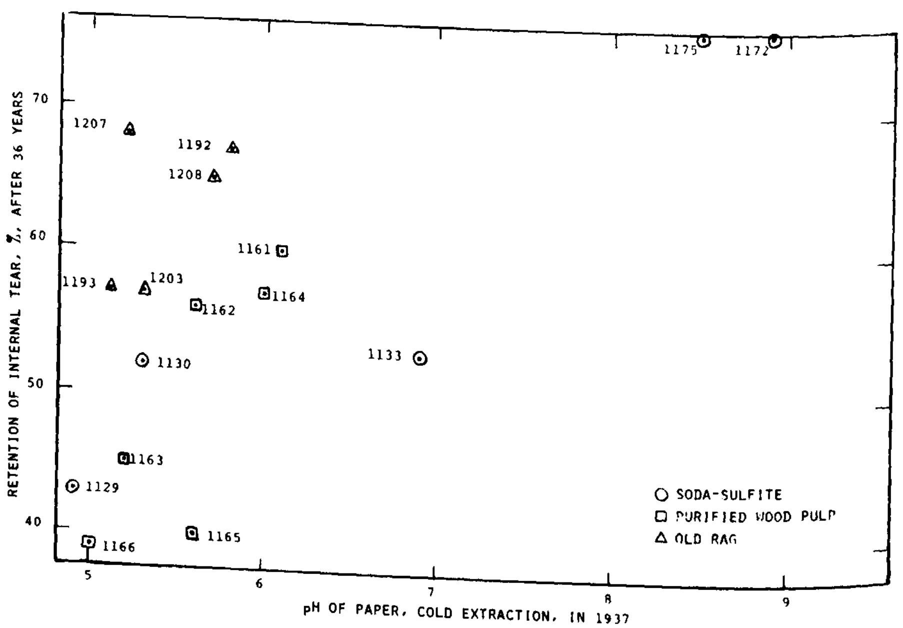


Figure 10. Zero-span breaking length, calculated to 100% fiber, in 1973 vs. pH, cold extraction, in 1937.

Figure 10. Allongement à la rupture à tension nulle rapporté à 100% de fibre en 1973 contre le pH de l'extrait à froid en 1937.

Abb. 10. Null-Spannungs-Bruch-Länge, berechnet für 100% Fasern, im Jahre 1973 gegenüber pH, Kaltextraktion im Jahre 1937.

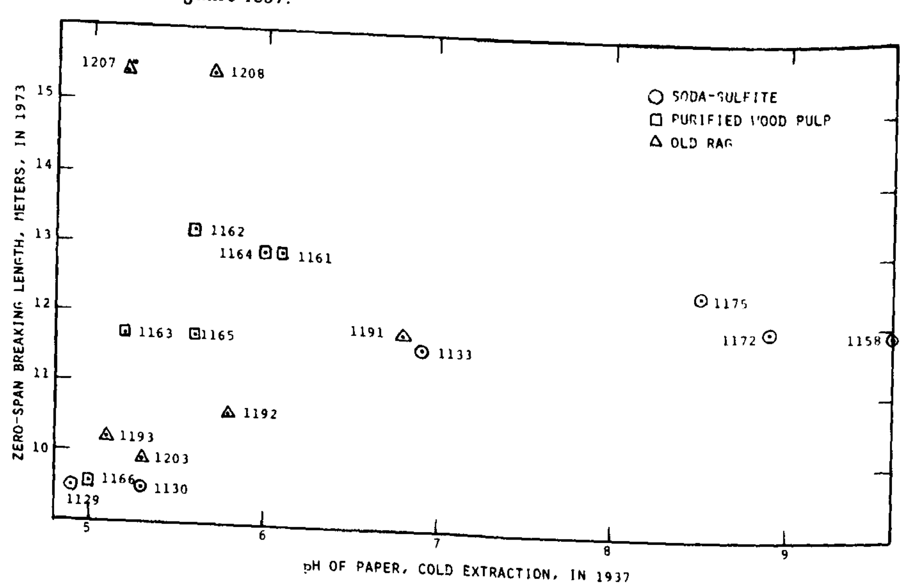


Table 23[1]. Load at break (kg) and retention of load at break of experimental handsheets, as percent of unaged paper, with time at 90°C in air or nitrogen at 50% or 0% relative humidity.

Table 23. Charge à la rupture (kg) et rémanence de la charge à la rupture de feuilles de papier expérimental en pourcentage du papier neuf en fonction du temps de séjour à 90°C à l'air ou à l'azote, à 50 ou à 0% d'humidité relative.

Tabelle 23. Belastung bei Bruch (kg) und Beibehaltung der Belastung bei Bruch von Versuchs-Handbögen als Prozent von ungealtertem Papier mit einer Zeit bei 90°C in Luft oder Stickstoff bei 50% oder 0% relativer Feuchtigkeit.

Pulp Treatment	Aging Atmosphere	Aging Period, days: Breaking Load, kg^2: 0	1	6	12	24	Retention, %: 1	6	12	24
Untreated	Dry air	8.83	8.55	8.30	8.73	8.83	97	94	99	100
	Dry nitrogen	8.96	8.70	8.53	8.75	9.22	97	95	98	103
	Humid air	8.62	8.25	8.04	8.25	7.21	96	93	96	84
	Humid nitrogen	8.45	8.69	8.46	8.24	8.12	103	100	98	96
Deashed	Dry air	8.23	8.21	8.76	7.98	7.66	100	106	97	93
	Dry nitrogen	8.19	8.27	7.85	7.90	7.88	101	96	96	96
	Humid air	8.17	7.58	4.19	2.99	2.22	93	51	37	27
	Humid nitrogen	7.57	7.22	6.19	4.83	3.90	95	82	64	52
Aluminum treated	Dry air	7.92	7.81	7.73	7.40	7.30	99	98	93	92
	Dry nitrogen	7.43	7.31	7.49	7.18	6.68	98	101	97	90
	Humid air	7.32	7.27	3.63	2.28	1.81	100	50	31	25
	Humid nitrogen	7.45	7.00	5.90	4.23	3.54	94	79	57	48

[1] Data from Table 5, NBS Report 10 628.
[2] 1 kilogram force = 9.80665 newton.

The data show that pH is not the only indicator of stability of paper and that folding endurance is not a universal method of measuring degradation. For example, using pH as a criterion of stability, one would have expected the three alkaline papers to retain a much higher percentage of their initial folding endurance. Number 1161 has a very high folding endurance retention, so it has retained its bonding and fiber strength with time. It would appear that some sizing material is desirable to maintain folding endurance with time even though the acidity may be higher.

Data in Table 18 on correlations of fold after natural aging with retention of elongation after natural aging are very good for purified sulfite and rag. Elongation probably could be used in place of fold as a routine test. This would be especially desirable as, 1) fold is a very time-consuming test and, 2) elongation usually is determined as a part of the determination of tensile properties.

Table 24[1]. MIT folding endurance and retention of folding endurance of experimental handsheets, as percent of unaged paper, with time in air or nitrogen at 90°C and 50% or 0% relative humidity.
Table 24. Résistance MIT au pliage et rémanence de la résistance au pliage de feuilles de papier expérimental exprimées en pourcentage du papier neuf, en fonction du temps de séjour à l'air ou à l'azote à 90°C et à 50 ou 0% d'humidité relative.
Tabelle 24. MIT Falzfestigkeit und Bewahrung der Falzfestigkeit von Versuchs-Handbögen als Prozent von ungealtertem Papier, mit einer Zeit in Luft oder Stickstoff bei 90°C und 50% oder 0% relativer Feuchtigkeit.

Pulp Treatment	Aging Atmosphere	Aging Period, days 0	1	6	12	24	1	6	12	24
		Number of Folds					Retention, %			
Untreated	Dry air	2102	2108	2087	1972	1767	100	99	94	84
	Dry nitrogen	2126	1953	1926	2044	1839	92	91	96	87
	Humid air	1920	1776	1382	1392	483	93	72	73	25
	Humid nitrogen	2215	2065	1722	2102	1761	93	78	95	80
Deashed	Dry air	1678	1721	1523	1352	1299	103	91	81	77
	Dry nitrogen	1768	1541	1484	1448	1351	87	84	82	76
	Humid air	1701	737	0	0	0	43	0	0	0
	Humid nitrogen	1838	1214	150	5	2	66	8	0	0
Aluminum treated	Dry air	1622	1469	1173	925	705	91	72	57	43
	Dry nitrogen	1980	1492	1100	1076	699	75	56	54	35
	Humid air	1923	823	0	0	0	43	0	0	0
	Humid nitrogen	1451	996	75	1	0	69	5	0	0

[1] Data from Table 2, NBS Report 10 628.

Internal tearing resistance

Data on retention of internal tearing resistance* after 36 years natural aging are given in Table 11. These data are plotted against accelerated aging data in Figure 8 and against pH in Figure 9. Two of the alkaline papers for which data are available (insufficient sample to test 1158) are superior to all others. Again, 1133 is somewhat exceptional, as one would expect a paper that has maintained its fiber strength and folding endurance to have maintained its tearing strength. Obviously, the bonding strength has deteriorated. Some papers at the bottom of Figure 11 are somewhat acid and show very poor retention of tear. However, several other papers in the same acidity range retained a much higher percentage of their tearing strength.

*As the name implies, internal tearing resistance is the energy required to tear a specimen, under specified conditions, after the tear has been started.

Table 25[1]. Internal tearing resistance (g) and retention of tearing resistance of experimental handsheets, as percent of unaged paper, with time in air or nitrogen at 90°C and 50% or 0% relative humidity.
Table 25. Résistance interne au déchirement (g) et rémanence de la résistance au déchirement de feuilles de papier expérimental exprimées en pourcentage du papier neuf, en fonction du temps de séjour à l'air ou à l'azote à 90°C et à 50 ou 0% d'humidité relative.
Tabelle 25. Interne Reissfestigkeit (g) und Bewahrung der Reissfestigkeit von Versuchs-Handbögen als Prozent von ungealtertem Papier, mit einer Zeit in Luft oder Stickstoff bei 90°C und 50% oder 0% relativer Feuchtigkeit.

Pulp Treatment	Aging Atmosphere	Aging Period, days 0	1	6	12	24	1	6	12	24
		Tearing Resistance, g					Retention, %			
Untreated	Dry air	93.2	87.4	95.0	87.4	92.0	94	102	94	99
	Dry nitrogen	96.0	98.0	95.0	90.8	101	102	99	95	105
	Humid air	87.0	83.2	80.7	77.2	60.4	96	93	89	69
	Humid nitrogen	92.0	84.2	85.0	82.8	78.6	92	92	90	85
Deashed	Dry air	91.0	88.4	90.0	73.4	82.8	97	99	81	91
	Dry nitrogen	95.2	87.8	93.8	79.0	75.8	92	99	83	80
	Humid air	91.4	65.4	14.6	7.6	5.2	72	16	8	6
	Humid nitrogen	93.4	79.8	46.2	28.0	16.4	85	49	30	18
Aluminum treated	Dry air	98.0	89.6	76.6	63.8	63.8	91	78	65	65
	Dry nitrogen	99.4	96.6	78.0	69.6	69.6	97	78	70	70
	Humid air	93.8	72.0	13.0	5.0	3.4	77	14	5	4
	Humid nitrogen	92.2	78.6	41.6	10.8	5.4	85	45	12	6

[1] Data from Table 3, NBS Report 10 628.

Correlations between internal tear after natural aging with other parameters are given in Table 19. Correlations between tear retention after, 1) accelerated aging and, 2) pH cold extraction, are not especially good, but correlations for the soda-sulfite and pruified sulfite populations are fairly good. Correlations between retension of tear after natural aging and retention of elongation after natural aging are surprisingly good.

Change in acidity

pH values, hydrogen ion concentrations (H+) calculated from pH values, and the changes that have occurred due to natural aging are given in Table 7. It is obvious that most of the papers, except the ones that are practically neutral, exhibit significant changes in hydrogen ion concentration of the extract after natural aging. The data on acidity in Table 7 are not as meaningful as they might be as pH values are expressed only to the nearest 0.1 pH unit. Massive

Table 26[1]. Paper acidity (cold extraction pH) and hydrogen ion concentration ($[H^+]$) after accelerated aging in air or nitrogen at 90°C and 50% or 0% relative humidity.
Table 26. Acidité du papier (pH de l'extrait à froid) et concentration des ions hydrogène (H^+) après un test de vieillissement accéléré à l'air ou à l'azote à 90°C et à 50 ou 0% d'humidité relative.
Tabelle 26. Papierazidität (Kaltextraktion pH) und Hydrogenionenkonzentration (H^+) nach beschleunigter Alterung in Luft oder Stickstoff bei 90°C und 50% oder 0% relativer Feuchtigkeit.

