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Paper Evaluation Section
Product Evaluation Technology Division
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Technical Report

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# 1. INTRODUCTION AND SUMMARY

A reliable accelerated aging method would be desirable for determining paper permanence, since natural aging requires long periods of time to generate meaningful trends in the decrease of paper strength. However, it is questionable which is better suited to simulate natural aging--a dry or a humid accelerated aging environment. It has been shown that the presence of a high percentage of moisture promotes oxidative degradation of paper at 90°C [1]. It is known, furthermore, that paper retains a significant amount of moisture at ordinary temperatures and relative humidities. It is not known whether the same chemical reactions which occur in paper at an elevated temperature also occur at an ambient temperature.

The surest way to resolve this and related questions would be to age a supply of papers covering a wide range of stabilities in a humid and in a dry accelerated aging atmosphere, then store other representative samples for natural aging, to be tested periodically over a number of years. Correlations of the results of selected physical tests before and after all types of aging might indicate which accelerated aging environment is more suitable for forecasting paper permanence in natural aging environments.

Unfortunately, the few systematic comparisons which are currently available are based only on short-term dry accelerated aging versus natural aging for periods of time up to about 30 years, and are usually limited to fold, burst, and tensile tests. There are no data with which to compare humid accelerated aging and natural aging.

The present report describes the results of tests performed on 13 samples of drawing and tracing papers for which data on dry accelerated aging were obtained in 1940. The papers include commercial rag and sulphite papers. It has been shown previously that decreases in MIT folding endurance, observed after the dry accelerated aging of a number of rag and sulphite papers, were highly correlated with natural aging processes for periods of 4, 8, and 26 years [2]. Data included in the present report complement the older study, since changes in tearing resistance observed after accelerated aging are similarly correlated with changes observed after natural aging.

This report also discusses results of differential thermal analysis (DTA) on aged papers. DTA has been shown to be very sensitive to the presence of trace amounts of metals in paper [3] and to functional groups such as aldehydes and carboxylic acids in modified cellulose [4]. Thus, it was of considerable interest to note that the present work shows a high correlation between a DTA parameter, $T_2$ (the temperature at which massive decomposition of cellulose begins), and the changes in tearing resistance observed after natural aging. Since the samples were not analyzed by DTA in 1940, soon after they were manufactured, it was impossible to know whether their thermal stability had changed. The absence of a correlation between $T_2$ and the magnitude of tearing resistance also implies the absence of correlations between $T_2$ and those structural factors that determine tearing resistance. The only evident correlation involves $T_2$ and the magnitude of change in tearing resistance and, therefore, relates DTA to permanence.

The pH of the aged papers is included in this report, as the pH of paper is thought to influence permanence. The data do not support this correlation. However, since pH may change as a paper is aged, the data cannot be interpreted with complete confidence.

# 2. RESULTS AND DISCUSSION

## 2.1 Results

### Initial Properties

The sample numbers, fiber content, and the initial bursting strength, folding endurance and internal tearing resistance of all of the papers, as determined in 1940, are given in Table 1. Tables 2, 3, and 4 summarize the changes in physical properties due to accelerated and natural aging.

### Correlation of Accelerated and Natural Aging

Bursting strength. Both increases and decreases in bursting strength are observed after 20 and 32 years of natural aging, and are plotted in Figures 1 and 2, against the decreases observed after 72 hours of accelerated aging. No correlation is evident.

Schopper folding endurance. Decreases in Schopper folding endurance observed after 20 and 32 years of natural aging are plotted in Figures 3 and 4 against the decreases observed after 72 hours of accelerated aging. Again, no correlation between natural and accelerated aging is evident. However, the original tests were interrupted at 2500 double folds. Only a limited number of samples, which had an initial folding endurance below 2500 double folds in at least one direction, can be used in calculating changes in folding endurance, and the useful data are limited to the weaker paper direction. For these reasons, little meaning can be attached to the changes in folding endurance.

Internal tearing resistance. The data listed in Table 4 indicate a high correlation between the changes in tearing resistances observed after 20 years of natural aging and changes observed after 72 hours of accelerated aging. One of the samples (No. 178) is extremely resistant to accelerated aging but does not prove to be especially stable under natural aging conditions, and a second (No. 58) is exceptionally unstable under accelerated aging conditions but not under natural aging conditions. Omitting these two extremes, the linear correlation of the data plotted in Figure 5 has a magnitude of about 0.89, which implies an explained variation of about 80 percent. The linear correlation of 0.67 for the

data plotted in Figure 6, involving measurements taken after 32 years of natural aging, is considerably lower probably because of the use of different instruments in making the measurements. It is also possible that the rates of decrease in tearing resistance are significantly changed after a given aging period, and that the 32 year data do not correlate as well as the 20 year data for reasons involving inductive processes that became important after 20 years. This point can be surmised but not verified at present. Very few data are available on natural aging periods beyond 25 years.

Differential thermal analysis (DTA). The DTA thermograms of various types of paper are usually characterized by a decomposition endotherm beginning and ending within the temperature range of about 220 to 400°C. A typical thermogram is shown in Figure 7. The first endotherm (range about 90° to 200°C) is due to desorption of moisture and gases and is not important. In the decomposition endotherm, there are at least three transitions: the beginning of the endotherm ($T_2$); the approximate end of exothermic reactions ($T_3$, located at the intersection of the straight portions of the slopes just above the lowest point in the endotherm); and the highest point on the curve just after $T_3$, which is usually the peak of a mild exothermic reaction ($T_4$).

Figures 8-10 show the relation of $T_2$ to the magnitude of changes in internal tearing resistance. One sample (No. 22) for unknown reasons shows an extremely high resistance both to natural and accelerated aging, but not an exceptionally high $T_2$. This point is taken to be nontypical and is omitted from the calculated slopes. Considering the data obtained for the other 12 samples after 20 years of natural aging, the correlation with $T_2$ is remarkable.

Tearing resistance depends partly on the weight of paper per unit area [5]. For example, the plot of tearing resistance in grams against basis weight, in grams, shown in Figure 11, roughly indicates a one-to-one correspondence. $T_2$ is independent of weight but might conceivably be affected by structural variables that also affect strength. In order to compare $T_2$ directly with tearing resistance, all of the tearing resistance data were placed on a common weight basis. The calculated tearing resistances are plotted in Figures 12 and 13 against $T_2$. The result is a nearly random scatter of points showing that $T_2$ is not correlated directly with the magnitude of the tearing resistances of these papers either before or after aging. The only evident correlation involves $T_2$ and the percent of decrease in tearing resistance or, in other words, the permanence of the papers.

It would be very desirable to know whether or not $T_2$ has changed since 1940. If $T_2$ were essentially constant over the years, Figure 8 indicates that the thermograms could have been used empirically, in 1940, to predict the relative aging stability of these samples. If $T_2$ has changed concurrently with tearing resistances, however, the thermograms and the attendant correlation indicate properties as they are now and are not necessarily closely related to properties as they were 32 years ago.

The correlations between $T_2$ and the tearing resistance changes after 32 years of aging and after accelerated aging both are relatively low. For the 32-year samples, the reason may be that the calculations are based on data obtained with two different instruments. For the accelerated aging data, however, all of the data were obtained with the same tearing tester, and one could expect a higher correlation with $T_2$. The situation is seriously impaired by the low correlation between $T_2$ and accelerated aging data because an accelerated aging method might have provided an empirical means to check out correlations of DTA and changes in tearing resistance with a number of papers tested before and after aging. Figure 10 shows that this approach might not work very well.

Figure 14 shows no correlation between $T_3$ and changes in tearing resistance, in marked contrast to $T_2$. The resistance to pyrolysis of the 32-year old papers is more closely related to $T_3$ than $T_2$ since extensive pyrolysis precedes $T_3$ and little or none precedes $T_2$. A logical inference is that permanence and resistance to pyrolytic decomposition are not closely related.

pH. Paper pH is often considered to be a criterion of paper stability, and acid paper is generally less stable than neutral or alkaline paper. However, the original pH values of these papers are unknown. The pH values listed in Table 7 were determined on the present set of papers after 32 years of aging. Paper pH can change substantially during accelerated aging, and probably also during natural aging, so that the values listed in Table 7 may reflect the original pH only approximately. Positive rank correlations between the pH values, tearing resistances, and Schopper folding endurances are still evident after 32 years of aging, but they are too weak to indicate whether the original acidity or the amount of acid generated in the present case has anything to do with stability.

## 2.2 Discussion

The question of what type of accelerated aging environment is best suited to simulate natural aging is a very important one that has not been successfully resolved. It may be addressed in a number of different ways.

One of the ways is to characterize the types of change that actually occur in the different aging environments and then examine old papers for evidence of similar types of change. For example, it has been shown in recent studies [1, 6, 7] that the accelerated aging process in a dry air environment leads to increases in the wet tensile strength of laboratory handsheets which are concurrent with slight loss of dry tensile strength, and that MIT folding endurance and internal tearing resistance decreases as wet strength increases. In humid air, at the same temperature, the principal change is a rapid decrease in dry tensile strength, with consequent very rapid decreases in folding endurance, tearing resistance, and bursting strength. One seldom knows the initial wet strength or tensile strength of an old paper, but if old paper should prove to have a much higher wet strength than papers of their composition usually have initially, but a normal tensile strength for papers of their type, it might be inferred that their natural aging process was similar in type to dry accelerated aging. But, if the dry tensile strength were quite low, it might be inferred that humid accelerated aging processes more closely resembled natural aging than dry accelerated aging processes.

A second approach is to determine if the nature of changes and the rates of change in a number of physical properties observed in a given type of paper during accelerated aging can be correlated with changes occurring over a much longer period of natural aging. This might involve tests after several accelerated aging periods and over several decades of time.

The third approach is used in the present study. That is, to subject a number of papers, having widely different stabilities, to natural and to accelerated aging and then try to develop correlations between the amount of change detected after one or two periods of accelerated aging and after natural aging.

All three approaches have advantages and disadvantages, and a combination of the three would certainly be preferable to any single approach. A rational choice of testing methods also is important for a fine perspective on the aging process. Decreases in folding endurance and tearing resistance, for example, can provide only crude information. These changes may be observed after either dry or humid accelerated aging, as a consequence of very different types of reactions. Dry aging results in crosslinks that can cause fold and tear both to drop because of the embrittlement of paper. Humid aging results in fiber degradation that also causes fold and tear to decrease. While the rates of decrease are quite different, it would not be surprising if either aging method could be correlated with natural aging. It is more significant that tensile strength declines very slowly in dry aging and very rapidly in humid aging. Therefore, if folding endurance should drop rapidly while tensile strength changes much more slowly, or not at all, during natural aging, a similarity to dry aging would be indicated. But if both fold and tensile strength should decline fairly rapidly, a parallel with humid aging would be indicated. This is not to imply that fold, tear, and tensile tests are recommended by the present authors, but that several different tests may provide a much finer perspective on aging than a few conventional tests can possibly provide.

The stumbling block in deciding which type of accelerated aging method to employ is the very reason that an accelerated aging method is needed: it takes so long to determine the stability of paper by natural methods. One must put some of the paper through an accelerated aging process, test it, and store other samples against future testing after natural aging processes. While it is true that experiments of this type were initiated long ago--in the thirties and forties--all of them have involved dry oven aging. No data are presently available that would permit a correlation of the effects of humid accelerated aging and natural aging.

