Abstract

The efficacy of strengthening and deacidification processes in increasing the permanence and durability of paper are examined. The permanence increase following treatment is found to be strongly dependent upon properties of the untreated paper, its strength at the time of treatment, the particular mode of strengthening employed, and the process parameters specific to each treatment process. Relationships among these variables are displayed in convenient graphical form and algebraically.

It is shown that addition of strength alone is of relatively little effect in increasing paper permanence but deacidification treatment of acidic papers can, for all but the weakest papers, significantly increase paper permanence. Most importantly it is shown that combined strengthening and deacidification treatments can result in large synergistic permanence increases.

The results obtained also suggest criteria for process selection, processing conditions and treatment priority as well as areas for further research and development. These aspects will be discussed in a subsequent paper (Part II). The relationship of strengthening and deacidification is to be addressed in a subsequent publication.

The Effects of Strengthening and Deacidification on Paper Permanence: Part I--Some Fundamental Considerations

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I. Introduction

In recent years much attention in addressing the "brittle book problem" has focused upon extending the useful life, i.e., increasing the permanence, of paper by reducing the rate of acid catalyzed hydrolysis of cellulose through the use of various deacidification processes which combine neutralization of acid and incorporation of an alkaline reserve[1-8]. Since acid catalyzed hydrolysis is considered to be the major, though not only, cause of paper degradation under library and archive storage conditions[9-11] this approach, properly employed, can be of enormous value in extending the life of paper-based artifacts. Concurrently, though at a lower level of funding and manpower resources, there have been investigations into mass processes for adding strength to already weakened paper[12-15]; these studies have sometimes had an increase in paper permanence as well as increased strength as a stated or implicit objective. Paper strengthening has come to be viewed by some[4] as a universally effective, desirable, and applicable means of increasing paper permanence whose application would be limited only by cost considerations and concern for possible deleterious effects upon materials, users, and the environment.

In early attempts to define and establish Library of Congress requirements for mass paper strengthening[12] it became apparent that limited attention had previously been given to the subject either in terms of its fundamental characteristics or in matters of detail. Examples of important questions which had not been seriously addressed include: What is the minimum amount of strengthening which is useful and economically justifiable? Is it adequate to give all papers an equal increase in strength or should the weakest papers be strengthened most? If strengthening is a one-time event with no change in the rate of paper deterioration, how much is the permanence of the paper extended? What, if any, are the relationships among paper strengthening, paper deacidification and paper permanence? If different strengthening processes result in different distributions of strengths in various papers what criteria can be developed to choose among them?

The objective of this paper is to address these kinds of questions through a general exposition of the relationship among strengthening, deacidification, and permanence. After stating operational definitions for several terms, useful general graphical methods of depicting paper strength, paper permanence, deacidification and strengthening will be introduced. These graphical methods will then be applied to deacidification and to three model types of strengthening processes both alone and in combination with deacidification. Some conclusions are drawn

regarding efficacy in enhancing paper permanence utilizing the different strengthening modes and deacidification both singly and in combination. Mathematical details are confined to an appendix. A subsequent paper will develop criteria for economic mass strengthening and evaluate the presently developed and available strengthening processes using these criteria.

It should be noted that although the origins of this article lie in mass treatment of library and archives paper collections the concepts are equally applicable to treatment of single sheets of paper and, in fact, to any materials whose permanence can be enhanced by strengthening and/or a decrease in the deterioration rate.

II. Paper Strength and Permanence

Discussion of paper strengthening would be greatly aided if a single universally accepted objective measure of paper strength was available. However, not only are there strong advocates for one strength measurement technique over another, there is profound disagreement about what constitutes paper strength[16]. Therefore, in the absence such agreed upon definitions and quantifications we shall adopt for present purposes the definition of paper strength: the ability of a paper to endure without failure the forces of physical handling.

Paper strengthening processes may be expected to increase paper permanence as well as (at least initially) paper durability. Once again universally accepted definitions of paper permanence and paper durability are absent and in this paper we shall adopt the definitions:[*]

> paper permanence: how long a paper retains its physical integrity when subjected to chemical deterioration under museum, archives, or library storage conditions.

> paper durability: how long a paper retains its physical integrity when subjected to the physical forces of use.

These two definitions recognize the different needs of museums, archives and research libraries for most of their collections, i.e., availability over long time periods for infrequent use and handling, compared to those of circulating libraries, publishers of dictionaries, printers of currency, etc., who require a paper which must endure repeated, often abusive handling but which need only be in service for a relatively few years. The issue of strengthening very weak or brittle papers to provide sufficient strength to enable format transfer will be addressed later. The primary focus of this paper will be on paper permanence rather than durability.

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[*]A subsequent paper will explore the relationships among paper strength, paper permanence, and paper durability. In that publication a more rigorous definition of durability will be given.

The concepts of strength, permanence, and durability need to be expressed as measurable quantities if objective statements and comparisons are to be made, therefore, the following measures* of those properties will be utilized:

> paper strength: the number of MIT double folds (0.5 kg load) to failure.

> paper permanence: the time required under natural (or equivalent accelerated aging) storage conditions for paper strength to drop to 1 MIT (0.5 kg load) double fold.

> paper durability: the time required under natural (or equivalent accelerated) use conditions for the paper strength to drop to 1 MIT (0.5 kg load) double fold.

This choice of MIT fold as the measure of strength, permanence and durability properties is largely based upon its widespread historical use and familiarity within the library, archives and preservation communities and, despite the time and cost of the required replicate measurements, its ability to provide reasonable reproduceability and sensitivity to strength changes[16-19]. Among other test methods, tensile energy absorption (TEA) is probably of comparable validity but currently still lacks wide acceptance and familiarity. In any event, though the details of the mathematical treatment would be different if TEA or some other strength measurement were adopted rather than MIT fold endurance, the general aspects of the development, discussion and conclusions contained in this paper would remain unchanged.

III. Deacidification/Strengthening Graphical Overview

Before proceeding to a detailed consideration of the relationships among strength, permanence and durability it will be helpful to introduce graphical methods of expressing these relationships. Although the variables plotted are familiar ones, the interpretations which are drawn can provide new insights and methods of expressing concepts and relationships. The graphs, though quantitative, will be general or generic in character; subsequent sections will quantify them for specific deacidification effects and modes of paper strengthening.

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* These measures may alternatively be taken as operational definitions of the paper properties in contrast to the theoretical definitions previously given.

A. Strengthening and Aging

Figure 1 displays for four different papers the decrease in paper strength, i.e., numbers of MIT double folds to failure, plotted logarithmically as a function of aging time. Pairs of papers have the same initial strength (100 and 1,000 MIT folds) but deteriorate (lose strength) at different rates under the same assumed aging conditions. The steeper the downward slope[*] of the aging curve the more rapidly the particular paper deteriorates. Eventually all papers drop to a value of 1 MIT double fold; the time taken to reach the 1 MIT value under library storage conditions we have defined as the permanence of the paper.

What qualitative and quantitative information can be gleaned from the graph? First, papers A & B deteriorate at the same logarithmic rate, i.e., they have the same downward slopes; however, paper A has greater permanence than B (325 years vs. 225 years) because initially paper A was stronger. Paper C, however, which has the same initial strength as paper A, has less permanence than A because its rate of deterioration (downward slope) is greater. In fact, paper C has less permanence than paper B although it initially started out with more strength. Paper D has the same permanence as C because, although it was initially weaker, its rate of deterioration is also less. We conclude, not surprisingly of course, that paper permanence is related to both the initial strength of the paper and the rate at which it loses that strength. Finally, it is useful to have a quantitative measure of the rate of deterioration. The slope of the deterioration line is given by:
(1)

$$rate\ of\ deterioration = slope = k = \frac{\log f_2 - \log f_1}{t_2 - t_1} = \frac{\log \frac{f_2}{f_1}}{t_2 - t_1}$$

where f_2 and f_1 are the numerical values of the MIT fold at times of aging t_2 and t_1. Numerical values of slopes for the four papers are displayed in Figure 1; the values are negative (less than 0) indicating the lines slant downward; the more rapid the deterioration the steeper the slope and the more negative the k value.

Clearly both papers A and B would be considered to be relatively permanent whereas C and D would more nearly represent the properties of acidic -- perhaps alum-sized -- papers which

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[*] Experimentally, most graphs are not perfectly straight lines and show some small curvature, most commonly during the initial period of aging. For the purposes here we shall ignore these initial induction periods and subsequent small curvature and consider the graphs to be straight lines.
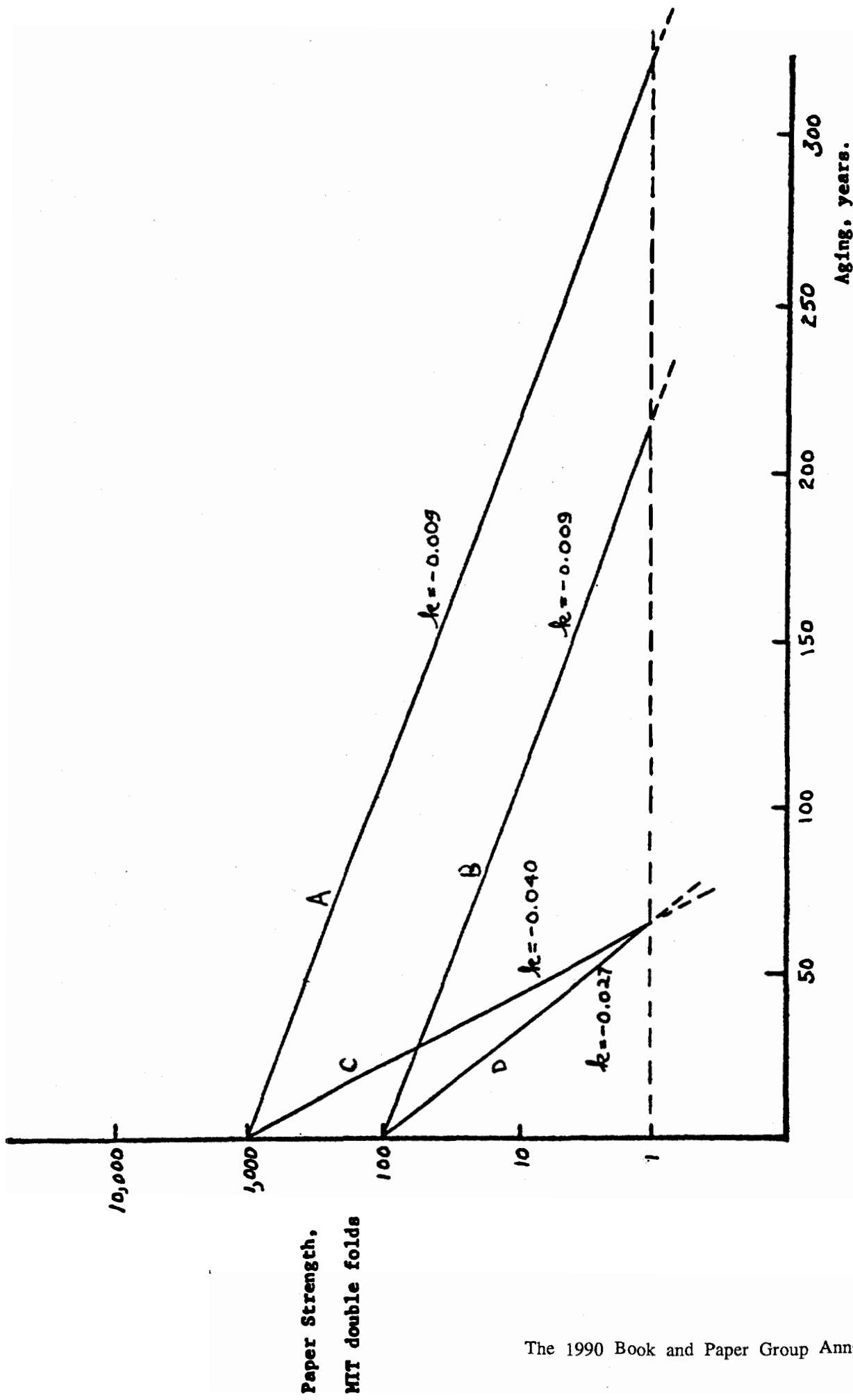
Fig. 1   Decrease in strength of four papers (A-D) upon aging. Graphs depict natural aging in library environment; accelerated aging behavior will be similar but loss of strength more rapid. Small curvature, commonly observed in graphs, is ignored. Paper β will be used hereafter as the model paper.

almost irrespective of initial strength become very weak in 75 years and ultimately brittle and unusable. In terms of the deterioration slopes, k's of in the range of 0 to -0.010 year^{-1} or more represent papers of considerable permanence while those of about -0.03 year^{-1} or less are characteristic of short-lived papers.

With respect to durability, graphs similar to Fig. 1 can be drawn to represent paper durability. The main differences between the permanence and durability graphs are that years of use rather than years of storage would be plotted and that a linear rather than logarithmic change in strength might be employed. However, without going into (important) details here, we can generally recognize that a stronger paper is probably a more durable paper; hence paper A, which retains its high strength for a relatively long period of time, will be more durable than paper D, which rapidly loses (through chemical deterioration) the relatively little strength it initially had.

The use of graphs like Figure 1 can be helpful in illustrating and clarifying relationships among permanence, durability and strength.

B. Deacidification and Permanence

Figure 2 displays the effects of deacidification on an acidic paper. For continuity in the discussion here and later we shall employ a model paper with characteristics not too different from those of typical papers.* This model paper initially has a strength of 1,000 MIT double folds which after 75 years of natural aging under library storage conditions has dropped to 1 fold; the untreated paper therefore has a permanence of 75 years and a slope value of k = -0.040 years^{-1}. Deacidification** alone of acid papers we have assumed to have no effect upon paper strength but to function only to reduce the rate of deterioration. Typically, deacidification can reduce the deterioration rate of acidic papers by factors of 3-6 so the k value of our model paper is reduced to (say) k = -0.010 years^{-1}, i.e., one-fourth of -0.040 years^{-1}.

As shown in Figure 2, the deacidification treatment reduces the deterioration rate thereby extending the length of time required

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* A somewhat smaller initial fold strength may be more representative but would not show up as clearly in graphs.