Pulp Treatment	Aging Atmosphere	Aging Period, days: pH 0	1	6	12	24	$[H^+] \times 10^7$ 0	1	6	12	24
Untreated	Dry air	6.34	6.24	6.25	6.21	6.21	5	6	6	6	6
	Dry nitrogen	6.29	6.36	6.34	6.30	6.22	5	4	5	5	6
	Humid air	6.58	6.44	6.10	5.97	5.23	3	4	8	11	59
	Humid nitrogen	7.05	6.70	6.76	6.73	6.36	1	2	2	2	4
Deashed	Dry air	5.32	5.08	5.04	4.97	4.88	48	82	91	107	133
	Dry nitrogen	5.11	5.05	4.80	4.97	4.94	77	90	159	107	115
	Humid air	4.82	4.44	3.95	3.87	3.86	151	363	1120	1350	1380
	Humid nitrogen	5.10	4.94	4.52	4.35	4.12	80	115	302	447	759
Aluminum treated	Dry air	5.14	5.20	4.92	4.96	4.88	73	63	121	110	132
	Dry nitrogen	5.24	4.89	4.93	5.07	4.82	58	129	117	85	151
	Humid air	5.01	4.53	4.02	3.86	3.78	98	295	955	1380	1660
	Humid nitrogen	5.36	4.87	4.46	4.29	4.25	44	135	347	513	562

[1] Data from Table 1, NBS Report 10 627.

amounts of acid were not generated during natural aging. Correlations between acid generated and initial pH are very poor except for the three acid soda-sulfite papers. These correlations are not shown. Poor correlation between initial pH and generation of acid is not surprising. The acid may arise from hydrolysis of aluminum on the carboxyl groups in cellulose or rosin, from hydrolysis of excess alum that may be in the paper, from carboxyl groups, from acid-lignin resudues, from oxidation of cellulose, and probably other causes.

Zero span breaking length

Zero span breaking strength is considered to be a function of the strength of the fibers in a paper. It is common practice to convert breaking strength data to breaking length by factoring in the basis weight of the paper. Breaking length is defined as the length that would cause the specimen to break under its own weight. Although zero span tensile was not measured in 1937, differences within the paper subsets, obtained in the current testing program, may be meaningful.

Table 27[1]. Changes in hydrogen ion concentration ($[H^+]$) after accelerated aging of experimental handsheets in air or nitrogen at 90°C and 50% or 0% relative humidity.
Table 27. Changements de concentration en ions hydrogène (H^+) après un test de vieillissement accéléré de feuilles de papiers expérimentaux, à l'air ou à l'azote, à 90°C et à 50 ou 0% d'humidité relative.
Tabelle 27. Veränderungen der Hydrogen-Ionen-Konzentration (H^+) nach beschleunigter Alterung von Versuchs-Handbögen in Luft oder Stickstoff bei 90°C und 50% oder 0% relativer Feuchtigkeit.

Pulp Treatment	Aging Atmosphere	Aging Period, days: 1	6	12	24
		Change in $[H^+] \times 10^7$			
Untreated	Dry air	1	1	1	1
	Dry nitrogen	−1	0	0	1
	Humid air	1	5	8	56
	Humid nitrogen	1	1	1	3
Deashed	Dry air	34	43	59	85
	Dry nitrogen	13	82	30	38
	Humid air	212	969	1199	1229
	Humid nitrogen	35	222	367	679
Aluminum treated	Dry air	−10	48	37	59
	Dry nitrogen	71	59	27	93
	Humid air	197	857	1282	1562
	Humid nitrogen	91	303	469	518

[1] Data from Table 1, NBS Report 10 627.

Zero span breaking length data obtained after 36 years natural aging (Table 14) are plotted against cold extract pH, measured in 1937 (Figure 10). The correlation coefficients in Table 20 show that it is fruitless to try to treat all of the papers as belonging to the same statistical population. The subsets show some degree of correlation. Removal of 1207 and 1208 from the rag subset, both of which contain titanium pigment, results in a surprising increase in correlation for this subset.

An examination of papermaking procedures suggests that the high zero span values of 1207 and 1208 may be indicative of stable papers. The first three rag papers contain varying amounts of alum, but no rosin. Number 1203 contains 2% rosin and a large amount (4%) of alum. Numbers 1207 and 1208 contain rosin and probably nearly stoichiometric amounts of alum (with respect to rosin). Therefore, there is an opportunity for some of the carboxyls in the first four rag papers to be covered with aluminum, but it is unlikely that the carboxyls in 1207 and 1208 are covered with aluminum. One would except the

Table 28[1]. Zero span breaking load (kg) and retention of breaking load of experimental handsheets, as percent of unaged paper with time, at 90°C in air or nitrogen at 50% or 0% relative humidity.
Table 28. Charge de rupture à tension nulle (kg) et rémanence de la charge de rupture de feuilles de papiers expérimentaux exprimées en pourcentage du papier neuf, en fonction du temps à 90°C et à 50 ou 0% d'humidité relative.
Tabelle 28. Null-Spannungs-Bruch-Belastung (kg) und Bewahrung der Bruchbelastung von Versuchs-Handbögen als Prozent von ungealtertem Papier mit einer Zeit bei 90°C in Luft oder Stickstoff bei 50% oder 0% relativer Feuchtigkeit.

Pulp Treatment	Aging Atmosphere	Aging Period, days								
		0	1	6	12	24	1	6	12	24
		Breaking Load, (kg)[2]					Retention, %			
Untreated	Dry air	11.4	11.4	11.2	11.0	10.6	100	98	96	93
	Dry nitrogen	10.2	10.5	10.7	10.9	10.4	103	105	107	102
	Humid air	9.1	9.6	9.6	8.4	9.0	105	105	92	99
	Humid nitrogen	10.6	9.3	9.0	8.9	8.7	88	85	84	82
Deashed	Dry air	11.4	11.1	11.1	12.4	11.7	97	97	109	103
	Dry nitrogen	11.4	11.4	10.9	12.0	11.1	100	96	105	97
	Humid air	13.0	12.4	6.4	3.0	2.2	95	49	23	17
	Humid nitrogen	15.2	14.4	12.2	8.4	6.4	95	80	55	42
Aluminum treated	Dry air	11.1	10.1	9.4	9.4	10.4	91	85	85	94
	Dry nitrogen	10.6	10.0	9.9	11.0	10.3	94	93	104	97
	Humid air	15.5	13.9	5.2	2.4	1.3	90	34	15	8
	Humid nitrogen	14.5	15.2	10.6	6.6	6.1	105	73	46	42

[1] Data from Table 6, NBS Report 10 627.
[2] 1 kilogram force = 9.80665 newton.

latter two papers to be more stable than the other four, if an excess of aluminum sulfate effects destabilization. This is indicated by the much higher zero span tensile strength of these papers. The papers that contain alum alone, and no rosin, (1129, 1130, 1191, 1192, 1193) or an excess of alum (1203) exhibit lower zero span tensile strength than the other papers in the subsets. Another factor that could be of paramount importance is that aluminum is strongly sorbed by titanium dioxide filler.[29*]

The three alkaline papers are somewhat higher in MD zero span tensile than the other soda-sulfite papers. Data on zero span breaking length were plotted (not shown) against acid generated after 36 years of natural aging, but no relationship was apparent.

*This was pointed out to me by Dr. E. L. Graminski, National Bureau of Standards.

Table 29[1]. Wet breaking load as percent of dry breaking load of experimental handsheets after accelerated aging at 90°C in various atmospheres.
Table 29. Charge à la rupture à l'état humide en pourcentage de la charge à la rupture à sec de papiers expérimentaux après un test de vieillissement accéléré à 90°C dans des atmosphères diverses.
Tabelle 29. Bruchbelastung im nassen Zustand als Prozent der trockenen Bruchbelastung von Versuchs-Handbögen nach beschleunigter Alterung bei 90°C in verschiedenen Atmosphären.

Pulp Treatment	Aging Atmosphere	Aging Period, days				
		0	1	6	12	24
Untreated	Dry air	0.8	1.5	1.7	2.8	3.7
	Dry nitrogen	0.7	1.3	2.1	2.5	3.1
	Moist air	0.8	1.3	2.0	2.9	4.8
	Moist nitrogen	1.1	1.1	1.8	2.2	3.1
Deashed	Dry air	1.4	2.8	3.7	8.1	10.4
	Dry nitrogen	1.3	2.8	4.2	7.6	9.6
	Moist air	2.2	5.5	9.7	7.9	6.1
	Moist nitrogen	1.6	4.0	4.4	9.0	8.8
Aluminum treated	Dry air	1.3	4.1	9.4	12.7	14.7
	Dry nitrogen	2.0	4.3	8.1	11.3	14.2
	Moist air	1.8	4.7	9.7	6.6	4.2
	Moist nitrogen	1.1	3.7	7.4	9.0	9.1

[1] Data from Table 2, NBS Report 10 627, and Table 5, NBS Report 10 628.

Tensile properties of wetted specimens

Measurement of specimens in the wet state gives an indication of the crosslinking that occurs in the aging of paper. Paper in which no crosslinking has occurred has a very low strength when wet.

Data on wet breaking load as a percent of dry breaking load (Table 15) are plotted against cold pH, 1937, in Figure 11. As indicated in Table 21, correlations within subsets are much better than the correlation coefficient that includes all of the papers. As the development of strength of wet specimens is a function of initial acidity,[6] fairly good correlations of the development of breaking strength of wet specimens with initial pH are to be expected. Correlations between energy at break of wet specimens (Figure 12) and extensional stiffness of wet specimens with initial cold extract pH show the same trends as correlations between breaking strength of wet specimens and pH (Table 21).

Moisture regain

Papers within each fiber subset (Tables 14 and 15) exhibit very similar mois-

Table 30[1]. Percent moisture regain and change in moisture regain for experimental handsheets aged in air or nitrogen at 90°C and at 50% or 0% relative humidity.
Table 30. Taux de réhumidification en pourcent et changement du taux de réhumidification de papiers expérimentaux vieillis en atmosphère d'air ou d'azote, à 90°C et à 50 ou 0% d'humidité relative.
Tabelle 30. Prozentuale Feuchtigkeits-Wiedergewinnung und Veränderung der Feuchtigkeits-Wiedergewinnung von Versuchs-Handbögen, die in Luft oder Stickstoff bei 90°C und bei 50% oder 0% relativer Feuchtigkeit gealtert sind.

Pulp Treatment	Aging Atmosphere	Aging Period, days								
		0	1	6	12	24	1	6	12	24
		Moisture Content, %					Change, %[2]			
Untreated	Dry air	7.2	7.0	7.0	6.9	7.0	0.2	0.2	0.3	0.2
	Dry nitrogen	7.4	7.0	6.9	6.8	7.0	0.2	0.3	0.4	0.2
	Humid air	7.2	6.6	6.5	6.2	6.0	0.6	0.7	1.0	1.2
	Humid nitrogen	7.2	6.7	6.5	6.5	6.2	0.5	0.7	0.7	1.0
Deashed	Dry air	7.1	6.8	6.9	6.7	6.7	0.2	0.1	0.3	0.3
	Dry nitrogen	7.0	6.9	6.8	6.6	6.7	0.1	0.2	0.4	0.3
	Humid air	7.0	6.3	5.3	4.9	4.3	0.7	1.7	2.1	2.7
	Humid nitrogen	6.8	6.6	5.8	5.4	5.1	0.4	1.2	1.6	1.9
Aluminum treated	Dry air	7.0	7.1	6.8	6.7	6.6	0.0	0.3	0.4	0.5
	Dry nitrogen	7.1	7.0	6.8	6.8	6.7	0.1	0.3	0.3	0.4
	Humid air	7.2	6.1	5.3	4.7	4.6	1.0	1.8	2.4	2.5
	Humid nitrogen	7.1	6.4	6.0	5.4	4.7	0.7	1.1	1.7	2.4

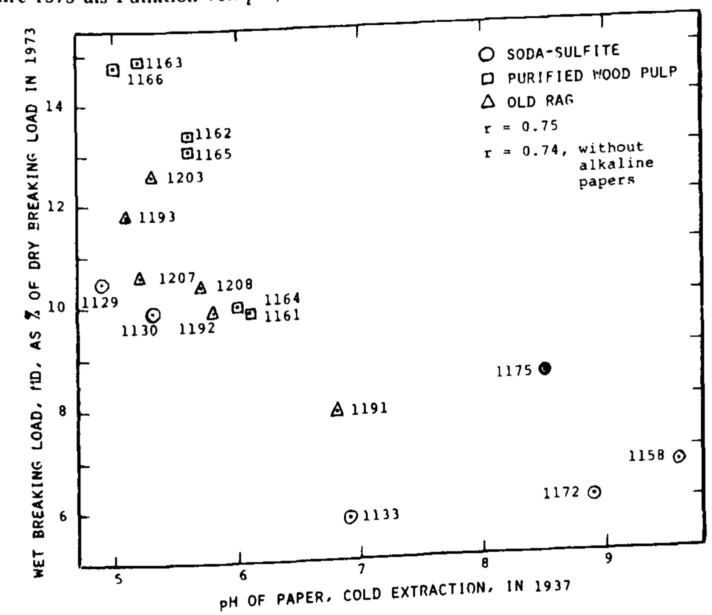
[1] Data from Table 5, NBS Report 10 687.
[2] Decrease in analytical value for zero time of aging, average values of 7.2% for untreated, 7.0 for deashed, and 7.1 for aluminum treated papers were used.

ture regains. Moisture regain of the rag papers averages about 1% lower than moisture regain of the wood pulp papers. This is in keeping with differences in crystallinity between wood fibers and cotton fibers. The data show no correlation between wet breaking load as a percent of dry breaking load and moisture regain. This is in keeping with data already reported[4] for dry aging of handsheets.

pH at head box

Graminski[30] has found after reviewing the data in this report that high correlations exist between, 1) head box pH and changes in folding endurance after natural aging and, 2) head box pH and wet strength as a percent of dry strength after natural aging. It is anticipated that this will be included in a publication by Graminski, which is in preparation.