In their study of the aging of a number of rag and sulphite papers, Wilson, et al [2] reported changes in the tensile strength and the MIT folding endurance determined before and after accelerated aging at 100°C in dry circulating air for periods of 24, 48, and 72 hours, and after 4, 8, and 26 years of natural aging. Significantly, they found little change in tensile strength, but a whole spectrum of changes in folding endurance, suggesting a similarity to dry accelerated aging. The samples which were least stable in the

accelerated aging environment also were least resistant to natural aging, and for both rag and sulphite papers, there was approximately the same equivalence between accelerated and natural aging times--i.e., 48 hours of accelerated aging produced about the same amount of decrease in folding endurance as 12.5 years of natural aging.

Some of Wilson's data are replotted in Figures 15 and 16, in order to show the fit of points determined by all of the papers to a common slope*. Fold is more sensitive to aging than is tear. Nevertheless, there is a remarkably similar correlation between the effects of natural and accelerated aging for both folding endurance and tearing resistance. Together with the lack of change in tensile strength, the coefficients of linear correlation strongly indicate that dry accelerated aging and natural aging are comparable.

Wilson's data include a comparison of rates; a test which may differentiate between dry and humid aging processes (the dry tensile test); and a selection of samples having a wide variety of stabilities. His tests permit all three of the types of comparison listed at the beginning of this discussion. Unfortunately, his data are limited only to two physical tests--fold and tensile. It could be especially interesting to know what changes in wet strength may have occurred.

The present experiments are also limited in range but complement Wilson's data in that the correlations are equally high. The same conclusions can be drawn from them, even though they involve a different physical property.

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*It should be noted that the high intercept apparent in Figure 15 means little. It is due to the fact that the least stable of the samples had suffered a loss of more than 90 percent of their folding endurance after 8 years, at the same time that the more stable samples had lost less than 20 percent. The more stable samples continued to lose folding endurance during the next 18 years of aging, whereas the least stable ones are unable to sustain much more loss after 8 years. So the slope determined by changes in the folding endurance of all of the papers decreases with time, and the intercept increases. This is immediately evident in comparing Figure 16 for the 8 year term and Figure 15 for the 26 year term.

## 3. DTA

The time required to obtain a DTA thermogram is less than 1 hour. Because of the rapidity of the method, any reproducible type of correlation between permanence and DTA would be very useful, however empitical it might be. The principal difficulties lie in the interpretation of thermograms. DTA is sensitive in different ways to many components of paper. For example, aluminum metal can promote endothermic reactions. Mineral acids also do this. $T_2$ may be affected by functional groups located in cellulose chains and by hemicelluloses in paper in qualitatively similar ways.

Most of the DTA performed in this laboratory has tended to show a correlation between $T_3$ and aging stability. The correlation between changes in internal tearing resistance and $T_2$, especially as indicated in Figure 8, was not anticipated. It is significant that $T_2$ is not related to the magnitude of the tearing strength of paper, but instead to the rate of change during natural aging. It also is interesting that Wilson's samples, which are quite similar to the ones tested by DTA, show little change in tensile strength. Where tensile strength is constant, fiber strength is nearly so, and the observed $T_2$-tear correlation evidently is not related to changes in fiber strength. This is helpful negative information, even though no explanation of the correlation is directly suggested by the present data.

## 4. pH

The pH data are of little value in the absence of knowledge of the original pH data for comparison. It would, for example, be possible for acid to be generated during the aging process. This is particularly characteristic of humid, accelerated aging, though not dry accelerated aging [1].

# 5. APPENDIX

## 5.1 Samples and Aging Conditions

The sample numbers, fiber content, and the physical properties that were determined in 1940 are listed in Table 1. The samples were subjected to accelerated aging at 100°C for 72 hours in circulating air. They were conditioned prior to tests according to recommendations given in TAPPI Method T 402 [8].

For natural aging, the samples were stored in the dark at ordinary temperatures and relative humidities for 20 and 32 years, respectively.

## 5.2 Methods of Test

Schopper folding endurance. Schopper folding endurance was determined in machine and cross directions according to TAPPI Method T 423 [8]. Originally, folding endurance measurements were interrupted at 2500 double folds. Most of the samples exceeded 2500 double folds in the stronger direction, but in the weaker direction, 10 out of 13 had folding endurances below 2500. Only those measurements, in the weaker direction, which were below 2500 are used in the calculations of subsequent changes in folding endurance.

Internal tearing resistance. Internal tearing resistance was determined according to TAPPI Method T 414 [6].

Bursting strength. Bursting strength was determined according to TAPPI Method T 413 [8].

pH, hot extraction. The hot extraction pH was determined according to TAPPI Method T 435 [8].

pH, cold extraction. The cold extraction pH was determined according to TAPPI Method T 509 [8].

Differential thermal analysis. A commercial differential thermal analyzer was used which has a temperature range of -100° to +500°C with a precision of 0.2°C and a sensitivity of 0.0025°C, according to manufacturer's data. Glass beads served as the reference material. The specimens and reference material were heated in a dry nitrogen atmosphere at a flow rate of 1.0 liter per minute and a heating rate of 20°C per minute.

Calculation of percent change in physical properties. The calculations of percent change in tearing resistance are based on measurements taken in both directions. Those Schopper folding endurances which were interrupted at 2500 double folds, however, are considered to be undefined, and the changes are calculated only for measurements in the weaker direction, which are usually less than 2500 double folds. The original data do not indicate whether measurements taken in the weaker direction were in the cross or the machine direction; but for the naturally aged papers, it was found to be the cross direction. It is assumed that, originally, the weak direction always refers to the cross direction.

Constancy of testing conditions. The same industrial laboratory and the same instruments were employed for Schopper folding endurance, internal tearing resistance, and bursting strength determinations throughout the first 20 years of this study, but the tests after 32 years of aging were performed with different instruments in a laboratory at the National Bureau of Standards.

## 6. CONCLUSIONS

1. Correlations of the accelerated dry aging of rag and sulphite paper and their natural aging are discussed.

2. Changes in the internal tearing resistance indicate a wide range of stabilities in both accelerated and natural aging.

3. Changes in internal tearing resistance indicate a high correlation between dry accelerated aging and natural aging.

4. Changes in Schopper folding endurance indicate no correlation between dry accelerated aging and natural aging, but these are of little value because many tests were interrupted before completion.

5. Changes in bursting strength are low, both in dry accelerated aging and natural aging.

6. Data on changes in the MIT folding endurance of the same types of paper used in this study are cited in the literature showing that a high correlation exists between dry accelerated aging and natural aging [2].

7. Differential thermal analysis indicates a surprisingly high correlation between $T_2$ and the magnitude of changes in tearing resistance due to natural aging.

8. Positive rank correlations between the pH of aged papers and rates of decrease in folding endurance and internal tearing resistance exist but are too weak to be meaningful.

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Table 1. Description of samples and summary of initial bursting strength, folding endurance, and internal tearing resistance.

| Sample No. | Type | Bursting Strength (points) | Schopper Folding Endurance* (double folds) | | Internal Tearing Resistance (g) | |
|---|---|---|---|---|---|---|
| | | | (a)** | (b)** | (a)** | (b)** |
| | **Drawing Paper** | | | | | |
| 22 | 100% rag, white, imported | 75 | 10 | 14 | 163 | 162 |
| 25H | 100% rag, white, domestic | 86 | 2500 | 2500 | 387 | 382 |
| 53 | 100% rag, cream, domestic | 78 | 2500 | 2500 | 208 | 202 |
| D28 | 50% rag, white, domestic | 59 | 1348 | 2500 | 180 | 164 |
| 8023 | All-sulphite, white, domestic | 61 | 1288 | 2500 | 200 | 198 |
| 58 | All-sulphite, buff, domestic | 80 | 2500 | 2500 | 192 | 180 |
| | **Tracing Paper** | | | | | |
| 181 | 100% rag, natural, domestic | 30 | 645 | 2500 | 46 | 46 |
| D172 | 100% rag, natural, domestic | 14 | 96 | 492 | 24 | 19 |
| N176L | 50% rag, natural, domestic | 14 | 49 | 296 | 27 | 33 |
| D179L | All-sulphite, natural, domestic | 17 | 261 | 2500 | 23 | 18 |
| 178L | All-sulphite, natural, imported | 34 | 1032 | 2500 | 21 | 19 |
| 195M | 100% rag, prepared, domestic | 49 | 1267 | 2500 | 67 | 64 |
| 198 | 100% rag, min. oil prepared, imported | 42 | 331 | 2500 | 52 | 46 |

* Folding endurance tests were interrupted after 2500 double folds.
** (a) and (b) refer to either machine direction or cross direction, not specified in the original data.

Table 2. Bursting strength observed after aging paper for 72 hours at 100°C and after 20 and 32 years of natural aging, and changes as a percent of the original bursting strength.

| Sample No. | Aging Conditions | | | | | |
|---|---|---|---|---|---|---|
| | 72 hours at 100°C | | 20 years, natural | | 32 years, natural | |
| | Bursting Strength (points) | Change (%) | Bursting Strength (points) | Change (%) | Bursting Strength (points) | Change (%) |
| 22 | 75 | 0 | 72 | -4 | 70 | -6.7 |
| 25 | 86 | 0 | 94 | +8.5 | 99 | +15.1 |
| 53 | 74 | -5 | 78 | 0 | 75 | +4.0 |
| D28 | 57 | -3 | 60 | +1.7 | 57 | -3.0 |
| 8023 | 56 | -8 | 60 | +1.6 | 56 | -8.0 |
| 58 | 49 | -39 | 63 | -21 | 56 | -3.0 |
| 181 | 29 | -3 | 31 | +3.0 | 31 | +3.3 |
| D172 | 13 | -7 | 14 | 0 | 13 | -7 |
| N176L | 14 | 0 | 16 | -14.3 | 17 | +21.4 |
| D179L | 17 | 0 | 17 | 0 | 20 | +17.6 |
| 178L | 32 | -6 | 26 | -23.5 | 34 | 0 |
| 195M | 49 | 0 | 45 | -8.2 | 42 | -14.3 |
| 198 | 36 | -14 | 31 | -26.2 | 40 | -4.8 |

Table 3. Schopper folding endurance observed after aging paper for 72 hours at 100°C in dry air and after 20 and 32 years of natural aging and changes as percent of the original folding endurance.

| Sample No. | Aging Conditions | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 72 hours at 100°C | | | 20 years, natural | | | 32 years, natural * | | |
| | Folding** Endurance (double folds) | | Change*** (%) | Folding Endurance (double folds) | | Change*** (%) | Folding Endurance (double folds) | | Change*** (%) |
| | a **** | b | | a | b | | a | b | |
| 22 | 7 | 9 | -30.0 | 1 | 1 | -90 | 1 | 1 | -90 |
| 25H | 1764 | 2500 | -- | 779 | 1216 | - | 981 | 1216 | - |
| 53 | 2500 | 2500 | -- | 59 | 346 | - | 513 | 545 | - |
| D28 | 338 | 439 | -73.8 | 10 | 28 | -99 | 19 | 46 | -98.6 |
| 8023 | 760 | 790 | -41.0 | 3 | 7 | -99.7 | 33 | 60 | -97.6 |
| 58 | 5 | 570 | -99.9 | 19 | 29 | -99.0 | 14 | 32 | -- |
| 181 | 429 | 2500 | -33.5 | 396 | 662 | -33.3 | 154 | 599 | -76.1 |
| ?172 | 32 | 344 | -66.7 | 26 | 64 | -72.9 | 12 | 29 | -87.5 |
| N176L | 37 | 203 | -24.5 | 23 | 49 | -53.1 | 14 | 66 | -71.4 |
| D179L | 104 | 1058 | -60.2 | 64 | 133 | -75.4 | 76 | 365 | -70.9 |
| 178I | 1227 | 2500 | +19 | 105 | 233 | -89.6 | 500 | 674 | -51.6 |
| 195M | 669 | 2500 | -47.2 | 233 | 283 | -47.2 | 221 | 256 | -82.6 |
| 198 | 171 | 1200 | -48.3 | 187 | 354 | -43.5 | 182 | 349 | -45.0 |

* Tests after 32 years performed with a different instrument from that used originally, after accelerated aging and after 20 years of natural aging.