** By deacidification is mean a process which neutralizes acids present in a paper and deposits an alkaline reserve which provides for future neutralization of any acids formed or introduced. For our present purposes, deacidification is assumed to have no effect upon the strength of the paper. Some deacidification processes described in the literature may affect strength immediately following treatment or for extended periods afterwards; such processes are considered generically below in the section on strengthening.
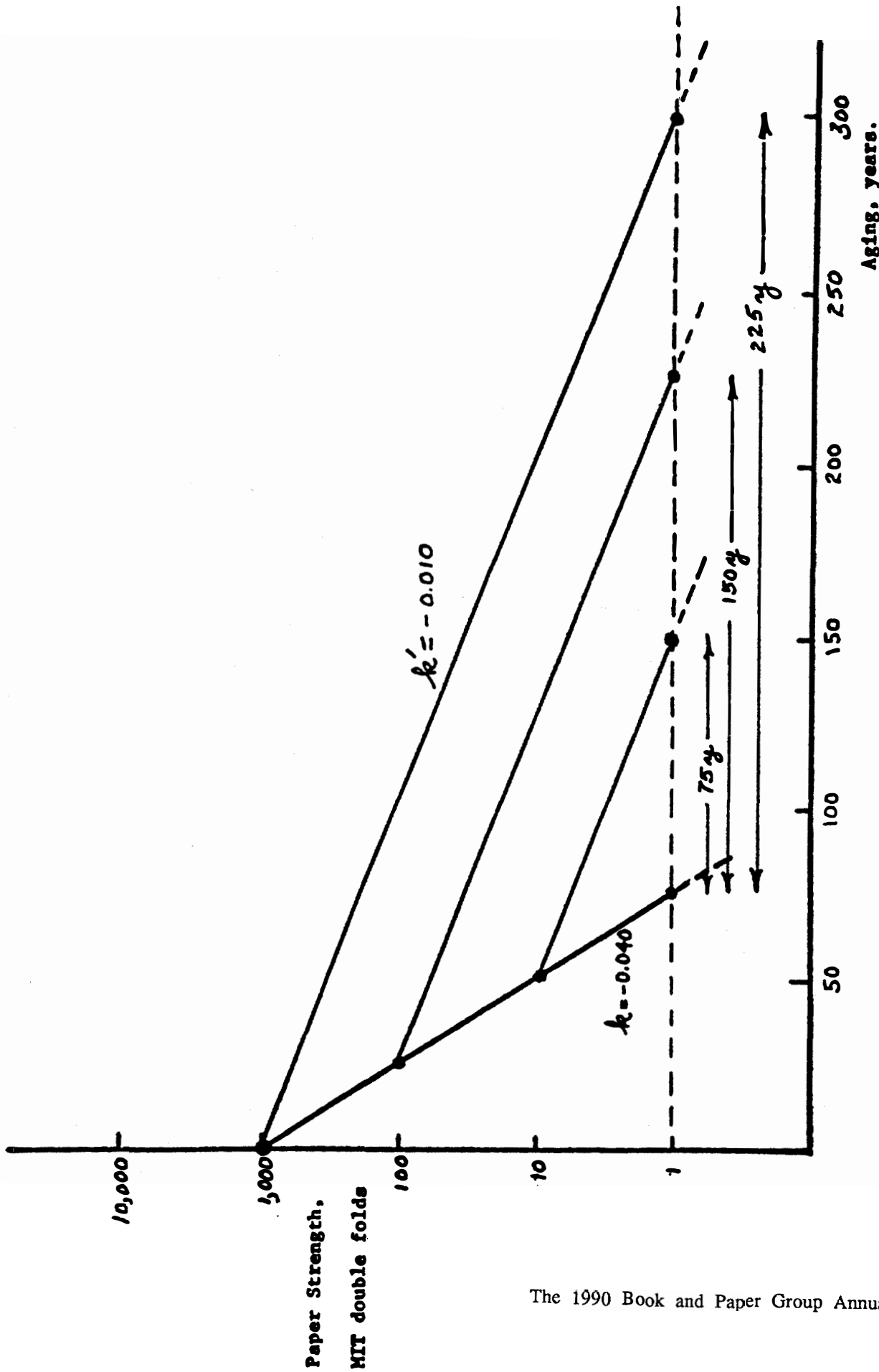
Fig. 2   Increased permanence of acidic paper resulting from deacidification. Shown is the result of decreasing the deterioration rate by a factor of 4 at various times in the aging of the originally acidic paper.

for the paper strength to drop to 1 MIT double fold, i.e., increasing the paper permanence. The model paper which, after 25 years of natural aging, has a remaining strength of 100 MIT double folds, if untreated would have a permanence of 50 years, but if treated would have a permanence of 225 years; deacidification has resulted in a permanence _increase_ of 150 years. Clearly, if deacidification reduced the slope by a factor larger than 4 the permanence increase would be greater than 150 years; equally clearly, if the deacidification treatment was carried out earlier (after less than 25 years, when the paper was stronger) a larger permanence increase would result.

C. Strengthening and Permanence

Figure 3 displays the result of strengthening (by 200 folds) the model paper after 50 years of aging when its strength has already dropped to 10 MIT double folds. Depicted is a model strengthening process which only increases strength but does not affect the rate of deterioration, hence, after treatment the paper deteriorates along a line parallel (the same k value) to that of the untreated paper. We see that the treatment has added approximately 37 years to the permanence of the paper. This graphical presentation of strengthening quickly allows one to assess the permanence consequences of strengthening by various amounts at different times in the life of the untreated paper. In a subsequent section this assessment will be made quantitatively for different modes of model strengthening. But we already see in this example that substantial strengthening, i.e., expressed as a 20x multiplicative factor or a 200 fold additive term, does not greatly impact on paper permanence.

D. Combined Strengthening/Deacidification and Permanence

Paper permanence can also be enhanced when strengthening processes are combined with deacidification or if the strengthening process itself results in a paper which is not only stronger but has a lower _rate_ of strength loss than the untreated paper. Figure 4 displays the results of combining strengthening and deacidification with the processes already shown in Figure 2 and 3. The figure shows the great _increase_ in permanence of the combined treatment, $\Delta^1 t^{S+D}$, compared with deacidification alone, $\Delta^1 t^D$ or strengthening alone, $\Delta^1 t^S$. Figure 4 also shows that deacidification results in the strengthened paper retaining a major portion of its enhanced strength for a much longer period of time under storage conditions. Section IV below addresses combined processes for three modes of strengthening employing this graphical representation as well as quantitative algebraic expressions.

IV. Quantitative Analysis of Permanence Relationships

The graphs shown in Figures 1, 2, 3 and 4 contain the essence of the relationships among strength, permanence, strengthening and deacidification. Apart from any detailed or quantitative considerations, they allow one to easily understand and utilize the relationships in a variety of situations. However, if one is to establish criteria for or measurements of treatment efficacy or to evaluate the comparative economic benefits of alternative treatment processes the more quantitative analysis of this section and the mathematical appendix are required. In all the discussions the model paper defined earlier will serve as a common example and treatment process parameters will be selected within ranges known to be attainable in present treatment processes or which would appear possible for alternative processes. These choices, made to emphasize the current state of development, are not restrictive and can easily be modified by using other values for paper deterioration rate, strengthening factors, etc.

A. Deacidification

Figure 4 displays the increased permanence of our model paper when deacidified at various times. Deacidification is shown decreasing the deterioration slope by the average factor of 4. It is seen that early deacidification, when the paper retains more of its initial manufactured strength, yields larger increases in permanence suggesting that an appropriate mass deacidification treatment strategy for archives and libraries would be deacidification of materials as soon as possible after acquisition with priority given (if necessary) to items most recently manufactured.

Figure 5 displays in a different form the relationships between increased permanence, paper strength at the time of treatment, and efficacy of the deacidification treatment in reducing the deterioration rate. Shown is increased permanence where the model paper deterioration rate is reduced by factors of
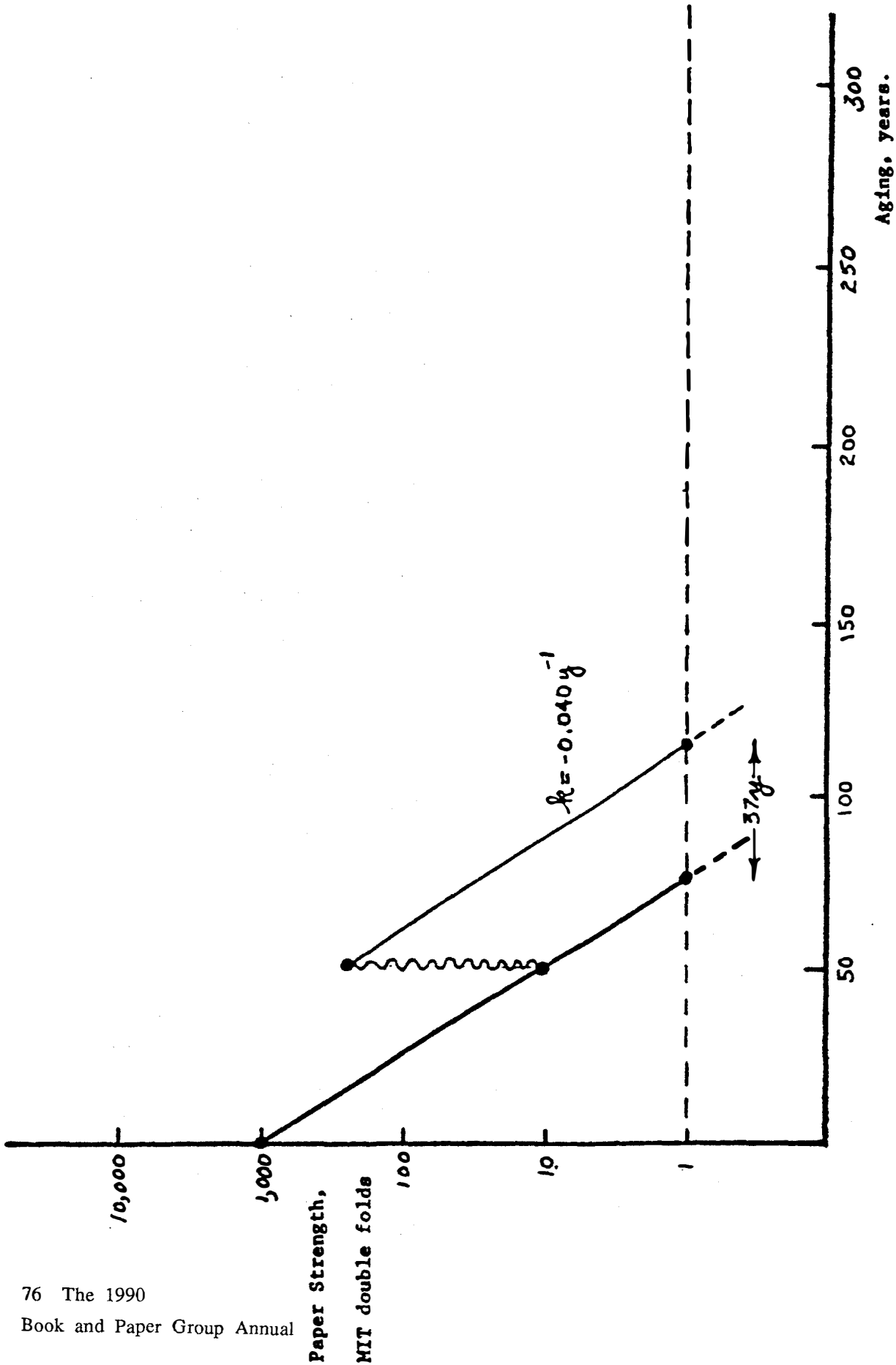
Fig. 3   Increase paper permanence resulting from strengthening. The model paper is strengthened by 200 MIT double folds (to 210 folds) after 50 years of natural aging when its pre-treatment strength has dropped to 10 folds.
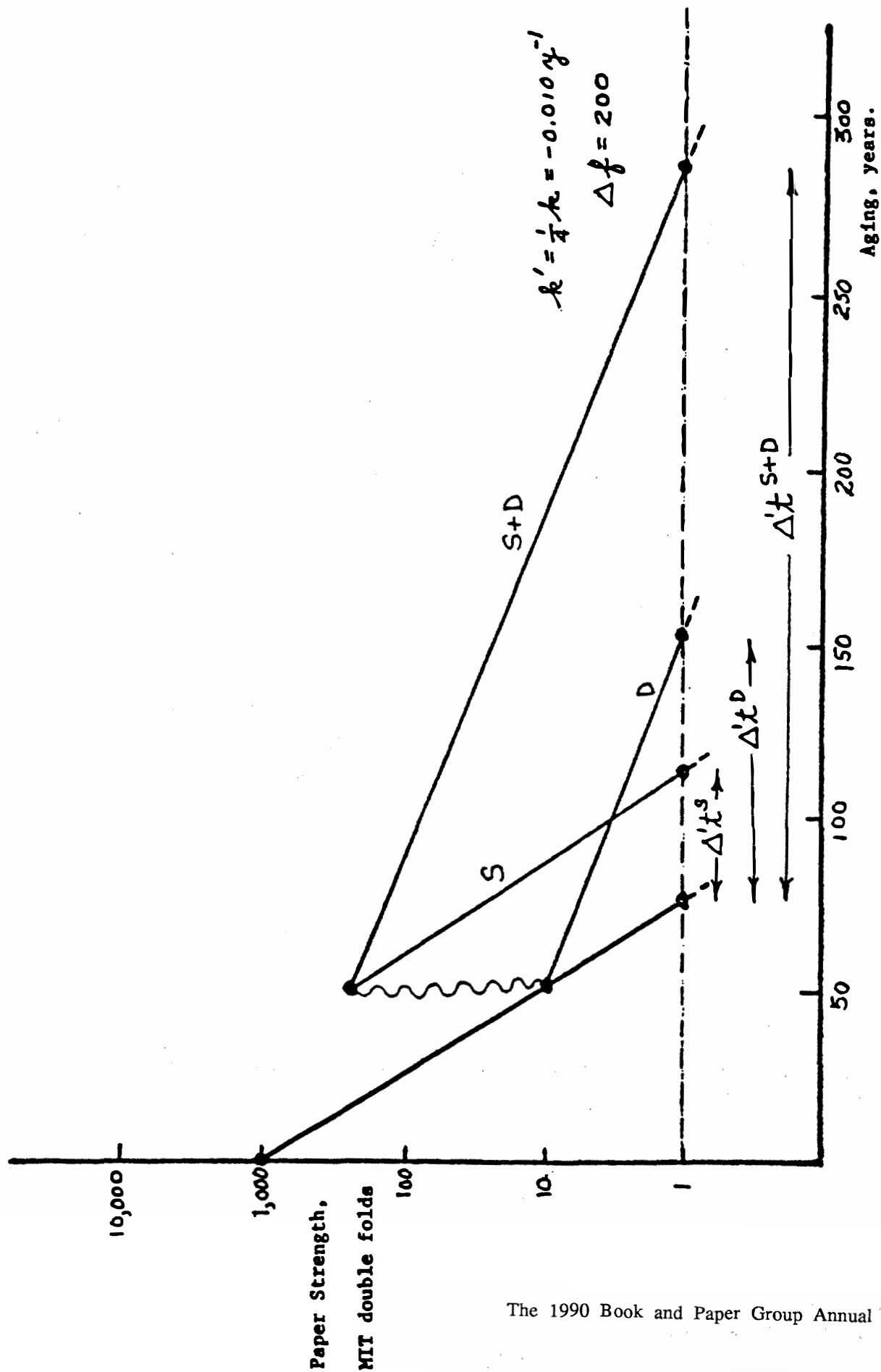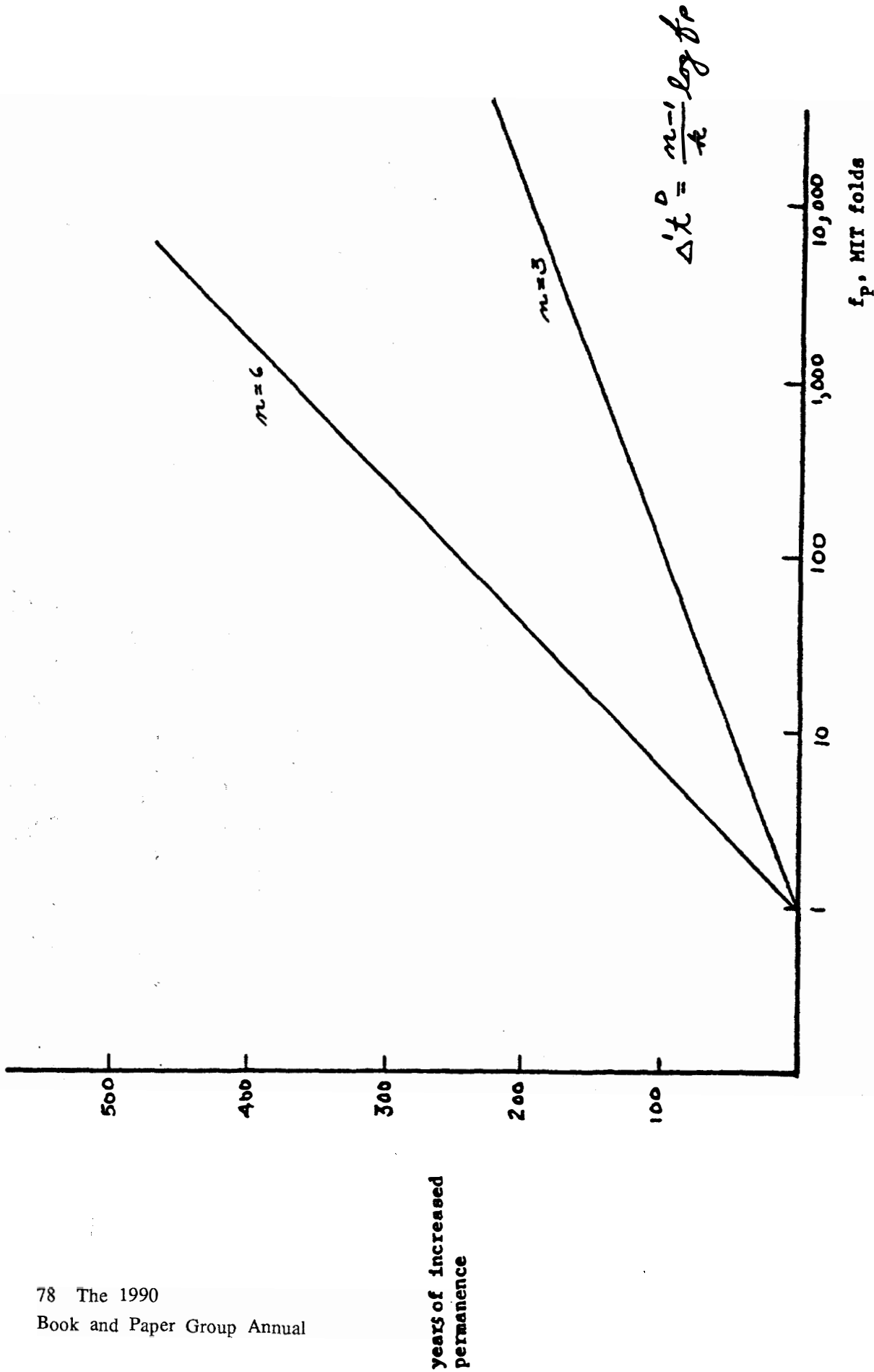
Fig. 4   Increased paper permanence resulting from combined strengthening and deacidification of model acidic paper. Graphs show effect of deacidification alone (D), strengthening alone (S), and combined strengthening and deacidification (S+D).