Figure 11. Wet breaking load as percent of dry breaking load in 1973 as a function of pH, cold extraction, in 1937.
Figure 11. Charge à la rupture à l'état humide en pourcentage de la charge à la rupture à sec en fonction du pH de l'extrait à froid en 1937.
Abb. 11. Bruchbelastung im nassen Zustand als Prozent der Bruchbelastung im trockenen Zustand im Jahre 1973 als Funktion von pH, Kaltextraktion, im Jahre 1937.



5. Relationship to Specifications

Specifications for permanent record papers should include tests that indicate the quality of the paper for immediate use, and tests that indicate the longevity of the paper. Assuming that the physical and chemical tests made in 1937 were adequate to indicate the performance of the paper for immediate use, we are concerned today only with the retention of properties with time. Potential indicators of retention of properties with time are pH and retention of properties after accelerated aging. On the basis of experience, one might make arbitrary decisions about minimum initial pH values and retention of properties with accelerated aging as indicators of stability, and thus select one or more indicators as requirements for a specification.

In Table 22 four categories have been arbitrarily selected, based on pH data and changes after accelerated aging, for possible specification requirements. The degree of success depends on the restrictions placed on the definition of stable paper after natural aging as shown in the right side of Table 22. From these data it is obvious that one could have selected stable papers in 1937 with considerable success.

The ranks of the summations of retentions of properties after accelerated aging and after natural aging (Table 22) suggest that some relationship exists between the dry oven accelerated aging procedure and natural aging. The correlation coefficeint is 0.79. Retentions for alpha cellulose and copper number were obtained by expressing maximum change as 0% retention, no change as 100% retention, and normalizing the changes between these extremes. Retentions for alpha cellulose, copper number, fold and tear were totaled to obtain Σ of retentions.

The correlation coefficient (0.79) or the ranks in Table 24 can not be considered conclusive, as uncertainties in sampling and uncertainties in laboratory technique spanning almost 40 years must be kept in mind. The overall picture, however, indicates that accelerated aging is a potentially useful tool in the selection of stable papers for permanent records. On the other hand, it is not claimed that the accelerated aging procedure used in 1937 is necessarily the best available at present. More extensive changes occurred during natural aging than during dry aging in 1937. Dry oven aging excludes the chemistry of carbohydrate hydrolysis which appears to be a significant factor in natural aging. This is taken up in detail in the next section.

6. Should an Accelerated Aging Atmosphere be Moist or Dry?

The object of this section is to develop information on whether an accelerated aging atmosphere for paper should be dry or moist, and if moist, some idea of the amount of moisture. It is not the purpose of this paper to recommend specific aging conditions. Enough data probably are available to do this, but a thorough analysis of the data from several publications will be required. Such an effort is beyond the scope of this publication.

Data on accelerated aging of handsheets at 90°C and at 0% and 50% relative humidity already have been reported.[2,3,4] Part of the data in these reports, some of which have been recalculated to a different form, are reproduced in Tables 23–31. In the three groups of handsheets (untreated, deashed, and alum-treated), those made from deashed pulp were much less stable, and those made from alum-treated pulp were somewhat less stable than the deashed. Different tests responded differently to moist and dry aging, but moist usually resulted in much greater and more rapid changes than dry aging. It is not possible to draw definite conclusions from these data and the data obtained

Table 31[1]. Percent blue reflectance and change in blue reflectance of experimental handsheets with time in air or nitrogen at 90°C and 50% or 0% relative humidity.

Table 31. Pourcent réflecteur bleu et changement du pourcent réflecteur bleu de feuilles de papier expérimental en fonction du temps de contact à l'air ou à l'azote à 90°C et à 50 ou 0% d'humidité relative.

Tabelle 31. Prozentuales Blau-Reflexionsvermögen und Veränderung des Blau-Reflexionsvermögens von Versuchs-Handbögen mit einer Zeit in Luft oder Stickstoff bei 90°C und 50% oder 0% relative Feuchtigkeit.

Pulp Treatment	Aging Atmosphere	Aging Period, days								
		0	1	6	12	24	1	6	12	24
		Blue Reflectance, %					Change, %[2]			
Untreated	Dry air	82.0	80.4	80.5	79.6	78.2	1.6	1.5	2.4	3.8
	Dry nitrogen	82.5	80.3	78.9	79.4	77.2	2.2	3.6	3.1	5.3
	Humid air	79.0	74.1	70.4	67.7	57.1	4.9	8.6	11.3	21.9
	Humid nitrogen	84.9	79.1	74.1	71.7	66.9	5.8	10.8	13.2	18.0
Deashed	Dry air	85.2	82.9	81.6	81.1	78.7	2.3	3.6	4.1	6.5
	Dry nitrogen	86.1	82.8	80.2	78.9	75.3	3.3	5.9	7.2	10.8
	Humid air	86.9	72.6	52.3	44.9	38.7	14.3	34.6	42.0	48.2
	Humid nitrogen	86.1	74.6	57.6	54.5	45.8	11.5	28.5	31.6	40.3
Aluminum treated	Dry air	86.5	84.4	83.2	81.2	80.3	2.1	3.3	5.3	6.2
	Dry nitrogen	86.1	84.6	82.8	80.9	77.9	1.5	3.3	5.2	8.2
	Humid air	86.4	78.5	57.5	42.0	27.7	7.9	28.9	44.4	58.7
	Humid nitrogen	85.9	78.1	66.0	57.3	49.7	7.8	19.9	28.6	36.2

[1] Data from Table 1, NBS Report 10 687.
[2] Decrease in measured value.

on the 36 years papers regarding an accelerated aging atmosphere, but a trend is obvious.

In comparing the four sets of data: 1) from natural aging, 2) from accelerated aging in 1937, 3) from dry accelerated aging at 90°C, and, 4) from accelerated aging at 90°C and 50% relative humidity, some judgement is necessary with respect to the aging times in (3) and (4) to use in the comparisons. Direct comparisons are possible between (1) and (2) and between (3) and (4), but not between (1) and (3) or (1) and (4) or between (2) and (3) or (2) and (4). Only the type of change can be categorized, and not always with certainty.

Tensile strength

The data in Table 23 show that aging at 50% relative humidity at 90°C seriously degraded the tensile strength of handsheets made from deashed and alum-treated pulps within 6 days. Very little degradation occurred in 24 days during aging in dry atmospheres and the handsheets made from untreated pulps were especially stable. The data in Table 8 indicate that the degradation in tensile strength that occurred during 36 years of natural aging more nearly approximate dry accelerated aging than accelerated aging at 50% relative humidity. A clear cut decision is not possible, but it would appear that a small amount of moisture should be present in an accelerated aging procedure.

Folding endurance

The data in Table 24 on changes in MIT folding endurance with time of aging show that accelerated aging in a moist atmosphere is devastating, even after one day of aging. On the other hand, even the alum-treated samples did not degrade as much during dry accelerated aging as the NBS mill papers after 36 years of natural aging. From this it appears that some moisture in an accelerated aging procedure is indicated but that 50% relative humidity at 90°C may be excessively severe.

Internal tearing resistance

The data on internal tearing resistance in Tables 11 and 25 lead to the same conclusion as with the folding endurance data.

Change in acidity

Data in Table 7 show that large amounts of acid were not generated during 36 years of natural aging. The data in Tables 26 and 27 show that little acid is generated during dry aging, but massive amounts of acid are generated during extended accelerated aging at 50% relative humidity. Again this indicates that some moisture is desirable in an accelerated aging atmosphere but that prolonged aging at 50% relative humidity at 90°C is excessive.

Zero span breaking length

Data on zero span breaking length in Tables 14 and 28 cannot be conclusive because zero span data were not obtained in 1937. The data in Table 28 show that the changes that occur during accelerated aging in a dry atmosphere are not great, but the changes that occur at 50% relative humidity are considerable. The only way one can draw inferences from the data in Table 14 is to compare papers in the same subset. Number 1129, a very acid paper in the soda-sulfite subset, is decidedly lower in zero span tensile than the other papers in the subset. Number 1130, also an acid paper, is somewhat low. The three alkaline papers, 1158, 1172, and 1175, are the highest in the group. Number 1133, a slightly acid paper, lies between the alkaline papers and the two acid papers. The average machine direction breaking length of the three alkaline

papers is about 12 km. The breaking length of 1129 is about 80% of this average value. A value this low does not appear in Table 28 except with samples aged at 50% relative humidity. Again, it appears that some moisture is desirable in an accelerated aging atmosphere.

Number 1166 in the purified sulfite subset is an acid paper. Numbers 1161 and 1164 in the same subset are only slightly acidic, and their zero span breaking lengths in the machine direction are about 12.9 km. The zero span breaking length of 1166 is about 75% of 1161 and 1164.

The zero span breaking length data for the six rag papers are very interesting. The first three papers (1191, 1192, 1193) contain increasing amounts of alum, but no rosin. The fourth paper, 1203, contains 2% rosin but a massive amount (4%) of alum. The zero span breaking lengths decrease with increasing amounts of alum from 1191 to 1203. The value for 1203 is about 85% of that of 1191. Numbers 1207 and 1208 are different from the other rag papers in that they contain titanium pigments and were sized with rosin without an excess of alum. They have outstandingly high zero span breaking lengths. It would be difficult to attribute this to the presence of titanium pigment. On the other hand, these two papers were sized by a procedure that was not likely to allow appreciable attachment of aluminum to carboxyls. Numbers 1191, 1192, 1193, and 1203 could have aluminum attached to the carboxyls. Therefore, the values for 1207 and 1208 may indicate the values that these rag papers would have if they were manufactured strictly with stability in mind. The zero span breaking length values for 1191 through 1203 range about 65–75% of the average value of 1207 and 1208. In any case, the data indicate that some moisture is necessary to produce the changes that occur during natural aging.

Breaking strength of wet paper

Data on breaking load of wet specimens as percent of dry breaking load in Table 15, when compared with tensile properties of wet specimens in Table 29, are not definitive.

Moisture regain

The data in Table 30 show that great changes in moisture content occurred during moist accelerated aging, but very little change occurred during dry accelerated aging. Moisture regain data were not obtained in 1937. The moisture regain on the 36 year papers in Table 14 show that variations within each of the three subsets is not at all large, and probably is within experimental error. As each subset contains papers with a wide spectrum of stability, one would expect much greater variation than the data show, when compared with the data in Table 30, if moist accelerated aging were indicative of that which occurs during natural aging. In terms of moisture regain, one can conclude that the atmosphere should either be dry or contain only a small amount of moisture.

Brightness

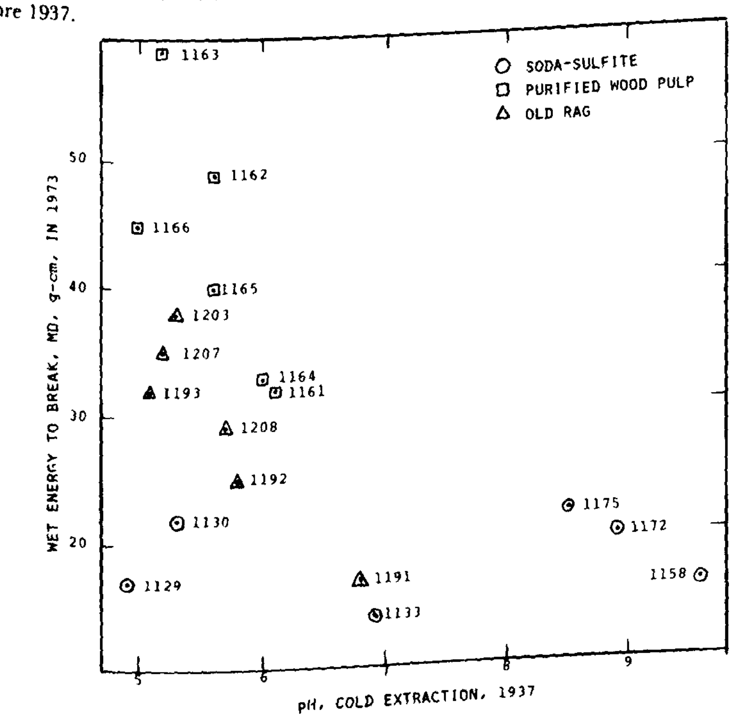
Data on changes in blue reflectance (brightness) of experimental handsheets in Table 31 show very definite differences between moist and dry accelerated aging. The changes that occurred during dry accelerated aging are comparatively minor but the changes that occurred during extended periods of moist aging are massive. Data on brightness of the 36 year papers in Table 16 are confused by the fact that, 1) brightness data are not available on the original papers and, 2) the presence of fillers in some of the papers. Comparisons within subsets of the same fiber composition show that differences in brightness are minimal, and that changes due to differences in stability are more indicative of dry accelerated aging than moist accelerated aging.

7. Accelerated Aging and Prediction of Permanence

Prediction of the permanence of paper is not an exact science, but several investigators have directed their efforts toward approaching this goal.[31] The usual approach is to determine rates of degradation at several temperatures and apply some form of the Arrhenius equation to an evaluation of the data. Graminski has published the most recent work on this subject,[5] and his work includes extensive data on the effect of moisture on the aging of paper.

