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SUMMARY

The purpose of an accelerated aging test is to predict the useful life of the material in question. Investigations on the permanence of paper by means of accelerated aging at elevated temperatures have been conducted over the past 50 years.

The conventional method, quite prevalent in permanence investigations, assesses permanence in terms of the extent of degradation occuring a fixed time after aging at a single temperature. This method, however, has been criticized as being potentially misleading (1). It was argued that, although the rate at which a paper degrades depends on temperature, this temperature dependence might not be the same for all papers. In such a case the degradation of one paper relative to another as determined by accelerated aging would differ from the relative degradation observed at room temperature. The suggestion was made that permanence be assessed in terms of the degradation rate at room temperature. This rate could be obtained from the Arrhenius equation using rates determined at several elevated temperatures.

Although the Arrhenius approach towards estimating paper permanence appears simple and straightforward, predictions of permanence may be just as misleading as those obtained in the single temperature method. More than one reaction contributes to the degradation of paper while the Arrhenius concept is applicable in a simple manner only to single reactions. The rates of

deterioration of paper at elevated temperatures, estimated by the decline of physical properties with time of aging, are for the system as a whole and unless the reaction rates for all the degradative reactions are increased in the same proportion with temperature the determined rates will be anamolously high or low depending on a number of factors. Similarly, the slope of the Arrhenius plot, generated from the determined rates, will be anamolously high or low and extrapolation of the plot to ambient conditions will yield degradation rates which are appreciably different from the actual rate of degradation.

It has been known for some time that moisture has a profound effect on the results obtained from accelerated aging tests for paper (2,3,4). Eventually studies on the accelerated aging of paper were conducted at some chosen relative humidity or at some constant moisture content of paper. Accordingly, much disagreement arose between investigators since the results of an investigation were dependent on the environmental conditions of the aging system. The only opportunity for agreement between investigators occurred when the moisture content of the papers used by two investigators was maintained the same.

It became very clear that much information had to be developed on the effect of moisture in accelerated aging of paper. In order to develop such information it would be necessary to age paper at a multitude of humidities and temperatures. Such a study would not only provide critical information on a very important variable in accelerated paper aging but the data might be also used to evaluate the validity of using the Arrhenius concept for assessing paper stability.

Handsheets were prepared from a Northeastern softwood kraft pulp which has been deashed with 0.1N HCl. The handsheets were aged at 60°, 70°, 80°, and 90°C and at 0, 10, 25 and 50% RH for all temperatures except 60° where the humidities were 0, 25, 50 and 75%. The reason for the change in humidity conditions at 60°C was because the partial pressure of water at 10% RH was so low very little increase in rate could be expected over that occurring at 60°C and 0%RH. The rates of deterioration were determined by plotting the log of the property in question against time for all properties except alkali solubility, copper number, hydrogen ion concentration and wet strength which were plotted on a linear scale against time. The slope of the plot was considered to be a measure of the degradation rate. Linear relationships were found between the degradation rate and the amount of moisture in the aging atmosphere, expressed as the partial pressure of water, for each temperature investigated. The plots were expected to pass through the origin since little if any degradation occurred at 0% R.H. regardless of the temperature. However plots for the 90°C series did not pass through the origin for any of the properties investigated. In the 80°C series the plots passed through the origin only for the chemical properties and for brightness while all of the plots passed through the origin for the 60°C and 70°C series. This suggests that the mechanism of degradation changes appreciably at some temperature above 70°C.

Although the results of this investigation indicate that atmospheric moisture and not bound water affects the degradation rate of paper it must be recognized a linear relationship usually exists between relative humidity and the amount of water bound to cellulose in the humidity range employed in this investigation. In the two instances where the R.H. range was broadened the results conflicted with each other. It will be necessary to expand this study to include humidities substantially above 50% for all the temperatures investigated before an indication of the type of water affecting degradation rates can be obtained. The expanded investigation should also provide additional information on the possibility of a change in degradation mechanism above an optimum temperature.

The results of this investigation clearly demonstrate the need to establish the optimum temperature and moisture conditions for accelerated aging tests for paper. Unless the functionality of moisture and the limits for temperature are established there is little hope for obtaining agreement between investigations on paper permanence or for designing an accelerated test for paper which will produce meaningful results.

INTRODUCTION

For over fifty years attempts have been made to predict the permanence of paper by means of accelerated aging. The earliest accelerated aging involved placing paper in an oven at 100-105°C for times ranging from 20 to 125 hours (5,6). The decline in physical properties resulting from exposure to elevated temperatures was considered a measure of paper permanence. The papers having a high retention of the original properties were considered to be permanent while those exhibiting an appreciable decline in properties were considered to be impermanent. The degree of impermanence was proportional to the extent of decline in properties. No attempt was made at predicting the service life of paper.

It was eventually recognized that the degradation rate for all papers might not remain constant and that the estimated permanence of paper could change with longer aging periods. This led to the practice of aging paper for longer periods of time with multiple withdrawals during the course of aging. The physical properties were plotted for the various time intervals. If necessary the data were suitably transformed in order to obtain straight lines. The slopes of these lines were considered to be a measure of the degradation rate and were used to assess the permanence of paper. The papers having the lowest degradation rates were judged to be the most permanent.

Generally speaking it is assumed that the degradative reaction in paper at elevated temperatures are not significantly different from those at ambient conditions, because for an accelerated aging method to be valid it must duplicate the chemical and physical changes occurring naturally. Within the limitation of this assumption attempts have been made at establishing a relationship between natural and accelerated aging. The results of several investigations concluded that three days oven aging at 100°C was equivalent to 20-28 years of natural aging (18,19). Barrow suggested that for convenience three days oven aging could be considered equivalent to 25 years natural aging (8). However, the most recent investigation comparing accelerated and natural aging clearly indicates that the degradation occuring during three days oven aging of paper frequently does not correspond to a specific number of years of natural aging(9).

The situation became more complex when it was discovered that moisture had a significant effect on the rate and extent of degradation of paper (2,3,4). To date no study, fully interpreting the relationship between moisture and degradation rate in accelerated aging, has been conducted. For the most part the choice of atmospheric conditions by various investigators has been based on an empirical rather than on a fundamental basis. Some investigators considered the control of relative humidity to be most important with no consideration of the amount of water bound to cellulose. Other investigators considered the "bound water" to be most important. At the present time there appears to be no consensus as to the type and amount of water to be controlled in an accelerated aging test.

Most recently the single temperature aging methods have been criticized as being potentially misleading(1). The decline in the physical properties of paper is caused by a variety of chemical reactions. Since different reactions that might occur in different papers have different responses to temperature it was argued that aging at a single temperature does not provide a means for detecting the differences in temperature dependence of the rate constants. It was suggested that the rate of degradation be measured at several elevated temperatures and that the well known Arrhenius equation then be used to extrapolate to the rate of deterioration at room temperature. In this way an estimate of the half-life of paper could be determined and a predication of the lifetime of paper could be made.

Although the Arrhenius approach towards estimating paper permanence appears simple and straightforward, predictions of permanence may be just as misleading as those obtained with single temperature methods. As mentioned previously, more than one reaction contributes to the degradation of a paper while the Arrhenius concept is applicable in a simple manner only to single reactions. The determined rate of deterioration at elevated temperatures is of the system as a whole and unless the reaction rates of all of the degradative reactions increase in the same proportion with temperature the determined rate will be anamolously high or low depending on a number of factors. Similarly, the slope of the Arrhenius plot generated from the determined rates will be anamolously high or low and extrapolation of the plot to ambient conditions will yield degradation rates which are appreciably different from the actual rate of degradation.

The question at hand is how do we evaluate paper permanence with precision? Essentially everything that has been said in the literature about the factors affecting paper permanence has been based on results obtained from accelerated aging tests. There is no assurance that accelerated aging duplicates the chemical and physical changes in natural degradation. Unless more fundamental knowledge of the aging process is known, assessment of paper permanence by means of accelerated aging will be more empirical than fundamental.

The purpose of this investigation was to develop information on the relationship between moisture and degradation rates in accelerated aging and to determine whether the temperatures commonly used in accelerated aging are excessive.

EXPERIMENTAL

Handsheets, prepared from a northeastern bleached kraft pulp containing approximately 85 percent alpha cellulose and 15 percent hemicellulose were used in this investigation. Six kilograms of the pulp were torn into pieces of approximately two square inches area and divided into three two-kilogram samples. Each sample was demineralized by soaking in 0.1N hydrochloric acid at a five percent consistency. After one hour the acid was drained and fresh acid was added to the pulp. After the fourth acid treatment the pulp was washed with distilled water on a large Buchner funnel until the pH of the filtrate was identical to the pH of the distilled water and remained at that pH for an additional three to four rinses.

Following demineralization, the three two-kilogram samples were blended thoroughly, and washed four additional times with carbon dioxide-saturated distilled water. The bulk of the water was removed by filtration and the treated pulp was placed in a covered glass jar and stored at -18°C until used.

The pulp was beaten in a laboratory mill at 10 percent consistency with no clearance between bedplate and roll for 5,000 revolutions at 33.3N (3.4 kilograms force) and a relative velocity of roll to bedplate of 6m/sec. The beating was done in distilled water using sufficient wet pulp to provide 40g of dry pulp for each charge. One kilogram of pulp was beaten (25 beater charges) and placed in a large stainless steel container, diluted to approximately one percent consistency and blended for approximately one hour prior to preparing handsheets.

Aliquots, containing sufficient pulp to make a 30.5 x 30.5 cm handsheet having a weight of 70 g/m^2 ± 5% were placed in a British Disintegrator, diluted with distilled water to a consistency of approximately 0.5 percent and disintegrated for 3000 revolutions. The disintegrated pulp was placed in a 30.5 x 30.5 cm deckle box containing approximately 28 liters of distilled water. The contents were agitated by moving a perforated plate up and down five times followed by a pause of approximately 10 seconds then drained through a 100 mesh monel wire screen. The wire containing the formed sheet was placed on a blotter, covered with wool felt and consolidated by pressing with a 33 cm long roller weighing 22.5 kg. The sheet was carefully removed from the wire, placed between wool felts and passed through a roll press at a pressure of approximately 7 kg/per linear cm. The pressed sheet was then dried on a drum dryer at 95°C for approximately four minutes. The tension on the endless felt of the drum dryer was adjusted to restrict sheet shrinkage to a minimum. The sheets were stress relieved by suspending them in a humidity chamber at 30°C and 95% relative humidity for approximately 16 hours.

Accelerated Aging

All of the handsheets were randomized out of the order in which they were manufactured in order to obtain samples, representative of the lot, for the various combinations of aging time, temperature and relative humidity. All of the handsheets were randomized into sets of 12 handsheets. Six sets of 12 handsheets, selected at random, were designated for each of the four temperatures. Each sheet in the sets was cut into four quaters and each quarter was designated at random. The quarters from each sheet having the same designation were then grouped together and each set of quarters were then aged for the same time period at four different relative humidities. Following aging the specimens were conditioned according to TAPPI T402 OS-70 before testing.

Constant temperature oil baths of internal dimensions, 30 cm in width by 60 cm length and 37 cm in depth, were constructed of stainless steel. A heating coil, immersed in the bath, was an auxiliary source of heat, with current input controlled by a variable transformer. An immersion heater controlled by a relay box and thermoregulator was the principal source of heat and provided the desired temperature control with ±0.1°C. The oil was continuously pumped in the bath with an immersion type pump to ensure uniform distribution of temperature.

Two baths were used in series. One bath (prehumidifier) was maintained at a temperature that would provide the desired partial pressure of water and the other (aging bath) was maintained at one of the four temperatures employed in this investigation.

To provide a vented atmosphere at a specific relative humidity in the aging vessels, 50 cm^3 of air per minute was metered through water in the prehumidifier, passed through glass tubing surrounded by a heating jacket at a temperature somewhat higher than the prehumidifier bath to avoid condensation, then through coiled glass tubing immersed in the aging bath and finally through the aging vessel containing the suspended paper specimens. To provide dry air (0% RH), air was passed over silica gel through a flowmeter to the aging vessel. The temperatures, the aging baths, the partial pressure of water vapor in the saturated air and the relative humidities in the aging vessels are given in Table 1. The baths were covered with black cloth to exclude light.

Testing Methods

The following Tappi methods were employed: Folding Endurance T511 Sn-69, Brightness T452 OS-58, Alkaline Solubility T212 OS-54, Copper Number T430 M-52, Tensile Strength T494 OS-70 using 1.5 cm wide specimens at a span of 10 cm and a rate of elongation of 1 cm/min, and pH by method T509 SU-68 with the exception that the pH measurement was made on the decantate (20).

Internal tear was performed on an Elmendorf tear tester having a 200 g capacity. A single ply was used unless the tear strength deteriorated considerably necessitating three or four plies in order to obtain a reading in the range suggested for the instrument.

Zero span tensile strength was determined on a commercially available zero-span tester. Sample size was 2 cm x 11 cm. The clamping pressure for each set of specimens was determined in advance to determine the minimum pressure at which slippage did not occur and the maximum pressure where fiber damage occurred. The clamping pressure chosen was midway between these two pressures.

Wet tensile strength was determined on a constant rate of elongation tensile tester using specimens 1.5 cm wide and a length of 10 cm. The samples were soaked for two hours in distilled water prior to testing.

Moisture regain specimens were first conditioned in a desiccator for 24 hours and then exposed to an atmosphere maintained at 23 ± 1°C and 50.0 ± 2.0% relative humidity for at least 24 hours. Specimens of approximately two grams were placed in weighing bottles and the total weight was determined to the nearest 0.1 mg. The sample was then dried in a vacuum oven at 105°C for one hour, covered immediately upon opening the oven, cooled in a desiccator for two hours and reweighed. This procedure was repeated until constant weight was obtained. The difference in weight between the conditioned and dried sample was due to the moisture in the specimen. The specimen was then removed from the weighing bottle, and the empty bottle was dried in the vacuum oven at 105°C for one hour, cooled in a desiccator for two hours and weighed. The difference between the weight of the bottle containing the dried specimen, and the empty weighing bottle was the weight of the anhydrous specimen. The weight of water divided by the weight of the anhydrous specimen multiplied by 100 was the percent moisture regain.

RESULTS

The results for all of the properties investigated in this study are given in Tables 2-12. Little if any change in physical properties occurred at any of the temperatures investigated when the aging atmosphere was desiccated. The one exception was a marked increase in wet strength. Possibly cross linking occurs under these conditions. As the relative humidity was increased to 25 and 50% the rate of wet strength formation also increased as shown in Figures 1-4. At the higher temperature and relative humidities the wet strength reached a maximum then declined indicating that more than one reaction was having an affect on wet strength.

In plotting the data it appeared that a better linear relationship was obtained by plotting the log of the property in question against time, rather than by merely plotting the physical property against time. Examples of this can be seen in Figures 5A, 5B, 6A and 6B. However, alkali solubility, copper number, hydrogen ion concentration and wet strength gave better linear relationships when plotted on linear coordinates. Therefore, the degradation rates were determined from the slopes of the plot of log property against time for all but alkali solubility, copper number, hydrogen ion concentration and wet strength. In every instance the rate of degradation of physical properties or change in chemical property increased with increasing relative humidity.

A plot of degradation rate as a function of relative humidity (Figures 7 and 8) resulted in a good linear relationship. However, relative humidity is not a fundamental expression for water vapor concentration and it is much better to express the amount of water vapor in the atmosphere in terms of partial pressure of water. When the degradation rate is plotted against the partial pressure of water an excellent linear relationship is also exhibited (Figures 9-19). The lines connecting the data points in Figures 9-19 were fitted by the least squares method.

DISCUSSION

Temperature and Humidity

It is interesting to note that the plots of degradation rate against the partial pressure of water for the 90°C series do not pass through the origin for any of the properties investigated. In the 80°C series the y intercept is at or near the origin for hot alkali extraction, brightness, copper number, pH, moisture regain but not for zero span, fold endurance, tear, breaking strength, wet strength and elongation to break. Inasmuch as little if any degradation occurs in the absence of moisture at each temperature investigated it would be reasonable to expect the y intercept for the plots of degradation rate against the partial pressure of water to be at or very near the origin. Since none of the 90°C plots and only some of the 80°C plots have a y intercept near zero it is possible that either the cellulose-water interaction or the degradation process changes at these conditions. There are several possible explanations for this phenomenon and it will be necessary to determine the exact causes for this occurrence.

This investigation demonstrates clearly that water has a profound effect on the degradation of paper in an accelerated test. The rate and extent of degradation apparently are directly dependent on the amount of moisture in the aging atmosphere. It is quite clear that any accelerated aging method must include some specification for moisture. Without such a specification the results will vary from investigator to investigator, however, it will be necessary to identify the role of moisture in the degradation process before it will be possible to specify the right quantity of moisture to be used in accelerated aging.

The object of an accelerated aging test is to speed-up the degradative process sufficiently to enable assessment of the stability of the material in question in a reasonable time interval. It is essential that only the degradative processes of interest are accelerated in the same ratio as they occur naturally and that degradative reactions which are insignificant at ambient conditions do not become significant at elevated temperatures.

Since there appears to be a linear relationship between the partial pressure of water in the atmosphere and degradation rate it could be argued that the amount of moisture to be employed in an accelerated aging test should be identical to that which paper is normally exposed to under natural conditions. The amount of moisture which could be specified is that equivalent to TAPPI standard conditions (50.0 ± 2.0% RH and 23.0 ± 1.0°C). In fact accelerated aging has been conducted in which air from a room at TAPPI standard conditions was piped into ovens to control the moisture in the aging atmosphere (8). Oven aging is frequently referred to as arid aging and the method has been criticized for its lack of moisture (1,4). However, in a recent study on the comparison of accelerated aging of book papers with natural aging it was concluded that oven or dry aging appeared to correspond more nearly to natural aging than accelerated aging at 90°C and 50% RH (9).

Bound Water

Some investigators consider that controlling the moisture content of paper in accelerated aging tests for paper is most important (1,10). The presumption here is that the water bound to cellulose is the moisture in question and that atmospheric moisture is important only in the sense that it must be present in sufficient quantity to assure a prescribed moisture regain (bound water). This presumption is quite divergent from the supposition that atmospheric moisture directly affects the degradation rate of paper.

The moisture content of paper is dependent on the amount of atmospheric moisture and on the temperature of the air in contact with the paper. Furthermore, the quantity of sorbed water at a particular set of conditions depends on whether the equilibrium conditions were appproached from a high or low relative humidity. A typical moisture sorption isotherm is shown in Figure 20. It is important to note that the isotherm is essentially linear between 10 and 50% RH which is the range of humidity conditions employed in this investigation with one exception. Consequently, the plot of degradation rate of paper as a function of moisture would be the same whether the moisture was expressed as relative humidity, partial pressure of water or as water bound to cellulose, providing the moisture isotherm was unchanged over the range investigated. The range of relative humidity employed in this investigation was too narrow to enable establishment of the type of water affecting the degradation rate of paper.

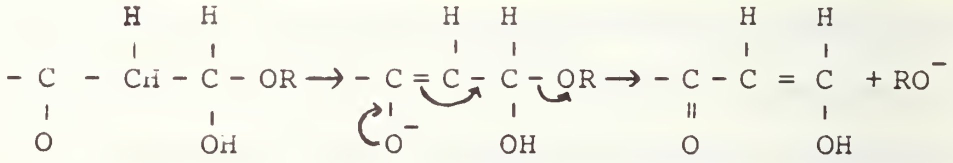
In one set of conditions in this investigation (60°C, 75% RH) the relative humidity was outside the 10-50% range. It can be seen in Figure 20 that the amount of water bound to cellulose under these conditions is considerably greater than it would be if the linear relationship between 10 to 50% was maintained. However, the various degradation rates for paper at 60°C and 75% RH fall very nicely on a straight line with the degradation rates at 25 and 50% RH (Figures 9-19). It might therefore be argued that atmospheric and not bound water is most important. Nevertheless it must be recognized that the slopes of the 60°C series plots are low and it would be difficlut to detect divergence from linearity unless the disparity were quite large.

In order to get a better insight into the type of water affecting degradation rate it was decided to conduct an additional experiment at 80°C and 75% RH. At these conditions the degradation rates were much higher than predicted by linear extrapolation of the rate-moisture plots. This result could be used to argue in favor of bound water as the important variable. However there is evidence that the degradation mechanism is different at 90° and 80°C and it may be that moisture may affect the degradation rate at these temperatures differently. It will be necessary to determine the effect of relative humidity on the degradation rate at several humidities above 50% RH before any conclusions can be made on the importance of atmospheric moisture as opposed to bound water.