Fig. 5 Paper permanence increase, Δ ltD, resulting from deacidification of model acidic paper. Paper of pre-treatment strength f_P folds has deterioration rate reduced by a factor of n, k = -0.04 year^{-1}.

$$\Delta' t^D = \frac{n-1}{k} \log f_P$$

f_P, MIT folds

years of increased permanence

1/3 and 1/6; we see again the importance of treating papers while they still retain significant strength.

Relationships expressed in these graphs can be generalized and quantified by mathematical analysis as shown in the Mathematical Appendix. There, assuming a deacidification process which does not affect the fold strength of the treated paper, f_p, but which reduces the deterioration rate of the treated paper, k', by a factor of n from the pre-treatment rate, k, i.e.,

(A-4)

$$k' = \frac{1k}{n}$$

the resulting <u>increase</u> in permanence, $\Delta^1 t^0$, is shown to be:

(A-7)

$$\Delta^1 t^D = -\frac{n-1}{k} \log f_p$$

Equation (A-7) can be used to construct graphs like Figure 5 for papers with properties different from those of the model paper and for deacidification processes of specific n values. Readers of a more mathematical bent will recognize in the form of (A-7) the great sensitivity of permanence increase to n values (doubling n will <u>more</u> than double the permanence increase) but (because of the logarithmic dependence upon f_p) the diminishing permanence increase as the pre-treatment paper strength increases.

B.   Strengthening

Paper strengthening processes are still mostly in the early stages of their development. Literature reports of process chemistry details are limited, as are data showing the degree of strengthening attainable. An especially important gap is definitive data for a wide variety of papers on the relationship of paper strength after treatment to its pre-treatment strength. For example, it has not been made clear whether a given process increases the strength of all papers by the same fixed amount or increases each in proportion to its pre-treatment strength. As we shall see below, the permanence consequences of a strengthening process are strongly dependent upon this pre-treatment/post-treatment strength relationship. In the absence of such details this paper will explore three types or modes of strengthening relationships which generally encompass the range of behavior we may expect to observe. If these three are inadequate or a more detailed analysis is desired for a specific process the techniques of the Mathematical Appendix can be applied to any specific process.

It should be mentioned again that though the comments and applications made in this and its subsequent paper mainly refer to mass treatment issues the results are generally applicable to all paper deacidification and strengthening applications. For example, if single sheets of paper are increased in strength by treatment with a sizing agent the permanence and durability of the treated paper may be characterized and evaluated using the graphs, equations and definitions developed here.

1. Incremental Strengthening

Generally, a strengthening process is considered as incremental strengthening if the treatment imparts a fixed strength increase to all treated papers irrespective of their pre-treatment strength. Identifying paper strength with MIT fold endurance as this paper does, we define:

> Incremental Strengthening Process: a strengthening process which imparts a fixed number of MIT double folds to all treated papers irrespective of their pre-treatment fold endurance.

This definition may be expressed mathematically as:

(A-8)

$$f^I = f_p + \Delta f$$

where f_p is the pre-treatment fold value, f^I is the fold value immediately after incremental strengthening and Δf is the common fold increase given to all papers.

Figure 6 shows the aging behavior of the model paper which has been incrementally strengthened by 100 folds. The wavy vertical lines (though of different length on a logarithmic graph) all show a 100 MIT double fold strength increase. It is seen that the maximum increase in permanence (50 years) is achieved with the weakest ($f_p=1$) paper; stronger papers give lesser increases. The definition (A-8) is developed in the Mathematical Appendix into a general expression for the increase in permanence, $\Delta^I t^I$, resulting
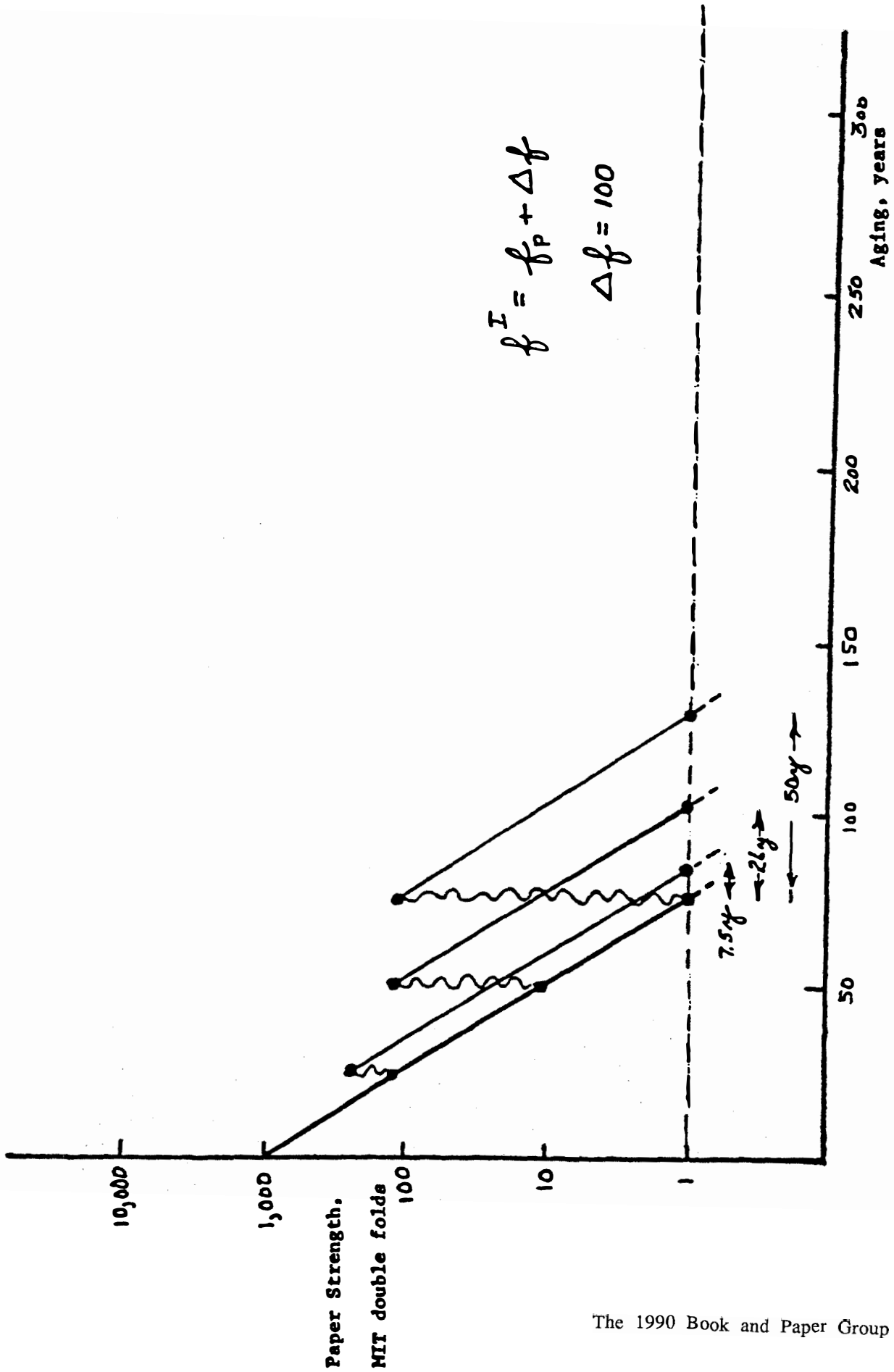
Fig. 6 Increased permanence resulting from incremental strengthening. Pretreatment strength of all papers increased by 100 MIT double folds. k = -0.04 years⁻¹.

$$f^I = f_P + \Delta f$$

$$\Delta f = 100$$

from the application of Δf MIT folds of incremental strengthening to a paper of strength f_p folds:

(A-11)

$$\Delta^1 t^{\,I} = -\frac{1}{k}\log\left(1+\frac{\Delta f}{f_p}\right)$$

The information of Figure 6 and values computed from (A-11) are compiled in Figure 7 which shows permanence increases which result from Δf values which might be commercially attainable. We see only very modest permanence increases resulting even from very large incremental strengthening. Indeed, using the aging characteristics of our model paper we must conclude that to achieve a permanence increase of 200 years the paper would require incremental strengthening by at least 100,000,000 MIT double folds! Even a paper which aged at half the rate of the model paper would require a minimum increment of 10,000 folds*.