Application of the Arrhenius equation presumes that plotting a function of degradation during accelerated aging against the reciprocal of the absolute temperature gives a straight line. This, in turn, implies that the same reaction, or reactions that occur at room temperature (or temperature at which the material is used) also occur at the elevated accelerated aging temperature, or temperatures. As one can write down about twenty variations of the anhydroglucose ring in cellulose, and as the physical structure of various papermaking fibers varies over a wide range, the likelihood of this happening for a wide spectrum of papers on an Arrhenius plot is somewhat remote. To this must be added another variable. Assuming that chain scission occurs in positions that cause the greatest damage, a sheet of paper could be reduced to powder by breaking less than 1% of the bonds between the anhydroglucose units. As chain scission probably would be random in the amorphous areas, the percentage of bonds that must be broken to render a paper useless might be larger than one,

Figure 12. Wet energy to break in 1973 as a function of pH, cold extraction, in 1937.
Figure 12. Energie de rupture à l'état humide en 1973 en fonction du pH de l'extrait à froid en 1937.
Abb. 12. Nasse Energie gegenüber Bruch im Jahre 1973 als Funktion von pH, Kaltextraktion, im Jahre 1937.



but it still would be small. Now when we use a test, physical or chemical, this is a function of the chain scission reaction and we have another variable.

It is the opinion of the authors that the situation is not all bad if we recognize the limitations of accelerated aging and not place too much confidence in complicated mathematical treatments of data that inherently have much greater variablility than a statistical analysis is likely to uncover. Under the following conditions, accelerated aging should be useful:

(1) Use accelerated aging only for ranking the stability of a group of papers relative to each other.

(2) The papers should be similar. Although useful data may be obtained by comparing, for example, the stability of a newsprint against a rag paper, comparisons of similar papers should have a higher degree of credibility.

(3) Don't try to predict permanence in years. This is not meant to imply that one cannot predict permanence in an absolute time frame, but the authors feel that the precision of such an exercise is not very great.

(4) Although a one-point (one aging time) test may be useful, a multiple-point test that will allow the calculation of a slope provides much more information. A multiple-time, multiple-temperature test is desirable, but time-consuming and expensive.

(5) Some moisture should be included in the aging atmosphere. A relative humidity in the range of 10–25% might be selected. This has been discussed by Graminski.[5b]

(6) The moisture content of the atmosphere should be controlled very precisely, as the rate of degradation of paper is greatly dependent on the moisture content of the paper.[5b]

(7) It appears that Graminski[5b] has defined the role of moisture in the aging of paper, and the important parameter is moisture content of the paper. This does not completely solve the problem, for different papers will have different moisture contents under the same natural aging conditions. This situation requires further attention.

(8) More than one test should be used in evaluating changes in paper after accelerated aging, and the tests should be related, if possible, to the end use of the product.

8. Recommendations for Further Work

(1) Old papers that have been in storage from a few (about ten) years to several hundred years should be examined. Preference should be given to papers on which some original data are available. Papers that have deteriorated should yield useful information. Older papers would require more intensive study, as no original data would be available.

(2) An in-depth review of the literature over the past ten years, especially the work of Graminski[5] and of Parks,[2,3,4] combined with the data in this report, should enable one to arrive at a recommendation for conditions for an accelerated aging procedure for paper. The selection of any procedure would be arbitrary and, to some extent, subjective. As much useful data have become available in the last few years, such a selection should have a fairly secure foundation.

9. Acknowledgements

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10. Abstracts

Comparison of Accelerated Aging of Book Papers in 1937 with 36 Years Natural Aging.

In 1937 a group of 72 book papers made in the National Bureau of Standards experimental paper mill was tested before and after accelerated aging for 72 hours at 100°C in a circulating oven. Some of these samples were retained for occasional testing, and in 1973 it was possible to assemble 18 of these papers from three fiber sources with 6 papers in each fiber group. Most of the papers were sized with rosin and alum, and some contained fillers.

These 18 papers were retested in 1973. Within the extensive limitations of the significance of accelerated aging (defined here as 72 hours at 100°C), the following conclusions may be drawn:

(1) Reasonably good correlations exist between changes in alpha cellulose after accelerated aging in 1937 and after 36 years of natural aging.

(2) The same is true for copper number.

(3) Correlations between cold extract pH in 1937 and changes after natural aging in alpha cellulose, copper number, fold, tear and elongation indicate that pH is a reasonably good criterion of stability.

(4) It appears from data after natural aging that zero span tensile and wet strength as a percent of dry strength should be useful criteria.

Data on the accelerated aging of handsheets at 90°C at 0% and at 50% relative humidity have been compared with changes in these 18 book papers after 36 years of natural aging, and it appears that an accelerated aging atmosphere should contain some moisture, but not as much as 50% relative humidity at 90°C. The data recently obtained by Graminski at various temperature and relative humidities support this conclusion.[5]

The following tests are potentially useful in evaluating changes that occur in the aging of paper: alkali solubility, reducing power, pH, internal tearing strength, elongation, zero span tensile strength, and strength when wet as a percentage of strength when dry.

Comparaison du vieillissement accéléré de papiers pour livres datant de 1937 au vieillissement naturel durant 36 années.

En 1937, une série de 72 types de papiers de librairie produits par la papeterie du National Bureau of Standards ont été testés avant et après un vieillissement accéléré de 72 heures à 100°C dans une

étuve à circulation d'air. Certains échantillons ont été conservés à fin d'essais sporadiques et, en 1973, 18 papiers provenant de 3 types de fibre ont pu être regroupés à raison de 6 types de papiers par type de fibre. La majorité des papiers avait été apprêtée à la collophane et à l'alun; certains papiers contenaient des charges.

Ces 18 papiers ont fait l'objet de nouveaux essais en 1973. Dans le cadre des limitations de signification présentées par la technique du vieillissement accéléré correspondant dans ce cas à 3 jours à 100°C, les conclusions suivantes ont pu être effectuées:

1. Un niveau assez bon de corrélation existe entre les changements de l'alfacellusose constatés sur un test de vieillissement accéléré en 1937 et à l'issue d'une période de vieillissement naturel de 36 ans.
2. Mêmes constatations dans le cas du taux de cuivre.
3. Les corrélations existant entre le pH de l'extrait à froid mesuré en 1937 et les changements intervenus aprés un vieillissement naturel au niveau de l'alfacellulose, du taux de cuivre, du pliage, du déchirement et de l'élongation indiquent que le pH représente un critère de stabilité assez valable.
4. Les données observées révèlent que lors du vieillissement naturel, l'élasticité à tension nulle et la résistance à l'état humide exprimée en pourcentage de la résistance à sec devraient représenter des critères utiles.

Les données concernant le vieillissement accéléré de feuilles de papier à 90°C sous une humidité relative de 50% ont été comparées avec les changements intervenus au niveau des 18 types de papier après 36 années de vieillissement naturel et il s'avère que l'atmosphère utilisée lors du vieillissement accéléré devrait contenir une certaine humidité, inférieure à 50% à 90°C. Les données présentées récemment par Graminski à des températures et à des humidités relatives diverses viennent corroborer cette conclusion.[5]

Les tests suivants présentent une utilité potentielle dans l'évaluation des changements survenus lors du vieillissement du papier: solubilité alcaline, pouvoir réducteur, pH, résistance interne au déchirement, élongation, coefficient d'élasticité à tension nulle et résistance à l'état humide exprimée en purcentage de la résistance à sec.

Vergleich zwischen beschleunigter Alterung von Buchpapier im Jahre 1937 und 36 Jahre langer natürlicher Alterung.

1937 wurde eine Gruppe von 72 Buchpapiersorten, die in der Versuchspapierfabrik des National Bureau of Standards hergestellt worden waren, vor und nach der beschleunigten Alterung von 72 Stunden in einem Umlaufofen bei 100°C getestet. Einige dieser Muster wurden zu späteren Tests bewahrt, und im Jahre 1973 war es möglich, 18 dieser Papiere aus drei Faserquellen mit 6 Papieren in jeder Fasergruppe zu sammeln. Die meisten Papiere waren mit Harz und Alaun planiert, während andere Füller enthielten.

Dise 18 Papiere wurden 1973 erneut getestet. Innerhalb der umfangreichen Begrenzungen der Aussagekraft der beschleunigten Alterung (hier definiert als 72 Stunden bei 100°C), können folgende Schlussfolgerungen gezogen werden:

1. Zwischen den Veränderungen in der Alpha Zellulose bestehen nach der beschleunigten Alterung im Jahre 1937 und den 36 Jahren natürlicher Alterung recht gute Korrelationen.
2. Das gleiche gilt für die Kupferzahl.

3. Die Korrelationen zwischen Kalt-Extrakt pH im Jahre 1937 und Veränderungen nach natürlicher Alterung in der Alpha-Zellulose, Kupferzahl, Falzfestigkeit, Reiss- und Dehnungsfestigkeit deuten darauf hin, dass pH ein durchaus geeignetes Stabilitätskriterium ist.
4. Es zeigt sich an Hand der Daten nach natürlicher Alterung dass die Null-Spannung-Dehnung und die nasse Festigkeit als Prozent der trockenen Festigkeit nützliche Kriterien darstellen sollten.

Die Daten über die beschleunigte Alterung der Handbögen bei 90° und bei 50% Feuchtigkeit sind mit den Veränderungen in diesen 18 Buchpapieren nach 36 Jahren natürlicher Alterung verglichen worden. Daraus ergibt sich, dass die Atmosphäre für die beschleunigte Alterung etwas Feuchtigkeit enthalten sollte, jedoch weniger als 50% Feuchtigkeit bei 90°C. Die Daten, die Graminski vor kurzer Zeit bei verschiedenen Temperaturen und unterschiedlicher Luftfeuchtigkeit erarbeitet hat, unterstützen diese Konklusion.

Die folgenden Tests sind besonders für die Bewertung der Veränderungen nützlich, die bei der Alterung von Papier vor sich gehen: Alkali-Löslichkeit, Reduzierfähigkeit, pH, interne Zerreissfestigkeit, Verlängerung, Null-Spannung-Dehnung und Festigkeit im nassen Zustand in Prozent zur Festigkeit im trockenen Zustand.

11. SUMMARIES

Comparison of Accelerated Aging of Book Papers in 1937 with 36 Years Natural Aging.

Keeping in mind the limitations of correlation coefficients, discussed in 3.3, and the limitations of accelerated aging procedures, the following inferences may be drawn from the data in this report:

1. The changes in alpha cellulose that occurred during accelerated aging for three days at 100°C correlated well with changes in alpha cellulose that occurred after 36 years of natural aging. Alpha cellulose, or perhaps some more convenient alkali solubility method, should be suitable as a criterion of resistance to accelerated aging.
2. Changes in copper number that occurred during accelerated aging for three days at 100°C correlated well with changes in copper that occurred after 36 years of natural aging.
3. Correlation of retention of folding endurance after natural and accelerated aging were fair only. Although fold is useful as an evaluation method after accelerated aging, one should not rely on it completely.
4. Correlations of internal tear after natural and accelerated aging were somewhat better than for folding endurance, but still not high.
5. Correlations between cold extract pH in 1937 and changes after natural aging in alpha cellulose, copper number, fold, tear, and elongation indicate that pH is a reasonably good criterion of stability, possibly for complex reasons.
6. Retention of tear after natural aging correlated well with retention of elongation after aging, except for rag papers.
7. Retention of fold after natural aging correlated fairly well with elongation after natural aging, but not as well as tear and elongation, except for soda-sulfite papers.
8. Correlation between pH and zero span tensile data for all 18 papers was very poor, but when the data were separated into statistically homogeneous subsets, the correlations were better.
9. The correlation between pH and breaking load of wet paper as a percent of breaking load when dry for the 18 samples was fair only. When the data were separated into statistically homogeneous subsets, the correlations were better.
10. The correlation between pH and energy at break for wet paper was fair only.

11. The correlation between pH and extensional stiffness for wet paper was very poor. When the data were separated into statistically homogeneous subsets, the correlation were fair.
12. It appears that *pH*, and changes in *alkali solubility, reducing power and tearing strength* after accelerated aging for 72 hours at 100°C are reasonable indications of stability. Fold is sensitive, but not as useful.
13. It appears from data after *natural* aging that *zero span tensile, elongation*, and *strength when wet as a percent of strength when dry* should be useful criteria.
14. When data in this report are compared with data obtained with hand sheets at 90°C and zero and 50% R. H., it appears that an accelerated aging atmosphere should contain some moisture, but not as much as 50% relative humidity at 90°C.

Comparaison du vieillissement accéléré de papiers pour livres datant de 1937 au vieillissement naturel durant 36 années.