** Tests were interrupted at 2500 double folds.

*** Each value represents change in the weaker direction.

****(a) and (b) refer to either machine direction or cross direction, not specified in the original data.

Table 4. Percent change in internal tearing resistance observed after aging paper for 72 hours at 100°C in dry air and after 20 and 32 years of natural aging.

| Sample No. | Aging Conditions | | | | | |
|---|---|---|---|---|---|---|
| | 72 hours at 100°C | | 20 years of storage | | 32 years of storage* | |
| | Tearing** Resistance (g) | Change (%) | Tearing Resistance (g) | Change (%) | Tearing Resistance (g) | Change (%) |
| 22 | 156 | - 3.7 | 148 | - 9.2 | 138 | -15.1 |
| 25H | 384 | -13.7 | 252 | -34.5 | 278 | -27.8 |
| 53 | 205 | -10.7 | 151 | -25.4 | 153 | -25.3 |
| D28 | 172 | - 9.6 | 127 | -24.2 | 116 | -32.6 |
| 8023 | 199 | -14.1 | 134 | -32.7 | 135 | -32.2 |
| 58 | 186 | -45.4 | 104 | -44.1 | 100 | -46.3 |
| 181 | 46 | - 3.3 | 39 | -15.2 | 33 | -28.3 |
| D172 | 22 | -16.3 | 14 | -37.2 | 12 | -44.2 |
| N176L | 25 | - 6.0 | 20 | -18.0 | 18 | -40.0 |
| D179L | 20 | -12.2 | 12 | -41.5 | 11 | -46.3 |
| 178L | 20 | - 2.5 | 14 | -32.5 | 13 | -35.0 |
| 195M | 65 | -13.0 | 49 | -25.2 | 46 | -29.8 |
| 198 | 59 | - 7.1 | 42 | -14.3 | 37 | -24.5 |

* Tests performed after 32 years with a different instrument than that used originally, after accelerated aging and after 20 years.
**Average of two directions.

Table 5. Half-lives calculated from decreases in internal tearing resistance observed after aging paper for 72 hours at 100°C in dry air and after 20 years and 32 years of natural aging.

| Sample No. | Aging Condition | | |
|---|---|---|---|
| | Accelerated* (half-lives, hours) | 20 years (half-lives, years) | 32 years** (half-lives, years) |
| 22 | 975 | 116 | 104 |
| 25H | 260 | 29 | 58 |
| 53 | 334 | 39 | 63 |
| D28 | 364 | 38 | 48 |
| 8023 | 256 | 31 | 50 |
| 58 | 96 | 23 | 34 |
| 181 | 900 | 66 | 57 |
| D172 | 251 | 30 | 35 |
| N176L | 450 | 56 | 54 |
| D179L | 240 | 25 | 35 |
| D178L | 1440 | 31 | 45 |
| 195M | 265 | 39 | 53 |
| 198 | 445 | 70 | 66 |

* 72 hours at 100°C in a laboratory oven with circulating air.
**Data obtained after 32 years performed with a different testing instrument from that used for earlier tests.

Table 6. Differential thermal analysis (DTA) of 13 samples of commercial paper after natural aging for 32 years.

| Sample No. | DTA Parameters | | |
|---|---|---|---|
| | $T_2$* (°C) | $T_3$** (°C) | $T_4$*** (°C) |
| 22 | 260 | 338 | 372 |
| 25H | 245 | 332 | 377 |
| 53 | 255 | 339 | 380 |
| D28 | 255 | 327 | 372 |
| 8023 | 240 | 308 | 333 |
| 58 | 223 | 341 | 360 |
| 181 | 287 | 363 | 385 |
| D172 | 255 | 347 | 380 |
| N176L | 262 | 321 | 368 |
| D179L | 235 | 372 | 392 |
| 178L | 240 | 308 | 333 |
| 195M | 267 | 372 | 392 |
| 198 | 295 | 369 | 391 |

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* $T_2$ is the approximate temperature of the onset of the principal decomposition endotherm.

** $T_3$ is the intersection of extrapolated slopes preceding and following the nadir of the decomposition endotherm.

***$T_4$ is the temperature of the exothermic peak immediately following $T_3$.

Table 7. pH values (cold and hot extraction) for 13 samples of commercial paper tested after natural aging for 32 years.

| Sample No. | pH (cold extraction) | pH (hot extraction) |
|---|---|---|
| 22 | 4.90 | 4.42 |
| 25H | 4.50 | 4.20 |
| 53 | 4.64 | 4.36 |
| D28 | 4.41 | 4.18 |
| 8023 | 4.75 | 4.34 |
| 58 | 4.70 | 4.14 |
| 181 | 4.80 | 4.53 |
| D172 | 4.40 | 4.14 |
| N176L | 4.68 | 4.22 |
| D179L | 4.80 | 4.47 |
| 178L | 5.04 | 4.38 |
| 195M | 4.09 | 3.98 |
| 198 | 5.40 | 5.01 |

Table 8. Rank correlations of pH (hot extraction, 32 years) with physical and thermal properties of the aged papers.

| Parameter Ranked Against pH | Aging Condition | | |
|---|---|---|---|
| | Accelerated | 20 Years Natural | 32 Years Natural |
| | Rank Correlation | | |
| tear | .45 | .51 | .43 |
| fold | .21 | .29 | .54 |
| burst | -.03 | .09 | .24 |
| $T_2$ | -- | -- | .25 |
| $T_3$ | -- | -- | .41 |
| $T_4$ | -- | -- | .17 |

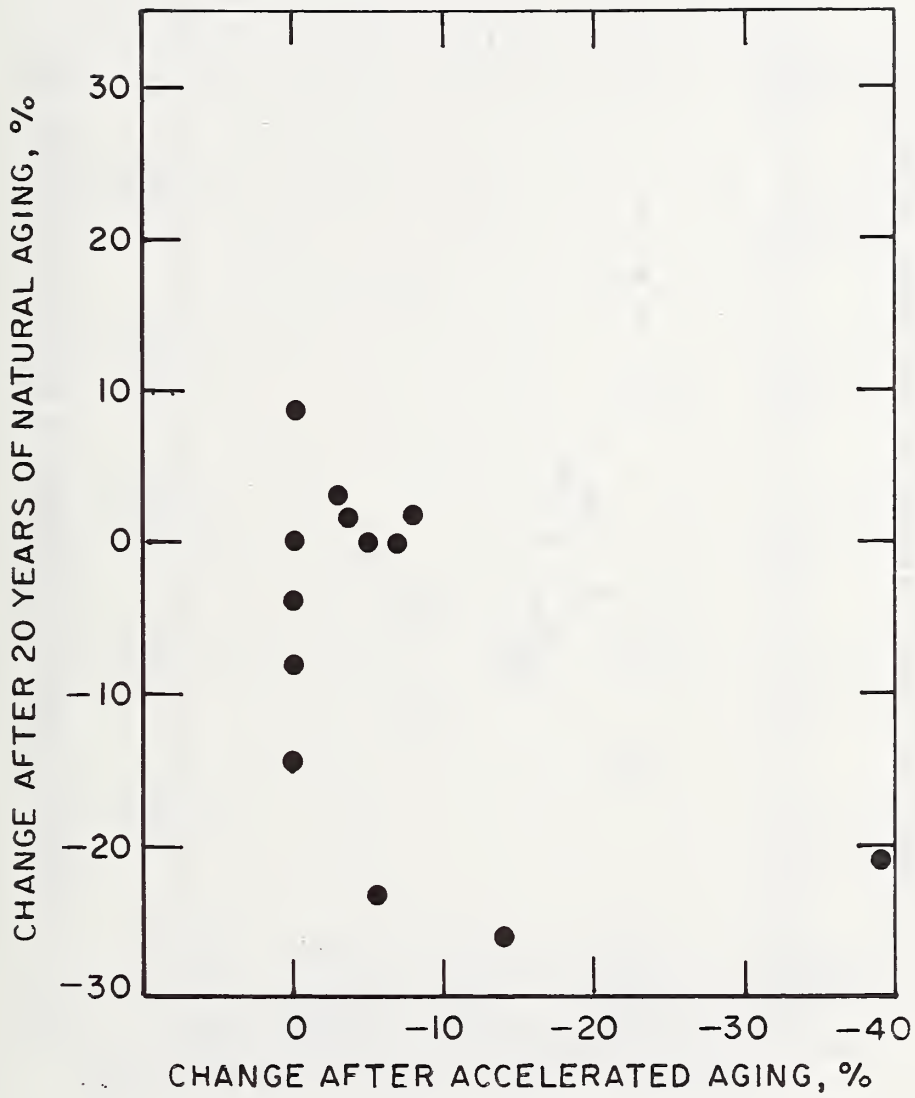



Figure 1. Relation of changes in bursting strength observed after accelerated aging to the changes observed after 20 years of natural aging.