Figure 7 presents a very somber picture for the practical utility of incremental strengthening in providing substantial permanence increases.
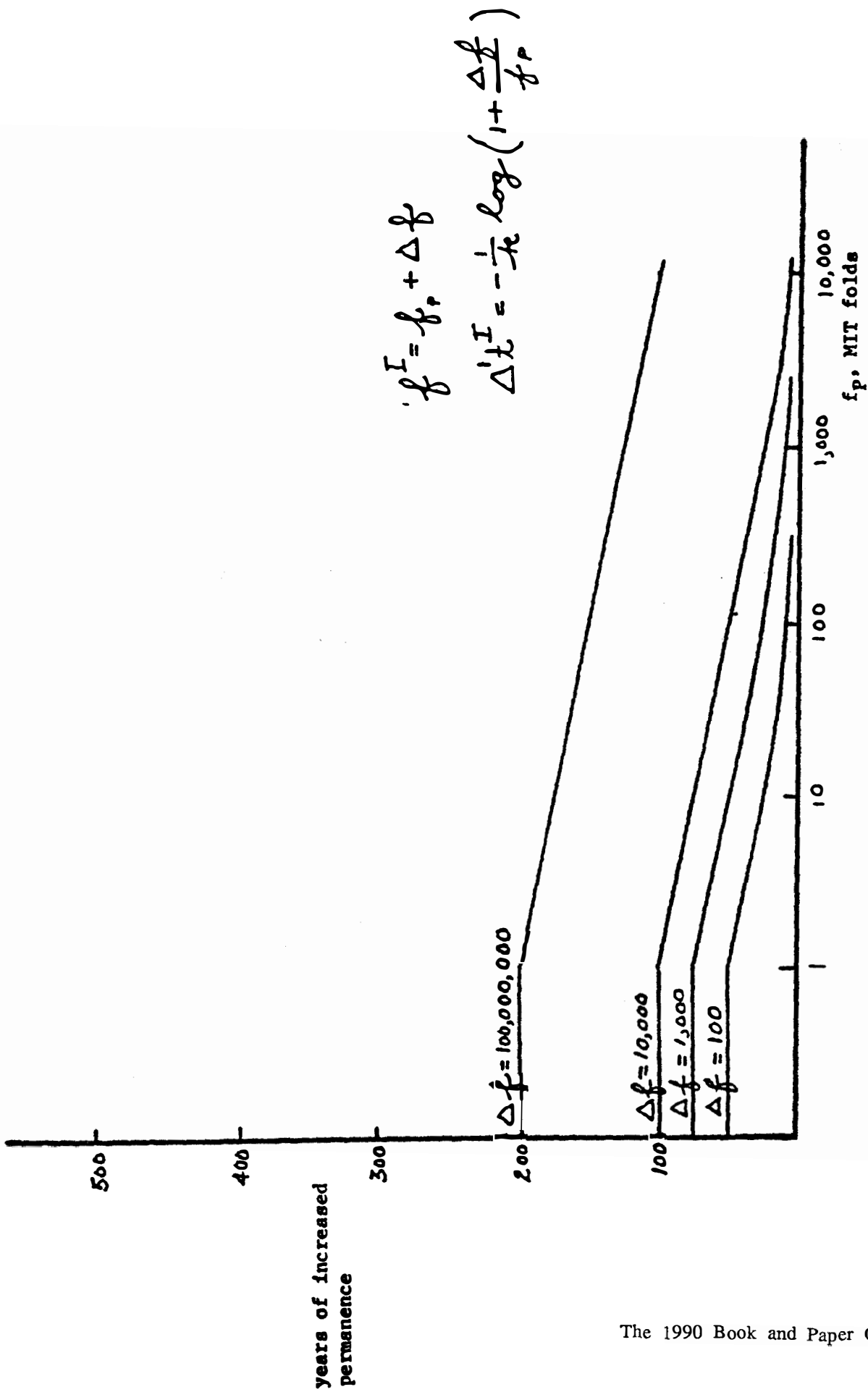
2. Proportional Strengthening

A second general type or mode of strengthening process which may be commercially available for mass treatment or employed in strengthening single sheets results in an increase in paper strength to a value proportional to its pre-treatment paper strength -- for example, all papers are increased in strength to a 50% higher value or to double their strength, etc. Again, using our definition of paper strength we define such a process:

> Proportional Paper Strengthening: a strengthening process which increases the MIT fold endurance of each treated paper to a fixed multiple of its pre-treatment fold value.

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* Perhaps a brief elaboration of these huge numbers to allay doubts of their validity is in order. Our model paper drops (logarithmically) in strength from 1,000 to 1 fold in 75 years. This means mathematically that its strength drops by a factor of 10 every 25 years, i.e., 1,000 folds initially, 100 folds after 25 years, 10 folds after 50 years, 1 fold after 75 years. Strengthening may be viewed as setting back the clock 25 years by every strength factor of 10. Therefore, our model paper with a lifetime of 75 years will have a permanence of 100 (75 + 25) years if its strength is increased to 10,000 folds. Similarly, 125 years for 100,000 folds, 150 years for 1,000,000 folds, and so on to 100,000,000 for a 200 year lifetime.

$$f^I = f_p + \Delta f$$

$$\Delta' t^I = -\frac{1}{k} \log\left(1 + \frac{\Delta f}{f_p}\right)$$

years of increased permanence

$\Delta f = 100,000,000$

$\Delta f = 10,000$

$\Delta f = 1,000$

$\Delta f = 100$

500

400

300

200

100

1   10   100   1,000   10,000

f_p, MIT folds

Fig. 7   Permanence increase, $_lt^I$, resulting from incremental strengthening of model paper (k = -0.04 year^{-1}). Paper of pre-treatment strength, f_p, are increased to a strength of $f_p + \Delta f$. Paper D of Fig. 1 would require a maximum Δf of 250,000 folds to attain a 200 year permanence increase. (minimum)

Expressed mathematically, we have:

(A-16)

$$f^P = Mf_p$$

where M is the multiplying factor (proportionality constant) by which all papers are strengthened.

Figure 8 displays the aging characteristics of our model paper when strengthened at various times in its useful life by a proportional strengthening process. Shown is the strengthening by a factor of 50 (M = 50) of papers of pre-treatment strength 100, 10, and 1 fold to 5,000, 500 and 50 folds respectively, and similarly papers whose strength is increased 10 times (M = 10) from initial values of 200, 40 and 4 to 2,000, 400 and 40. It is seen that all the strengthened papers of a given M value lie along the same aging line thus, unlike incremental strengthening which benefits weak papers more than strong ones, proportional strengthening gives all papers an equal increase in permanence. For our model paper the permanence increase resulting from even a large 50x strength increase is a modest 42 years.

As before, the mathematical definition of proportional strengthening can be used to obtain an algebraic expression for the increased permanence:

(A-15)

$$\Delta^1 t^P = -\frac{1}{k} \log M$$

The absence of f_p in the equation is an expression of what we have already seen in Figure 8 -- the permanence increase does not depend on the pre-treatment paper strength. The logarithmic dependence on M of permanence means that there is a rapidly diminishing value of increases in M on increasing permanence.

Figure 9 shows the increase in permanence of our model paper resulting from proportional strengthening by M factors of 10, 100 and 1,000. We see all papers equally share the permanence benefits of strengthening but even at what probably is an unrealizably large value of M = 1,000 the permanence increase of the model paper is only 75 years. For papers with the model deterioration rate (k = -0.04 y^{-1}) it would be required that all papers be increased in strength to a value 100,000,000 times their pre-treatment strength (M = 100,000,000) to achieve a 200 year permanence increase.
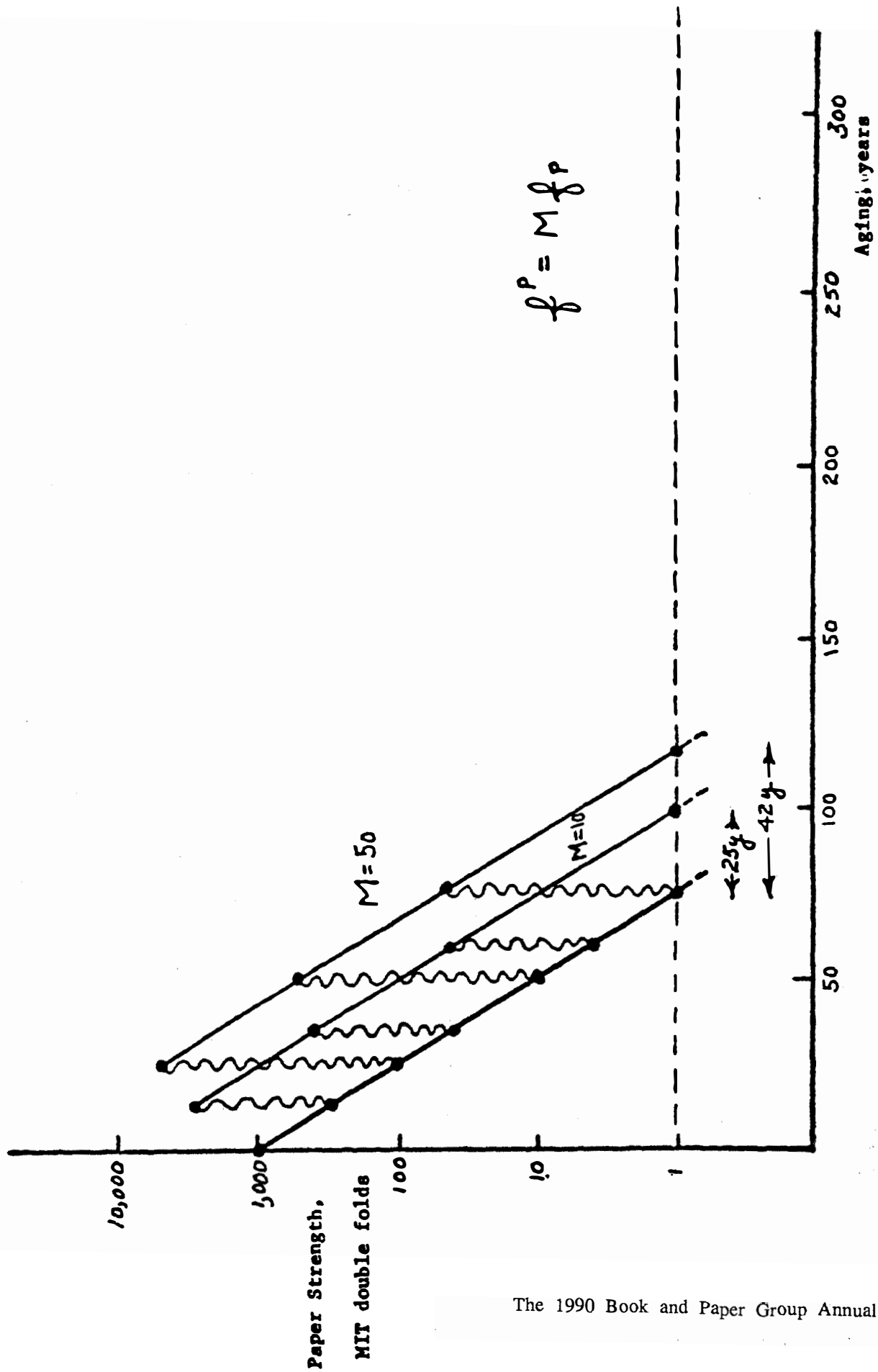
Fig. 8 Increased paper permanence resulting from proportional strengthening of model paper. All papers are increased in strength to a value M times the pre-treatment strength, fp. $k = -0.04$ year^{-1}.
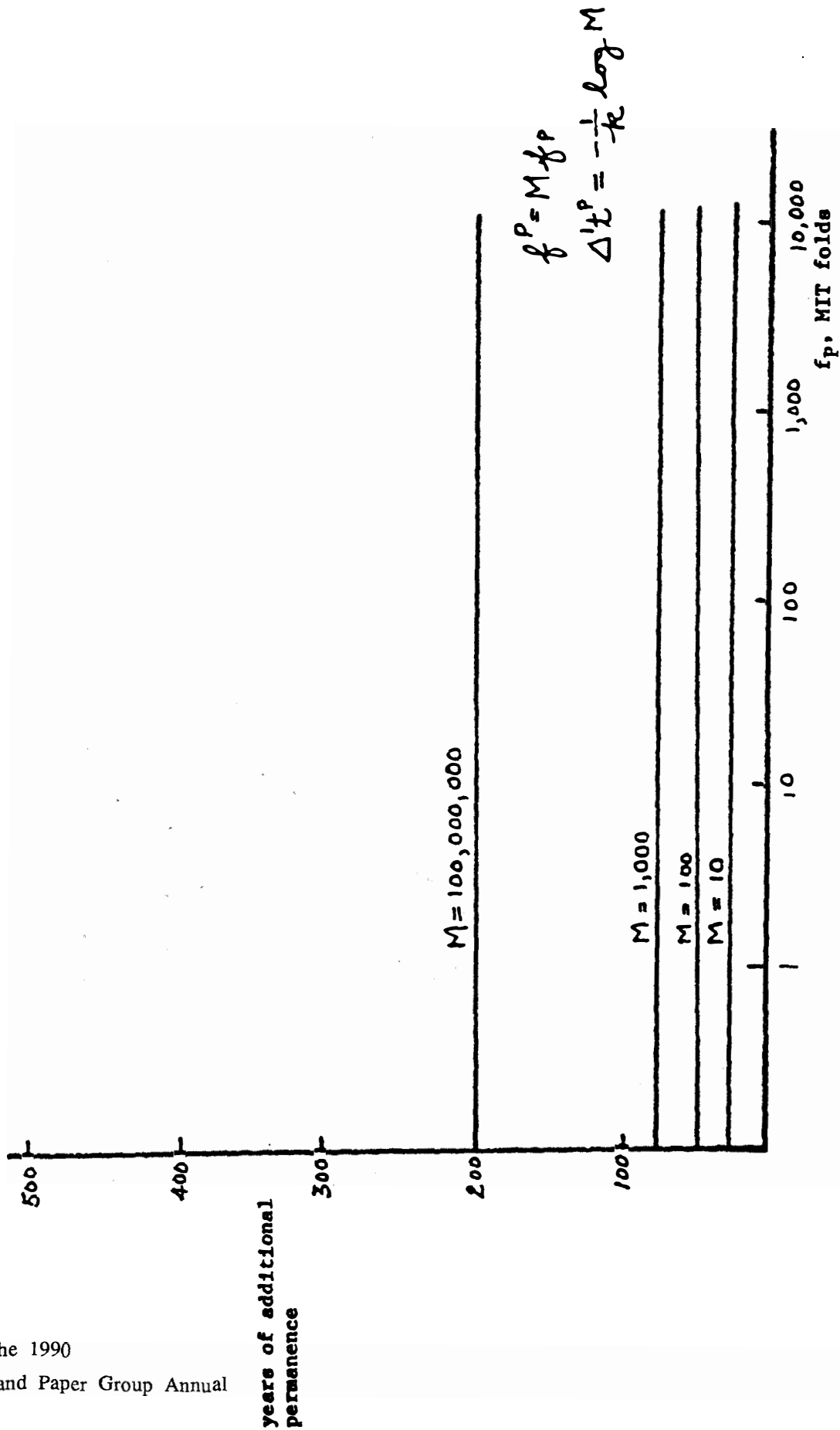
Fig. 9 Paper permanence increase resulting from proportional strengthening of model paper. If a more slowly deteriorating paper is strengthened, small M values are required to attain a given permanence increase. Paper D of Fig. 1 will have a 200 year permanence increase at M = 250,000.

3. Inverse Proportional Strengthening

Thus far we have investigated strengthening processes which one might reasonably expect, on chemical and physical grounds, to be capable of small scale and large scale development and use. There remains one major mode of strengthening which has been viewed as potentially the best -- papers would receive different strength increases with the weakest papers strengthened most. Though no such process is known to the author its general characteristics can be explored using the methods already developed. The process we shall call inverse strengthening is such a strengthening process which increases the strength by an amount inversely proportional to the pre-treatment strength. Inverse Proportional Strengthening: a strengthening process which increases the MIT fold endurance of each treated paper by an amount inversely related to its strength. Mathematically this is expressed:

(A-16)

$$f^{IP} = f_p + \frac{C}{f_p}$$

where C is the inverse proportionality constant characteristic of a given process for all treated papers. Table 1 selectively indicates strengthening for a few sets of conditions; it shows greater strengthening of weaker papers.

