NBSIR 74-632

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

W. K. Wilson and E. J. Parks

Paper Evaluation Section
Institute for Materials Research
National Bureau of Standards

December 18, 1974

Interim Report

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

NBSIR 74–632

COMPARISON OF ACCELERATED AGING OF BOOK PAPERS IN 1937 WITH 36 YEARS NATURAL AGING

W. K. Wilson and E. J. Parks

Paper Evaluation Section
Institute for Materials Research
National Bureau of Standards

December 18, 1974

Interim Report

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

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

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

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.

In 1937 a group of book papers made in the NBS 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" [1]. 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.

A copy of the original paper by Shaw and O'Leary is included as an Appendix to this report. 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 after accelerated aging for 72 hours at 100°C in 1937 are given in Table 4.

A group of commercial papers was tested before and after accelerated aging in 1929, and these papers were retested after 4, 8, 22, and 26 years of natural aging [2]. 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 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 probably can be explained by recent work in this laboratory [3, 4, 5] which showed that aluminum on the carboxyls in cellulose contributes 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 in this laboratory has shown that significant differences exist between moist accelerated aging and dry accelerated aging [3, 4, 5]. 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. A group of papers aged in air at 90°C and 50 percent relative humidity 10 years ago [6] has been tested, and it is expected that the data on these papers will be the subject of a separate report.

2. SAMPLES

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

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

Chemically these furnishes are very different. The soda-sulfite papers contain a high percentage of pentosans (hemicelluloses) (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 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 were determined by methods developed by Launer [7-9]. 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 percent relative humidity and 70°F.

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

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 [10]. Zero span tensile was measured using a commercial testing device 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 specimen) was determined at 50 percent relative humidity and 23°C [11]. Brightness (reflectance using a blue filter with peak transmittance at 457 nm) was determined by TAPPI Method T 452 [12].

3.3 Statistical Treatment of Data

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

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

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

Correlation coefficients were calculated according to the following formula:

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

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

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

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 parameter of a sample of paper, reflectance might vary enormously, but as long as thickness is maintained within allowable limits, the sample would be from the same statistical population. On the other hand, if the group of papers contained newsprint and a bond paper, 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 furnish. Each subset usually can be treated as belonging to the same statistical population. For some tests, one or more papers must be eliminated before the subset can be treated as a separate statistical entity. There is considerable scatter in most of the plots and one

cannot be sure that any relationship that may exist is a straight-line relationship, although such a relationship is assumed in calculating correlation coefficients.

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

3.4 Sampling

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

4. RESULTS AND DISCUSSION

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. 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 [6, 13]. Correlations among various properties are given in Tables 17-21.

Alpha cellulose and copper number

Data in Tables 4-6, the plots in Figures 1 and 2, and the correlation data in Table 17 show good correlations between 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. The correlation coefficients show that alpha cellulose and copper number, based on the data from these 18 papers, are suitable chemical tests for evaluating the stability of papers for permanent records.

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 place a value on 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. In general, the correlations between changes in alpha cellulose and copper number, after either accelerated aging or natural aging, with cold pH are not as good as the correlations between changes after natural aging with changes after accelerated aging. The correlations are fairly acceptable, 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 the overall trend is unmistakable. This is borne out by the correlation coefficients in Table 17.

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 strictly empirical.

By today's standards, these tests are considered to be archaic. Alpha cellulose [14] has been supplanted by other more convenient and supposedly more meaningful alkali solubility tests. The copper number test [15] 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 [16]. In addition, the copper number reagent causes further degradation of alkali sensitive cellulose during the copper number test.

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 retention of tensile strength.

The three alkaline soda-sulfite papers, 1158, 1172, and 1175, show good, but 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 percent, MD). With the exception of 1166 (79 percent, MD) all of the other papers show retention values of 94 percent 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 would 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 connection with other tests. Correlations of retention of elongation with cold pH are given in Table 20. Although the correlation for all 18 papers is not good, the correlation coefficients for the three subsets are much 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 are fairly good. 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 fairly high but correlations for the set of 18 papers are very low. 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 a function of alum added minus rosin retained are surprisingly good. 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 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 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 percent) or after accelerated aging (55-75 percent). 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 percent 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.

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, one would have expected the three alkaline papers to have retained a much higher percentage of their initial folding endurance. Number 1161 has a very high folding endurance, so it has retained its bonding 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.

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.

Correlations between internal tear after natural aging with other parameters are given in Table 19. Correlations between tear retention after natural aging and tear retention after (1) accelerated aging and (2) pH cold extraction, are not especially good. Correlations for specific populations are somewhat better. Correlations between retention 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. It has been shown earlier in this laboratory that significant changes in hydrogen ion concentration of the aqueous extract of the paper, especially

---

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

if the carboxyls are covered with aluminum, is a characteristic of moist aging. The magnitude of these changes in the naturally aged papers is not nearly as great as the magnitude of the acidity changes of handsheets with aluminum on the carboxyls aged at 90°C and 50 percent relative humidity. It appears, however, from these acidity data that some moisture in an accelerated aging procedure may be indicated.

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 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 residues, from oxidation of cellulose, and probably others.

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.

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 fairly good correlations, but 1207 and 1208, both of which contain titanium pigment, cannot be included in the rag 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 percent rosin and a large amount (4 percent) of alum. Numbers 1207 and 1208 contain rosin and probably nearly stoichiometric amounts of alum (with respect to rosin). Therefore, as there is an opportunity for some of the carboxyls in the first four rag papers to be covered with aluminum, and it is unlikely that the carboxyls in 1207 and 1208 are covered with aluminum, one would expect the latter two papers to be more stable than the other four. 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.

The three alkaline papers are somewhat higher in 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.

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 [17], 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 moisture regains. Moisture regain of the rag papers averages about one percent 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 [5] for dry aging of handsheets.

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. Indicators of retention of properties with time are pH and retention of properties after accelerated aging. On the basis of experience, one may make arbitrary decisions about minimum initial pH values and retention of properties with accelerated aging as indicators of stability. One thus can 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) show that some relationship exists between accelerated aging and natural aging. The correlation coefficient 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. 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 may 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 useful in the selection of stable papers for permanent records.

6. SHOULD AN ACCELERATED AGING ATMOSPHERE BE MOIST OR DRY?

Data on accelerated aging of handsheets at 90°C and at zero percent and 50 percent relative humidity already have been reported [3, 4, 5]. 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 untreated pulp were the most stable, those made from deashed pulp were much less stable, and those made from alum-treated pulp were the least stable. Different tests responded differently to moist and dry aging, but moist usually resulted in much greater changes than dry aging. It is not possible to draw definite conclusions from these data and the data obtained on the 36 year papers regarding an accelerated aging atmosphere, but a trend is obvious.

Tensile strength

The data in Table 23 show that aging at 50 percent relative humidity at 90°C seriously degraded the tensile strength of handsheets made from deashed and alum-treated pulps. Very little degradation occurred 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 approximates dry accelerated aging than accelerated aging at 50 percent 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. 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 not as much as is present at 50 percent relative humidity.

Internal tearing resistance

The data on internal tearing resistance in Tables 11 and 25 lead to the same conclusion as 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 accelerated aging at 50 percent relative humidity. Again this indicates that some moisture is desirable in an accelerated aging atmosphere but not as much as is generated at 50 percent relative humidity at 90°C.

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 percent 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 percent of this average value. A value this low does not appear in Table 28 except with samples aged at 50 percent relative humidity. Again, it appears that some moisture is desirable in an accelerated aging atmosphere, but that 50 percent relative humidity at 90°C is too high.

Number 1166 in the purified sulfite subset is an acid paper. Number 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 percent 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 percent rosin but a massive amount (4 percent) of alum. The zero span breaking lengths decrease with increasing amounts of alum from 1191 to 1203. The value for 1203 is about 85 percent 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 percent 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. As strength when wet is developed during both moist and dry aging, one cannot make a choice between the two by this test.

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 data 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 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. SUMMARY

Keeping in mind the limitations of correlation coefficients, discussed in 3.3, 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) The same is true for copper number.

(3) Correlations 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 great.

(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.

(6) Retention of tear after natural aging correlated well with retention of elongation after natural aging.

(7) Retention of fold after natural aging correlated fairly well with elongation after natural aging, but not as well as tear and elongation.

(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 correlations 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) Although changes after accelerated aging are not available, it appears from data after natural aging that zero span tensile 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 in earlier reports, it appears that dry accelerated aging more nearly corresponds to natural aging than accelerated aging at 50 percent relative humidity. The data indicate, however, that some moisture should be present.

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 in this age range that have deteriorated should yield useful information. Older papers would require more intensive study, as no original data would be available.

(2) In order to finalize recommendations for an accelerated aging procedure, handsheets should be aged at low relative humidity (perhaps 5 and 10 percent) at 90°C.

9. ACKNOWLEDGMENT

The authors are indebted to the writers, Merle B. Shaw and M. J. O'Leary (deceased), of the original publication, Effect of Filling and Sizing Materials on Stability of Book Papers. Their outstanding work and detailed reporting made this report possible.

10. REFERENCES

1. Shaw, M. B. and O'Leary, M. J., Effect of Filling and Sizing Materials on Stability of Book Papers, J. Res. NBS 21, 671 (1938).

2. Wilson, W.K., Harvey, J. L., Mandel, J., and Worksman, T. L., Accelerated Aging of Record Papers Compared with Natural Aging, Tappi 38, 543 (1955).

3. Parks, E. J. and Hebert, R. L., NBS Report 10 627, Accelerated Aging of Laboratory Handsheets: Changes in Acidity, Fiber Strength, and Wet Strength (Dec. 1971).

4. Parks, E. J. and Hebert, R. L., NBS Report 10 628, Accelerated Aging of Laboratory Handsheets: Retention of Folding Endurance, Internal Tear, Bursting Strength, and Tensile Strength (Dec. 1971).

5. Parks, E. J. and Hebert, R. L., NBS Report 10 687, Accelerated Aging of Laboratory Handsheets: Reflectance, Moisture Regain, Sonic Modulus, and DTA (Feb. 1972).

6. Wilson, W. K. and Hebert, R. L., Evaluation of the Stability of Record Papers, Tappi 52, No. 8, 1523 (1969).

7. Launer, H. F., Simplified Determination of Resin in Pulps and Papers, J. Res. NBS 18, 227 (1937).

8. Launer, H. F., Volumetric Determination of Alpha, Beta, and Gamma Cellulose in Pulps and Papers Containing Sizing, Filler, and other Materials, J. Res. NBS 20, 87 (1938).

9. Launer, H. F., Determination of the pH Value of Papers, J. Res. NBS 22, 553 (1939).

10. TAPPI Method T456 os-68, Wet Tensile Breaking Strength of Paper and Paperboard.

11. ASTM Method D 1348, Standard Method of Test for Moisture in Cellulose.

12. TAPPI Method T452, Brightness of Paper and Paperboard.

13. Wilson, W. K. and Hebert, R. L., Evaluation of the Stability of Manifold Papers, Tappi 55, No. 7, 1103 (1972).

14. TAPPI Method T429, Alpha Cellulose in Paper.

15. TAPPI Method T430 su-68, Copper Number of Paper and Paperboard.

16. Lidman-Safwat, S. and Theander, O., Determination of Carbonyl Groups in Modified Celluloses--A Comparison of the Borohydride and Copper Number Methods, Svensk Papperstidning 61, 42 (1958).

17. Wilson, W. K. and Parks, E. J., An Analysis of the Aging of Paper: Possible Reactions and Their Effects on Measurable Properties, NBSIR 74-499 (April 1974).

Table 1. Papermaking details on book papers made in NBS mill in 1937.[1]

Machine Run No.	Fiber	Filler			Alum Added	Rosin[2]		pH at Headbox
		Kind	Added	Retained		Added	Retained	
			%	%	%	%	%	
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	"	titanium pigment	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.

Table 2. Chemical test data obtained in 1937 on book papers made in NBS mill in 1937.[1]

Machine Run No.	pH		Alpha Cellulose	Copper No.	Pentosans
	cold	hot	%		%
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.

Table 3. Physical test data obtained in 1937 on book papers made in NBS mill in 1937[1]

Machine Run No.	Thickness		Weight		Burst	Breaking Load		Elongation		Fold, MIT		Tear	
	μm	mils	g/m^2	25x40,500 lb	points	kg^2		%		0.5 kg^2 tension		g	
						MD	CD	MD	CD	MD	CD	MD	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.

Machine Run No.	Alpha[1] Cellulose change	Copper Number change[2]	Fold Retention %	Tear Retention %
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.

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.

Machine Run No.	Alpha Cellulose, %		S[1], %	Change[2], %, After:	
	1937	1973	1973 data	36 Years Natural Aging	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	+.1
1158	75.5	68.6	0.3	6.9	.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	.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.

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.

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	.05	.8	.4
1133	3.2	3.2	.14	.0	-.1
1158	3.3	3.9	.14	.6	.0
1172	3.4	4.2	.17	.8	.4
1175	3.3	4.1	.22	.8	.3
1161	0.8	1.8	.05	1.0	.3
1162	0.9	2.1	.10	1.2	.5
1163	0.9	2.8	.07	1.9	.7
1164	0.9	1.7	.06	.8	.2
1165	0.8	2.4	.07	1.6	.4
1166	0.9	2.6	.07	1.7	.5
1191	0.3	0.9	.04	.6	.1
1192	0.4	1.1	.02	.7	.1
1193	0.5	1.6	.12	1.1	.2
1203	0.7	2.3	.07	1.6	.9
1207	0.5	1.5	.07	1.0	.5
1208	0.4	1.7	.04	1.3	.4

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

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.

Machine Run No.	pH Cold Extract		pH Hot Extract		$[H^+]x10^{-7}$ calculated from extract pH					
					Cold Extract			Hot Extract		
	1937	1973	1937	1973	1937	1973	Change	1937	1973	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	-

Table 8. Effect of 36 years of natural aging on the tensile strength of book papers made in NBS mill in 1937.

Machine Run No.	Tensile Strength kg				Standard Deviation, kg[1] 1973 data		Retention of Tensile After Natural Aging, %			No. of Specimens
	1937		1973							
	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.

Table 9. Effect of 36 years of natural aging on the elongation of book papers made in NBS mill in 1937.

Machine Run No.	Elongation, %				Standard Deviation, % 1973 data		Retention of Elongation After Natural Aging, %			No. of Specimens
	1937		1973							
	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

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.

Machine Run No.	Folding Endurance				Standard Deviation 1973 data		Retention of Fold After Natural Aging, %			Retention of Fold After Accelerated Aging in 1937, %
	1937		1973							
	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

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.

Machine Run No.	Tearing Resistance		Retention of Tearing Resistance, %, after	
			36 Years Natural Aging	Accelerated Aging
	1937	1973[1]		
	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.

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.

Machine Run No.	Natural Aging, 36 Years				Accelerated Aging in 1937	
	Increase in $[H^+]$		Alpha Cellulose, Decrease	Copper Number, Increase	Alpha Cellulose, Decrease	Copper Number, Increase
	Cold	Hot				
1129	190	293	16.7	1.2	7.6	0.6
1130	108	240	13.4	.8	3.3	.4
1133	49	75	2.2	0.0	+ .1	- .1
1158	-	-	6.9	.6	.4	0.0
1172	-	-	5.4	.8	2.1	.4
1175	-	-	6.4	.8	3.3	.3
1161	92	138	3.9	1.0	.8	.3
1162	175	348	5.8	1.2	3.6	.5
1163	188	478	12.9	1.9	4.6	.7
1164	90	180	4.0	.8	1.8	.2
1165	226	531	12.1	1.6	2.9	.4
1166	151	233	13.6	1.7	5.0	.5
1191	3	-	7.0	.6	3.1	.1
1192	63	-	8.0	.7	3.0	.1
1193	47	-	15.1	1.1	8.1	.2
1203	108	185	16.5	1.6	9.6	.9
1207	63	-	9.1	1.0	4.4	.5
1208	106	-	10.7	1.3	3.7	.4

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.

Machine Run No.	Natural Aging				Accelerated Aging	
	Fold	Tear	Tensile	Elongation	Fold	Tear
	Ave.	MD	Ave.	Ave.	Ave.	MD
1129	10	43	76	58	19	58
1130	15	52	82	66	56	80
1133	4	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

Table 14. Zero span breaking length and moisture regain of book papers made in NBS mill in 1937 after 36 years of natural aging.

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	.58	.27	89.5	10.02	7.80	6.30
1133	11.61	8.81	.72	.27	99.7	11.64	8.84	6.89
1158	10.84	7.24	.49	.34	91.2	11.89	7.94	6.36
1172	10.56	7.71	.66	.40	87.7	12.04	8.79	6.45
1175	11.02	8.28	.73	.34	88.7	12.42	9.33	6.45
1161	11.33	7.71	1.13	.43	87.8	12.90	8.78	6.26
1162	11.55	7.60	.55	.61	87.6	13.18	8.68	6.26
1163	10.34	6.79	.64	.42	88.4	11.70	7.68	6.09
1164	11.39	7.98	.85	.42	88.5	12.87	9.02	5.91
1165	10.22	7.36	.68	.43	87.6	11.67	8.40	5.90
1166	8.44	6.54	.51	.36	88.3	9.56	7.41	6.00
1191	10.10	7.77	.66	.35	85.5	11.81	9.09	5.27
1192	9.12	7.56	.44	.32	85.7	10.64	8.82	5.33
1193	8.76	6.43	.47	.28	85.7	10.22	7.50	5.26
1203	8.50	6.49	.60	.33	86.0	9.88	7.55	5.23
1207	14.62	10.93	.68	.68	95.0	15.39	11.51	5.29
1208	13.30	10.22	.42	.39	86.7	13.34	11.79	5.27

Table 15. Wet tensile properties of book papers made in NBS mill in 1937.

Machine Run No.	Breaking Load		Std. Deviation of Break		Elongation at Break		Std. Deviation of Elongation		Energy at Break		Std. Deviation of Energy		Extensional Stiffness		Std. Deviation of Stiffness		Wet Breaking Load as % of Dry Breaking Load		No. of Specimens
	g		g		%		%		g-cm		g-cm		kg		kg				
	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.

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	.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.

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.

Correlation Variables	Papers Included in Calculations	r, Correlation Coefficients	m, Slope
X alpha-natural aging Y alpha-accelerated aging	all	0.86	0.49
	soda-sulfite	.88	.45
	purified sulfite	.82	.29
	rag	.97	.70
X alpha-natural aging Y pH, cold, 1937	all	-.57	-.18
	all except alkaline	-.81	-.10
	soda-sulfite	-.70	-.26
	soda-sulfite: 1129, 1130, 1133	-.99	-.14
	purified sulfite	-.89	-.08
	rag	-.69	-.11
X copper no.-natural Y copper no.-accelerated	all	.82	.44
	soda-sulfite	.91	.62
	purified sulfite	.86	.35
	rag	.87	.72
X copper no.-natural Y pH, cold, 1937	all	-.55	-1.67
	all except alkaline	-.72	-.90
	soda-sulfite	-.28	-1.37
	purified sulfite	-.88	-.88
	rag	-.64	-1.07

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.

