The Getty Conservation Institute

research in conservation

Accelerated Aging

Photochemical and Thermal Aspects

Robert L. Feller

Editor: Dinah Berland
Production coordinator: Anita Keys
Cover designer: Garland Kirkpatrick
Designer: Irina Averkieff
Illustrator: Ad • Infinitum
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The Getty Conservation Institute

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Research in Conservation

This reference series is intended to make available the findings of research conducted by the Getty Conservation Institute and its individual and institutional research partners, as well as state-of-the-art reviews of conservation literature. Each volume covers a separate topic of current interest and concern to conservators. Other volumes in the Research in Conservation series include: *Cellulose Nitrate in Conservation* (1988), *Statistical Analysis in Art Conservation Research* (1988), *Evaluation of Cellulose Ethers for Conservation* (1990), *Protection of Art from Atmospheric Ozone* (1990), *Epoxy Resins in Stone Conservation* (1992), and *Airborne Particles in Museums* (1993).

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Robert L. Feller

Contents

Foreword

The difficulties inherent in accelerated-aging procedures are nicely represented by the egg. Age it at one temperature, and you get a rotten egg; at a much higher temperature, a fried one; and in between, a chicken. These three conditions produce markedly different results in ranking eggs, predicting the texture of omelets, or describing the deterioration mechanisms of chickens.

In his preface, Robert L. Feller remarks that after many years of writing, he must conclude that "one most often writes for oneself" in trying to understand a new field—hence, the author becomes his or her most important audience. While this is certainly a penetrating observation and defines Feller's lifelong dedication to his science, it only partially explains the genesis of this book, which I came to understand through numerous conversations with the author over the years.

At the start of his career, when Feller was just beginning to grapple with the issues of ranking products, estimating service life, and studying the mechanisms of deterioration of conservation materials, what he would have wished for most in the 1950s and '60s was a review in hand that presented a path through the problems and potentialities of accelerated aging. Such a review was yet to be written, but the pitfalls were clearly known to exist. In those days, the unnerving inadequacies of accelerated aging must have hung like the sword of Damocles over the heads of both the cautious and the foolhardy researcher alike. The only difference being that the foolhardy never looked up, and Feller did—doubtlessly terrified at the relationship between the suspending hair's tensile strength and his own vulnerability to error. Scientists working in industry or producing consumer products can perhaps be largely forgiven for their oversight, because it's normally not in their best interests to produce goods that will not need to be replaced. But for scientists advocating materials that will be applied to priceless works of art, not looking up can be disastrous.

Those pitfalls still exist, and the audience that needs to consider their depth has grown enormously. At one time the total fraternity of full-time individuals carrying out technical studies of works of art in the United States could all get into one taxicab together. By the time Robert Feller began working on protective coatings, this group had soared to around twenty, and the concept of "conservation science" slowly began to emerge. So new, unfettered, and interdisciplinary was this "science," George Stout characterized it as little more than a "mongrel pup that had clawed through the academic fence." Since then, however, the growth worldwide has expanded by a factor of ten, and the pup now has an academic pedigree.

From this vantage point, a carefully considered treatment on accelerated aging is long overdue, for it is our ultimate desire and dream that materials and practices should last as long as the objects to which they are applied. If that were the case today, we would have no need for conservation scientists; but the increase in research over the last two decades and the concerns and doubts many conservators openly voice clearly illustrates how far short of that goal conservation remains. This book is written for those who will use accelerated aging, particularly photochemical and thermal aging, to push the performance envelope for these products as far as possible and assist in making their results more meaningful and relevant. Does this mean, then, that the audience is limited to conservation scientists? We at the Getty Conservation Institute believe the audience is much wider. For most people, a book such as this will require a degree of dedication, and some conservators may encounter difficulties. Yet Robert Feller brings a rather unique and refreshing gift for communicating the concepts of accelerated aging against the backdrop of materials science development. He selects literature and materials in order to reinforce his points and weaves a discourse that is both informative and a recurring call back to fundamentals. The persistent reader will certainly find a wealth of interrelated material that simply does not exist in one place elsewhere.

James R. Druzik
Conservation Scientist
The Getty Conservation Institute

Preface

When I first began my work in the 1950s and '60s on the underlying causes of the deterioration of organic coatings of interest to conservators, and also began the accompanying search for types that possessed high stability, there was surprisingly little information in the literature concerning the chemical mechanisms of the deterioration of protective coatings. Today, publications in the field abound. With each passing year knowledge and understanding grows so rapidly that it is difficult to keep abreast. The journal *Polymer Degradation and Stability* is now in its sixteenth year; *Polymer Testing* is in its fourteenth. Just in the past two or three years, internationally acclaimed authorities from industry and academia have begun to make significant contributions to our understanding of the degradation of conservation-related polymers: N. S. Allen, N. Grassie, J. Lemaire, and D. M. Wiles to name a few. The latter two lectured at the Canadian Conservation Institute's Symposium '91, the proceedings of which were not yet in print at the time that the bulk of this writing was done (Grattan 1993). Also just published, the Royal Society of Chemistry's conference proceedings *Polymers in Conservation* contains important reviews on degradation chemistry by N. S. Allen, J. S. Crighton, I. C. McNeill, D. J. Priest, and other scientists from academia. These and others have written on various aspects of photochemical deterioration with greater experience and authority than I. What, then, can I hope to accomplish in the present overview? In 1987, I published a brief review titled "Some Factors to Be Considered in Accelerated-Aging Tests." In a sense, that which follows represents an expansion of that subject; the same title would be appropriate. Rather than simply decrying the difficulties in making predictions of service lifetimes by means of accelerated-aging tests, it should prove useful to describe the well-recognized difficulties and what can be done, and has been done, to circumvent them.

Who is the audience? In all truth, I must conclude after so many years that one most often writes for oneself. In an effort to grasp an unfamiliar subject, it is a useful exercise to organize the salient points and set down a summary. The material presented is based on the information compiled over a period of several decades in support of research conducted at the Research Center on the Materials of the Artist and Conservator at Mellon Institute (now Carnegie Mellon Research Institute). I trust that this overview will serve, as it has for me, as an introduction to the subject, particularly indicating its considerable breadth and its recognized limitations. Extensive references are provided to assist those who may wish to pursue various aspects in greater depth.

Individual topics will deserve more extensive and more didactically helpful discussion than achieved here. A number of major topics are not covered at all. There is nothing to be found here on the subject of experimental design, outdoor exposure per se, or of the intentional cycling of weathering conditions; also nothing on microbiological action or the effects of air pollutants. The application of ultraviolet absorbers and inhibitors is only lightly touched upon. There is nothing on the photophysics of the singlet and triplet excited states of molecules, nor on the possible role of the singlet state of oxygen. Chemical actinometry is scarcely mentioned. These topics must remain for others.

No attempt has been made to make an exhaustive search of the literature; much of it would prove to be repetitive or not particularly pertinent. Nor are the references cited necessarily the best and most significant. Instead, those selected serve mainly to support the exposition of the subject and to document the various statements and concepts put forth.

Considerable effort has been made to cite the contributions of colleagues in conservation science who have previously written concerning some of these matters; nevertheless omissions undoubtedly occur for which I must apologize.

Robert L. Feller

Acknowledgments

The opportunity provided by the Getty Conservation Institute to conduct a research project on accelerated aging problems and to compile this overview of the subject is much appreciated. Frank Preusser, former associate director of Programs at the Institute, is especially thanked for his interest in and support of the research and the preparation of this manuscript, much more extensive than originally envisioned. Throughout, James R. Druzik of the Institute's Scientific Department, has given much encouragement and advice. Paul Whitmore, director of the Research Center on the Materials of the Artist and Conservator at Carnegie Mellon Research Institute, and Eric Hansen of the Getty Conservation Institute provided a number of pertinent references to recent literature as well as helpful discussions. Also much appreciated is the editorial and design work of the Getty Conservation Institute's Publications department and the assistance, at various stages in the process, of Irina Averkieff, Dinah Berland, Jacki Gallagher, and Peter Hoffman.

The author thanks the many copyright holders for their kind permission to reproduce numerous graphs and charts that were considered to be especially useful in illustrating particular points. As she has done for so many years in the past, Mary Curran continued to be of great assistance in gathering and checking the literature. More recently, Catherine Bailie has been called upon in this effort and her cheerful, prompt response to hurried calls for help is much appreciated. Thanks also go to the librarian at Carnegie Mellon Research Institute, Lynn Labun, and her staff for much assistance and patience. As always, Sandra Melzer has typed, corrected, organized, and kept track of the numerous drafts of this and related manuscripts with much skill, speed, and steadfast good spirit.

Objectives of Accelerated Aging

So-called accelerated-aging tests are carried out for three major purposes. The first is to establish in a conveniently short time the relative ranking of materials, or physical combinations of materials, with respect to their chemical stability or physical durability. The second is to estimate or "predict" potential long-term serviceability of material systems under expected conditions of use. Thirdly, processes of deterioration are speeded up in the laboratory in order to elucidate the chemical reactions involved (the "mechanism" of the degradation) and the physical consequences thereof. An important facet of this effort is the disclosure of the overall pattern of deterioration, that is, whether the processes accelerate in time, whether there is an induction period, or whether a number of distinct stages are observable before failure occurs. The ultimate objective of this third area of investigation is the development of techniques that can monitor the extent of degradation and methods by which the useful lifetime of materials can be extended. These three major objectives are cited in the approximate order of the ease in which they can be achieved.

Introduction

In the effort to estimate the potential long-term serviceability of materials—the "maintenance of performance above a threshold level that is regarded as acceptable" (Sereda and Litran 1980)—two aspects can be distinguished. One is the stability of a material or composite of materials, that is, their resistance to environmental factors such as oxygen, ozone, moisture, heat, and light, which primarily bring about chemical changes. The other is durability, largely the physical resistance to change with respect to the stress and strain of use.

By far the most extensive literature on accelerated aging deals with the chemical stability or chemical resistance of specific materials. One may regard this emphasis as a fundamental approach, for it is generally held that it is chemical changes that are ultimately responsible for the physical disintegration and failure of materials. Much more rarely do conservators focus their attention on the physical stresses of use unless they are concerned with the maintenance of monuments and historic sites, the ruggedness of bookbindings, or the design of shipping containers and earthquake-resistant display cases.

This review primarily discusses the chemical aspects of photochemical stability, particularly the ways in which the oxidative deterioration induced by exposure to visible and near-ultraviolet radiation takes place and the ways in which the underlying chemical processes can be speeded up in order to estimate the long-term serviceability of materials. Acceleration of thermally initiated deterioration will also be discussed briefly.

In the past decade or two, industrial and academic research has made major strides in revealing the chemical processes involved in the deterioration of specific polymers, that is, the "mechanism" of deterioration reactions (McNeill 1992). However, in spite of the deluge of seemingly pertinent titles that turn up in a search of the literature, one finds that many of the research reports are not readily applicable to problems faced by the conservator and conservation scientist. Many studies involve the use of vacuum, unsuitably high temperatures, or inappropriately short wavelengths of radiation. One of the chief objectives in preparing this review, then, is to begin to extract from the vast technical literature those aspects and contributions that may be applicable in the conservation of historic and artistic works. As Brown said in a recent review (1991): "It is possible that the need to transfer what is known in research circles to testing circles is greater than the need for what is yet to be discovered."

The need for standard test procedures for lightfastness and artificial aging was cited in the extensive list of "Proposed Priorities for Scientific Research in Support of Museum Conservation" compiled in 1984 by a committee of the National Institute for Conservation. Nevertheless, for all the recent advances, authorities still must concede that “lifetime prediction is in its infancy” (Edge et al. 1992). It is really too soon to expect to find extensive, well-founded recommendations for specific testing procedures. This may be possible in the not-too-distant future for specific materials such as paper, dyed textiles, and artists’ pigments. It appears most useful at this point in time to present an overview of this considerable subject, introducing some of the reasoning, limitations, and principles underlying the concept of accelerated aging. No attempt has been made to propose a how-to-do-it handbook.

The desire to carry out accelerated-aging tests and perhaps thereby to understand and predict the long-term behavior of materials is a research activity that has long excited the interest and imagination of both the theoretically oriented and the practical-minded. Unfortunately, the achievement of these objectives is a difficult matter, so much so that “one could be forgiven for writing the whole concept off as impossible” (Brown 1991). Moreover, the effort to conduct sensible accelerated-aging tests is time consuming and expensive. As far as the presently available test methods are concerned, it has been claimed that “the majority of users do not believe that they properly simulate or predict service” (Brown 1991). Numerous such pessimistic statements could be cited, particularly in the literature of the 1960s and 1970s (Brand et al. 1968). Nonetheless, today progress is being made. It is in the effort to assemble some of this information that the present review has been prepared.

An attempt will be made to answer a number of the questions regularly encountered whenever the subject of accelerated aging is raised:

- “Evidence gathered so far indicates little likelihood of a universal accelerated weathering method . . . .” (Patel 1991). What are the reasons for such a statement?
- Why are changes in chemical rather than physical properties more commonly measured and what are the recognized limitations in so doing?
- What are the limitations that must be kept in mind concerning the application of very short wavelengths of ultraviolet radiation, correlation coefficients, and the Arrhenius and reciprocity relationships?
- What are some of the methods for predicting service lifetime that are currently generating increased interest, methods such as isothermal calorimetry, electron spin resonance, and residual thermo-oxidative stability?

The chapter headings list the various facets of the subject addressed. The references and supplemental bibliography cited should assist those who need to delve more deeply into the subject and will introduce the names of the active contributors to the field that may not yet be widely familiar: Stoll and Fengel; Allen and Edge;

Martin and McKnight; Gerlock and Bauer; and Krochmann, Aydinli, and Hilbert, just to name a few. In the last chapter, a brief summary will be given of significant tasks that await attention.

This is an introductory survey, indicating the scope of the subject. It must remain for others to treat individual aspects more fully and with greater didactic utility and practical immediacy.

1 Classes of Stability

Range of Stability

Some materials that one may wish to evaluate are very much more stable than others. Pihlajavoara presented a table pointing out that strong ceramic materials can give good service as much as 1,000 to 10,000 times longer than ordinary paints and natural textile fibers (Sereda and Litram 1980:9). The fact that three to four decades of stability can be encountered in materials to be tested becomes particularly important in designing accelerated-aging tests. Under a bank of ordinary fluorescent lamps, fugitive pigments and dyes can fade in a few weeks. On the other hand, many modern coatings can withstand ten, fifteen, or more years of exposure outdoors (Schmid 1978, 1988). If the latter were to be exposed under the same fluorescent-lamp bank as the former, they would require an inordinately long time before a significant change in properties could be measured. Practically speaking, highly stable materials need to be tested under a high-wattage xenon-arc lamp, at a perhaps higher-than-normal temperature, if not also humidity, in order to induce changes in properties in a reasonable length of time. The wide range of stability in materials is one of the chief reasons why it is impractical to specify a standard accelerated-aging test that can effectively evaluate both highly fugitive and highly stable materials.

Changes in properties with time are perhaps most often envisioned on a linear scale in terms of the hours of exposure in a Fade-ometer or hours of heating at an elevated temperature. (Largely for convenience, but not solely for that reason, time is sometimes expressed on a logarithmic scale [see "Functions Nonlinear in Time," page 31.]) The time scale in any set of accelerated-aging tests is commonly intended to relate to a similar scale in terms of years of satisfactory service life or years-to-failure. Thus, in Figure 1.1 the scale is marked off below in tic marks labeled 20, 100, 200, and 500 years. The lowercase letters above indicate various times or endpoints during laboratory exposure tests which the experimenter might hope would correspond reasonably well with a given number of years of actual exposure or use.

Unfortunately, when one reads a research report in which a particular change is plotted against time, one is often not immediately aware of whether the data refer to an exposure as mild as between zero and point *b* in this example, or as severe as between zero and *d* or *g*. Kühn's study of the influence of humidity and temperature on fading involved an exposure of only about 800,000 lux hours (Kühn 1968). From the point of view of Figure 1.1, this valuable study involved the mild exposure of fugitive pigments. In contrast, Johnston-Feller's study of alizarin fading involved 350 hours of exposure in a xenon-arc Fade-ometer, an exposure amounting to 5500 kJ/m^2 at 420 nm (Johnston-Feller et al. 1984). It might not be immediately apparent to readers of the two publications that Kühn referred to an exposure in the very earliest portion of the timeline in Figure 1.1, whereas the Johnston-Feller study related to an exposure at least twenty times greater.

In considering technical reports of accelerated-aging tests, it is useful to have in mind some concept of the relative severity of the exposure described. The use of control specimens can often be helpful in this regard (see "Controls," page 42).

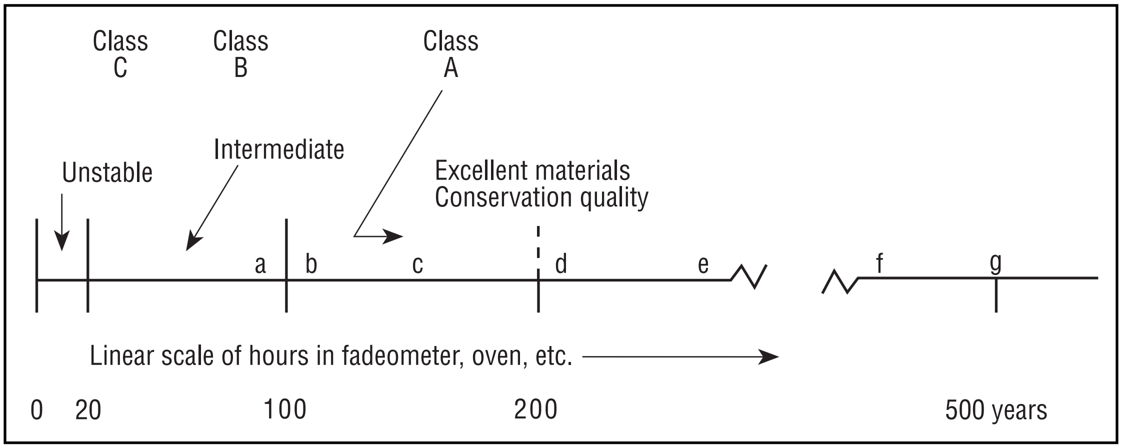


Figure 1.1. Useful lifetimes of materials as estimated crudely on the basis of accelerated-aging tests.