Table 1
Inverse Proportional Strengthening of Paper

Inverse Proportionality	Pre-Treatment Fold Strength,	Folds Added by Treatment,	Fold Strength of Treated Papers
Constant, C	f_p	$\dfrac{c}{f_p}$	f^{Ip}
10	1	10	11
10	10	1	11
10	100	0.1	100.1
10	1,000	0.01	1,000.01
1,000	1	1,000	1,001
1,000	10	100	110
1,000	100	10	110
1,000	1,000	1	1,001

Computations of the type used in compiling Table 1 can be used to obtain aging curves (Figure 10) for inverse proportional strengthening. Figure 10 shows that for C values of 10, 100 and 1,000 our model papers will obtain a <u>maximum</u> increase in permanence of 25, 50 and 75 years respectively.

Mathematical analysis demonstrates the permanence increase, $\Delta^1 t^{IP}$, relationship:

(A-19)

$$\Delta^1 t^{IP} = -\frac{1}{k} \log \left(1 + \frac{c}{f_p^2}\right)$$

Figure 11 shows the permanence extension for various values of C. Like proportional strengthening there is a logarithmic dependence upon the proportionality constant so once again any increase in C yields diminishing returns in permanence. As with incremental strengthening, the permanence increase is less for stronger papers. We again recognize the futility of attempting to achieve a 200 year permanence increase by strengthening alone; even if an inverse strengthening process were developed a C value of at least 100,000,000 would be required.
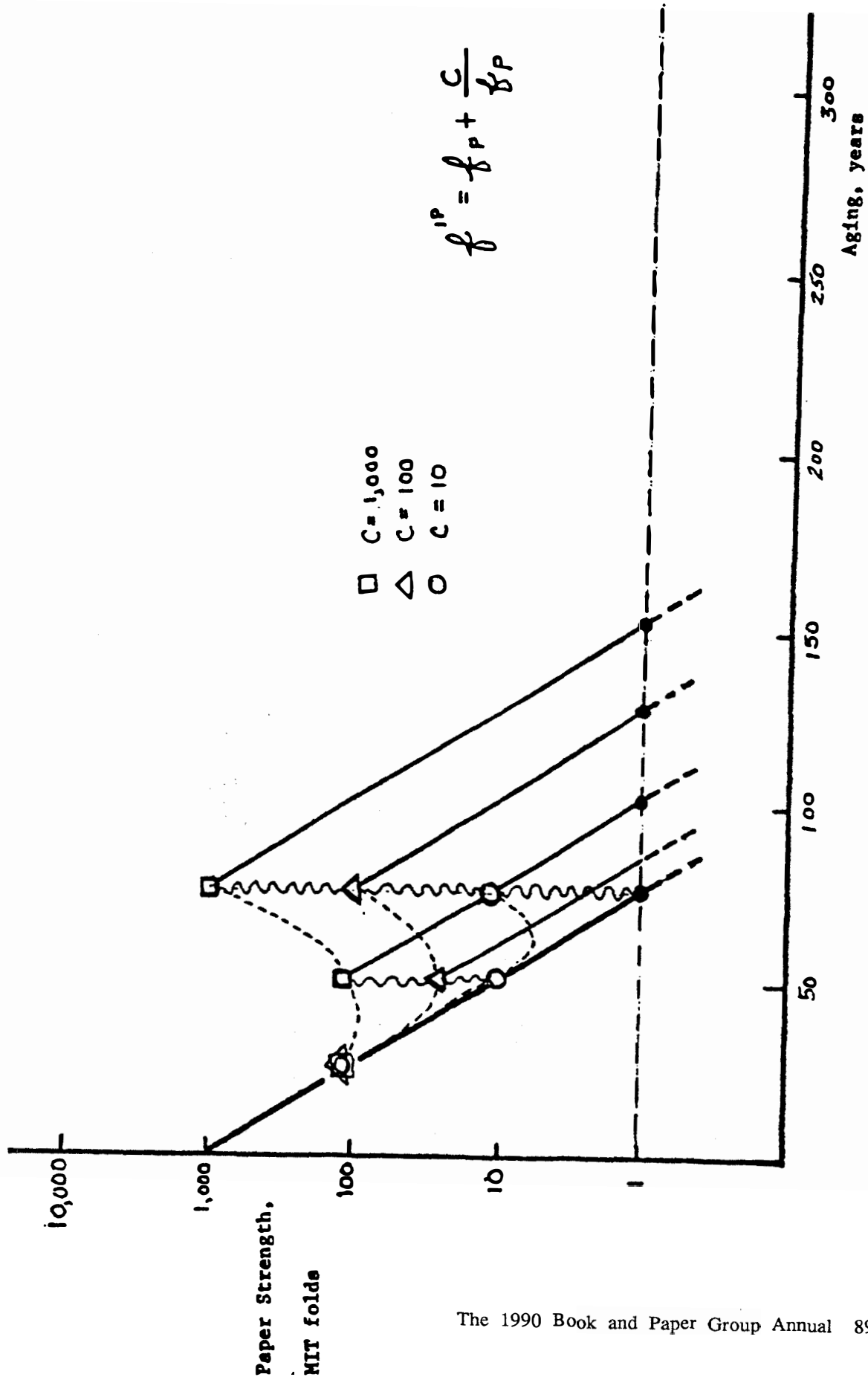
Fig. 10 Increased paper permanence resulting from inverse proportional strengthening. Papers of pre-treatment strength, fp, values 1, 10, and 100 MIT double folds are each increased in strength by the amount c/fp for C values of 10, 100, and 1,000. k = -0.04 year⁻¹.

$$f^{'p} = f_p + \frac{c}{f_p}$$

□ C = 1,000
△ C = 100
○ C = 10

Paper Strength, MIT folds

Aging, years

years of additional
permanence

500

400

300

200

100

C = 100,000,000

C = 10,000

C = 100

C = 10

$$f^{IP} = f_P + \frac{C}{f_P}$$

$$\Delta t^{IP} = -\frac{1}{k} \log\left(1 + \frac{C}{f_P^2}\right)$$

10   100   1,000   10,000
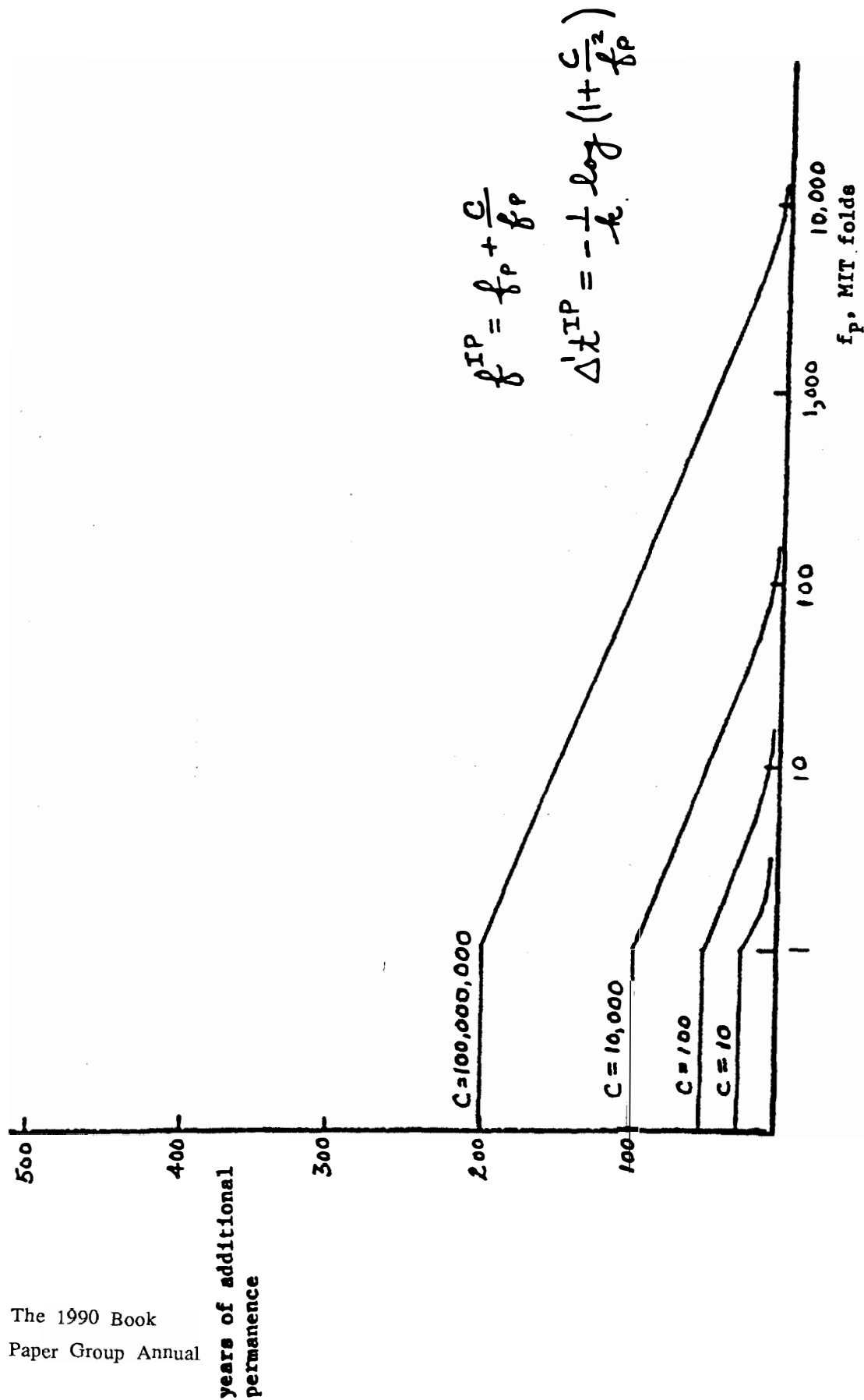
f_P, MIT folds

Fig. 11   Paper permanence increase resulting from inverse proportional
strengthening of model paper. If a more slow deteriorating paper is
strengthened small C values are required to attain a given permanence
increase. Paper D of Fig. 1 will have a 200 year permanence increase
for C values greater than 250,000. k = 0.04 year^{-1}.

V. Combined Deacidification and Strengthening

In this section the permanence effects of processes which combine strengthening with a change in the deterioration rate will be explored. The most important practical case is the one in which the slope is decreased but the discussion will be able to encompass slope increases as well[*]. Though the strengthening process itself may induce a slope change (either positive or negative), the discussion will be conducted by considering a combined strengthening/deacidification process. This approach is chosen because deacidification is a process which is certain to produce the desired slope decrease when acidic papers are treated.

The discussion will primarily utilize the graphical representations and notation previously employed; Figure 4 should be referred to for a general picture of how deacidification combined with strengthening greatly extends paper permanence. Detailed mathematical derivations can be found in the Mathematical Appendix.

The increase in permanence associated with a combined _incremental_ strengthening and deacidification process is:

(A-22)

$$\Delta^1 t^{I+D} = -\frac{1}{k} \log \left[\frac{(f_p + \Delta f)^n}{f_p} \right]$$

The strength/aging curve for this system is omitted (it would resemble Figure 4) but (A-22) is plotted for several values of n and Δf in Figure 12.

Combined _proportional_ strengthening and deacidification produces a permanence increase expressed algebraically as:

(A-28)

$$\Delta^1 t^{P+D} = -\frac{1}{k} \left[(n-1) \log f_p + n (\log M) \right]$$

which is displayed graphically in Figure 13.

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[*]   The mathematical equations can also be used to evaluate the permanence consequences of employing deacidification treatments which cause an initial increase or decrease in strength.

Finally, combined <u>inverse proportional</u> strengthening and deacidification yields permanence increases given by:

(A-32)

$$\Delta^1 t^{IP+D} = -\frac{1}{k} [n \log (f_p^2 + C) - (n+1) \log f_p]$$

and shown in Figure 14.

Figures 12, 13 and 14 all show the very large increase in permanence resulting from combined deacidification and strengthening compared with each treatment alone. Moreover, the <u>combined effect</u> is seen to be <u>greater than the sum of the effects of each treatment alone</u>. Processes in which the combination of parts is greater than the sum of the individual parts are said to be exhibit <u>synergism</u>. In practical applications it would obviously be advantageous to select treatment conditions which, among other relevant factors, would maximize the synergistic effect. Mathematically the magnitude of the synergistic effect is given by:

(A-34)

$$synergistic \; permanence \; increase \equiv \Delta^1 S^{S+D} = \Delta^1 t^{S+D} - (\Delta^1 t^S + \Delta^1 t^D)$$

Derivations of the synergistic permanence increases are found in the Mathematical Appendix; the results are presented algebraically below and in Figures 15, 16 and 17:

(A-36)

$$\Delta^1 S^{I+D} = -\frac{n-1}{k} \log [1 + \frac{\Delta f}{f_p}]$$

(A-38)

$$\Delta^1 S^{P+D} = -\frac{n-1}{k} \log M$$

(A-40)

$$\Delta^1 S^{IP+D} = -\frac{n-1}{k} \log [1 + \frac{C}{f_p^2}]$$

Figures 12-17 consolidate a great deal of information concerning the relationships of strengthening and deacidification to practical preservation problems. In a subsequent paper the
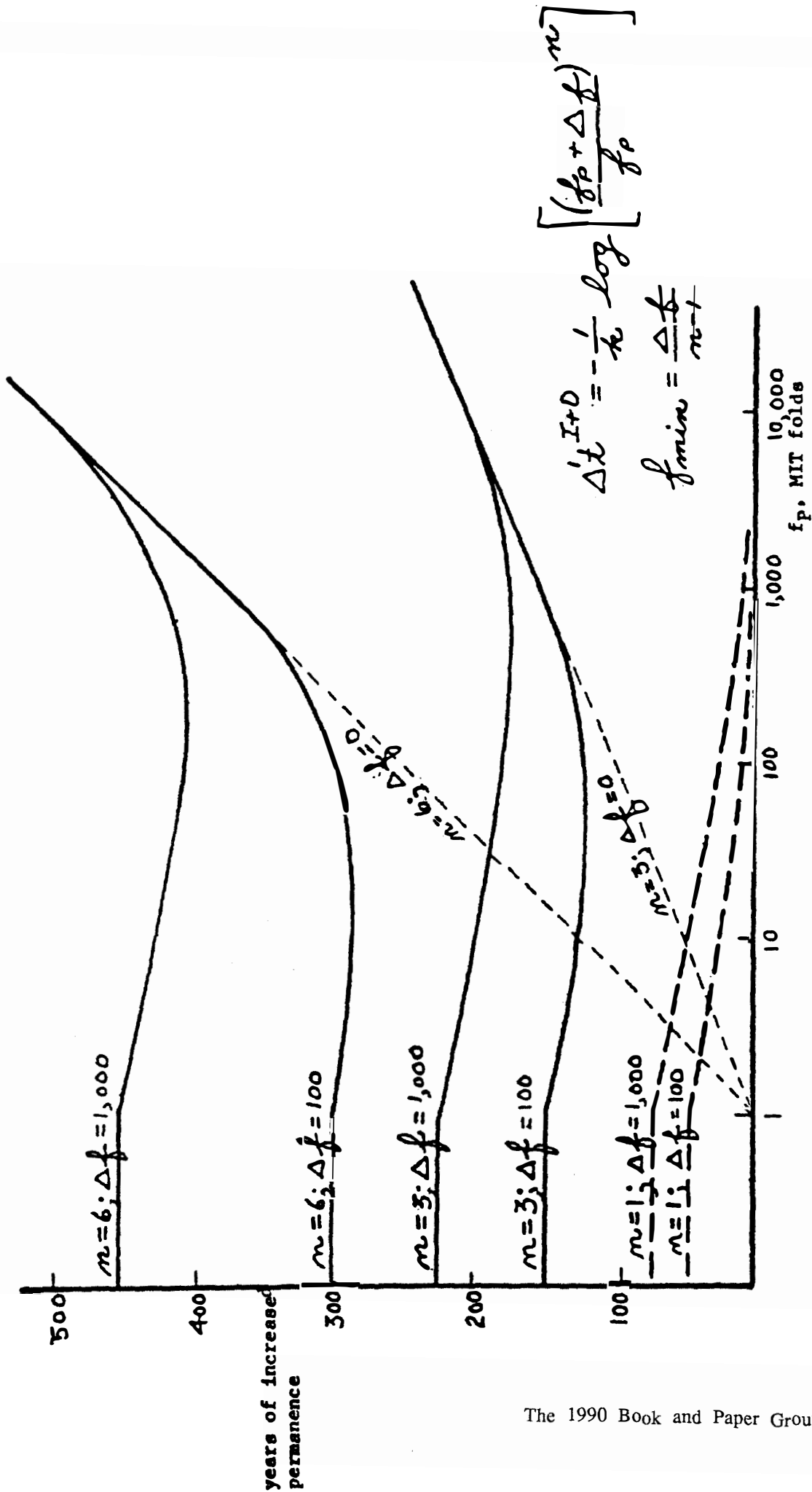
Fig. 12 Paper permanence increase resulting from combined incremental strengthening and deacidification (————). Also shown are effects of strengthening alone, $n = 1$ (————) and deacidification alone, $f = 0$ (— — — —). $k = -0.04$ year^{-1}.

$$\Delta t'^{I+D} = -\frac{1}{k} \log \left[\left(\frac{f_{fp} + \Delta f}{f_p} \right)^m \right]$$

$$f_{min} = \frac{\Delta f}{n-1}$$

years of increased permanence

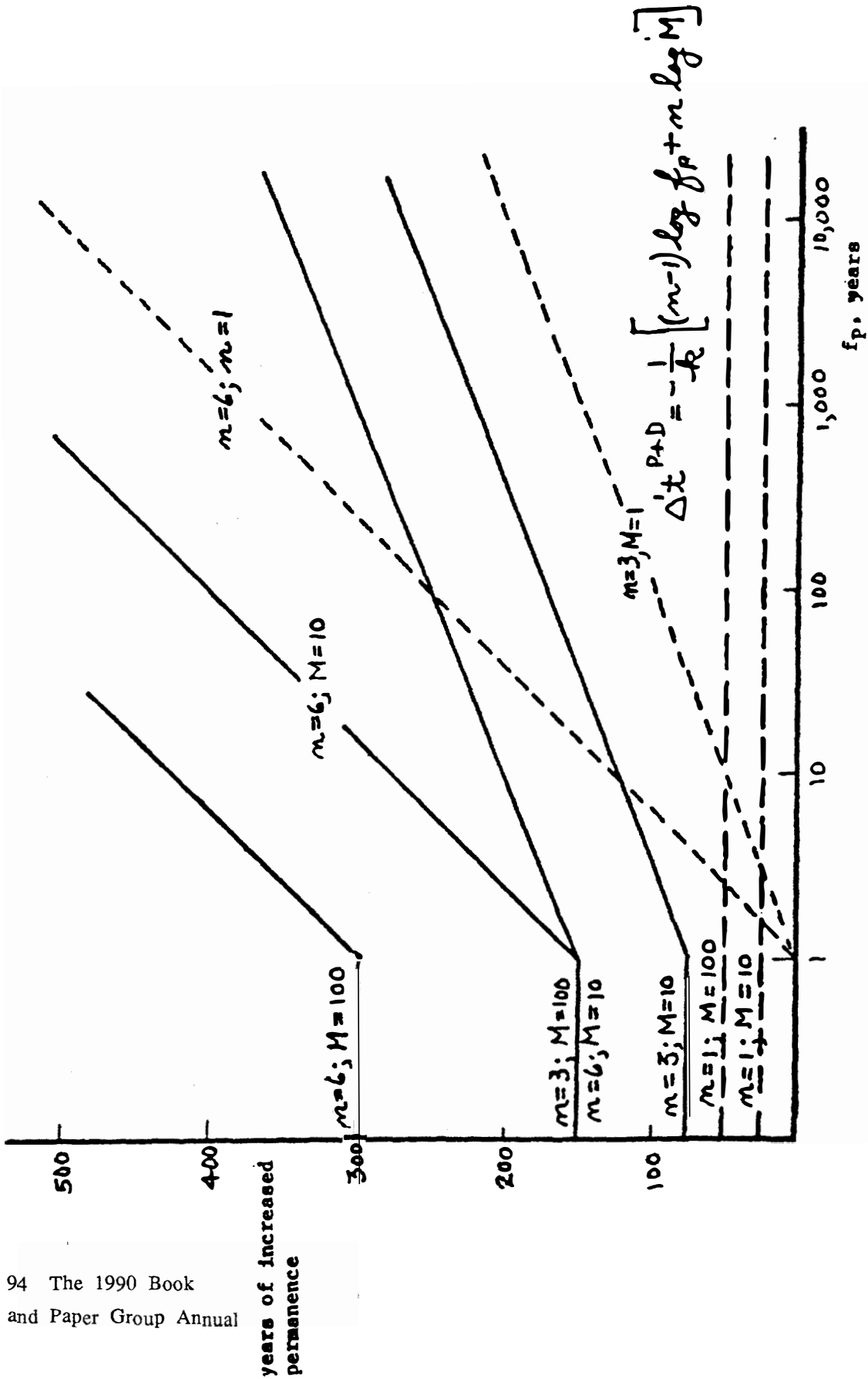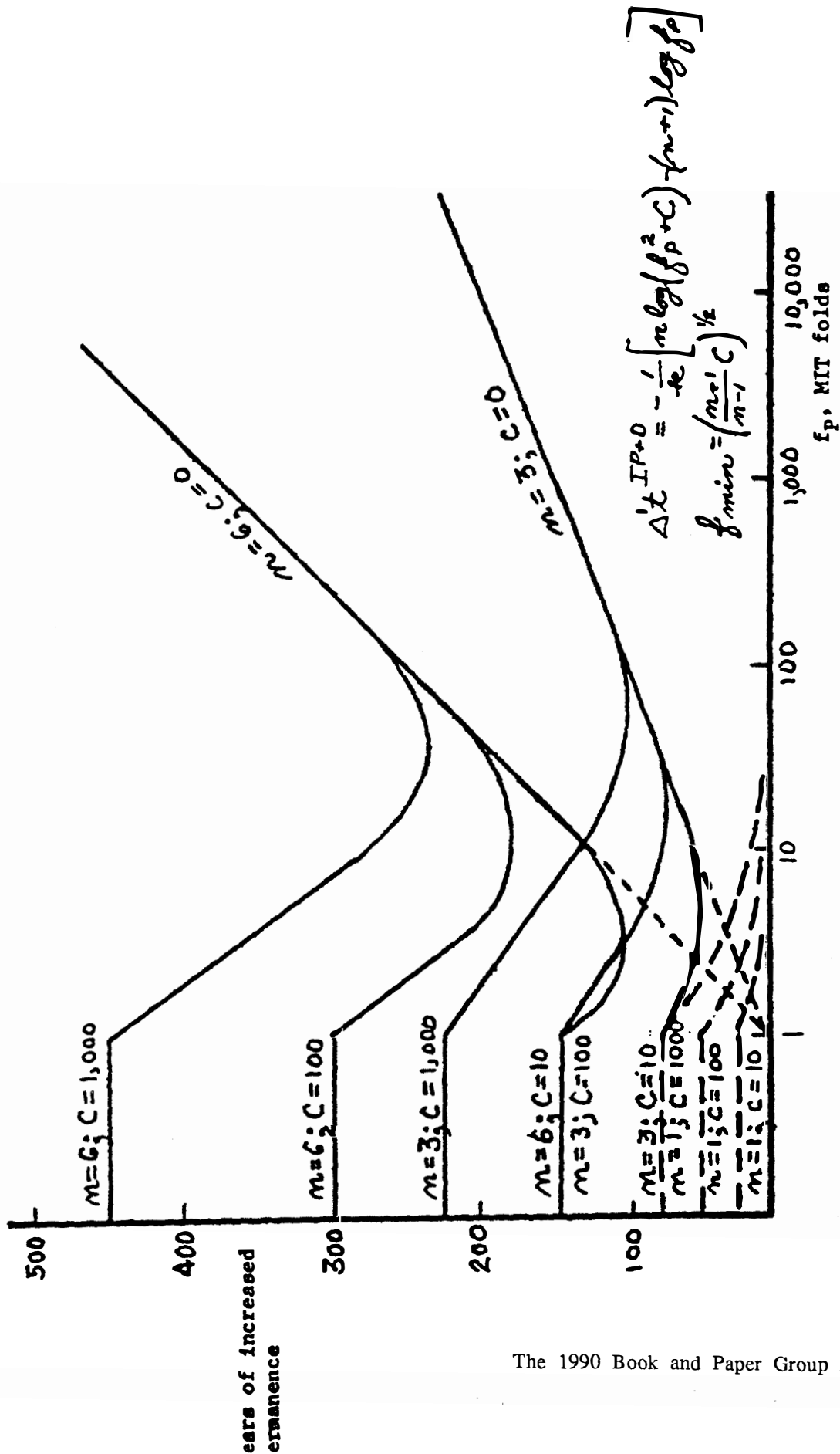$$\Delta t^{P+D} = -\frac{1}{k}\left[(m-1)\log f_P + m\log M\right]$$

Fig. 13   Paper permanence increase resulting from combined proportional strengthening and deacidification (_____). Also shown are effects of strengthening alone, $n = 1$ (_____) and deacidification alone, $M = 1$ (_____). $k = -0.04$ year^{-1}.

m=6; C=0

m=3; C=0

m=6; C=1,000

m=6; C=100

m=3; C=1,000

m=6; C=10

m=3; C=100

m=3; C=10
m=3; C=1000
n=1; c=100
n=1; c=10

$$\Delta't^{IP\to0} = -\frac{1}{k}\left[n\log(\beta_p^2+C)-(n+1)\log\beta_p\right]$$

$$f_{min}=\left(\frac{m+1}{m-1}C\right)^{1/k}$$

f_p, MIT folds

ears of increased
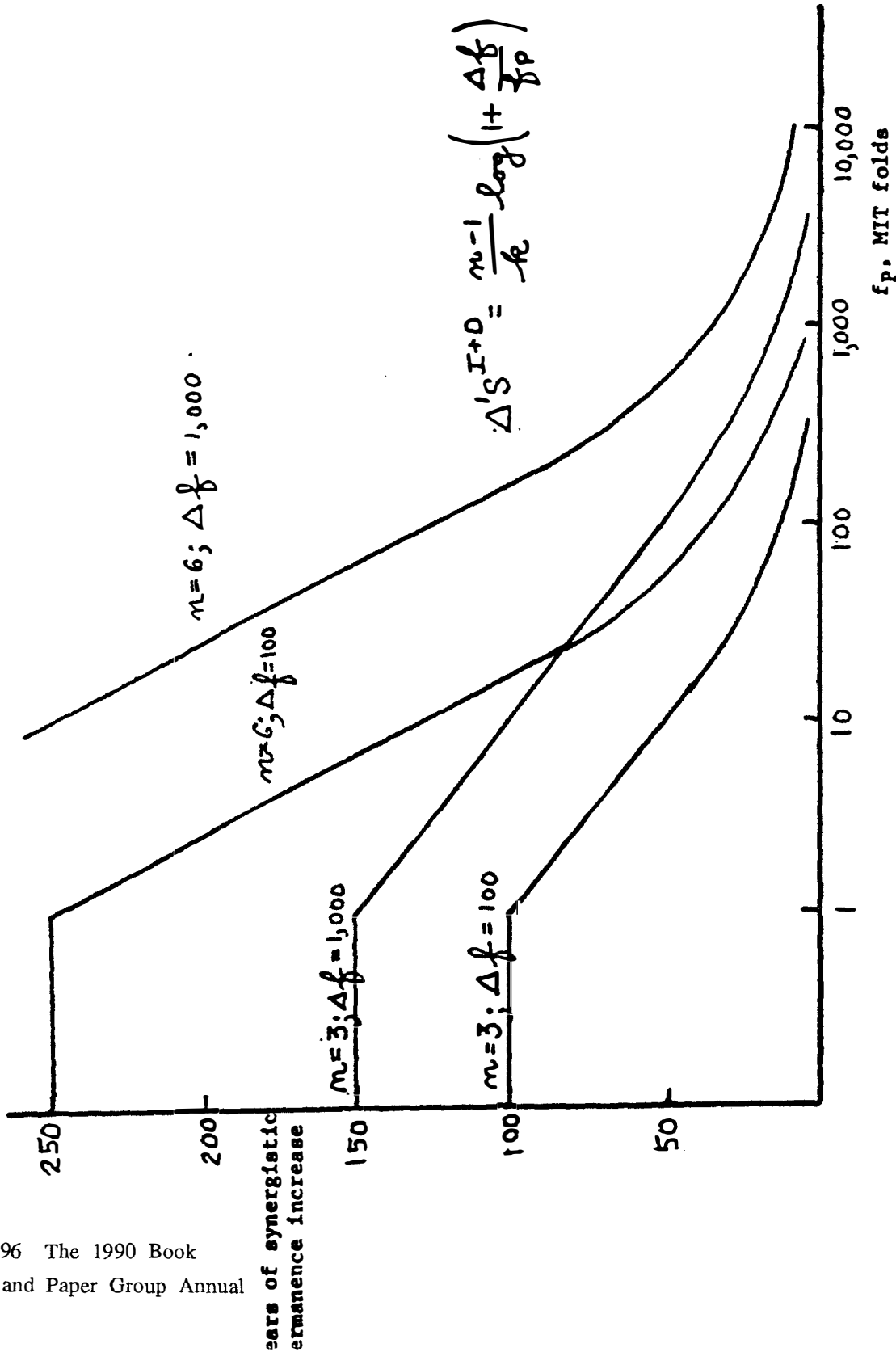ermanence

500
400
300
200
100

Fig. 14   Paper permanence increase resulting from combined inverse proportional strengthening and deacidification (———). Also shown are effects of strengthening alone, n = 1 (———) and deacidification alone, C = 0 (– – – – –). k = -0.04 year^{-1}.