Correlation Variables	Papers Included in Calculations	r, Correlation Coefficients	m, Slope
X fold retention after natural aging Y fold retention after accelerated aging	all	0.63	0.54
	all except alkaline	.71	.60
	all except 1129 and alkaline	.65	.41
	soda-sulfite	.79	.50
	purified sulfite	.83	.36
	rag	.92	.67
X fold retention after natural aging Y pH, cold, 1937	all	.41	.02
	all except alkaline	.75	.01
	soda sulfite	.69	.04
	purified sulfite	.88	.01
	rag	.89	.05
X fold retention after natural aging Y alum added, %, minus rosin retained, %	all	-.50	-.02
	soda sulfite: 1129, 1130, 1133	-.98	-.02
	purified sulfite	-.82	-.02
	rag	-.73	-.05
X retention of fold after natural aging Y retention of elongation after natural aging	all	.52	.31
	soda sulfite	.40	.33
	purified sulfite	.87	.23
	rag	.95	.65

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.

Correlation Variables	Papers Included in Calculations	r, Correlation Coefficients	m, Slope
X tear retention after natural aging Y tear retention after accelerated aging	all[1] except 1158 and 1191	0.76	0.62
	all except 1158, 1191, and 1129	.84	.47
	soda-sulfite except 1158	.90	.83
	purified sulfite	.96	.73
	rag except 1191	.51	.14
X tear retention after natural aging Y pH, cold, 1937	all except 1158 and 1191	.68	.07
	soda-sulfite except 1158	.95	.11
	purified sulfite	.82	.04
	rag except 1191	.54	.03
X tear retention, MD, after natural aging Y retention of elongation, MD, after natural aging	all except 1158	0.88	1.69
	soda-sulfite except 1158	.86	1.90
	purified sulfite	.95	1.27
	rag except 1191	.82	1.19

[1]No sample available for 1158 and 1191.

Table 20. Correlation of (1) zero span tensile, MD, and (2) retention of elongation, ave., with pH, cold extraction, of papers in 1937.

Correlation Variables	Papers Included In Calculations	r, Correlation Coefficient	m, Slope
X zero span tensile, MD Y pH, cold, 1937	all	0.22	.20
	all except 1207 and 1208	.48	.57
	soda-sulfite	.91	1.48
	purified sulfite	.82	.26
	rag	-.02	-.01
	rag except 1207 and 1208	.96	.87
X elongation retention after natural aging Y pH, cold, 1937	all	.53	.04
	soda-sulfite	.65	.04
	purified sulfite	.81	.04
	rag	.86	.07

Table 21. Correlation of wet tensile properties with pH, cold extraction, in 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	- .74	- .18
	soda-sulfite	- .72	- .70
	soda-sulfite: 1129, 1130, 1133	- .99	- .41
	purified sulfite	- .96	- .16
	rag	- .90	- .35
X wet energy at break, CD Y pH, cold, 1937	all	-0.56	-0.04
	all except alkaline	- .56	- .02
	soda-sulfite	- .62	- .10
	purified sulfite	- .72	- .02
	rag	- .89	- .05
X wet extensional stiffness, MD Y pH, cold, 1937	all	- .26	- .01
	all except alkaline	- .54	- .01
	soda-sulfite	- .57	- .04
	1129, 1130, 1133	- .99	- .03
	purified sulfite	- .82	- .02
	rag	- .79	- .04

Table 22. Arbitrary definitions of stable papers based on 1937 data compared with retention of properties in 1973.

Machine Run No.	Arbitrary definitions of stable papers based on pH, cold extraction, and changes[1] in properties after accelerated aging in 1937.						Arbitrary definitions of stable papers based on changes[1] in properties after 36 years of natural aging.						
	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	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
1129					131	18						90	17
1130					258	14						145	13
1133	1133	1133	1133	1133	349	5	1133	1133	1133	1133	1133	330	1
1158	1158	1158			365	2	1158[3]			1158[3]	1158[3]	255	8
1172	1172	1172			280	12	1172			1172	1172	262	5
1175	1175	1175			301	8	1175	1175	1175	1175	1175	283	4
1161	1161	1161	1161	1161	357	4	1161	1161	1161	1161	1161	299	2
1162	1162		1162		294	10	1162			1162	1162	224	10
1163					235	15						94	16
1164	1164	1164	1164	1164	343	6	1164			1164	1164	259	7
1165	1165		1165		300	9						117	15
1166					229	16						86	18
1191	1191	1191	1191	1191	368	1	1191[3]	1191[3]	1191[3]	1191[3]	1191[3]	294	3
1192	1192		1192		364	3	1192	1192		1192		260	6
1193					279	13	1193					164	12
1203					191	17	1203					130	14
1207					286	11	1207			1207		225	9
1208	1208		1208		318	7	1208					205	11

[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.

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

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.

Pulp Treatment	Aging Atmosphere	Aging Period, days								
		0	1	6	12	24	1	6	12	24
		Breaking Load, kg[2]					Retention, %			
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.

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.

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.

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.

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.

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.

Pulp Treatment	Aging Atmosphere	Aging Period, days									
		0	1	6	12	24	0	1	6	12	24
		pH					$[H^+] \times 10^7$				
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.

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.

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.

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.

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.

Table 29[1]. Wet breaking load as percent of dry breaking load of experimental handsheets after accelerated aging at 90°C in various atmospheres.

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	.7	1.3	2.1	2.5	3.1
	Moist air	.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	8.3
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.

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.

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.

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.

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.

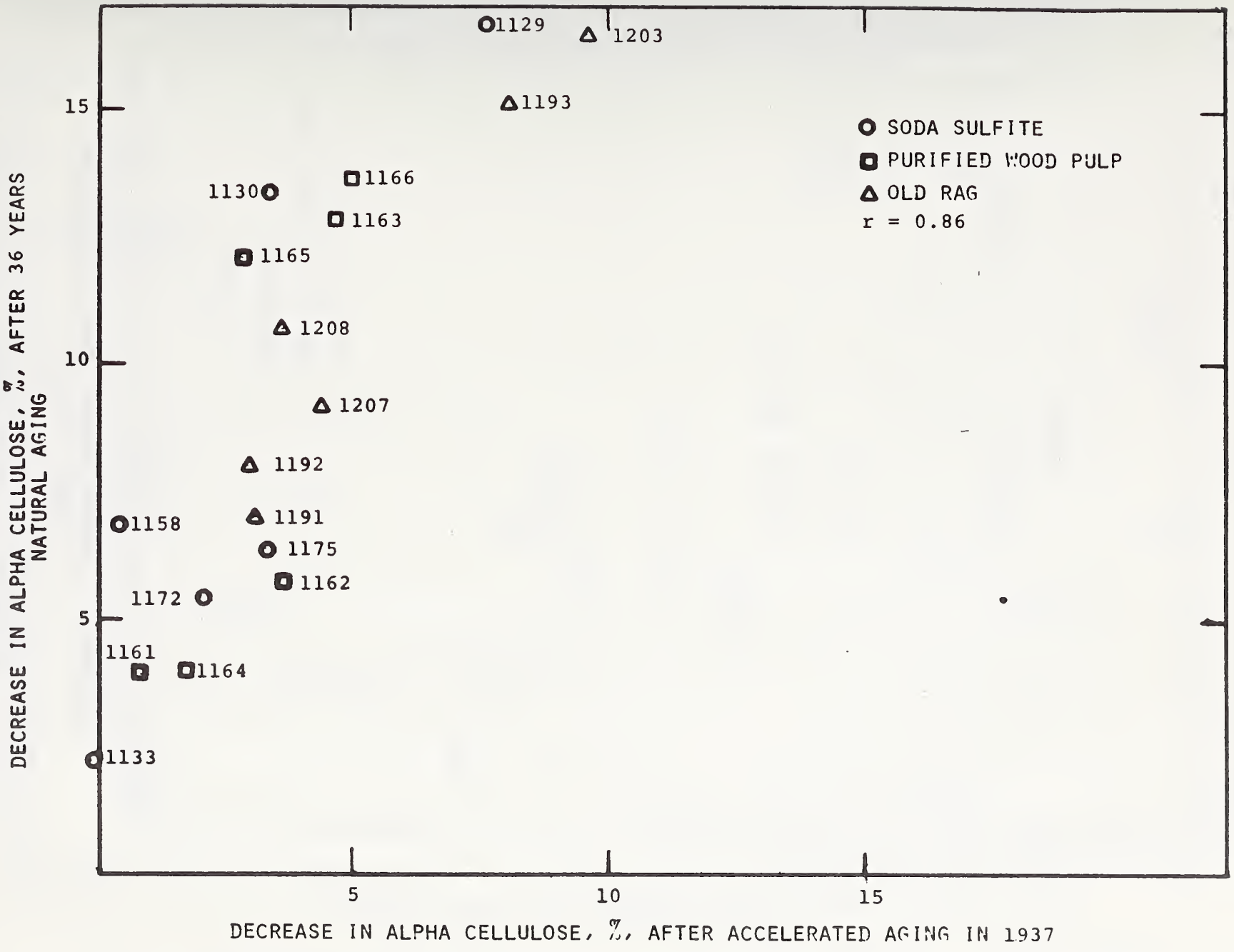

Figure 1. Decrease in alpha cellulose: natural aging for 36 years vs. accelerated aging in 1937.

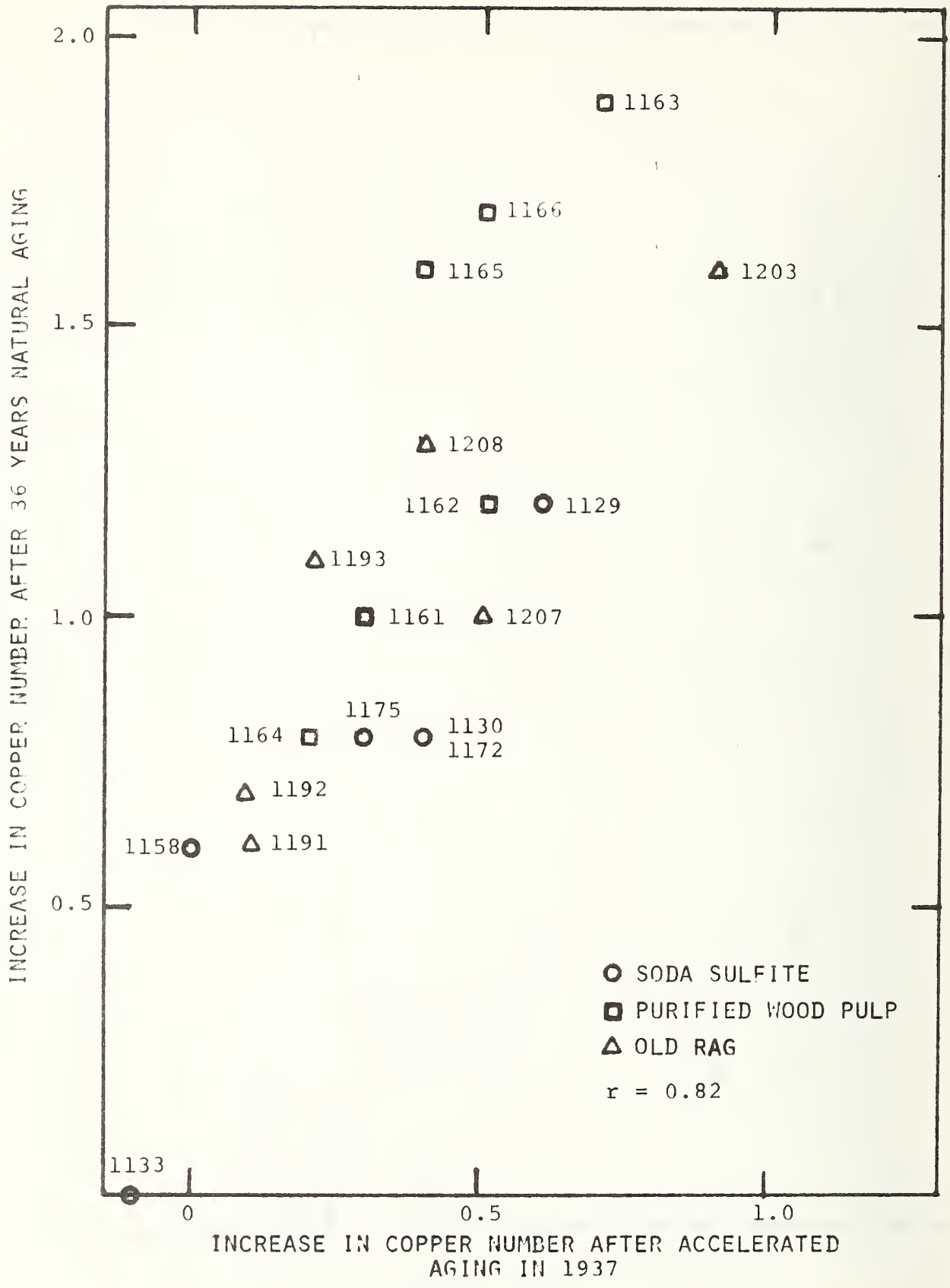

Figure 2. Increase in copper number: natural aging for 36 years vs. accelerated aging in 1937.

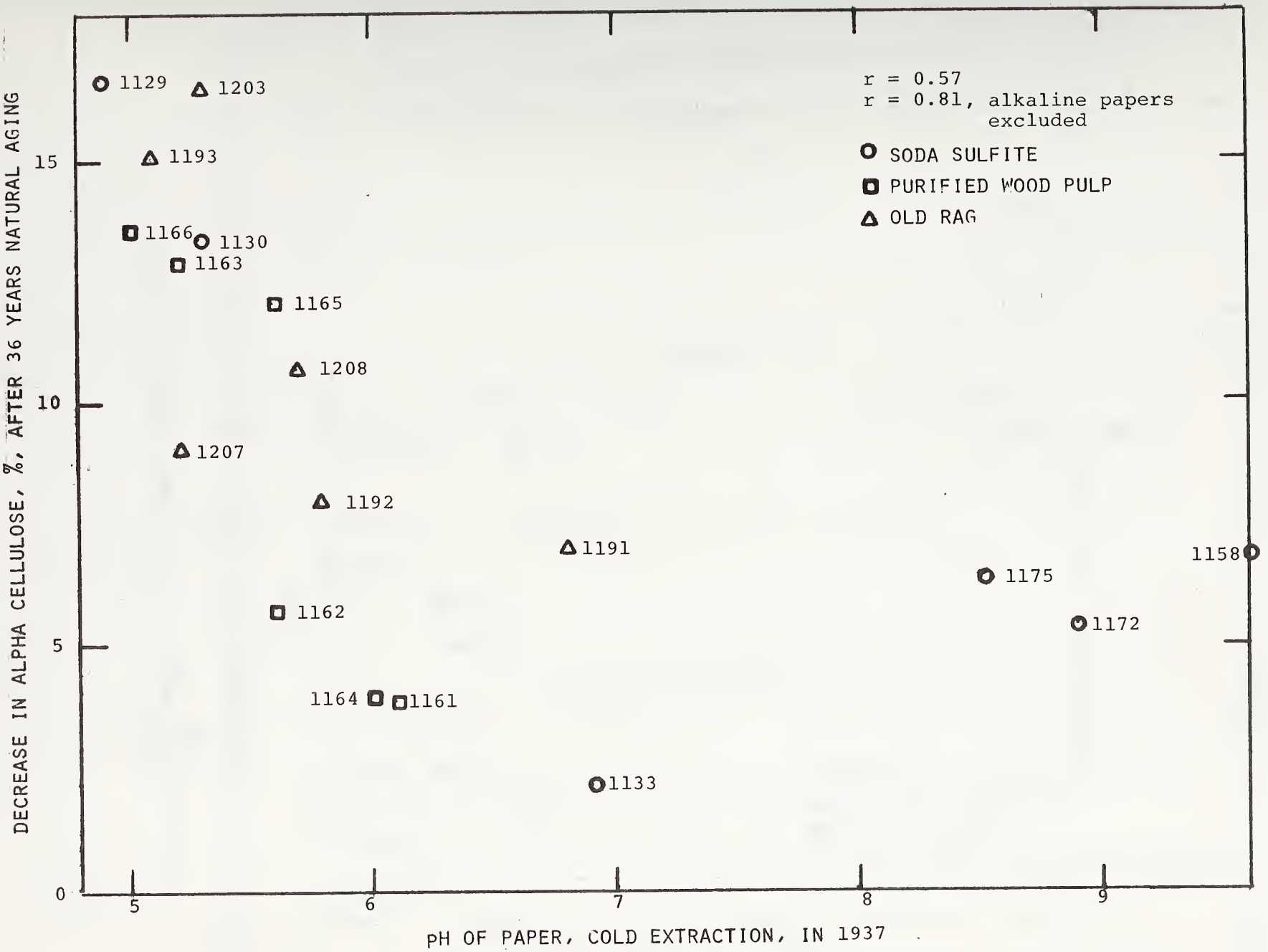

Figure 3. Decrease in alpha cellulose after 36 years natural aging as a function of pH, cold extraction, in 1937.

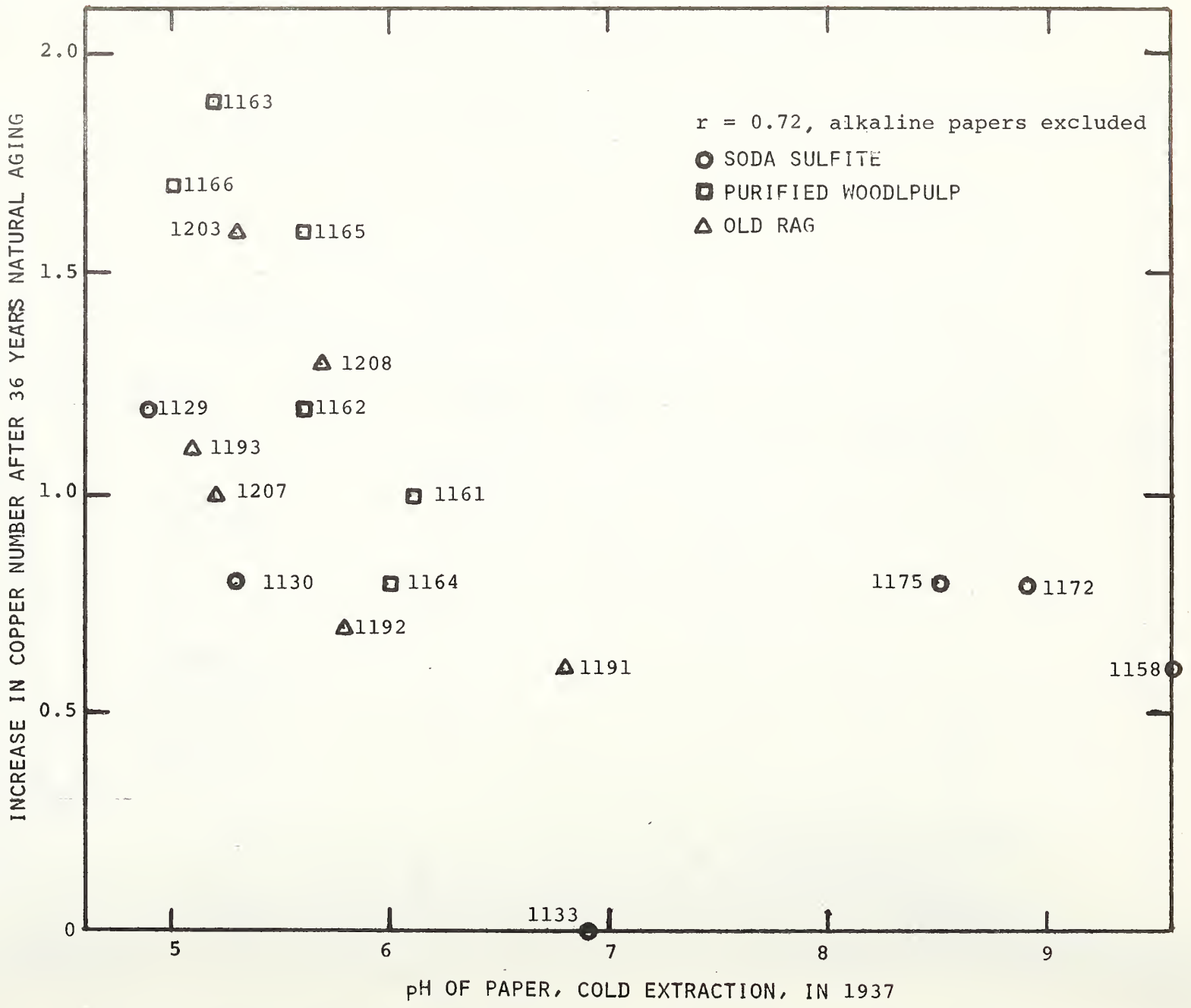

Figure 4. Increase in copper number after 36 years natural aging as a function of pH, cold extraction, in 1937.