Alkali Solubility, Copper Number and Acid Generation

The bulk of material that dissolves in the hot 1% alkali solubility test is low molecular weight carbohydrates consisting mainly of hemicellulose and degraded cellulose. One might assume then that the increase in alkali solubility which occurs during accelerated aging in a humid atmosphere is a consequence of hydrolysis. The increase in copper number which is also characteristic of accelerated aging would seem to support this premise. However, the unusually high increase in alkali solubility at the higher temperatures and humidities seems to indicate other processes are occurring.

The degradation rate for paper is considerably lower in a moist nitrogen atmosphere than in moist air (11,12,13). Apparently, cellulose is oxidized during accelerated aging with the formation of β-alkoxyl groups. The β-alkoxycarbonyl grouping occurs in all possible situations where a carbonyl group is introduced into a cellulose molecule. Whenever a β-alkoxycarbonyl group is present in alkali, a rapid elimination of the alkoxyl group will occur as follows:



$$-\underset{O}{C}-\overset{H}{CH}-\overset{H}{\underset{OH}{C}}-OR \rightarrow -\underset{O^-}{C}=\overset{H}{C}-\overset{H}{\underset{OH}{C}}-OR \rightarrow -\underset{\overset{\|}{O}}{C}-\overset{H}{C}=\overset{H}{\underset{OH}{C}}+RO^-$$

It may be assumed that rapid chain scission will occur by the above mechanism in dilute alkali. If β-alkaxycarbonyl groups do form during aging chain scission will occur during the alkali solubility test producing alkali soluble material exceeding that present prior to chain scission. This could account for a significant portion of the material dissolved in the hot alkali.

The copper number indicates the relative number of reducing groups in paper. Aldehydes as well as the reducing end groups of a number of sugars reduce copper but ketones do not. However, the copper number test is conducted under alkaline conditions and ketones promote chain rupture in alkali by means of the beta elimination mechanism described above. Chain rupture produces new reducing end groups and increases the copper number. As in alkali solubility, copper number is affected by a number of variables and is not indicative of any one specific reaction.

The production of acidity during aging is likely to be caused by a combination of oxidation and hydrolysis. However, the hydrogen ion concentration was derived from pH measurements and the quantities reported do not necessarily represent the total hydrogen ion concentration in the paper. A variety of acids are probably formed during the aging process each having a different pK value. Therefore, there is the possibility some weak organic acids are not dissociated at the time of pH measurement and the only way the total acidity could be determined is by complete extraction of all acids and a titration of the extract.

Strength Properties

Folding endurance deteriorates at the fastest rate and to the greatest extent of all the physical properties investigated. There is even an appreciable decline in fold in desiccated air at the higher temperature. This decline may be due to the formation of crosslinks which appear to form quite prevalently in the absence of moisture. Due to the great variance commonly associated with folding endurance a specially designed experiment would have to be conducted to determine if the observed differences are significant.

The deterioration of strength properties of paper during aging is apparently due in large part to the decline in fiber strength as assessed by zero span tensile measurements. The decline of fiber strength is undoubtedly due to hydrolysis.

Oxidation may also be an indirect cause for fiber degradation. It has been reported that the rate of hydrolysis of cellulose is increased two to three fold by the introduction of aldehyde groups in the 2 and 3 positions (14). A carbonyl group in the 6 position can lead to an increase of from 20 to 70 times the normal rate of hydroylsis (15).

Physico-Chemical Properties

The decrease in brightness is probably due to hydrolytic processes. The formation of uronic acids is know to cause color reversion (16). Oxidation may also play a role in color reversion not only through an increase in hydrolysis rate because of carbonyl formation at the 2, 3 or 6 positions but also by the formation of chromophoric groups.

The decrease in moisture regain strongly suggests a decrease in the accessibility of moisture in the amorphous regions of cellulose. Apparently, strain induced by crystallization forces is relieved by chain splitting during hydrolysis and a rapid crystallization results (17). As crystallinity increases, accessibility and consequently the moisture regain will decrease. This premise will have to be tested in specially designed experiments.

Wet Strength

The changes which occur in wet strength with time are critically dependent on the temperature and humidity conditions. In desiccated air as well as at 10% RH wet strength increased continuously at all temperatures. There was very little difference in the amount of wet strength developed at 0 or 10% RH for any of the individual temperatures investigated but the rate of wet strength development increases with temperature.

As the humidity increased to 25 and 50% RH the rate of wet strength development increases also. However, at 80° and 90°C wet strength reached a maximum, plateaued and finally declined. Plots of wet strength as a function of aging time are given in Figures 1-4.

It is quite apparent that wet strength development is affected by more than one process. It is reasonable to assume that the eventual decline of wet strength under certain conditions is the result of competing reactions. Since the decline in wet strength occurs only at the higher humidity conditions it may be assumed hydrolysis is the cause for the decline in wet strength.

Frequently wet strength is expressed as a fraction of the dry strength. When wet strength is expressed as fractional dry strength and plotted against time (Figures 21-24) the character of the plots changes appreciably. In fact a decline in wet strength is observed only at conditions of 50% RH, 90°C and 75% RH, 80°C after the paper has degraded extensively. In expressing wet strength as fractional dry strength, some compensation for fiber degradation is made. This is an important consideration as fiber degradation is extensive at the higher temperatures and humidities.

Presumably the mechanisms for the fracture of wet paper changes as the fibers degrade. Fracture of wet paper is presumed to occur primarily by breaking interfibers bonds as they are quite weak in wet paper. As fiber degradation becomes extensive it is probable that an appreciable number of very weak fibers break in wet tensile failure. This would especially be true if inter-fiber bonds became more hydrophobic and fiber strength decreased. This hypothesis could be verified by determining the ratio of broken to whole fibers at the fracture line of unaged and highly degraded accelerated aged paper.

Rates for wet strength development may be obtained by plotting wet strength as fractional dry strength against time. Only the time intervals were used when a substantial increase in wet strength development occurred over the preceeding time interval. For example, only time intervals 0-6 days were used at 90°C and 50% RH while all but the 42 day interval was used at 80°C and 50% RH.

Plots of wet strength development rate versus the partial pressure of water in the aging atmosphere were linear (Figure 19). Neither the 80° or the 90°C plots passed through the origin indicating once again that the optimum temperature in accelerated aging of paper is in the vicinity of 70°C.

Estimation of Permenance

Since moisture has a profound effect on the rate of degradation of paper and possibly on the degradation mechanism itself it could be anticipated that evaluation of permanence by the Arrhenius approach will also be affected by the moisture conditions in the aging system. The water in question, affecting the degradation rate, is either atmospheric moisture or bound water. If atmospheric moisture is at issue then the partial pressure of water must be kept constant at all temperatures. If bound water is in question then the relative humidity must be set to provide a constant moisture content at every temperature investigated.

Neither bound water nor partial pressure of water was maintained constant in this investigation. However, the degradation rates at a given partial pressure of water can be extrapolated from the plots in Figures 9-18. Furthermore, the moisture content of paper, in the temperature range of this investigation, should be approximately the same for each temperature at a constant relative humidity (16). Therefore, it is possible to calculate an approximate heat of activation and an ambient degradation rate at a constant partial pressure of water or a constant moisture content of paper from the data generated in this investigation.

It was impossible to extrapolate degradation rates at 1405 N/m^2, which is the partial pressure of water at 23°C and 50% RH, with any precision. However, since the plots are linear, extrapolation can be done at higher moisture conditions since the rates at one partial pressure are proportional to those at another partial pressure. An estimate of degradation rate at 1405 N/m^2 and 23°C is also possible since the degradation rates are proportional to the partial pressure of water.

Arrhenius plots were made for zero span tensile strength and brightness at 25% and 50% RH and at 5333 and 14932 and N/m^2 (Figures 25 and 26). The heats of activation and degradation rates at 23° and 50% RH are given in Tables 13 and 14. It is obvious that the heat of activation and the extrapolated degradation rate at ambient conditions are dependent on the amount of water in the aging system.

At constant partial pressures of water the heat of activation is approximately 13-18 kcal/mole while at constant relative humidity it is between 25-29 kcal/mole. These heats of activation should correspond to the heats of activation usually observed in oven and humid aging respectively. In previous work the heat of activation was reported to be higher in oven than in humid aging in contrast to that seen here (1). One possible explanation for this divergence is that extrapolation from the rate-moisture plots at a constant partial pressure of water gives rise to a significant error in the estimated rates at 80° and 90°C as these plots do not pass through the origin. In actual oven aging the determined rates may differ significantly from those obtained by extrapolation.

CONCLUSIONS

Moisture has a profound effect on the degradation rate of paper. The exact relationship between moisture and degradation rate must be established before a satisfactory accelerated aging method for estimating paper permanence can be specified. Without precise knowledge of the function of water in accelerated aging the choice of moisture conditions will be based purely on empirical rather than on a fundamental basis.

Evidence also exists which indicates that accelerated aging should not be conducted at temperatures above 70°C, however additional work is necessary before an upper boundary on temperature can be specified.

The likelihood of developing an accelerated aging method for paper which will assess permanence in close agreement with actual long term natural aging is critically dependent on establishing the function of moisture and the limits for temperature in artificial aging.

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* Reports marked with an asterisk may be ordered from:

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Table 1. Partial Pressure of Water Vapor at Various Temperatures and Relative Humidities

Aging Temperature	Relative Humidity - %				
	10	25	50	75	100
°C	N/m^2	N/m^2	N/m^2	N/m^2	N/m^2
90	7010	17524	35047	52571	70095
80	4734	11834	23672	35507	47343
70	3116	7789	15579	23368	31157
60	1992	4979	9958	14937	19916
23	281	702	1405	2107	2809

Table 2. Effect of Aging on Folding Endurance

Aging Temp.	Time	Relative Humidity, Percent														
°C	Days	0			10			25			50			75		
		Avg* Double folds	s** Double folds	Retention %	Avg Double folds	s Double folds	Retention %	Avg Double folds	s Double folds	Retention %	Avg Double folds	s Double folds	Retention %	Avg Double folds	s Double folds	Retention %
90	1	1620	330	85	1730	400	91	1630	300	86	1270	300	67			
	3	1730	410	91	1630	280	86	1030	200	54	270	100	14			
	6	1640	370	87	1240	250	65	290	100	15	4	3	0.2			
	12	1310	200	69	650	150	34	11	9	0.5	0	0	0			
	18	1540	280	81	560	170	29	3	7	0.1	0	0	0			
	Control	1900	370	-												
80	3	1860	250	101	1630	280	90	1530	160	83	1240	300	68	874	218	48
	6	1420	260	77	1430	420	78	1340	240	73	600	150	33	210	71	11
	9	-	-	-	-	-	-	-	-	-	-	-	-	24	9	13
	12	-	-	-	-	-	-	-	-	-	-	-	-	2	1	0
	15	-	-	-	-	-	-	-	-	-	-	-	-	0	0	0
	18	1500	320	82	1160	160	64	530	140	29	4	2	0.2			
	30	1870	320	102	760	210	41	58	28	3	1	0	0			
	42	1560	380	85	440	210	24	6	3	0.2	0	0	0			
	Control	1830	280	-										1600	277	-
70	9	1750	290	110	1410	250	95	1330	340	90	1190	320	80			
	18	-	-	-	-	-	-	-	-	-	819	160	52			
	27	1600	260	101	1380	260	92	910	200	61	260	60	17			
	54	1560	340	98	1250	350	84	503	120	34	10	6	1.2			
	72	-	-	-	-	-	-	-	-	-	4	2	0.2			
	90	1510	250	95	930	260	58	75	30	5						
	126	1660	360	104	540	120	34	26	22	2						
	Control	1590	250	-												
60	24	1580	460	94	-	-	-	1490	350	88	1470	280	87	1180	200	70
	36	-	-	-	-	-	-	-	-	-	-	-	-	920	250	54
	48	1880	390	111	-	-	-	1550	300	92	1220	340	70	520	190	31
	60	-	-	-	-	-	-	-	-	-	-	-	-	458	121	27
	72	1800	230	107	-	-	-	1180	240	70	192	100	10	236	90	14
	117	1560	410	92	-	-	-	740	200	44	95	34	6			
	162	1660	300	98	-	-	-	440	180	26	7	3	0.4			
	Control	1690	390	-												

* Average of 12 specimens

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

Table 3. Effect of Aging on Zero Span Tensile Strength

Aging Temp.	Time	Relative Humidity, Percent														
°C	Days	0			10			25			50			75		
		Avg* Kilo-metres	s** Kilo-metres	Retention %	Avg Kilo-metres	s Kilo-metres	Retention %	Avg Kilo-metres	s Kilo-metres	Retention %	Avg Kilo-metres	s Kilo-metres	Retention %	Avg Kilo-metres	s Kilo-metres	Retention %
90	1	15.05	.61	103	15.00	.84	103	14.73	.43	101	13.99	.66	96			
	3	14.88	.62	102	14.71	.79	101	13.71	.87	94	11.86	1.03	81			
	6	14.56	1.42	100	14.31	.61	98	12.01	.52	82	8.83	.43	60			
	12	14.20	.93	97	12.69	.62	87	9.25	.65	63	5.62	.33	38			
	18	15.62	.86	107	12.67	.95	87	8.20	.90	56	4.71	.37	32			
	Control	14.62	.42	-												
80	3	14.13	.72	98	14.44	.79	100	14.32	.89	99	13.74	.71	95	12.89	.62	88
	6	14.01	.68	97	13.63	.81	94	13.59	.93	94	12.15	.63	84	11.55	.68	79
	9	-	-	-	-	-	-	-	-	-	-	-	-	9.11	.42	62
	12	-	-	-	-	-	-	-	-	-	-	-	-	7.36	.44	50
	15	-	-	-	-	-	-	-	-	-	-	-	-	6.41	.24	44
	18	14.49	.20	100	13.32	.95	92	12.15	.43	84	8.45	.61	59			
	30	14.38	.82	100	13.55	.89	94	10.08	.59	70	6.96	.44	48			
	42	14.04	.79	97	12.61	.92	87	9.20	.64	64	5.56	.26	39			
	Control	14.44	.98	-										14.62	.73	-
70	9	14.87	1.23	98	14.87	.56	98	14.35	.75	98	14.57	.93	96			
	18	-	-	-	-	-	-	-	-	-	12.69	.66	83			
	27	15.24	1.19	100	14.45	.51	95	13.39	.85	95	11.86	.68	78			
	54	14.37	.75	94	13.54	.73	89	12.18	.57	89	9.53	1.12	63			
	72	-	-	-	-	-	-	-	-	-	8.92	.25	57			
	90	13.72	.66	90	13.09	.81	86	10.15	.44	64	-					
	126	13.83	.21	91	12.53	.68	82	9.70	.54	64	-					
	Control	15.22	.92	-												
60	24	14.84	.68	102	-	-	-	14.66	.66	101	13.87	.55	96	14.09	.75	97
	36	-	-	-	-	-	-	-	-	-	-	-	-	13.03	.70	91
	48	14.10	.91	104	-	-	-	13.96	.67	96	13.10	.40	96	12.12	.50	84
	60	-	-	-	-	-	-	-	-	-	-	-	-	13.49	.68	93
	72	15.03	.57	101	-	-	-	13.86	.66	96	11.14	.72	77	11.10	60	77
	117	14.57	1.11	99	-	-	-	12.82	.97	86	10.62	.64	73			
	162	14.37	.85	97	-	-	-	12.61	1.18	87	9.02	70	62			
	Control	14.48	.72													

* Average of 12 specimens

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

Table 6. Effect of Aging on Wet Strength

Aging Temp.	Time of Aging	Relative Humidity, Percent																			
		0				10				25				50				75			
°C	Days	Avg kN/m	s* kN/m	n**	Retention %	Avg kN/m	s kN/m	n	Retention %	Avg kN/m	s kN/m	n	Retention %	Avg kN/m	s kN/m	n	Retention %	Avg kN/m	s kN/m	n	Retention %
90	1	.163	.020	12	218	.165	.014	12	220	.182	.020	12	243	.194	.018	10	259	-	-	-	-
	3	.244	.036	12	325	.222	.033	12	296	.280	.033	11	373	.330	.039	13	440	-	-	-	-
	6	.312	.033	12	416	.308	.037	11	411	.385	.047	12	513	.348	.025	12	464	-	-	-	-
	12	.378	.030	12	504	.387	.031	12	516	.406	.033	12	541	.231	.021	12	308	-	-	-	-
	18	.429	.048	12	572	.374	.054	11	499	.375	.037	12	500	.180	.023	11	240	-	-	-	-
	Control	.075	.014	12	-																
80	3	.144	.008	12	215	.150	.011	11	224	.156	.011	12	233	.192	.012	12	287	.217	.008	12	252
	6	.189	.018	11	282	.186	.032	12	278	.227	.024	12	339	.269	.034	12	401	.287	.025	12	334
	9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.292	.019	12	340
	12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.244	.025	12	284
	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.230	.025	12	267
	18	.279	.024	12	416	.299	.028	12	446	.346	.028	12	516	.331	.028	12	494	-	-	-	-
	30	.370	.045	12	552	.393	.025	11	587	.375	.024	11	560	.289	.012	12	431	-	-	-	-
	42	.404	.054	12	603	.422	.054	12	603	.378	.027	12	564	.180	.058	11	269	-	-	-	-
	Control	.067	.016	11	-													.086	.012	12	-
70	9	.135	.012	9	144	.144	.023	12	153	.159	.017	12	169	.188	.015	12	200	-	-	-	-
	18	-	-	-	-	-	-	-	-	-	-	-	-	.263	.058	11	280	-	-	-	-
	27	.194	.016	12	206	.203	.022	12	216	.254	.018	12	270	.299	.026	12	318	-	-	-	-
	54	.235	.039	12	250	.269	.038	12	286	.327	.010	12	348	.320	.025	12	340	-	-	-	-
	72	-	-	-	-	-	-	-	-	-	-	-	-	.375	.037	11	399	-	-	-	-
	90	.286	.018	12	304	.311	.033	12	331	.370	.032	12	394	-	-	-	-	-	-	-	-
	126	.331	.044	12	352	.415	.054	12	441	.356	.033	12	379	-	-	-	-	-	-	-	-
	Control	.094	.010	12	-																
60	24	.123	.011	12	162	-	-	-	-	.137	.010	12	180	.153	.018	12	201	.167	.020	10	220
	36	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.226	.020	12	297
	48	.157	.031	12	207	-	-	-	-	.197	.025	12	259	.221	.024	12	291	.260	.028	12	392
	60	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.271	.023	12	357
	72	.186	.025	12	245	-	-	-	-	.223	.039	12	293	.300	.020	12	395	.288	.026	12	379
	117	.225	.033	12	296	-	-	-	-	.301	.026	12	396	.316	.029	12	416	-	-	-	-
	162	.225	.029	12	296	-	-	-	-	.325	.015	12	428	.321	.026	11	422	-	-	-	-
	Control	.076	.013	12	-																

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

**n = number of specimens

Table 7. Effect of Aging on Elmendorf Tear

Aging Temp.	Time of Aging	Relative Humidity, Percent														
		0			10			25			50			75		
°C	Days	Avg* N	s** N	Retention %	Avg N	s N	Retention %	Avg N	s N	Retention %	Avg N	s N	Retention %	Avg N	s N	Retention
90	1	.85	.12	104	.87	.10	106	.79	.09	96	.77	.06	94	-	-	-
	3	.87	.09	106	.80	.10	98	.73	.08	89	.46	.05	56	-	-	-
	6	.73	.09	89	.69	.10	84	.52	.06	63	.22	.02	27	-	-	-
	12	.74	.11	90	.65	.08	79	.25	.03	30	.07	.02	9	-	-	-
	18	.76	.10	93	.59	.09	72	.20	.03	24	.06	.01	7	-	-	-
	Control	.82	.10	-												
80	3	.84	.11	91	.86	.11	93	.78	.08	85	.75	.08	82	.66	.09	78
	6	.77	.08	84	.84	.09	91	.73	.09	79	.53	.06	58	.50	.05	59
	9	-	-	-	-	-	-	-	-	-	-	-	-	.27	.02	32
	12	-	-	-	-	-	-	-	-	-	-	-	-	.20	.01	24
	15	-	-	-	-	-	-	-	-	-	-	-	-	.14	.01	16
	18	.83	.14	90	.88	.07	96	.54	.06	59	.22	.01	24	-	-	
	30	.77	.10	84	.82	.07	89	.34	.12	37	.12	.02	13	-	-	-
	42	.89	.12	97	.84	.05	91	.22	.02	24	.08	.01	9	-	-	-
	Control	.92	.09											.85	.10	
70	9	.80	.09	98	.85	.10	104	.82	.09	100	.67	.09	82	-	-	-
	18	-	-	-	-	-	-	-	-	-	.71	.08	87	-	-	-
	27	.80	.09	98	.80	.07	98	.64	.06	78	.50	.08	61	-	-	-
	54	.90	.14	110	.77	.11	94	.60	.06	73	.31	.04	38	-	-	-
	72	-	-	-	-	-	-	-	-	-	.25	.02	30	-	-	-
	90	.87	.11	106	.70	.10	85	.37	.04	45						
	126	.74	.09	90	.52	.06	63	.30	.03	37						
	Control	.82	.07	-												
60	24	.83	.11	89	-	-	-	.88	.13	95	.77	.10	83	.77	.10	83
	36	-	-	-	-	-	-	-	-	-	-	-	-	.69	.06	74
	48	.84	.08	90	-	-	-	.82	.10	88	.67	.09	72	.55	.07	59
	60	-	-	-	-	-	-	-	-	-	-	-	-	.55	.07	59
	72	.85	.12	91	-	-	-	.67	.08	72	.47	.07	51	.47	.04	51
	117	.83	.10	89	-	-	-	.62	.08	67	.43	.04	46	-	-	-
	162	.80	.11	86	-	-	-	.58	.08	62	.32	.06	34	-	-	-
	Control	.93	.10	-	-	-	-									