Compte tenu des limitations inhérentes aux coefficients de corrélation discutés au paragraphe 3.3 et des limitations des processus de vieillissement accélér; les conclusions suivantes peuvent être déduites des données présentées dans ce rapport:

1. Les modifications de l'alfacellulose survenus durant le processus de vieillissement accéléré durant 3 jours à 100°C présentent une bonne corrélation avec les changements de l'alfacellulose survenus après 36 années de vieillissement naturel. La détermination de l'alfacellulose ou éventuellement une méthode de solubilité en milieu alcalin d'un emploi plus commode représenterait un critère approprié de résistance au vieillissement accéléré.
2. Les modification du taux de cuivre survenues durant le processus de vieillissement accéléré pendant trois jours à 100°C présentent une bonne corrélation avec les changements du taux de cuivre survenus après 36 années de vieillissement naturel.
3. Les coefficients de corrélation du maintien de la résistance au pliage après vieillissement naturel et accéléré ne sont qu'acceptables. Bien que le pliage soit utile en tant que méthode d'évaluation après un vieillissement accéléré, il ne représente pas un paramètre complètement sûr.
4. Les coefficient de corrélation de déchirement après vieillissement naturel et accéléré étaient, quoique légèrement supérieurs à la résistance au pliage, toujours trop faibles.
5. Les coefficients de corrélation entre le pH d'un extrait effectué à froid en 1937 et les modification par vieillissement naturel du niveau d'alfacellulose, du taux de cuivre, des résistances au pliage, au déchirement et du coefficient d'élongation indiquent que le pH représente un critère relativement valable de stabilité et ce, du fait de raisons complexes.
6. La rémanence du coefficient de déchirement après un vieillissement naturel présente une bonne corrélation avec la rémanence du coefficient d'élongation après vieillissement naturel, sauf dans le cas des papiers de chiffons.
7. La rémanence de la résistance de pliage après vieillissement naturel présente une assez bonne corrélation avec l'élongation après vieillissement naturel, inférieure toutefois à la corrélation présentée par la résistance au déchirement et à l'élongation, à l'exception des papiers alcalins au sulphite.
8. Le coefficient de corrélation entre le pH et l'élasticité à tension nulle de l'ensemble des 18 papiers était très bas, mais une fois les données regroupées en des sous-groupes présentant une certaine homogénéité d'ordre statistique, les coefficients de corrélation étaient meilliurs.
9. Le coefficient de corrélation entre le pH et la charge à la rupture de papier humide exprimé en pourcentage de la charge de rupture à sec des 18 échantillons était assez bon. Lorsque les

données ont été regroupées en des sous-groupes présentant une certaine homogénéité d'ordre statistique, les coefficients de corrélation étaient meilleurs.

10. Le coefficient de corrélation entre le pH et la force de rupture du papier humide était seulement assez bon.
11. Le coefficient de corrélation entre le pH et l'allongement élastique du papier humide était très faible. Lorsque les données étaient regroupées en sous-groupes d'une certaine homogénéité statistique, les corrélations étaient assez bonnes.
12. Il s'avère que le *pH* et les changements de *solubilité alcaline*, de *capacité réductrice* et de *résistance au déchirement* après un test de vieillissement accéléré durant 72 heures à 100°C représentent des critères raisonnables indicatifs de la stabilité. La résistance au pliage est un paramètre sensible mais dont l'utilité n'est pas comparable.
13. Les données de vieillissement naturel telles que *l'élasticité à tension nulle, l'élongation* et *la résistance à la rupture mesurées à l'état humide en pourcentage des valeurs à sec* devraient être des critères d'évaluation utiles.
14. Lorsque les données de ce rapport sont comparées aux donnés obtenues avec des feuilles traitées à 90°C sous une humidité relative de 0 et 50%, il s'avère que l'atmosphère utilisé durant le vieillissement accéléré nécessite une certaine teneur en humidité, inférieure à 50% RH à 90°C.

Vergleich zwischen beschleunigter Alterung von Buchpapier im Jahre 1937 und 36 Jahre langer natürlicher Alterung.

Unter Beachtung der Begrenzungen der Korrelations-Koeffizienten, die in Punkt 3.3 beleuchtet werden, sowie der Begrenzungen von beschleunigten Alterungsverfahren, können aus den Daten dieses Artikels folgende Schlussfolgerungen gezogen werden:

1. Die Veränderungen der Alpha-Zellulose, die sich bei der beschleunigten Alterung von drei Tagen bei 100°C zeigten, stimmten gut mit den Veränderungen der Alpha-Zellulose überein, die sich nach 36 Jahren natürlicher Alterung zeigten. Die Alpha-Zellulose, oder vielleicht eine geeignetere Alkali-Löslichkeits-Methode, sollte als Resistenzkriterium gegenüber beschleunigter Alterung geeignet sein.
2. Die Veränderungen der Kupferzahl, die sich bei der beschleunigten Alterung von drei Tagen bei 100°C zeigten, stimmten gut mit den Veränderungen der Kupferzahl überein, die sich nach 36 Jahren natürlicher Alterung ergeben hatten.
3. Die Korrelationen der Beibehaltung der Falzfestigkeit nach natürlicher und beschleunigter Alterung waren nur gering. Obwohl der Falz als Beurteilungs-Methode nach beschleuigter Alterung nützlich ist, sollte man sich nicht ganz auf ihn verlassen.
4. Die Korrelationen von inneren Rissen nach natürlicher und beschleunigter Alterung waren etwas besser als bei der Falzfestigkeit, sie waren jedoch nicht hoch.
5. Die Korrelation zwischen Kalt-Extrakt pH im Jahre 1937 und Veränderungen nach natürlicher Alterung in der Alpha-Zellulose, Kupferzahl, Falzfestigkeit, Reiss- und Dehnungsfestigkeit deuten darauf hin, dass pH ein durchaus geeignetes Stabilitätskriterium ist.
6. Die Beibehaltung der Reissfestigkeit nach natürlicher Alterung stimmte gut mit der Beibehaltung der Dehnung nach der natürlichen Alterung überein, abgesehen von Hadernpapier.
7. Die Beibehaltung der Falzfestigkeit nach der natürlichen Alterung entsprach der Dehnung nach der natürlichen Alterung recht gut, jedoch nicht so gut wie Reissfestigkeit und Dehnung, abgesehen von Soda-Sulfit-Papier.
8. Die Korrelation zwischen pH und den Null-Spannungs-Dehnungs-Daten war fü alle 18 Pa-

pierarten nur gering. Nach einer Einteilung der Daten in statistisch homogene Untergruppen waren die Korrelationen besser.

9. Die Korrelation zwischen pH und der Bruchbelastung von nassem Papier in Prozent der Bruchbelastung von trockenem war für alle 18 Muster nur spärlich. Nach einer Einteilung in statistisch homogene Untergruppen waren die Wechselbeziehungen besser.
10. Die Korrelationen zwischen pH und Energie bei Bruch bei nassem Papier waren nur gering.
11. Die Korrelation zwischen pH und Dehnungsfestigkeit bei nassem Papier war sehr gering. Nach einer Einteilung der Daten in statistisch homogene Untergruppen waren die Korrelationen genügend.
12. Es zeigt sich, dass pH und Veränderungen der Alkali-Löslichkeit, Reduzierfähigkeit und Zerreissfestigkeit nach einer beschleunigten Alterung von 72 Stunden bei 100°C angemessene Stabilitätsindikationen sind. Der Falz ist empfindlich, aber nicht so wertvoll.
13. Es zeigt sich an Hand der Daten nach natürlicher Alterung, dass die Spannungs-Dehnungs-Daten bei Null, die Verlängerung und die Festigkeit im nassen Zustand in Prozent zur Festigkeit im trockenen Zustand wertvolle Kriterien sind.
14. Wenn in diesem Artikel die Daten mit den Daten verglichen werden, die durch Handbögen bei 90°C, Null und 50% Feuchtigkeit erreicht werden, so zeigt sich, dass die Atmosphäre für eine beschleunigte Alterung etwas Feuchtigkeit enthalten sollte, jedoch weniger als 50% bei 90°C.

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William K. Wilson
Preservation Services Division
National Archives and Records Service
Washington, DC 20408, U.S.A.

E. J. Parks
National Bureau of Standards
Washington, DC 20234
U.S.A.

Conservation and Restoration of Manuscripts and Bindings on Parchment

by M. V. YUSUPOVA

Parchment is an extremely durable material which has made it possible to preserve early manuscript books and documents (acts, deeds, diplomas, office patents) up to the present time. These materials usually pertain to the most ancient part of a collection and have great scientific, cultural, historic and artistic value.

The physical condition and preservation of manuscripts and manuscripts on parchment are, to a large extent, determined by the nature and specific physico-chemical properties of this material. Parchment is untanned leather of special dressing, which possesses some alkalinity. The latter property lends it a certain resistance to the effect of acid components of air and creates a certain protection against microorganisms, which prefer a lightly acid substrate. Nevertheless, its extremely high hygroscopicity substantially diminishes the stability of this material: moisture content in it fluctuates from 10% to 40%, the changes in the relative humidity of the ambient air ranging from 40% to 80%.[9]

When preserved in an atmosphere of relative humidity of 40% and less, parchment undergoes deformation and becomes stiff, its surface decreases appreciably and the ink and dyes can fall off. Yet greater deformations and crumbling of leaves are brought about when manuscripts are preserved in conditions of high humidity as parchment is an anisotropic material and adsorbed water spreads unevenly on its surface and in volume. In a bound manuscript, kept in a damp place for some time, the edges of the leaves, which absorb atmospheric humidity most heavily, become so deformed that the edge area increases to a significant degree with the result that it is not always easy to close the book.

In this way the most widely spread damages of parchments are different kinds of deformations. This is precisely why the main attention in restoration practice is paid to softening and straightening, i.e. the elimination of deformations.

To other frequently encountered damages belong: decay and deterioration of manuscripts, written in acid ferrogallic inks; fading of non-water-resistant and ferrogallic texts; the falling off of texts and colour layer of miniatures; appearance of fragility and transparency; pigment spots of different colour and intensity, different losses, ruptures and cuts. The elimination and prevention of

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development of damages of different kinds make up the main problems of contemporary restoration and conservation of parchments.

1. Examination of Reasons Leading to the Heightening of Transparency of Parchments in the Course of Eliminating Deformations and Softening

The softening and straightening of parchments is a difficult problem, and many researchers and restorers have given much time and effort to its solution. Compositions recommended for softening are many and varied. Among them are different emulsions such as spermaceti,[1,7] stearic,[12] castor,[13] lanolin,[11] spermaceti-lanolin[21] and egg emulsions.[12,13]

The qualitative and quantitative composition of emulsions varies greatly,[1,7,12,13] but the technique of their use is practically invariable. The emulsion is spread on a small area of the parchment with a tampon or soft brush and this area should, as soon as possible, be smoothed out. The surplus of the emulsion is removed with a gauze tampon and filter paper, which is then pressed with an iron heated up to 45–50°C.[13] In order to protect the text against mechanical effects of the tampon or brush, the impregnation should be made through a thin sheet of long-stapled paper.[11] Emulsion treatment, to a certain degree, compensates the fatty substances which were lost by the parchment in the process of natural ageing and preservation in unfavourable conditions. Nevertheless, the use of emulsions is limited because they do not always ensure the necessary softening effect and frequently, due to the difficulty in determining the dosage, their application leads to the stickiness and transparency of parchments. Restoration practice and later research show that it is feasible to do the softening and straightening with the help of water and some water-containing systems.[3,10] The efficiency of their action is, apparently, stipulated by the restoration of optimal moisture content and its sufficiently even distribution in the parchments. Among water-containing systems, aqueous solutions of glycerine, potassium acetate, and gelatins with small additions of spermaceti in an organic solvent are especially well known.[7,20] Yet the most popular substances are aqueous-alcoholic solutions of urea,[2] and the most approved method is that of softening the parchment by moistening it.[2,5,7,10,13] When urea is used the parchment is either moistened thoroughly or dipped in its 5%–10% solution after which it is simultaneously dried and pressed in wax paper. After the parchment has partly dried additional treatment with 1–2% alcoholic benzol suspension of spermaceti is recommended.[1] In cases of moistening with water the deformed parchment sheet or fastened block is held for some hours under permanent control in a thermostat with indoor temperature and 90–98% humidity. When the parchment has sufficiently softened it is recovered from the

thermostat, carefully smoothed out and dried in a press.[5,7,10,13] Similar results can be attained more rapidly if the parchment is placed between moist sheets of filter paper. The paper is moistened with a piece of cloth either with water or 50% ethyl alcohol.[3,7] The softened parchment is also dried in the press. Filter paper or a piece of cloth, which should be regularly changed, is used as a pad. Moistening with water is usually recommended for parchments with waterproof texts.

The mechanism of moistening in water or in urea seems to be the same as the water, present in both softening systems, and should adsorb on the hydrophilic surface of the parchment mainly due to its high surface energy. Urea solutions, the main reaction of which is weak, are, probably, capable of provoking an additional effect: partial hydrolysis of collagen (the main protein of which parchment is composed). Probably, it is precisely this phenomenon that ensures the quick ungluing of some fastened manuscripts with the help of aqueous-alcoholic solutions of urea. Nevertheless, both methods have a serious drawback as after restoration, transparency can increase and sometimes the outward appearance of parchments suffer. In order to find out and eliminate conditions which bring about the appearance of transparency, we carried out a comparative analysis of methods of softening with the help of water and urea and examined the effect of pressure, padding material and different reagents on the physico-mechanical and physico-chemical properties of parchments under conditions of natural and accelerated ageing. The subjects of study were binder's parchments of the 17–19th centuries and writing parchments of the 19th century. The effects of different methods and conditions of restoration were assessed by the changes in transparency (light transmission coefficient with the effective wave length of 633 mm), elasticity (of the specific elongation), hygroscopicity, moisture yield, porosity and the value of the pH of parchment. The transmission coefficient was also measured with a universal photometer. All the other characteristics were determined according to standard methods used for leather. Samples for the assessment of durability and elasticity were prepared by the asymmetric fringe method. Accelerated ageing was produced by ultraviolet illumination during 200 hours. In these conditions the appreciable fall in durability and porosity and the heightening of the transparency of parchments discovered in special experiments are all indications of ageing (destruction).