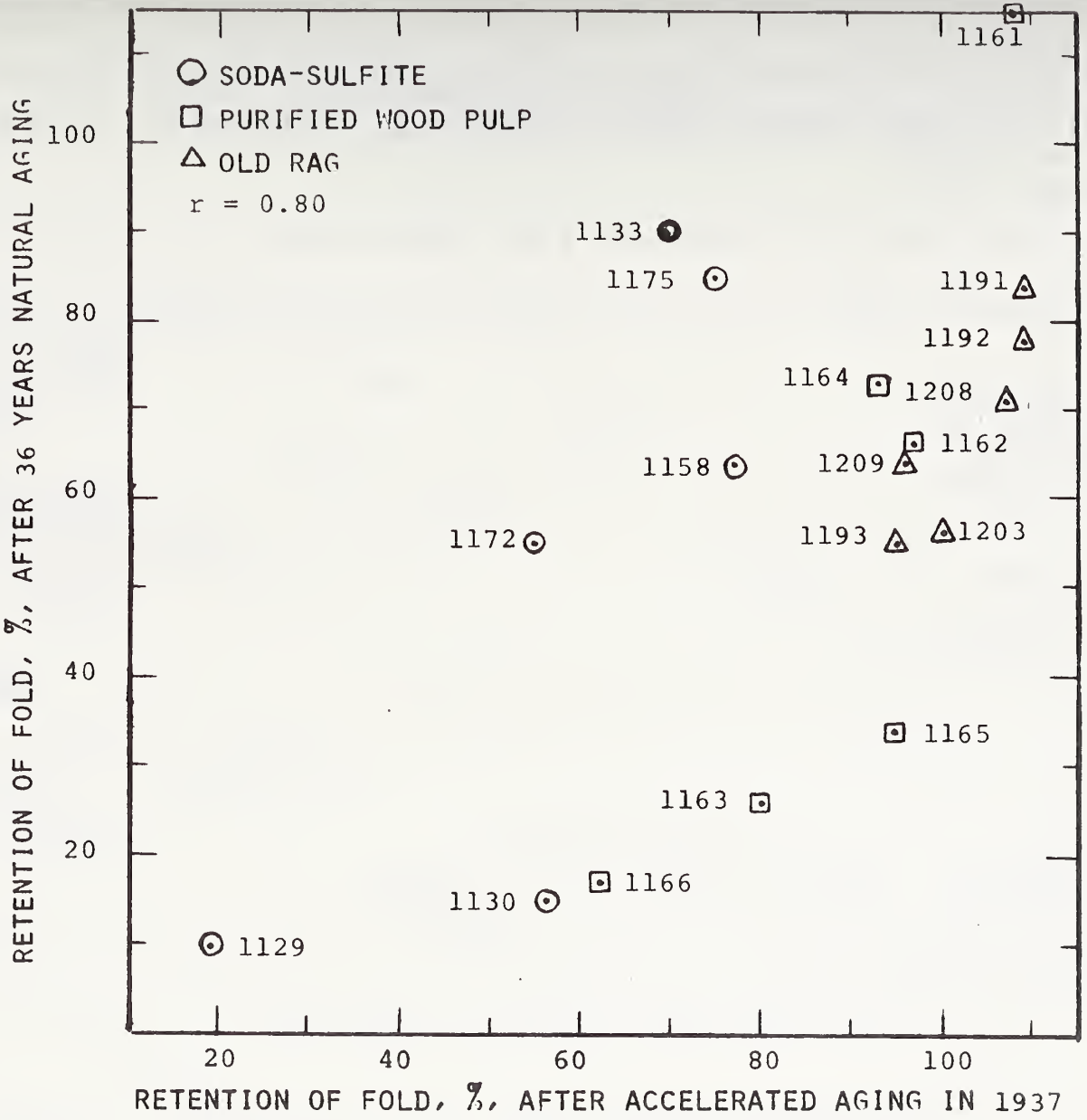

Figure 5. Retention of fold: natural aging for 36 years vs. accelerated aging in 1937.

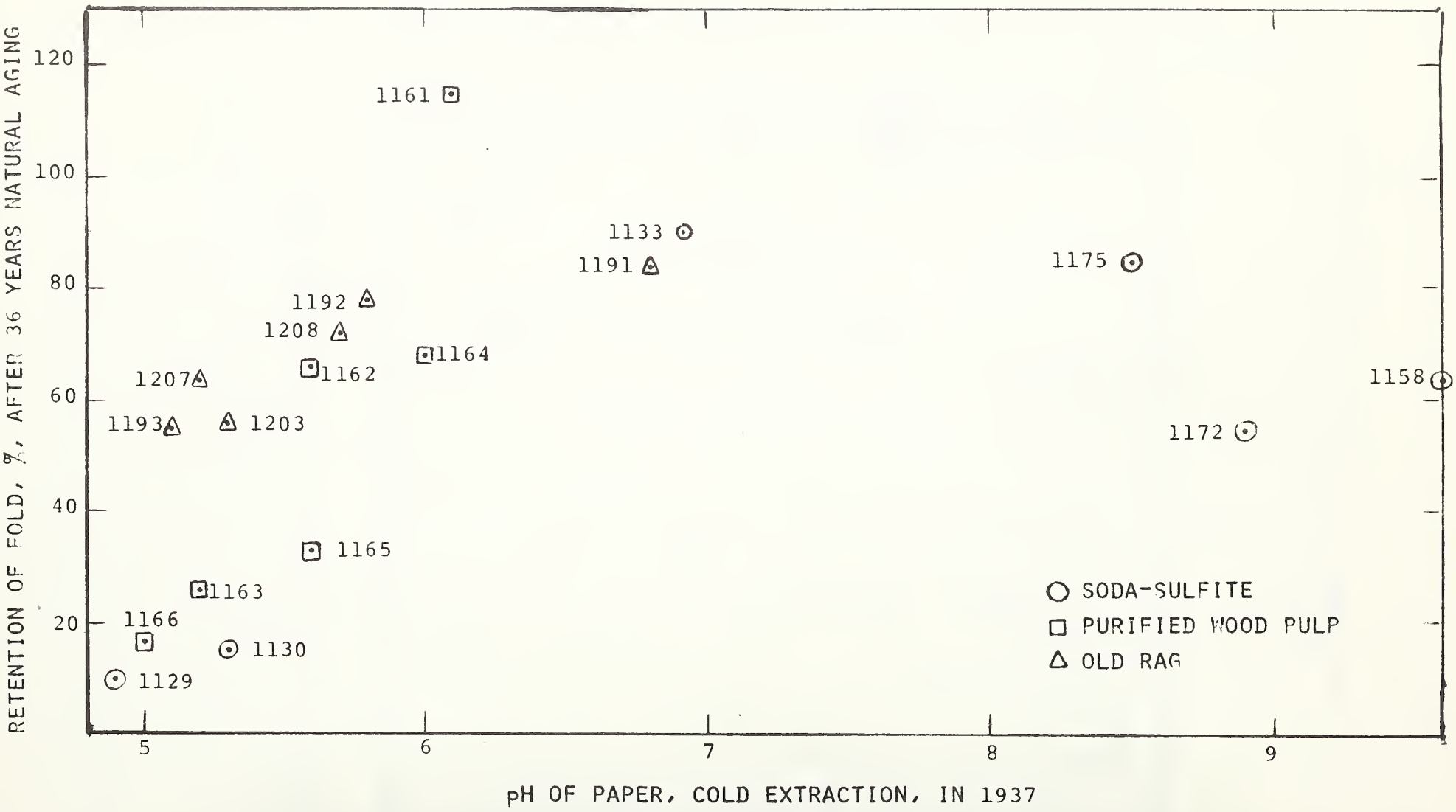

Figure 6. Retention of fold after 36 years natural aging as a function of pH, cold extraction, in 1937.

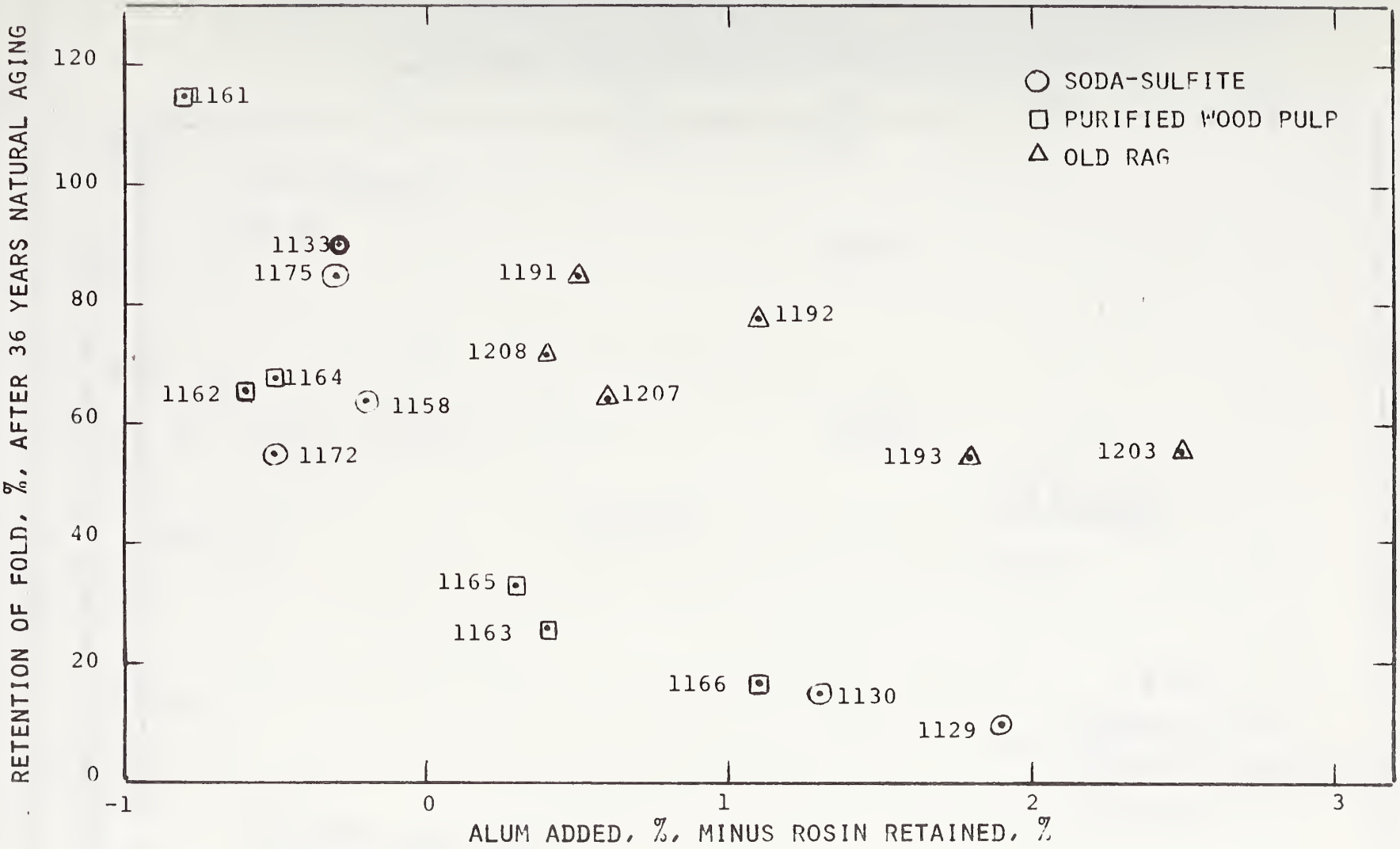

Figure 7. Retention of fold after 36 years natural aging as a function of alum and rosin added during manufacture.

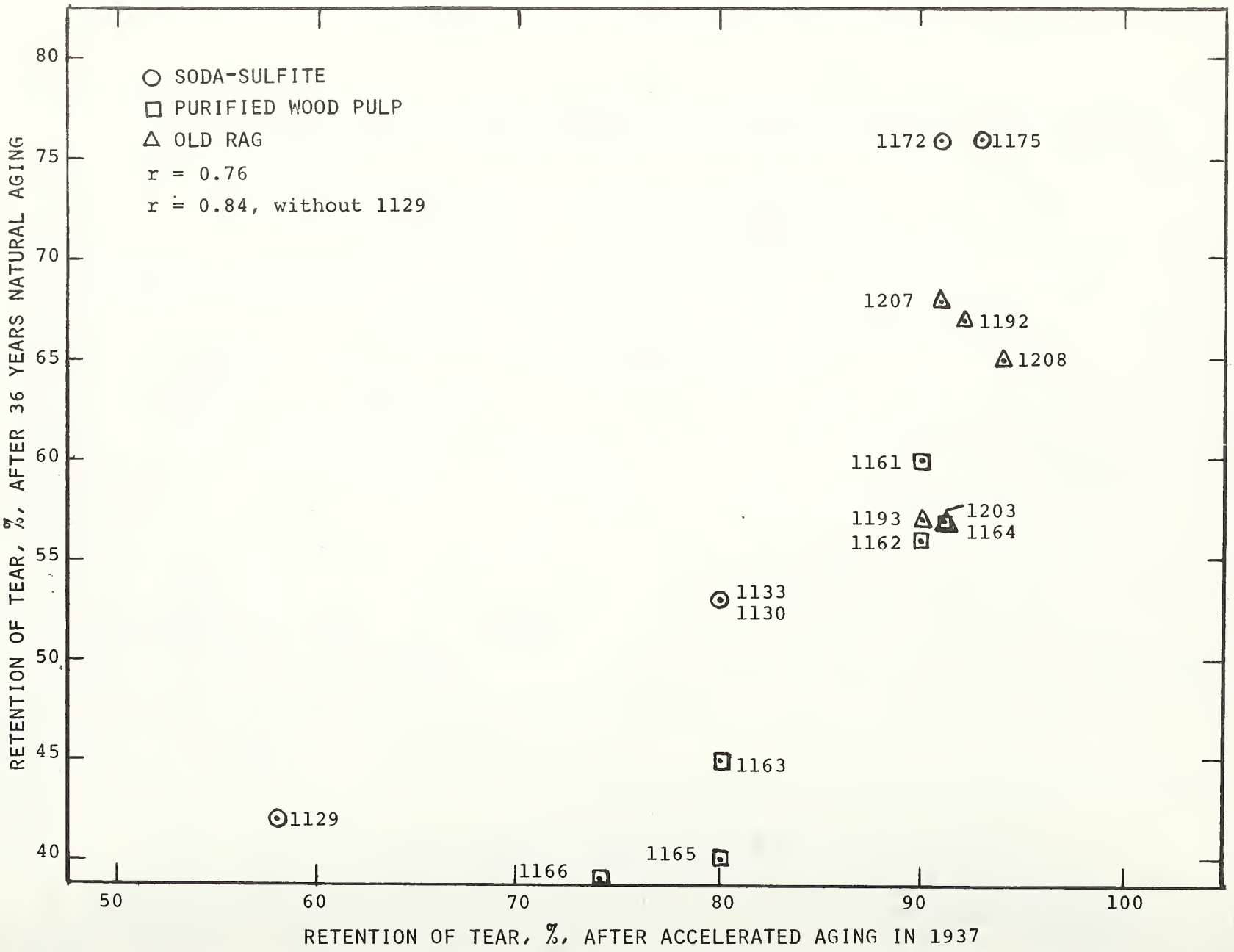

Figure 8. Retention of internal tear: natural aging for 36 years vs. accelerated aging.

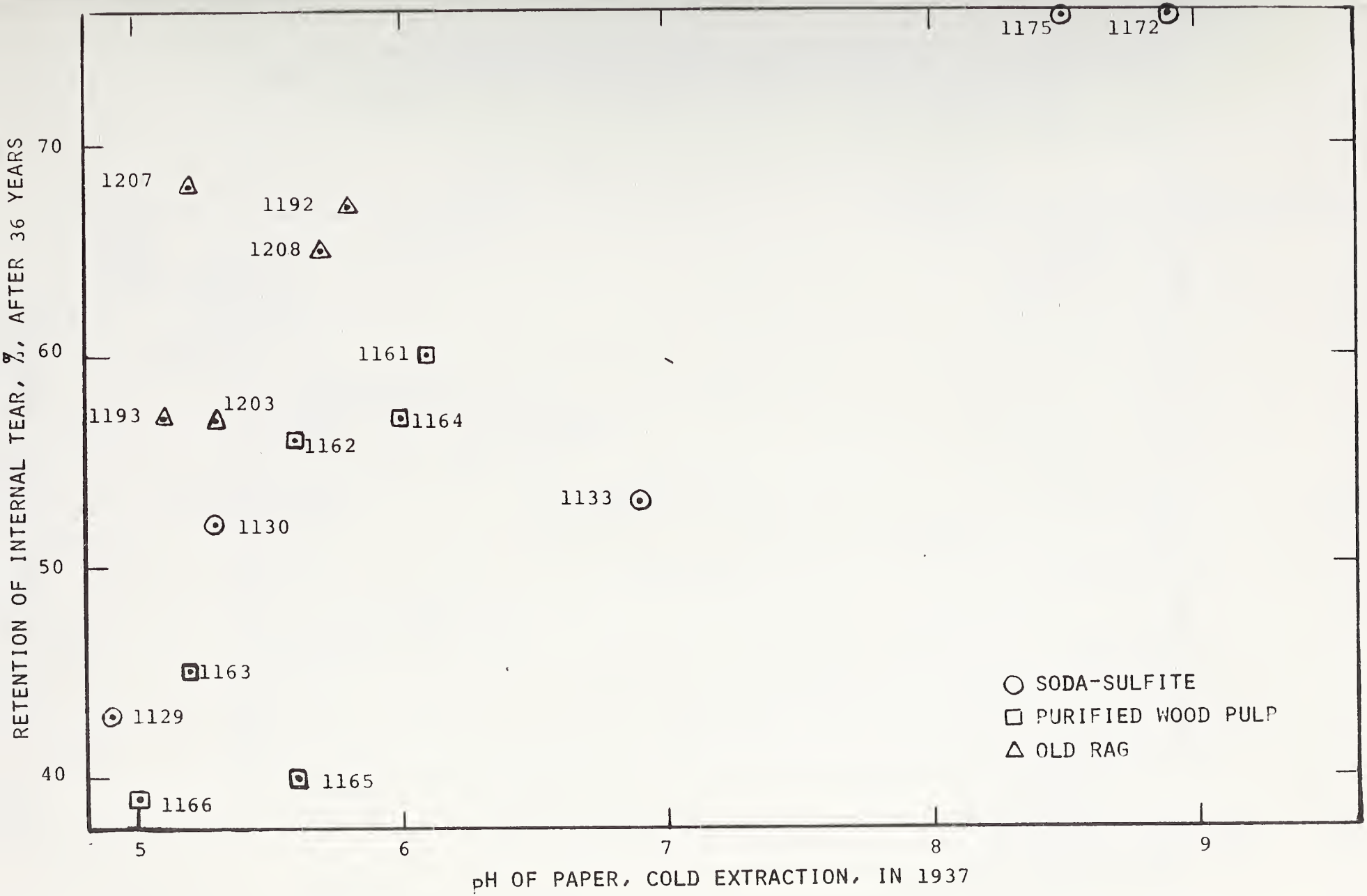

Figure 9. Retention of internal tear after 36 years natural aging as a function of pH, cold extraction, in 1937.