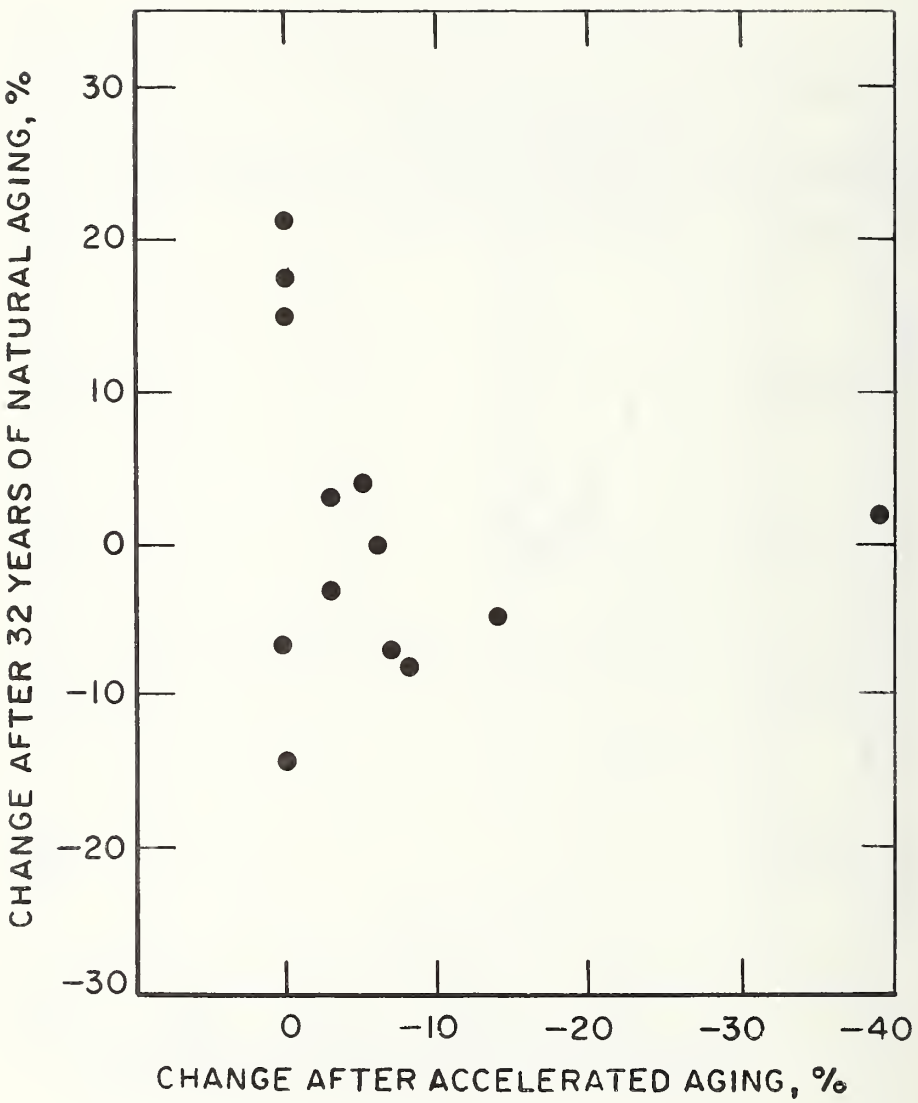



Figure 2. Relation of changes in bursting strength observed after accelerated aging to the changes observed after 32 years of natural aging.

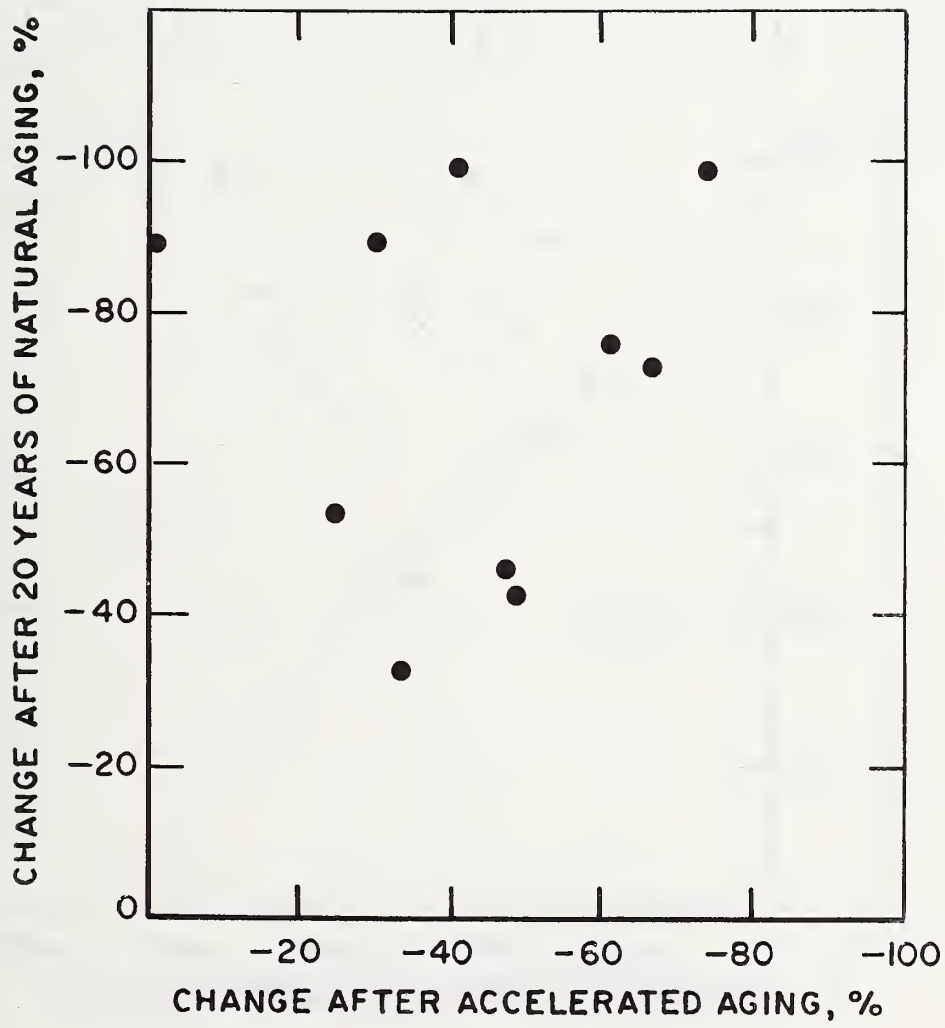



Figure 3. Relation of percent decrease in Schopper folding endurance after 20 years of natural aging to percent decrease after accelerated aging.

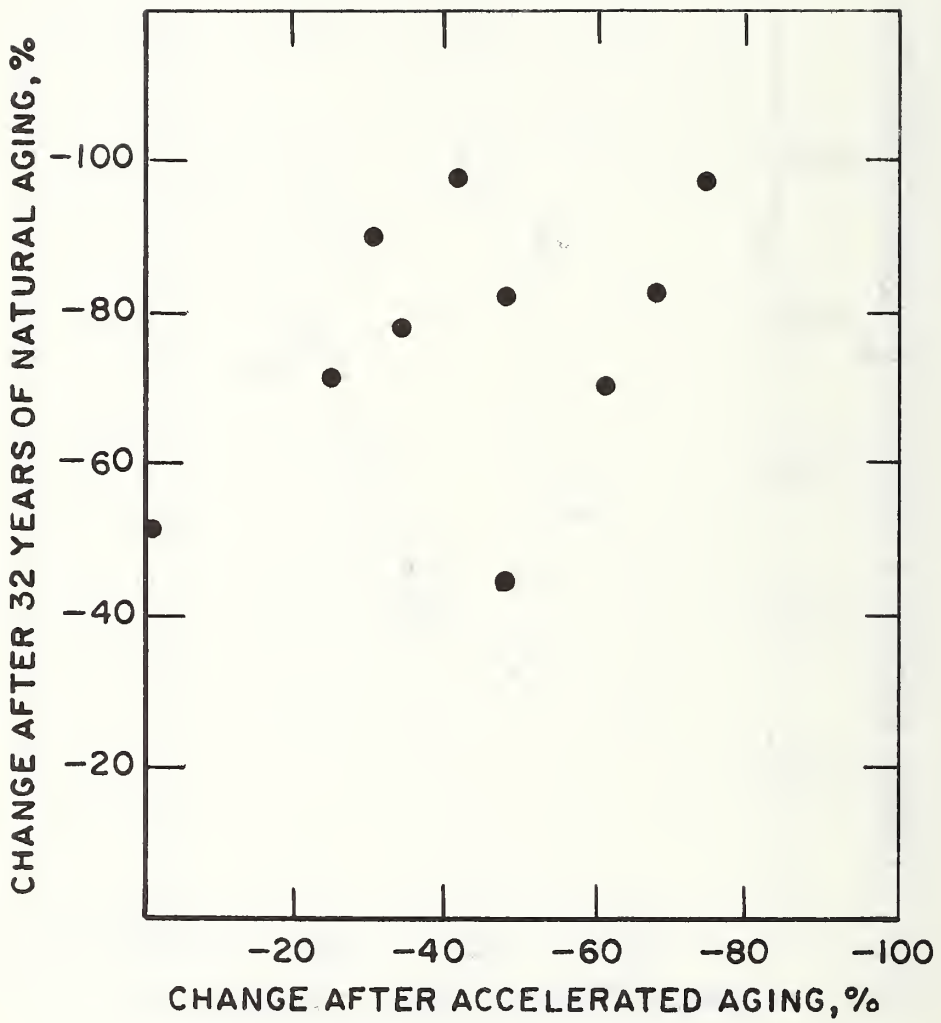



Figure 4. Relation of percent decrease in Schopper folding endurance after 32 years of natural aging to percent decrease after accelerated aging.

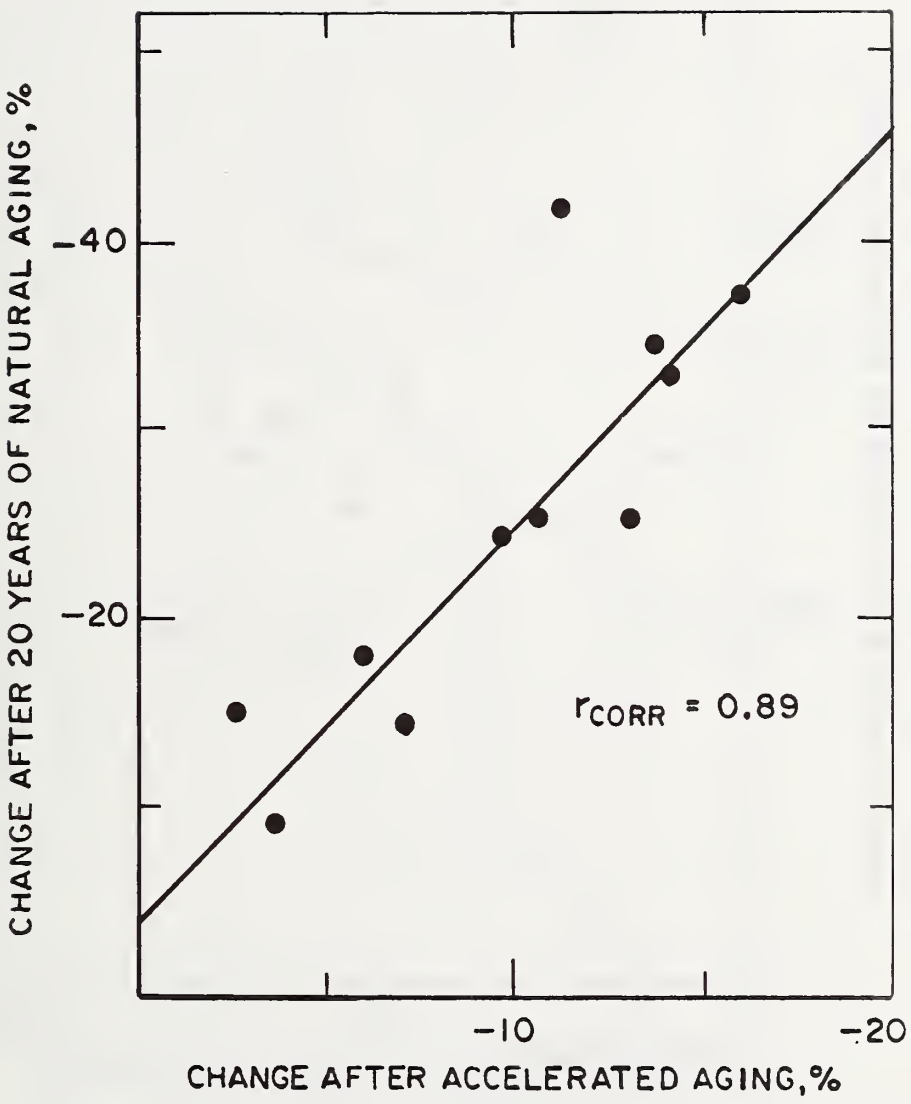



Figure 5. Relation of decreases in internal tearing resistance observed after accelerated aging to the decreases observed after 20 years of natural aging.