Class of Stability

In an effort to initiate recognition of this situation, Feller (1975) suggested three classes of photochemical stability. These are noted in Figure 1.1 and in Table 1.1. Unstable materials, Class C, were considered to be those that would seriously degrade in less than 20 years of normal usage in a museum. Class A materials, of "excellent" quality suitable for use in conservation practice, were considered to be materials that might give at least 100 years of satisfactory service. Class B materials were those falling between the two, materials that possibly would give from 20 to 100 years' service. In order to define these classifications somewhat objectively, a comparison with the fading of the ISO R105 blue-wool standards 3 and 6 was proposed.

To obtain some perspective on the proposed classes, one may recall that Thomson (1967) estimated the average annual exposure in the National Gallery, London, to be about $1\frac{1}{2}$ Mlxh (million lux hours). Hence, materials that will withstand 100 years of exposure on the average gallery wall there would be exposed to 155 Mlxh (about 15 million footcandle hours). A fugitive colorant, proposed as one that would fade considerably in 20 years under average exhibition conditions, is thus likely to seriously fade in about 30 Mlxh. Modern coatings that are able to withstand 10 years of exposure outdoors in Washington, D.C. would be exposed to about 1,600 Mlxh, 1,000 times more than the annual exposure on Thomson's average gallery wall, to say nothing of the added harmful effects of heat and moisture under exterior conditions. Thomson also reported that the average proportion of daylight reaching representative walls in the National Gallery was about 1.5% of the annual exposure outdoors. Such figures may provide convenient points of reference.

Class	Classification	Intended useful lifetime	Approximate equivalent standard of photochemical stability
T	Materials in temporary contact	Less than 6 months?	–
C	Unstable or fugitive	Less than 20 years	BS1006 class 3 or less
B	Intermediate	(20–100 years)	(3 to 6)
A	Excellent	(A2?) greater than 100 years	Greater than BS1006
		(A1?) greater than 500 years	?

Table 1.1. Standards of Intended Use and Photochemical Stability for Materials in Conservation (Feller 1975).

One could, of course, specify a greater number of classes than three. How many is an arguable point, but in view of the difficulties in predicting aging characteristics, it seems sensible to have as few subclasses as convenient. Rånby and Rabek (1979b) were satisfied with three classes of stability, as was apparently Winslow (1977).

It is a relatively easy matter for a testing laboratory to determine those materials that fall in photochemical Class C, "unstable." The period of testing such materials, even under conditions close to normal, can be conveniently short. Moreover, if accelerated tests are employed to investigate Class C materials, one does not have to use such intense light, humidity, or heat that an extrapolation of the data to normal conditions needs seriously to be questioned. If so desired, several decades of exposure under normal museum and archival conditions can even be accomplished in order to confirm the behavior of materials of poor to moderate stability (recall Wilson and Parks [1974] 36 years).

It is also a relatively easy task to determine those materials that would fall in the "excellent" class (A). Many materials are able to withstand particularly severe test conditions. From the conservator's point of view, the conditions used to rank Class A materials might even be considered "absurdly severe," such as the temperatures that might be used to cause nylon and Kevlar to degrade in a convenient length of time: 90% RH and 100° to 250 °C (Auerbach 1989). It should not be difficult for an experimenter to entertain the idea that a particular material might give “at least 100 years” of good service indoors, its having withstood particularly severe test conditions. Nevertheless, it must not be forgotten that all predictions of long-term behavior are essentially educated guesses. Fundamentally, accelerated-aging tests simply rank materials and systems with regard to their stability relative to one another under a given set of conditions.

As mentioned, reports of accelerated-aging studies customarily place materials on a ranking scale such as that seen in Figure 1.1. A basic question then arises as to whether the conservator should be overly concerned with the relative ranking of a material that falls at *b* versus *a*, *g* versus *f*, or perhaps *d* versus *e*. One should not place too much emphasis on such slight differences in durability unless careful attention has been paid to the uncertainty and repeatability of the results (Reedy and Reedy 1992). In Down’s study of the life expectancy of epoxy adhesives, the uncertainty of the estimated lifetimes is clearly noted (Down 1984, 1986).

In addition, it must not be overlooked that very stable materials, those falling in positions *e*, *f*, and *g* in our example, may all be equally serviceable in many conservation applications, in spite of the fact that the laboratory is able to report significant differences in behavior.

In accelerated testing, there is always a basic difficulty. This concerns whether samples showing small differences in ranking (samples *a* versus *b*, or samples *f* versus *g*, for example) will remain in the same relative positions under more moderate (normal) conditions of usage. This aspect of accelerated-aging tests is not always fully discussed. It is never wise to reject a sample falling at *a* relative to *b* on the basis of one particular experiment or type of test. The above-normal conditions of temperature and humidity usually employed in accelerated-aging tests might be such that these materials would not fall in the same relationship under “normal” conditions.

A pertinent example comes to mind: Many years ago, Feller and Bailie (1966) encountered an acrylic terpolymer that underwent a significant amount of cross-linking as well as chainbreaking when it was tested in a xenon-arc Fade-ometer. In order to be conservative with regard to the potential for cross-linking, the use of this particular polymer was never suggested to conservators. Years later, when it was realized that heat increased the tendency of certain acrylic polymers to cross-link (Feller et al. 1981), the product was again tested, this time not in the Fade-ometer, where the sample temperature often was above 60 °C, but under a bank of “daylight” fluorescent lamps, where the temperature of the samples reached no more than 28 °C. Under the milder conditions, cross-linking of the polymer proved to be negligible. By the time the later test was made it was considered that this particular polymer had no advantage over others already in use. Nonetheless, the exposure at the lower temperature clearly indicated that cross-linking in this polymer, detected in the xenon-arc Fade-ometer, really would not be a serious hazard under typical museum conditions. This experience serves as a clear example of the difficulty in predicting the behavior of materials under "normal conditions" of usage on the basis of a commonly employed "standard" accelerated-aging test. At the time of the initial studies, our knowledge of the effect of heat on the photochemically initiated process of cross-linking had not been developed.

Statistical Approach to the Probability of Failure

Increasingly today, modern techniques in failure analysis are being applied to answer some of the problems just described. When a set of nominally the same textile, coating, or adhesive is exposed to a particular aging condition, it is very much to be expected that there will be variations in the experimentally measured time to failure. Sometimes variations can span as much as a decade in time or more. Hence, predictions of service life based on an average time to failure often have little practical significance. Martin (1984), Martin and McKnight (1985), McKnight et al. (1985), and others now suggest that a better criterion for service-life predictions would be to state the maximum time beyond which a specified fraction of the population of a given material or system of materials is likely to survive. This criterion is stated in a probabilistic format. The probability for a set of test samples to survive above an acceptable value of a measured property such as tensile strength is represented in Figure 1.2 by $\overline{H}t$, the shaded areas under the curves of probability density. The shape of the curve shows the probable frequency of a given level of the measured property, that is, the distribution of measured values of tensile strength, discoloration, etc. To emphasize the variability and uncertainty in measured properties as systems age, Nelson (1990) makes frequent use of similar illustrations.

Martin demonstrated this concept with a relatively simple system—the photolytically initiated chainbreaking of polymethylmethacrylate. Applying this concept with mathematical precision to more complex degradation situations will require considerable understanding of statistical principles and techniques. Nonetheless, the principle is a sound one. Consideration of Figure 1.2 should serve to warn the experimenter how basically difficult it is to issue a simple statement stating that, under specific aging conditions, a given material can be expected to fail at a specific time. Instead, one finds that it is possible to state only that it is probable that a given fraction of a set of samples will fail in a given time. (The statistical approach to predicting failure is further discussed in Chapter 4.)

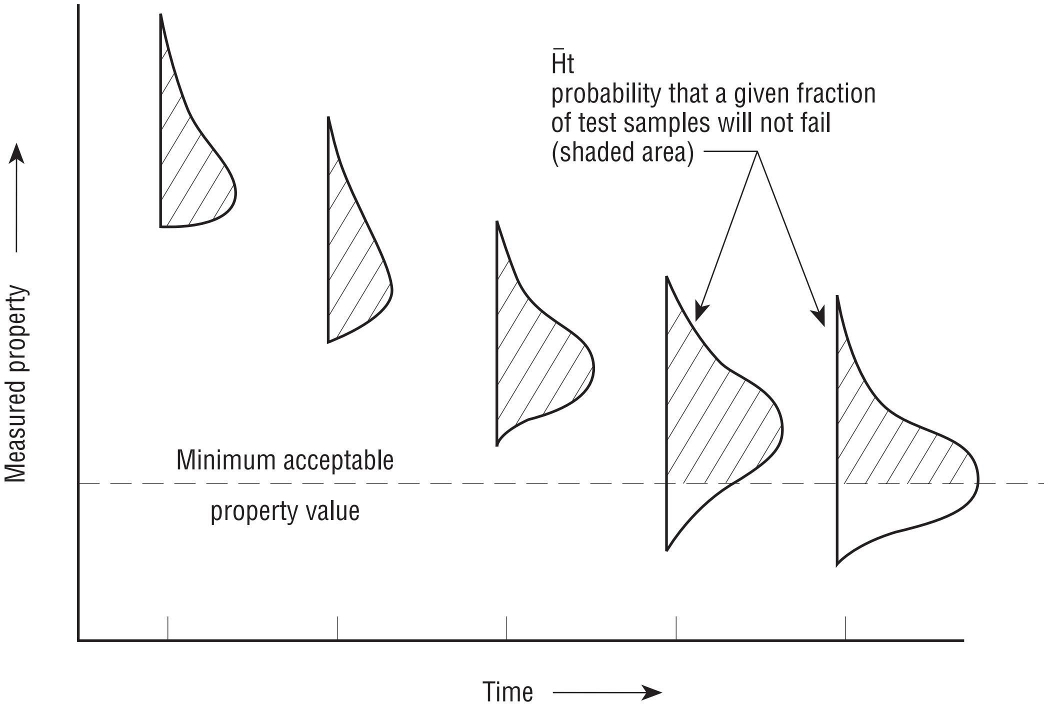


Figure 1.2. Change in set of data for measured property at increasing times of exposure (after Martin 1984). Reproduced with permission of the publisher.

Materials of Moderate or Intermediate Stability

A challenging question facing the field of conservation science concerns whether to employ materials that fall in an "intermediate" class in the course of accelerated-aging tests. There are many materials that the conservator will find attractive, particularly from the point of view of ease of handling. Some, however, will exhibit properties that are noticeably less stable than those possessing Class A stability.

A fundamental question thus arises with respect to Class B materials, however one wishes to define them. Are materials of intermediate stability "good enough" for a particular application in conservation? Colleagues may not have understood that over many years at the Research Center at Mellon Institute, a formal research decision had been made to devote primary attention to polymers of the highest class of stability (Feller 1987). As a consequence, little laboratory attention was devoted to materials such as polyvinylalcohol or the organic-soluble ethylhydroxyethylcellulose. Nonetheless, some of their immediate properties appear to be suitable for specific conservation uses.

In spite of the primary focus in this monograph to long-term stability, it is good to recognize that certain materials that the conservator may wish to use are indeed intended only to be in temporary contact with an artifact. Adhesives used to attach facing papers to paintings or to attach stronger facing materials to frescos represent two examples. For such uses the long-term stability requirements need not be great. Such applications might be designated as Class T, materials intended to be in temporary contact with an artifact, perhaps for no more than six months (Feller 1975).

Summary

The range of inherent stability to be found in the materials of interest to conservators is so great that no single accelerated-aging test procedure is likely to be effective. The wide variety of test procedures in present use serve at the very least to establish the relative ranking of carefully characterized materials or surrogate systems regarding their tendency to maintain their desired properties under the particular conditions of the test.

When choosing test procedures, it can prove useful to have some concept of the general class of stability under evaluation, whether relatively unstable, highly stable, or intermediate. The three classes of photochemical stability proposed nearly two decades ago were put forth to draw attention to the matter. Additional consideration and further refinements are certainly warranted (Michalski 1987).

Thus far there has been little formal discussion concerning standards of stability and durability of conservation materials except perhaps with respect to the degree of permanence of paper. If the target is not to be “at least 100 years of service under normal museum conditions,” then what should be the limit of acceptable lifetime and acceptable decline in properties for conservation-quality materials to be used in long-term contact with artifacts? The subject remains to be addressed.

2 Changes with Age That Are Measured

Chemical versus Physical

What are the properties of a material in a particular application that are desirable and that, when they change a certain degree, become unacceptable? This is the initial question that must be addressed in designing a program of accelerated-aging tests. Most often, one is concerned with the maintenance of certain physical properties such as tensile strength, adhesion, brittleness, and color. It is realized, however, that changes in physical properties are generally and fundamentally influenced by the chemical changes that occur with age. Hence, by far the most customary method of monitoring the changes that occur is to measure some chemical property (Brown 1991).

Heavy reliance on the measurement of chemical properties comes about for at least two practical reasons: Such measurements can usually be made (a) with conveniently small samples and (b) with considerable speed, sensitivity, and precision. In addition, changes in chemical properties can often be detected in advance of an obvious change in physical property. Moreover, the research investigator is well aware that physical properties such as brittleness, tensile strength, and folding endurance are difficult to measure with precision. Consequently, most discussions regarding the theory and practice of accelerated-aging tests deal primarily with the chemical changes that materials undergo and how these changes may be interpreted in an effort to explain and compare the chemical and physical stability of one material relative to another.

One of the early decisions that must be made in planning accelerated-aging tests is to decide the property to measure as an indication of the extent of aging. Unfortunately, with unfamiliar materials, it is usually not possible to decide in advance which chemical property will be most significant or revealing. Hence, it is the usual practice in initial studies to measure a number of properties, both chemical and physical; the recent report of Edge et al. (1992) provides an excellent example. As the critical aspect of aging, an investigator may be forced to focus upon a physical change, such as loss of tensile strength, adhesive strength, or folding endurance. Nevertheless, because it is a challenge to measure and describe changes in physical properties precisely, a well-planned research effort will usually include chemical tests that have been shown to be related to the critical physical change; Fromageot and Lemaire (1991) refer to the need to focus on a “critical photoproduct” or simply a “critical product” (Lemaire 1993:125).

After considerable experience has been gained concerning the aging of specific materials, it is usually possible to reduce the number and variety of tests used, relying on those that experience has shown to be most significant. For example, the loss of molecular weight in polymers can usually be related directly to loss of strength. For another example, the development of carbonyl groups or the quantity of oxygen absorbed has been related to increased brittleness in ethylene and propylene polymers (Winslow et al. 1972).

In the practical world, materials are used in *systems* with other materials: paper-adhesive-support, vehicle-pigment-volatile solvent, plaster-consolidant-supporting wall. Nonetheless, rather than attempt to measure with high precision the point of physical failure of such composite systems, it is far easier (and, as suggested, possibly more fundamental) to measure the chemical changes that occur within a specific component of the system. Thus, it is relatively easy to measure the decrease in molecular weight of cellulose and to state that, when the number-average degree of polymerization declines to about 200 to 250 (or, stated more precisely, when it reaches a value close to the leveling-off degree of polymerization), then unsized, lignin-free paper may have little practical strength. In this case, a precise molecular parameter, degree of polymerization, can be related to a practical physical property—loss of zero-span tensile strength or folding endurance (Swenson 1975; DuPlooy 1981).

There are potential problems in such an approach; that is, relying on measurement of one chemical property of one particular component of the system to follow the course of aging (Storp and Bock 1985). Opposing reactions—cross-linking and chain breaking, yellowing and bleaching—can take place concurrently. Hence, there is always the question of whether the particular chemical property chosen will provide a true indicator of the moment when an unacceptable change will have taken place. For example, the percentage of insoluble matter in a coating is not invariably the measure of its ease of removal in solvents, especially if the coating swells considerably (Feller 1963). In this instance, it has proved fruitful to measure at least three properties—ability to swell, insolubility, and the polarity of solvent required—in order to evaluate the onset of an unacceptable degree of difficulty in removal of a picture varnish (Feller, Stolow, and Jones, 1985:202).

In another example, the measurement of yellowness in a film may not closely relate to insolubility or brittleness. In the case of rubber cement, yellowness is a property that occurs at a late stage in the oxidative attack (Feller and Enke 1982). On the other hand, yellowness can take place in poly(vinylchloride) before a serious loss in strength has occurred (Gray and Cadoff 1967:87).

Such apparent contradictory results need not cause confusion in planning a testing program if some thought is given to the principal chemical changes that must be occurring within a material. In the case of rubber cement, for example, much of the colored material represents an accumulation of degradation products, an event that logically comes after the initial reactions with oxygen. In contrast, with poly(vinylchloride), color can arise owing to the development of a series of *conjugated double bonds* along the main chain of the polymer as hydrochloric acid, HCl, is lost; yellowing can thus occur without the polymer chain itself breaking.

Sometimes distinctly indirect methods can be used to estimate relative durability. For example, when it was found that titanium white pigment (TiO_2), upon exposure to ultraviolet, induced the formation of free radicals in vehicles (binders), leading to a destruction of the vehicle and chalking of the paint, it was suggested that the ability of TiO_2 to oxidize isopropyl alcohol to acetone, a similar chemical process, could be used to predict the photochemical activity of the pigment (Sullivan 1972). An even more indirect measure of this potential takes advantage of the fact that, in the presence of lead white the following reactions can take place:

$$\mathrm{TiO_2} + \text{ultraviolet light} \longrightarrow \mathrm{TiO_2^-} \text{ (thus } \mathrm{Ti^{+3}}\text{)}$$

$$2\mathrm{Ti^{+3}} + \mathrm{Pb^{++}} \longrightarrow 2\mathrm{Ti^{+4}} + \mathrm{Pb^0}$$

The formation of metallic lead (Pb^0) causes the mixture of lead white and titanium white to darken. As a result, the rate of darkening of a paste of the two pigments in glycerine has been used as a simple yet indirect indicator of the potential photochemical activity of titanium white pigments (Braun 1990). Wilska (1967) refers to mandelic acid and crystal violet methods for accomplishing the same objective.

Indirect measures of deterioration can yield precise analytical data. Nonetheless, care must be taken to see to it that the results relate to the mode of failure (cracking, embrittlement, or yellowing) of a particular system of materials under the practical conditions of use.