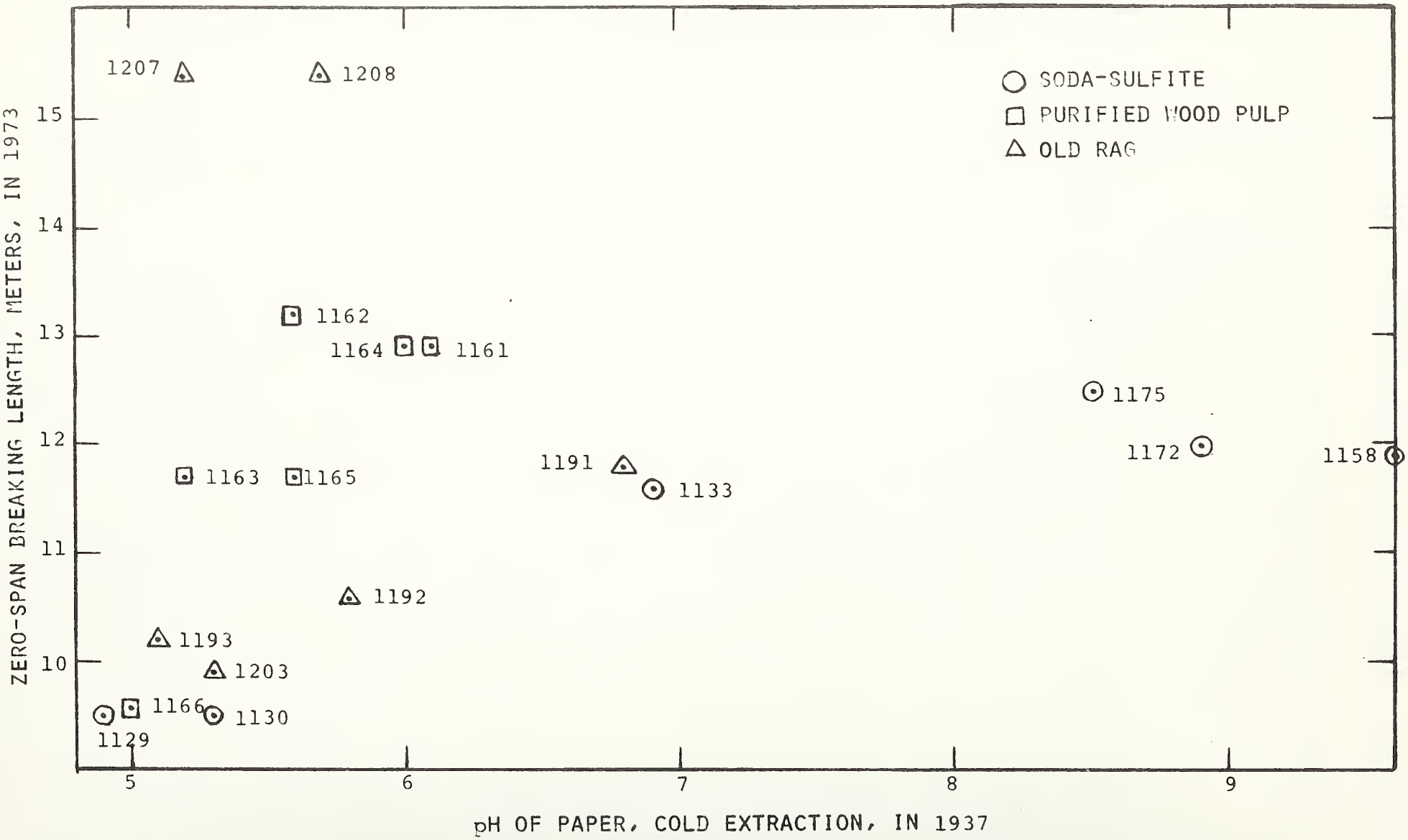

Figure 10. Zero-span breaking length, calculated to 100 percent fiber, in 1973 vs. pH, cold extraction, in 1937.

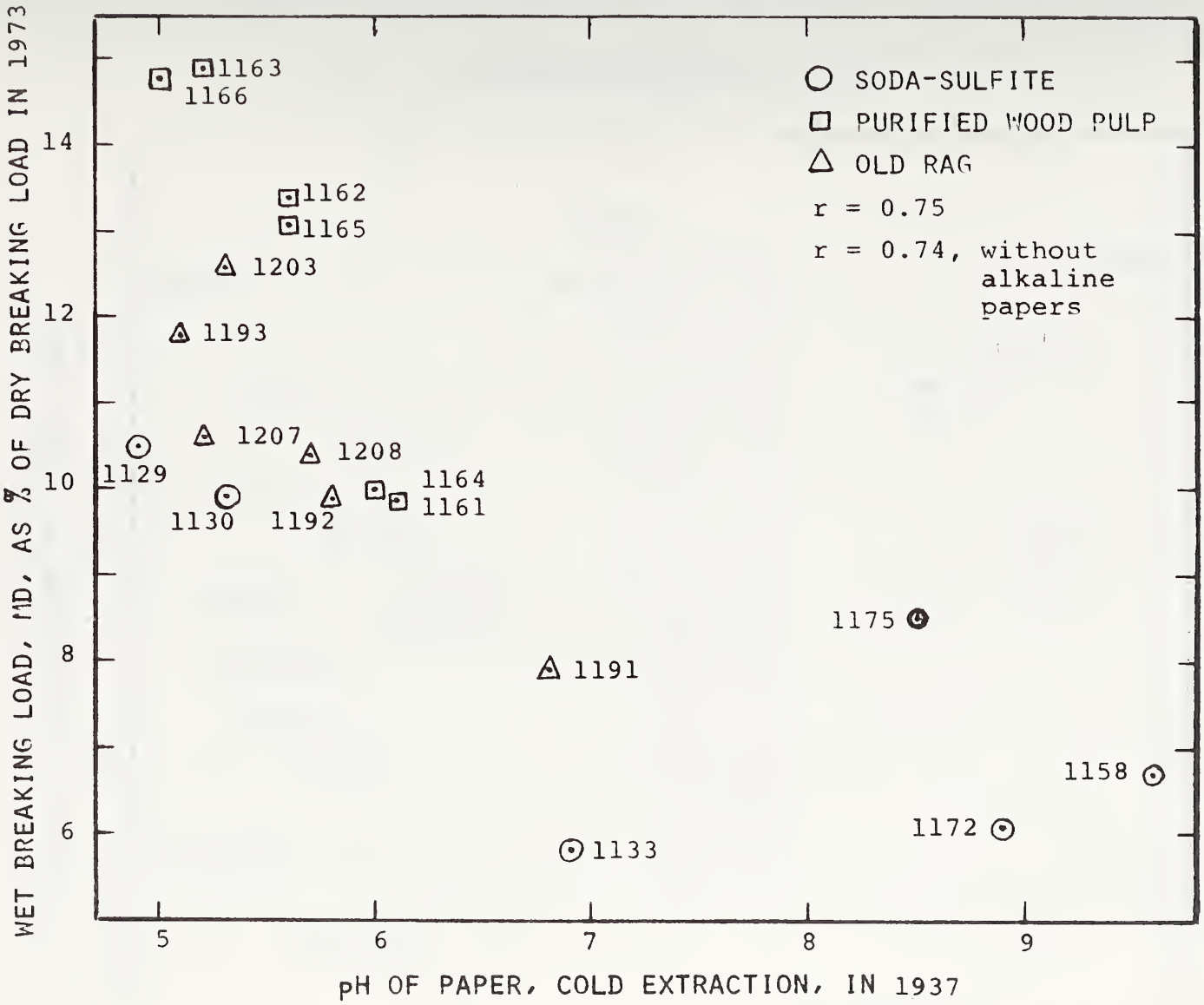

Figure 11. Wet breaking load as percent of dry breaking load in 1973 as a function of pH, cold extraction, in 1937.

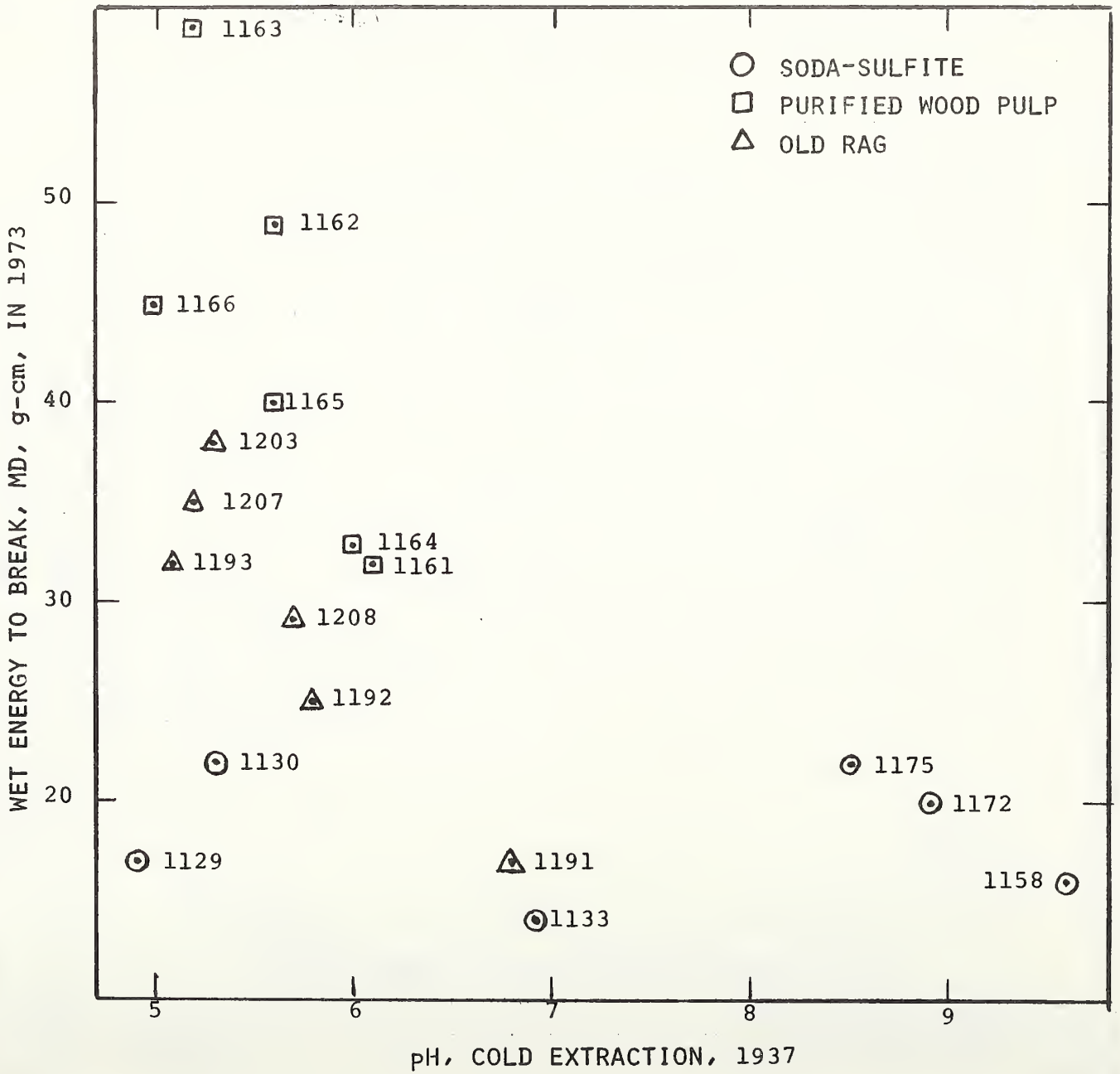

Figure 12. Wet energy to break in 1973 as a function of pH, cold extraction, in 1937.

APPENDIX

EFFECT OF FILLING AND SIZING MATERIALS ON STABILITY OF BOOK PAPERS, by Merle B. Shaw and Martin J. O'Leary, Journal of Research of the National Bureau of Standards, Volume 21, November 1938, Research Paper RP1149.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1149

Part of Journal of Research of the National Bureau of Standards, Volume 21, November 1938

EFFECT OF FILLING AND SIZING MATERIALS ON STABILITY OF BOOK PAPERS

By Merle B. Shaw and Martin J. O'Leary

ABSTRACT

The National Bureau of Standards has been carrying on research on the manufacture of papers to obtain information on composition and processes which have an important bearing on the stability of paper. Several publications have been issued as a result of these investigations. Three of them, Research Papers RP372, RP574, and RP794, present data for writing papers. Another Research Paper, RP949, reports the results on experimental unsized papers made from pulps commonly used in book papers. The present publication is an extension of the work on book paper, and relates primarily to the effect of filling and sizing variables introduced in manufacture.

The papermaking materials used were representative commercial products. Four types of fillers, including both natural materials and manufactured pigments, were used. They comprised one clay filler; two titanium dioxide pigments; two zinc sulfide pigments; and two calcium carbonates, one precipitated, the other a natural product, water-ground. The sizing agent, rosin soap prepared from rosin and soda ash, was precipitated by means of papermaker's alum, aluminum sulfate. The fibrous materials covered the range of those commonly used in the fine printing papers. They consisted of sulfite pulp and soda pulp of the ordinary book-paper grade; three "purified" wood pulps, produced by special cooking and bleaching treatments to obtain high purity and strength; new rags, the grade known commercially as No. 1 white shirt cuttings; and two grades of old rags, No. 1 old whites and "twos and blues."

Seventy-two experimental papers were manufactured in the Bureau's semicommercial mill. The papers were given extensive physical and chemical tests with particular reference to stability, both before and after an accelerated aging test made by heating the paper for 72 hours at 100° C.

The strength of the experimental papers decreased with increasing filler content, and was influenced by the amount, not the type, of filler present. There was no pronounced difference in the relative effect of the nonalkaline fillers on sizing. The nonalkaline fillers had less effect than calcium carbonate in reducing the degree of sizing. Although the sizing values of the carbonate-filled papers were not high, the papers were sized sufficiently to be written on with ink and for ordinary printing processes. Maximum clay retention was obtained in the purified wood and the rag papers when the pH at the head box was approximately 5, and decreased as the amount of alum was increased. For the sulfite-soda stock, retention of all the nonalkaline fillers increased as alum was increased. The papers containing titanium dioxide, zinc sulfide, or precipitated calcium carbonate pigments had the highest opacity. Preliminary printing tests made on a few of the filled papers indicated satisfactory printing quality.

The rag and purified wood-pulp papers were more stable to the heat test than the sulfite-soda. Nonalkaline fillers had no apparent harmful influence on the stability of any of the papers, and the calcium carbonate pigments had a protective or inhibiting effect in the aging test.

Acidity was an important factor in deterioration. The attack on the cellulose was increased as the amount of alum was increased, in either the unsized or the rosin-sized papers.

The effect of increasing the amount of alum in the beater and then neutralizing part of the alum with sodium carbonate as the stock was being pumped from

the beater chest to the machine chest was practically the same as having had the final pH value originally in the beater and maintained throughout the preparation of the stock.

CONTENTS

I. INTRODUCTION

As a part of its program of research relating to the stability of papers used for records, the National Bureau of Standards is making a study of the relation of papermaking materials and processes to the strength, stability, and other properties of book papers. This publication is the fifth in the series planned to include the more important types of fibrous and nonfibrous raw materials commonly used in the manufacture of record papers. Of the preceding publications, three [1, 2, 3] [1] related to writing papers and one [4] to fibers commonly found in book papers. The present publication is an extension of the work on book papers and deals primarily with the effect of filling and sizing materials on their stability.

II. PAPERMAKING RAW MATERIALS

The fillers selected were representative of several types, both natural materials and manufactured pigments, and were used as supplied by the manufacturers. They comprised one clay; two titanium pigments,

[1] Figures in brackets indicate the literature references at the end of this paper.

titanium dioxide and a composite of titanium dioxide and barium sulfate; two zinc sulfide pigments, zinc sulfide and a composite of zinc sulfide and barium sulfate; two calcium carbonates, one precipitated, and one water-ground. Fillers are not added to book paper to adulterate it but to improve the printing quality of the sheet. They fill the interstices of the fiber network of the paper thus producing a more even surface, lend softness, and improve the opacity and, generally, the color of the sheet. The number of types of important fillers on the market has increased considerably in the last few years, but little is known about their effect on the permanence of paper. The selection of fillers for the papermaking tests of this study was limited, however, to only the more important types, as a complete study of fillers, as such, was not planned at this time.

The sizing agent was that most generally employed, rosin soap. It was prepared from rosin and soda ash and was precipitated with papermaker's alum, aluminum sulfate.

The fibrous materials employed covered the range of those commonly used in the fine printing papers, and, like the fillers, were obtained from commercial manufacturers. They consisted of sulfite pulp and soda pulp of the ordinary book-paper grade; three "purified" wood pulps produced by special cooking and bleaching treatment to obtain high purity and strength; new rags, the grade known commercially as No. 1 white shirt cuttings; and two grades of old rags, No. 1 old whites and "twos and blues."

III. PAPERMAKING EQUIPMENT

The Bureau paper mill is equipped for experimental manufacture of practically all types of paper under conditions which in general simulate those of industrial mills. A complete description and photographs of the equipment may be found in previous publications [5].

IV. PAPERMAKING PROCESSES

1. PREPARATION OF RAG HALF STUFF

The procedure followed in the preparation of the rag "half stuff" (partially pulped rags that have been boiled, washed, drawn out of weave, and bleached) was essentially the same as the general practice in the commercial production of high-grade papers from rags. It was described in a previous publication [3] of the series.

The amount of bleaching powder, containing 35 percent of available chlorine, required to produce the desired degree of whiteness varied with the color of the rags. The amount used, based on the oven-dry weight of the rags, for No. 1 white shirt cuttings was 0.1 to 0.2 percent; for No. 1 old whites, 0.3 percent; and for twos and blues, 1.0 percent.

2. BEATER AND PAPER-MACHINE OPERATIONS

To afford comparison of the papers made in the numerous experimental runs it was necessary to follow a uniform procedure for handling the papermaking materials and the paper machine. It was desired that the procedure conform to customary or established general mill practice, but inasmuch as different mills differ widely as

to the relative time of adding the pulps, fillers, rosin, and alum to the beater, the method used was the one ordinarily followed at the Bureau and previously found to compare favorably with commercial mill methods.