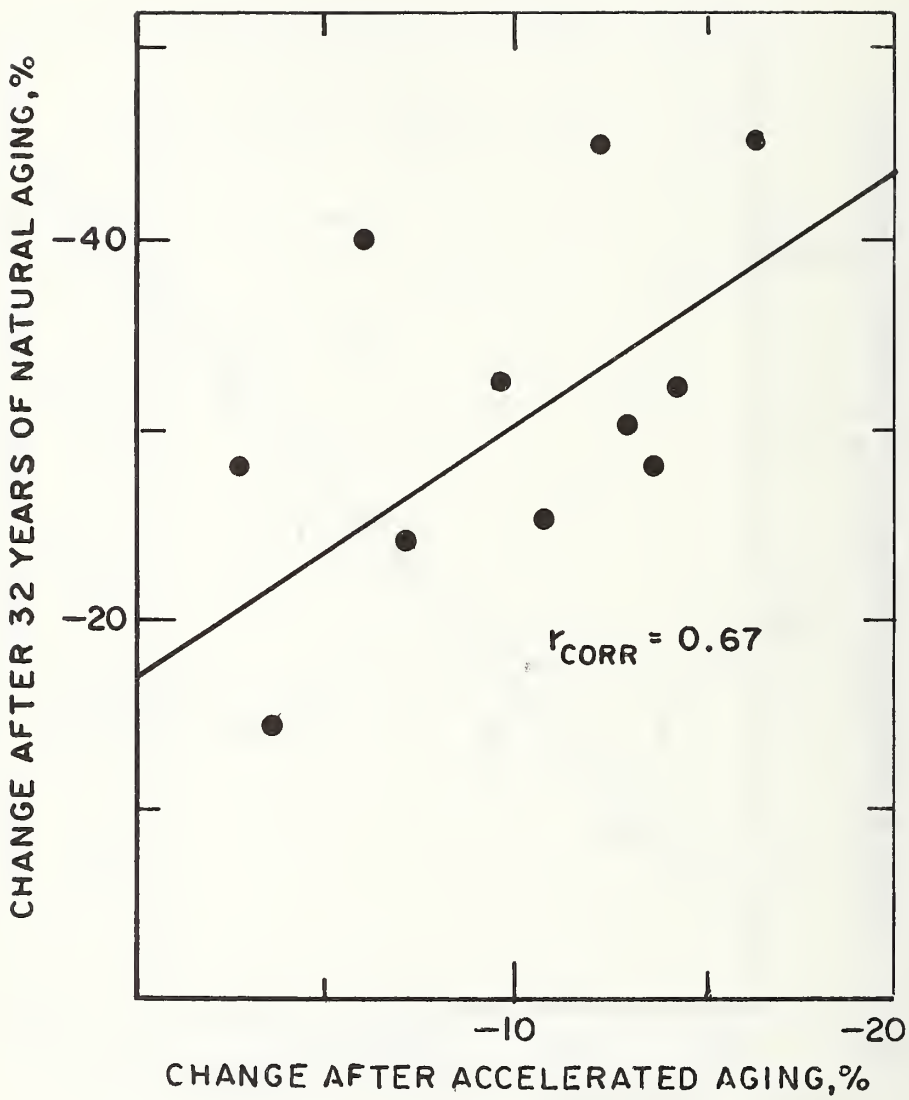
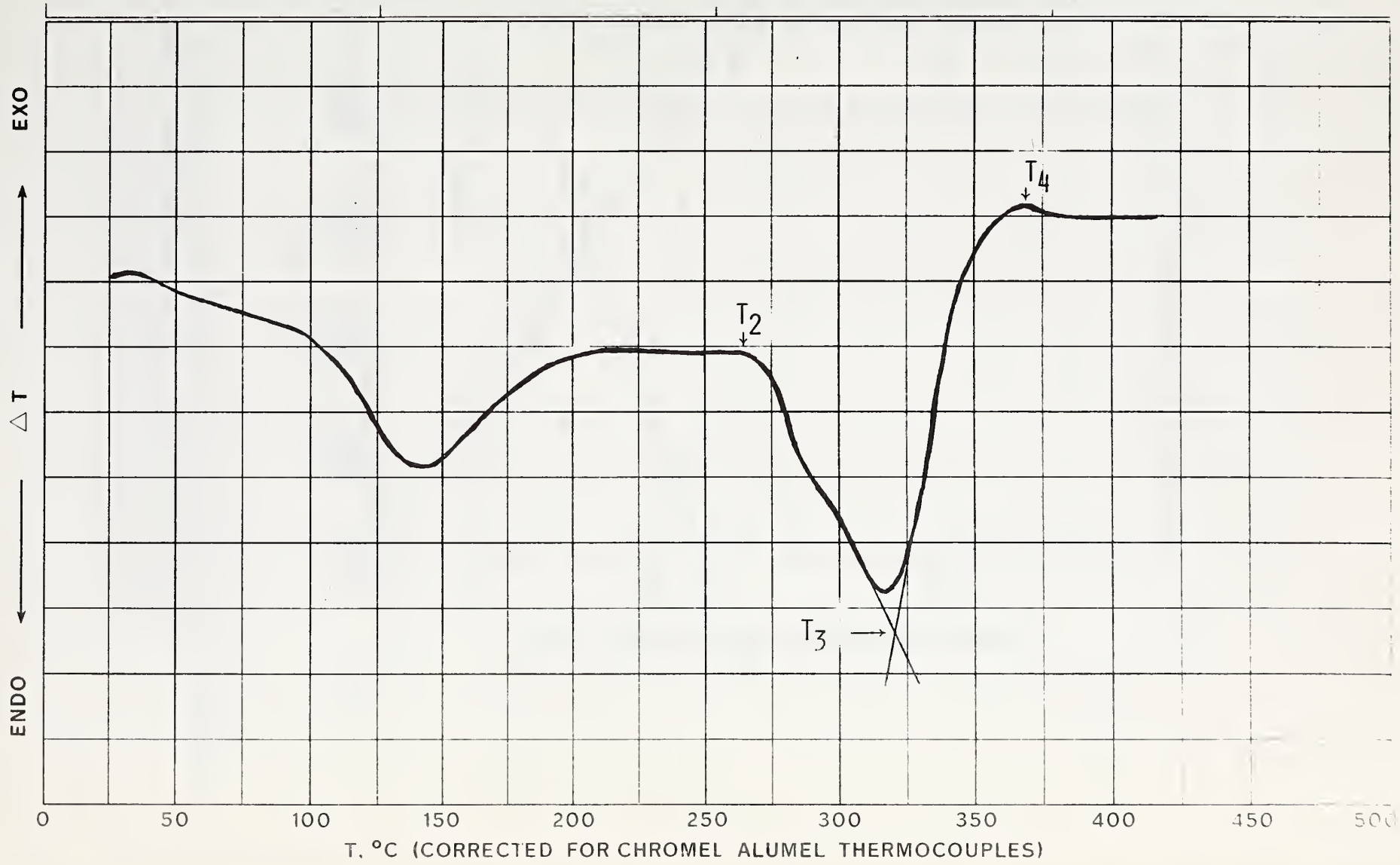



Figure 6. Relation of decreases in internal tearing resistance observed after accelerated aging to the decreases observed after 32 years of natural aging.

Figure 7. DTA thermogram of sample No. N176L. The initial deflection is due to desorption of moisture and is not significant. The endotherm beginning near 260° is due to massive decomposition of celluloses. $T_2$ is the beginning of this endotherm. $T_3$ is an intersection of tangents to the slopes preceding and following the lowest point in the endotherm. $T_4$ is the highest point following $T_3$.



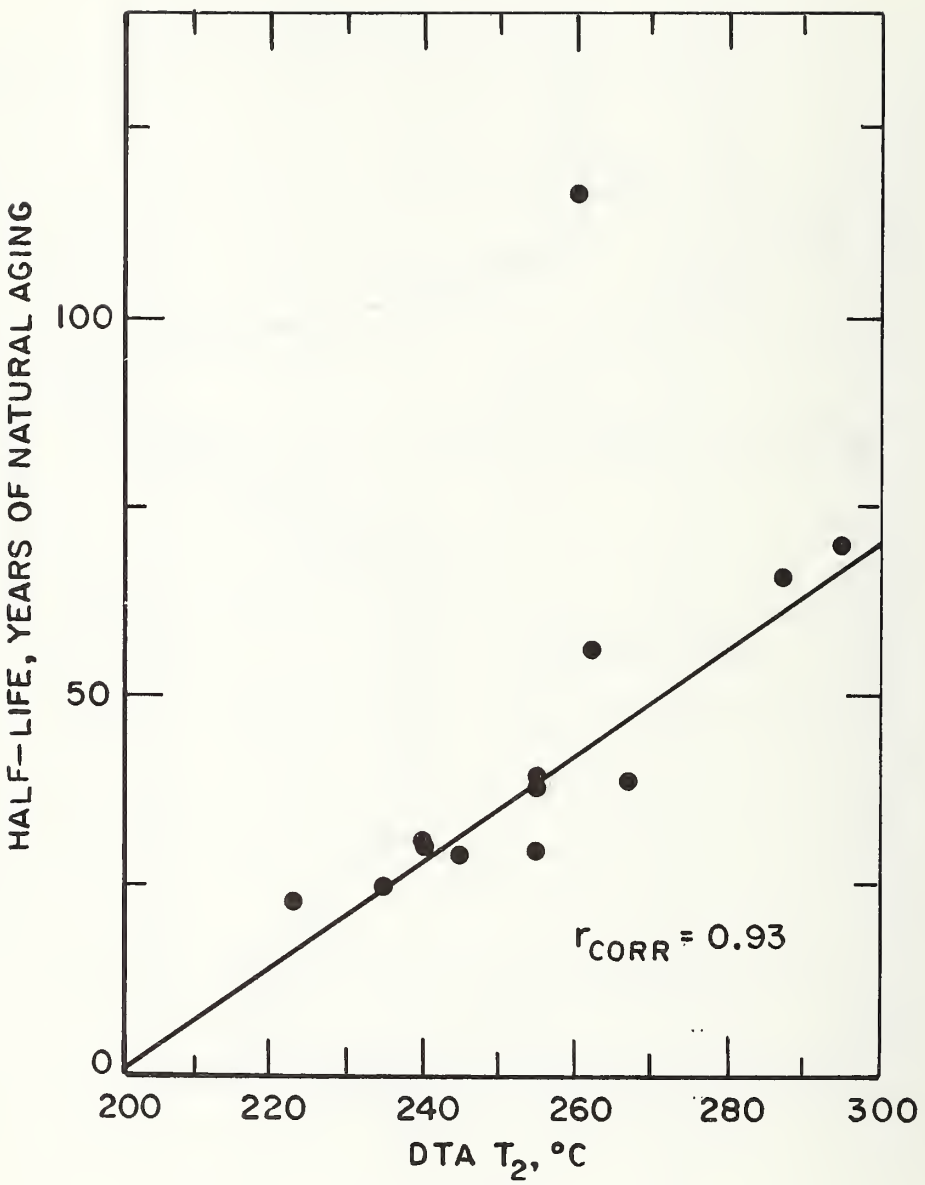



Figure 8. Half-lives in internal tearing resistance plotted against DTA $T_2$ in degrees Centigrade. The calculated half-lives are based on decreases in tearing resistance observed after 20 years of aging.