* Average of 12 specimens

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

Table 8. Effect of Aging on Acidity

Aging Temp.	Time of Aging	Relative Humidity, Percent														
°C	Days	0			10			25			50			75		
		Avg* (pH)	s** (pH)	$[H^+]$***	Avg (pH)	s (pH)	$[H^+]$	Avg (pH)	s (pH)	$[H^+]$	Avg (pH)	s (pH)	$[H^+]$	Avg (pH)	s (pH)	$[H^+]$
90	1	5.24	.04	4.0	5.19	.01	4.5	4.99	.01	7.0	4.78	.04	11.6			
	3	5.15	.18	5.0	5.09	.01	5.7	4.78	.03	11.6	4.51	.02	21.6			
	6	5.11	.06	5.4	4.95	.04	7.9	4.45	.06	24.8	4.18	.03	46.3			
	12	5.04	.10	6.4	4.80	.01	11.1	4.22	.06	42.2	3.98	.06	73.4			
	18	5.16	.03	4.8	4.76	.01	12.2	4.18	.02	46.3	4.00	.00	70.0			
	Control	5.45	.01	2.5												
80	3	5.49	.00	2.3	5.29	.02	3.6	5.14	.01	5.1	4.49	.01	8.1	4.60	.13	17.6
	6	5.29	.04	3.6	5.05	.03	6.2	4.9	.01	8.6	4.68	.00	14.6	4.36	.03	32.5
	9	-	-	-	-	-	-	-	-	-	-	-	-	4.20	.01	44.2
	12	-	-	-	-	-	-	-	-	-	-	-	-	4.16	.05	48.4
	15	-	-	-	-	-	-	-	-	-	-	-	-	4.02	.02	59.8
	18	5.17	.04	5.7	4.84	.03	10.1	4.6	.02	16.8	4.22	.01	42.2	-	-	-
	30	5.10	.01	5.6	4.72	.00	13.3	4.4	.03	27.9	4.16	.03	48.4	-	-	-
	42	5.06	.01	6.1	4.67	.03	15.0	4.3	.00	33.5	4.03	.00	65.3	-	-	-
	Control	5.45	.07	2.5										4.99	.08	7.2
70	9	5.10	.05	5.6	5.13	.01	5.2	5.00	.01	7.0	4.92	.01	8.4			
	18	-	-	-	-	-	-	-	-	-	4.79	.01	11.3			
	27	5.13	.03	5.2	4.94	.01	7.2	4.74	.02	12.7	4.50	.05	21.1			
	54	5.24	.08	4.0	4.97	.04	7.5	4.59	.01	18.0	4.32	.05	33.5			
	72	-	-	-	-	-	-	-	-	-	4.29	.07	35.9			
	90	5.20	.01	4.4	4.76	.08	12.2	4.33	.01	32.8	-	-	-			
	126	5.06	.01	6.1	4.59	.01	18.0	4.26	.04	38.4	-	-	-			
	Control	5.42	.03	2.7												
60	24	5.40	.05	2.8	-	-	-	5.24	.06	4.6	5.17	.04	4.7	4.97	.03	7.5
	36	-	-	-	-	-	-	-	-	-	-	-	-	4.67	.03	15.0
	48	5.22	.02	4.2	-	-	-	5.02	.07	6.7	4.75	.02	12.7	4.50	.03	22.1
	60	-	-	-	-	-	-	-	-	-	-	-	-	4.50	.01	22.1
	72	5.23	.01	4.1	-	-	-	4.86	.01	9.7	4.51	.00	21.6	4.38	.05	29.2
	117	5.21	.02	4.4	-	-	-	4.66	.02	15.3	4.47	.00	23.7			
	162	5.19	.01	4.5				4.57	.00	18.8	4.24	.04	40.3			
	Control	5.49	.08	2.3												

* Average of 2 specimens

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

*** $[H^+]$ calculated from pH values and expressed in milliequivalents per hundred grams of paper.

Table 9. Effect of Aging on Solubility in Hot 1% Alkali

Aging Temp.	Time of Aging	Relative Humidity, Percent				
		0	10	25	50	75
		Avg* %	Avg %	Avg %	Avg %	Avg %
90	1	3.51	3.66	5.14	7.29	
	3	4.49	4.76	7.04	12.87	
	6	4.18	5.79	11.68	21.51	
	12	4.82	7.43	17.88	31.38	
	18	4.52	7.54	21.42	32.69	
	Control	3.50				
80	3	3.92	4.23	5.07	7.46	9.63
	6	4.01	4.42	5.96	9.93	15.02
	9	-	-	-	-	19.90
	12	-	-	-	-	24.17
	15	-	-	-	-	27.69
	18	4.23	6.56	9.46	20.70	-
	30	4.98	9.07	16.06	28.23	-
	42	5.14	8.50	18.05	31.00	-
	Control	4.00				4.49
70	9	4.73	5.28	6.62	8.52	
	18	-	-	-	9.25	
	27	3.97	4.96	7.57	13.85	
	54	4.80	6.28	9.22	18.40	
	72	-	-	-	26.50	
	90	4.80	7.67	14.98		
	126	4.82	9.41	22.91		
	Control	4.17				
60	24	3.84	-	5.16	5.80	6.88
	36	-	-	-	-	10.08
	48	4.42	-	6.50	7.97	12.84
	60	-	-	-	-	-
	72	4.43	-	7.80	13.50	13.52
	117	4.45	-	11.49	15.64	
	162	4.57	-	10.18	20.85	
	Control	3.30				

* Average of 2 specimens

Table 10. Effect of Aging on Copper Number

Aging Temp.	Time of Aging	Relative Humidity, Percent				
°C	Days	0	10	25	50	75
		Avg* Cu No.	Avg Cu No.	Avg Cu No.	Avg Cu No.	Avg Cu No.
90	1	.72	.82	1.20	1.63	
	3	.73	.88	1.32	3.04	
	6	.85	1.13	2.42	6.06	
	12	.81	1.44	4.79	10.39	
	18	.80	1.39	5.99	13.13	
	Control	.61				
80	3	.73	.76	.89	1.60	3.19
	6	.65	.85	1.18	2.40	4.14
	9	-	-	-	-	5.49
	12	-	-	-	-	6.51
	15	-	-	-	-	8.58
	18	.72	1.00	1.86	5.50	-
	30	.73	1.36	3.65	8.44	-
	42	.79	1.76	4.72	10.62	-
	Control	.61				0.58
70	9	.70	.71	.81	1.40	
	18	-	-	-	2.30	
	27	.66	.92	1.23	3.37	
	54	.70	1.00	2.47	5.04	
	72	-	-	-	5.82	
	90	.84	1.31	3.37		
	126	.79	1.90	4.46		
	Control	.61				
60	24	.76	-	.82	1.03	1.39
	36	-	-	-	-	2.33
	48	.68	-	1.17	1.61	2.95
	60	-	-	-	-	2.97
	72	.62	-	1.23	3.47	3.60
	117	.60	-	1.87	4.28	
	162	.60	-	2.05	6.15	
	Control	.54				

* Average of 2 specimens

Table 11. Effect of Aging on Brightness

Aging Temp.	Time of Aging	Relative Humidity, Percent														
°C	Days	0			10			25			50			75		
		Avg* %	s** %	Retention %	Avg %	s %	Retention %	Avg %	s %	Retention %	Avg %	s %	Retention %	Avg %	s %	Retention %
90	1	83.2	0.3	97.4	82.9	0.3	97.1	80.5	.3	94.3	75.5	0.5	88.4			
	3	82.0	0.4	96.0	81.5	0.4	95.4	74.6	.5	87.4	62.5	1.6	73.2			
	6	81.2	0.4	95.1	78.9	0.5	92.4	69.0	1.2	80.8	51.8	1.8	60.7			
	12	80.0	0.4	93.7	76.6	0.4	89.7	57.9	2.2	67.8	40.4	2.5	47.3			
	18	79.8	0.5	93.4	75.9	0.7	88.9	52.3	2.8	61.2	33.7	2.3	39.5			
	Control	85.4	0.5	-												
80	3	83.1	0.4	98.2	82.7	0.5	96.6	80.8	0.5	95.5	74.6	0.4	88.2	70.9	0.7	83.6
	6	82.9	0.4	98.0	82.0	0.4	95.8	77.8	.3	92.0	67.7	0.4	80.0	62.7	0.8	73.9
	9	-	-	-	-	-	-	-	-	-	-	-	-	54.8	1.1	64.6
	12	-	-	-	-	-	-	-	-	-	-	-	-	50.9	1.3	60.0
	15	-	-	-	-	-	-	-	-	-	-	-	-	49.1	1.3	57.9
	18	81.8	0.4	95.6	79.4	0.4	92.8	71.4	.6	83.4	54.0	1.7	63.1	-	-	-
	30	81.2	0.4	94.8	77.2	0.7		62.9	1.2	73.5	47.3	2.0	55.3	-	-	-
	42	81.5	0.5	95.2	75.6	0.5	88.3	59.1	1.2	69.0	39.9	3.2	46.6	-	-	-
	Control	85.6	0.4	-										84.8	0.6	-
70	9	84.1	0.5	99.4	83.3	0.6	98.5	81.2	0.6	96.0	76.7	0.6	90.7			
	18	-	-	-	-	-	-	-	-	-	69.5	0.5	82.1			
	27	83.2	0.5	98.9	82.3	0.4	97.3	76.7	.4	90.7	63.1	0.8	74.6			
	54	82.3	0.4	97.3	80.5	0.5	95.2	71.6	.7	84.6	54.9	2.0	64.9			
	72	-	-	-	-	-	-	-	-	-	49.6	1.9	58.6			
	90	82.2	0.4	97.2	79.3	0.5	93.7	63.5	1.0	75.0	-	-	-			
	126	80.9	0.5	95.6	73.5	0.6	86.9	59.9	1.3	70.8	-	-	-			
	Control	84.6	0.1	-												
60	24	83.8	0.4	98.6	-	-	-	82.3	.4	96.8	79.8	0.5	93.9	75.6	1.2	88.9
	36	-	-	-	-	-	-	-	-	-	-	-	-	71.9	1.1	84.6
	48	83.8	0.6	98.0	-	-	-	78.7	.5	92.6	72.9	0.8	86.2	66.4	1.4	78.1
	60	-	-	-	-	-	-	-	-	-	-	-	-	68.9	0.6	81.0
	72	83.8	0.4	98.1	-	-	-	77.5	.4	91.2	64.7	1.0	76.1	63.9	0.7	75.2
	117	83.4	0.5	97.8	-	-	-	74.8	.5	88.0	61.3	0.9	72.5			
	162	83.1	0.4	98.6	-	-	-	73.4	.4	86.4	58.8	0.4	69.5			
	Control	85.0	0.8	-												

* Average of 12 specimens

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

Table 12. Effect of Aging on Moisture Regain

Aging Temp.	Time of Aging	Relative Humidity, Percent				
°C	Days	0	10	25	50	75
		Avg* %	Avg %	Avg %	Avg %	Avg %
90	1	6.87	7.06	6.81	6.66	
	3	6.73	6.80	6.62	6.63	
	6	6.63	6.63	6.18	5.40	
	12	6.42	6.53	5.39	4.48	
	18	6.21	6.77	5.50	5.32	
	Control	7.37				
80	3	6.64	6.67	6.47	6.23	6.35
	6	6.74	6.66	6.27	6.25	
	9	-	-	-	6.03	
	12	-	-	-	-	5.86
	15	-	-	-	-	5.9
	18	6.68	6.68	6.48	5.72	
	30	6.60	6.43	6.07	5.22	
	42	6.49	6.43	5.74	5.02	
	Control	7.17				6.69
70	9	6.80	6.58	6.58	6.38	
	18	-	-	-	6.53	
	27	6.68	6.29	6.20	5.89	
	54	6.58	6.55	6.66	5.80	
	72	-	-	-	5.40	
	90	6.88	6.57	5.51	-	
	126	6.44	6.22	5.79	-	
	Control	7.26				
60	24	6.82	-	6.69	6.52	6.74
	36	-	-	-	-	6.91
	48	6.83	-	6.40	6.50	6.47
	60	-	-	-	-	6.16
	72	6.66	-	6.55	6.03	6.00
	117	6.80	-	6.56	6.21	
	162	6.96	-	6.30	5.87	
	Control	7.03				

* Average of 2 specimens

Table 13. Heats of Activation and Degradation Rates for Zero Span Tensile at Various Conditions

Moisture Conditions	Heat of Activation	Degradation Rate at 23 °C 50% RH
	kcal/mole	x10^6
25% RH	29.0	1.7
50% RH	26.5	7.8
1405 N/m^2	——	*4.6 - 6.8
14932 N/m^2	18.3	49.8
29330 N/m^2	16.3	141.1

*Estimated

Table 14. Heats of Activation and Degradation Rates for Brightness at Various Conditions

Moisture Conditions	Heat of Activation	Degradation Rate at 23 °C
	kcal/mole	x10^6
25% RH	27.3	2.16
50% RH	25.4	8.06
1405 N/m^2	——	*11.7 - 12.8
14932 N/m^2	13.2	136.1
29330 N/m^2	13.8	243.9

*Estimated

Fig. 1 Change in wet breaking strength of paper with time when aged at 60°C and various relative humidities.

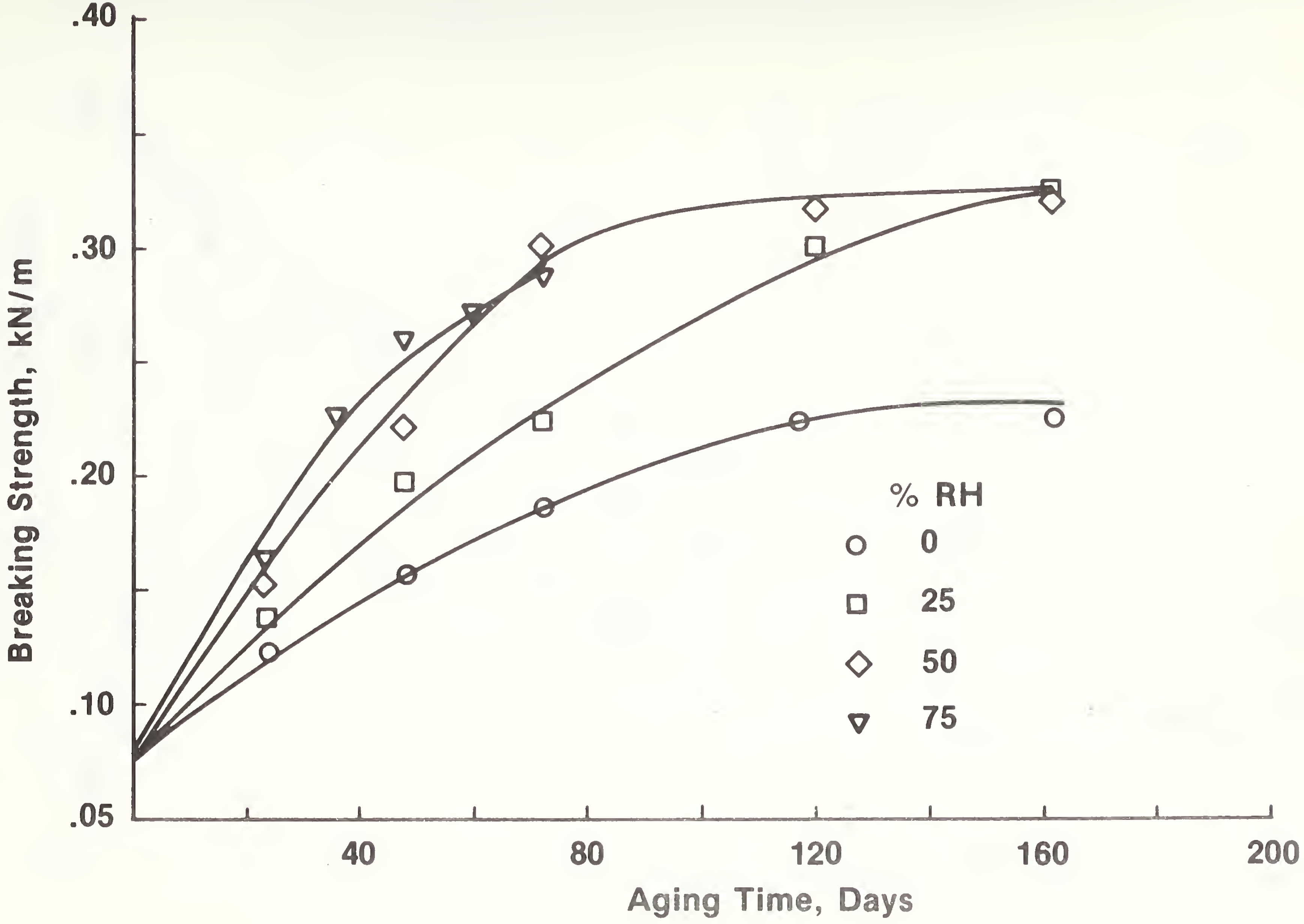


Fig. 2 Change in wet breaking strength of paper with time when aged at 70°C and various relative humidities.

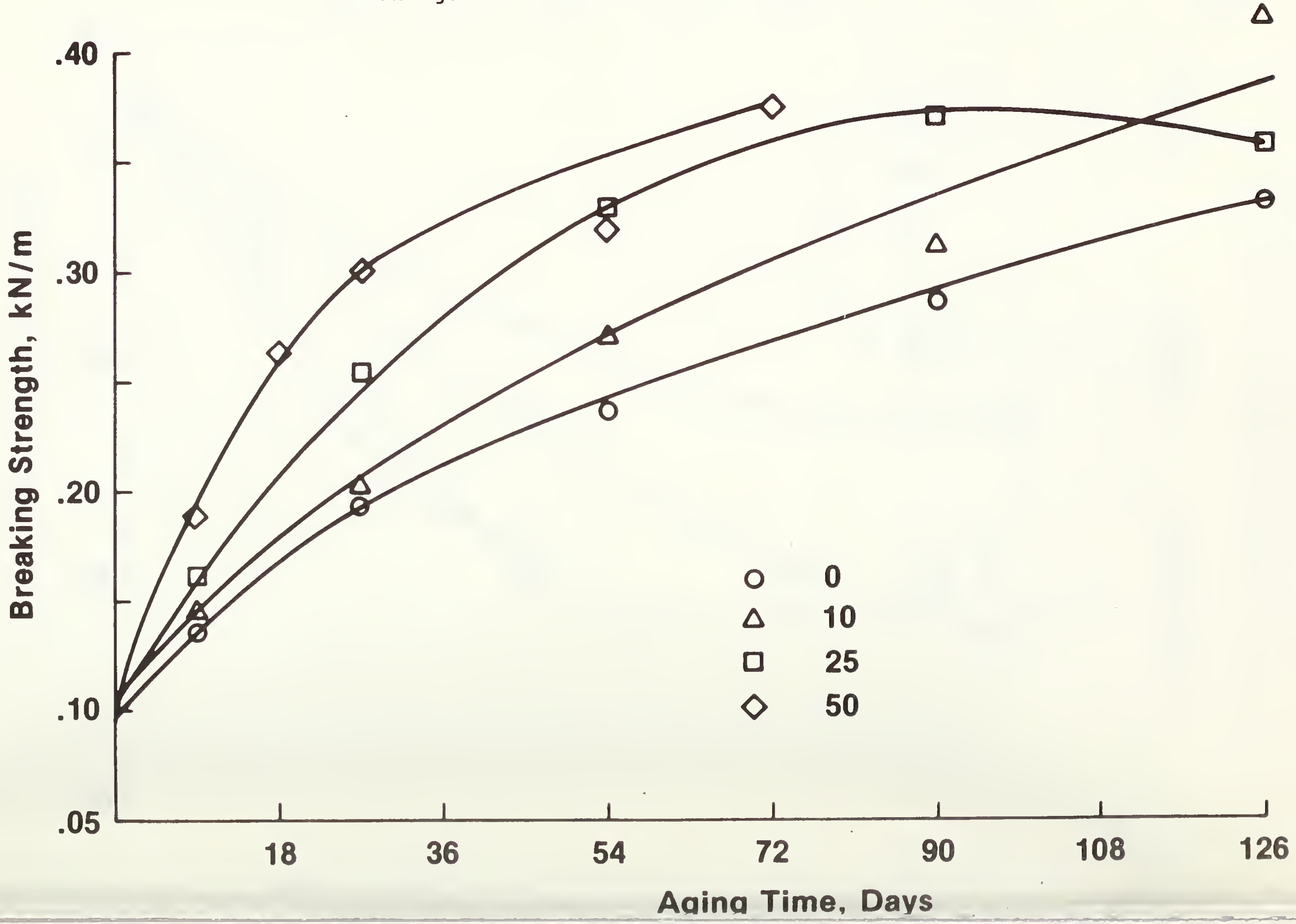


Fig. 3 Change in wet breaking strength of paper with time when aged at 80°C and various relative humidities.