The fillers were mixed with water (made into "slips") and the mixture agitated a fixed length of time and then run through an 80-mesh screen to remove dirt and impurities before being added to the beater.

The procedure followed in furnishing the beater, unless noted otherwise elsewhere in the text, was as follows: The pulps or fibrous materials and the filler slip were put in at the time of furnishing (which required about 15 minutes), and the rosin size was added to the stock 1 hour, and the alum ½ hour, before it was dropped to the beater chest. Variation from this procedure might have affected the characteristics of the finished sheet as to bulk, opacity, etc., but it is believed that it did not affect the permanence of the paper, which is the property of primary interest in this study.

The beating procedure was adjusted to the peculiarities of the different papermaking fibers. The paper-machine operations were the same for all runs. The methods of beating and paper-machine operation followed very closely those described in the other publications of this investigation [1, 2, 3].

The temperature of the stock at the head box of the paper machine was maintained at 90° F ±2°.

V. TESTING METHODS

All the physical and most of the chemical tests of the pulps and papers were made by the official methods[2] of the Technical Association of the Pulp and Paper Industry. For the determinations of the amounts of alpha-, beta-, and gamma-cellulose, pentosans, and acidity in the cellulosic materials, the methods used were modifications recently developed at the Bureau [6].[3] Although all papers were tested for acidity by the modified method (cold extraction), some of them were tested also by the TAPPI method (hot extraction), and for the latter the values obtained by both methods are reported. For the mill waters—in the beater and the head box—the pH determinations were made electrometrically, using the quinhydrone method except for the runs with calcium carbonate, for which a glass electrode was used because of the alkalinity.

The relative stability of papers can be judged by determining their chemical characteristics, but in addition it is desirable to subject them to some form of accelerated aging. Therefore, the pertinent physical and chemical tests were applied not only to the original papers but also to samples that had been submitted to an accelerated aging test considered to closely simulate the effects of natural aging. This test is made by heating specimens of the papers for 72 hours at 100° C and then conditioning and determining to what extent the paper has been altered in folding endurance, tearing strength, alpha-cellulose content, and copper number. For details of the accelerated aging test the reader is referred to previous discussions of the method [7].

---

[2] Copies of the methods can be obtained from the Technical Association of the Pulp and Paper Industry, 22 East 42d Street, New York, N. Y.

[3] Pentosans and acidity determined by unpublished methods.

VI. ANALYSES OF PAPERMAKING MATERIALS USED

1. FIBERS

Analyses showing the degree of cellulosic purity of the wood pulps and the rag half stuffs used in the manufacture of the papers are given in table 1. The fibrous material ranged in quality from 74 to 95 percent of alpha-cellulose and from 4.4 to 0.3 in copper number.

TABLE 1.—*Chemical test data on fibrous materials used*

Fibrous material	Alpha-cellulose [1]	Beta-cellulose [1]	Gamma cellulose [1]	Pentosans	Copper number	Ash [2]	Resin [2]
	%	%	%	%		%	%
Sulfite pulp	82.0	5.8	12.2	5.8	3.4	0.1	0.6
Soda pulp	74.4	21.3	4.3	18.7	4.4	.3	.2
Purified wood pulp *A* [3]	91.0	4.2	4.8	3.2	0.6	.1	.2
Purified wood pulp *C* [3]	88.3	6.3	5.4	4.3	.8	.1	.2
Purified wood pulp *D* [3]	84.2	4.3	11.5	8.4	.6	.2	.1
No. 1 new white rags, bleached half stuff	94.8	4.7	0.5	----	.3	.1	.2
No. 1 old white rags, bleached half stuff	90.3	9.4	.3	----	.4	.2	.2
Twos and blues, bleached half stuff	91.1	8.6	.3	----	.4	.3	.3

[1] Based on total cellulose.
[2] On oven-dry basis.
[3] Produced commercially by special cooking and bleaching treatment to obtain improved quality.

2. FILLERS

The chemical composition of the fillers used is shown in table 2.

TABLE 2.—*Composition of fillers used* [1]

Test	Clay	Titanium dioxide pigment *A*	Titanium dioxide pigment *B*	Zinc sulfide pigment *A*	Zinc sulfide pigment *B*	Precipitated calcium carbonate	Water-ground natural calcium carbonate
	%	%	%	%	%	%	%
Loss at 105° C	0.3	None	0.09	0.09	0.07	0.15	0.03
Further loss on ignition	13.7	0.15	None	16.1	9.0	43.6	43.8
Silica (SiO_2)	45.3	----	----	----	----	----	----
Iron oxide (Fe_2O_3)	0.2	----	----	----	----	----	----
Alumina (Al_2O_3)	38.8	----	----	----	----	----	----
Titanium dioxide (TiO_2)	1.8	98.2	30.4	----	----	----	----
Calcium carbonate ($CaCO_3$)	----	----	----	----	----	97.6	99.8
Barium sulfate ($BaSO_4$)	----	----	69.5	----	44.9	----	----
Zinc sulfide (ZnS)	----	----	----	99.8	54.8	----	----

[1] Analyses by Chemistry Division, National Bureau of Standards.

VII. DATA ON PAPERS MADE

1. PHYSICAL AND CHEMICAL MEASUREMENTS

Data relative to the composition of the beater furnishes (materials blended in the beater) and the various physical and chemical measurements on the papers made are given in tables 3 and 4.

The percentage of filler in paper is sometimes determined from the ash content, and sometimes, when possible, by chemical analysis. In the case of clay it was determined from the ash of the paper, corrected for the loss of water of composition from the clay during ignition. The values for the pigments were obtained by chemical analysis.

The amount of retention of filler is that proportion of the filler added to the beater furnish which appears in the finished paper. The different methods used in different laboratories for computing retention account in some degree for the varying results reported by them. The formula used in this work was developed by Edwin Sutermeister of the S. D. Warren Co., Cumberland Mills, Maine, and has been used in previous studies [8] carried on at the Bureau, in which it was found to check the determinations by weight. The formula is:

$$\text{Retention} = \frac{0.94(100-C-A)}{A(100-C-B)},$$

in which A is the percentage of ash in bone-dry stock going to machine (that is, the stuff box stock); B is the percentage of ash in bone-dry paper at reel; and C is the percentage of bone-dry filler lost on ignition.

Before being adopted for general use in a mill, however, this or any retention formula should be tested to determine whether it is suited to the particular conditions with which that mill has to deal. Many factors other than filler influence retention, but it is impossible to estimate their effects except in a general way. Some of the conditions which affect the retention of fillers are the kind of stock used, the extent of its beating (hydration), consistency of pulp and the amount of filler added, acidity, weight of paper made, speed of machine, chemicals used (such as starch, sodium silicate, or viscose materials), the use of save-alls, etc.

(a) CLAY-FILLED PAPERS

(1) *Sulfite pulp, 50 percent; soda pulp, 50 percent.*—Two paper-machine runs were made of sulfite and soda pulps without filler—one (run 1133), without rosin size or alum; the other (run 1143), with rosin size and alum added. The test data on the runs are given in tables 3 and 4. For the paper made from pulp alone (run 1133) the chemical test data for the heat-treated paper differ little from those for the original sheet, but when rosin and alum were added the alpha-cellulose content decreased and the copper number increased for the aged or heat-treated paper. The stability as regards retention of folding endurance and tearing strength is not high for either of the papers, with or without rosin size and alum.

TABLE 3.—*Papermaking details and physical test data on the book papers*

Paper machine run number	Beater furnish: Fiber	Beater furnish: Filler: Kind	Beater furnish: Filler: Amount [1]	Beater furnish: Rosin [1]	Beater furnish: Alum [1]	Acidity at headbox (quinhydrone method)	Tests of unheated papers [2]: Weight: 25 by 40 inches, 500 sheets	Bursting strength [3]	Tensile properties: Breaking load [4]: Machine direction	Tensile properties: Breaking load [4]: Cross direction	Tensile properties: Elongation at rupture: Machine direction	Tensile properties: Elongation at rupture: Cross direction	Thickness	Sizing value (dry-indicator method)	Opacity (contrast ratio)	Folding endurance [5]: Schopper: Machine direction	Folding endurance [5]: Schopper: Cross direction	Folding endurance [5]: MIT: Machine direction [7]	Folding endurance [5]: MIT: Cross direction [7]	Tearing strength: Machine direction	Tearing strength: Cross direction	Tests of heat-treated papers [8]: Folding endurance: Schopper	Folding endurance: MIT	Tearing strength
			%	%	%	pH	lb.	Points	kg	kg	%	%	in.	sec.	%	Double folds	Double folds	Double folds	Double folds	g	g	% of initial	% of initial	% of initial
1133	Sulfite pulp, 50%; soda pulp, 50%.	None	None	None	None	7.3	57.6	31	7.6	4.6	2.0	5.5	0.0035	----	81	247	141	2,828	1,228	55	54	39	69	80
1143	do	do	None	1	1.3	5.1	55.9	28	7.0	4.0	2.0	5.5	.0037	49	83	403	118	2,884	683	59	70	36	60	75
1134	do	Clay	15	None	0.5	7.0	55.8	26	6.0	3.6	2.0	5.0	.0035	----	86	101	38	1,749	395	47	51	57	72	89
1135	do	do	15	None	1.0	6.0	55.8	26	6.1	3.4	2.0	4.5	.0036	----	87	72	33	913	416	48	55	64	93	87
1130	do	do	15	None	1.5	4.6	55.5	24	5.5	3.7	1.8	5.0	.0035	----	87	53	33	548	423	48	49	46	56	80
1129	do	do	15	None	2.1	4.2	54.9	23	5.7	3.3	1.7	4.6	.0035	----	87	54	18	599	140	46	51	21	19	58
1136	do	do	15	2	1.1	5.8	56.8	25	5.8	3.3	2.0	5.0	.0037	41	87	71	25	857	355	49	57	58	78	80
1137	do	do	15	2	1.4	4.9	55.6	24	5.6	2.9	2.0	5.0	.0037	40	88	36	14	505	97	50	60	68	63	83
1138	do	do	15	2	2.3	4.2	57.3	18	3.8	2.9	2.0	4.5	.0037	59	90	41	14	443	111	53	57	49	53	73
1139	do	do	15	1	0.8	6.2	54.9	21	5.7	3.2	2.0	5.0	.0036	45	87	83	30	1,341	340	49	56	62	69	87
1140	do	do	15	1	1.3	5.1	56.1	20	5.3	3.0	2.0	4.5	.0036	42	88	47	23	731	142	51	52	59	70	84
1141	do	do	15	1	2.4	4.2	57.6	16	5.1	2.7	2.0	5.0	.0037	47	89	29	15	346	87	50	57	37	40	68
1142 [9]	do	do	15	1	[9] 2.4	[9] 6.1	55.7	18	4.6	2.7	2.5	5.0	.0036	48	89	27	13	329	96	46	53	77	76	90
1147	do	Titanium pigment *A*	15	1	1.3	4.8	54.9	16	4.9	2.6	1.5	5.0	.0035	38	94	29	14	317	82	49	54	61	77	82
1145	do	do	5	1	1.6	5.0	57.1	23	6.7	3.7	2.0	5.0	.0037	59	90	140	51	1,467	572	56	61	46	82	78
1148	do	Titanium pigment *B*	15	1	1.1	5.0	56.8	19	5.6	3.2	2.0	5.0	.0037	55	90	72	23	1,241	227	49	56	38	47	80
1149	do	do	15	1	2.2	4.2	56.5	16	5.2	2.7	2.0	5.0	.0035	45	92	39	15	540	132	47	54	32	32	72
1150	do	Zinc sulfide pigment *A*	15	1	1.2	4.9	56.0	19	5.2	2.9	2.0	5.5	.0035	44	94	52	22	832	172	54	58	63	69	77
1151	do	do	5	1	1.3	5.0	55.1	25	6.7	3.9	2.0	5.0	.0034	59	88	163	52	2,200	834	58	63	49	53	78
1152	do	Zinc sulfide pigment *B*	15	1	1.2	5.0	54.5	18	5.3	2.8	2.0	5.0	.0034	47	92	42	21	808	221	56	59	69	56	85
1153	do	do	15	1	2.3	4.2	55.0	14	4.6	2.5	1.5	4.5	.0033	47	94	20	10	250	64	50	58	52	60	72

See footnotes at end of table.

100928—33——10

TABLE 3.—*Papermaking details and physical test data on the book papers*—Continued

Paper machine run number	Beater furnish					Acidity at headbox (quinhydrone method)	Tests of unbeated papers [8]														Tests of heat-treated papers [9]		
	Fiber	Filler		Rosin [1]	Alum [2]		Weight: 25 by 40 inches, 500 sheets	Bursting strength [3]	Tensile properties				Thickness	Sizing value (dry-indicator method)	Opacity (contrast ratio)	Folding endurance [4]				Tearing strength		Folding endurance		Tearing strength
		Kind	Amount [1]						Breaking load [4]		Elongation at rupture					Schopper		MIT				Schopper	MIT	
									Machine direction	Cross direction	Machine direction	Cross direction				Machine direction	Cross direction	Machine direction [7]	Cross direction [7]	Machine direction	Cross direction			
			%	%	%	*pH*	*lb*	*Points*	*kg*	*kg*	%	%	*in.*	*sec*	%	*Double folds*	*Double folds*	*Double folds*	*Double folds*	*g*	*g*	% *of initial*	% *of initial*	% *of initial*
1158	Sulfite pulp, 50%; soda pulp, 50%.	Prec. calcium carbonate.	15	None	None	[10] 8.2	56.0	20	5.3	3.1	3.0	5.0	.0037	0	90	57	23	644	150	51	55	67	77	92
1159	do	do	15	2	1.1	[10] 9.0	56.6	16	4.8	2.6	2.5	5.0	.0038	21	92	33	12	201	70	51	59	76	98	90
1172	do	do	15	2	1.1	[10] 8.0	56.9	19	4.2	2.6	1.5	3.0	.0039	13	92	21	17	251	122	50	52	74	55	91
1173	do	do	30	2	1.0	[10] 8.0	55.9	15	3.1	1.9	1.0	3.0	.0037	6	93	8	5	47	28	44	45	84	90	97
1174	do	Natural calcium carbonate *A*.	30	None	None	[10] 7.7	56.7	22	4.7	3.0	1.5	4.5	.0037	0	86	26	20	462	250	42	41	73	57	91
1175	do	do	15	2	1.0	[10] 7.7	56.4	23	5.0	3.3	1.0	4.5	.0037	23	87	38	21	445	135	45	47	66	75	93
1220	do	Natural calcium carbonate *C*.	30	2	1.0	[10] 7.8	55.4	14	3.3	2.0	2.0	4.0	.0034	11	93	10	6	59	26	42	45	82	78	92
1160	Purified wood pulp: *A*, 75%; *C*, 25%.	Clay	15	None	None	7.0	58.0	25	5.8	3.2	3.5	7.0	.0037	0	87	840	118	5,310	1,890	83	95	90	110	99
1161	do	do	15	2	0.8	5.9	55.0	21	5.0	2.5	2.5	5.5	.0034	24	88	260	43	2,270	474	82	96	106	108	90
1162	do	do	15	2	1.1	4.8	57.4	21	4.8	2.6	2.0	5.5	.0036	31	87	211	37	1,734	428	79	84	92	97	90
1163	do	do	15	2	2.3	4.2	57.0	22	5.3	2.7	2.5	6.0	.0036	25	87	325	47	2,328	556	77	87	69	81	80
1164	do	do	15	1	0.6	5.6	56.5	23	5.2	2.6	2.5	6.0	.0033	13	87	274	41	3,506	487	79	86	109	93	91
1165	do	do	15	1	0.8	4.7	58.1	23	5.1	2.6	3.0	5.5	.0036	22	88	242	47	2,480	592	83	91	84	95	80
1166	do	do	15	1	2.1	4.2	56.0	23	5.3	2.5	3.0	6.0	.0037	24	88	221	45	2,646	695	75	85	69	62	74
1167	Purified wood pulp: *D*, 100%.	do	15	None	None	7.0	55.8	37	9.0	4.7	4.5	9.0	.0034	4	80	2,800	2,313	[11] 1,763	[11] 1,761	97	101	101	86	102
1168	do	do	15	1	0.7	6.1	55.1	37	8.3	4.4	4.0	9.0	.0033	14	83	2,633	2,077	[11] 1,490	[11] 1,441	99	101	89	84	99
1169	do	do	15	1	1.0	4.9	56.9	36	8.0	4.8	4.0	10.0	.0036	17	84	1,952	1,920	[11] 1,118	[11] 1,297	112	126	91	77	81
1170	do	do	15	1	2.3	4.2	56.6	36	8.0	4.4	4.0	8.0	.0034	22	84	2,067	1,688	[11] 1,096	[11] 752	108	108	46	47	66