Mechanism

When a chemist proposes the series of chemical steps or reactions involved in the process of initiation and ultimate degradation, he or she is speaking about the *mechanism* of deterioration. With the great advances made in the last few decades in our understanding of how chemical reactions take place and how the components of chemical systems can be identified, description of deterioration in terms of the process of activation and the chemical changes that occur has today almost subconsciously entered into the polymer chemist's day-to-day language. There has been a question as to where in this manuscript the subject of mechanism should be formally introduced. It is a major topic. Brown (1991) states that "a much greater appreciation of the mechanisms of degradation is needed." Fromageot and Lemaire (1991), introducing the subject of accelerated aging in a few succinct paragraphs, state at one point that "a better insight into polymer aging can only be gained if a correct description is given of the ongoing chemistry in the matrix." The point has been stressed again by Lemaire (1993).

One could say that the most fundamental objective of deterioration studies is to discover the mechanism of deterioration in a given system. As well as the chemistry involved this would also include the physical character or mode of failure. To disclose the mechanism, however, is a task requiring much time and skill on the part of the chemist and his team. Fromageot and Lemaire (1991) describe a detailed mechanism for the photodeterioration of soluble nylon. This is possible because the laboratory under Lemaire's direction has been devoted to photochemical studies for many years. Five previous publications are referenced regarding studies of amide-containing polymers related to the nylon structure, studies involving four different collaborators with Lemaire and dating back to 1982.

This example points to the fact that it is no simple matter to establish the mechanism of deterioration in specific systems. With our general knowledge of deterioration processes today it is relatively easy to *propose* a mechanism. Admittedly, that is a useful exercise. But it is quite another matter to demonstrate and to confirm beyond much doubt the mechanism (the chemical steps) involved. The field of conservation perhaps will largely have to continue to rely on experienced and well-equipped laboratories in academia to develop such information. The field is already fortunate to have gained the interest and attention of authorities such as Lemaire, N. S. Allen, and others that will be cited (Allen et al. 1992).

In the discussions that follow, mechanisms will frequently be alluded to without much elaboration. Most if not all such citations will have been based on authoritative studies found in the chemical literature. Nonetheless, a word here is warranted to stress to the reader that the establishment of thoroughly confirmed mechanisms is a challenging task, primarily to be consigned to the dedicated and well-trained chemist.

Sensitivity of Measurement

An important point to be considered in choosing the property to measure is to select one, depending on the objectives, that will either (a) change markedly at a very early stage, (b) change dramatically near the time of failure, or (c) change in a predictable manner throughout the entire useful life span of the material being tested. Figure 2.1 illustrates this point, comparing the relative values of various physical parameters at different levels of the degree of polymerization of cellulose (Lawson et al. 1977). It has long been known, for example, that folding endurance decreases markedly in the early stages of thermal aging of paper, whereas tensile strength does not.

Numerous examples of the limitations in particular measurements can be cited. For example, Mead et al. (1982) concluded that "infrared examination of aged nylon yarns with various degrees of degradation showed only slight differences for the most severely degraded samples when compared to controls"; the authors found only slight differences in the infrared absorption spectra of samples that had lost as much as 40% in tensile strength. In another situation, because the discoloration of many polymers is often bleached by the same light source that is used to initiate deterioration, Bendaikha and Decker (1984) point out that "discoloration, although an important parameter in testing the light sensitivity of a polymer, may actually reflect quite imperfectly the extent of photodegradation occurring." Down (1986) cites a reference to the fact that carbonyl group formation in epoxy resins need not relate to yellowing.

Renschler (1985) provides a clear example of how the sensitivity of the measurement of a change in physical property can be investigated; in his case the loss of tensile strength of nylon 6,6 was compared objectively to the sensitivity of an alternative measurement—the change in optical absorption at 245 nm. Plots were made of absorbance versus time and also of tensile strength versus time. The slopes of the two curves and their standard deviations were then calculated. The relative sensitivities of the two analytical tests were estimated by the time of exposure necessary to have either property change more than three times the standard deviation. Renschler further showed how the *student's t* test would be applied to estimate the significance between the sensitivity determined for one type of measurement versus another.

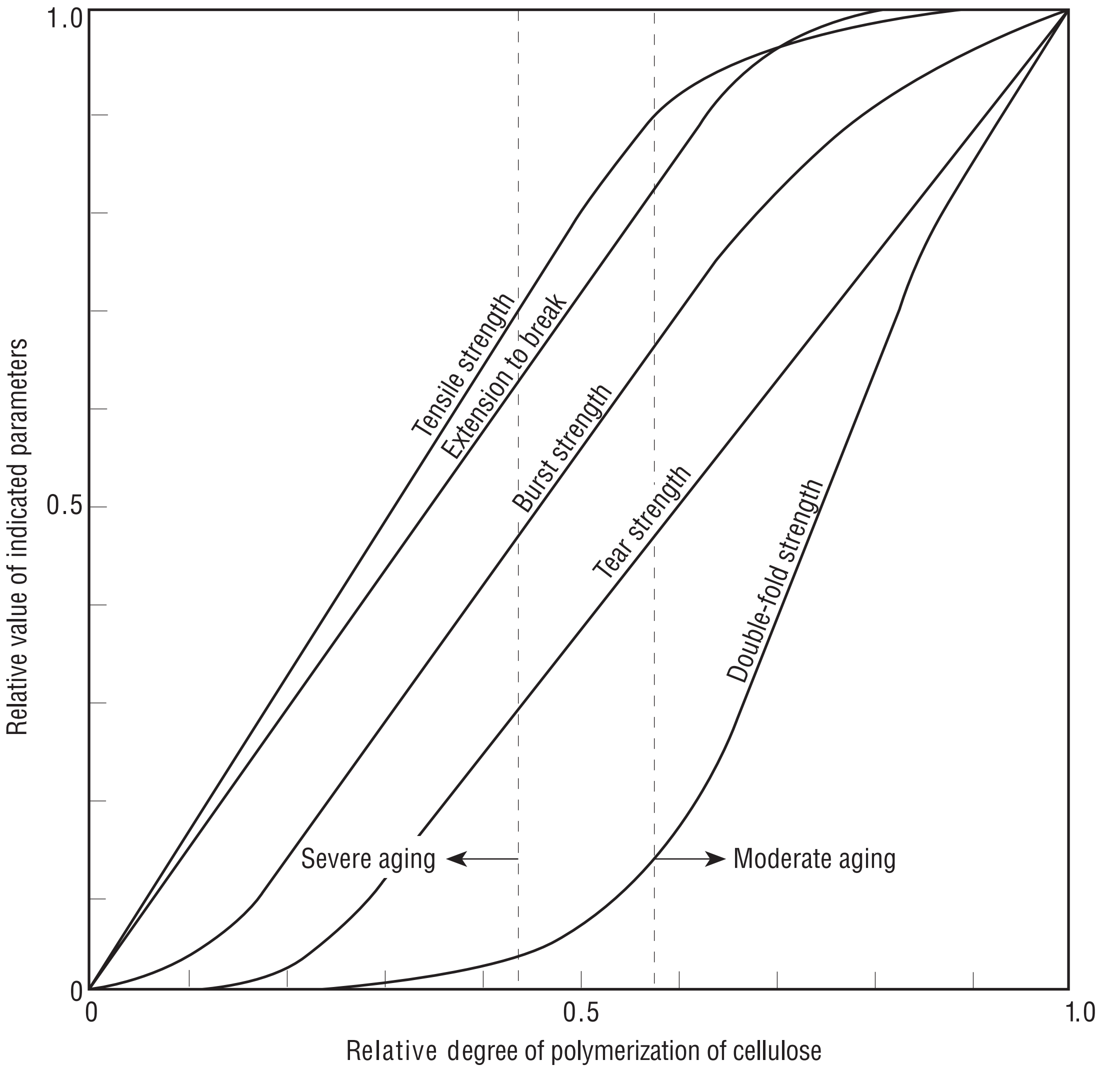


Figure 2.1. Illustration of the different sensitivities of various physical property measurements as a function of the degree of polymerization of cellulose (Lawson et al. 1977). Reproduced with permission of the publisher.

Choosing an Acceptable and Unacceptable Degree of Change

Subjective judgments of the point at which a material is "too matte," "too faded," or "too yellow" are bound to vary even among any group of experienced observers. Down's initial study of the yellowing of epoxy resins provides an example of one way in which a subjectively adjudged unacceptable degree of change can be established (Down 1984). A set of twenty coatings having various degrees of yellowness was presented to a panel of thirty observers. It was found that those panels in which the absorbance (*A* = log [I_O/I]) at 380 nm of a 0.1 mm-thick film relative to the reference absorbance at 600 nm (*A* 380 nm - *A* 600 nm) was less than 0.1 were always considered acceptable and that those having a relative absorbance greater than 0.25 were always considered unacceptable. These values then were used as criteria to determine the approximate acceptable life expectancy of the epoxy formulations. It was fully acknowledged that judgments were uncertain when the relative absorbance at 380 nm fell between 0.1 to 0.25.

Objectively obtained physical measurements also will vary. Because of this, a number of authors now suggest that the maximum service life be considered as the time beyond which some specified percentage of the sampled population survives; i.e. their critical property remains satisfactory (Martin 1984; Martin and McKnight 1985; McKnight et al. 1985). Frequently, the time for increasing fractions of a selected number of samples to fail is observed, up to the point at which 50 to 80% of the samples have failed. It is further assumed that the distribution of failures will follow a statistical law of probability. Thus the accumulative percentage of failures is plotted versus time and the data fitted to the probability function. The predicted probability of a given percentage of failure having occurred by a certain time is then read from the curve. This approach was mentioned in Chapter 1 (Fig. 1.2) when the problem of borderline cases was discussed. It is referred to again in Chapter 4.

Summary

Because chemical changes are basically the underlying cause of the physical changes that occur in organic materials during deterioration and because such changes can usually be measured with considerable ease and precision, accelerated-aging studies usually involve studies of chemical change. Nonetheless, considerable effort must be made to demonstrate the relationship between a particular chemical constituent and its potential reactions and the degree of change in a critical physical property. The measured property needs to be suitably sensitive to reveal either (a) significant early changes in a material or system of materials, (b) incipient failure, or (c) a predictable course of change.

In planning a program of accelerated-aging tests, a decision must be made concerning the degree of change that is acceptable and that which is unacceptable. It is recognized that this is not likely to be a precise or completely objective value. Moreover, it is important to recognize that objective physical or chemical measurements will vary; the degree of uncertainty can nonetheless be treated statistically.

3 Kinetic Analysis of Change

How should the chemical and physical changes that take place over a period of time be interpreted if they do not occur simply in a linear fashion, but instead apparently slow down or speed up in time? In the desire to predict the condition of a material at a future time, it is frequently possible to express the nonlinear behavior by a mathematical formula that can then be used to calculate the expected level of a property at some later time. The basic approach to the problem of nonlinear as well as linear changes in properties with time involves the extensive subject of the kinetics of change; more precisely, the principles of *chemical kinetics* are commonly applied (Bamford and Tipper 1975). This is defined as the study of the rates at which reactions occur and the influence of conditions—temperature, humidity, concentration of reactants—on the rates. Numerous textbooks deal with this specific subject, a major topic in physical chemistry (Bamford and Tipper 1969, for example, extends to fourteen volumes).

On the basis of a kinetic analysis, one finds, for example, that the fundamental way to follow the degradation of cellulose is not to focus on the decrease in degree of polymerization (DP) with time but to follow instead the change in the inverse of this, 1/DP, for this is related to the number of bonds being broken in the chain (see Feller, Lee, and Bogaard 1986). In the fading of pigments and dyes, the change can often be evaluated effectively, not by plotting the decrease in concentration of colored matter with time of exposure to light, but instead by considering the change in the logarithm of the concentration with time (Giles et al. 1974; Johnston-Feller et al. 1984). Thus, it is necessary not only to select the particular property that will measure the changes meaningfully, but also to make a sensible judgment on how to *plot* or interpret the change in the measured property against time. The decision to evaluate the changes that occur over time in terms of the logarithm of the concentration of a key component, the concentration itself, its inverse, or some other measure, is based primarily on an analysis of the processes of deterioration in terms of chemical kinetics.

When only one principal chemical reaction is responsible for the change being monitored, an interpretation in terms of chemical kinetics often serves rather well. However, when more than one chemical process is going on in the course of aging, and this is the usual case, one can expect occasionally to encounter confusing degradation data unless careful consideration is given to the experimental circumstances. For example, in the action of light on ordinary paper, the lignin component may darken under the influence of ultraviolet radiation emitted by a particular light source. At the same time, another component of the paper, the discolored remnants of the degradation of cellulose and hemicelluloses, may be bleached either by visible or ultraviolet radiation. Alternatively, additional discoloration may occur through the action of temperature and humidity. Thus, both bleaching of certain components and discoloration of others can be going on at the same time. In this situation the net discoloration measured at any given time will depend on which of these chemical processes is the dominant one under the particular conditions of illumination, temperature, and humidity.

The case of wool provides an excellent example of the complexity of the problem of accounting for color changes. Exposure to one light source may cause principally bleaching; another, yellowing. Figure A.2 in Appendix A shows the effect of various light sources on five different types of wool (Lennox and King 1968). Exposure to the Xenotest apparatus and to the sunlamp, sources high in ultraviolet, results in increased yellowing. A fluorescent blue light, with radiation peaked at 420 nm radiation, results chiefly in bleaching. Sunlight, which contains both ultraviolet and visible radiation, also results in bleaching. It is further noted that the path which the curve of yellowness follows during exposure depends in part on the initial yellowness of the wool. The latter observation provides a clear example of the need for the research investigator to have knowledge of the whole course of change rather than relying simply on a measurement of the net change after a fixed time of exposure (a *single-point determination*).

Whenever the particular change in a property that one is concerned with (yellowness, fading) is the result of more than one chemical process—and, as stated, most outward manifestations of deterioration are just that—it is logical to expect that a rise in temperature, an increase in humidity, or a change in the relative severity of ultraviolet radiation will not speed up each of the underlying chemical steps to the same extent. It is fully expected that exposure to different light sources and different conditions of temperature and humidity will give rise to behavior that differs. With some thought to the matter, however, as in the cases of wool and paper cited, the results can usually be explained and, in future tests, controlled.

Equations Expressing Changes in the Concentration of Reactants

When experimental data such as shown in curves *b*, *c*, and *d* in Figure 3.1 are encountered, scientists usually begin to try out various mathematical equations to see if one can be found that mimics the changes in time most precisely—that is, one that gives the best fit, so to speak, between the experimentally observed data and the mathematically calculated values. Some of these equations can be quite elaborate, even accommodating S-shaped curves similar to that seen in curve *d* (Auerbach 1989 provides an excellent example). Such equations, often developed more or less by mathematical trial and error, can be very effective in allowing one to predict the extent of change at some time in the future. Equations that simply "fit the data" can be classified as *empirical* rather than *theoretical* in their derivation.

Scientists are seldom completely satisfied with an empirically derived equation. Usually they do their best to consider the underlying reasons why a particular equation should work so well in predicting behavior. Often an analysis based on the principles of chemical kinetics allows one to say, on the basis of the theory of how chemical reactions take place and a model for what may be taking place in a particular case, that one equation or another should indeed account for what happens. Such mathematical expressions of the rates of change can be said to be theoretically based, grounded on the principles of chemical kinetics, rather than empirical. A number of commonly encountered mathematical expressions for the way changes occur are discussed in the following section.

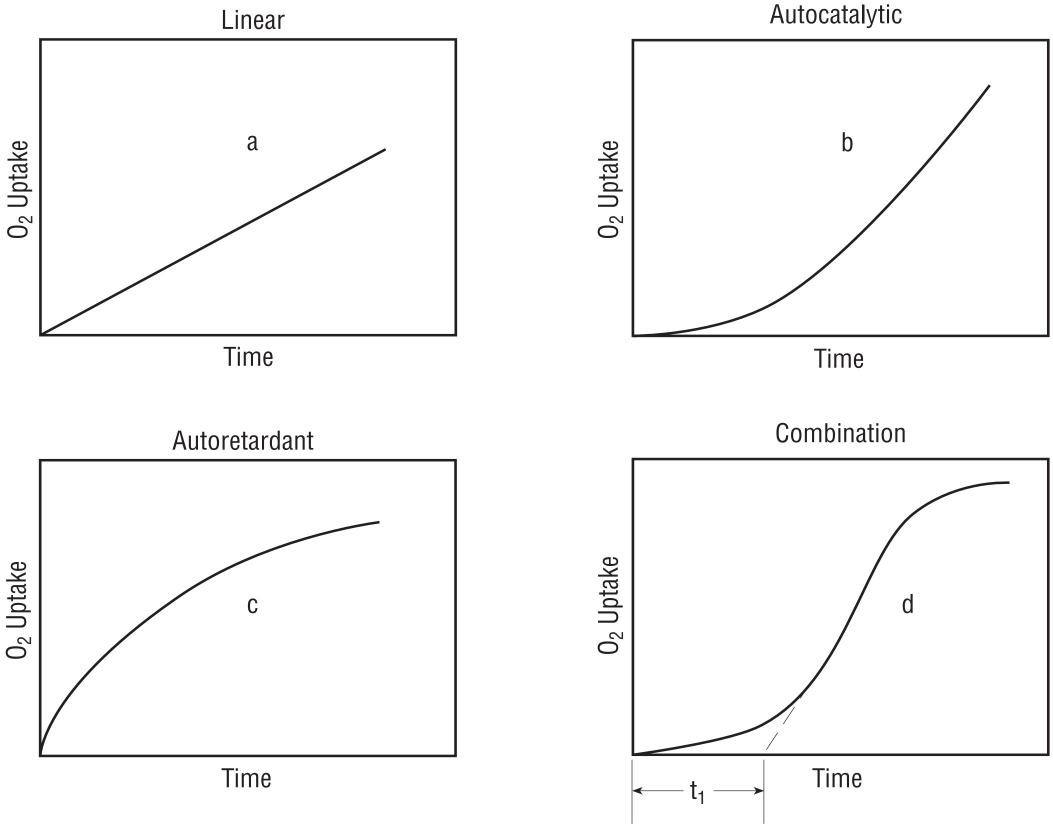


Figure 3.1a–d. Various forms of aging curves representing oxygen uptake (after Kelleher 1966). Reproduced from Feller (1977) with permission of the publisher.