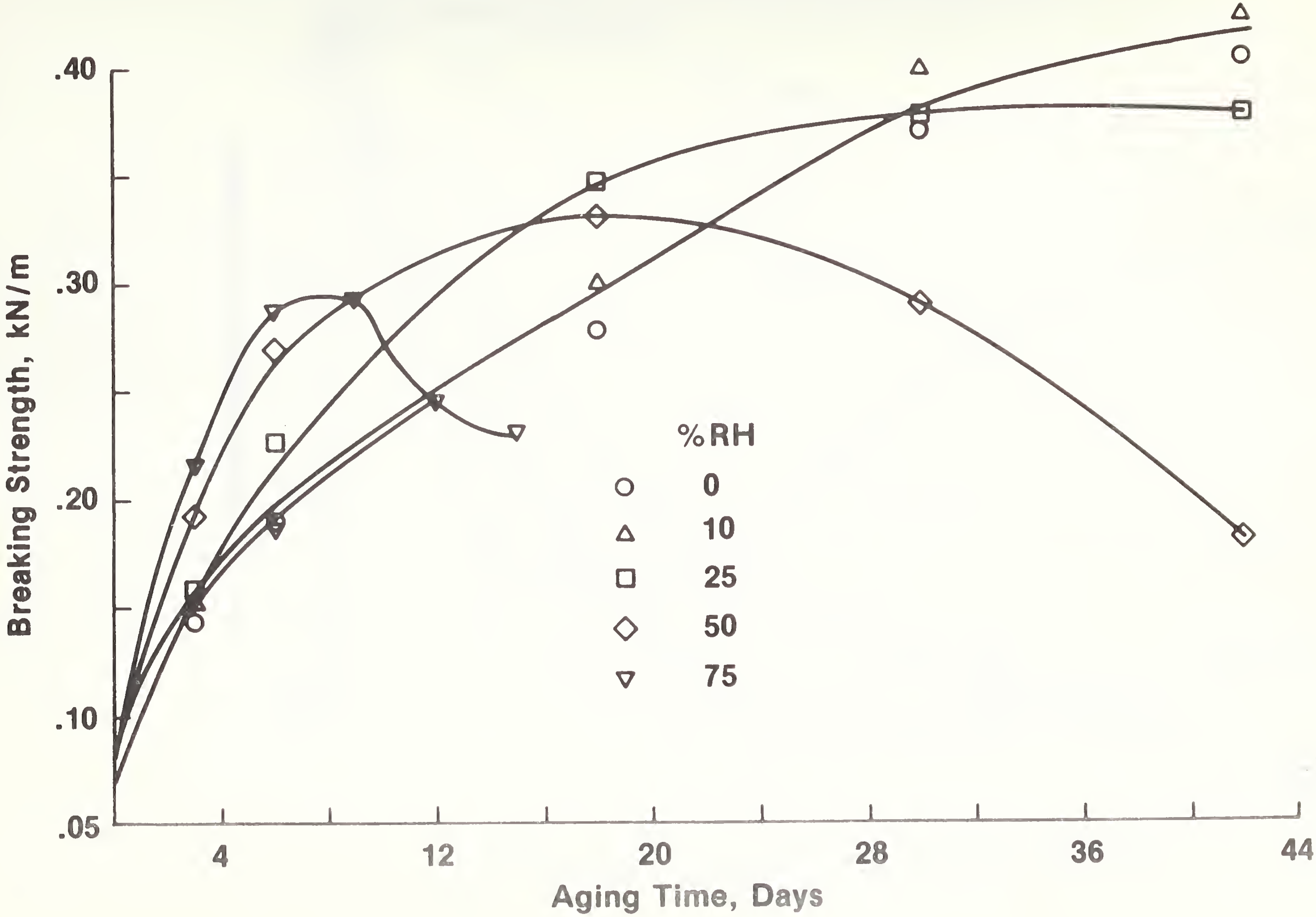


Fig. 4 Change in wet breaking strength of paper with time when aged at 90°C and various relative humidities.

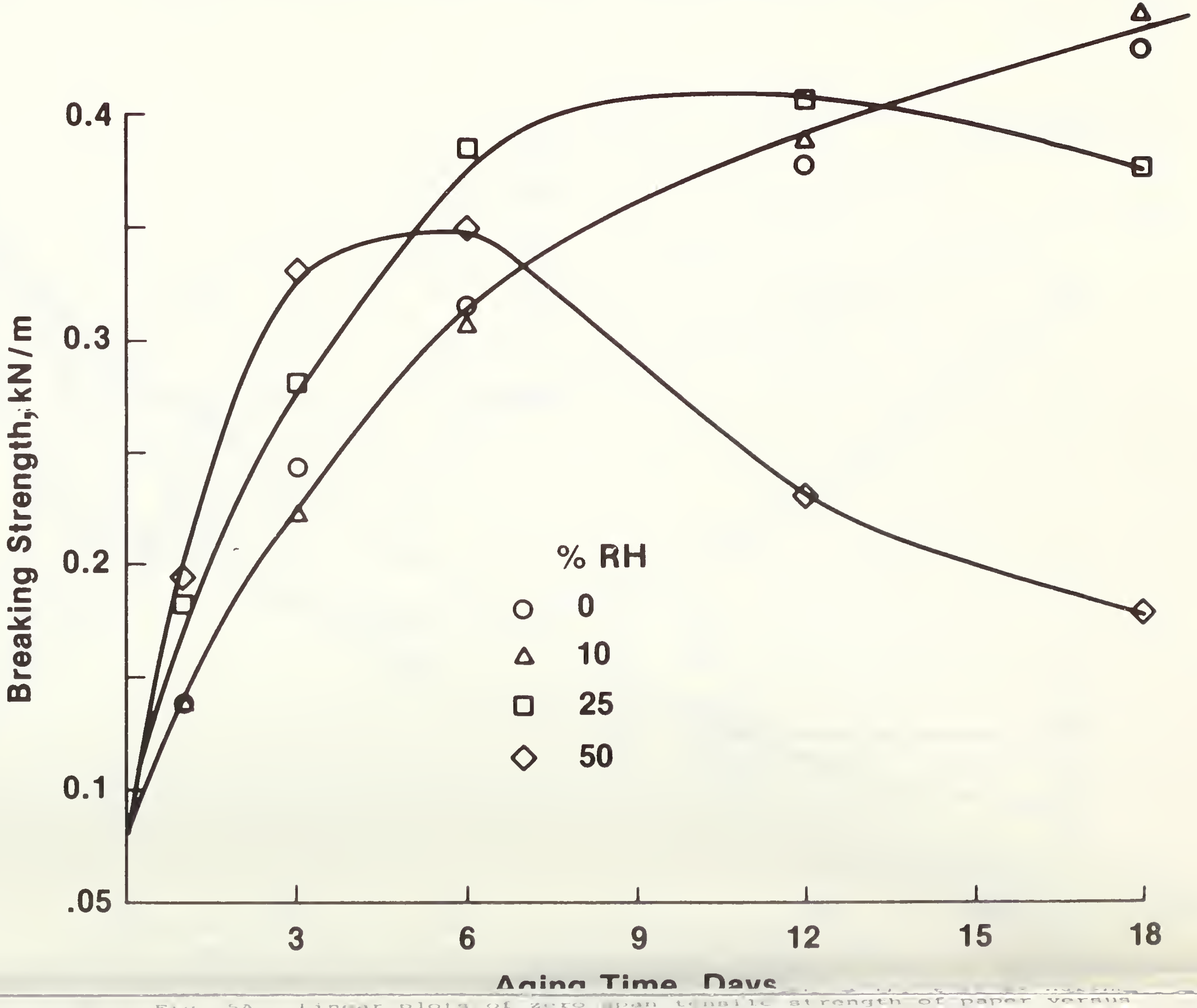


Fig. 5A. Linear plots of zero span tensile strength of paper versus time when aged at 90°C and various relative humidities.

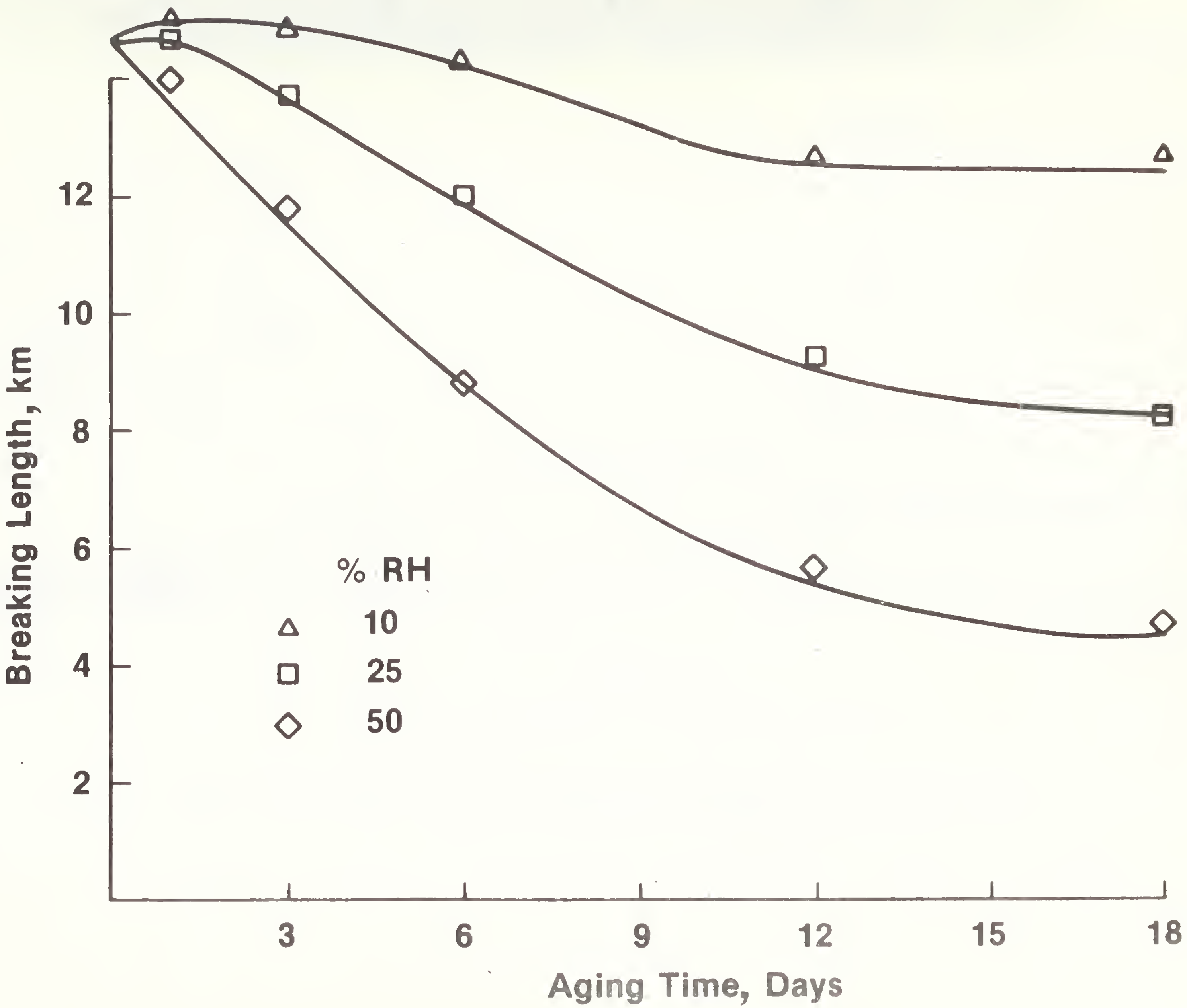


Fig. 5B. Semi-logrithmic plots of zero span tensile strength of paper versus time when aged at 90°C and various relative humidities.

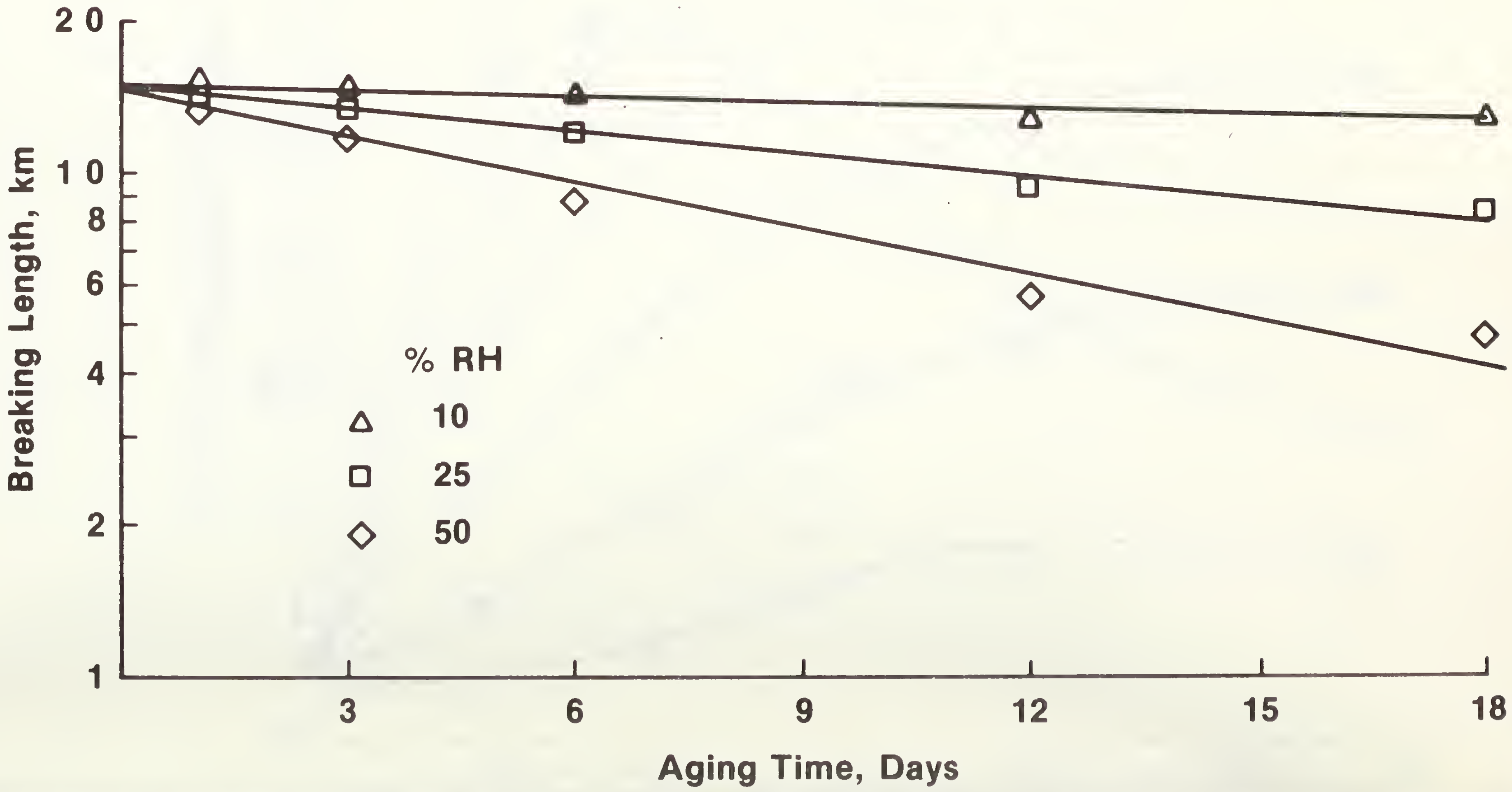


Fig. 6A. Linear plots of Elmendorf tear of paper versus time when aged at 90°C and various relative humidities.