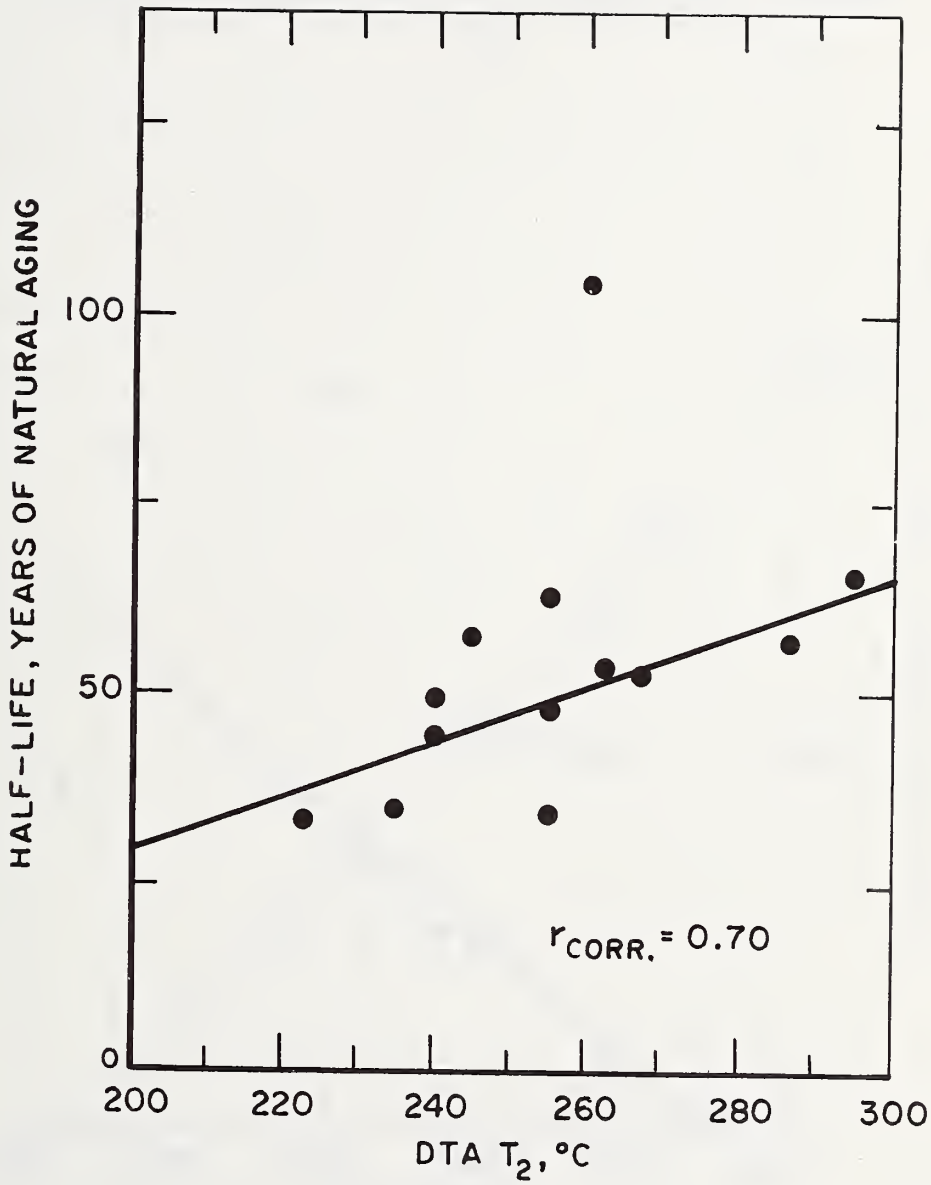



Figure 9. Half-lives in internal tearing resistance plotted against DTA $T_2$ in degrees Centigrade. The calculated half-lives are based on decreases in tearing resistance observed after 32 years of aging.

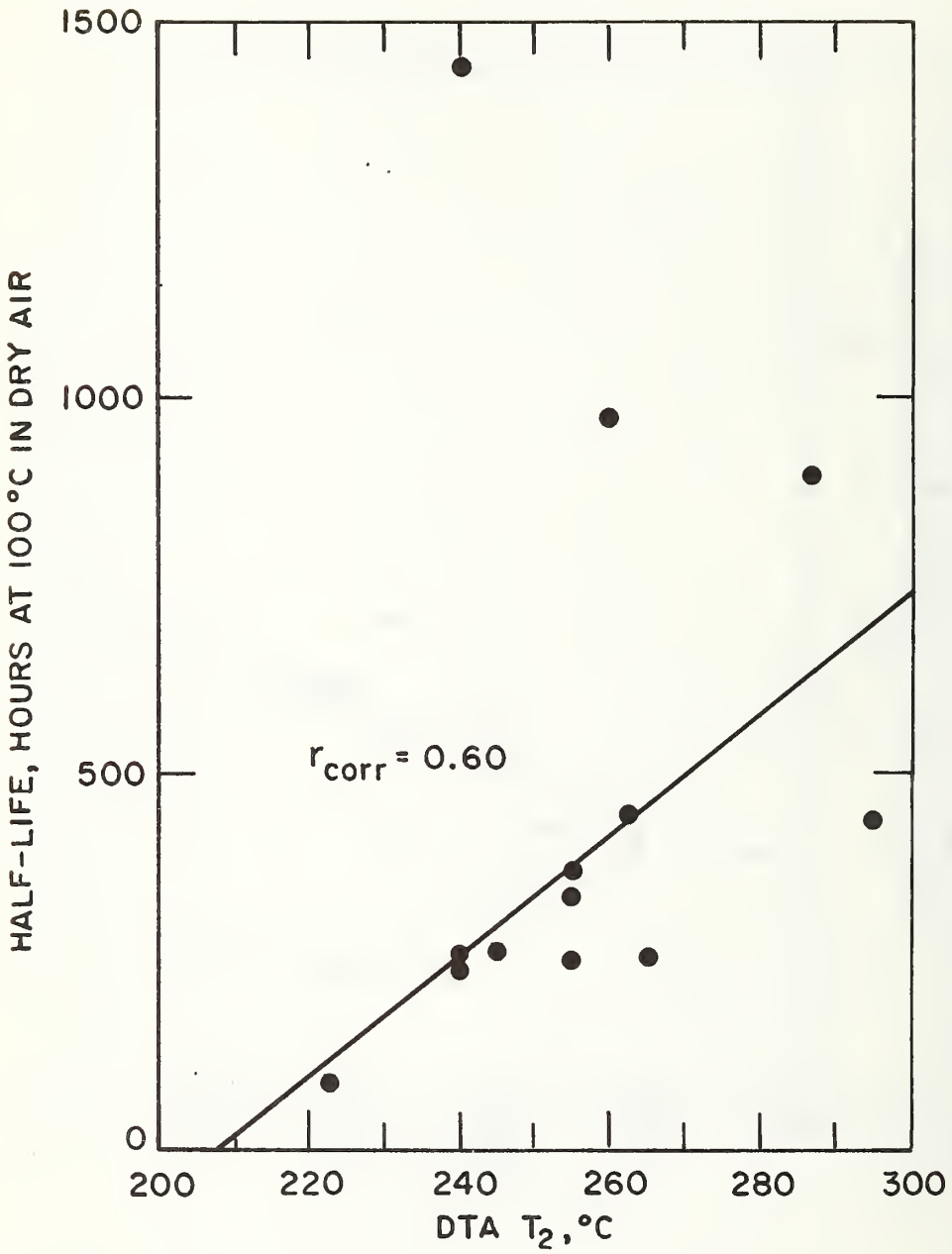



Figure 10. Half-lives in internal tearing resistance plotted against DTA $T_2$ in degrees Centigrade. The calculated half-lives are based on decreases in tearing resistance observed after 72 hours of accelerated aging.

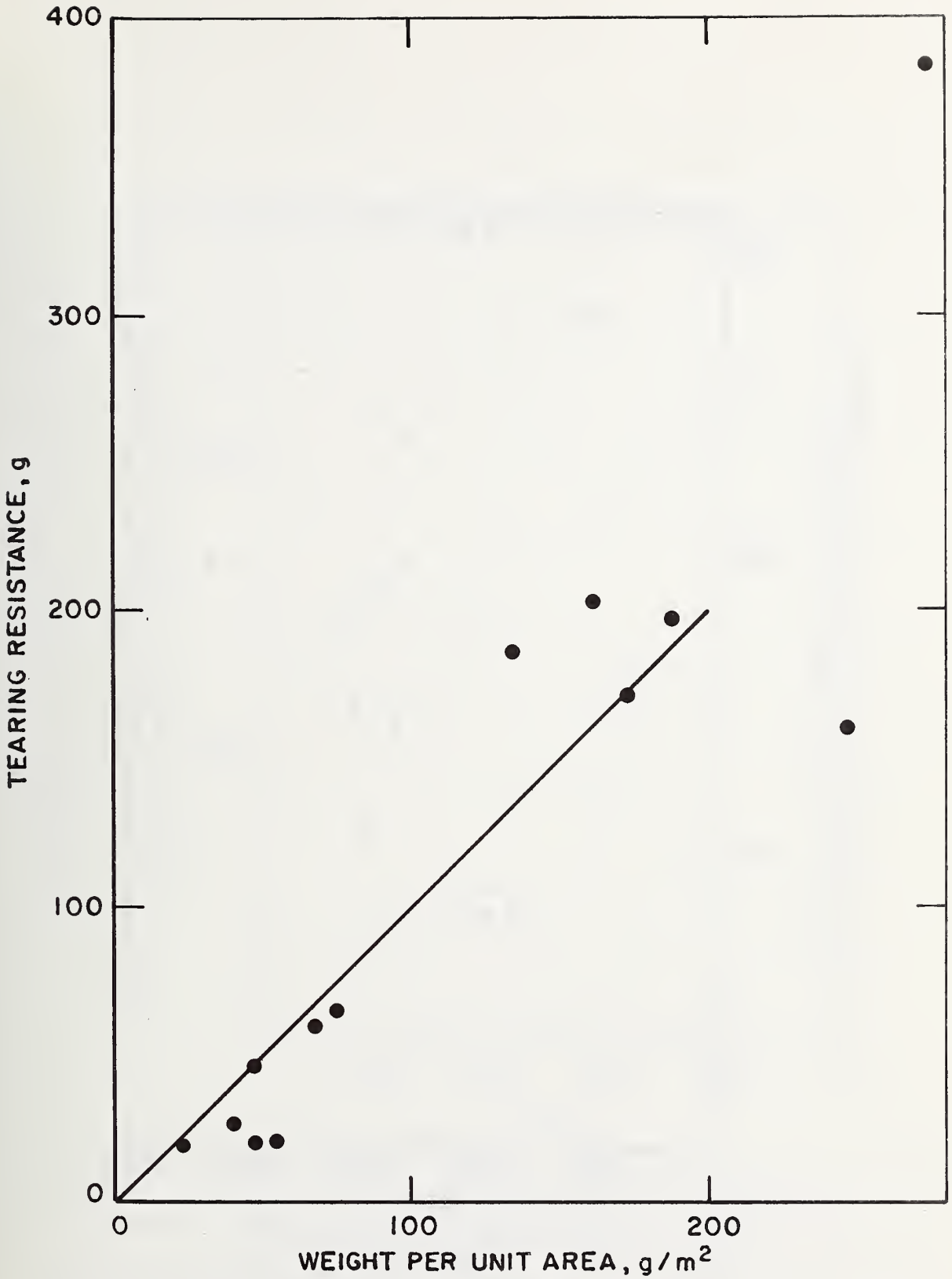



Figure 11. Internal tearing resistance, as a function of weight per unit area.