In order to determine transparency dependence in relation to the pressure, which varied greatly (from dozens of $kgf/sec/m^2$ to pressures, developed in a squeezing binder's press) samples of two types were used, the first of which were earlier kept in natural conditions and the second aged under the action of ultraviolet illumination. Some control samples of each type were only pressed while others were moistened (water and 50% ethyl alcohol) or treated with urea (moistening or dipping in a 10% aqueous-alcoholic solution). It was discovered that transparency dependence in relation to the pressure was manifest in the region of pressures in the order of hundreds of kgf/sec/m². Increase in transparency was observed not only in samples of the first type, which were either subjected to treatment or were softened by moistening. In the rest of the cases with the heightening of pressure the transparency increased, the more so when urea was used. The transparency of artificially aged samples grows on an equal level, after pressing and after softening. Optimal pressure for artificial ageing of writing parchment, which does not provoke an increase of transparency and frequently ensures a satisfactory quality of pressure, is 130–150 kgf/sec/m². In a number of cases an increase in the duration of pressing also brings about a heightening of transparency.

As it turned out, the degree of change in transparency also significantly depends on the character of the padding material used in pressing. Filter, or waxed paper, kapron cloth in combination with filter paper and broadcloth were used as padding materials. The effect of the pad was discovered on the level of pressures in the order of hundreds of kgf/sec/m² and was connected with the previous treatment of parchment. With the use of all padding materials the transparency increases, but when urea and not moistening with water is applied the transparency increases still more strongly. The heightening of transparency is less marked when parchment is pressed in broadcloth and kapron with filter paper.

The method of softening with urea consists of a number of operations: cleansing with water followed by rapid drying with ethyl alcohol, treatment with aqueous-alcoholic solutions of urea, treatment with alcoholic-benzol suspension of spermaceti.[1] But the increase of transparency at all stages of restoration is not excluded and therefore we studied the effects of different components (water, ethyl spirit, aqueous, alcoholic and aqueous-alcoholic solutions of urea of different concentrations, benzol, alcoholic-benzol suspension of spermaceti), used in accordance with the given method, on the softening and transparency of parchments. It was established in an organoleptic way that softening resulted only when water and systems containing water: aqueous and aqueous-alcoholic solutions of urea, were used. Photometric measurements showed that suspension of spermaceti, benzol, alcohol and alcoholic solutions of urea do not affect the transparency and only alcohol diluted with water (1:1 ratio) leads to its slight growth. And though treatment with spermaceti does not change the transparency it is frequently accompanied by the formation of an uneven white coating which can, nevertheless, be easily removed with benzol for it is merely the surplus of spermaceti. Water and aqueous solutions of urea,

while not raising the transparency during moistening to any significant degree, increase it 1.5–2 times when parchments are soaked in them for half an hour. Aqueous-alcoholic solutions of urea provoke a larger increase in transparency. Nevertheless, precisely these solutions were recommended for restoration as it was assumed that the presence of alcohol in them should favour the fixing of texts.[1]

The increase of transparency in cases when urea was used was probably stipulated by structural and mechanical changes and partial hydrolysis of collagen, though substantial changes of pH were not discovered. The observed substantial decrease (1.5–2 times) of their porosity alone, speaks of structural changes. When gradually moistened with water or 50% alcohol, the transparency and porosity remain unchanged, a fact which makes it possible to assume the absence of structural and chemical changes in parchments under such conditions of softening.

Physico-mechanical tests showed that when softened by water and urea the limit of durability in relation to extension and the hygroscopicity of parchments do not change. Relative extension, characterizing elasticity, in the case when water is used, appears to be somewhat lower than in the case of urea. Nevertheless, this fault is compensated by a less than half water yield, i.e. the capability of parchments to bind water more durably and, apparently, remain in a softened state longer.

In this way the results of research show that it is simpler, easier and more reliable to perform the softening and straightening of deformed parchment manuscripts and bindings by gradually moistening them with water ("remote" moistening). The use of aqueous-alcoholic solutions of urea should, probably, be limited to cases of ungluing of fastened manuscripts, the parchment of which has already become transparent in the process of ageing.

2. Removal of General Soiling and Pigment Spots from Parchments

Frequent damages of parchments include general soiling and pigment spots of microorganisms. There are comparatively few works devoted to cleaning and they usually contain the most general recommendations which lack the necessary methodological instructions. In particular, these works suggest that spots from thin parchments of bindings can be removed by cleaning them with a sponge wetted in water with a slight addition of glue,[9] but the concentration and nature of the glue are not mentioned and it can only be supposed that what is meant is an aqueous solution of gelatin. If parchment is soiled by mineral or organic substances it is recommended to clean it with water,[19] soap alcohol,[18] a weak solution of soap,[7] or an alcohol solution of the mixture of borax and boric acid with a slight addition of the antiseptic – nipagin.[30] In cases where there are yellow and brown spots some authors suggest that parchment should be carefully treated with hydrogen peroxide,[21] an aqueous solution of alum or chlorine water[7] followed by careful washing and neutralization of whitening agents. All surface soils in the form of mycelium and spores of fungi, adipose matter and other substances are carefully removed mechanically[7] and then disinfected. Large-size documents are padded by paper sheets of appropriate size, impregnated with fungicide. This method is particularly useful in cases when manuscripts need constant protection for a long period of time.[9]

Analysis of literature shows that works dealing with the removal of soil from parchments are, as a rule, purely practical and do not contain sufficient information on structural and mechanical and physico-chemical changes of the material to be cleaned. Since it is necessary to establish reliable, scientifically grounded restoration methods, we have explored the possibility of performing a general cleaning and the removing of pigment spots of a microorganism nature from parchment manuscripts and bindings.

Subjects of investigation were parchment bindings of the 17th-19th centuries, made in different ways, and old parchments with texts. Since all parchments possess some alkalinity, the choice of cleaning and whitening systems to a great extent depended on their hydrogen content, the change being allowed within the 7–10 range. The following substances were tested as cleaning and whitening agents: water, suspensions of subalkali soap (5 and 10%) dissolved in 50 and 90% ethyl alcohol; multicomponent paste for removing spots of unknown origin (the composition of the paste: ammonia (10%) – 80 ml; chipped subalkali soap – 15 gm, borax – 5 gm, ethyl alcohol (96%) – 6,2 ml, water – 120 ml); 6–10% water solution of chloramine B. (It is made by dissolving 10 gm. of chloramine in 90 ml. of water. The solution should be filtered through a paper filter. A transparent filtrate is used for whitening.)

The parts of parchments that had been soiled were treated with appropriate cleaning means, after which they were washed with water or alcohol; the treated samples were dried in a press. To remove spots, the parchment was placed on glass, cleaned with a gauze tampon wetted with a chloramine solution, then two or three layers of gauze, also impregnated with chloramine, polyethylene film, glass and a small weight placed on it. In the case of through spots a compress was put on both sides of the parchment. When needed, gauze was again wetted in the process of whitening. The overall duration of whitening amounted to 1–5 hours, depending on the thickness and quality of the whitening material, the intensity of the spot or soiling and demands made on the degree of cleaning. The cleaning and whitening effect of the systems was assessed in an organoleptic way. The protection of texts and fixing of borders of

cleaned areas were ensured with the help of the same polymer materials, which are suitable for the fixing of non-water-resistant and crumbling texts, alcoholic solution of vinyl acetate copolymer with ethylene and fluorolon H6 mixed with organic solvents.[16]

Water, alcohol suspensions of soap and ammoniacal-alcohol soap paste with a small addition of borax are inactive enough towards parchment, the probability of their affecting the parchment properties being practically the same because the use of the two latter systems shall be followed by water or alcohol washing. The use of chloramine naturally presupposes the possibility of physico-mechanical and physico-chemical changes in parchment as prolonged action of the alkali system can lead to hydrolysis of collagen, the main albumen making up any leather, and parchment in particular. In this connection we studied the effect of whitening with chloramine on tensile strength, elasticity (relative elongation), hydroscopicity, moisture yield and acidity of parchments both immediately after treatment and after artificial ageing. The characteristics of parchments were determined in accordance with standard methods used for leathers. Accelerated ageing was effected with ultraviolet illumination during 200 hours. The investigation showed that all the tested systems can be used for general cleaning of parchments, the most effective being paste and chloramine. After being treated with paste, parchments acquire a lighter colouring. If cleaned with chloramine the colouring becomes still lighter.

In the case of prolonged treatment with chloramine (whitening), intensely coloured, through pigment spots can be removed; if texts are fixed beforehand, general soiling of bindings and manuscripts can also be removed. Whitening with chloramine practically does not effect physico-chemical properties or the value of pH of parchments either in ordinary conditions or in the case of accelerated ageing. This testifies to the fact that various soiling of parchments can be removed, their durability remaining unchanged.

In conclusion it should be pointed out that in view of the great variety of parchments and of the nature of their soiling, a differentiated approach to the choice of means and methods of cleaning should be adopted. A preliminary sample should be made for each parchment document to be restored, as the materials ensuring the positive effect in a certain case can lead to undesirable results in another one (for instance, some parchments can turn yellow due to the effect of chloramine).

3. FIXING OF TEXTS AND ELIMINATION OF MECHANICAL DAMAGES OF PARCHMENTS.

In the course of natural ageing and particularly in unfavourable conditions of preservation many parchment manuscripts and documents deteriorate and become damaged in different ways. The most widely spread damages are: loss of certain fragments, breaks, cuts, lace-like falling out of parchment under acid ferrous-gall texts, crumbling of texts, scattering and crumbling of the paint layer of miniatures.

Problems of elimination of such damages and particularly those which concern the fixing of parchment, conservation and restoration of losses have been a subject of research for many years now. In our opinion the spraying of deteriorated parchments with parchment glue[21] is one of the oldest and best known methods. According to the opinion of some restorers this treatment makes it possible to fix not only parchment, but also the paint layer of miniatures. The drawback of this method is the vague composition of the glue to the lack of a universal means and raw materials for its preparation.

It is recommended for purposes of conservation of burnt and lace-like parchments to impregnate them with a dammar wax paste, 1–3% alcoholic solution of methylolpolyamide PFE 2/10 or a mixture of melted amber with spermaceti in benzol.[2] It is also possible to use PFE 2/10 for fixing texts and paint on parchment.[6] In cases when only a part of the text on the sheet needs fixing, solution PFE 2/10 is laid with a brush on the area and separate capital letters and miniatures that need fixing.[10] Nevertheless, practice shows that the film of PFE 2/10, apart from lending a gloss to the documents well nigh immediately after it has been laid on, is apt to become yellow with time and it is very difficult to remove this yellowness. This is why PFE 2/10 should, probably, be rejected as a conserving and fixing material. The use of amber with spermaceti in benzol is also not recommended.

The recipe for fixing suggested by German restorer Thamm deserves special mention.[20] It includes casein, borax, acid ammonium carbonate, cedar-nut oil, hexan, water, alcohol and a small dose of the antiseptic – nipagin. But since the qualitative assessment of its fixing effect and the principle of selection of the components are lacking this compound should be used with caution.

There are very many different compounds that are recommended for the fixing (impregnation) of painting on parchment. All of them are based on substances of organic and synthetic origin. The best known impregnators are: gelatin, shellac, Canadian balsam, starch, latex and paraffin emulsions,[13] (Microcrystal wax, mixture of bees wax with dammar [5:4 ratio]), wax-pistachio paste, polyvinylacetate,[14] soluble nylon.[17]

The gelatin is prepared in the form of a 1–2% solution in a water bath at 40–50°C. Before use, the following components are added: antiseptic (1:3 ratio) – a weak solution of parachlormetacresol or 2% ethyl alcohol solution of thymol with a small addition of peppermint or clove oil. Sometimes 1–2% of neutral

untinted soap is added as a softening agent. The object is impregnated with the solution by dipping; it can also be laid on with a brush or roller. The surplus of the solution is removed with a roller. The gelatin impregnator is suitable for one-sided and two-sided objects. Its main drawbacks are: hygroscopicity and difficult proportioning as a surplus of gelatin provokes the formation of glossy spots and the darkening of paintings.

Shellac in the form of an aqueous solution and Canadian balsam, dissolved in benzol, is sprayed with a sprayer a number of times. Like gelatin, these substances should be used in moderation. They are suitable for the treatment of two-sided parchments. According to Farmakovsky,[13] Canadian balsam is the best impregnator. When fixing the paint layer with wax or wax resins it is necessary to quickly remove the surplus of the impregnator in order to prevent the appearance of transparent spots on the parchment (the surplus is usually removed with a tampon wetted with gasoline).

The starch impregnator is prepared by dissolving corn starch in cold water which is then warmed in a water bath, and a hot solution of antiseptic (Parachrolmetacresol, for instance) is gradually added. Soap can be used as a softening agent. Starch glue is laid on in the same way as gelatin, but unlike the latter it is used for the treatment of one-sided parchments only as it overshades the text. Latex and paraffin emulsions are also used for one-sided documents for the same reason.