“Order” of Reaction

Under homogeneous conditions, such as in solutions and gaseous mixtures, the rate that a chemical process takes place at any moment is related to concentration of the substances undergoing reaction. In the study of chemical kinetics, reactions can be considered either according to the *molecularity,* that is, the number of atoms or molecules taking part in each specific chemical reaction or according to the *order of the reaction*. The latter refers to the number of atoms or molecules whose concentrations seem clearly, on the basis of empirical evidence, to determine the velocity of the process. As shall be pointed out, the two are not always the same. The latter is the more common approach to the question of participation.

The rate of change in the concentration of a substance at any given moment in time can be expressed mathematically in a general way as:

$$dC / dt = kC^n \tag{3.1}$$

This equation states that the change in concentration of a substance, *dC*, over a very small interval of time, *dt*, that is, the *instantaneous* rate of change, is proportional to its concentration at that time, *C*, raised to some power, *n*. The factor or *constant* relating one side of the equation to the other is *k*. When *n* is zero, one, or two, the reaction is said to be zero, first, or second order. These are the most commonly encountered modes of chemical change.

Zero Order. If one should find that the decrease in concentration of a particular chemical substance proceeds at a constant rate, that is, that a substance is lost or destroyed at a constant rate, this represents the case in which *n* in Equation 3.1 is zero. The change in concentration with time is constant, expressed in this manner:

$$dC / dt = k \tag{3.2}$$

In this case, a graphical plot of change in concentration of a chemical substance over time is a straight line, the slope of which is *k*.

$$C = C_0 - kt \tag{3.3}$$

In this *integrated* form of Equation 3.2, C_0 is the concentration of substance *C* at zero time, the initial concentration.

In the hydrolytic degradation of cellulose in the presence of a fixed concentration of acid, the acid is a catalyst and is not used up in the process. Its concentration remains constant and does not seem to enter into the equation accounting for the loss of molecular weight of the cellulose. The concentration of water in the solution also remains effectively unchanged. Nonetheless, we know that the *molecularity* of this reaction involves both a hydrogen ion and a molecule of water. To calculate the loss of molecular weight of the cellulose in a dilute solution of acid at a given pH, the concentration of acid and of water remains sufficiently constant so that it does not need to be considered in following the rate of degradation of the cellulose. The rate of degradation in this situation is said to be *pseudo zero-order* with respect to the concentration of water and hydrogen ion.

If studies were made at different concentrations of dilute acid, one would find that the rate is indeed almost directly related to the concentration of hydrogen ion (not to pH, which is the negative logarithm of the concentration; Arney and Chapdelaine 1981). More precisely, it is the "activity" of the hydrogen ion and other reactants that needs to be considered in kinetic equations rather than concentration. In concentrated solutions of acids, the Hammett acidity function, H_0, reflects activity very well (Hammett 1970; Vink 1966). Nonetheless, the nominal concentration of substances is used in all but the most critical treatments of the subject.

First Order. If one finds that the disappearance of a substance with time is clearly related to its concentration at any given time, this is called a *first-order reaction*; *n* is 1 in Equation 3.1. The fading of a dye or pigment (the decline in concentration of the colored substance with time) often takes place in this manner. We say that it obeys *first-order kinetics* (Giles et al. 1974; Johnston-Feller et al. 1984; Johnston-Feller 1986). The rate of degradation obeys the equation:

$$dC / dt = kC \tag{3.4}$$

This equation tells us that, at any given moment, a certain fraction (k) of the concentration of colorant that is present, C, is being lost; k is called the *specific first-order reaction constant*.

The integrated form of equation 3.4 is:

$$2.303 \log C = 2.303 \log C_0 - kt \tag{3.5}$$

On this basis, in cases of first-order decay, a plot of the logarithm of C against time, t, is a straight line, the negative slope of which is k; C_0 is the concentration at time (t) zero (Fig. 3.2).

The factor 2.303 converts to the natural logarithm (to the base e) to the logarithm to the base 10. The fact that the data for a loss of property over time yields a straight line in such a plot is customarily taken as a test or proof of first-order behavior.

In the fading of pigments and dyes, oxygen is often involved; the molecularity of the reaction involves oxygen. However, since the amount of oxygen in the air surrounding an exposed paint panel or textile is practically limitless under normal conditions, its concentration remains virtually constant. Hence, the concentration of oxygen usually does not appear to enter into a calculation of the rate of fading; the reaction is then said to be *pseudo first-order* in its behavior, involving only the change in the concentration of colored matter.

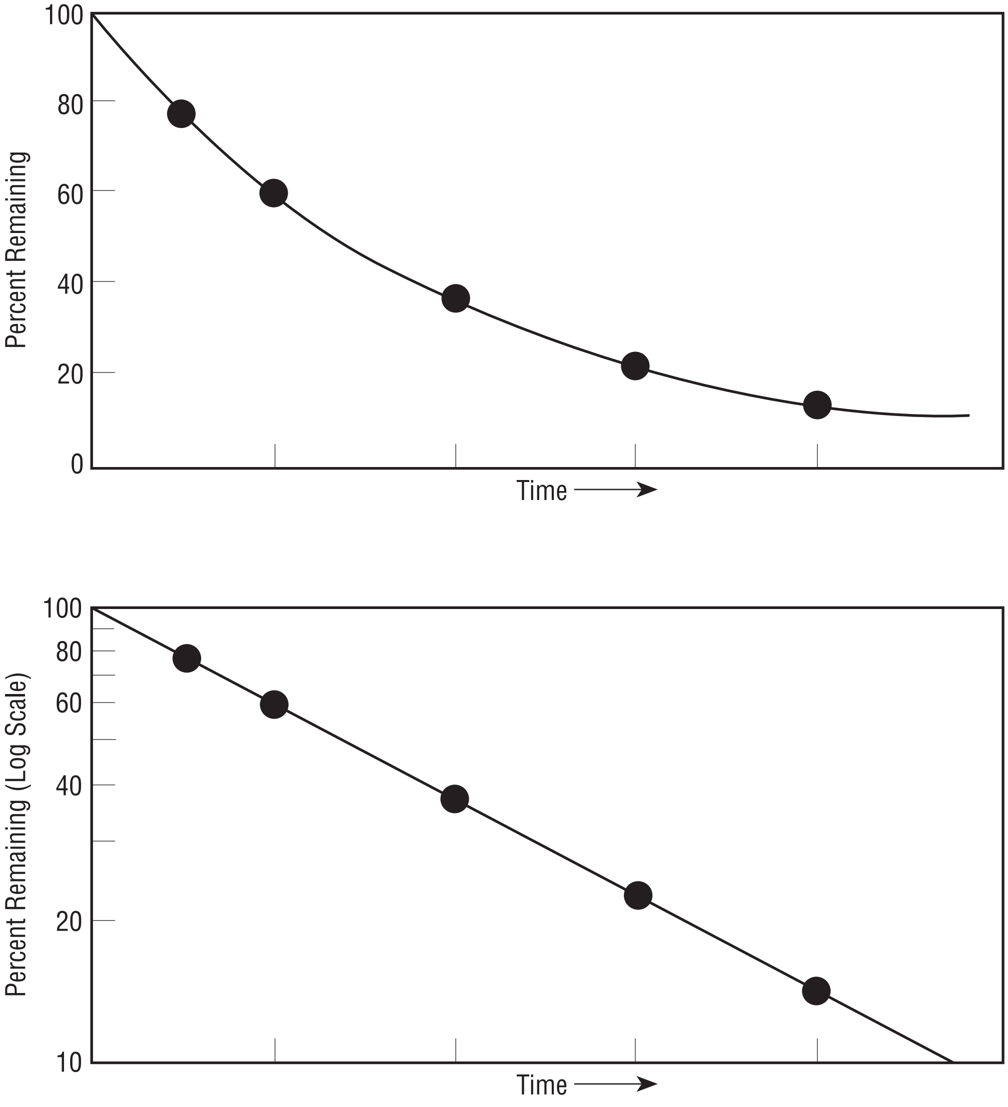


Figure 3.2a, b. Example of first-order decay of a component: (a) percent of original quantity remaining versus time (linear scale); (b) same data plotted in terms of logarithm of quantity remaining versus time (semilog plot).

In degradation reactions that take place in air, evidence that oxygen is involved can easily be overlooked. Its role can be disclosed, however, if the reaction is carried out under atmospheres in which different amounts of oxygen are present (Arney et al. 1979). A quick method to detect the participation of oxygen is simply to carry out an experiment under oxygen and then under nitrogen, argon, or a vacuum. An interesting example is provided in the case of nylon. Based on the most obvious chemical reaction, the degradation of nylon was at first considered to primarily involve hydrolysis of the amide bonds in the polymer, not involving oxygen (zero order with respect to oxygen). However, when Peters and Still (1979) and others have sought to confirm this, it was discovered that hydrolytic reactions did not occur under nitrogen but required the presence of oxygen. Thus, the mechanism of nylon degradation turned out to be more complicated than first imagined. The process was not purely hydrolytic.

The utility of experiments in which the concentration (partial pressure) of oxygen is varied is discussed in Chapter 9, "The Role of Oxygen."

Second Order. Instances of *second-order kinetics* in degradation can be demonstrated in many common processes if one takes into consideration the concentration of the chief reactant and also a second compound such as water, acid, or oxygen. Two components can be shown to control the rate. The hydrolytic breakdown of poly(ethylene terephthalate), for example, has been found to be autocatalytic because the carboxylic acid groups liberated by hydrolysis catalyze further degradation. Hence, a second-order equation, one involving both the concentration of ester bonds and the concentration of acid groups produced by the hydrolysis, is necessary to account for the rate (Zimmerman and ThacKim 1981).

Cases where the concentration of one of the components must be squared, a special case of second-order kinetics, are more rarely encountered. In a well-known situation, however, it has been found important in free-radical termination reactions. Here two free radicals must unite:

$$R\bullet + R\bullet \rightarrow RR$$

Fractional Order. Occasionally the overall chemical equations result mathematically in a situation where the square root (half order) or even some other fractional power of the concentration of a particular component seems to relate to the rate of degradation. The rate of degradation of high-density polyethylene, for example, has been found to be related to the square root of the carbonyl groups formed (Chew et al. 1977). The reasons for this can usually be found in the complexity of the reactions involved. Flynn (1957, 1960) describes a number of ways to determine *fractional orders*.

Sequential, Simultaneous, and Reversible Reactions

Deterioration processes are generally the result of a series of reactions. Thus, if one measures the change in concentration of a particular chemical end-product of the series, the kinetic analysis often will not reflect the result of one specific chemical step but instead will reflect the net result of the overall set of chemical reactions. For example, the maximum rate of consumption of oxygen in a process that goes through a hydroperoxide intermediate may depend on the square of the concentration of the compound being oxidized. The reason for this is not obvious without going through an analysis of the chemical steps involved (see Appendix A).

A widely encountered situation is a sequence of reactions such as:

$$A \xrightarrow{k_1} Y \xrightarrow{k_2} C \tag{3.6}$$

The change in concentration of the three components commonly varies in time, as seen in Figure 3.3. One often observes, for example, situations in which a yellow (discolored) component at first increases then decreases in time. Likewise, the buildup of peroxides during thermal deterioration usually goes through a maximum; Feller and Enke (1982) illustrated this in the case of rubber cement. The kinetics of this type of change can often be interpreted in terms of the sequence illustrated in Equation 3.6. The rate constants for each step, k_1 and k_2, can be determined. Feller, Johnston-Feller, and Bailie (1986) illustrated such behavior during the fading of alizarin lake pigment.

If the overall rate is the result of two first-order reactions, one of which proceeds faster than the other, the rate constants of each can also be determined, as Shelton and Winn (1946) did in accounting for the rate of oxidation of rubber vulcanizates. Today, high-speed computers can calculate the concentrations of many components that may be present as the result of a great number of concurrent reactions (Guillet et al. 1983).

If products A and B are formed from the same starting material and decompose by reactions of the same order, kinetic analysis shows that the ratio of their concentrations, B/C, tends to remain the same

$$\begin{tikzcd} & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd} \tag{3.7}$$

regardless of the time that the reaction has gone on. A possible example of this behavior was suggested by Lee et al. (1985), in which the rate of formation of carbonyl groups and the rate of chainbreaking appeared to be independent reactions during the photochemical oxidation of cellulose.

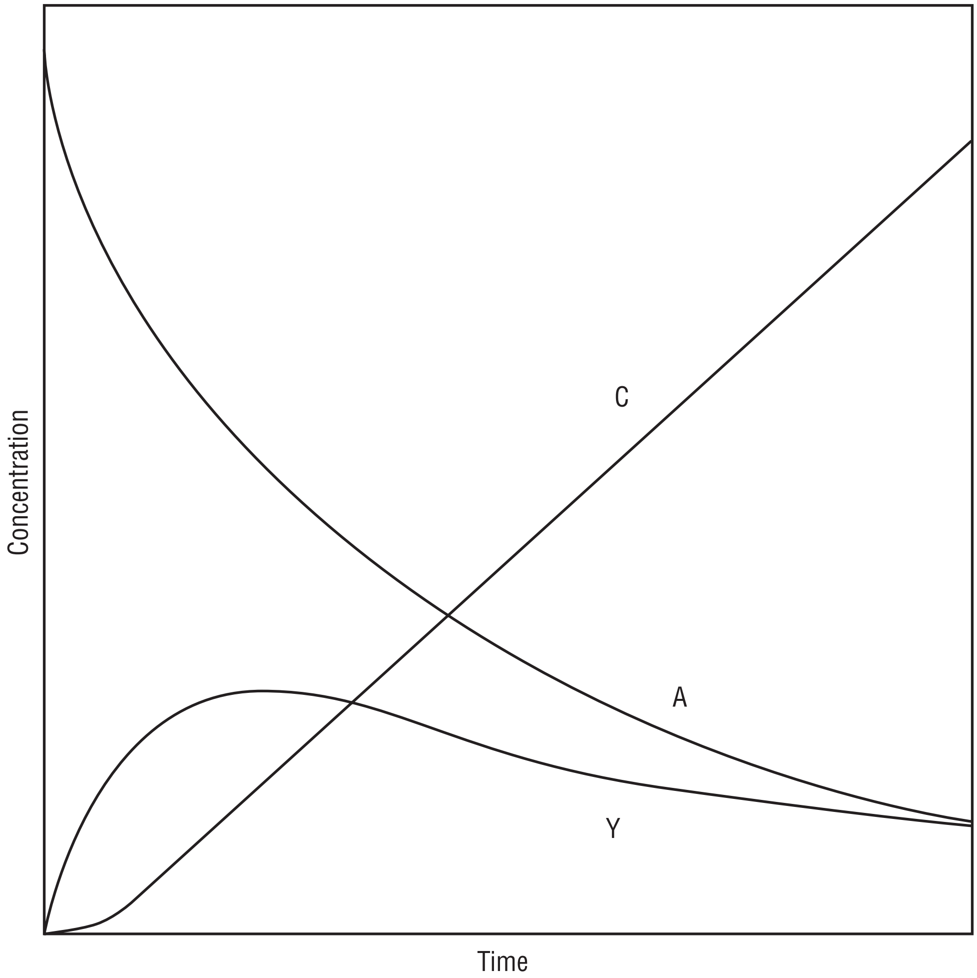


Figure 3.3. Relative concentrations of three substances present at various times when undergoing a consecutive-reaction series $A \longrightarrow Y \longrightarrow C$ in which A and Y decay by first-order kinetics.

Another common situation occurs in which a reversible reaction takes place:

$$A \rightleftarrows B \tag{3.8}$$

Kinetic analysis can account for the change in concentration of *A* or *B* with time until equilibrium is reached. The author knows of no example of a conservation problem in which the kinetics of a reversible reaction has been utilized. Perhaps, however, the apparent reversible darkening and bleaching of discolored paper will someday be profitably studied from this point of view.

These brief remarks serve only to introduce the extensive subject of kinetic analysis. Pointed out is the basic fact that there are a number of well-recognized kinetic explanations to account for the rate at which chemical changes proceed in time. As shall be seen in later chapters, these principles have been repeatedly and effectively applied to account for the rates at which deterioration takes place in numerous systems.

How Properties Change in Time

Linear

It would be very convenient indeed if the decline in the chemical concentration, or in the physical properties dependent upon such concentrations, would decrease (or the decomposition products would increase) at a constant rate. Such a change, *linear* in time, is more the exception than the rule. As noted, the disappearance of a chemical substance in this manner is said to be *zero order*.

Cases can indeed be found in which the rate of deterioration is constant, illustrated as curve *a* in Figure 3.1. The formation of C9 dicarboxylic acid, a decomposition product in linseed oil paints exposed to ultraviolet radiation, seems to occur in such a manner (Rasti and Scott 1980). One must always check, however, to verify whether the rate is only apparently linear over the relatively short period of time in which the experimenter has observed the process or whether, if the test were carried out over a much longer period of time, the rate would be found not to be constant. Incidentally, the frequently used calculation of the correlation coefficient is not a device to demonstrate linearity.

Situations frequently occur in which a process appears linear but if the very first moments of change are observed, an initial change may be noted that is particularly rapid. One can be alerted to this possibility if, when extrapolated to zero time, the apparently linear set of data points does not intercept at the initial concentration (or physical property) at time zero. Thus, in the homogeneous hydrolysis of cellulose, the apparently rapid initial breaking of bonds has been considered to represent *weak links* (Michie et al. 1961; Rånby 1961). In the thermal decomposition of various cellulose products the general process of weight loss is considered to be a *first-order* reaction (as defined earlier in this chapter). A rapid initial stage which seems to occur has been taken to represent degradation that takes place in the amorphous fraction (Peters and Still 1979).

In cases where there is an induction time, as illustrated in Figures 3.1d and 3.4, the experimenter might only have observed the slight change during an initial (or steady-state) stage and yet consider that the experimental data had represented the whole process. If the reaction is not carried out far enough, the fact that there were actually two stages can easily be overlooked. The potential for such an oversight can be seen in the data of Wilson and Forshee (1959) regarding the degradation of cellulose acetate at 110 °C.

When analyzing a set of data as "obeying first-order kinetics," it is customary to state that the data "follow first-order kinetics until *n* percent of the product has been consumed." It is also well known that, if the net change is not more than 10%, one usually cannot distinguish whether the rate of change is zero or first order.

Research investigators can consider themselves fortunate if they find that they have a case of linear deterioration, a constant rate over time. Nevertheless, as pointed out, one must always consider the evidence carefully, particularly if one wishes to predict the behavior over a very long period of time. The presence of an induction time, or a rapid initial process, may go unnoticed. One will find authors sometimes having treated their experimental data as falling on a straight line when, upon closer inspection, the data suggest that there may have been an induction time or an initial rapid stage present.