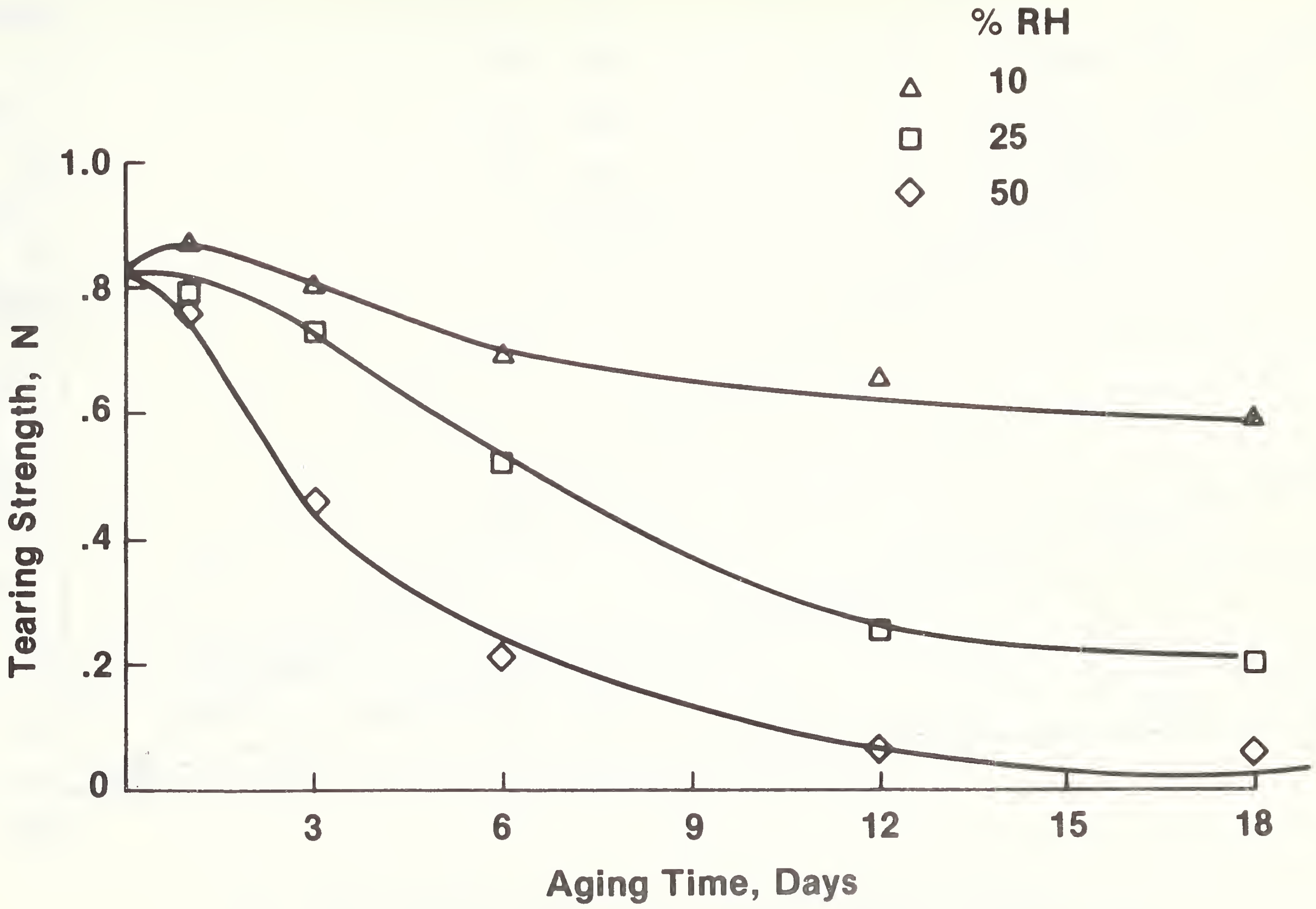
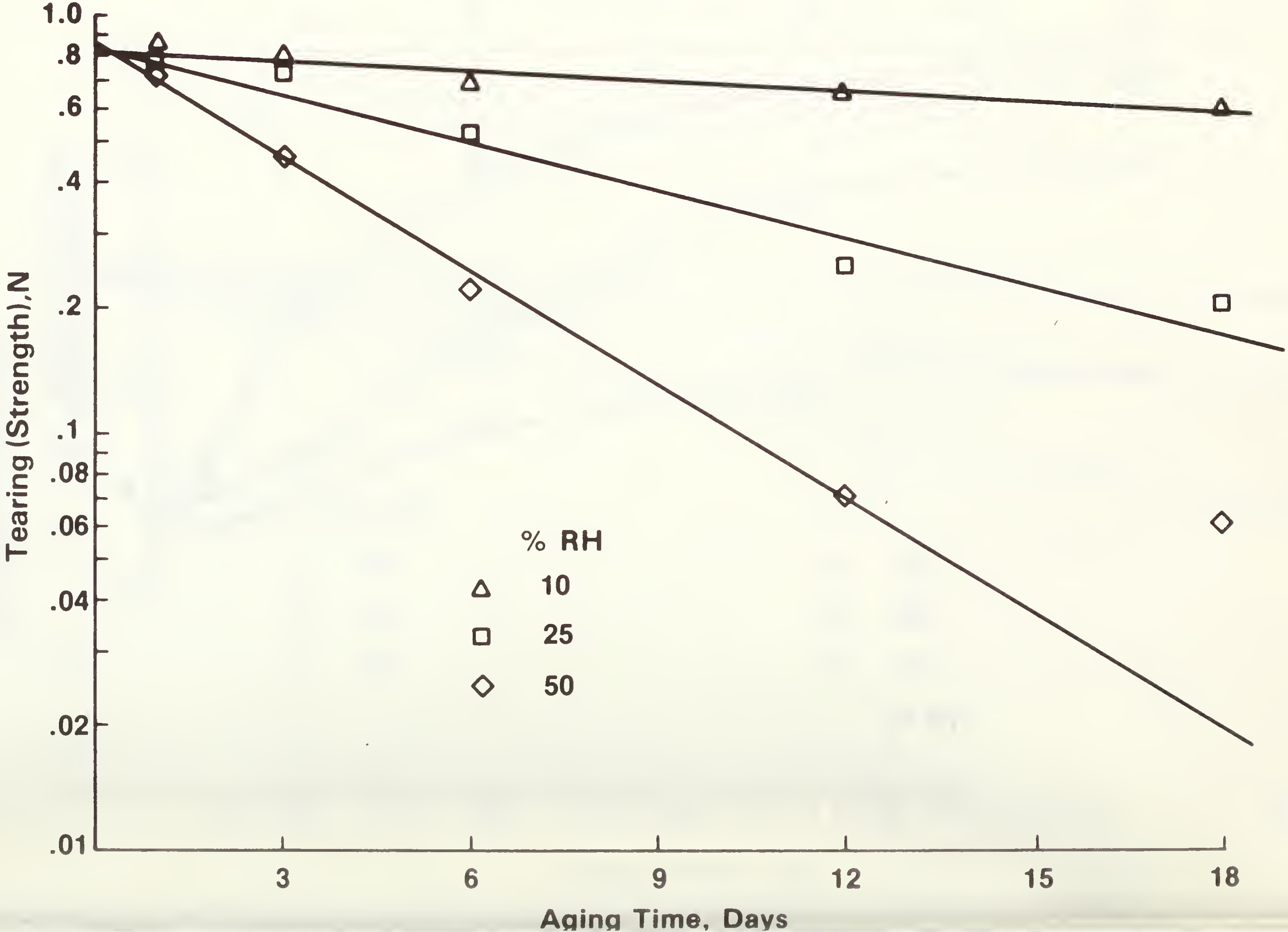


Fig. 6B. Semi-logrithmic plots of Elmendorf tear of paper versus time when aged at 90°C and various relative humidities.



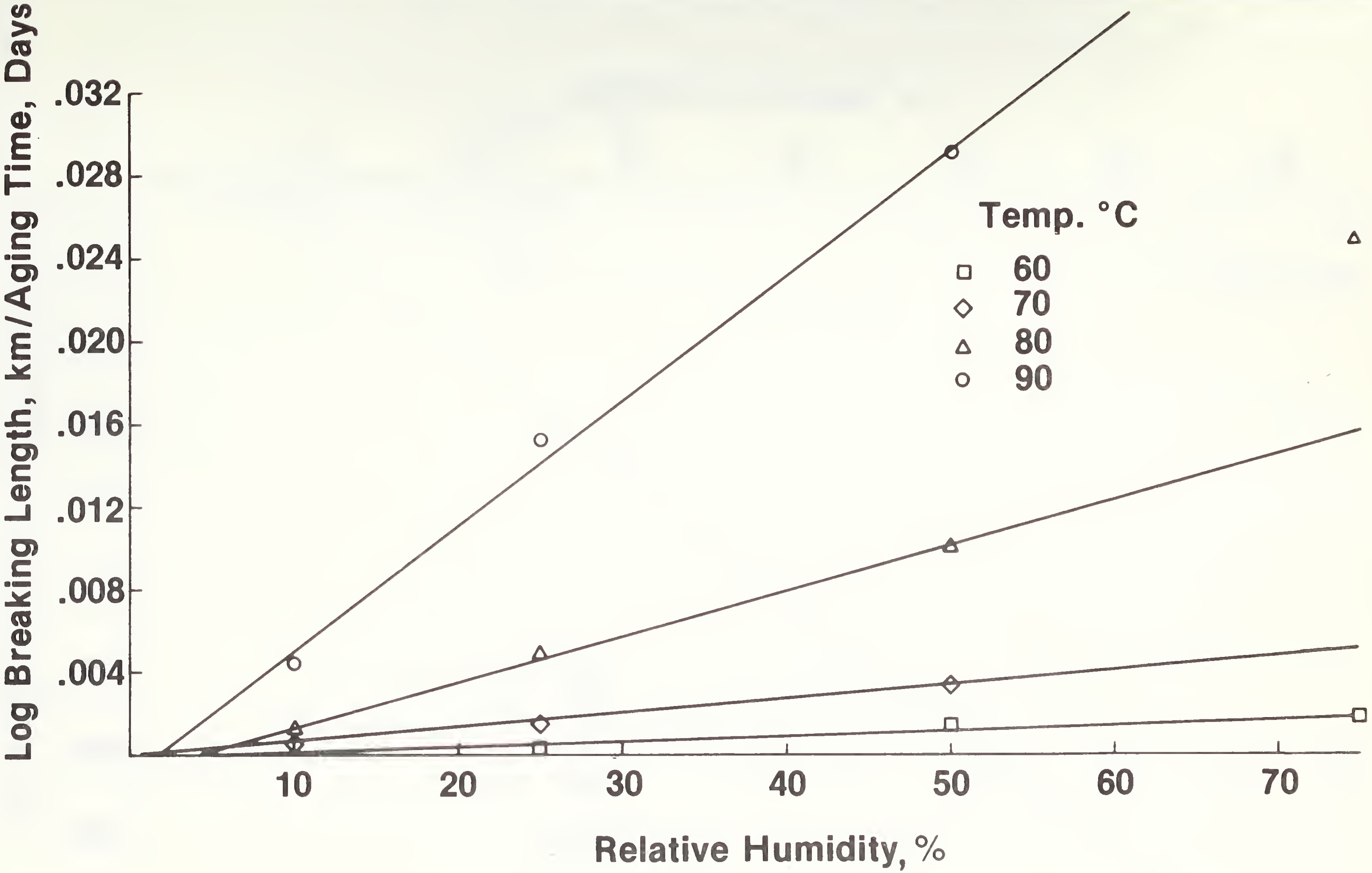


Fig. 7. Change in degradation rate of zero span tensile strength of paper with relative humidity when aged at various elevated temperatures.

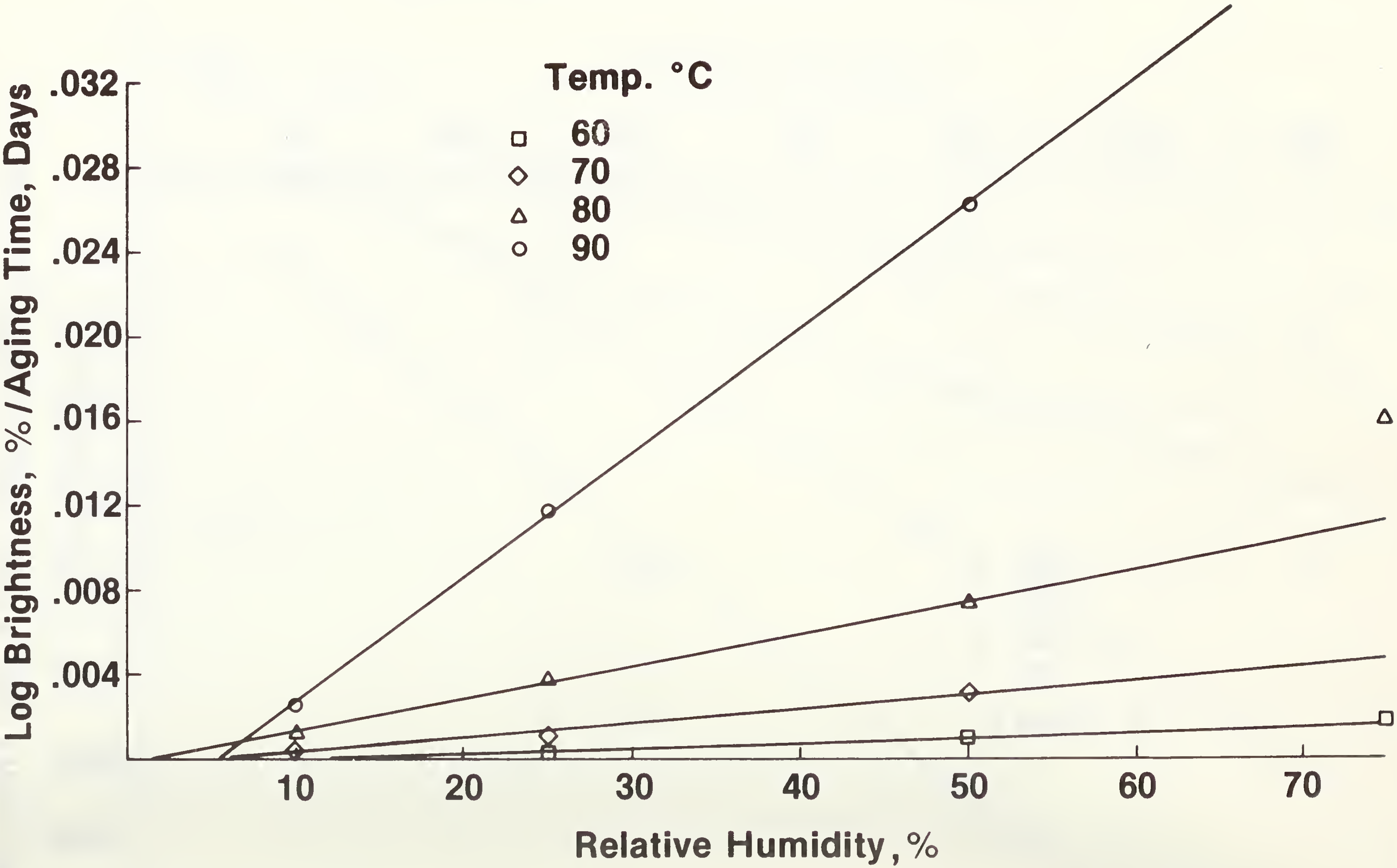


Fig. 8. Change in degradation rate of paper brightness with relative humidity when aged at various elevated temperatures.

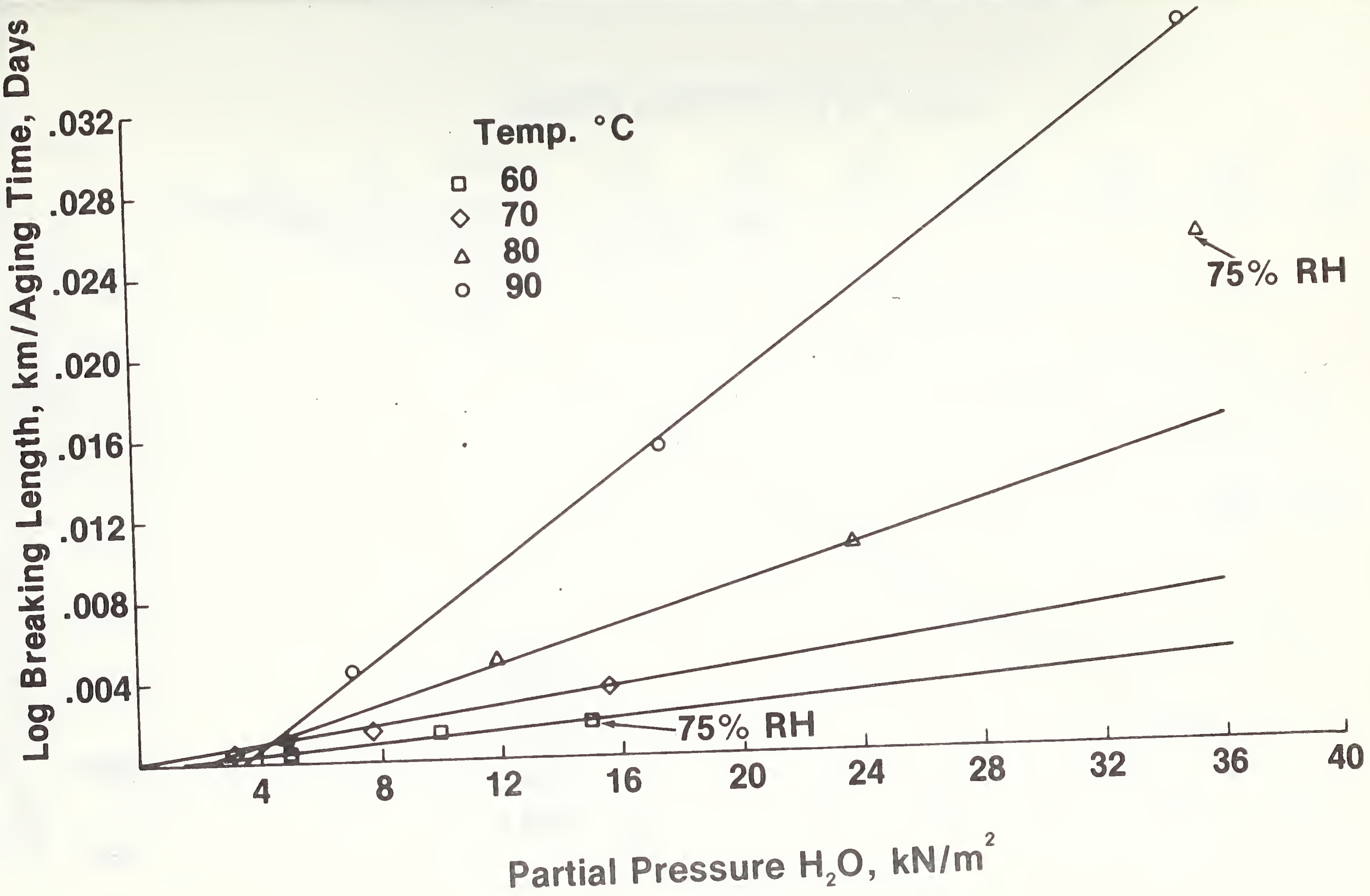


Fig. 9 Change in degradation rate of zero span tensile strength of paper with partial pressure of water when aged at various elevated temperatures.

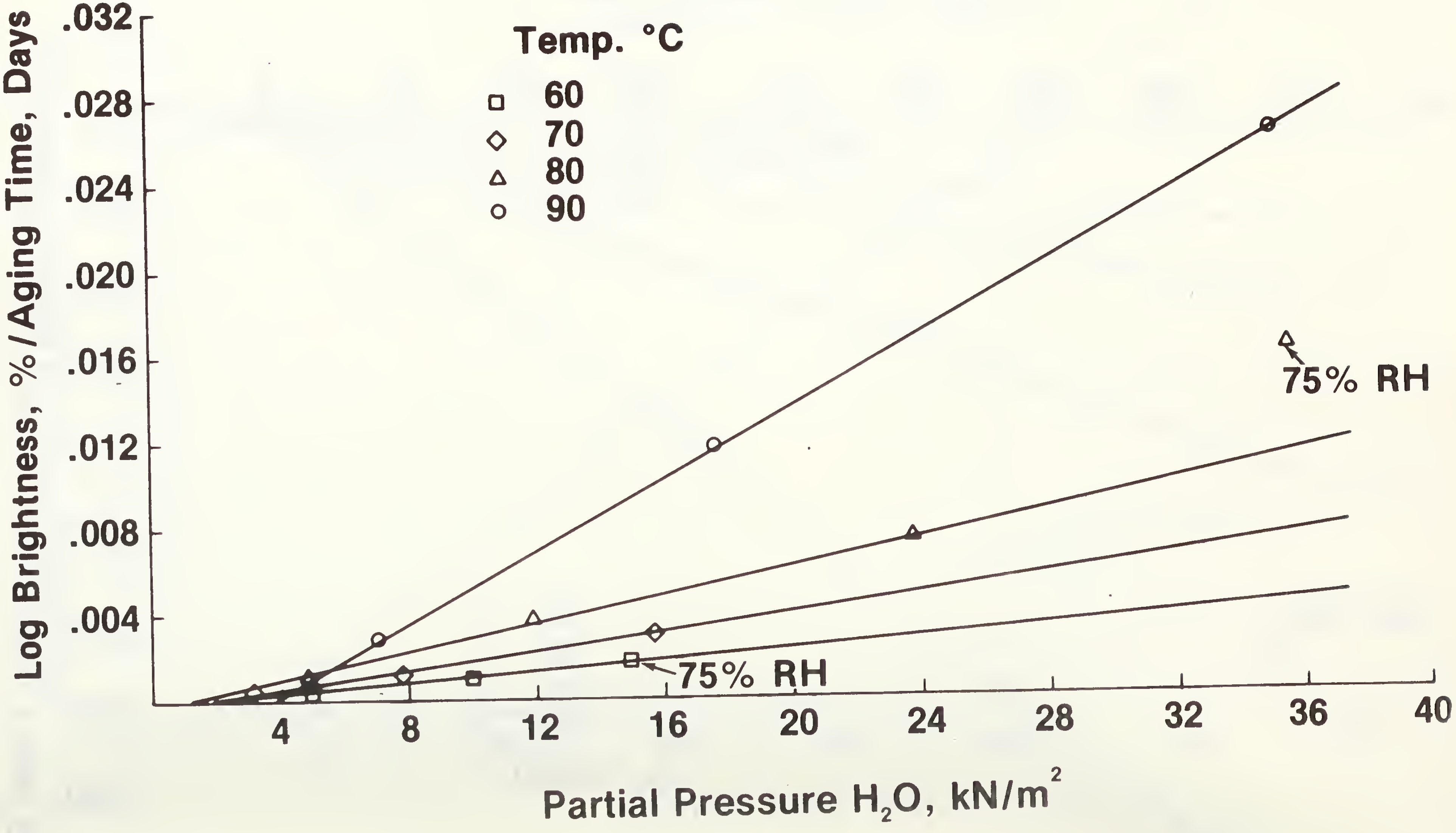


Fig. 10. Change in the degradation rate of paper brightness with partial pressure of water when aged at various elevated temperatures.