According to V. Filatov, polyvenylacetate is suitable for the fixing of the paint layer as its film is not too glossy. It is soluble in organic solvents (acetone) and should not damage paints and inks. Attempts to use water-soluble nylon failed because a tinted film, which was difficult to remove, appeared.[14] According to certain data[17] only an alcoholic solution of nylon of a special brand has a positive effect.

In order to fix a peeling and crumbling paint layer synthetic polymers – aqueous dispersion of copolymer of polylacetate with 2 ethylhexilacrilate and organic solutions of fluorolons – have become particularly popular in recent years.[14] Among materials recommended and suitable for restoration and conservation of parchments, synthetic polymers seem to be extremely promising because they can form colourless, elastic, water-proof films with good adhesion, high chemical stability and resistance to light ageing; they can also be easily removed. Nevertheless, a universal material which would fully satisfy the complex of the listed demands has not yet been found.

In cases when it is necessary to restore lost fragments of parchments in order to supplement the lacking parts, as for gluing, many different materials are used. Formerly paper, cloth, caecum of animals, casual parchment and parchment shavings were used; cuts were sewed up with flax and silk thread. In recent years some workshops have begun to use substitute parchment.[8] This subsitute is made of printing paper impregnated with an alcoholic solution of methylolpolyamide PFE 2/10 with filler (chalk) under low pressure. As opposed to materials known earlier this substitute coincides well with different kinds of parchments in colour, thickness and texture. Nevertheless, when restoring parchment documents and manuscripts, which are usually of high value, it is better to use parchment. Recently some Soviet industrial enterprises have begun to manufacture parchment especially intended for restoration.[15]

For the gluing of parchments the following substances are used: parchment glue,[2] aqueous solution of acetic acid,[9] mixture of gelatin, acetic acid and a small quantity of alcohol,[20] composition of animal glue and water with an addition of formalin as an antiseptic, a composition made up of rubber, shellac and rosin in carbon bisulphide, solution of celluloid and citric acid in acetone.[7] Nevertheless, all these glues have substantial shortcomings among which are an indefinite character of composition (parchment glue), chemical effect upon parchment (acetic acid, composition with formalin), toxicity and inflammability (compositions with carbon bisulphide and celluloid). In this way the analysis of literature shows that, notwithstanding a fair amount of recommendations, satisfactory materials and methods of removal of mechanical damages to parchment have not yet been discovered. Nonetheless, in connection with the need of performing work of this kind, we examined the possibility of fixing crumbling texts of manuscripts and the gluing of parchments with the help of some synthetic polymers.

The subject of study was a one-sided manuscript on smooth parchment, written in soot ink. Of polymers fluorolon H6, dissolved in acetone and copolymer vinylacetate with ethylene in an alcoholic solution – CVEB were used. Special interest in CVEB was stipulated by its capability of dissolving in ethyl alcohol because alcohol does not practically affect old inks and when it is necessary to remove the polymer film there is no risk that this will weaken the intensity of their colour. Fluorolon and CVEB in the form of solutions of different concentrations (1–10%) were laid on the parchment a number of times. The effect of fixing was assessed either by the presence or the intensity of the imprint on filter paper, or after remote moistening or after keeping the parchment in water for 30 minutes.

In order to characterize the properties of parchments in accordance with methods accepted for leathers, their durability (tensile test), elasticity (relative elongation), hygroscopicity, moisture yield, value of pH and porosity in conditions of usual preservation and accelerated ageing were tested. Accelerated ageing was accomplished through ultraviolet illumination during 200 hours.

The experiment showed that fluorolon and CVEB are capable of ensuring

satisfactory fixing of soot-ink texts, which, in cases when polymers were lacking, immediately fell off when the samples were dipped in water. With the increasing of the concentration of polymers the quantity of impregnators needed for fixing diminished. The physico-mechanical indices of the value of pH of parchments, when films were laid on, did not change even in conditions of artificial ageing. Nevertheless, in cases when remote moistening was used fluorolon showed a higher adhesion to parchment as compared to CVEB, the films of which frequently came off in one piece after moistening. For this reason when fixing crumbling texts it is better to use fluorolon H6.

In order to weaken the gloss, which films made up of highly concentrated solutions of polymer impart to parchment, it is recommended to select the optimal concentration of a solution and the necessary quantity of impregnators in each separate case. In cases when very glossy films form they can be removed (entirely or partially) with filter paper, wetted with an organic solvent (acetone, for example).

The materials we chose for gluing in our research were binding parchment of the 17th-19th centuries, writing parchment of the late 19th century and new contemporary parchment. The gluing substances we tested were an alcoholic solution of methyl polyamide PFE 2/10 (29.4%), which we compared with a 10% aqueous solution of acetic acid. We chose PFE 2/10 by reason of its capability of forming water-proof films, possessing high adhesion to parchment. These films do not lead to the deformation of parchment, which is also its positive characteristic.

The gloss and yellowness of films that impede the use of PFE 2/10 when fixing texts and ink do not, apparently, in the case of gluing, have much importance. The comparison of the gluing action of PFE 2/10 and acetic acid is explained by the satisfactory durability of the glued places, ensured by acetic acid, due to the simultaneous hydrolysis of collagen, the main and additional material.

The gluing was carried out in the following manner: the edges of cuts (holes) and patches were ground off with a sharp scalpel or abrasive paper. We then moistened them with glue, fitted the pieces together and padded them with filter paper and put them in the press to dry. After drying, the place of gluing was brought to the needed thickness with the help of pumice or abrasive paper. When removing small punctures, particularly fall-outs under the acidic text, parchment shavings mixed with a small quantity of glue, were used.

Tests showed that methylolpolyamide PFE 2/10 ensures reliable gluing of parchments. Moreover, the parchments do not become deformed and do not call for additional limitations when moisture treated (remote moistening, for instance). Neither do they become yellow or transparent in glued-up areas. It is much more difficult to stick the pieces together as reliably and neatly when acetic acid is used. Yet another drawback here is that patched-up areas always prove to be transparent. In this way methylpolyamide has important advantages over acetic acid and other systems suggested earlier. Apparently it can be recommended as the best glue to use when missing parts of parchments are added.

Abstracts

Conservation and Restoration of Manuscripts and Bindings on Parchment

This article contains short descriptions of the main damages of manuscripts and bindings on parchment. Literature dealing with problems of their conservation and restoration is analyzed.

Reasons of increase in transparency of parchments, which is the result of removal of deformations and softening, are examined. The possibility of eliminating this fault is discussed. Materials for the effective removal of different soiling, the fixing of texts and elimation of mechanical damages of parchments are suggested.

Conservation et restauration de manuscrits et de reliures sur parchemin

Cet article comporte une série de descriptions brèves des dégâts principaux survenant aux manuscrits et aux reliures sur parchemin. Les publications traitant des problèmes de conservation et de restauration font l'objet d'une analyse.

Les raisons de l'accroissement de transparence des parchemins résultant de l'élimination des déformations et de l'assouplissement sont passées en revue. La possibilité d'élimination de ces défauts est discutée. Les produits d'élimination efficace de divers souillants, la fixation des textes et l'élimination des dégâts d'ordre mécanique survenus à des parchemins sont suggérés.

Konservierung und Restaurierung von Manuskripten und Einbänden auf Pergament

Dieser Artikel enthält eine kurze Beschreibung der wichtigsten Angriffe, denen Pergamentmanuskripte und -einbände ausgesetzt sind. Die Literaturquellen, die sich mit der Konservierung und Restaurierung von Pergament befassen, werden analysiert.

Die Ursachen für das Anwachsen der Transparenz von Pergament als Ergebnis der Beseitigung von Verformungen und Weichmachung werden untersucht. Die Möglichkeit, diesen Fehler zu vermeiden, wird diskutiert. Es werden Materialien für die effektive Entfernung von verschiedenen Verunreinigungen, die Haltbarmachung der Texte und die Beseitigung von mechanischen Beschädigungen von Pergamentseiten vorgeschlagen.

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M. V. Yusupova
Department of Hygiene and Restoration of Books
State V. I. Lenin Library of the U.S.S.R.
SU-101000 Moscow
U.S.S.R.

Biodeterioration and Biostability of Library Materials

by J. P. NYUKSHA

There are over 300 species of fungi causing damage to library stocks. Owing to the process of evolution, the fight against their destructive action is growing more and more complicated. A differentiated system of protection has been worked out to make prints and manuscripts less vulnerable to biological attack: a) conservation in the usual storage conditions; b) protection from the effect of temporary increase in humidity and temperature; c) the imparting of greater biostability during exposure to prolonged unfavourable influences. In selecting the preservatives, account is taken not only of the commonly accepted requirements, but also of the capacity of biocides to combine with other materials to provide durability of paper, and of the changing microstructure of the paper under the influence of these compounds, and of their specific influence on the various microfungi, etc. Preference is given to polymeric substances. In the USSR a new polymeric antifungal substance is being synthesized – a guanidine derivative which has been tested exhaustively in the laboratory of the Saltykov-Shchedrin State Public Library, Leningrad. Its advantages as a preservative have been proved.[5,6] Guanidine preparations have different toxicity depending on their chemical structure. The preparation which we use, polyhexamethyleneguanidine, was synthesized in the USSR and was subjected to careful toxicological, medical and hygienic testing. It is considered to be harmless to warm-blooded animals, so its use in medicine is allowed. For instance, for disinfection of surgeon's hands, in paper for sanitary and hygienic purposes, etc. The evaluation of the preparation is made by the Institute of Disinfection and Sterilization of the Academy of Medical sciences of the USSR. The subject of this paper is the use of this substance for the protection of library materials.

Books and documents are complex chemical combinations of both natural origin and of artificial and synthetic polymers. During storage they undergo the processes of aging, alteration and destruction. This leads to the appearance of new destructive substances in their composition.

Books undergoing restoration are combined with materials that are more or less similar to the original. With the years, more and more techniques appear, using new chemically synthesized polymers to restore the lost properties of the objects in question, and to imbue them with new properties. This corresponds to the general trends in contemporary restoration.

Restaurator 4 1980: 71–77
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The restorer, nonetheless, always prefers using natural materials and of interfering as little as possible in the original structure of manuscripts and ancient books. Many of the materials used, particularly the adhesives, are aqueous systems, in which the content and form of the water changes easily in accordance with the level of relative humidity of the air. In restoring paper, the use of hydrophilic compounds has proved to be reliable, being compatible with its colloidal system. It is mainly these compounds that are subject to biodeterioration. Therefore the problem of susceptibility, protection and biostability of objects of cultural value always takes first priority with researchers. However, it can never be solved completely or simply. This is due to two reasons: one, the fact that the organisms adapt themselves to living on materials containing antifungal substances, and that this process is endless and has, so far, not succumbed to prognosis; and two, more and more efforts are required for biostability as a result of the constant widening choice of chemicals used for restoration purposes. The history of restoration records the fact that preservation of the first adhesives was only required to act for a few days, while the work was going on. Subsequently the task was complicated by the necessity to give protection not only to the adhesive, but also to the objects being restored. This led to the use of higher concentrations of antifungal substances and to the rejection of some of them. Later on, rigid standards were established for substances to be used for conserving valuable manuscripts and prints. Meanwhile, things were happening that influenced restoration work in the whole world. At the same time the range of activity in the field of protection of objects of cultural value was widening. The system of biological protection was subdivided along three main lines:

1. Conservation of the parts of the objects (these parts are mainly adhesives) most susceptible to the action of microorganisms, for the purpose of ensuring their conservation in ordinary storage conditions;

2. Conservation of objects with a view to protecting them in an emergency, when some accident temporarily upsets normal storage conditions;

3. Conservation providing for the protection of objects from prolonged exposure to damaging elements: sudden changes in temperature and humidity, repeated periods of high temperature and high humidity.

In practice there is, naturally, no such strict differentiation. Many protection systems are transitional.

In the new conditions for library economy we consider it advisable to implement restoration and conservation processes that simultaneously solve the problem of durability, biostability and resistance to wear. From this point of view optimal results can be achieved by the use of mainly polymer compounds compatible with material of natural origin.

Our work may serve as an example of this. We used polymerous guanidine compounds for the protection of adhesives and the paper of manuscripts and prints.

Guanidines are derivatives of imino-urea. The formula for guanidine is

$$HN = C \begin{smallmatrix} \diagup NH_2 \\ \diagdown NH_2 \end{smallmatrix} .$$

It is a strong base, it has the same strenght as NaOH. One of the guanidine derivatives, arginine, occurs in protein. The formula for natural guanidine derivative (isoamilene-guanidine) is

$$HN = C \begin{smallmatrix} \diagup H_2 \\ \diagdown NHCH_2CH = C\ (CH_2)_3 \end{smallmatrix}$$

The seeds and leaves of broom contain it.