Functions Nonlinear in Time

Occasionally the rate of a process will be found to be related to the square root of time. This often occurs to the situation in which the rate is controlled by diffusion (Auerbach and Sanders 1969; Fukushima 1983). The relaxation of internal stresses in coatings also proceeds according to the square root of time (Saarnak et al. 1976). The reader may also recall that some of the original studies on the discoloration of paper plotted the change in the Kubelka-Munk K/S value against square root of time, largely because this seemed to yield linear plots (Tongren 1938); this practice continues today (Kim et al. 1990).

Changes in properties are also sometimes plotted against the logarithm of time, but this is often done simply for convenience, to compress the data. There is at least one theoretically based situation, however, where the use of log time is entirely valid. Based on the Hurter-Driffield Law for photographic materials, Zerlaut and Ellinger (1981) showed that a linear relationship between the loss of gloss of coatings was obtained when plotted against the logarithm of exposure to the ultraviolet component of sunlight. Hirt et al. (1959) reported the same relationship for the yellowing of polyesters.

Stages

As mentioned, when a single, rather well-defined, chemical substance or process is studied, it is usually a relatively easy task to describe the course of its deterioration by a well-known kinetic equation. The fading of dyes in solution, for example, has been extensively studied and repeatedly found to obey first-order kinetics. However, textiles, paints, varnishes, and adhesives represent complex mixtures of substances; one finds that specific chemical constituents and their general physical properties usually deteriorate in a manner that is not constant or even monotonic from time zero up to the point where all useful properties are lost. Instead of changing as in curve *a*, *b*, or *c* in Figure 3.1, frequently a combination of all three types of behavior is observed, as in curve *d*.

It has proven useful to consider that most materials tend to deteriorate in *stages* (Feller 1977). These may be the generalized stages designated in Figure 3.4 (Grassie 1956) or they may be considered in terms of specific chemical-process steps designated as initiation, propagation, and termination reactions (reviewed by Feller 1976). There may also be specific subsidiary reactions such as inhibition or chain transfer in free-radical processes. In the alkaline degradation of oxidized cellulose, a "chain-stopping" chemical reaction has long been known (Feller, Lee, and Curran 1985).

Because substances tend to deteriorate not in a linear fashion but by one of the other pathways illustrated in Figure 3.1, it is absolutely necessary, in designing and conducting accelerated-aging tests, that the character of the overall pattern of changes in physical properties or specific chemical substances with time be determined up to the point of failure. To state this in another way, it is absolutely necessary to determine whether the system follows one of the paths shown in Figure 3.1 up to the point in time at which failure occurs or the degree of change becomes unacceptable. Nonetheless, during any particular stage the principal reactions often can be evaluated in terms of zero-, first-, or second-order kinetics.

One of the time-honored ways of carrying out accelerated-aging tests is used on so-called single-point measurements; that is, heating a substance or exposing it to light for a given length of time and noting how much it has changed in strength or color relative to another. The major fault of this procedure can be seen in Figure 3.5a, where, based on a single point in time, one would rate product *A* as the better one, changing less than *B*. If, however, the overall behavior of these materials is as shown in 3.5b, product *A*, when exposed just a bit longer, would have drastically changed, whereas the decline in properties of *B* would have practically leveled off. This example, which the author first encountered many years ago in a lecture by W. K. Wilson,

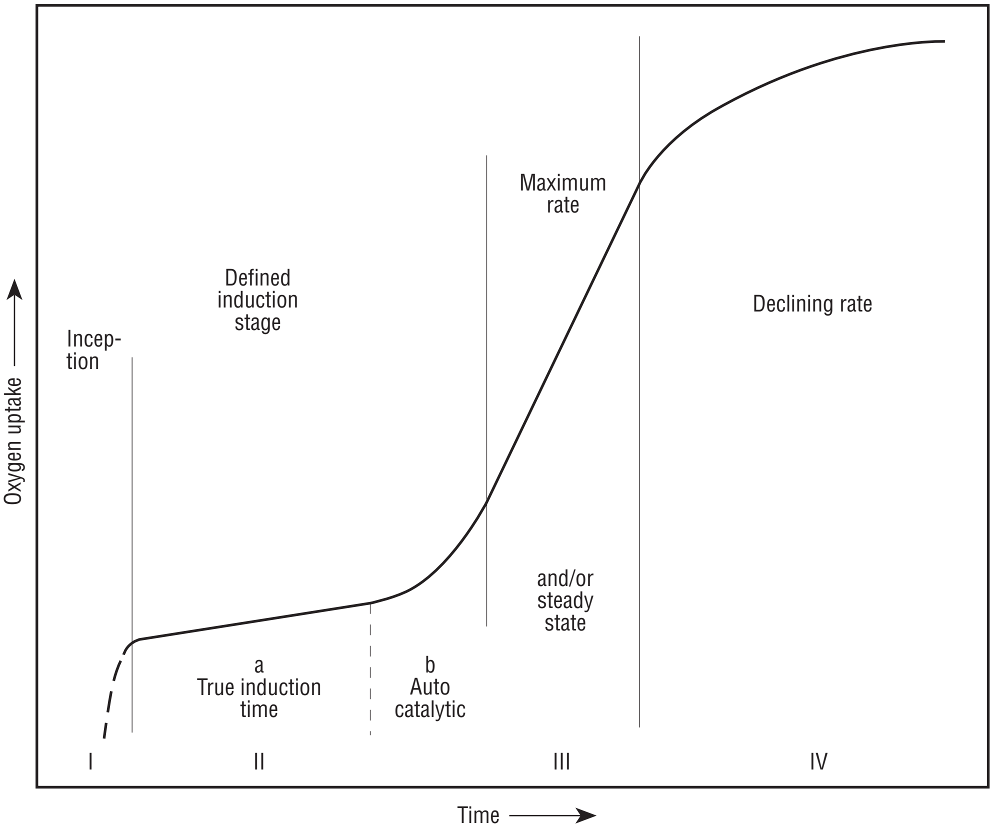
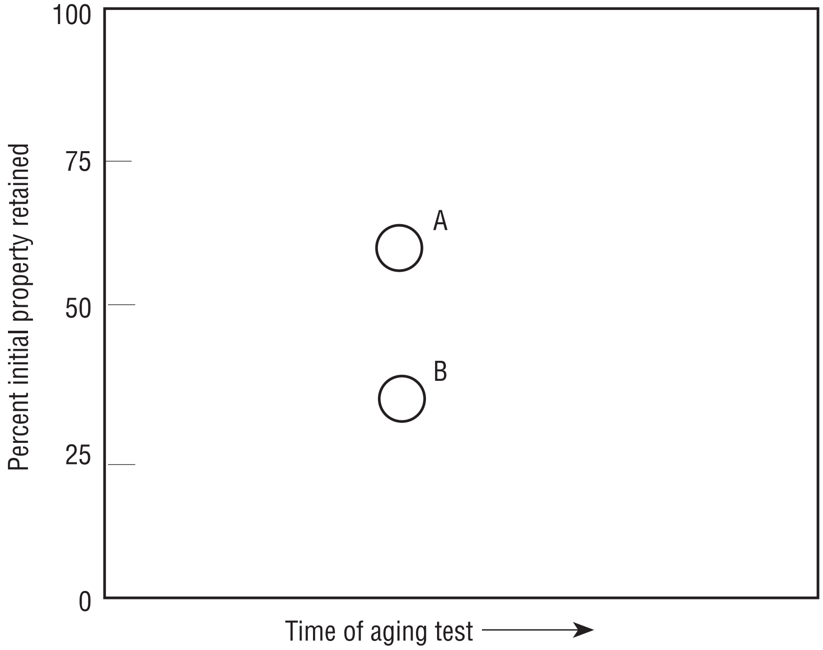


Figure 3.4. Possible stages of oxidative history (after Grassie 1956). Reproduced from Feller (1977) with permission of the publisher.

clearly illustrates the need to know more than is revealed by the measurement of the degree of change at a single point in time.

There is another aspect of the single-point method of evaluation that is not often thoroughly discussed: it is generally more fundamental to measure the relative time to reach a given degree of change rather than measure the degree of change after a fixed aging time (Sizman and Frank 1963; Arney and Chapdelaine 1981).

In the practical case, if a series of materials were under investigation all of which exhibit behavior similar to either product *A* or product *B* in Figure 3.5, then indeed it might be feasible to test them by only measuring their properties at a particular point in time. Thus, the effectiveness of various inhibitors applied to one particular class of polymer, behaving as in the case of example *B*, are often rated according to the apparent induction time; that is, the time in which the precipitous loss in strength, or precipitous increase in oxygen uptake, occurs. One might also compare the merits of various periods of washing of a bleached wool textile or a



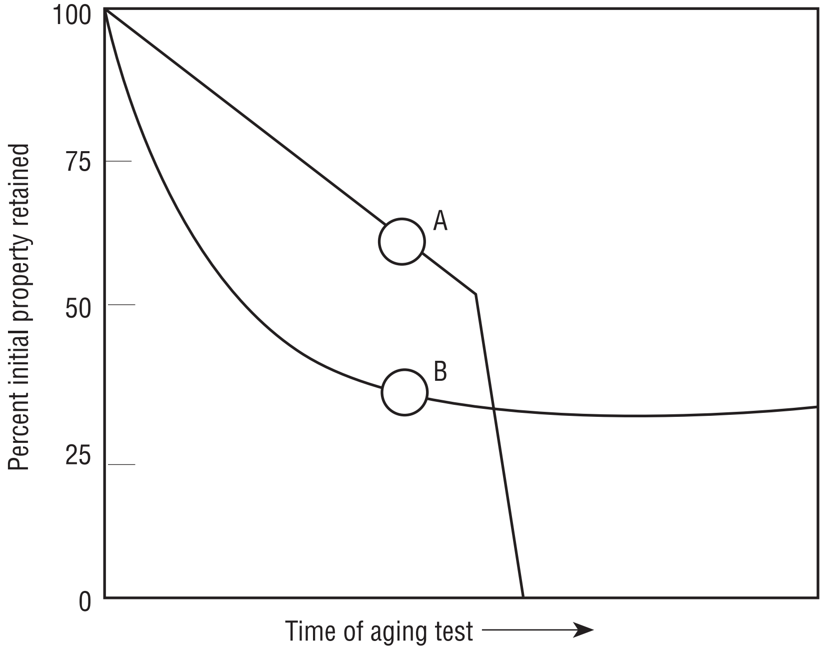


Figure 3.5a, b. Example of the problem of evaluating the relative stability of two materials. Chart on top (a) shows "single point" determination of the retention of initial property with time Product. A rated more stable than B. Chart on bottom (b) gives information regarding the entire course of aging.

low-lignin paper, evaluating each after a fixed time. However, employing the shortcut of a single measurement is not advisable when the behavior of dissimilar materials or systems is to be compared—the behavior of high-alpha-cellulose versus a paper of high-lignin-content or the behavior of a thermoplastic adhesive system versus a thermosetting one. It is to be expected that widely different types of materials will deteriorate by different paths, such as those in Figure 3.1 or products *A* and *B* in Figure 3.5. Measuring a single point would not properly characterize such diverse behavior.

Summary

In planning accelerated-aging tests one of the first steps is to determine whether the deterioration of the system under study follows one of a number of pathways such as those illustrated in Figures 3.1, 3.4, and 3.5. The whole course of degradation up to the point of failure of the system must be determined. If the task is to routinely compare closely similar treatments on the same substrate (cloth, paper, polymer), perhaps the complete course of deterioration (requiring many measurements) need not be monitored in future tests; some simplification in the test protocol can usually be devised. On the other hand, if the merit of a variety of materials or systems of materials is to be compared, significant features of the whole course or character of their deterioration must be known. A rapid inception (or weak-link stage), an induction time, or a maximum rate of deterioration may reveal themselves as major features that must be monitored. If one system exhibits an induction time and another an initial rapid stage, or if one exhibits retardant behavior and the other autocatalytic, considerable thought has to be given to the aging criteria that will be used to compare the merits of the one system relative to the other with respect to their long-term serviceability.

4 Prediction of Useful Lifetime

A recent survey of laboratories engaged in accelerated-aging tests resulted in the statement that "the majority of users do not believe that they can properly simulate or predict service" (Brown 1991). Dozens of similar pessimistic remarks can be cited. Admitting that there are difficulties, it is nonetheless useful to review the approaches that chemists and engineers have regularly employed in the effort to meet the objective of predicting long-term behavior and time to failure.

As stressed in the previous chapter, it is necessary to determine the whole course that the deterioration of a particular material or system follows over time before graphs and equations can be developed by which the change in its properties in time can be predicted. The course of deterioration must be established up to the point of failure or unacceptable change. Useful equations may predict the progress of aging in an early or intermediate stage yet fail to conform to the whole pattern of deterioration.

Empirical Equations

Kamal (1966) and Kamal and Saxon (1967) proposed the following empirical equation to calculate the change in thirteen different properties (P) in ten different plastics during exposure in xenon-arc radiation:

$$\log P = b_0 - b_1 (t - 250) + b_2 (I - 0.710) \tag{4.1}$$

Here, t is time, I the average intensity of the light source and b_0, b_1, and b_2 constants. In the 1966 publication, Kamal provided tables of predicted and measured results of outdoor exposure confirming the effectiveness of the equation. Tooke (1980) has reviewed several other types of equations.

Computer programs exist today that allow one to develop equations that best fit a curve of the change in properties over time (Hamid and Prichard 1991). However, a word of caution: Nelson (1990:533) points out that polynomial equations are often adequate for *interpolation* "but are notoriously bad for *extrapolation*" [italics added].

Change According to Laws of Chemical Kinetics

If it can be shown on the basis of accelerated-aging tests that the observed change in chemical properties tends to follow one of the principal kinetic processes discussed in Chapter 3 (zero-, first-, or second-order individually, sequentially, or reversibly), then the pertinent equations are often applied to predict the progress of additional accelerated aging as well as the course of aging under normal conditions. Such equations might be said to be theoretically based rather than empirical, conforming to a "model," as some authors say, of what must be taking place. Thus, Shelton and Cox (1954) derived an equation for the rate of oxygen absorption by Hevea rubber based on kinetic principles and showed that the theoretical explanation conformed to the empirical behavior. Using a first-order kinetic plot for the loss of ether bands in the infrared, Hartshorn (1987) considered it possible to predict a five-and-a-half to six-year lifetime of melamine-acrylic enamels on the basis of twelve to sixteen months' monitoring the changes in the infrared spectra of the coatings during exposure outdoors. Another significant application of first-order decay is seen in the work of Stoll and Fengel (1981, 1988) in their interest in dating ancient linen and cotton by the decrease in the degree of polymerization of the cellulose. These are just a few examples of the many that could be cited.

Even if the change in properties does not conform perfectly in accord with one of these equations up to the point of failure, the course of deterioration can often be analyzed in terms of a given kinetic process. Thus, plotting the loss of DP of polystyrene (Gupta and Nambiar 1983) and cellulosic textiles (Daruwalla et al. 1967) in terms of the fraction of bonds broken (1/DP), the data often showed a break in the theoretical straight-line behavior. One might consider this as a failure to conform to the rate law. However, the discontinuity has been interpreted not as a failure to obey a zero-order law, but instead to represent the existence of two stages, the first taking place through easily broken "weak links" in the polymer chain. Similarly, a first-order plot (log concentration versus time) that has two or more linear segments, has often been interpreted profitably in terms of a rapid initial first-order change superimposed on one or more slower ones. Shelton and Winn (1946) provide an example of the application of this concept.

Predictions regarding the effect of temperature based on the Arrhenius equation are discussed in Chapter 10, "Thermally Induced Oxidative Deterioration."

Sizmann and Frank Method

As mentioned earlier, in carrying out accelerated tests it has often been the custom to age two materials for a given length of time and then to compare their relative loss of strength or degree of yellowing. A more fundamental approach is to compare the length of time to reach the same degree of change (Sizmann and Frank 1963). For example, the time required for a given loss of dye was used extensively in the early studies of dye fading (Giles and McKay 1963). However, when this point of view has been employed, the fundamental reasons behind it have not often been pointed out. Arney has provided a convenient discussion of the principles and practical consequences of applying this approach (Arney and Chapdelaine 1981).

Statistical Analysis of Probability of Failure

In recent years changes in properties and the distribution of test results have become increasingly analyzed from a statistical point of view. One might wish to classify this approach also as an empirical one for it is not based on the theoretical kinetic reasons for the rate of chemical reactions. Nonetheless, statistical behavior is also based on theory: on the assumption, not an unreasonable one, that experimental results will usually obey the principles of statistics and probability (recall Figure 3.2). One such technique is used in business forecasting and in the analysis of the lifetime of engineering products: Time Series Analysis (Rehfeldt 1987). The Box-Jenkins analysis adapted for this purpose is called an autoregressive integrated moving average model (Box and Jenkins 1976).

Gaining wide recognition is an approach to the prediction of service life based on the assumption that the probable distribution of times-to-failure, F_t, will follow the Weibull cumulative distribution function:

$$F_t = 1 - e^{-(t/\beta)\alpha} \tag{4.2}$$

and the probability density function is:

$$f(t) = (\alpha / \beta)(t / \beta)^{\alpha-1}\, e^{-(t/\beta)\alpha} \tag{4.3}$$

In this equation, t is time, e the base of natural logarithms, and values of α and β are selected that fit the data (Bekker 1980; Martin and McKnight 1985, Part II). Figure 4.1 shows how the Weibull probability density changes with the values α and β. Note how this one equation fits considerably different response curves depending on the values of α and β. Figure 4.2 shows a plot of experimental data and the Weibull curve fitted to the data. A significant point made by proponents of this approach is that all the samples do not need to fail before useful predictions are made.

Correlation

Mathematical measures of correlation can be found in any standard text regarding statistics. The reader is referred particularly to the text by Reedy and Reedy (1992) published by the Getty Conservation Institute.

Before it can be claimed that any accelerated-aging protocol or analysis of degradation products suitably leads to the prediction of aging behavior under what are considered normal conditions of exposure, comprehensive data on the behavior under those conditions must be obtained so that the correlation of the behavior under accelerated and normal conditions can be satisfactorily demonstrated. (Tahan [1974] and Tahan et al. [1975] provide extensive examples comparing the loss of gloss of various coatings under natural and artificial weathering.) Many elaborate mathematical treatments have been applied to determining how well the results of accelerated-aging tests correspond with the behavior of materials during outdoor aging (Nelson 1983). However, examples of extensive data on indoor aging under normal museum conditions with which to correlate with accelerated tests are extremely rare.