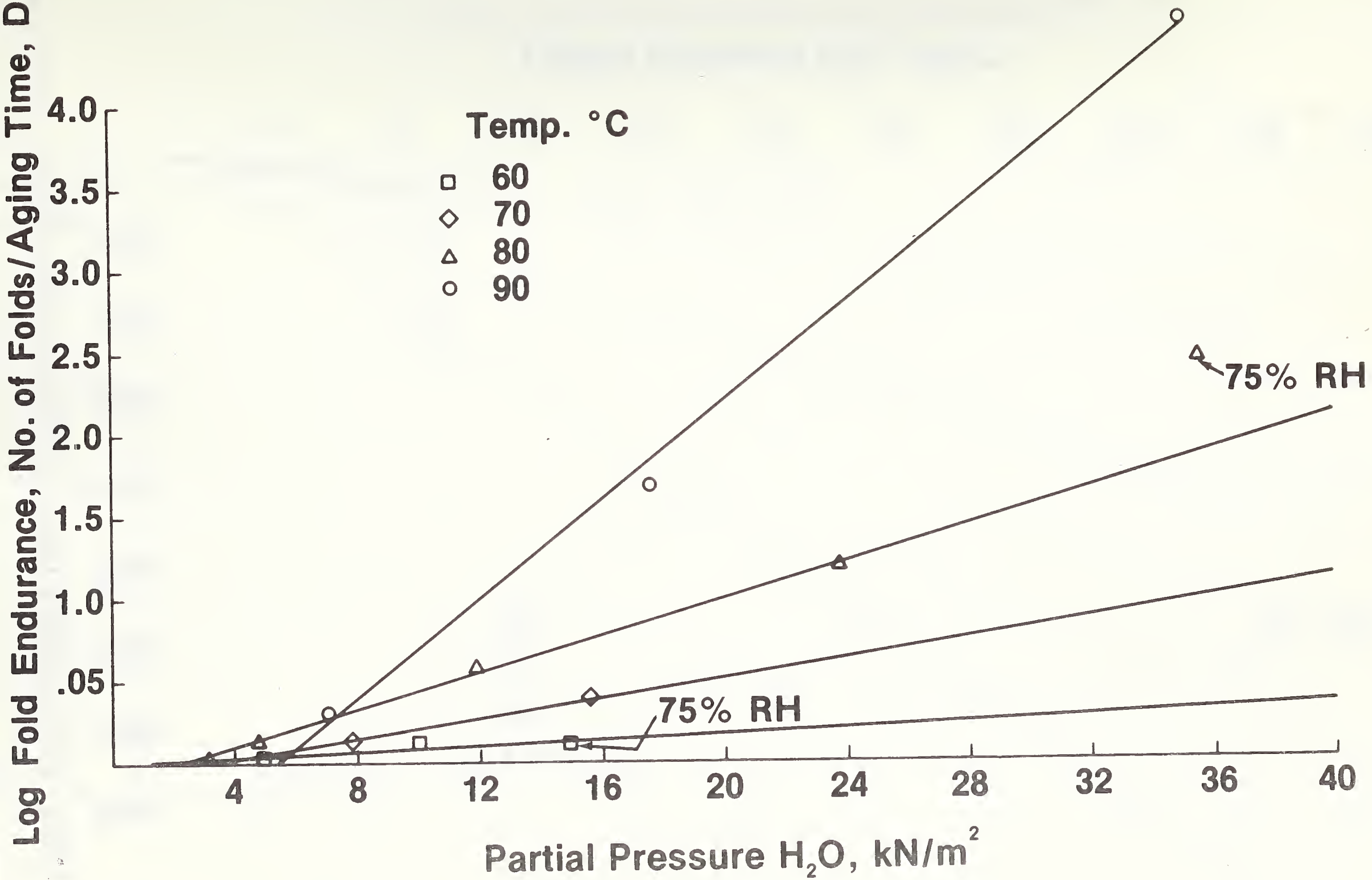


Fig. 11. Change in degradation rate of folding endurance of paper with partial pressure of water when aged at several elevated temperatures.

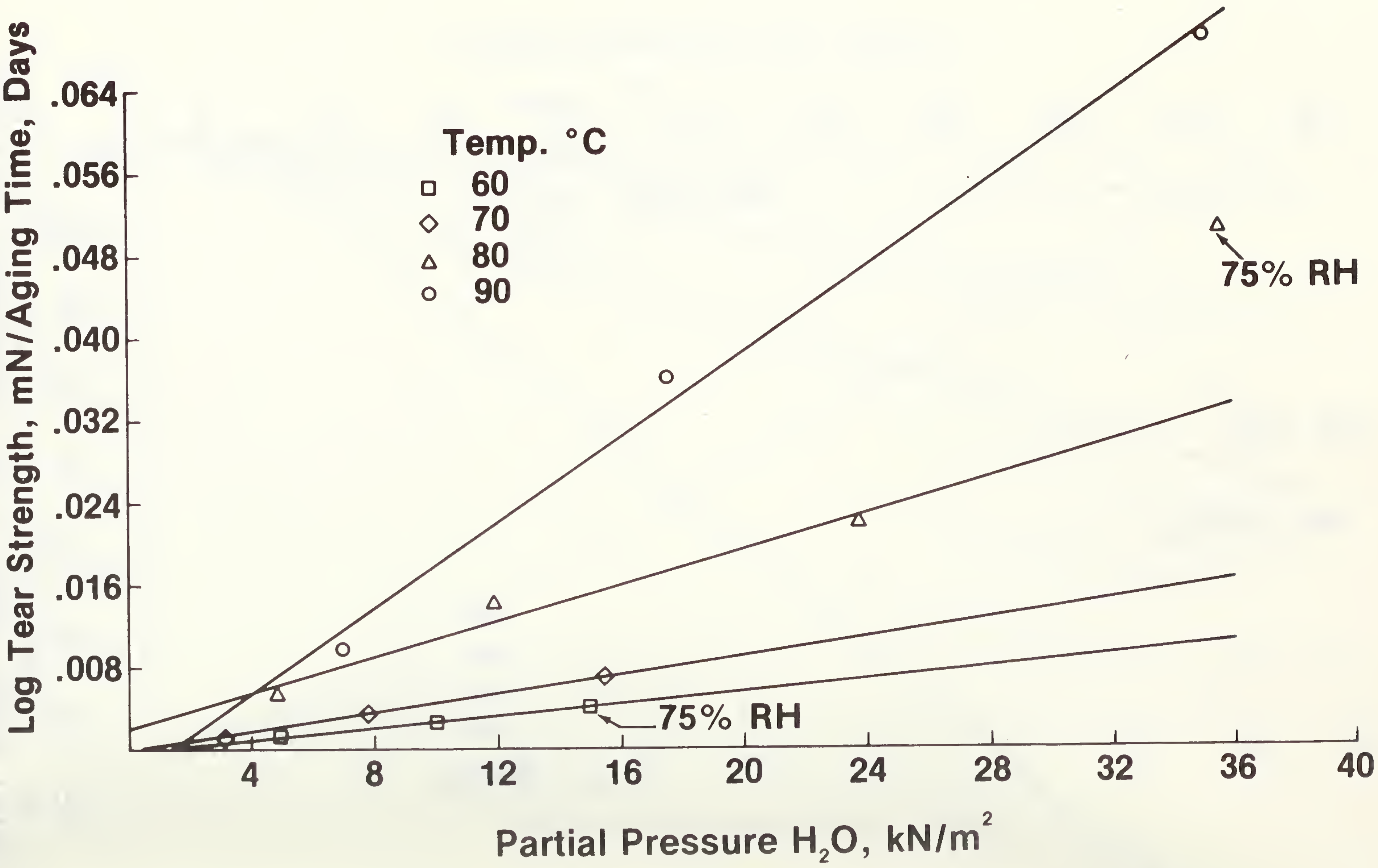
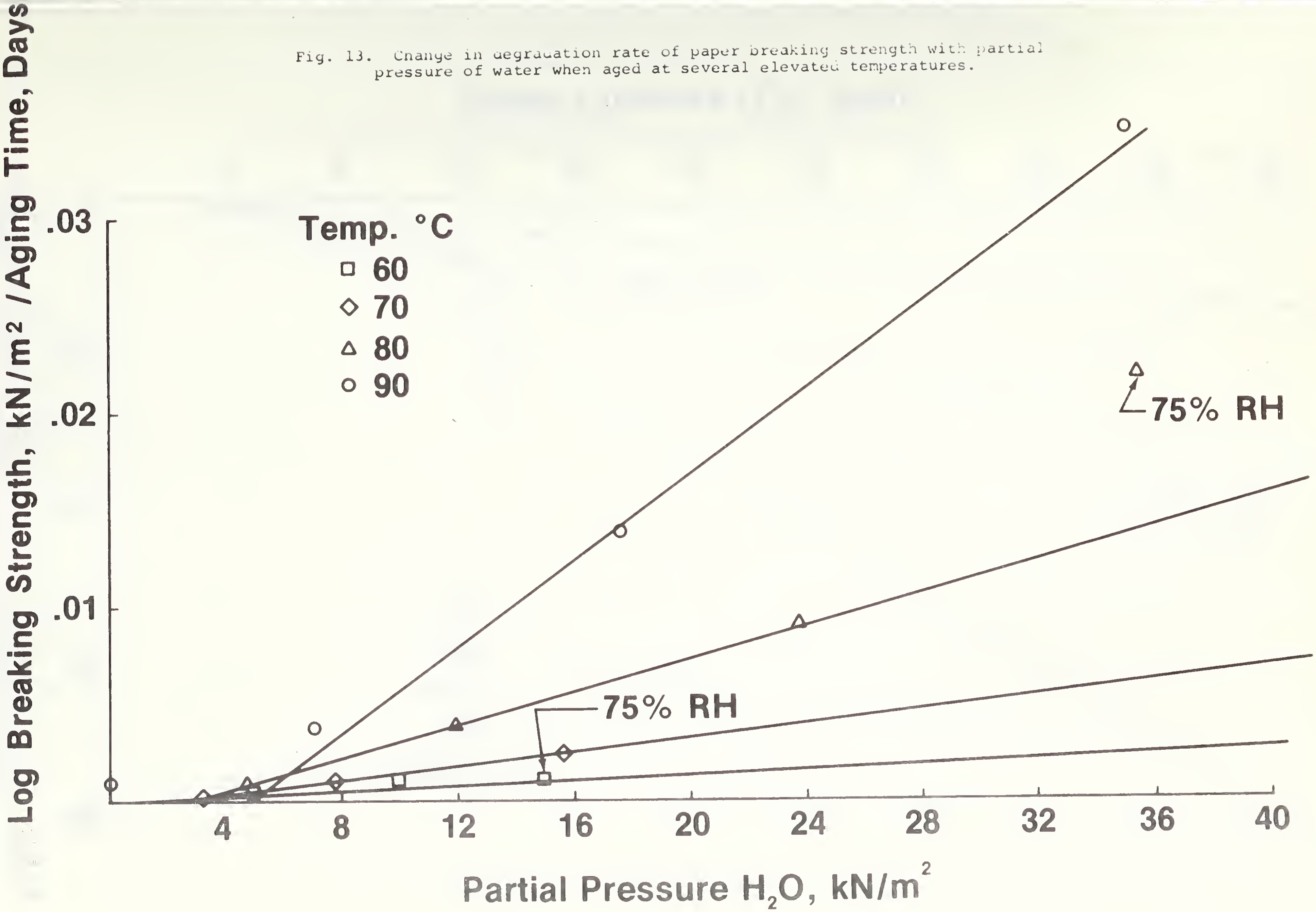


Fig. 12. Change in degradation rate of Elmendorf tear of paper with partial pressure of water when aged at several elevated temperatures.

Fig. 13. Change in degradation rate of paper breaking strength with partial pressure of water when aged at several elevated temperatures.



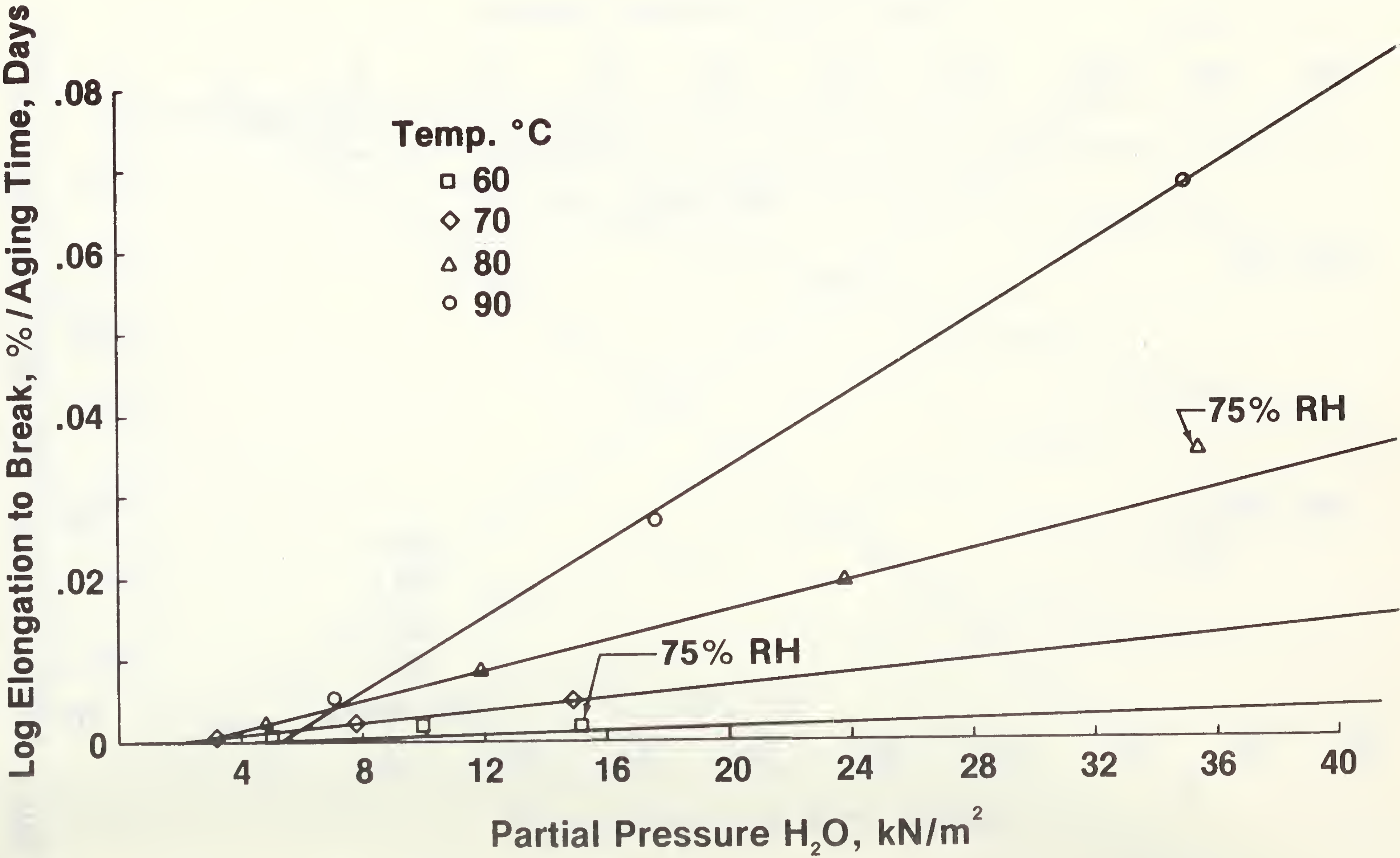
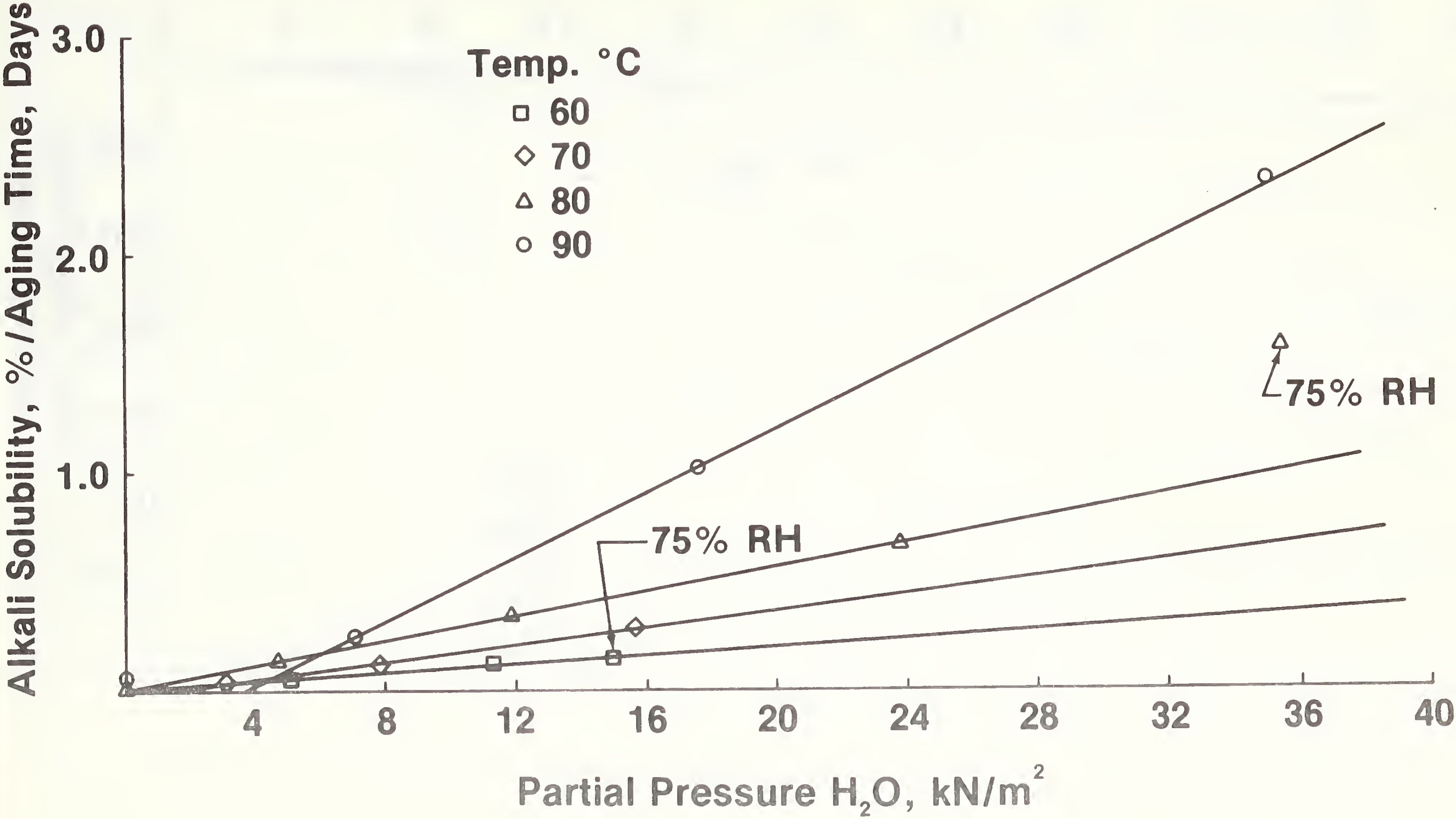


Fig. 14. Change in the degradation rate of elongation to break of paper with partial pressure of water when aged at several elevated temperatures.

Fig. 15. Change in the rate of alkali solubility of paper with partial pressure of water when aged at several elevated temperatures.



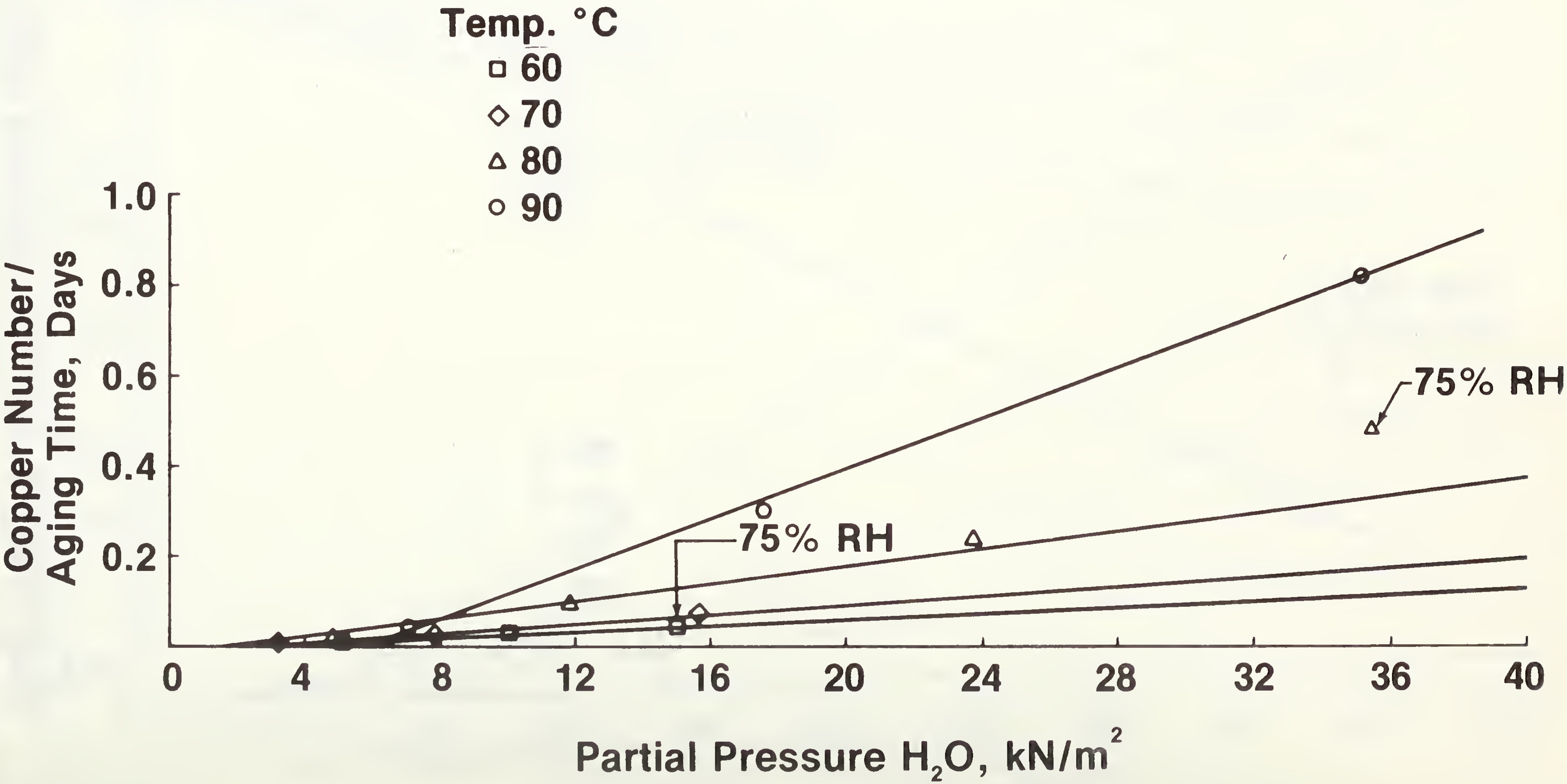


Fig. 16. Change in the copper number rate of paper with partial pressure of water when aged at several elevated temperatures.