Polymerous guanidine compounds are more stable than monomers and have a number of useful properties. Some of them have been developed in the USSR[2]. For example, polyhexamethyleneguanidine – a water-soluble polymer of the kation type. Its chemical structure is

$$NH_2 \left[(CH_2)_6\ NHCNH \atop \diagdown NH.HCl \right]_n H, \quad n = 4 \pm 6$$

HCl may be replaced by other acids, among them lauric acid. This substance is a transparent, hard, yellowish, odourless resin with a softening temperature of 80–100°C. The resin is hygroscopic, watersoluble, any concentrations are possible and is in a 1% water solution of polyhexamethyleneguanidine, has pH 8–10, stable in storage. Alkaline pH is caused by basic groups NH_2. When heated for a short time and exposed to sunlight the polymer does not change its properties. In decomposition polymerous carbamide (urea) $(NH_2 - CO - NH_2)_n$ and NH_4Cl are formed. Thus polyhexamethyleneguanidine does not have a bad influence on the physical and chemical state and properties of paper during artificial aging and prolonged storage. Owing to its polymerous structure and kationic properties polyhexamethyleneguanidine is regularly distributed in the material. A microexamination of paper impregnated with polyhexamethyleneguanidine shows that the substance fills the spaces between fibers evenly and covers the fiber surface completely. Polyhexamethyleneguanidine has a fungicidal and fungistatic effect on book-damaging fungi[3].

These fungi do not grow on paper which contains 1% of the substance: *Chaetomium globosum* Kunze ex Fr., *Penicillium cyclopium* Westling, *P. roqueforti* Thom, *Sporotrichum bombycinum* Cda., *Aspergillus terreus* Thom, *A. amstelodami* (Mang.) Thom et Church, *Verticillium tenerum* Nees ex Lk., *Myxotrichum deflexum* Berk., *Stachybotrys chartarum* (Ehr. ex Lk.) Hughes. The conidio spores of *Penicillium purpurogenum* Stoll, *Trichoderma viride* Pers. ex Fr. perish. *Rhizopus nigricans* Ehr. ex Cda., *Aspergillus flavus* Lk. ex Fr., *A. niger* v. Tiegh., *Myrothecium verrucaria* (Alb. et Schw.) Ditm. ex Fr. need higher concentrations of polyhexamethyleneguanidine, up to 1.5–2% and even 3%.

The paper samples impregnated with a 2% solution of the polymers at pH level 8.5 showed themselves fungi-resistant under controlled conditions at relative humidity of 100%. This protection of the materials is ensured under accident conditions.

A valuable property of polyhexamethyleneguanidine is its compatibility with other polymers including proteins. The latter reduce the fungi static effect only 1.5–2 times. While it is known that in the presence of proteins other (monomeric) substances reduce their antifungal effect dozens of times. In connection with this the use of 1.5–2% preparation is advisable for conservation of water compositions containing protein and starch. The pH level of paper restored with this adhesive is 5–5.5.

Polymerous guanidine derivatives are compatible with the polymers which strengthen the paper and impart hydrophobic nature to it: polyethylenimine[1], polyamidamine, polyacrylamide[4], and other modifications of these polyelectrolytes. The latter form complexes with cellulose and polyhexamethyleneguanidine. This improves the retention of the substance in the paper during moulding and water processing during restoration.

Cotton paper (48° Schopper-Riegler freeness, mass of 40 g/m^2) containing polyhexamethyleneguanidine, polyamidamine and polyacrylamide was made in the laboratory. The structure and test results of the paper samples are shown in Table 1.

The results summarized in Table 2 show that pH level of the laboratory-made paper is equal to 6 or a little bit more. In spite of the distinct alkaline reaction of a 1% initial product solution the low pH of the paper indicates that the suggestion of binding its amine groups with cellulose is correct. Polyhexamethyleneguanidine (samples 1 and 2) does not impart durability to paper. In the presence of polyacrylamide and polyamidamine (samples 3 and 4) folding strength increases 5–7 times, biostability being satisfactory (better than other samples show). The biostability was evaluated by means of the cellulasae of *Trichoderma viride*.

Polyhexamethyleneguanidine did not increase moisture content of paper.

Table 1: Paper composition.
Table 1: Composition du papier.
Tabelle 1. Zusammensetzung des Papiers

Polymer		Number of paper samples								
Name	Concentration, %	1	2	3	4	5	6	7	8	9
Polyhexamethyleneguanidine	1					x	x			
	2	x						x	x	
	3		x							
Polyacrylamide	1			x		x		x		
Polyamidamine	1				x		x		x	

Table 2: Properties of paper samples
Table 2: Caractéristiques des échantillons de papier.
Tabelle 2: Eigenschaften der Papiermuster

pH	6.6	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3
Folding strength, number of double folds	28	31	168	215	186	223	238	256	16
Bioproofness, relative retain of strength, div.	2	2	5	6	7	8	7	8	1
Moisture content, %	4.4	4.7	5.0	4.9	4.1	4.8	4.2	4.2	4.7

The filter paper impregnation with 1.5% polyhexamethyleneguanidine solution led to a decrease in its moisture content from 46.7% to 17.7% at air rH of 100%, i.e. 3 times. When the humidity of the air is 45–50% the moisture content of this paper impregnated with adhesives based on NaCMC, polyvinylalcohol, polyvinylacetate became lower after introducing polyhexamethyleneguanidine into the paper composition.

The considerable increase of durability was achieved by means of paper impregnation with a 1% polyacrylamide solution and a 2% polyhexamethyleneguanidine solution in strict succession. The paper became 20 times more durable and obtained biostability. If paper contains even 5% of polyhexamethyleneguanidine the character of its luminescence under the influence of mercury line radiation with wave-length 365mm remained unchanged. Polyacrylamide and polyamidamine impart luminescence of a dingy-pink tint to paper.

Summaries

Biodeterioration and Biostability of Library Materials

The antifungal substance polyhexamethyleneguanidine has been proved safe for paper and may be used for restoration of library materials of any value. Polyhexamethyleneguanidine has an evenly spaced distribution in paper. It does not increase paper moisture content. The substance supports biostability of paper and of natural compositions containing protein and starch for 2–3 years. It is notable for its specific action on cellulose-deteriorating fungi and inhibits the activity of their cellulases. At the same time it does not inhibit the effect of proteinase and amilase which are used in restoration. Polyhexamethyleneguanidine does not change paper durability, but in combination with polyacrylamide and polyamidamine it increases paper permanence and resistance to wear considerably. Content of the antifungal substance does not prevent subsequent optical and photographic researches of documents. Labour and health protection of those working with polyhexamethyleneguanidine or using the documents processed with it is guaranteed.

Deterioration et stabilite biologiques des materiels de bibliotheque

La polyhexaméthylineguanidine, substance à caractère fongicide, s'est avérée être un agent sûr pour le traitement du papier et elle peut être utilisée pour la restauration de documents de bibliothèques de valeur. La polyhexaméthylineguanidine présente un degré de répartition régulier dans le papier et n'accroît pas le taux d'humidité du papier. Cette substance maintient la biostabilité du papier et des composés naturels contenant des protéines et de l'amidon pendant 2 à 3 ans. Propriété remarquable d'action spécifique sur les champignons dégradant la cellulose et inhibition de l'activité de leur cellulases. Concomitament, ce produit n'inhibe pas l'effet des protéinases et des amylases utilisées dans les travaux de restauration. La Polyhexaméthylineguanidine n'altère pas la durabilité du papier, mais combinée à la polyacrimide et à la polyamidamine elle accroît considérablement la stabilité et la résistance du papier à l'usure. La teneur en substance fongicide n'altère pas les travaux de recherche ultérieurs optiques et photographiques sur ces documents. Les conditions de protection sanitaire des personnels travaillant avec la polyhexaméthylineguanidine ou utilisant des documents traités avec ce produit sont garanties.

Biodeterioration und Biostabilität von Bibliotheks-Materialien

Die Anit-Pilz-Substanz Polyhexamethyleneguanidin ist nachweislich sicher für Papier und kann zur Restaurierung von Bibliotheks-Materialien, auch von sehr wertvollen, verwendet werden. Polyhexamethyleneguanidin verteilt sich gleichmässig in dem Papier. Es erhöht den Feuchtigkeits-

gehalt von Papier nicht. Die Substanz unterstützt die Biostabilität von Papier und von natürlichen Zusammensetzungen, die Protein und Stärke enthalten, f4ur 2–3 Jahre. Sie zeichnet sich durch ihre spezifische Einwirkung auf die Pilze aus, die die Zellulose verschlechtern und unterbindet die Aktivität ihrer Zellulase. Gleichzeitig bremst sie die Wirkung von Proteinase und Amilase, die zur Restaurierung verwendet werden, nicht Polyhexamethyleneguanidin verändert die Haltbarkeit von Papier nicht, in Verbindung mit Polyacrylamid und Polyamidamin verbessert sie jedoch die Beständigkeit und Widerstandsfähigkeit von Papier gegenüber Verschleiss wesentlich. Der Gehalt an Anti-Pilz-Substanz verhindert die nachfolgende optische und photographische Untersuchung der Dokumente nicht. Der Arbeits- und Gesundheitsschutz derer, die mit Polyhexamethylenguanidin arbeiten oder die die Dokumente verwenden, die mit der Substanz behandelt worden sind, ist garantiert.

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Yu. P. Nyuksha, Dr. (biol.sc.)
Chief of the Restoration and Conservation Department
M. E. Saltykov-Shchedrin State Public Library of Leningrad
SU-191069 Leningrad
U.S.S.R.

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The Smithsonian Institution is offering a one year fellowship in materials analysis in residence at the Smithsonian, dealing with the application of techniques of the physical sciences to problems in art history, anthropology, archeology and the history of technology. Requirements for eligibility are a Ph.D. in a relevant scientific field or a degree/certificate in the conservation of artifacts or art objects. Sites: Smithsonian conservation facilities, departments of Anthropology, Mineral Sciences at the National Museum of Natural History. The deadline for application is January 15, 1981. The fellowship carries an award of $14,000 plus allowances. For more information write:

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Restaurator 4 1980: 78
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Special Conference on Fumigants Plans Broad Strategy Covering Staff Safety and Collections Care

Report Will Recommend Specific Steps Applicable to All Museums regarding Fumigation Procedures, Government Responsibility, Research and Training

Specific recommendations for the careful, legal use of fumigants to protect people and museum collections are expected by Fall from a recent special inter-disciplinary conference, "Fumigation in Museums, Preservation or Extinction," organized by the Association of Systematics Collections and sponsored by the National Museum Act.

The recommendations, compiled in a report presenting analyses of fumigation procedures; chemicals involved; governmental, legal and ethical considerations, and manufacturers' concerns, will be broadly applicable to the museum community.

Preliminary results of a pre-conference survey conducted by the New York State Museum disclosed widespread disregard among respondents, chiefly in natural history and anthropology museums, for the effects of powerful fumigants on staff and visitors. The findings strongly suggest that many curators and conservators worry more about the collections than even their own health and safety in the use of fumigants.

Ironically, the survey indicated, users of chemicals often lack knowledge of the potentially harmful effects of fumigants upon collections as well as of the hazards to human health.

The conference was directed by Dr. Stephen R. Edwards, executive director, Association of Systematics Collections, with Dr. Bruce M. Bell, Head of the Collections Management Section, New York State Museum, and Dr. M. Elizabeth King, Keeper of Collections, The University Museum, University of Pennsylvania, and chairperson of the Curator's Committee of the American Association of Museums. Brought to the Smithsonian Institution's Belmont Conference Center, Elkridge, Maryland, were some 30 museum scientists, legal experts and chemical manufacturers who assessed present museum fumigation conditions in the United States and Canada. Joining them were authorities in pest control and officials from federal regulatory agencies.

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Most of the participants represented professional and scholarly organizations whose opinions on the conference report and recommendations will be sought.

According to Dr. Edwards, the conference was convened to begin resolution of several difficulties. These arise, he said, from the pursuit of museum responsibilities in maintaining collections of the cultural and natural heritage in the face of government strictures on use of fumigants. Moreover, the problem is worsened by lack of knowledge about chemicals and procedures for their proper use, extensive specialization among museums, and absence of communication among museum professionals and with government agencies and manufacturers, Dr. Edwards observed.

Principal outcomes of the conference were decisions to seek creation of a program leading to fumigant research, staff training, appropriate facilities and equipment development, a comprehensive data clearinghouse, executive museum administrators' more complete understanding, and presentation of coherent information to government authorities. Strategies are being formulated to secure funding.

Availability of the final conference report and recommendations, including the survey findings and an annotation of federal pesticide regulations, will be announced in several museum professional publications and related journals.

Dr. Stephen R. Edwards
Executive Director
Association of Systematics Collections
Museum of Natural History
University of Kansas
Lawrence, KS 66045
U.S.A.

Dr. Bruce M. Bell
Head of the Collections Management Section
New York State Museum
Albany, NY 12230
U.S.A.

Dr. M. Elizabeth King
Keeper of Collections
The University Museum
University of Pennsylvania
33rd & Spruce Streets
Philadelphia, PA 19174
U.S.A.

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Contents 4:1

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RESTAURATOR. *International Journal for the Preservation of Library and Archival Material*, will bring original papers on the subjects mentioned in the titles (including etchings and engravings), as well as reviews and news of interest to scientists, conservators, archivists, and librarians.

Contributions will be accepted in English, French, or German. Abstracts and figure legends will be printed in these languages. Contributors not writing in their mother tongue are particularly asked to have their manuscripts checked for linguistic and stylistic errors.

Manuscripts should be original typescripts (not carbon copies), in double spacing and on one side only of the paper. They must be carefully revised, as alterations in print are expensive. The paper used must be non-absorbent. Author's name should be accompanied by the title, position and working place of the author.

An abstract of no more than 200 words should be sent with the manuscript. The abstract should be in the same language as the article. The publisher will provide translation into the two other languages, of the abstract and the figure legends.

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