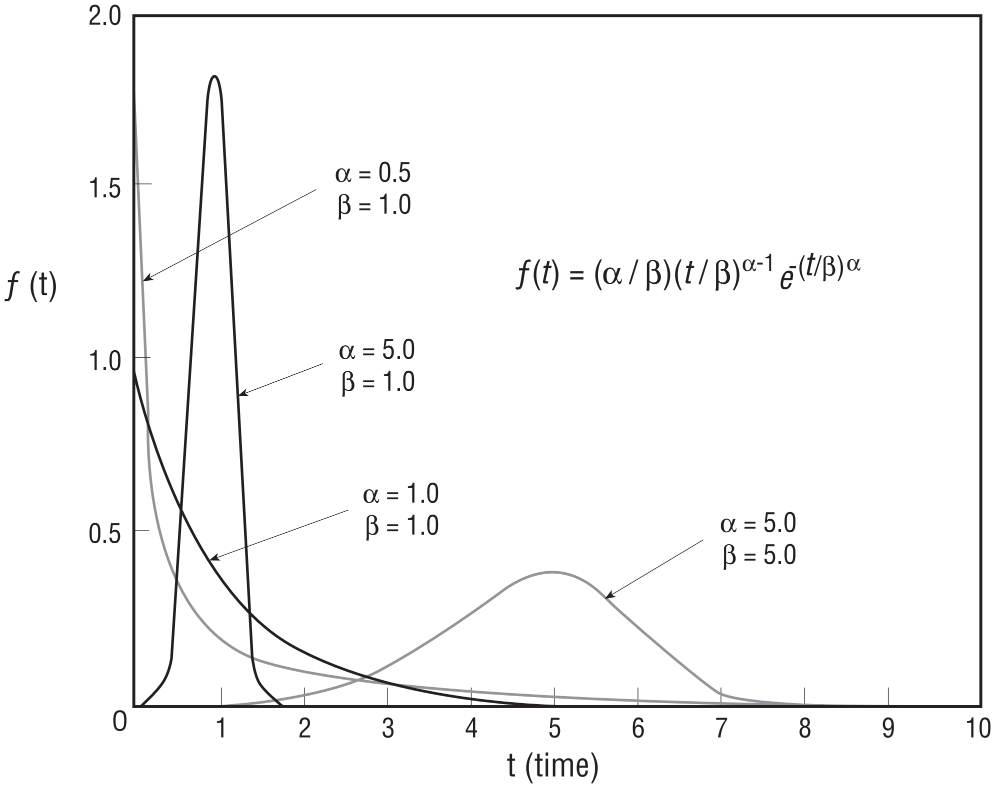


Figure 4.1. Weibull probability density function plots for different shape (α) and scale (β) parameter values (Martin and McKnight 1985). Reproduced with permission of the publisher.

Ranking. When there are no exact (numerical) measurements available, one can verify if one accelerated-aging procedure is yielding virtually the same effects as another or

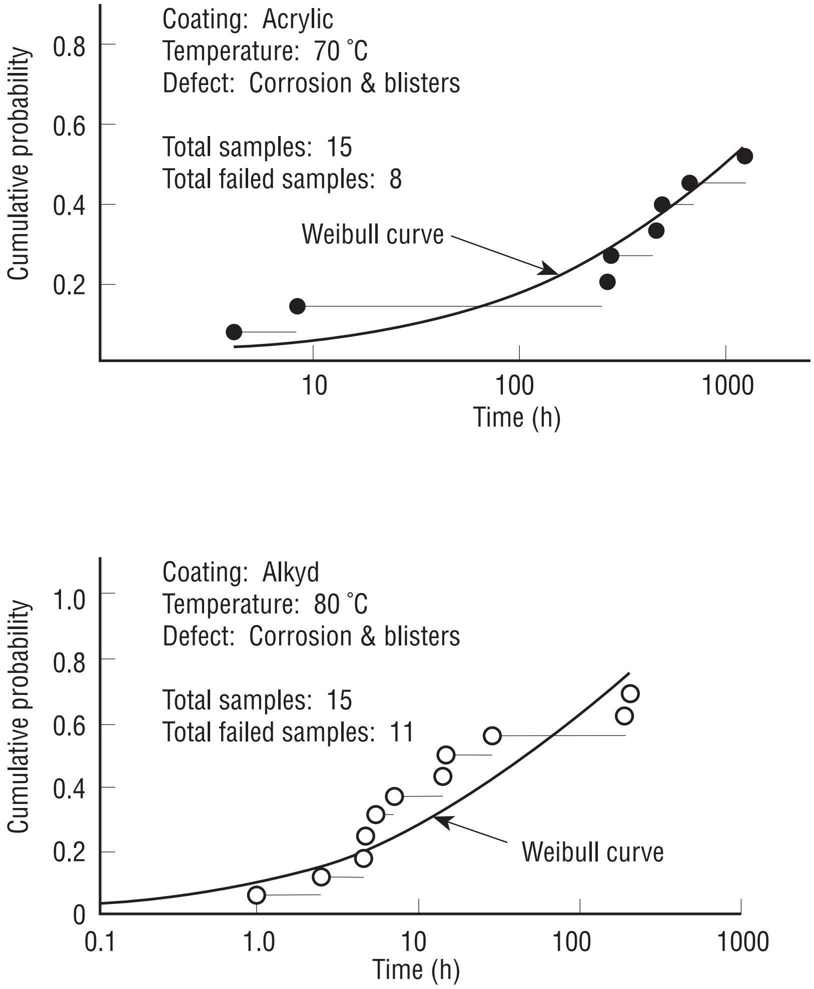


Figure 4.2a, b. Cumulative probability of failure for (a) an acrylic coating system at 70 °C and 95% RH and (b) an alkyd coating system at 80 °C and 95% RH. Experimental data compared to Weibull distribution function (Martin and McKnight 1985). Reproduced with permission of the publisher.

as natural aging, by comparing the relative ranking of failure of a set of samples under each circumstance. Most commonly this is expressed as the Spearman Rank Correlation Coefficient, ρ:

$$\rho = 1 - \frac{6\Sigma d^2}{N(N^2-1)}$$

Here, d^2 is the square of the difference in ranking between items in the first test series and the second. N is the number of test items in the set.

Controls

When there is doubt as to how well the conditions used in an accelerated-aging test will lead to a duplication of the results observable under ordinary conditions of usage, it is useful to include controls in a testing program, materials whose behavior and effective lifetime under normal conditions of usage is reasonably well known. DeTommaso et al. (1980) state that it is a "cardinal rule to always include appropriate pass and fail controls with documented . . . history" (of behavior under actual conditions of exposure). The Dioxide Group, manufacturers of titanium dioxide pigments, regularly includes a reference pigment in every program of exposure (Blakey 1985), taking full recognition of the difficulty in controlling the conditions of temperature and humidity in carbon-arc Fade-ometer as well as other accelerated weathering procedures. In evaluating the tendency of cellulose ethers to darken during thermal aging, Arney compared their behavior with that of rag paper, cellulose acetate, and newsprint (Feller and Wilt 1990:51).

When selecting controls, it will be found useful to choose some that exhibit very poor stability, others that exhibit intermediate behavior, and still others that possess exceptional stability, as discussed in "Classes of Stability" (page 5). Materials whose composition is well characterized or controlled in manufacture can be considered as primary standards; others less well characterizable may be considered secondary controls.

It has been suggested the ISO R105 blue-wool fading standards, Paraloid® B-72, and butylmethacrylate polymers might serve as material standards in photochemical-aging tests (Feller 1978). Artists' alizarin lake is a widely encountered pigment of moderate lightfastness; alizarin lake-titanium white mixtures often exhibit a lightfastness equivalent to ISO 105 blue wools 4 to 5 and have therefore sometimes served in the past as a convenient control (Levison 1976). Nevertheless, one must regard alizarin as a secondary standard because its characteristics vary depending on the manufacturer.

In recent years the National Research Institute of Cultural Properties, Tokyo, has begun to use filter papers dyed with Rhodamine B as a monitor of light exposure (Kenjo 1986a, b; 1987). The American Association of Textile Colorists and Chemists (AATCC) has a standard fading cloth, XRF-1, that has long been used to monitor exposures in xenon- and carbon-arc devices (AATCC test method 16-1982). Tennent et al. (1982) have described a dosimeter to monitor ultraviolet radiation. The yellowing of a polystyrene reference white (available from Testfabrics, Inc., Middlesex, NJ 08846) is currently being used in the United States as a standard monitor/control for exposures in Fade-ometers and weatherometers (J. W. Scott 1991). However, this dosimeter seems chiefly sensitive to ultraviolet (C. W. Bailie, pers. comm. 1992).

Summary

In view of the variety of polymeric materials available, the complexity of the coating and adhesive systems in which they are employed, and the varied effects of temperature and humidity, it is not surprising that few claims are made regarding our ability to predict their long-term behavior and stability. In any given system it is fundamentally necessary to determine the whole path or course of deterioration up to the point of failure or unacceptable change. With this knowledge, it is often possible to develop mathematical equations, either from an empirical or theoretical point of view, that will closely mimic the decline of particular properties with time. The theory and principles of chemical kinetics provide the basis for many such expressions. There are also mathematical techniques to confirm how well the equations correlate with the changes that occur during natural aging or during alternative methods of testing. Statistical methods are increasingly being applied to the problem of prediction, particularly calculations of the probability that a given percentage of the samples under consideration will reach a certain level of degradation in a given time. Because of the variability of test conditions and response of systems to them, the use of controls of known behavior is much to be recommended.

5 Theoretical Aspects of Photochemical Deterioration

To Activate Molecules, Radiant Energy Must Be Absorbed

Visible and ultraviolet radiation, with which this monograph is primarily concerned, exhibit properties characteristic of both waves and particles[1]. The particle, bundle, or bullet of electromagnetic radiation is called a photon. Its energy is given by the equation $E = h\nu^3$. The energy of photons in the infrared range (long wavelength, low frequency) is seldom sufficiently great to induce the chemical reactions that are normally encountered in photochemical deterioration. However, as the wavelength of radiation gets shorter and shorter, through the blue and violet region of the visible and into the ultraviolet, the photons possess an increasing amount of energy and are capable of inducing significant photochemical changes.

A key principle of photochemical phenomena is the Grotthus-Draper Law. This states that only radiation that is absorbed by a substance may cause a chemical reaction. This, of course, is axiomatic: light must be absorbed, or taken up, so to speak, by a substance in order to act upon it.

The Grotthus-Draper Law may seem obvious but it is not always clear just how this principle can be applied in a particular case. Two examples can be cited. First, the spectral absorption curve of a colored pigment or dye can be readily measured, and the wavelengths that are strongly absorbed by the colored substance are often assumed to be responsible for its deterioration. Suppose, however, the destruction of the colored compound (fading) is caused by the absorption of radiation by some other substance which then passes its energy on to the colorant. This would be called *photosensitized* fading. Under such circumstances, the absorption curve of the most obvious compound, the colored substance, would not be indicative of the wavelengths that initiated the process. Berger (1972) states: "Not every type of light absorption causes changes in the material."

A second example illustrating the difficulty of identifying the key act of absorption is the case where a trace of carbonyl or other absorbing impurity is responsible for initiating the photochemical reactions in a clear and practically colorless plastic film. Thus, polyethylene, poly(vinylchloride), nylon 6,6, cellulose, and many other polymers do not appear to absorb significant radiation above 290 nm when their absorption is recorded on a scale of 0 to 100%. One might, therefore, propose that these polymers would not be affected by near-ultraviolet radiation. However, materials often contain traces of impurities that may absorb far less than 1%. Such a low degree of absorbance would generally pass unnoticed when the percentage of spectral absorption or transmission is recorded. The light-absorbing entities in trace contaminants may be carbonyl groups, double-bond unsaturation, oxygen-polymer charge-transfer complexes, metallic impurities, and various catalyst residues (McKellar and Allen 1979:13). A typical quote regarding this situation is that of Andrady and Searle (1989): "Since PVC (polyvinylchloride) itself does not absorb ultraviolet light in the wavelength range . . . 280–400 nm, and the photoinitiation is dependent upon the nature and concentration of impurities and additives and on any thermal degradation products formed during processing . . . discrepancies [in reported 'active wavelengths'] are to be expected."

Somersall and Guillet (1975) have classified polymers that have chromophoric (light-absorbing, color-producing) groups present either at the chain ends or attached along the chain as type A. Polymers in which the monomeric units comprising the main chain are themselves able to absorb photochemically significant wavelengths were designated type B; polystyrene and poly(ethylene-teraphthalate) provide examples of the latter. One would expect the type B polymers to be affected by ultraviolet radiation. It is far more challenging to identify the critical absorbing entity in polymers of type A, situations in which trace photosensitive groups or impurities are responsible for initiating photodeterioration. Thus, to say that no photochemical or photolytic reaction can take place without absorption is perfectly correct. Nevertheless, there often is difficulty in deciding just what the chemical entity is whose spectral absorption characteristic is critical in any given situation.

Why should radiation be absorbed by some molecular structures and not by others? Sir William Bragg used the analogy to tuning forks which can be set in vibration when sound waves of the appropriate frequency pass through them (Bragg 1959). In a similar manner, certain musical instruments possess strings or resonant chambers which, though not directly touched, are set in sympathetic vibration when other parts of the instruments are played upon. Correspondingly, it may be said that molecules tend to absorb electromagnetic energy when their electronic system is in tune with a particular frequency of light that passes through them.

Tweedie et al. (1971) succinctly sum up the subject of the critically absorbed wavelengths thusly: "The rate of photodegradation of the material . . . depends primarily on the energy available at those wavelengths which one or more components of the material can absorb and which, when absorbed, are capable of directly degrading that component (e.g., a dye or the fiber substance) and/or initiating a reaction which may or may not damage the absorbing component but does damage other components (e.g., the effects . . . of photosensitizing dyes and . . . pigments such as titanium dioxide). Subsidiary factors . . . are the temperature and humidity. . . ."

Photolysis

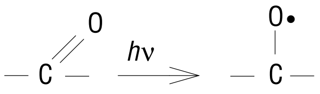
A second key principle, the Stark-Einstein, states that a molecule can only absorb radiation in terms of a discrete quanta of energy (photon). It is well known that the shorter the wavelength the higher the energy of the photons, the packets, or bullets of electromagnetic radiation. Their energy is expressed by the equation $E = h\upsilon$ or hc/λ where υ is the frequency of the electromagnetic energy, λ the wavelength, c the speed of light, and h Planck's constant.[2]

Many introductory discussions of photochemical deterioration show tables of chemical bond strengths and the energy of a photon. Figure 5.1 essentially implies that the absorption of a photon by a chemical substance is capable of the direct breaking (dissociation) of a bond, such as in the case of a hydroperoxide shown in Equation 5.1:

$$\mathrm{ROOH} \xrightarrow{h\nu} \mathrm{RO}\bullet + \bullet\mathrm{OH} \qquad (5.1)$$

Such a process would be called *photolysis* or the *photolytic* breaking (scission) of a bond. Equation 5.1 is described as a *homolytic* breaking of the bond; one electron remains on each of the two atoms separated. This is the type of change familiarly induced by 254 nm radiation, the short wavelength principally emitted by *germicidal* mercury vapor (low-pressure mercury vapor) lamps. For convenient reference, the ultraviolet has been divided into different wavelength regions: UV-A 400 to 315 nm, UV-B 315 to 280 nm, and UV-C 280 to 100 nm. These regions are similar to those that used to be called near, middle, and far ultraviolet (Fig. 5.1).

Wavelengths in the UV-C region have the greatest potential of inducing photolytic scission. When wavelengths of near ultraviolet and visible are involved, however, photolysis is a relatively rare occurrence. Far more frequently, the absorption of a photon of near-ultraviolet radiation leads to the excitation of the electrons in a chemical bond, raising them to a higher level of energy. This is often indicated by a chemical equation such as Equation 5.2:



(5.2)

The single dot on C and O implies a lone electron in the outer orbit, a free-radical site. Excitation of a structure such as the carbonyl group shown here more often than not leads to *photochemical* processes rather than photolytic. Kämpf et al. (1991) sum up the situation clearly: "As far as light-induced bond breaking in a polymer is concerned, it is important to distinguish between the excitation of a molecule into a binding bound state with the possibility of further reaction (for example, with atmospheric oxygen [photo-oxidation]) and the excitation of a molecule in a non-binding state with immediate dissociation. In the visible spectral range, the probability of a dissociative [photolytic] process occurring in polymer solids is extremely low."

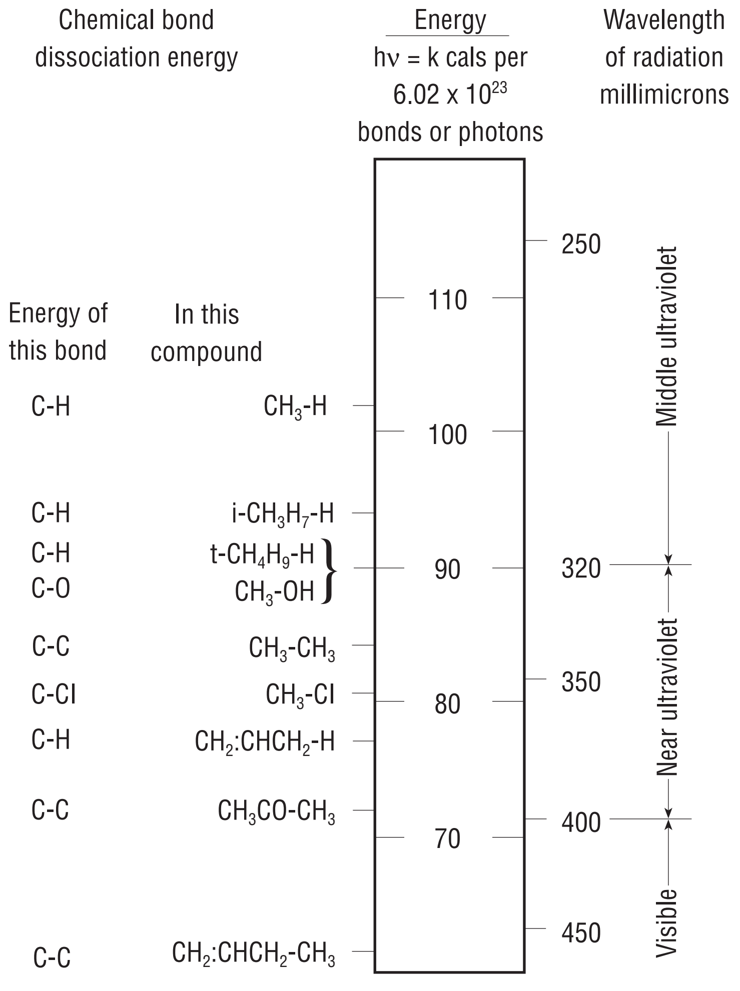


Figure 5.1. Chart relating the energy of radiation at various wavelengths to the dissociation energy of various chemical bonds. After Feller(1964). Reproduced with permission of the publisher.