Fig. 17. Change in the rate of extractable acidity of paper with partial pressure of water when aged at several elevated temperatures.

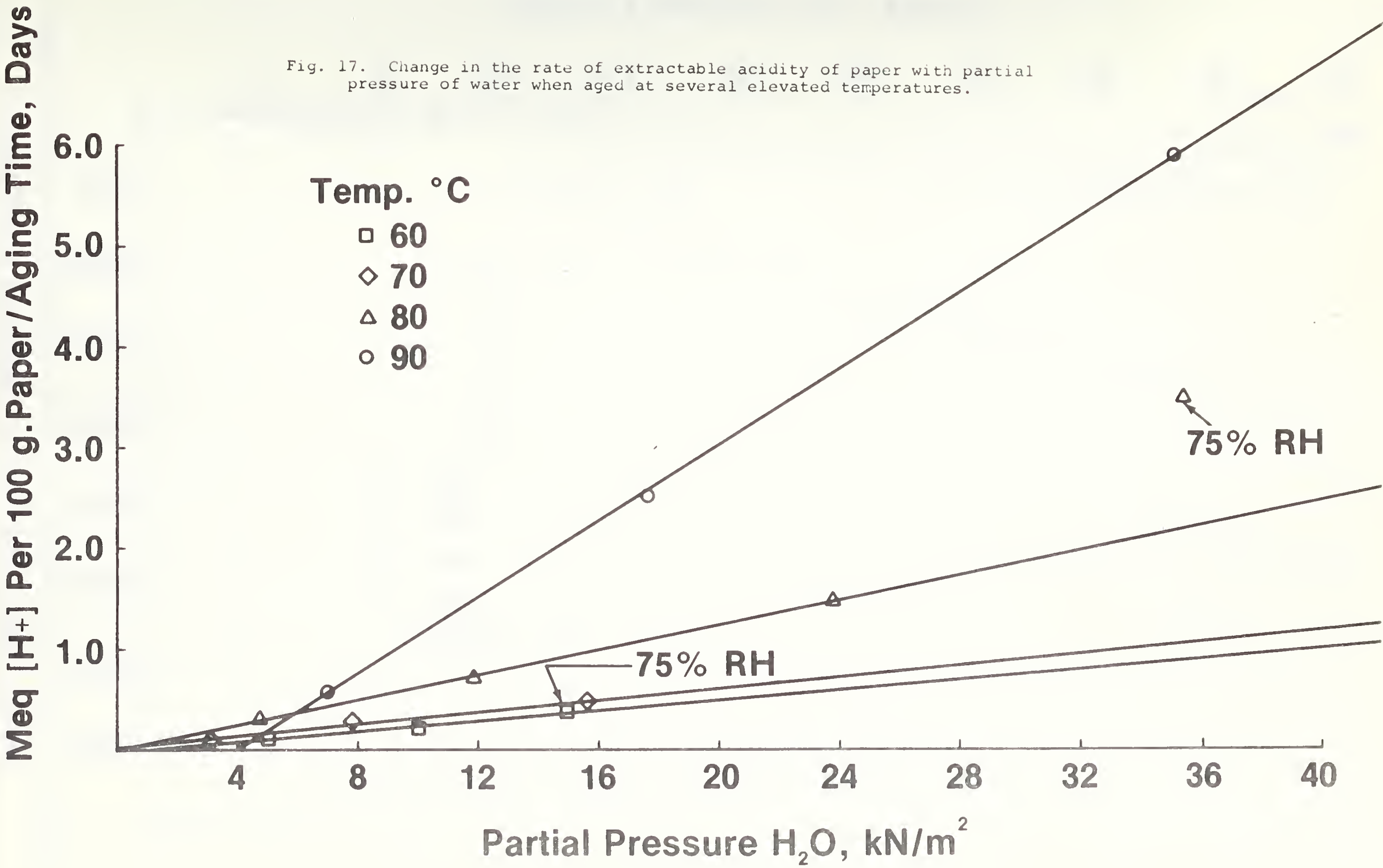


Fig. 18. Change in the rate of moisture regain of paper with partial pressure of water when aged at several elevated temperatures.

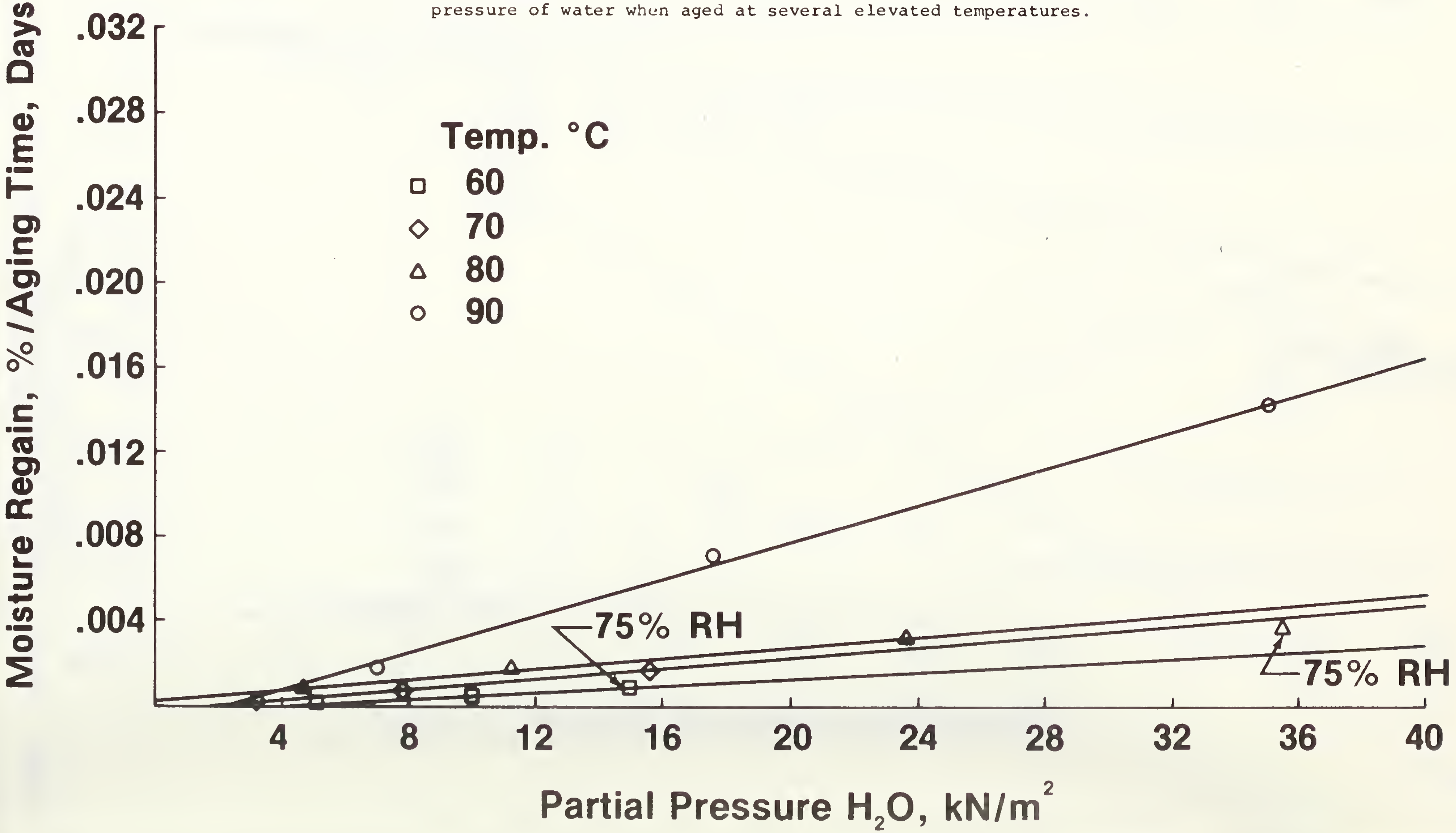
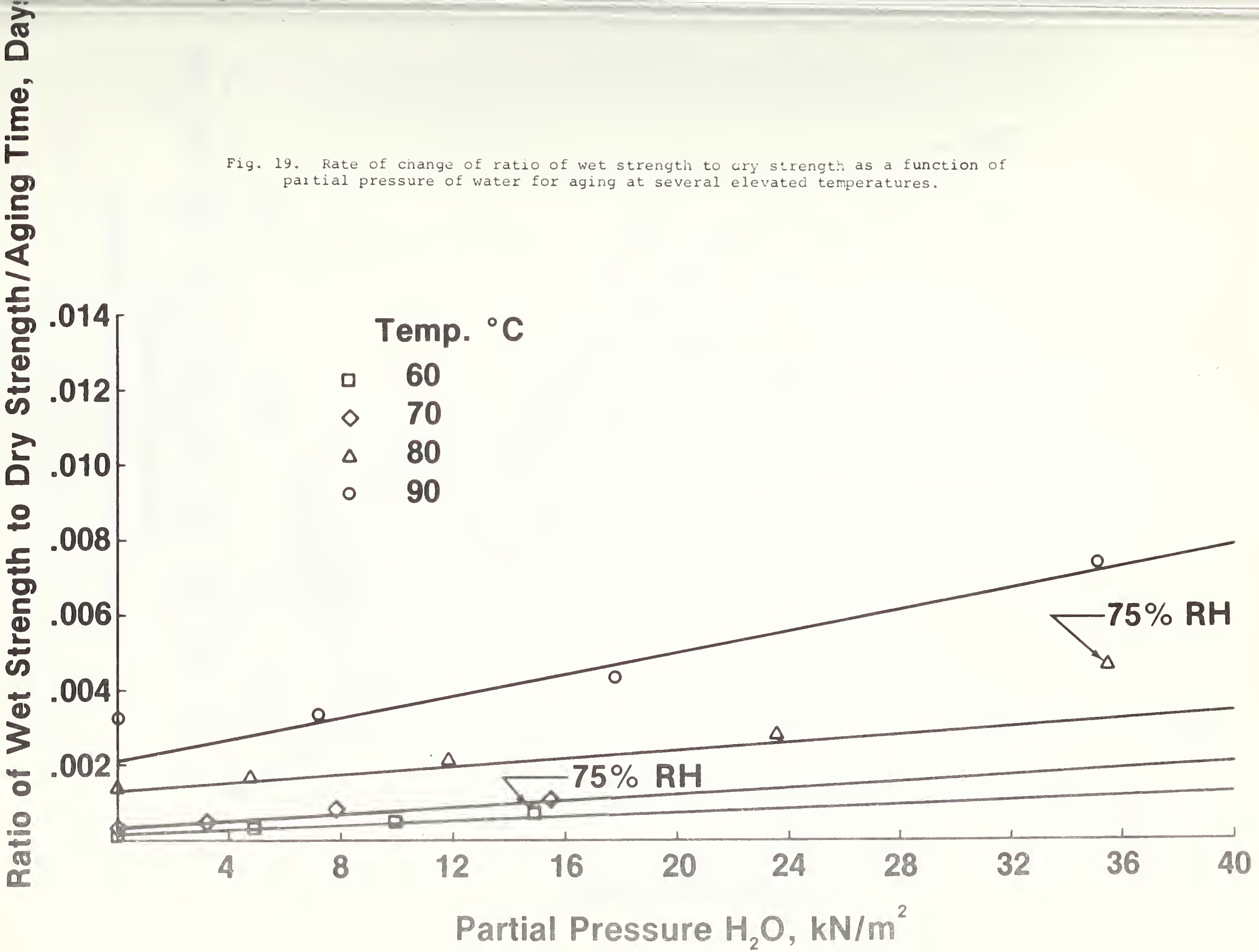


Fig. 19. Rate of change of ratio of wet strength to dry strength as a function of partial pressure of water for aging at several elevated temperatures.



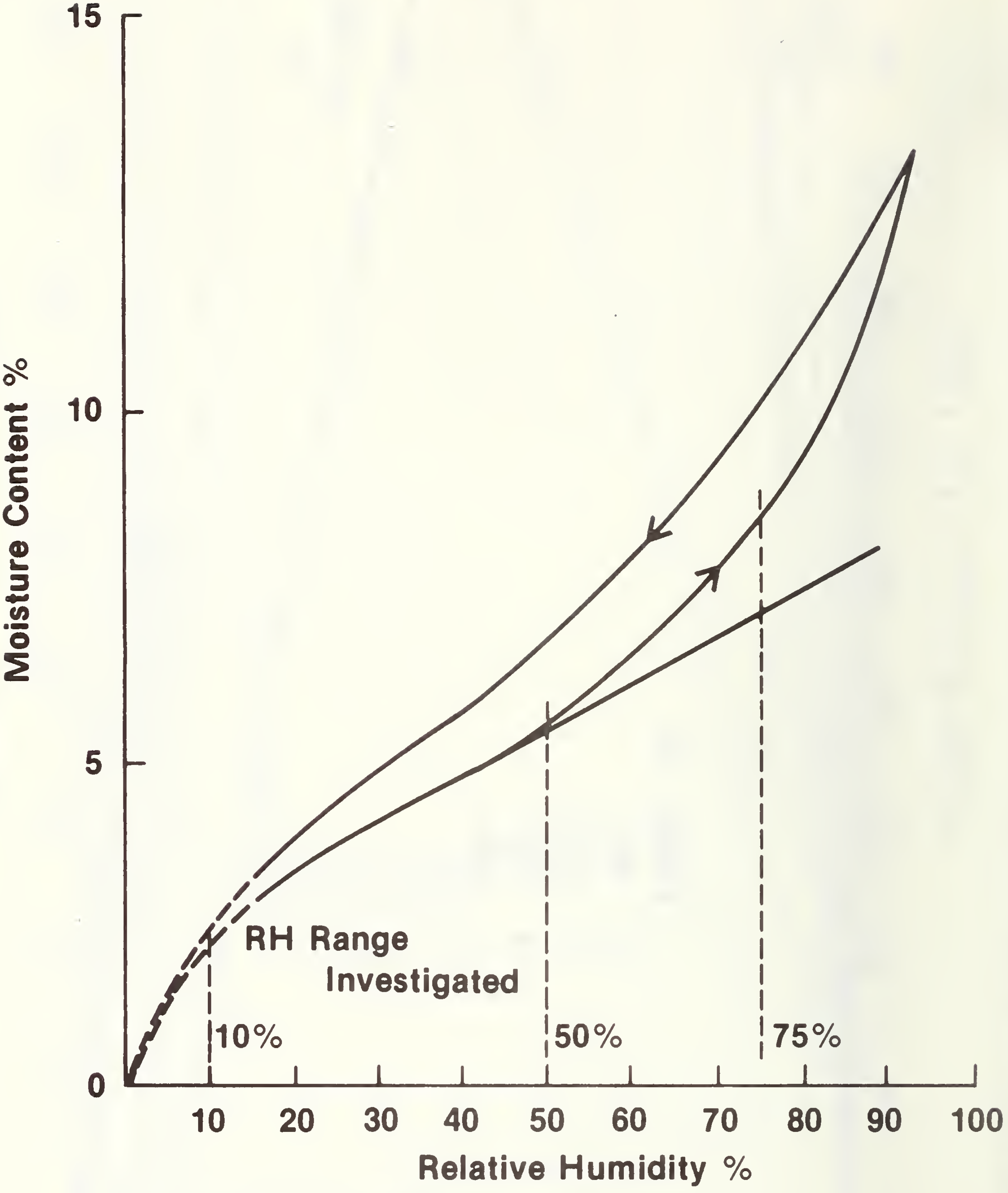


Fig. 20. A typical water sorption isotherm for paper.

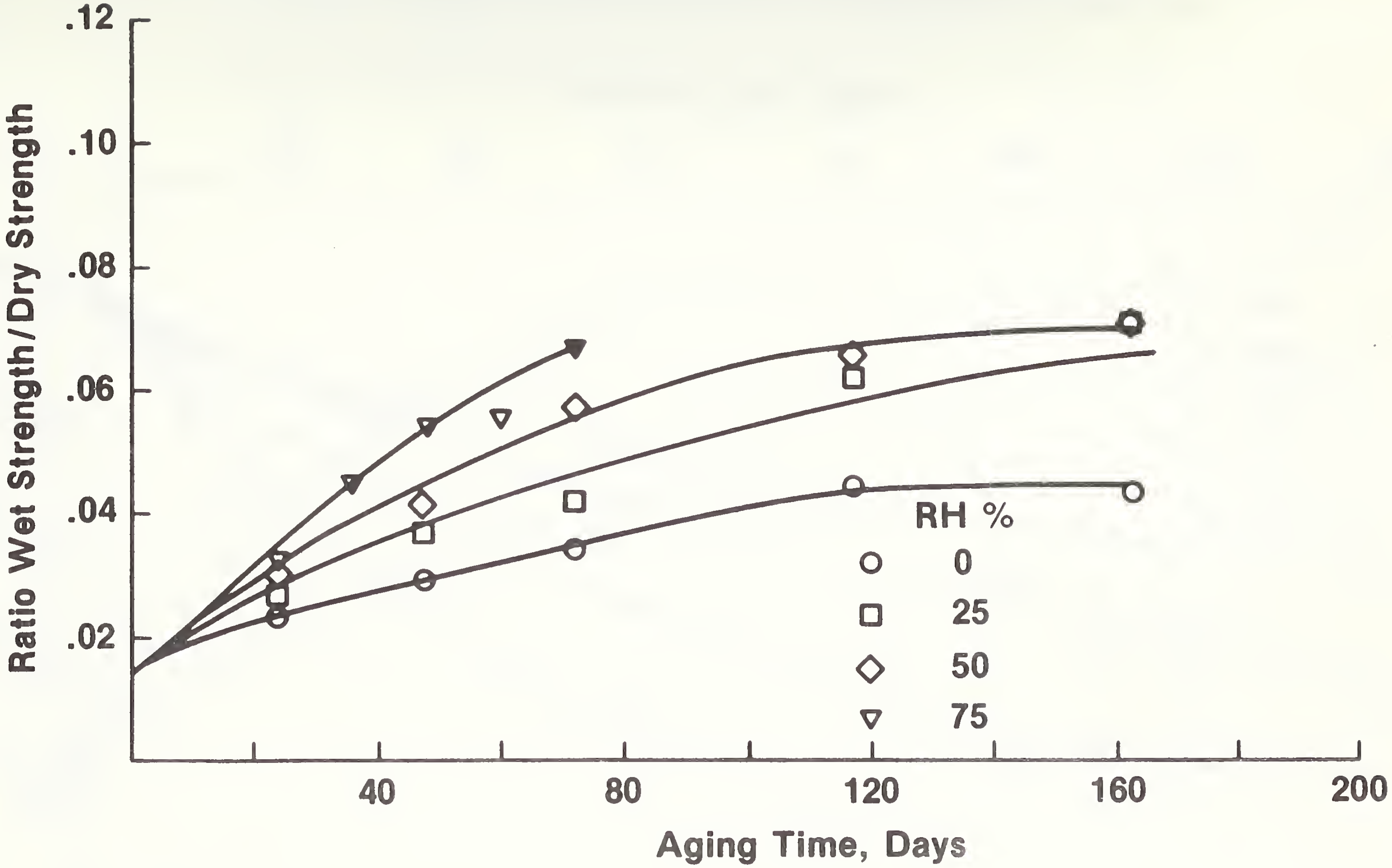


Fig. 21. Ratio of wet strength to dry strength of paper when aged at 60°C and various relative humidities.