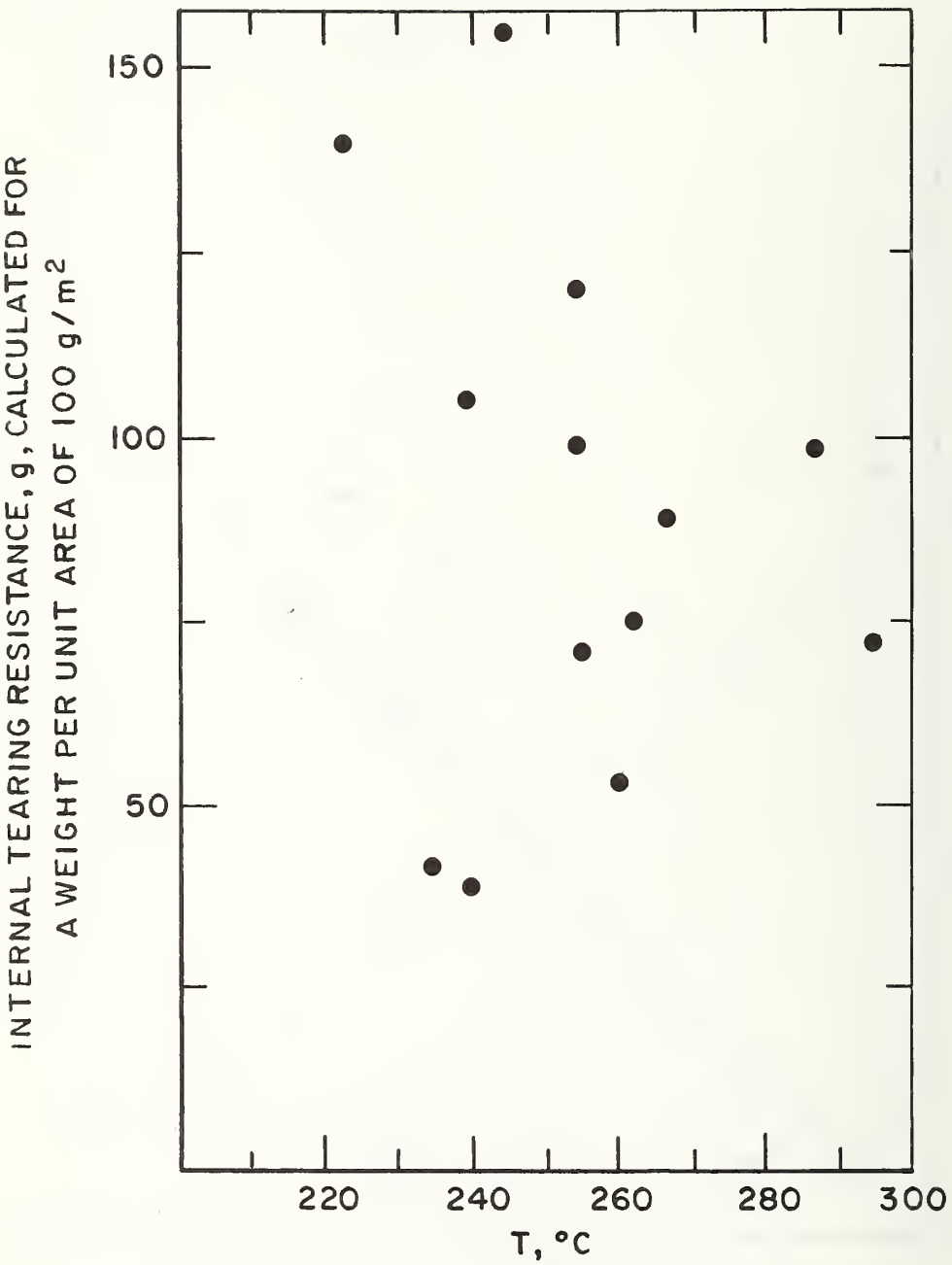



Figure 12. Relation of magnitude of the tearing resistance of unaged samples to DTA $T_2$, °C, of same samples aged 32 years.

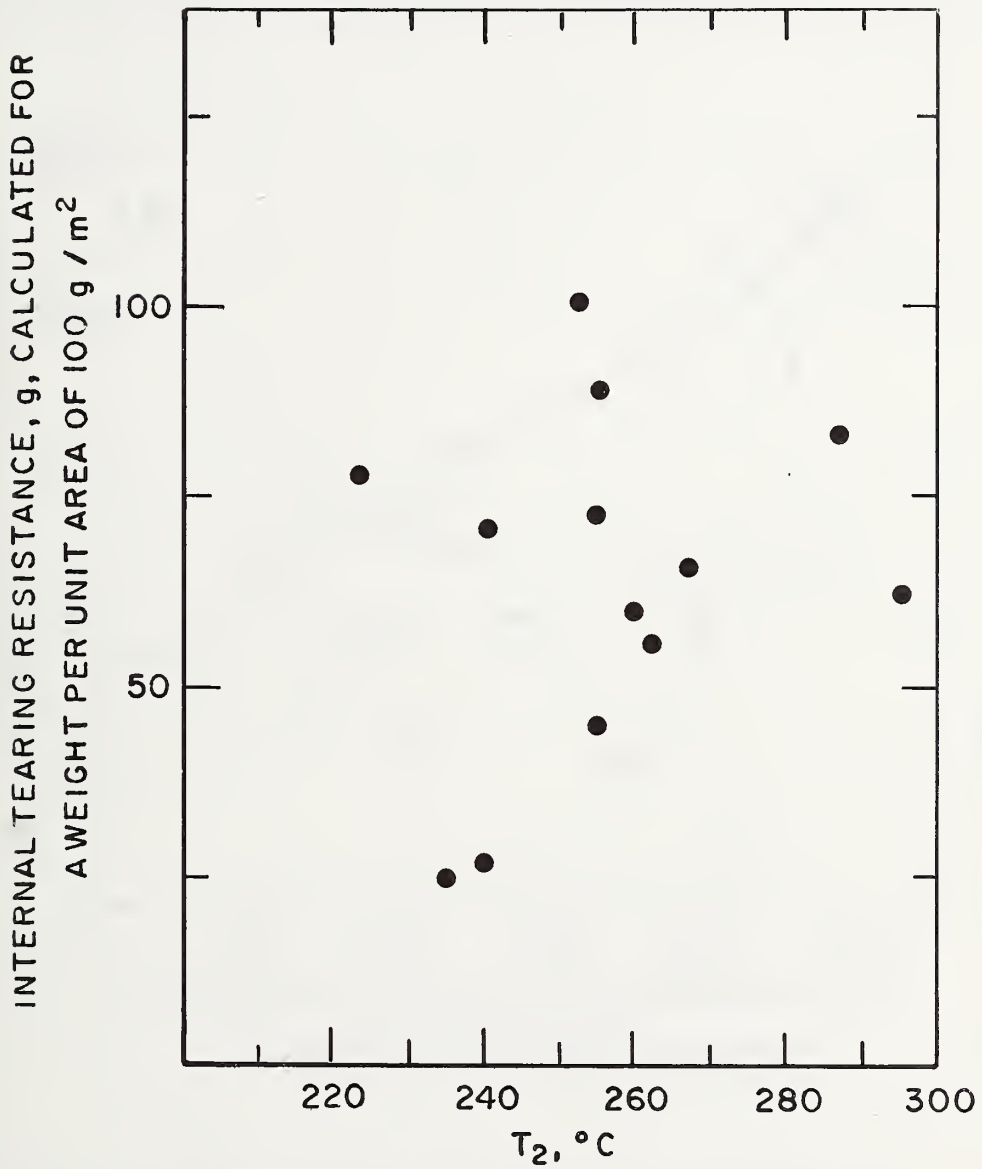



Figure 13. Relation of the magnitude of the tearing resistance of samples aged 20 years to DTA $T_2$, °C, of same samples aged 32 years.