So-called accelerated-aging tests carried out with short wavelengths such as 254 nm, which generally induce photolytic deterioration, lead to different results than exposure to longer wavelengths. The latter primarily induce photochemical processes. Thus, in a famous example, Launer and Wilson (1949) showed that, in the deterioration of paper induced by 254 nm radiation, water vapor retarded chain-breaking. On the other hand, under near ultraviolet, moisture accelerated deterioration.

In searching and reading the scientific literature on photochemical deterioration, particular care must be taken to verify the kind of ultraviolet radiation involved in the research. If low-pressure mercury vapor lamps have been used without special filtration, or if mercury vapor lamps have been used with solely a quartz envelope, the type of deterioration described and the conclusions reached, particularly with 254 nm radiation, are likely to have little to do with photochemical deterioration problems encountered in a museum or library. This point was stressed many years ago (Feller 1975). (Photochemical studies are often carried out with the 313 nm radiation. The author believes that reactions induced by this wavelength would, in general, be pertinent to conservation science problems.)

A practical or operational definition of photolysis would be any photo-initiated reactions observed to take place in the absence of oxygen (McKellar and Allen 1979:31; Lemaire 1993:126). Gardette and Lemaire (1986), for example, have carried out exposures under vacuum as a technique to detect whether photolytic reactions were occurring at particular wavelengths. In conducting such a test under inert conditions, one must always be on guard against the possibility that traces of absorbed oxygen might unknowingly be present which could contribute to an initial photo-oxidative stage of degradation, rather than photolytic.

The Primary Process

When a photon is absorbed by a molecule, the energy thus supplied is said to excite the electronic system of the molecule, or to *activate* the molecule. The excited molecule may then lose the absorbed energy (a) by heat, (b) by the emission of radiant energy in the form of fluorescence or phosphorescence, (c) by undergoing a chemical change within the molecule, (d) by the breaking of chemical bonds (photolysis), or (e) by transfer of the energy to another atom or molecule. It is essentially the acquisition of the energy and its loss through these five principal ways that may be considered to be the primary process of photochemistry. The first two are considered photophysical processes (Geuskins 1975); the other three are considered photochemical. Rabek (1982:854) has itemized ten primary photochemical processes.

A fundamental law governing this event is the Stark-Einstein Law, also known as the law of photochemical equivalence. This states that one atom or molecule is activated for every photon that is absorbed. To study the details of a photochemical reaction, the chemist often looks at the products of the reaction to determine the number of chemical transformations that have occurred for a given number of photons absorbed. If one molecule is changed or decomposed for every photon of light absorbed, the photochemist says that the *quantum yield* or quantum efficiency is equal to 1, as predicted by the Stark-Einstein Law.

Photochemical processes in the deterioration of paints, varnishes, and textiles are highly complex; the result is that the quantum efficiency of the overall photochemical effect is often very much lower than 1 (Knowles 1973). For example, long ago the quantum efficiency had been reported to be only about 0.002 in the bleaching of certain dyes by light; in other words, two dye molecules are bleached for every thousand photons absorbed (Bodenstein 1913). In another example, the quantum yield was found to be 0.03 in the phototendering (embrittlement) of certain textiles (Bamford and Dewar 1949). Quantum yields as low as 10^{-4} and 10^{-5} are widely reported in the deterioration of plastics and drying oil vehicles (Gusman and Spell 1956; Miller 1958). In contrast, if a chain reaction is initiated, as in photopolymerization, the quantum yield can be very high. (The *chain length* of peroxide formation is discussed in Appendix C.)

The number of quanta impinging upon a sample is usually determined by the use of chemical reactions whose quantum efficiency has been well established. These are called *quantum counters* or *chemical actinometers*. Since the determination of quantum efficiency or quantum yield requires some effort and experience, it is best to consult authoritative texts such as that by Rabek (1982:920–959).

Lowering the intensity of illumination lowers the number of photons per minute but does not alter their energy, for this is a function of their wavelength. It is the *energy* of the photons absorbed that is able to initiate a photochemical change. As a consequence, there is theoretically no threshold of intensity of light below which photochemical reactions will cease to take place.[3] This conclusion is of considerable importance to the museum curator. No hope can be extended that if sensitive objects are exhibited under an intensity lower than a particular level, photochemical deterioration will cease. At low intensities, the processes of photochemical deterioration will be retarded, very possibly according to the reciprocity principle. However, photochemical action will not be arrested. The idea of a possible threshold of photochemical activity is discussed again in Chapter 6.

Secondary Processes

As mentioned, the literature on photochemical processes often compares the energy of chemical bonds with the energy of the photons in a simple chart, as shown in Figure 5.1. By such a chart it is intended that one may readily see that radiation of short wavelength would be sufficiently energetic that it can break or dissociate a number of chemical bonds of lower energy. As stated, in spite of the frequency with which such charts are presented, the direct breaking apart of molecules (photolysis or photolytic cleavage) is rarely the predominant effect in the deterioration of solids and liquids activated by visible and near-ultraviolet radiation. Far more often, transfer of energy with neighboring molecules takes place. This was noted in the previous section as the fifth possible result of the primary photochemical process.

Collision with neighboring molecules may dissipate the excitation energy so thoroughly that the quantum efficiency falls off. Nonetheless, of particular significance are the cases in which the transfer of energy starts a chain of chemical events, the so-called secondary processes in photochemistry. Secondary reactions are sometimes discussed under the heading of *post-irradiation effects.*

Examples of reactions that may occur in secondary processes are outlined in the following series of highly simplified chemical steps proposed to account for the formation of hydrogen peroxide on dyed cloth:

Primary Process:

Excitation

$$\text{HD (dye)} + h\nu \text{ (light)} \rightarrow \text{HD}^* \text{ (activated dye)} \quad (5.3)$$

Transfer of excitation energy

$$\text{HD}^* + \text{O}_2 \text{ (oxygen)} \rightarrow \text{HD} + \text{O}_2^* \text{ (activated oxygen)} \quad (5.4)$$

Secondary Processes:

Excited oxygen converts water to hydrogen peroxide summarized in the following equation:

$$\text{O}_2^* + 2\text{H}_2\text{O (water)} \rightarrow 2\text{H}_2\text{O}_2 \text{ (hydrogen peroxide)} \quad (5.5)$$

Ordinary chemical reactions between hydrogen peroxide and cellulose, or the dye, may then follow:

$$\text{H}_2\text{O}_2 + \text{Cellulose} \rightarrow \text{H}_2\text{O} + \text{Oxycellulose} \quad (5.6)$$

and/or

$$\text{H}_2\text{O}_2 + \text{HD} \rightarrow \text{H}_2\text{O} + \text{HOD (bleached dye)} \quad (5.7)$$

These much simplified equations are intended to show that, in the primary process, a molecule of dye, HD, is activated by absorption of light having energy, $h\upsilon$; the asterisk in Equations 5.3 and 5.4 signifies a molecule in an activated or excited state. The energy of the activated molecule of dye can then be transferred to oxygen, as indicated in Equation 5.4. Through a complex series of reactions, summed up here in a single step (Eq. 5.5), the activated oxygen molecule is able to convert water to hydrogen peroxide. The last two equations indicate that the resultant hydrogen peroxide can react with either the cellulose of the cotton fibers or the dye. Far more precisely verified examples from modern literature perhaps should have been selected. Nonetheless, the various steps suggested, taken from an early publication by Egerton (1949), serve conveniently to indicate the complexity of photochemical processes. Here, three different secondary reactions are involved.

The primary process is generally little dependent upon temperature (as discussed in "General Influence of Temperature in Photochemical Reactions," this chapter). Any one of the steps in the secondary (chemical) processes, however, may be considerably dependent. This is one of the fundamental reasons why it is difficult to accelerate photochemical deterioration in a completely satisfactory manner. Raising the temperature of the samples—which usually occurs in most accelerated-aging tests—does not necessarily speed up each of the various secondary processes to the same degree. Shimada and Kabuki (1968a), for example, report that the activation energy for the initiation step in the thermal degradation of acrylonitrile-butadiene-styrene (ABS) polymer was lower than that of the propagation step. (Initiation and propagation steps are discussed in "Initiation" page 55, and in Appendix E.) One approach to maintaining the same ratio of the thermal reactions to oxidation and hydrolysis as the temperature is raised is the "The Equalized-Aging Process," page 155.

The above series of chemical equations also suggests why the quantum yield of the overall photochemical effect (the number of molecules affected for every photon absorbed in the primary process) may not always be one: After going through the many intermediate steps, it may not be that one molecule of dye will be bleached (Eq. 5.7) for every photon absorbed in the first step (Eq. 5.3).

One can also see why the presence of oxygen and water vapor often profoundly influence many photochemical processes: These substances are directly involved in the secondary steps shown. When water is not consumed in such an event (water is regenerated again in Eqs. 5.6 or 5.7), it is said to have a *catalytic* action; its presence is able to speed up the oxidation of the cellulose or the dye, yet it, itself, is not consumed.

In conservation science, a most significant point must be mentioned: If molecules are destroyed (for example, if the oxygen should break off pieces of molecules and convert them to volatile gases, such as carbon dioxide, water, and formaldehyde), the original molecules cannot readily be put together again; they would be irreversibly altered. To be sure, embrittled fibers can be consolidated by adhesives, but the broken chains of the fiber molecules themselves cannot be joined again at the original sites in the molecules. Once faded, most dyed objects cannot be converted back to their original colorant compounds; the molecular fragments diffuse away from the site. Linseed oil broken down into volatile substances cannot be effectively reconstituted.

The museum curator should realize that, on a fundamental chemical basis and in a very practical sense, photochemical damage is irreversible damage.

Reciprocity Principle

An important generality is implied in the concepts presented in "How Properties Change in Time" (page 30). This states that the net exposure, that which influences the total amount of photochemical damage, is represented by the product of the intensity of the irradiance (or the illumination, the luminous flux) times the time, other factors being negligible. In other words, 100 lux of intensity for 1 hour is considered to produce as much damage as 1 lux of the same radiation for 100 hours. The product in each case is the same: 100 lux hours. The total number of photons striking the sample would be the same. This is referred to as the principle of reciprocity.

It is of importance in connection with the museum problem that the research investigator be aware that the reciprocity principle is not always precisely followed. (Hence reference to principle rather than law.) There are theoretical reasons why the reciprocity relationship may occasionally fail; these are discussed in the next section. There is also a practical reason for the appearance of failure; the high intensities of illumination employed in accelerated testing often raise the temperature of the samples and may also lower the samples' moisture content. Such an alteration of condition readily accounts for numerous apparent failures of the reciprocity principle (Wilhelm 1993:236-37).

Discontinuous exposure, that is, exposure under alternate conditions of light and dark, may also give results that are noticeably different from those obtained under continuous exposure for the same number of kilowatt hours. This behavior has been observed in the case of the National Bureau of Standards' light-sensitive papers (Launer 1948), and in the case of oil paints formulated with alizarin (Henry Levison, Permanent Pigments Company, pers. comm. 1975). Clark and Munro (1984) provide an interesting example relating to the photo-oxidation of polystyrene. Nonetheless, a common reason for the apparent discrepancy in the reciprocity principle under discontinuous exposure is that the samples cool down when the radiation source is turned off, resulting in a buildup of moisture content during this time. In other words, the average moisture content in the samples can be higher under alternate conditions of exposure in comparison to continuous.

Reactions Proportional to the Square Root of Intensity

There are photochemical reactions that do not follow the reciprocity principle, but instead the chemical step of chief interest is found to be proportional to the square root of the intensity (Kollmann and Wood 1980). Perhaps the best-known example of such a response to intensity is in the photochemical processes involved with the generation of free radicals on the surface of titanium white pigments leading to the deterioration of the paint vehicle and chalking. Egerton and King (1979) provide a detailed kinetic explanation of why the square-root relationship may be observed at high intensities of exposure as opposed to low.

In the rather common case in which two radicals are formed in the initiation step, it is known that, if the pair can diffuse away from the site and separately develop long chain processes, the rate of oxygen consumption will be proportional to the square root of the initiator concentration or the intensity of the radiation wavelength that initiates the reaction (Cicchetti 1970). This possibility can become particularly important in accelerated-photochemical testing, in which the stability of a stabilized polymer is compared to the unstabilized case. Vink and van Veen (1978) cite a situation where the induction time in the stabilized case was almost directly proportional to the intensity. In the unstabilized condition, however, the induction time was found to be proportional to the square root of the intensity.

Few if any examples of behavior with respect to the square root of intensity have thus far been demonstrated in practical problems involved in the deterioration of museum objects.

General Influence of Temperature in Photochemical Reactions

As has been mentioned, the primary step in photochemistry is the absorption of radiation followed by the dissipation of that energy through heat, emission of radiation (fluorescence or phosphorescence), transfer of the energy to another molecular entity, or the direct breaking of bonds. These processes require little or no heat. Hence, temperature has little effect on the primary step. Thermally induced chemical reactions are commonly found to have energies of activation (calculated by means of the Arrhenius equation) of from 28 kilocalories per mole (hydrolysis of cellulose) to as much as 50. In the case of photochemical processes, however, numerous examples can be found in which the Arrhenius-based energy of activation is calculated to be only about 2.0 to 10 kilocalories per mole (Giles et al. 1974; Shah and Srinivasan 1976). Jellinek (1967) cites an example in which the photolysis of polystyrene by 254 nm radiation exhibited an energy of activation of 2.9 kilocalories per mole. In the case of values found to be in the upper range, 10 to 20 kilocalories per mole, the explanation is often given that the observed photochemical changes are the result of diffusion, a thermally activated process, or of secondary chemical reactions.

Moisture often plays a significant role in the changes brought about by exposure to light. As noted earlier, temperature can markedly influence the moisture content of the system; more will be said about this in Chapter 8. Other than for this reason, one does not generally expect photochemically-induced changes to be strongly affected by temperature. If a moderate effect of temperature is found, one can suspect that the net reaction being observed is the result of secondary chemical steps or that it is controlled by diffusion (see Chapters 8 and 9).

Initiation

Exposure to near-ultraviolet and visible radiation seldom directly *causes* fading, embrittlement, or yellowing unless, of course, it causes a molecular bond to rupture (photolysis). Exposure to light more properly can be said to *induce* or *initiate* a chain of events that lead to chemical changes. Light "excites" or "activates" certain groups within molecules.

Absorption of radiation takes place in what chemists call an *initiation* step. In the oxidation of polymers through the mechanism of peroxide formation, this step is followed by what has become known as *propagation* and *termination* reactions (see Appendix C). This proposed sequence of three principal steps may be disrupted by *chain transfer* reactions or reactions with substances that act as *inhibitors*. To help analyze the process further, in his authoritative review of the mechanisms of oxidative photodegradation, Cicchetti (1970) drew attention to two types of initiation: *primary*, when ultraviolet or visible radiation is directly absorbed by functional groups in the oxidizable material, and *secondary*, when the radiation is absorbed by certain of the oxidation products (peroxides and carbonyls). In the case of polyolefins, for example, the secondary mode is by far the most important mode of initiation, particularly in latter stages of deterioration (Cicchetti 1970; Carlsson and Wiles 1974). Unfortunately, Cicchetti's terms are the same as those used to designate primary and secondary reactions in photochemical deterioration; nonetheless, he makes an interesting point.

> Because light primarily influences the initiation but not the propagation steps, a general effect of exposure to light often is to shorten, if not eliminate, an induction period but not the rate (technically the *maximum rate*) of the chief degradation reaction if that occurs among the secondary reactions (see Appendix C). Today, advanced technology is available by which photo-initiation rates can specifically be determined (Gerlock et al. 1984; see Appendix E).

Depth of Penetration of Light into Coatings

It has long been recognized that photochemical damage is largely a surface phenomenon. It is, therefore, of basic interest to consider how deeply visible and ultraviolet radiation can penetrate into transparent or translucent materials. For systems that practically do not scatter radiation, but principally absorb it, the Beer-Lambert Law is usually considered to hold:

$$I = I_0 e^{-\alpha x} \text{ or } 2.303 \log_{10} I_0 / I = \alpha x \tag{5.8}$$

Here, I_0 is the incident intensity and I is the intensity at depth x; α is known as the absorption coefficient of the medium. Heller (1969) has discussed this equation in relation to the efficiency and protective action of ultraviolet absorbers; Jellinek (1967, 1981) has discussed it in relation to chain scission.

Many materials tend to absorb an increasing amount of radiation as the wavelength decreases. As a consequence, the depth of photodegradation is markedly influenced by the wavelengths of radiation used to induce degradation. In a syllabus of the Atlas Electric Devices short course, Norma Searle presented data regarding an aromatic polyester, stating that the depth of penetration of 320 nm radiation was only 1/10 that of 350 nm.

Figure 5.2 shows the increase in carbonyl-group concentration in pressed test sheets of high-density polyethylene with increased exposure to radiation in a Xenotest 1200 exposure device (Müller 1983). Note that the depth of photodegradation falls off rapidly in the outer 200 micrometers. Thomson (1965, 1979) made calculations that showed a similar sharp fall-off of photochemically unreacted material with depth during increased exposure. The decrease is particularly precipitous, Thomson pointed out, when photodeterioration leads to discoloration owing to the generation of substances that increasingly absorb the damaging radiation with the passage of time.