1176	Rags: No. 1 new whites, 100%.	do	15	None	0.5	6.6	56.4	21	4.4	2.8	2.5	5.0	.0036	0	88	140	40	1,675	642	94	110	108	92	100
1177	do	do	15	None	0.8	4.9	55.9	21	4.4	2.7	2.0	5.0	.0035	0	88	103	29	1,059	416	84	94	102	118	101
1178	do	do	15	None	1.5	4.2	55.0	20	4.4	2.6	2.0	5.0	.0035	0	88	100	29	1,541	474	89	95	101	101	88
1179	do	do	15	2	0.9	6.6	55.7	20	4.4	2.7	2.0	4.5	.0034	2	88	83	32	1,062	351	85	90	100	113	98
1180	do	do	15	2	1.2	4.9	56.1	20	4.4	2.5	2.0	5.0	.0034	9	89	71	20	543	220	85	90	129	109	94
1181	do	do	15	2	2.0	4.2	54.9	16	4.1	2.6	2.0	5.0	.0033	7	89	55	25	460	253	80	85	96	99	87
1182	do	do	15	2	4.0	4.0	54.8	17	4.2	2.7	2.0	5.0	.0033	11	88	63	28	651	291	82	81	96	86	89
1183	do	do	15	1	0.7	6.5	55.5	19	4.3	2.8	2.0	5.5	.0033	2	87	90	36	1,482	403	88	85	106	92	95
1184	do	do	15	1	1.1	4.8	55.0	18	4.2	2.7	2.0	5.5	.0035	3	88	76	28	810	246	81	90	99	108	96
1185	do	do	15	1	2.0	4.2	56.0	17	4.1	2.8	2.0	5.5	.0035	5	88	68	36	735	357	87	92	101	93	87
1186	do	do	15	1	4.0	4.0	54.3	19	4.5	2.9	2.0	6.0	.0034	5	86	79	37	1,090	517	86	85	77	69	80
1191	Rags: No. 1 old whites, 50%; two and blues, 50%.	do	15	None	0.7	6.7	56.4	15	3.3	2.2	2.5	4.0	.0036	0	91	13	8	71	55	55	60	107	114	97
1192	do	do	15	None	1.3	4.9	57.1	14	3.2	2.2	2.0	4.0	.0038	1	91	11	7	66	48	57	61	100	114	92
1193	do	do	15	None	2.1	4.2	56.0	15	3.4	2.2	2.5	4.5	.0036	1	92	13	7	76	53	56	59	78	95	90
1200	do	do	15	2	1.0	6.5	57.2	16	3.6	2.2	2.5	4.0	.0037	3	91	14	7	80	61	58	63	107	130	93
1201	do	do	15	2	1.5	4.8	56.5	14	3.1	2.2	2.5	4.5	.0035	6	92	10	6	56	38	54	53	105	98	93
1202	do	do	15	2	2.1	4.2	54.8	14	3.2	2.1	2.5	4.5	.0037	5	91	11	6	51	33	52	56	87	100	92
1203	do	do	15	2	4.0	4.0	56.1	14	3.0	2.2	2.5	4.5	.0037	6	91	11	7	64	37	54	57	84	100	91
1214	do	None	None	1	1.1	5.0	55.1	22	4.1	3.0	2.5	5.0	.0038	3	86	49	22	524	267	62	67	96	138	93
1204	do	Clay	15	1	1.0	6.3	56.9	17	3.2	2.3	2.5	4.5	.0039	3	91	13	8	87	61	56	55	92	86	95
1205	do	do	15	1	1.3	4.9	55.9	15	3.1	2.2	2.5	4.5	.0038	3	91	13	6	66	42	53	57	89	109	91
1206	do	do	15	1	2.2	4.2	56.9	16	2.9	2.3	2.5	4.5	.0039	4	91	12	7	72	47	55	57	87	102	86
1207	do	Titanium pigment A	5	1	1.4	4.9	57.4	19	3.7	2.7	2.5	5.0	.0038	6	92	24	12	217	113	60	64	96	96	91
1208	do	Titanium pigment B	15	1	1.3	4.9	56.0	15	3.1	2.2	2.5	5.0	.0035	4	93	12	7	94	47	54	56	104	107	94
1209	do	do	15	1	2.2	4.2	57.1	15	3.1	2.3	2.5	5.0	.0037	5	93	14	7	97	53	55	57	103	97	93
1210	do	Zinc sulfide pigment A	5	1	1.6	4.9	56.4	17	3.3	2.5	2.5	5.0	.0039	5	94	19	10	130	88	60	64	95	108	90
1211	do	Zinc sulfide pigment B	15	1	1.5	4.9	57.5	15	3.0	2.1	2.5	4.5	.0037	3	95	12	6	78	47	56	58	108	112	91
1212	do	do	15	1	2.3	4.2	57.4	14	3.0	2.1	2.5	4.5	.0037	3	95	12	6	62	39	57	56	96	114	85
1215	do	Prec. calcium carbonate	15	None	None	[10] 8.1	55.2	15	3.3	2.2	3.0	4.5	.0036	----	91	19	9	102	65	54	57	100	125	98
1216	do	do	30	None	None	[10] 8.4	55.3	11	2.2	1.7	2.0	4.0	.0033	----	93	6	4	28	25	45	49	92	92	97
1217	do	Natural calcium carbonate C.	15	None	None	[10] 8.1	56.4	17	3.7	2.5	2.5	4.5	.0037	----	90	16	10	191	95	58	62	120	85	95
1218	do	Natural calcium carbonate B.	15	None	None	[10] 8.1	55.6	17	3.6	2.5	3.0	4.5	.0037	----	89	23	13	200	136	57	54	102	96	99
1219	do	Natural calcium carbonate A.	15	None	None	[10] 8.0	55.9	18	3.5	2.5	2.5	5.0	.0037	----	89	23	11	277	106	53	59	113	88	98

[1] Based on dry weight of fiber and filler.
[2] Based on dry weight of fiber, filler, and rosin.
[3] Bursting pressure, in pounds per square inch, through a circular orifice 1.2 inches in diameter.
[4] For test specimen 15 mm wide and 100 mm between jaws.
[5] All physical tests made at 65-percent relative humidity and 70° F.
[6] Test specimen 15 mm wide.
[7] Tests made at 0.5-kg tension unless noted.
[8] Samples heated at 100° C for 72 hours.
[9] See text, p. 683. An excessive amount of alum was added in the beater to give pH 4.2, but later sodium carbonate was added to neutralize part of the acidity.
[10] Glass-electrode method.
[11] Tests made at 1.0-kg tension.

TABLE 4.—*Papermaking details and chemical test data on the book papers*

Paper machine run number	Beater furnish					Acidity at head box (quinhydrone method)	Original papers											Heat-treated papers [9] (change in content)				
	Fiber	Filler		Rosin [1]	Alum [2]		Ash [3]	Filler	Retention of filler [4]	Resin [5]	Acidity (glass-electrode method)		Alpha-cellulose [6]	Beta-cellulose [6]	Gamma-cellulose [6]	Pentosans	Copper number	Alpha-cellulose	Beta-cellulose	Gamma-cellulose	Pentosans	Copper number
		Kind	Amount [1]								Cold-water extraction	Hot-water extraction										
			%	%	%	pH	%	%		%	pH	pH	%	%	%	%		%	%	%	%	
1133	Sulfite pulp, 50%; soda pulp, 50%.	None	None	None	None	7.3	0.3			0.3	6.9	6.4	75.8	17.3	6.9	11.2	3.2	+0.1	−0.5	+0.4	0	−0.1
1143	do	do	None	1	1.3	5.1	.4			.9	5.8	5.1	75.4	17.2	7.4	10.7	3.3	−2.0	+1.7	+.3	+0.3	+.3
1134	do	Clay	15	None	0.5	7.0	7.8	8.6	0.56	.3	6.6	6.2	74.8	18.0	7.2	11.1	3.0	−1.0	+0.2	+.8	−.1	−.1
1135	do	do	15	None	1.0	6.0	8.0	8.9	.60	.3	6.4	5.7	74.4	17.6	8.0	10.2	3.2	−1.2	+.7	+.5	+.2	.0
1130	do	do	15	None	1.5	4.6	9.1	10.1	.66	.2	5.3	4.8	75.7	16.8	7.5	11.4	3.6	−3.3	+2.8	+.5	+.9	+.4
1129	do	do	15	None	2.1	4.2	10.1	11.2	.77	.2	4.9	4.3	76.0	16.3	7.7	11.4	3.6	−7.6	+7.2	+.4	+.6	+.6
1136	do	do	15	2	1.1	5.8	7.8	8.5	.52	1.2	6.0	5.3	77.0	14.7	8.3	10.3	3.5	−4.0	+2.9	+1.1	+.5	+.7
1137	do	do	15	2	1.4	4.9	9.7	10.6	.67	1.6	5.5	4.9	76.8	15.0	8.2	10.6	3.6	−5.0	+4.6	+0.4	+.2	+.7
1138	do	do	15	2	2.3	4.2	10.2	11.2	.71	1.9	5.4	4.5	77.6	13.9	8.5	10.8	3.5	−5.8	+4.9	+.9	+.4	+.7
1139	do	do	15	1	0.8	6.2	8.1	8.8	.53	0.9	6.2	5.5	77.8	14.5	7.7	10.5	3.1	−2.6	+2.3	+.3	+.4	+.5
1140	do	do	15	1	1.3	5.1	9.2	10.0	.64	1.0	5.9	5.1	76.4	16.5	7.1	10.5	3.3	−3.2	+2.5	+.7	−.1	+.4
1141	do	do	15	1	2.4	4.2	10.8	11.8	.73	1.2	5.2	4.6	74.3	18.1	7.6	9.7	3.2	−6.3	+6.8	−.5	+1.2	+.7
1142 [7]	do	do	15	1	[7] 2.4	[7] 6.1	11.4	12.6	.80	1.0	6.5	5.3	75.0	17.6	7.4	10.7	3.2	−2.6	+2.5	+.1	+0.1	+.7
1147	do	Titanium pigment A.	15	1	1.3	4.8	9.7	9.0	.59	1.0	5.2	----	73.6	18.2	8.2	11.0	3.3	−5.0	+4.8	+.2	+.4	+.6
1145	do	do	5	1	1.6	5.0	3.8	3.1	.68	0.9	5.6	4.9	75.2	15.8	9.0	----	3.0	−5.2	+5.8	−.6	----	+.8
1148	do	Titanium pigment B.	15	1	1.1	5.0	7.4	[8] 2.1; 4.6	.44	.9	5.4	4.6	73.5	19.3	7.2	10.6	3.0	−6.0	+5.6	+.4	.0	+.3
1149	do	do	15	1	2.2	4.2	10.5	[8] 3.2; 6.6	.64	1.1	5.2	4.6	72.2	20.6	7.2	10.6	3.0	−8.2	+7.3	+.9	.0	+1.1
1150	do	Zinc sulfide pigment A.	15	1	1.2	4.9	8.5	9.4	.60	1.1	5.8	----	78.2	13.6	8.2	10.4	(10)	−3.7	+2.9	+.8	.0	(10)
1151	do	do	5	1	1.3	5.0	2.5	2.3	.52	0.9	5.7	----	76.8	15.0	8.2	9.6	(10)	−2.0	+1.2	+.8	−.7	(10)
1152	do	Zinc sulfide pigment B.	15	1	1.2	5.0	8.6	[8] 5.0; 4.0	.55	1.1	5.8	5.1	77.4	15.7	6.9	10.3	(10)	−3.7	+3.5	+.2	+.6	(10)
1153	do	do	15	1	2.3	4.2	11.2	[8] 6.2; 5.1	.74	1.2	5.1	4.6	77.3	13.9	8.8	10.7	(10)	−1.3	+0.1	+1.2	+.1	(10)

1158	....do	Prec. calcium carbonate.	15	None	None	[11] 8.2	4.2	7.2	[13] .48	0.5	9.6	....	75.5	15.3	9.2	10.5	3.3	−0.4	+3.0	−2.6	0.0	+0.
1159	....do	....do	15	2	1.1	[11] 8.0	6.3	11.2	[13] .75	1.5	9.2	....	76.6	15.7	7.7	10.1	3.3	−1.5	+1.0	+0.5	−1.3	+.1
1172	....do	....do	15	2	1.1	[11] 8.0	6.5	11.2	[13] .75	1.6	8.9	....	75.6	15.2	9.2	10.8	3.4	−2.1	+1.5	+.6	+0.5	+.4
1173	....do	....do	30	2	1.0	[11] 8.0	12.1	21.1	[13] .70	1.6	8.8	....	76.4	14.6	9.0	10.7	3.4	−2.3	+2.0	+.3	+.2	+.4
1174	....do	Natural calcium carbonate *A*.	30	None	None	[11] 7.7	10.0	16.4	[13] .55	0.3	9.2	....	74.2	18.3	7.5	9.7	3.3	−2.2	+1.8	+.4	+.9	+.3
1175	....do	....do	15	2	1.0	[11] 7.7	6.0	9.9	[13] .66	1.3	8.5	....	74.2	17.4	8.4	10.7	3.3	−3.3	+2.9	+.4	+.1	+.3
1220	....do	Natural calcium carbonate *C*.	30	2	1.0	[11] 7.8	12.6	21.2	[13] .70	1.1	8.8	....	75.0	17.5	7.5	.....	3.8	−2.7	+1.7	+1.0	.....	+.5
1160	Purified wood pulp: *A*, 75%; *C*, 25%.	Clay	15	None	None	7.0	7.6	8.4	.53	0.2	6.9	7.2	89.8	4.6	5.6	.....	0.7	−0.4	−0.1	+0.5	.....	+.1
1161	....do	....do	15	2	0.8	5.9	10.5	11.5	.76	1.6	6.1	5.7	90.2	4.0	5.8	.....	.8	−.8	−.2	+1.0	.....	+.3
1162	....do	....do	15	2	1.1	4.8	10.7	11.9	.79	1.7	5.6	5.3	90.2	2.8	7.0	.....	.9	−3.6	+3.5	+0.1	.....	+.5
1163	....do	....do	15	2	2.3	4.2	10.0	11.1	.74	1.9	5.2	4.5	90.0	3.4	6.6	.....	.9	−4.6	+4.2	+.4	.....	+.7
1164	....do	....do	15	1	0.6	5.6	10.9	12.1	.81	1.1	6.0	5.7	89.8	4.8	5.4	.....	.9	−1.8	+1.5	+.3	.....	+.2
1165	....do	....do	15	1	.8	4.7	10.7	11.9	.79	1.1	5.6	5.0	89.9	4.9	5.2	.....	.8	−2.9	+2.5	+.4	.....	+.4
1166	....do	....do	15	1	2.1	4.2	10.1	11.2	.74	1.0	5.0	4.4	89.6	4.7	5.7	.....	.9	−5.0	+5.1	−.1	.....	+.5
1167	Purified wood pulp: *D*, 100%.	....do	15	None	None	7.0	9.8	10.8	.71	0.1	6.8	7.0	82.4	4.2	13.4	8.5	.7	−0.2	+0.2	.0	+.3	+.1
1168	....do	....do	15	1	0.7	6.1	12.1	13.5	.88	.9	6.4	6.0	83.2	4.4	12.4	8.5	.8	−.7	+.5	+.2	+.1	+.2
1169	....do	....do	15	1	1.0	4.9	12.5	13.9	.87	.9	5.8	5.0	82.6	4.4	13.0	8.4	.7	−.8	+.8	.0	+.1	+.1
1170	....do	....do	15	1	2.3	4.2	12.3	13.7	.84	1.0	5.2	4.4	82.4	4.6	13.0	8.3	1.1	−1.4	+2.9	−1.5	+.2	+.3
1176	Rags: No. 1 new whites, 100%.	....do	15	None		0.5	6.6	11.4	12.6	.81	0.3	7.2	7.3	96.0	3.2	0.8	.....	0.2	−.03	+0.3	0.0	.....	+.1
1177	....do	....do	15	None		.8	4.9	12.6	14.0	.89	.3	6.4	5.5	95.8	3.4	.8	.....	.2	−0.9	+.7	+.2	.....	+.2
1178	....do	....do	15	None		1.5	4.2	11.6	12.7	.82	.2	5.5	4.8	95.2	4.1	.7	.....	.3	−3.2	+3.0	+.2	.....	+.2
1179	....do	....do	15	2	0.9	6.6	11.2	12.4	.80	1.6	6.4	5.9	96.0	2.6	1.4	.....	.4	−2.0	+1.6	+.4	.....	+.4
1180	....do	....do	15	2	1.2	4.9	12.3	13.6	.87	1.8	5.6	5.0	94.8	3.7	1.5	.....	.5	−4.6	+4.1	+.5	.....	+.5
1181	....do	....do	15	2	2.0	4.2	11.8	13.0	.83	1.7	5.4	4.7	95.1	3.6	1.3	.....	.4	−5.3	+4.7	+.6	.....	+.6
1182	....do	....do	15	2	4.0	4.0	11.8	13.0	.83	1.7	5.0	4.4	94.8	4.0	1.2	.....	.5	−7.0	+6.2	+.8	.....	+.7
1183	....do	....do	15	1	0.7	6.5	11.6	12.7	.82	0.8	6.3	6.0	93.8	3.4	0.8	.....	.3	−1.4	+1.1	+.3	.....	+.2
1184	....do	....do	15	1	1.1	4.8	12.3	13.6	.87	.9	5.6	5.0	95.4	3.6	1.0	.....	.3	−2.9	+2.7	+.2	.....	+.4
1185	....do	....do	15	1	2.0	4.2	11.6	12.7	.84	.9	5.1	4.5	95.1	4.1	0.8	.....	.4	−4.9	+4.6	+.3	.....	+.4
1186	....do	....do	15	1	4.0	4.0	10.8	12.0	.82	.9	4.9	4.3	95.0	4.2	.8	.....	.4	−8.0	+7.6	+.4	.....	+.5
1191	Rags: No. 1 old whites, 50%; twos and blues, 50%.	....do	15	None		0.7	6.7	12.5	13.9	.84	.2	6.8	....	92.3	7.5	.2	.....	.3	−3.1	+1.4	+1.7	.....	+.1
1192	....do	....do	15	None		1.3	4.9	12.4	13.8	.83	.2	5.8	....	91.1	8.7	.2	.....	.4	−3.0	+1.8	+1.2	.....	+.1
1193	....do	....do	15	None		2.1	4.2	12.4	13.8	.83	.3	5.1	....	91.6	8.3	.1	.....	.5	−8.1	+7.3	+0.8	.....	+.2
1200	....do	....do	15	2	1.0	6.5	11.7	13.0	.79	1.4	6.7	....	90.4	8.2	1.4	.....	.5	−4.0	+3.6	+.4	.....	+.5
1201	....do	....do	15	2	1.5	4.8	12.3	13.7	.85	1.4	5.9	5.1	89.0	9.5	1.5	.....	.5	−6.6	+5.9	+.7	.....	+.9
1202	....do	....do	15	2	2.1	4.2	12.3	13.7	.84	1.5	5.5	4.8	89.1	9.3	1.6	.....	.7	−8.3	+7.6	+.7	.....	+.8
1203	....do	....do	15	2	4.0	4.0	12.1	13.4	.83	1.5	5.3	4.5	89.2	9.3	1.5	.....	.7	−9.6	+8.8	+.8	.....	+.9

See footnotes at end of table.

TABLE 4.—*Papermaking details and chemical test data on the book papers*—Continued

Paper machine run number	Beater furnish					Acidity at head box (quinhydrone method)	Original papers											Heat-treated papers [9] (change in content)				
	Fiber	Filler					Ash [3]	Filler	Retention of filler [4]	Resin	Acidity (glass-electrode method)		Alpha-cellulose [5]	Beta-cellulose [5]	Gamma-cellulose [5]	Pentosans	Copper number	Alpha-cellulose	Beta-cellulose	Gamma-cellulose	Pentosans	Copper number
		Kind	Amount [1]	Rosin [1]	Alum [2]						Cold-water extraction	Hot-water extraction										
			%	%	%	pH	%	%		%	pH	pH	%	%	%	%		%	%	%	%	
1214	Rags: No. 1 whites, 50%; twos and blues, 50%.	None	None	1	1.1	5.0	0.4			0.5	6.2		90.3	8.6	1.1		.4	−3.0	+2.8	+.2		+.3
1204	do	Clay	15	1	1.0	6.3	12.1	13.4	.82	.5	6.2		90.4	8.6	1.0		.4	−2.9	+2.8	+.1		+.3
1205	do	do	15	1	1.3	4.9	12.6	14.0	.87	.5	5.4		89.6	9.5	0.9		.6	−4.2	+3.6	+.6		+.4
1206	do	do	15	1	2.2	4.2	12.2	13.5	.84	.7	5.0		90.0	9.1	.1		.6	−6.7	+6.4	+.3		+.4
1207	do	Titanium pigment *A*.	5	1	1.4	4.9	5.0	4.6	.87	.8	5.2		90.2	8.8	1.0		.5	−4.4	+3.9	+.5		+.5
1208	do	Titanium pigment *B*.	15	1	1.3	4.9	13.4	[6] 4.2; 8.1	.82	.9	5.7		90.5	9.5	0.0		.4	−3.7	+3.6	+.1		+.4
1209	do	do	15	1	2.2	4.2	13.7	[6] 4.2; 8.4	.83	.8	5.6		89.8	10.1	.1		.6	−4.3	+4.4	−.1		+.4
1210	do	Zinc sulfide pigment *A*.	5	1	1.6	4.9	4.2	4.3	.85	.8	6.1		90.5	9.0	.5		[10]	−5.1	+4.4	+.7		[10]
1211	do	Zinc sulfide pigment *B*.	15	1	1.5	4.9	12.8	[7] 7.2; 5.8	.85	.9	6.2		91.0	8.1	.9		[10]	−4.7	+4.3	+.4		[10]
1212	do	do	15	1	2.3	4.2	12.4	[8] 6.9; 5.6	.83	.9	5.5		90.7	8.8	.5		[10]	−6.8	+6.1	+.7		[10]
1215	do	Prec. calcium carbonate.	15	None	None	[11] 8.1	8.3	14.0	[12] .93	.1	9.5		92.8	6.7	.5		.4	−0.6	+0.3	+.3		.0
1216	do	do	30	None	None	[11] 8.4	16.5	28.2	[12] .94	.1	9.5		92.7	6.6	.7		.3	+.1	−.3	+.2		+.1
1217	do	Natural calcium carbonate *C*.	15	None	None	[11] 8.1	6.9	11.8	[12] .79	.1	9.4		92.5	6.9	.6		.3	−2.1	+2.1	.0		+.1
1218	do	Natural calcium carbonate *B*.	15	None	None	[11] 8.1	7.3	12.4	[12] .82	.2	9.4		92.4	7.0	.6		.4	−2.7	+2.5	+.2		+.1
1219	do	Natural calcium carbonate *A*.	15	None	None	[11] 8.0	7.3	12.2	[12] .81	.2	9.4		92.1	7.3	.6		.4	−1.4	+1.5	−.1		+.1

[1] Based on dry weight of fiber and filler.
[2] Based on dry weight of fiber, filler, and rosin.
[3] On oven-dry basis.
[4] For method of calculating retention see text, p. 676.
[5] Based on total cellulose.
[6] Samples heated at 100° C for 72 hours.
[7] See text, p. 683. An excessive amount of alum was added in the beater to give pH 4.2, but later sodium carbonate was added to neutralize part of the acidity.
[8] Titanium dioxide and barium sulfate, respectively.
[9] Zinc sulfide and barium sulfate, respectively.
[10] Presence of zinc sulfide interferes with the chemical reactions in the test.
[11] Glass-electrode method.
[12] Approximated, did not have data required for use of formula. Obtained by dividing percentage in paper by percentage furnished.