Fig. 15   Synergistic paper permanence increase resulting from combined incremental strengthening and deacidification of model paper. Synergistic effect is zero if $n = 1$ and/or $\Delta f = 0$. $k = -0.04$ year^{-1}.

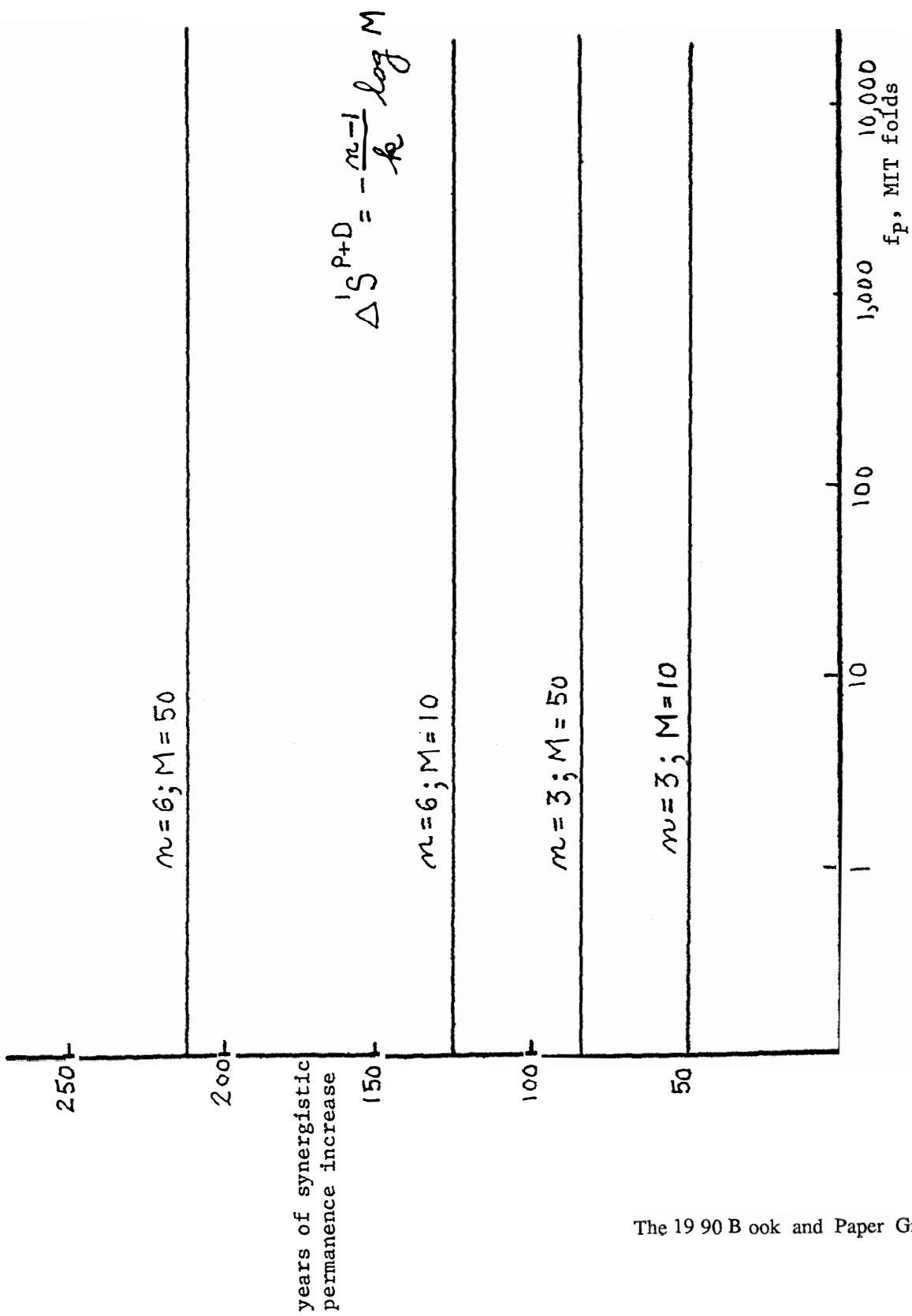$$\Delta'S^{P+D} = -\frac{m-1}{k}\log M$$

Fig. 16   Synergistic paper permanence increase resulting from combined proportional strengthening and deacidification. Synergistic effects are zero if n = 1 and/or M = 1. k = -0.04 year^{-1}.

$$\Delta' S^{IP+D} = -\frac{m-1}{k} \log\left(1 + \frac{C}{f_P^n}\right)$$

$m = 6; C = 200$

$m = 6; C = 20$

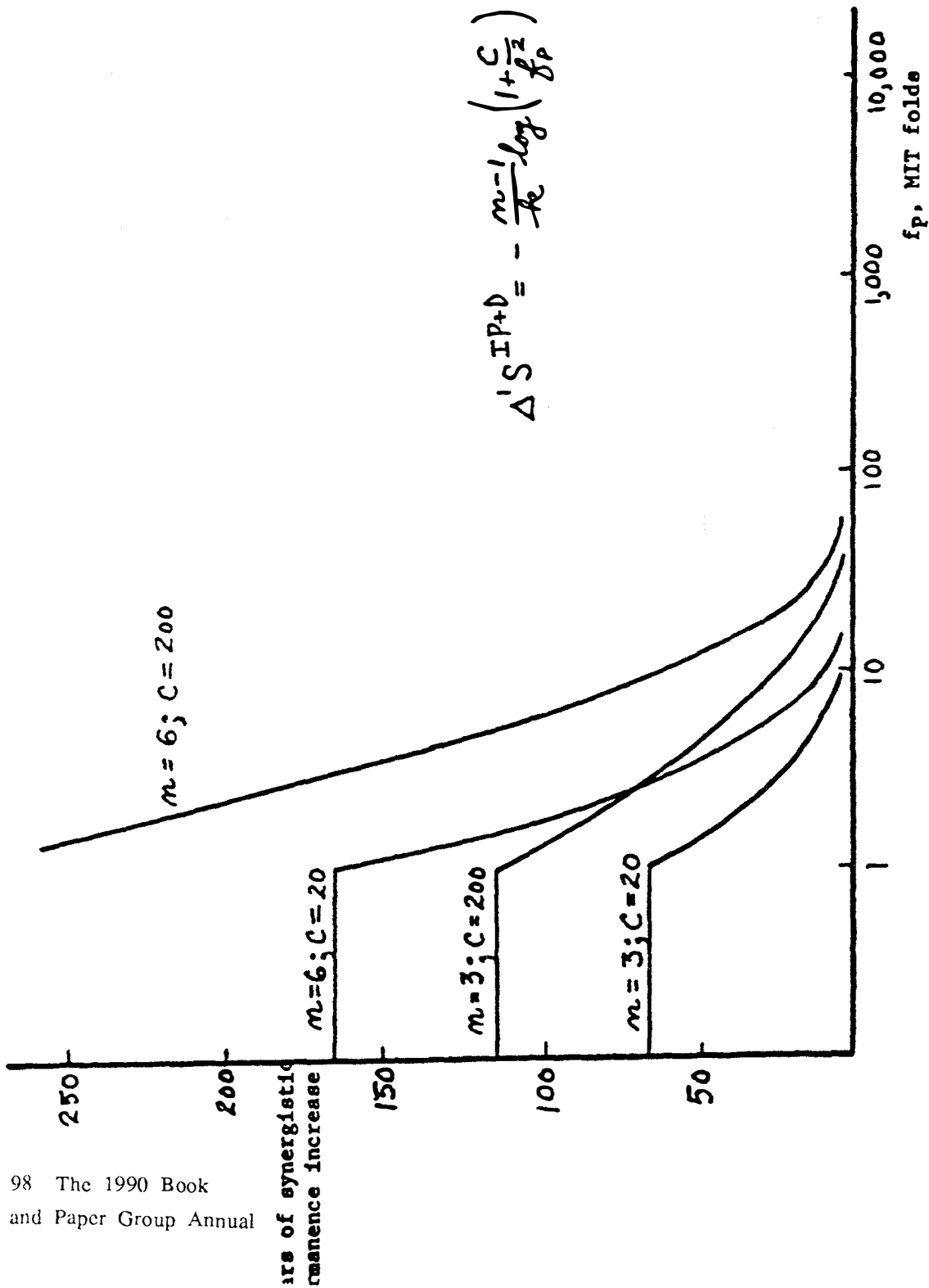$m = 3; C = 200$

$m = 3; C = 20$

Fig. 17   Synergistic paper permanence increase resulting from combined inverse
proportional strengthening and deacidification. No synergistic effects
are observed if n = 1 and/or C = 0.

author will utilize the concepts and relationships developed here in conjunction with published strengthening and deacidification process data to evaluate the efficacy of the processes for various types of library and archives collections, to suggest strategies for employment these processes and to provide guides for future research and development efforts. The conclusions drawn here will be more general but two points must be emphasized. First, the conclusions drawn refer specifically to papers whose deterioration rate upon aging is predominately determined by the acidity in the paper which is reduced when the papers are deacidified. Second, the model processes are "pure": deacidification processes change only the acidity deterioration rate but have no effect on paper strength; strengthening processes only add strength to the paper but have no effect upon the rate of paper strength loss.

VI. Conclusions

1. By making use of reasonable approximations and assumptions about paper permanence, rates of paper deterioration, and characteristics of strengthening and deacidification processes it is possible to develop mathematical relationships which provides estimates of paper permanence increases associated with a variety of strengthening and deacidification procedures.

2. Presently available deacidification processes (which can achieve n values of 3 or greater) can significantly extend the anticipated storage life of average or stronger papers. However, deacidification processes alone do little to increase the permanence of very weak papers.

3. Strengthening processes alone do relatively little to increase the permanence of papers of any strength except for proportional mode processes, and for them limited efficacy decreases with increasing pre-treatment paper strength. Treatment parameters (Δf, M and C) sufficient to achieve useful increases in permanence by strengthening alone are probably unattainable.

4. Combining deacidification and strengthening treatments can provide substantial increases in paper permanence with presently available or probably attainable process parameters.

5. Maximum permanence increases result when deacidification and strengthening procedures are carried out in combination. Ideally one would want a single processing procedure in which both strengthening and deacidification took place; however, the same permanence benefits (synergistic and otherwise) will accrue if two separate processes are completed over a time period during which the paper resulting from the first treatment loses little strength before the second treatment is undertaken. In practical terms, essentially the full permanence benefits of the combined treatment will be obtained if the two procedures are separated by 5-10 years or less.

6. The sequence in which the two processes are carried out does not affect the magnitude the permanence increase. This conclusion suggests a strategy of performing at once whichever process is currently available with the subsequent treatment following after research and development of the other process has been completed. Again, little of the potential permanence increase will be lost if the interval between treatments is less than 10 years.

7. Some combined processes exhibit a minimum in permanence extension in the mid-ranges of paper strength. If possible, process parameters should be adjusted so the minimum does not coincide with average paper strength of library collections.

8. Although the development and discussion here has focused on deacidification, other processes which decrease the rate of deterioration in a similar logarithmic manner will exhibit similar behavior. For example, investigation may show incorporation of an antioxidant into paper decreases the rate of oxidative deterioration by some factor n ; the oxidative contribution to the overall deterioration rate could be described by the equations and graphs presented above.

9. Although the relationships developed follow from the known behavior of paper and the assumptions and approximations made, it would be valuable to confirm them with experimental observations. The next paper will incorporate the very limited data currently available but it would be extremely useful if more strengthening and deacidification data were obtained and published. The definitions and the graphical and algebraic expressions presented here may be helpful to process developers in describing the characteristics and merits of their processes.

10. The relationships of strengthening and deacidification to paper durability are more complex and will be described in another publication.

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Mathematical Appendix

This appendix describes the mathematical procedure employed to obtain the relationship displayed in tables and graphs of the main text. It also states the assumptions and approximations made.

I. Deacidification Alone

Figure 1 shows graphically the assumption that the logarithm of paper strength as measured by MIT fold endurance, f, decreases linearly with the time for both accelerated and natural aging. The slope of the decrease is a function of temperature, relative humidity and pH for all papers as well as being a function of various individual paper qualities, e.g., fiber length, filler, size, etc. This relationship is expressed algebraically as:

(A-1)

$$\log(f_t) = \log(f_p) + kt$$

where f_p is the initial pre-treatment paper strength, f_t is its strength after a time t, and k is the slope of the deterioration curve.

If we define permanence, ^1t, as the time required for the paper to drop to an MIT double fold value (0.5 Kg load) of 1:

(A-2)

$$\log(^1f) = \log(f_p) + k(^1t)$$

and:

(A-3)

$$(^1t) = \frac{1}{k}[\log(^1f) - \log(f_p)]$$
$$= \frac{1}{k}\log[1 - \log(f_p)]$$
$$= -\frac{1}{k}\log(f_p)$$

If an acidic paper is deacidified the deterioration rate (- slope) will decrease to the smaller value k'. If the rate of fold strength loss drops by a factor of n:

(A-4)

$$k' = \frac{1}{n} k$$

$$k = nk'$$

After deacidification treatment the time for the neutral pH paper strength to drop to 1 MIT fold, $^1t^D$, will be:

(A-5)

$$(^1t^D) = -\frac{1}{k'} \log(f_p)$$

$$= -\frac{n}{k} \log(f_p)$$

The _increase_ in permanence resulting from deacidification, Δ^1t^D, is the difference between A-5 and A-3:

(A-6)

$$\Delta(^1t^D) = (^1t^D) - (^1t) = -\frac{1}{k'} \log(f_p) - \frac{1}{k} \log(f_p)$$

$$= \frac{k-k'}{kk'} \log(f_p)$$

which, using A-4, becomes:

(A-7)

$$\Delta(^1t^D) = -\frac{n-1}{nk'} \log(f_p)$$

$$= -\frac{n-1}{k} \log(f_p)$$

In order to provide numerical examples illustrating various deacidification (and strengthening) effects a _model paper_ will be defined which has an initial (newly manufactured) strength of 1,000 MIT folds (an initial strength of 50-200 folds would be more typical of book papers but would produce less easily interpreted graphs) which drops to 1 fold after 75 years; this paper has a k value of -0.04 year^{-1}. Deacidification of acid papers

typically can reduce the rate of deterioration by a factor of 3-6 times hence n values will range from 3-6.