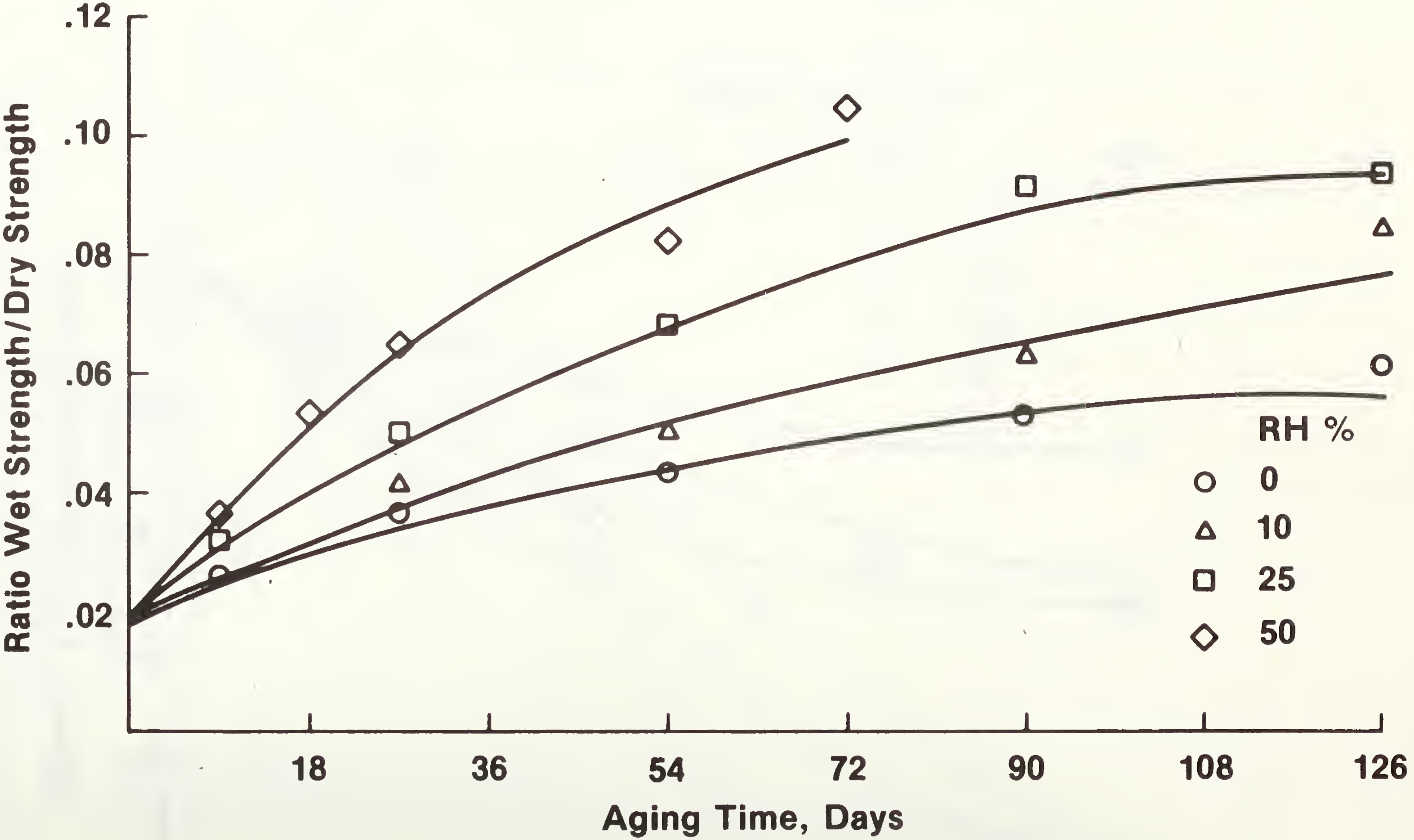
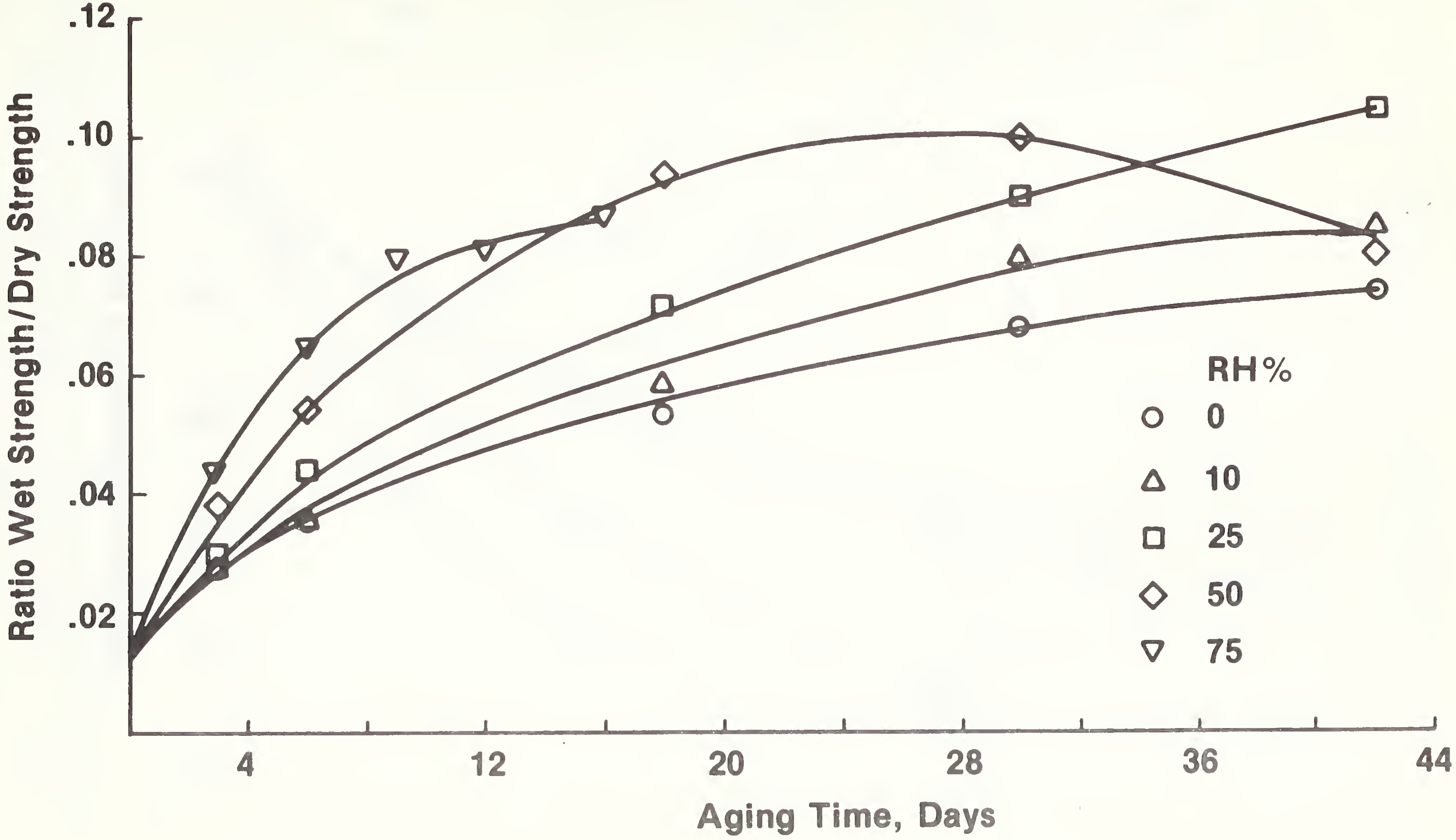


Fig. 22. Ratio of wet strength to dry strength of paper when aged at 70°C and various relative humidities.

Fig. 23. Ratio of wet strength to dry strength of paper when aged at 80°C and various relative humidities.



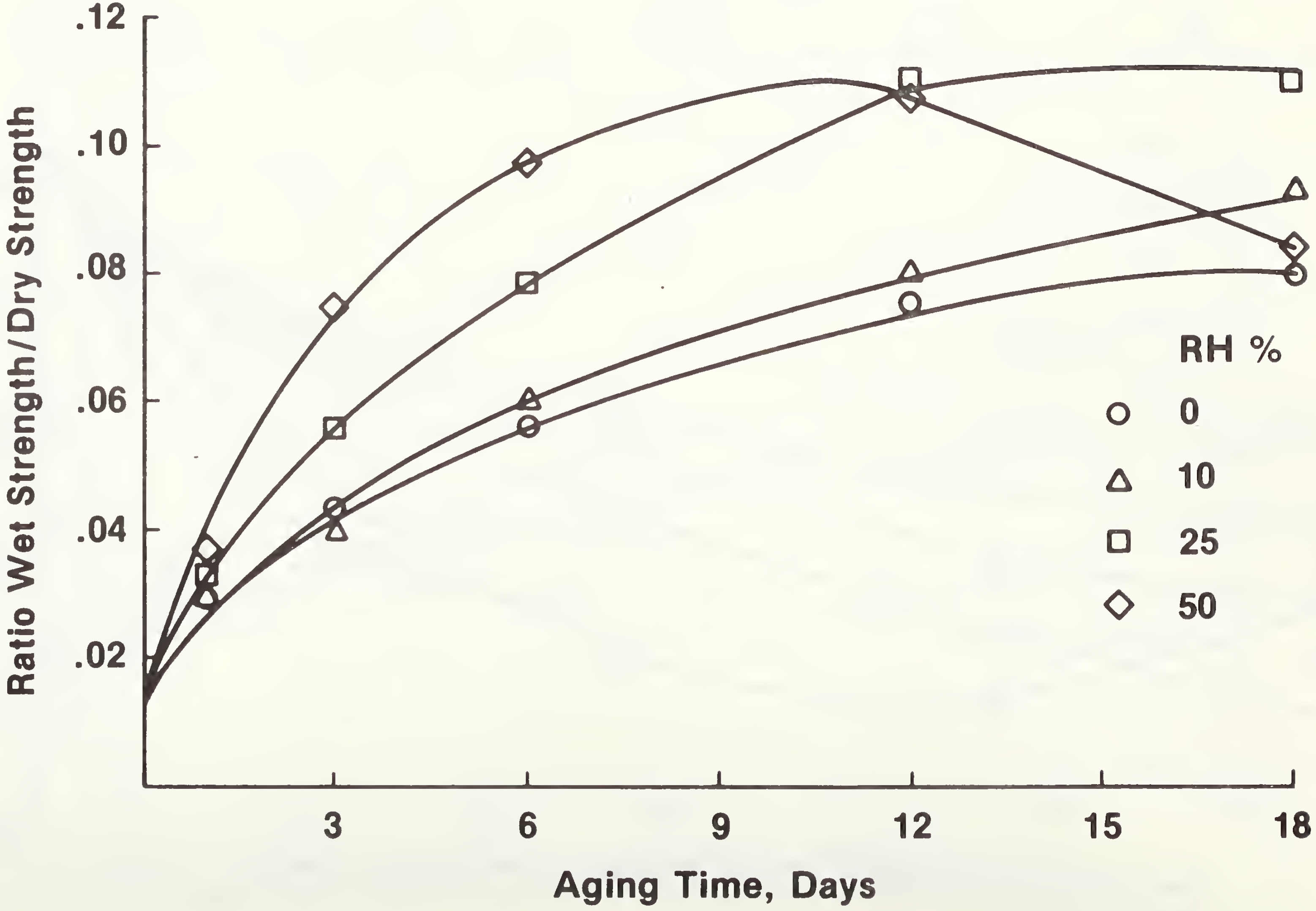


Fig. 24 The ratio of wet strength to dry strength of paper when aged at 90°C and various relative humidities.

Fig. 25. Arrhenius plot for the degradation rate of zero span tensile strength for various environmental moisture conditions.

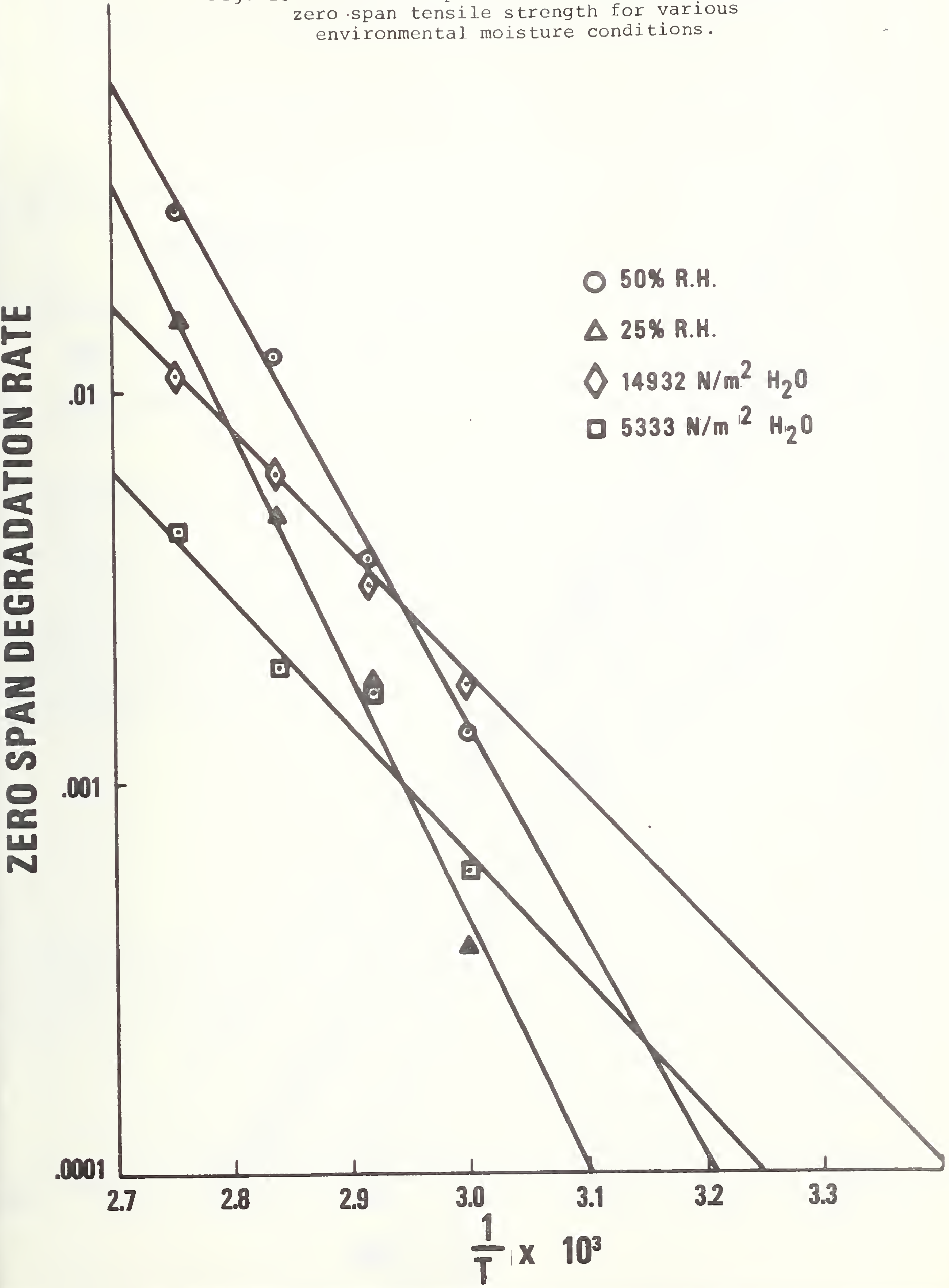
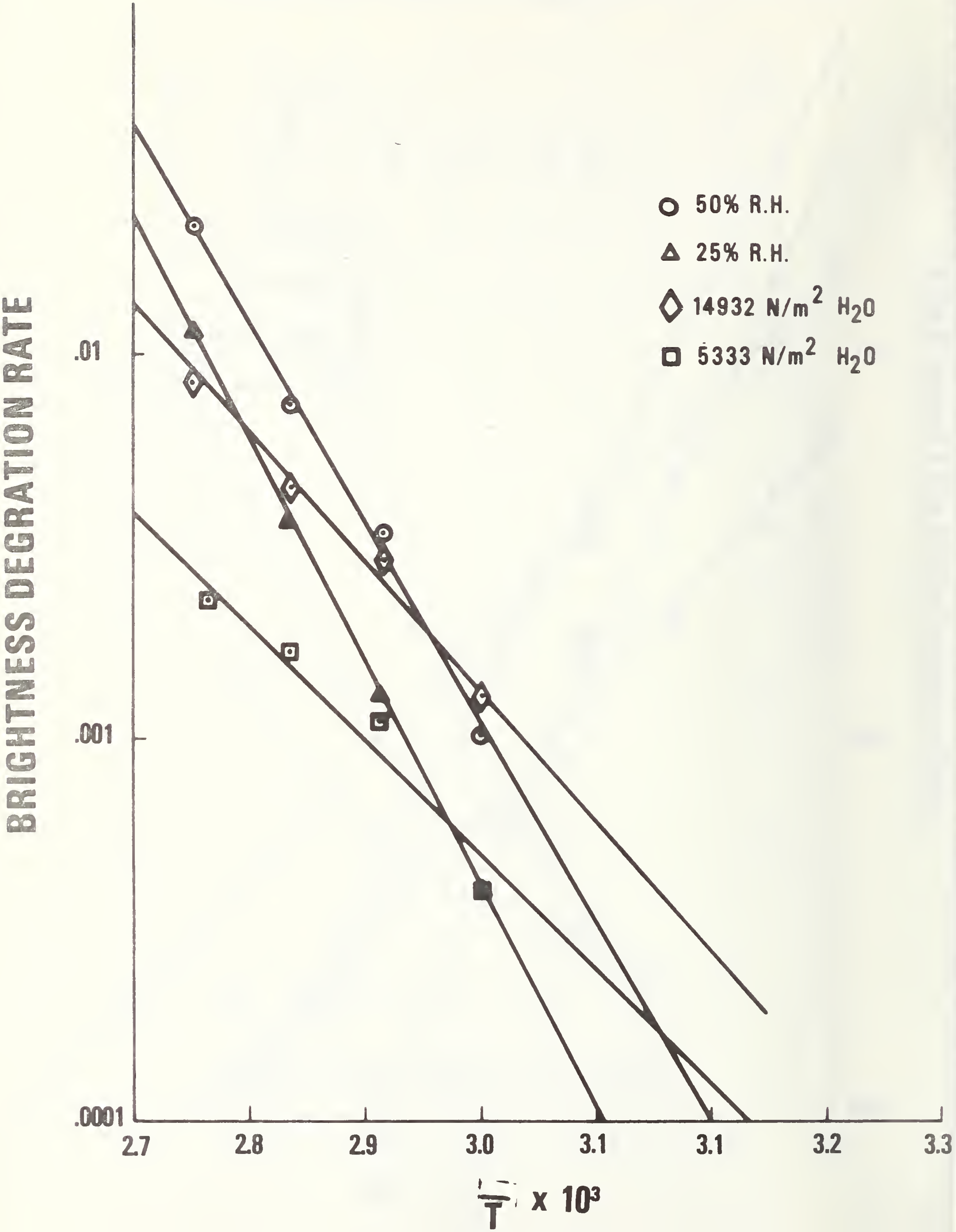


Fig. 26. Arrhenius plot for the degradation rate of paper brightness for various environmental moisture conditions.



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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.)*

The rate of paper degradation at elevated temperatures appears to be directly proportional to the partial pressure of atmospheric water up to 50% relative humidity. This linear relationship continues to exist at higher humidities at 60°C but not at 80°C. It is uncertain at this time whether the water in question is bound to cellulose or is atmospheric moisture. Additional degradation studies at relative humidities above 50% must be conducted in order to identify the type of water affecting the degradation rate. There is also an indication that either an optimum temperature exists for accelerated aging of paper or that the cellulose-water interaction at the higher temperatures and lower humidities differs significantly from that at ambient temperatures.

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; alkali solubility; fiber degradation; paper degradation; paper permanence; wet strength

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