A series of runs (1134, 1135, 1130, and 1129) of unsized papers containing clay was made in which the amount of alum added was varied. The effect of acidity on the stability of the unsized clay-filled papers is shown by the decrease in alpha-cellulose content and increase in copper number of the heat-treated papers as the amount of alum in the furnish increased, and the decrease in retention of folding endurance and tearing strength. In general, the agreement between the pH values of the water from the stock at the head box and of the hot-water extraction of the finished paper was fairly good, the differences probably being due to differences in buffer conditions, the head-box sample being well buffered and the water extraction of the finished paper poorly buffered. The clay retention of the runs increased with increased amounts of alum.

To study the effect of rosin sizing on the stability of sulfite-soda papers containing clay several machine runs were made in which the amounts of alum and rosin size were varied.

The test data on the runs (1136 to 1138) in which the amount of rosin was kept constant at 2 percent and the amount of alum was varied show that the change in alpha-cellulose content of the heat-treated papers increased as the alum was increased, but that the increase in copper number remained constant, although large. The percentage of retention of folding endurance and tearing strength gradually decreased as acidity increased but to less extent than for the unsized papers, to which rosin was not added (runs 1134, 1135, 1130, and 1129). The rosin seems to have hindered deterioration. This phenomenon was noted also in a previous study [2] of sulfite pulps for writing papers. As a possible reason for this apparent disagreement, it is suggested that for pulps in the low stability range, rosin sizing may actually have a protective effect. The indications are that, within the range studied, the amount of rosin employed in sizing sulfite-soda papers is not an important consideration as far as stability is concerned. Retention of clay in runs 1136 to 1138 increased as alum was increased.

For the series of papers (runs 1139 to 1141) in which the amount of rosin was kept constant at 1 percent and the amount of alum was varied, the stability falls between that of papers with no rosin in the beater furnish and those with 2 percent of rosin added. The data on the heat-treated papers of this series are shown graphically in figure 1.

Although the folding strength of the original clay-filled papers decreased as the amount of alum was increased, some of the decrease was due to the increased retention of clay. The increased filler content should not affect the strength retention of the heat-treated papers, however, since clay is an inert substance which has been previously found to have no harmful effect on the stability of paper.

To determine whether paper made from stock having high acidity in the beater but subsequently adjusted at the paper machine to low acidity would remain stable, a paper-machine run (1142) was made similar to run 1141 in the preparation of the stock in the beater. An excessive amount of alum was added in the beater to give a pH of 4.2, but a solution of soda ash (sodium carbonate) was added to neutralize some of the acidity as the stock was being pumped from the beater chest to the machine chest. The pH at the head box of

the paper machine was 6.1. The stability of the finished paper compared favorably with that of the run (1139) which had pH 6.2 at the head box without any treatment to reduce the original acidity. The retention of folding endurance and tearing strength was as good for the paper of the adjusted run as for the run in which only a small amount of alum was used (run 1139), and the change in alpha-cellulose content of the heat-treated paper was no greater. But the increase in copper number was the same as that of the paper with high acidity at the head box (run 1141). The sizing value was not materially affected, but the clay retention was increased. The improvement in clay retention may be attributable to the presence of

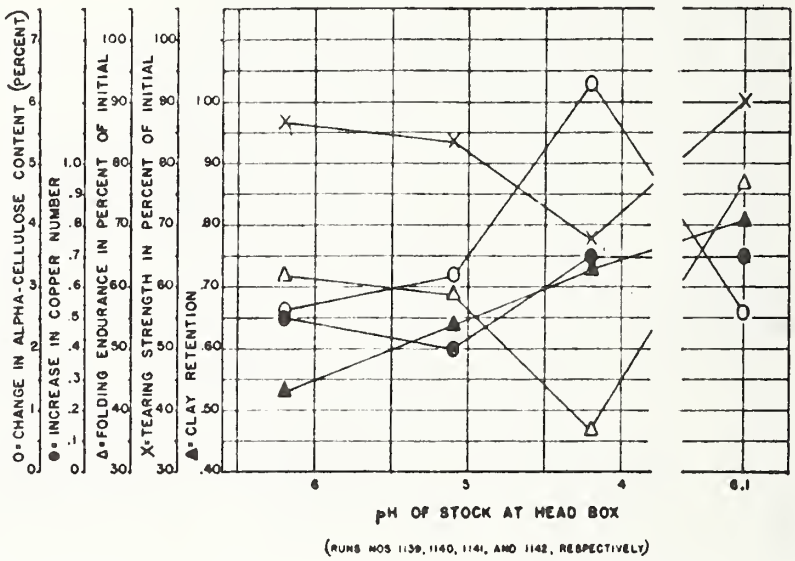

FIGURE 1.—*Effect of acidity on stability of rosin-sized, clay-filled book papers made from sulfite and soda pulps.*

Points at pH 6.1 are displaced to right of main graph to avoid confusion. For this run there was considerable difference between the initial and final pH values. An excessive amount of alum was used in the beater to give a pH of 4.2, but sodium carbonate was added to neutralize part of the acidity as the stock was being pumped from the beater chest to the machine chest.

aluminum floc formed when the acidity caused by the excessive amount of alum was neutralized with the soda ash. Retention has been shown by a number of writers to be partly the result of occlusion and fixation of the finer particles in the sheet by the rosin and the aluminum hydrate floc formed in the sizing operation.

In addition to the results obtained on the experimental paper, tests at the Bureau on commercial papers of known history show that with high acidity in the beater followed by treatment at the paper machine to obtain low acidity, paper of fair stability, as far as acidity is concerned, may be produced.

The pentosan content of the different sulfite-soda papers was not appreciably changed by the heat treatment. It is apparent that pentosans do not contribute to the deterioration of cellulose to the extent that modified celluloses do, and therefore that pentosan

determinations are comparatively unimportant in evaluating the relative stability of papers.

(2) *Purified wood pulp: A, 75 percent; C, 25 percent.*—In previous work [4] at the Bureau on purified wood pulps, papers made from pulp *A* without rosin and alum were relatively stable but had comparatively low folding strength. Pulp *B* produced a hard sheet, stronger but less stable to the heat test, and not as good in color as that made from pulp *A*. The use of a small amount (25 percent of furnish) of pulp *B* with the weaker but more stable pulp *A* increased the strength of the sheet without appreciably lessening its stability. Paper made from pulp *C* showed that although pulp *C* was not so strong as pulp *B*, it was considerably stronger than *A* and produced a softer paper of better color

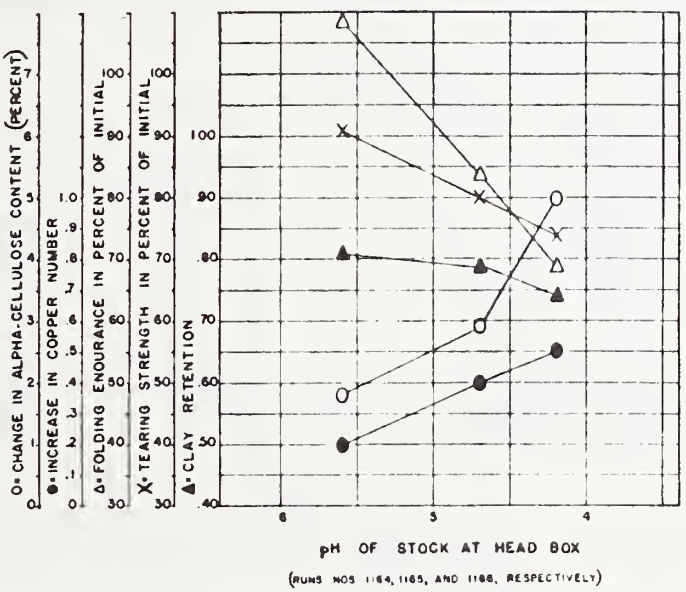

FIGURE 2.—*Effect of acidity on stability of rosin-sized, clay-filled book papers made from purified wood pulps A and C.*

and stability than *B*. Therefore, pulp *C*, rather than *B*, was selected for mixture with purified wood pulp *A* in the present study to obtain improved strength.

One run (1160) was made of the mixture of pulps *A* and *C* with clay filler but without rosin size or alum to obtain data on the quality of the pulp mixture. To determine the effects of rosin size and alum on the stability of papers from the mixture, two series of runs were made—one (runs 1161 to 1163), with 2 percent of rosin size and various amounts of alum; the other (runs 1164 to 1166), with 1 percent of rosin and various amounts of alum. The data on the papers are given in tables 3 and 4. The stability of the second series (furnish containing 1 percent of rosin) is also shown graphically in figure 2.

The stability of the papers to the heat treatment decreased as the amount of alum was increased, and was little affected by rosin size. The clay retention was highest when the pH at the head box was 5.0 to 6.0 and lowest at the highest acidity, pH 4.2. The papers were of

good formation, color, and strength, showed little change in color after oven-aging, and compared favorably with those made from new white rags, described herein later.

(3) *Purified wood pulp: D, 100 percent.*—In previous work [4] paper made from purified wood pulp *D* was hard, and therefore not suitable for book paper, but some of the hardness was attributed to the beater roll and beater tackle not being suited to produce from hard long-fibered pulp the desired character of sheet for book paper. It was believed, however, that if the beating could be effected quickly enough to preclude excessive hydrating or gelatinizing of the fibers without

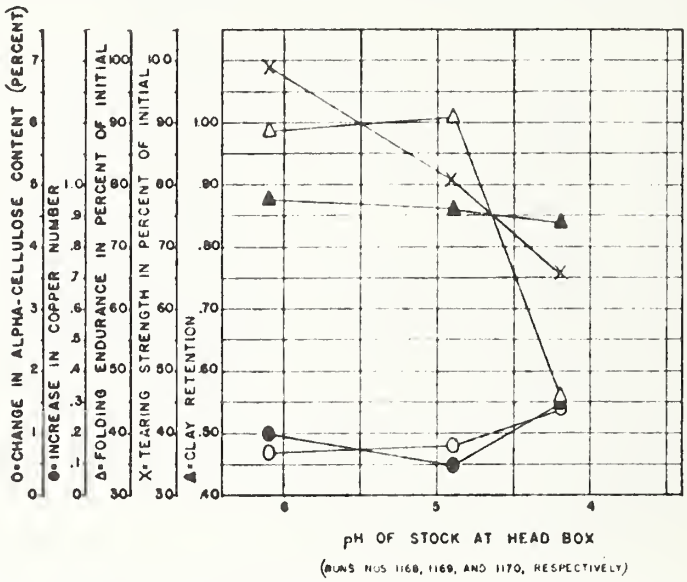

FIGURE 3.— *Effect of acidity on stability of rosin-sized, clay-filled book papers made from purified wood pulp D.*

sacrificing the desired fraying and fibrillation, a soft bulky sheet would result and would have the strength for severe service. Pulp *D* was therefore included in the present study.

One paper-machine run (1167) was made from the pulp with clay incorporated in the furnish but without rosin size or alum, and a series of runs (1168 to 1170) using 1 percent of rosin size and various amounts of alum. The stability of the sized papers is shown graphically in figure 3.

The papers showed less deterioration in the heat treatment than some of the other pulps, and better clay retention, but the retention decreased as the acidity was increased. Perhaps because of the unfavorable beating conditions, the alum affected the hydrating or binding properties developed in the beater, thereby reducing the slowness of the stock and the amount of filler retained mechanically. As would be expected, the opacity was low and the paper was comparatively hard—more like writing than book.

(4) *Rags: No. 1 new whites, 100 percent.*—Three series of papers were made from new rags and clay filler. One series (runs 1176 to

1178) was without rosin size but with various amounts of alum; the second (runs 1179 to 1182) contained 2 percent of rosin size and various amounts of alum; and the third (runs 1183 to 1186), 1 percent of rosin size and various amounts of alum.

The preparation of the rag half stuff and the method of beating the half stuff to prepare it for the paper machine followed the procedure described in previous publications [3, 4]. When beating the furnish for the rosin-sized papers, however, the stock became very hot as a result of hot weather and hard beating. To preclude any harmful influence of the high temperature on the sizing effect of the rosin, part of the stock was emptied into the chest after the beating was completed so that water could be added to the remainder in the beater before the rosin size was put in. After the rosin size was added, the

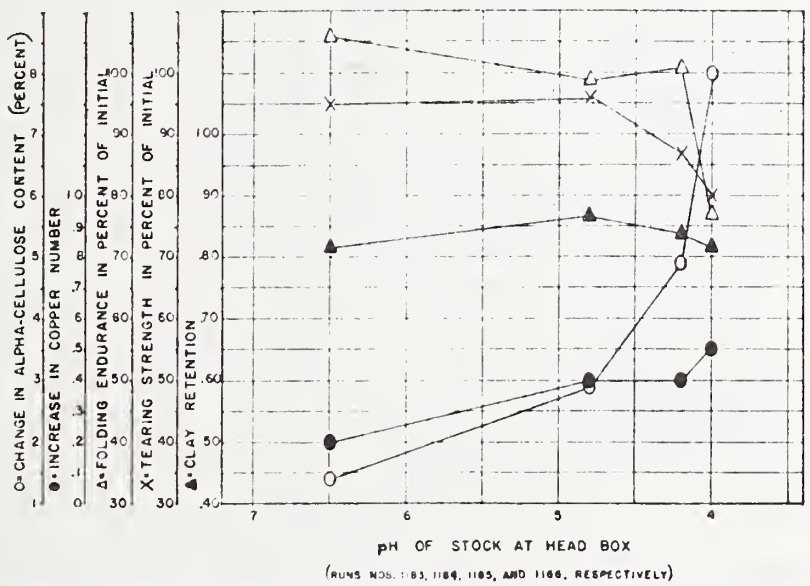

FIGURE 4.—*Effect of acidity on stability of rosin-sized, clay-filled book papers made from new rags.*

stock was circulated about 15 minutes (with the beater roll off the bedplate), the alum was added, and the stock finally mixed in the beater chest.

The folding endurance of the original papers decreased as the alum was increased, the decrease being greatest for the series with the highest rosin content. The unsized papers showed practically no reaction to the heat treatment in retention of folding endurance and tearing strength, and the rosin-sized papers decreased only slightly. An additional run in each of the sized series was made with the amount of alum increased to 4 percent. The resultant papers also were fairly stable. As is apparent from the test data of tables 3 and 4 and the curves of figure 4, if new white rags are properly prepared and the amounts of rosin size and alum added are not excessive, book paper of high stability can be produced.

The papers were not well sized but were satisfactory in this respect for printing. The color, formation, and finish were very good. The retention of clay was maximum when the pH of the stock at the head box was about 5.0. Also, at that acidity the tendency to foam was minimum, not only for the rag stocks but also for the other pulps when rosin size and alum were added.

(5) *Rags: No. 1 old whites, 50 percent; twos and blues, 50 percent.*— The preparation of the rag half stuff from No. 1 old whites and twos and blues also was the same as that used in previous studies [3, 4]. The half stuffs from the two kinds of rags were kept separate until blended in the beater at the time of furnishing. Three series of runs, comparable to the runs described for the preceding pulps in respect of the amounts of clay, rosin, and alum added, were made. One run

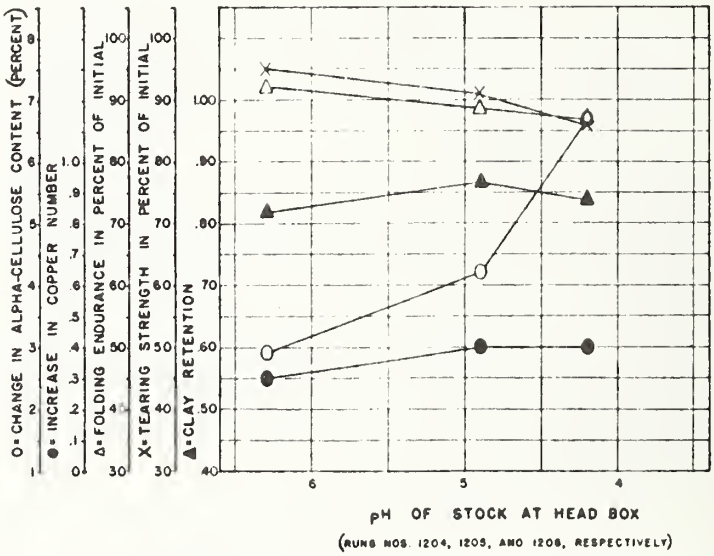

FIGURE 5.— *Effect of acidity on stability of rosin-sized, clay-filled book papers made from old rags.*

(1214) without clay filler but with rosin size and alum was also included.

The first two runs of old-rag papers (1191 and 1192) without rosin size but with alum showed little change in physical and chemical tests after heat treatment, but the paper of run 1193, with pH 4.2 at the head box, showed a decided decrease in alpha-cellulose content and retention of folding endurance. The clay retention was practically the same for all three runs.

For both series of the rosin-sized papers (2 percent, runs 1200 to 1203; 1 percent, runs 1204 to 1206) the measurements given in table 4 show increases in the change of alpha-cellulose and copper number as the alum was increased, but the initial folding endurance (table 3) of the papers was so low that the decrease for the heat-treated samples was not pronounced. Clay retention seems to be highest for the old-rag papers when the pH value at the head box is approximately 5. Characteristics of the series sized with 1 percent of rosin are shown in figure 5.

(b) TITANIUM-DIOXIDE-PIGMENTED PAPERS

Titanium dioxide pigments are manufactured pigments said to produce a high degree of opacity and brightness in paper. Although the manufacturer reported that only small proportions of titanium dioxide pigments are generally used in paper, since our study was concerned mainly with the effect of the pigments on stability, 5 and 15 percent were each used in the experimental runs. The method of furnishing the beater was the same for the titanium dioxide pigments as for the clay filler.