The calculated increase in paper permanence resulting from deacidification of papers of varying pre-treatment strengths and n values of 3 and 6 is displayed in Figure 2. The graph clearly show the desirability of applying a deacidification procedure of large n value to a paper when it possesses the maximum fraction of its initial strength, i.e., early in its life.

II. Incremental Strengthening

An incremental strengthening process is defined as a paper strengthening process which adds a fixed number of additional MIT folds, Δf, to all papers irrespective of their pre-treatment fold endurance:

(A-8)

$$f^I = f_p + \Delta f$$

If, after strengthening, the paper continues to lose strength at the same <u>rate</u> as before treatment, i.e., the k value remains the same, the increased permanence can be calculated as above:

(A-9)

$$\log(f_t^I) = \log(f_p + \Delta f) + kt$$

and

(A-10)

$$(^1t^I) = [\log(f_1^I) - \log(f_p + \Delta f)]$$
$$= \frac{1}{k}[\log(1) - \log(f_p + \Delta f)]$$
$$= -\frac{1}{k}\log(f_p + \Delta f)$$

The increase in permanence, Δ^1t^1, resulting from incrementally strengthening a paper of pre-treatment strength f_p therefore is:

(A-11)

$$\Delta(^1t^I) = (^1t^I) - (^1t)$$
$$= -\frac{1}{k}\log(f_p + \Delta f) - (-\frac{1}{k}\log f_p)$$
$$= -\frac{1}{k}\log(1 + \frac{\Delta f}{f_p})$$

Figure 4 shows the calculated paper permanence increase associated with various values of f and Δf which might be attainable in an incremental paper strengthening process.

III. <u>Proportional Strength Increase</u>

A <u>proportional</u> strengthening process is defined as one in which all papers, irrespective of their pre-treatment strength, are increased to some fixed multiple value of that strength:

(A-12)

$$f^P = Mf_p$$

where M is the proportionality constant. Again following the same procedures as above the time for the strengthened paper to drop to

1 MIT double fold, $^1t^P$, can be calculated as can the increased permanence of the strengthened paper, $_\Delta{}^1t^P$:

(A-13)

$$\log(^Pf_t) = \log(f^P) + kt$$

(A-14)

$$(^1t^P) = \frac{1}{k}[\log(f_1^P) - \log(Mf_p)]$$
$$= -\frac{1}{k}\log(Mf_p)$$

(A-15)

$$\Delta(^1t^P) = (^1t^P) - (^1t)$$
$$= -\frac{1}{k}\log(Mf_p) - [-\frac{1}{k}\log(f_p)]$$
$$= -\frac{1}{k}\log(M)$$

Figure 5 shows the calculated increases in permanence associated with values which might be attainable in a proportional strengthening process.

IV. Inverse Proportional Strengthening

An _inverse proportional_ strengthening process is defined as one which increases the strength of the paper by an amount inversely proportional to the pre-treatment strength:

(A-16)

$$f^{IP} = f_p + \frac{C}{f_p}$$

where C is the proportionality constant.

As before the time for the strengthened paper to drop to a 1 MIT fold endurance can be derived:

(A-17)

$$\log(f_t^{IP}) = \log(f^{IP}) + kt$$

(A-18)

$$(^1t^{IP}) = \frac{1}{k}[\log(f_1^{IP}) - \log(f^{IP})]$$

$$= \frac{1}{k}[\log(1) - \log(f_p + \frac{C}{f_p})]$$

$$= -\frac{1}{k}\log[\frac{C}{f_p}]$$

And the increase in permanence resulting from inverse proportional strengthening, Δ^1t^{IP} is:

(A-19)

$$\Delta(^1t^{IP}) = (^1t^{IP}) - (^1t)$$

$$= -\frac{1}{k}\left([\log(f_p) + \frac{C}{f_p}] - [-\log(f_p)]\right)$$

$$= -\frac{1}{k}\log(1 + \frac{C}{f_p^2})$$

Figure 6 displays increases in permanence for papers of various proportional strengths associated with a range of C values. The C values have been chosen to display a range of effects; no experimental data of inverse proportional strengthening is available.

V. Combined Deacidification and Strengthening

The increases in paper permanence calculated above for strengthened papers are based upon the assumption that the rate of deterioration following treatment is the same that prior to treatment. Strengthening processes may also have the effect of increasing or decreasing the deterioration rate; deacidification is known to decrease the rate for acid papers. The following sections consider the increase in permanence of strengthening processes accompanied by a change in the rate of deterioration from k to k'. In general k' may be larger, smaller or equal to k; for deacidified acidic papers k'<k. As before we express this relationship:

(A-4)

$$k' = \frac{1}{n}$$

$$k = nk'$$

where n may assume any positive value; i.e., n $\geq$ 0.

Slope change may be the result of deacidification or strengthening processes individually or in combination. For convenience, (and because we know deacidification decreases the slope) we shall describe all changes in k value associated with a treatment as the result of an accompanying deacidification.

VI. Combined Incremental Strengthening and Deacidification

Prior to treatment the paper of strength f_p will deteriorate at a rate given by the rate constant k; A-3 gives the time required for it to drop to strength of 1 MIT fold:

(A-3)

$$(^1t) = -\frac{1}{k}\log(f_p)$$

After treatment, the paper, now of strength $f_p + \Delta f$, deteriorates at a new rate governed by k'. Utilizing A-10, the time for the incrementally strengthened and deacidified paper to drop to 1 MIT double fold, $^1t^{I+D}$, is:

(A-20)

$$(^1t^{I+D}) = -\frac{1}{k'}\log(f+\Delta f)$$

The increase in permanence associated with a process combining deacidification and incremental strengthening, Δ^1t^{I+D}, is therefore:

(A-21)

$$\Delta(^1t^{I+D}) = (^1t^{I+D}) - (^1t)$$

$$= -\frac{1}{k'}\log(f_p+\Delta f) - [-\frac{1}{k}\log(f_p)]$$

$$= \frac{1}{kk'}\log[\frac{(f_p+\Delta f)^k}{f_p^{k'}}]$$

Combining A-21 and A-4, we obtain the general relationships for the increase in permanence:

(A-22)

$$\Delta(^1t^{I+D}) = -\frac{1}{nk}\left(\log[\frac{(f_p+\Delta f)^{nk'}}{f_p^{k'}}]\right)$$

$$= -\frac{1}{k}\log[\frac{(f_p+\Delta f)^n}{f_p}]$$

Figure 7 displays the permanence increase Δ^1t^{I+D} as a function of f_p for reasonable values of n, Δf and f_p. As seen in the figure the increase in permanence goes through a minimum. The pre-treatment fold value at the minimum, f_{min}, may be determined in

algebraic form by taking the first derivative of $\Delta^1 t^{I+D}$ with respect to f_p and setting it equal to 0:

(A-23)

$$\left[\frac{\partial (\Delta(^1 t^{I+D}))}{\partial f_p} \right]_{n,\Delta f} = -\frac{2.303}{k} \left[\frac{n}{f_p + \Delta f} - \frac{1}{f_p} \right]$$

(A-24)

$$-\frac{2.303}{k} \left[\frac{n}{f_{min} - \Delta f} - \frac{1}{f_{min}} \right] = 0$$

so:

$$f_{min} = \frac{\Delta f}{n-1}$$

Figure 7 clearly shows that at n values of 6 and 3 and Δf values of 1,000 and 100 in agreement with equation A-24 the minima lie at f values:

$$\frac{1,000}{6-1} = 200, \qquad \frac{100}{6-1} = 20,$$

and

$$\frac{1,000}{3-1} = 500, \qquad \frac{100}{3-1} = 50 \text{ folds.}$$

VII. Combined Proportional Strengthening and Deacidification

Prior to strengthening and deacidification the anticipated permanence is given by A-3 as :

(A-3)

$$(^1t) = -\frac{1}{k}\log(f_p)$$

After treatment the strengthened paper having Mf_p MIT folds degrades at a reduced rate:

(A-25)

$$\log(f_t^{P+D}) = \log(Mf_p) + k't$$

and it drops to a single 1 MIT double fold strength in the time:

(A-26)

$$(^1t^{P+d}) = \frac{1}{k'}[\log(f_1^{P+d}) - \log(Mf_p)]$$
$$= -\frac{1}{k'}\log(Mf_p)$$

The _increase_ in permanence associated with deacidification and proportional strengthening, Δ^1t^{P+D} is:

(A-27)

$$\Delta(^1t^{P+D}) = (^1t^{P+D}) - (^1t)$$
$$= -\frac{1}{k'}\log(Mf_p) - [-\frac{1}{k}\log(f_p)]$$
$$= \frac{k-k'}{kk'}\log(f_p) - \frac{1}{k'}\log(M)$$

which upon substitution from (A-4) yields:

(A-28)

$$\Delta(^1t^{P+D}) = -\frac{1}{k}[(n-1)\log(f_p) + n\log(M)]$$

Figure 8 displays Δ^1t^{P+D} as a function of f_p for several reasonable values of M and n. No minimum is observed in Δ^1t^{1P+D} _vs._ f_p.

VIII.   Combined   Inverse   Proportional   Strengthening   and Deacidification

The algebraic expression for the increase in permanence of a paper treated by a process which increase paper strength inversely to its pre-treatment strength and changes the rate of post-treatment rate of deterioration is derived in a manner similar to the previous examples:

(A-16)

$$f^{IP} = f_p + \frac{C}{f_p}$$

(A-29)

$$\log(f_t^{IP+D}) = \log(f_p + \frac{C}{f_p}) + K't$$

(A-30)

$$(^1t^{IP+D}) = -\frac{1}{K'}\log(f_p + \frac{C}{f_p})$$

and

(A-31)

$$\Delta(^1t^{IP+D}) = (^1t^{IP+D}) - (^1t)$$

$$= -\frac{1}{k}\log(f + \frac{C}{F_p}) - [-\frac{1}{k}\log(f_p)]$$

$$= \frac{1}{kk'}\log[\frac{(f_p + \frac{C}{f_p})^k}{f_p{}^{k'}}]$$

$$= \frac{1}{kk'}\log[\frac{(f_p + \frac{C}{f_p})^k}{f_p{}^{k+k'}}]$$

and utilizing (A-4):

(A-32)

$$\Delta(^1t^{IP+D}) = -\frac{1}{k}[n\log(f_p^2 + C) - (n+1)\log(f_p)]$$

Figure 9 displays $\Delta^1 t^{IP+D}$ as a function of f_p for several values of C and n. Minima are again observed as expected for a function (A-32) which combines increasing permanence with pre-treatment fold endurance arising from deacidification and the decreasing permanence extension with pre-treatment fold endurance of an inversely proportional strengthening process. Expressions for minima are derived as before:

$$\left[\frac{\partial(\Delta^1 t^{Ip+D})}{\partial f_p}\right]_{n,c} = 2.303\left[-\frac{n}{k}\left(\frac{1}{f_p^2+C}\right)(2f_p)+\left(\frac{n+1}{k}\right)\left(\frac{1}{f_p}\right)\right]$$

which when set equal to 0 for $f_p = f_{min}$ reduces to:

(A-33)

$$f_{min} = \left(\frac{n+1}{n-1}C\right)^{\frac{1}{2}}$$

The minima shown on Figure 9 correspond to those calculated from A-33.

IX. Synergistic Effects

Examination of Figures 7, 8 and 9 shows the increase in permanence from a combined strengthening and deacidification (or other slope decreasing process) procedures is greater than the sum of the effects of strengthening and deacidification alone. This synergistic effect is especially significant for the weakest papers, and is defined as the difference between combined and separate strengthening and deacidification permanence increases:

(A-34)

$$(^1S^{S+D}) \equiv \Delta^1 t^{S+D} - (\Delta^1 t^{S} + \Delta^1 t^{D})$$

A. Incremental Synergism

The synergistic increase in permanence resulting from combined incremental strengthening and deacidification $^1S^{I+D}$ is the difference between the increase in permanence of the combined processes, $\Delta^1 t^{I+D}$, and the sum of the increase in permanence of the individual treatments, $\Delta^1 t^I$ and $\Delta^1 t^D$:

(A-35)

$$\Delta^1 S^{I+D} = \Delta^1 t^{I+D} - (\Delta^1 t^{I} + \Delta^1 t^{D})$$

Substituting in A-34 from A-4, A-6, A-11 we have:

(A-36)

$$\Delta^1 S^{I+D} = -\frac{1}{k} \log \left[\frac{(f_p + \Delta f)^n}{f_p} \right] - \left[-\frac{1}{k} \log (1 + \frac{\Delta f}{f_p}) - \frac{n-1}{k} \log f_p \right]$$

$$= -\frac{n-1}{k} \log (1 + \frac{\Delta f}{f_p})$$

Figure 15 displays the synergistic effect for selected values of Δf, f_p and n.

B.   Proportional Synergism

The synergistic increase in permanence associated with a combined proportional strengthening and deacidification process is similarly defined and calculated from equations A-7, A-15 and A-25:

(A-37)

$$\Delta^1 S^{P+D} = -\frac{n-1}{k} \log M$$

(A-38)

$$\Delta S^{P+D} = \Delta^1 t^{P+D} - (\Delta^1 t^P + \Delta^1 t^D)$$

$$= \frac{n}{k} \left[\frac{n-1}{n} \log f_p + \log M \right] - \left[-\frac{1}{k} \log M + \frac{n-1}{k} \log f_p \right]$$

Figure 16 displays the synergistic effects for selected values of M, n and k; the effect is independent of the pre-treatment fold strength.

C.   Inverse Proportional Synergism

Synergistic effects associated with inverse proportional strengthening and deacidification can be defined and calculated from equations A-4, A-19 and A-31 as:

(A-39)

$$\Delta^1 S^{IP+D} = \Delta^1 t^{IP+D} - [\Delta^1 t^{IP} + \Delta^1 t^D]$$

$$= \frac{n}{k} \left[\log (f_p^2 + C) \right] - \left[-\frac{n-1}{k} \log f_p - \frac{1}{k} \log (1 + \frac{C}{f_p}) - \frac{n-1}{k} \log f_p \right]$$

(A-40)

$$\Delta^1 S^{IP+D} = -\frac{n-1}{k} \log \left[1 + \frac{C}{f_p^2} \right]$$

These effects are displayed in Figure 17 which, like incremental strengthening, shows a (deeper) minimum.