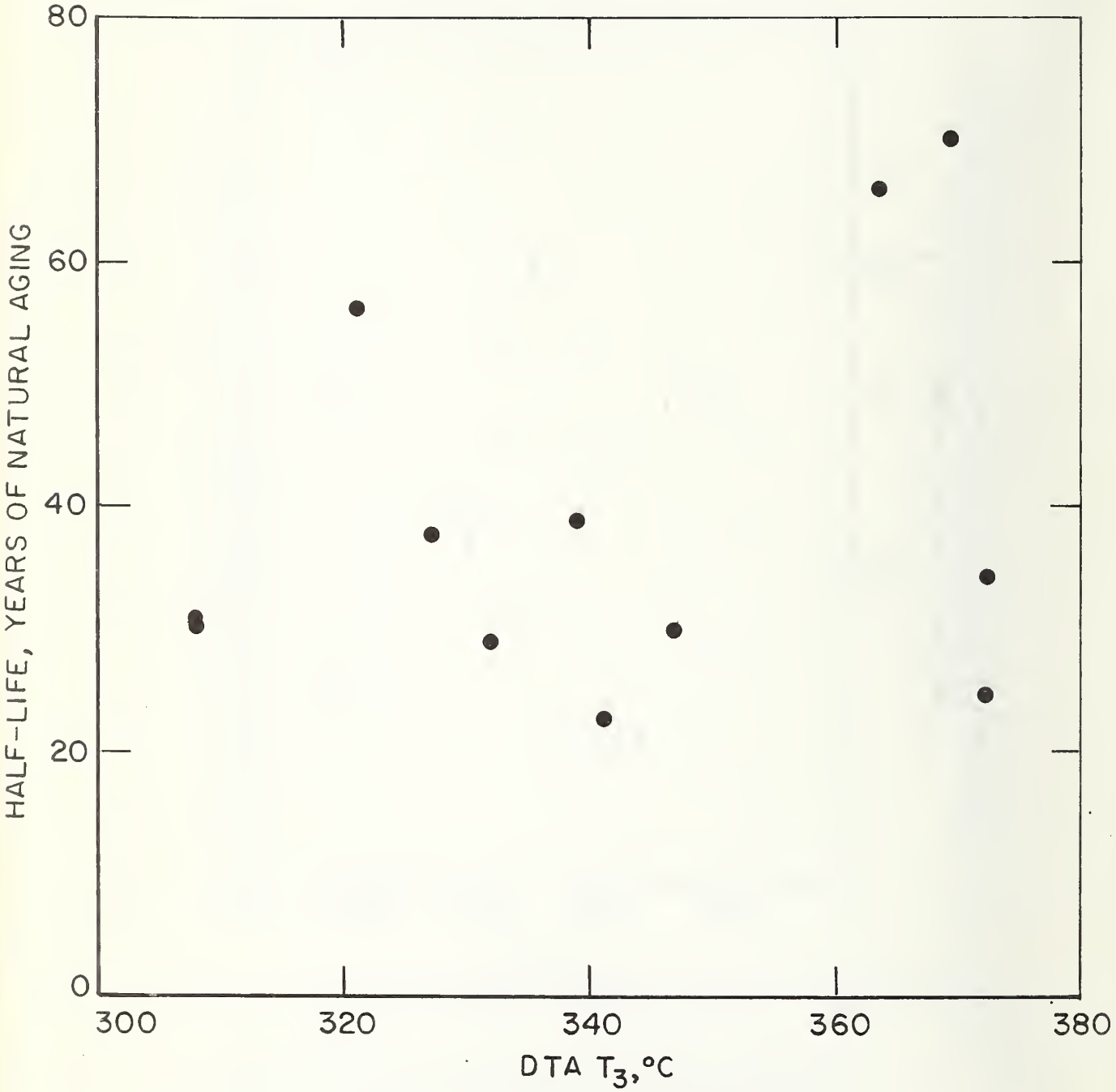



Figure 14. Half-lives in tearing resistance plotted against DTA $T_3$ in degrees Centigrade. The calculated half-lives, in years, are based on changes observed after 20 years of natural aging.

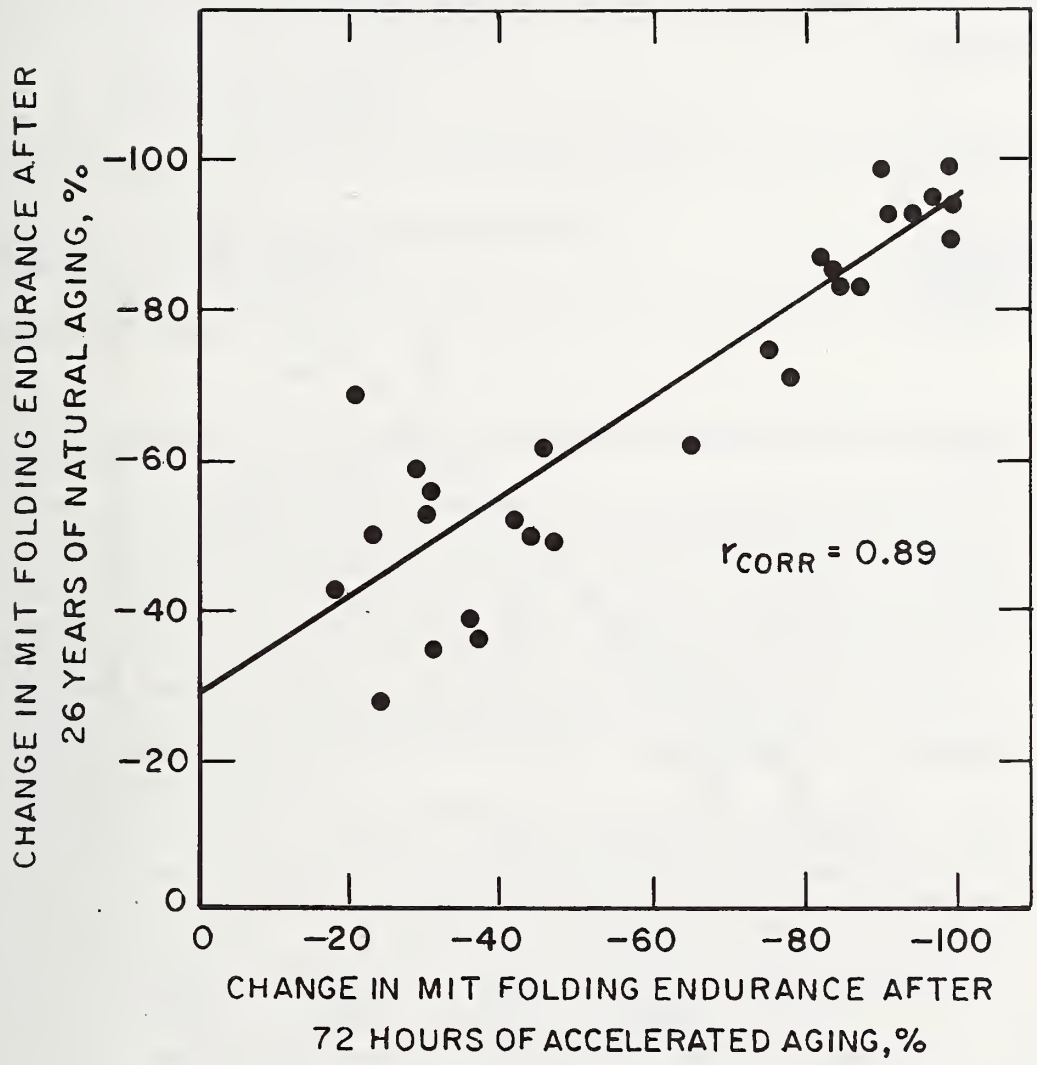



Figure 15. Relation of decreases in MIT folding endurance after accelerated aging (72 hours at 100°C, dry air) to decreases observed after 26 years of natural aging. Data of Wilson, et al [2].

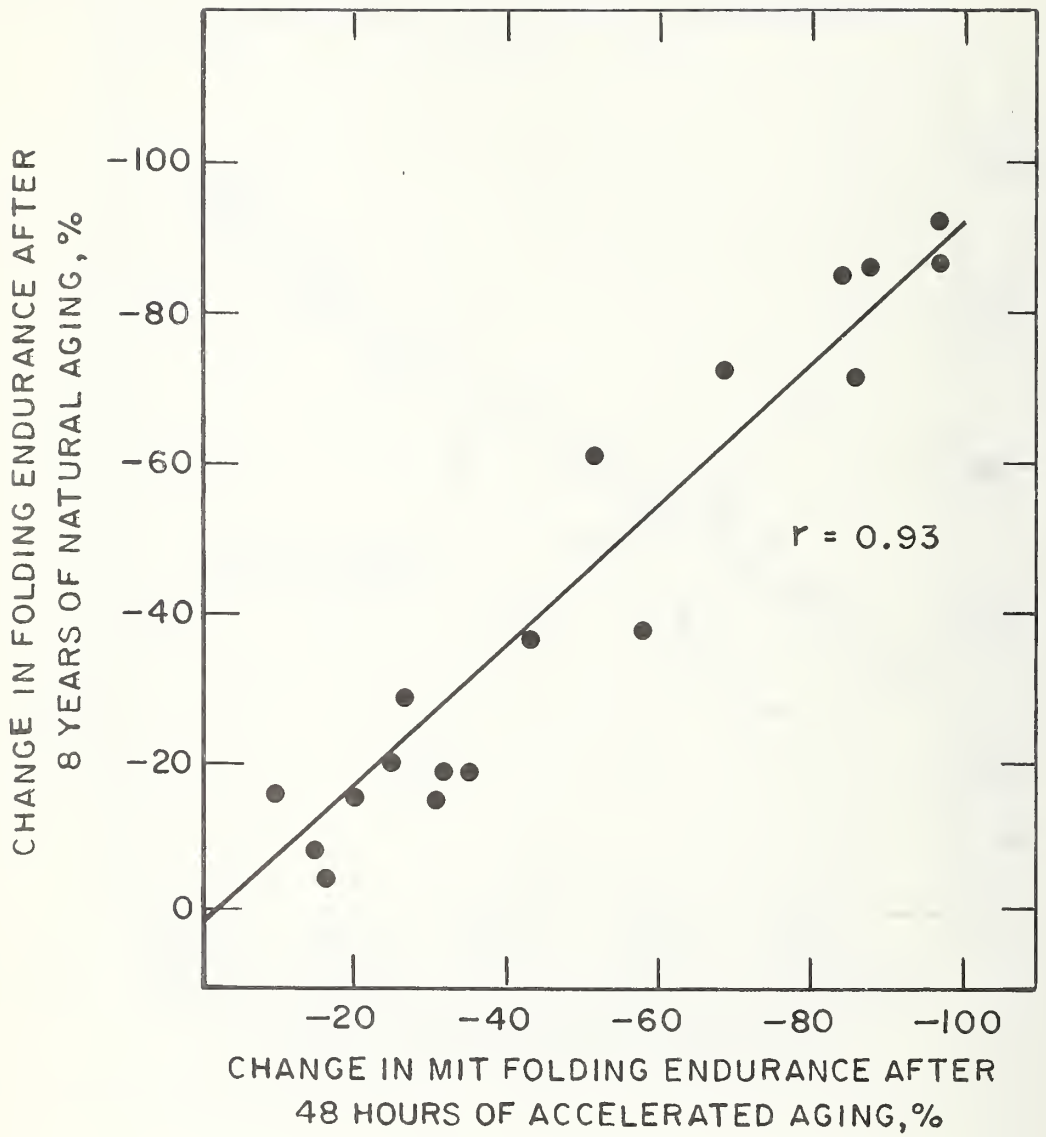



Figure 16. Relation of decreases in MIT folding endurance after accelerated aging (48 hours at 100°C, dry air) to decreases observed after 8 years of natural aging. Data of Wilson, et al [2].

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**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.)

An accelerated aging method is necessary for determining the permanence of paper, since natural aging requires long periods of time to generate meaningful trends in the decrease of paper strength. It is questionable which would be better suited to simulate natural aging--a dry or a humid accelerated aging environment. This report describes correlations of the dry accelerated aging of rag and sulphite paper and their natural aging for periods up to 32 years.

The tests performed include internal tearing resistance, Schopper folding endurance, bursting strength, differential thermal analysis, and pH determinations.

Changes in internal tearing resistance indicate a high degree of correlation between natural aging and dry accelerated aging. Differential thermal analysis is correlated with the change in tearing resistance. Bursting strength changes little during either natural or accelerated aging. The original acidities (pH) are unknown, but the acidities of the aged papers show little or no correlation with aging. Schopper folding endurance cannot be correlated with aging, perhaps because of interruption in the initial tests.

Data on changes in MIT folding endurance of similar types of paper are cited, which indicate an equally high correlation between dry accelerated aging and natural aging.

**17. KEY WORDS** (Alphabetical order, separated by semicolons) Bursting strength; differential thermal analysis; dry accelerated aging; humid accelerated aging; internal tearing resistance; MIT folding endurance; natural aging; pH; rag paper; Schopper folding endurance; sulphite paper.

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