(1) *Sulfite pulp, 50 percent; soda pulp, 50 percent.*—Two paper-machine runs (1147 and 1145) were made with 15 and 5 percent of titanium dioxide pigment *A*, at pH values 4.8 and 5.0, respectively, at the head box; and two runs (1148 and 1149) with 15 percent of titanium dioxide pigment *B* but with different amounts of alum. The beater furnishes all contained 1 percent of rosin size.

The opacity of the paper for which 5 percent of titanium dioxide pigment *A* was added in the beater was equal to that of the runs in which 15 percent of clay was used; and when 15 percent of titanium dioxide pigment, *A* or *B*, was used the opacity was better. The papers containing titanium dioxide pigments were whiter and brighter than the clay-filled sheets. The relative quality of the clay and of the other fillers should be regarded as applying only to materials that were representative at the time the work was done. The relationship may be changed with further improvement of fillers. The sizing values were not affected by the pigments. The stability of the titanium-dioxide-pigmented papers was about the same as that of the clay-filled papers.

The original folding endurance and tearing strength of the paper in which 5 percent of pigment *A* (run 1145) was used were higher than when 15 percent of clay or titanium dioxide pigment was used. To maintain high strength and at the same time obtain high opacity is a result desired in filled papers. Since strength is adversely affected as the amount of filler is increased, relatively high opacifying power is a very desirable property. The retention of titanium dioxide pigment *B* increased as the amount of alum added was increased.

(2) *Rags: No. 1 old whites, 50 percent; twos and blues, 50 percent.*—Runs comparable to those made from the sulfite-soda pulps were made from old rags also. The stock for one (run 1207) contained 5 percent of titanium dioxide pigment *A* and was at pH 4.9 at the head box; for two runs (1208 and 1209) the furnishes included 15 percent of titanium dioxide pigment *B* and varied amounts of alum. All contained 1 percent of rosin size.

As with the sulfite-soda papers, the opacity of the paper (run 1207) for which 5 percent of titanium dioxide pigment *A* was used was as high as that of the papers in which 15 percent of clay was used, and was higher for the runs containing 15 percent of pigment *B*. The finished titanium-dioxide-pigmented papers also were whiter and brighter. The effect of the titanium dioxide pigments on the stability of the papers, and the degree of retention of the pigments, were about the same as for clay.

(c) ZINC-SULFIDE-PIGMENTED PAPERS

Zinc sulfide pigments are manufactured materials said to have high brightening and opacifying value.

The supplier of the zinc sulfide pigments recommends as a precautionary measure that plants having considerable copper equipment "avoid acid conditions so excessive as to attack this equipment and to form a dilute copper solution, as such a condition can dull down the white pigment to an extent dependent upon the amount of copper in solution and the time available for the reaction." The 50-pound beater used at the Bureau is lined with copper, and the stock pipes and screen plates are brass. Since the program of study included the manufacture at pH 4.2 of some papers with each filler, dulling of the papers pigmented with zinc sulfide was expected.

The method of furnishing the beater was the same as that used with clay and with titanium dioxide pigments. The papers were all sized with 1 percent of rosin.

(1) *Sulfite pulp, 50 percent; soda pulp, 50 percent.*—Paper machine runs 1150 and 1151 were made with 15 and 5 percent of zinc sulfide pigment *A*, at pH 4.9 and 5.0, respectively, at the head box; runs 1152 and 1153, with 15 percent of zinc sulfide pigment *B* and various amounts of alum.

All four papers were darkened somewhat, but this condition may have been due to the copper and brass of the equipment and the degree of acidity of the stock. (The odor of hydrogen sulfide was detected at the higher acidities, lower pH's.) As a result the opacity would naturally be slightly higher because relatively more light would be absorbed than if the papers had been whiter and brighter in color. The opacity for the run using 5 percent of zinc sulfide pigment *A* is as high as that of papers made with 15 percent of clay, and the opacities for the runs with 15 percent of zinc sulfide pigments, *A* or *B*, are higher.

The stability of the zinc-sulfide-pigmented papers was as good as of the papers containing the other fillers. The usual copper number test as a measure of degradation is not applicable to papers containing zinc sulfide because it interferes with the chemical reactions in the test; therefore no values are given in the table. The retention of zinc sulfide pigment *B* increased as the proportion of alum in the furnish was increased.

(2) *Rags: No. 1 old whites, 50 percent; twos and blues, 50 percent.*—Runs comparable to the last three sulfite-soda runs with zinc sulfide pigments were made with old-rag half stuff also. The test data indicate that as to stability the zinc sulfide pigments had no harmful effect on the papers. But the papers were discolored, which could be attributed in part at least to the copper and brass equipment and the degree of acidity.

(d) CALCIUM-CARBONATE-PIGMENTED PAPERS

Two types of calcium carbonate pigments were used in this study, precipitated and water-ground natural material. When the work was begun only two samples were considered, one of each kind, the precipitated and sample *A* of the natural. Later two more samples, *B* and *C*, of the water-ground natural calcium carbonate were added. The producer of the water-ground natural pigments stated that the three samples differed only in fineness: "Sample *A*, average particle size 10 microns, nothing larger than 30 microns; sample *B*, average particle size 7 microns, nothing larger than 20 microns; sample *C*, average particle size 2 microns, nothing larger than 7 microns."

The precipitated calcium carbonate was soft and bulky, was more finely divided and more uniform in particle size, and when mixed with water stayed in suspension for a comparatively long time. The water-ground natural material was not so soft nor so bulky as the precipitated, and settled out of the water mixture more rapidly. The analyses (table 2) of the two kinds of calcium carbonate show them to be about the same chemically, and they were approximately alike in color.

Most book paper in which alkaline fillers are used is not sized, has no acidic material added, and consequently the stock is alkaline during its manufacture into paper. The general manufacturing practice is very much the same as for the usual clay-filled sheet except for the omission of size and alum. In the experimental work at the Bureau some of the calcium carbonate papers were made without sizing materials, but the pulp for some was rosin-sized first and the calcium carbonate was added later. Before calcium carbonate is used for commercial paper manufacture, however, the patent rights on the use of the material in sized papers should be examined.

(1) *Sulfite pulp, 50 percent; soda pulp, 50 percent.*—In preparing the sulfite-soda stock for the papermaking runs the pulp mixture was beaten first, and the subsequent operations depended on whether the stock was to be rosin sized. The procedure followed for each run is described under the discussion of the run.

The precipitated calcium carbonate was used in runs 1158 and 1159 and 1172 and 1173. In run 1158 the calcium carbonate slip was added when the stock was being discharged into the beater chest. No rosin size or alum was added.

The pulp for run 1159 was sized in the beater and the calcium carbonate was added later in the machine chest. Two percent of size was used, based on the weight of pulp and calcium carbonate, or 2.3 percent if based on pulp alone. The sized stock was allowed to stand overnight in the beater chest. The pH of the stock, before the calcium carbonate was added, was 5.0. The calcium carbonate was added 1 hour before the stock was run over the paper machine.

Run 1172 duplicated run 1159 except for the interval between the addition of the rosin size and the calcium carbonate. For run 1172 the rosin size was added to the pulp in the beater 1 hour before it was discharged into the chest and ½ hour before the alum was added. After being emptied into the beater chest the stock was agitated for a short time and then pumped to the machine chest. The pH of the stock in the beater chest was 5.0. The calcium carbonate slip was added in the machine chest and the stock was agitated for 1 hour to insure uniformity of the mixture. The pH of the stock at the head box was 8.0.

Run 1173 was similar to run 1172, except that 30 percent of precipitated calcium carbonate was added.

The water-ground natural calcium carbonate samples *A* and *C* were used with the sulfite and soda pulp mixture. The stock for run 1174 was prepared without rosin size or alum, but 30 percent of calcium carbonate sample *A* was added in the machine chest. The stock was then agitated for 1 hour to insure a uniform mixture for the paper machine.

For run 1175 rosin size was added to the pulp in the beater 1 hour before the stock was emptied into the beater chest and ½ hour before the alum was put in. After being discharged to the beater chest

the stock was agitated for a short time and then pumped to the machine chest. The pH of the stock in the beater chest was 5.0. Fifteen percent of natural calcium carbonate sample *A* was added in the machine chest, after which the stock was agitated for 1 hour and then pumped to the paper machine. The pH of the stock at the head box was 7.7.

Run 1220 differed from run 1175 only in that 30 percent of calcium carbonate sample *C* instead of 15 percent of sample *A* was added.

Natural calcium carbonate sample *A* (runs 1174 and 1175) settled out of the stock somewhat in the riffler, or sand trap, while being run to the paper machine. This condition was not observed when either the precipitated calcium carbonate or the more finely ground natural calcium carbonate sample *C* was used.

The stock containing calcium carbonate, precipitated or natural, but no size nor alum, did not foam on the paper machine. When rosin size and alum had been added in the beater, however, followed by calcium carbonate in the machine chest, there was foaming on the paper machine, more for the precipitated than for the natural samples, although the amount was not great and doubtless could have been kept down satisfactorily with a fine water spray. There is, of course, always the possibility when foaming has occurred of foam spots being left in the finished paper.

The sizing values reported in table 3 for the sized papers are not high, but appraised by personal opinions and judgment the papers were sized sufficiently to be written on with ink and for ordinary printing processes. There is no direct correlation between the resistance of paper to water penetration and its ink-receptiveness. The retention of the calcium carbonate and the opacity of the papers were good.

From the physical and chemical test data it appears that papers containing calcium carbonate are more stable than the usual rosin-sized papers, which are acid in character.

(*2*) *Rags: No. 1 old whites, 50 percent; twos and blues, 50 percent.*— In the runs with old rags the calcium carbonate slip was added to the stock in the machine chest and the resultant mixture was agitated for 1 hour before being pumped to the paper machine.

Precipitated calcium carbonate, 15 and 30 percent, respectively, was used in runs 1215 and 1216.

The three paper-machine runs (1217 to 1219) with water-ground natural calcium carbonate comprised 15 percent of samples *C*, *B*, and *A*, respectively. As previously stated, the only difference in the three samples was the fineness to which they had been ground, *A* being the coarsest and *C* the finest. In run 1219, as in the sulfite-soda runs with sample *A*, some of the carbonate settled out from the stock in the riffler, or sand trap, but samples *B* and *C* (runs 1218 and 1217) seemed to remain in suspension.

There was no foaming of the stock on the paper machine in any of the runs. The finish of the papers containing the carbonates was satisfactory. All the carbonate-filled papers were comparatively stable.

2. PRINTING TESTS

In the early part of the study, printing tests were made at the Government Printing Office on the experimental papers that had

been manufactured up to that time. The papers printed were representative samples of sulfite-soda runs containing clay (unsized and sized sheets), titanium dioxide pigment *A*, zinc sulfide pigment *A*, and calcium carbonate (precipitated and natural); and of purified-wood-fiber and new-rag papers containing clay.

The papers were printed from type on one side and by the offset process on the other. The fillers seemed well anchored to the fiber and did not dust out during printing. The papers caused no trouble in the operations and the printings were considered very satisfactory.

Now that the experimental paper-mill work on the book papers has been completed, extensive printing tests to evaluate the printing quality of papers representative of all the different pulp and filler furnishes is in progress and the results obtained will probably appear in a later publication. Final opinion as to the relative values of the different fillers and of the other different papermaking details should await the results of the printings.

VIII. DISCUSSION AND CONCLUSIONS

It is well known that fillers used in large amounts very appreciably reduce the strength of paper. The strength of the experimental papers decreased with increasing filler content, but was influenced by the amount, not the type, of filler present. Because of their effective opacifying quality, smaller amounts of titanium dioxide and zinc sulfide pigments than of clay were sufficient to obtain requisite opacity for printing processes, and the resulting papers were less reduced in strength. All the papers had sufficient strength to withstand the mechanical stresses to which book papers are ordinarily subjected.

There was no pronounced difference in the relative effect of the nonalkaline fillers on sizing. The degree of sizing was very much greater for the sulfite-soda papers than for the rag papers, and the purified wood-fiber papers were in an intermediate position. The nonalkaline fillers had less effect than calcium carbonate in reducing sizing. Although the sizing values of the carbonate papers were not high the papers were sized sufficiently to be written on with ink and for ordinary printing processes. There was no direct correlation between the resistance of the papers to water penetration and their ink-receptiveness.

When rosin size and alum had been added to the stock in the beater and followed by calcium carbonate in the machine chest, the stock foamed somewhat on the paper machine, although the amount of foam was not great and doubtless could have been kept down satisfactorily with a fine water spray.

Maxium clay retention was obtained in the purified wood and rag papers when the pH at the head box was approximately 5, and decreased as the amount of alum was increased. For the sulfite-soda pulp, retention of all the nonalkaline fillers increased as alum was increased. Retention of the calcium carbonate was satisfactory.

The papers containing titanium dioxide, zinc sulfide, or precipitated calcium carbonate pigments had the highest opacity values in the experimental work, and, by personal judgment, gave the best printing results. Only a few of the papers were submitted to the printing tests however. Further tests of the printability of representative samples

of all the papers are in progress, and rating of their printing qualities will probably be reported in a subsequent publication.

Aside from natural aging the best information on the inherent permanence of paper is based on changes in physical and chemical characteristics during accelerated aging tests. The Bureau believes that oven aging rapidly accelerates the slow deterioration caused by impurities in the paper, and that changes in alpha-cellulose content and copper number and the percentage of the original strength retained indicate the comparative resistance to degradation. The change in the cellulose in the accelerated aging seemed to have been from alpha- to beta-cellulose, with no appreciable difference in the percentage of gamma-cellulose. The rag and purified wood-pulp papers were more stable to the heat test than the sulfite-soda wood-pulp papers. Nonalkaline fillers had no apparent influence on the stability of any of the papers, and the calcium carbonate pigments had a protective or inhibiting effect in the accelerated aging.

Acidity was an important factor in deterioration. Attack on the cellulose was increased as the amount of alum was increased, in either the unsized or the rosin-sized papers. The rag fibers seemed to withstand acidity better than any of the other fibers used. Contrary to the reaction with the pulps of higher initial purity, sulfite-soda papers were more stable to the heat test when containing rosin sizing than when made with corresponding acidity but without size.

The effect on the stability of increasing the amount of alum in the beater and then neutralizing part of the alum with sodium carbonate as the stock was being pumped from the beater chest to the machine chest was practically the same as having had the final pH value originally in the beater and maintained throughout the preparation of the stock.

The necessity for employing only minimum amounts of rosin and alum in the sizing of papers intended to be used for permanent records is generally recognized. The optimum pH value for combining high stability with adequate sizing of papers containing nonalkaline fillers, however, varies in different mills because of hardness of water, white-water recovery, kinds of materials used, etc., but at the Bureau is approximately 5 at the head box of the paper machine. The pH (hot-water extraction) of the finished papers is in approximate agreement with that of the stock at the head box.

Resistance of paper to deterioration from internal causes is not sufficient to insure its stability, however. The conditions under which the paper is stored and used must also be considered. For a discussion of external deteriorative agencies—light, temperature, humidity, acidic pollution of air—and recommendations as to storage conditions for prolonging the life of paper, the reader is referred to a previous Bureau publication [9].

The authors acknowledge their indebtedness to R. W. Carr of this Bureau for the physical testing of the experimental papers, and to H. F. Launer, C. I. Pope, and W. K. Wilson, also members of the Bureau staff, for the chemical testing of the pulps and papers.

IX. REFERENCES

[1] R. H. Rasch, M. B. Shaw, and G. W. Bicking, *Highly purified wood fibers as papermaking material*, BS J. Research **7**, 765 (1931) RP372.

[2] R. H. Rasch, M. B. Shaw, and G. W. Bicking, *A study of some factors influencing the strength and stability of experimental papers made from two different sulphite pulps*, BS J. Research **11**, 7 (1933) RP574.

[3] M. B. Shaw, G. W. Bicking, and M. J. O'Leary, *A study of the relation of some properties of cotton rags to the strength and stability of experimental papers made from them*, J. Research NBS **14**, 649 (1935) RP794.

[4] M. B. Shaw and M. J. O'Leary, *Study of the effect of fiber components on the stability of book papers*, J. Research NBS **17**, 859 (1936) RP949.

[5] M. B. Shaw and G. W. Bicking, *Caroá fiber as a papermaking material*, Tech. Pap. BS **21**, 338 (1927) T340; *Further experimental production of currency paper in the Bureau of Standards paper mill*, BS J. Research **3**, 904 (1929) RP121; *Equipment and research work of the Bureau of Standards paper mill*, Paper Trade J. **89**, 19, 60 (1929).

[6] H. F. Launer, *Volumetric determination of alpha-, beta-, and gamma-cellulose in pulps and in papers containing sizing, filler, and other materials*, J. Research NBS **20**, 87 (1938) RP1068.

[7] R. H. Rasch, *Accelerated-aging test for paper*, BS J. Research **7**, 465 (1931) RP352; *Estimating stability of paper by heating*, Paper Trade J. **95**, 4, 28 (1932); R. H. Rasch and B. W. Scribner, *Comparison of natural aging of paper with accelerated aging by heating*, BS J. Research **11**, 727 (1933) RP620.

[8] M. B. Shaw and G. W. Bicking, *Comparison of American and foreign clays as paper fillers*, Tech. Pap. **18**, 337 (1924) T262; *A comparative study of paper fillers*, Tech. Pap. **19**, 733 (1925) T301.

[9] A. E. Kimberly and B. W. Scribner, *Summary report of the Bureau of Standards research on preservation of records*, Misc. Pub. BS M154 (1937).

WASHINGTON, August 10, 1938.

USCOMM-NBS DC

NBS-114A (REV. 7-73)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 74-632	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

Comparison of Accelerated Aging of Book Papers in 1937 With 36 Years Natural Aging

5. Publication Date December 18, 1974

6. Performing Organization Code

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

8. Performing Organ. Report No. NBSIR 74-632

9. PERFORMING ORGANIZATION NAME AND ADDRESS

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

10. Project/Task/Work Unit No. 3000442

11. Contract/Grant No.

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

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

13. Type of Report & Period Covered Interim

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

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

A group of 36 book papers made in the NBS paper mill in 1937 were tested in 1937 before and after accelerated aging for 72 hours at 100°C, and in 1973 after 36 years of natural aging. The data show that fairly good correlations exist between accelerated aging and natural aging when changes in alpha cellulose, copper number and, to a lesser extent, tearing strength, were used as criteria of change. pH is a reasonably good criterion of stability. It appears that zero span tensile strength, wet strength as a percentage of dry strength, and brightness are useful criteria for evaluating the aging of paper. When data in this report are compared with data from earlier reports, it appears that dry accelerated aging at 100°C more nearly corresponds to natural aging than accelerated aging at 90°C and 50 percent relative humidity.

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

Accelerated aging; aging; natural aging; paper, permanent; paper, stability; permanent papers; record papers; stability of paper.

18. AVAILABILITY

[X] Unlimited

[ ] For Official Distribution. Do Not Release to NTIS

[ ] Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Cat. No. C13

[XX] Order From National Technical Information Service (NTIS) Springfield, Virginia 22151

19. SECURITY CLASS (THIS REPORT)	21. NO. OF PAGES
UNCLASSIFIED	
20. SECURITY CLASS (THIS PAGE)	**22. Price**
UNCLASSIFIED	