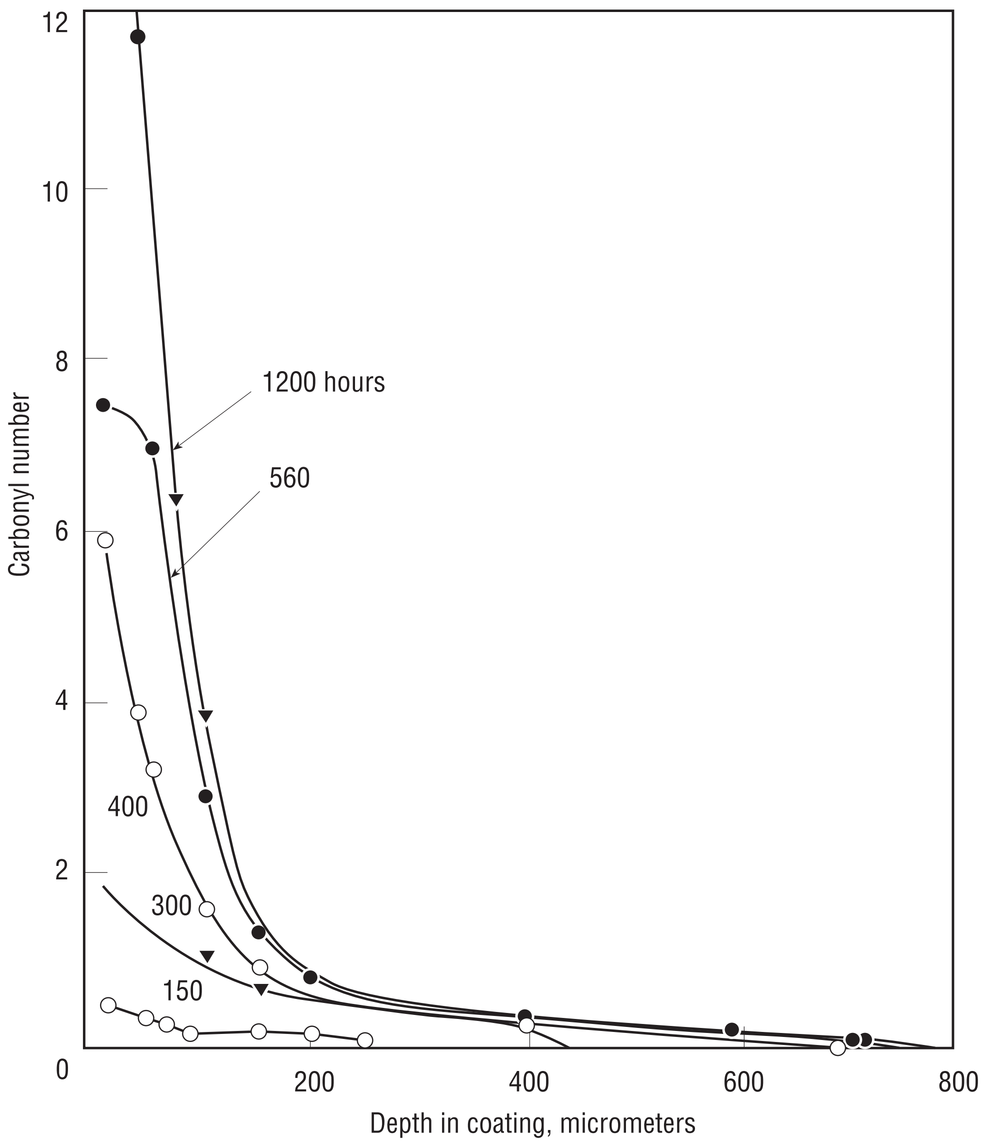


Figure 5.2. Extent of oxidation within samples of high-density polyethylene as measured by carbonyl number versus depth (after Müller). Reproduced with the permission of the publisher.

When measuring the initial formation of cross-linked material in normal butyl and isobutyl methacrylate polymers versus the thickness of the coatings, Feller (1963) proposed that the sharp fall off of cross-linking with film thickness in the case of exposure under carbon-arc radiation (Fig. 5.3b) was due to the presence of short wavelengths of ultraviolet which would have been absorbed sharply at increased

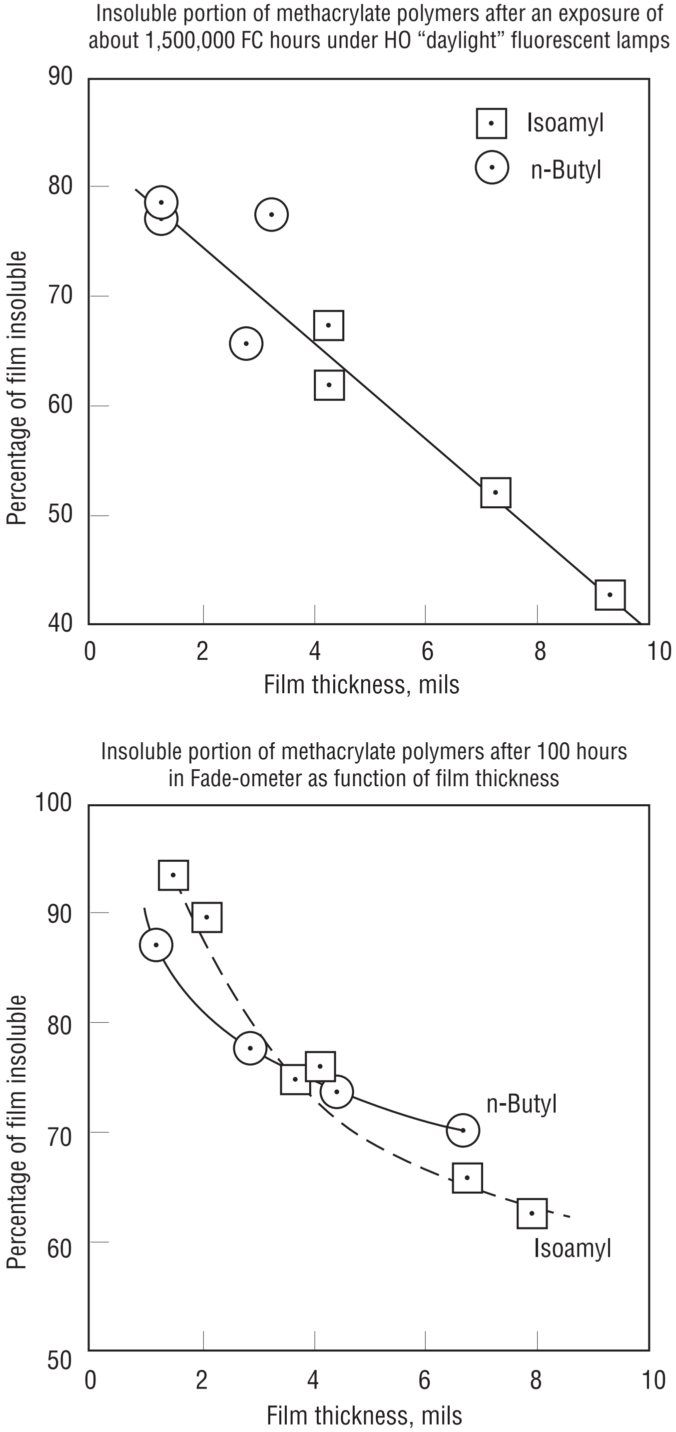


Figure 5.3a, b. Depth of cross-linking (insoluble matter) of poly(n-butylmethacrylate) and poly(isobutylmethacrylate) thermoplastics as a function of exposure to (a) high-output "daylight" fluorescent lamps and (b) xenon-arc Fade-ometer

(quartz/borosilicate filters; Feller 1963). Reproduced with permission of the publisher.

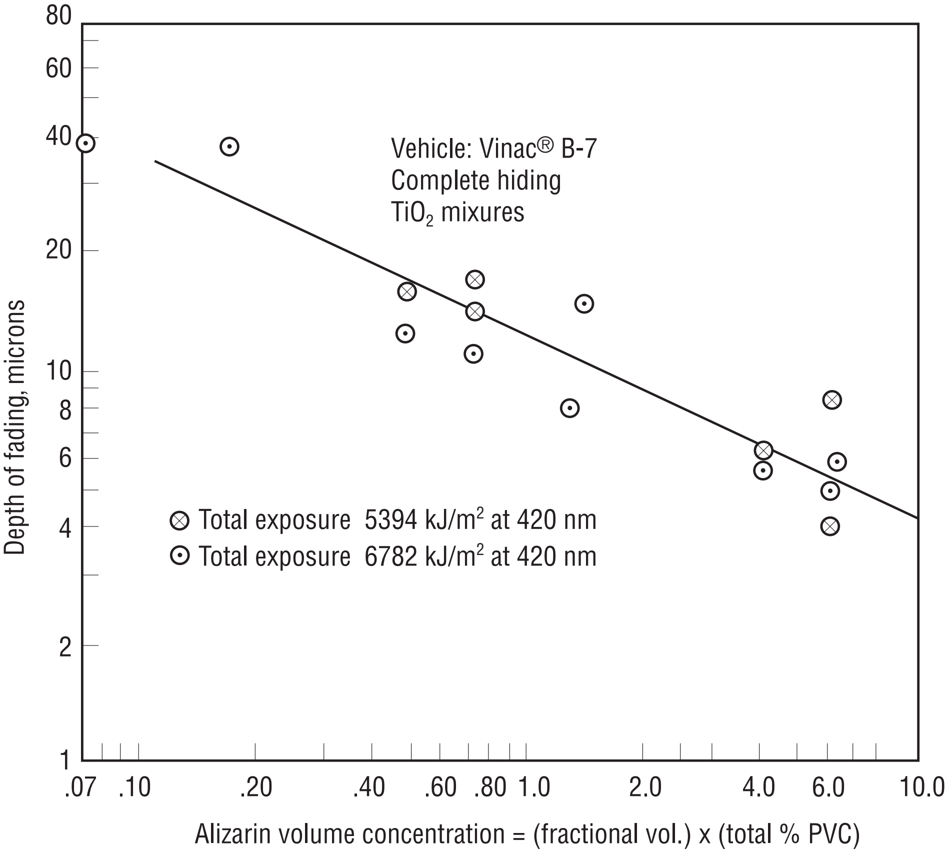


Figure 5.4. Depth of fading in alizarin-lake/titanium-white coatings as function of the volume fraction of alizarin lake (fractional volume of alizarin lake times total percent pigment volume concentration, PVC). Xenon-arc exposure. Polyvinylacetate vehicle. Johnston-Feller (1986). Reproduced with permission of the publisher.

depths. Under daylight fluorescent lamps, longer wavelengths of ultraviolet were involved; in this case the extent of initial cross-linking fell off more gradually with thickness (Fig. 5.3a).

The depth of photochemical action is, of course, reduced by the presence of pigments. In paints based on titanium white and alizarin lake, Johnston-Feller (1986) has shown, for example, that the depth of fading resulting from xenon-arc exposure is decreased from about 40 to as little as 4 micrometers as the concentration of alizarin lake is increased (Fig. 5.4).

Table 5.1 presents experimental data related to these conclusions. The data show that the depth of fading becomes greater as the pigment volume concentration (PVC) of the scattering pigment, titanium white, decreases. Light penetrates deeper into a paint formulated at 3.5% PVC than at higher percentages of PVC. Reading down the table one can see that, as the concentration of the absorbing pigment (alizarin lake) increases, the depth of fading also decreases. As observed with a microscope that has a micrometer eyepiece, the line of demarcation between the faded and unfaded portion of the paint becomes more sharply defined at higher concentrations of alizarin. This occurs because the intensity of light penetrating the film containing a high concentration of colorant is reduced more sharply with distance than occurs in the case of paler tints.

In discussing the absorption by photosensitizers in the ultraviolet curing of pigmented coatings, Wicks and Kuhhirt (1975) showed that most of the absorption took place in the first 5 to 10 micrometers. Calculations based on Kubelka-Munk equations clearly accounted for the more rapid decrease in photoactivity with depth in the case of pigmented systems.

The importance of photochemical deterioration occurring primarily on the surface was early recognized by textile scientists who noted that finer fibers deteriorated more rapidly than coarser (Little 1964). Indeed, because the action of sunlight is topochemical, Singleton et al. (1965) suggest that the surface-to-volume ratio of fibers should be similar when the photochemical stability of different textile fibers is under comparison.

Relative percent alizarin	14% PVC TiO_2	7% PVC TiO_2	3.5% PVC TiO_2
2.5	17.2 (D)		
5	11.6 ± 2.4 (D)		
10	9.7 ± 2.2 (T)	15 (T)	
20	6.4 (S)	10.8 (T)	28.0 ± 4.9 (D)
40		8.6 (S)	8.6 (S)
60			6.88 ± 2.8 (S)
80			6.5

Character of dividing line between faded and unfaded zones:(S) sharp demarcation, (T) tapered, (D) diffuse.

Table 5.1. Depth of faded zone (micrometers) in alizarin/titanium-white paints relative to both alizarin content and the pigment volume concentration (PVC) of titanium white based on Rhoplex AC-34 acrylic emulsion. Series 4 data (420 hrs. in Fade-ometer) (after Feller 1964).

Many reports are available to show that, in samples that are a few hundred micrometers thick, the zone of degradation can be seen to decrease rapidly from the surface of the sample (Carlsson and Wiles 1970; Müller 1983; Adam et al. 1989). This situation can pose a problem if the extent of deterioration is monitored by measuring infrared absorption spectra of such a sample. Estimates of quantum efficiency would contain inaccuracies because the measured absorption is the result not of a simple reaction but of a nonuniform change throughout the sample. This problem has been circumvented in recent years by taking microtomed thin slices through the relatively thick sample as shown in Figure 9.2. (Adam et al. 1989).

The fact that fading usually takes place only in the upper portion of a paint is of interest to those concerned with the deterioration of works of art. If one observes a faded paint, it may be that relatively unfaded material still exists underneath. It may thus be possible, by means of cross-sections, to provide reasonable evidence that a paint had or had not undergone serious fading. Moreover, it may be possible to identify many of the original colorants even though, on the outer surface, the colorant seems all but lost.

Changes in the degree of degradation with depth need not solely be the result of decreasing penetration of light. The phenomenon is also dependent on the diffusion of oxygen into the material, a subject taken up in Chapter 9.

Summary

An understanding of a number of basic principles should do much to explain important aspects of photochemical deterioration. Exposure to light activates molecules in a so-called primary step, normally initiating further chemical reactions. While it is true that ultraviolet or visible radiation must be absorbed in order to act upon molecules, the critical absorbing substance or chromophoric group is not always readily identifiable.

The primary absorption process is little affected by temperature, but varies greatly in effectiveness (quantum efficiency). The net practical effects of photo-initiated changes are usually the result of a series of secondary chemical reactions which are generally effected by heat and moisture. The principle of reciprocity suggests that the total photochemical action induced is equal to the product of the intensity of irradiance times time of exposure. There will be situations, however, in which this relationship will not strictly hold. Moreover, because it is not intensity but the frequency (inverse of wavelength) that determines the energy of electromagnetic radiation and its tendency to be absorbed by specific chemical structures, there is theoretically no threshold of intensity below which photo-activation will not occur. Light is absorbed in passing through a translucent material; the result is that the extent of photo action will ordinarily decrease rapidly with depth.

Notes

This chapter, up to “Reciprocity Principle,” largely from Feller (1964).

1. Early reviews of photochemical principles were made by Lodewijks (1963) and Brommelle (1962).
2. The frequency of the radiation, υ, is inversely related to the wavelength; and h is Planck’s constant, a number that relates the units of frequency to energy, equal to 6.6×10^{-27} erg-sec. The equation will yield the energy of the photon in terms of kilocalories per gram molecular weight (kilocalories per 6.02×10^{23} bonds or photons) if used in the form $E = 2.86 \times 10^{4}/\lambda$, where the wavelength of radiation, λ, is in nanometers. Values thus calculated for the energy of radiation at different wavelengths are given in Figure 5.1.
3. In practice, there are a number of investigators who have reported that they have found intensities below which no reaction will take place. However, upon careful study, such findings usually have been shown to be in error. For example, certain reactions may proceed at a negligible rate at low intensities of light, but proceed at a measurable rate in sunlight outdoors. In the latter case, the intensity is such that the samples attain higher-than-normal temperatures, causing noticeable deterioration to take place.

6 Influence of Wavelength

The two basic principles of photochemistry—that electromagnetic radiation must be absorbed in order to initiate a photochemical process and that absorption takes place in discrete quanta (photons) whose energy is determined by the frequency of the radiation—have led research laboratories to devote extensive attention to a search for the wavelengths that are responsible for the deterioration of specific materials. As potentially fruitful as this approach is in principle, the quest has not always yielded results as significant as initially expected. Berger (1971a, b; 1972) clearly states: "Absorption curves need not always be identical with the pertaining curves of damage, for not every type of absorption causes changes in the material." As mentioned in Chapter 5, when a dyed or pigmented material fades, it may not be the absorption of light by the most obvious absorber, the colored substance, that represents the wavelengths principally responsible for its deterioration (ISO R105 blue-wool fading cloth No. 7 provides a case in point [McLaren 1956]). Instead, it may be that absorption by chromophoric groups in a trace of impurity activates the vehicle in such a manner that this in turn leads to the degradation of the colorant. A second reason for misdirection is that determination of the activation spectrum, which is discussed in this chapter, may show an apparent wavelength of peak activity, not because of the maximum absorption of a particular component, but simply because the available energy of the light source falls off rapidly at the lower wavelengths.

Activation Spectra

Norma Searle who, along with R. C. Hirt, pioneered the concept of activation spectra, has defined two key terms: *activation spectrum*, the effect of wavelength on the extent of degradation, and *wavelength specificity*, the influence of wavelength on the mechanism and type of degradation. Andrady and Searle (1989) note that the activation spectrum does not involve correction for the intensity of irradiance at each wavelength and hence is dependent on the specific light source involved. On the other hand, if a correction is made for the intensity of each wavelength, the authors call this an *action spectrum*, independent of the light source. Determinations of activation spectra are more commonly encountered. Nonetheless, some examples of both action spectra and wavelength specificity will be cited below.

Tables of peak (the most damaging) wavelengths in the activation spectra of familiar polymers have been published on numerous occasions (Hirt and Searle 1967). As mentioned, however, the point of maximum activity at 290 to about 350 nm, seen in many reports, is often just a result of the falling off of energy at the shorter wavelengths in the source. This effective peak of activity is nonetheless important in the practical effort to protect coatings, for the information reveals the most active wavelengths under the commonly encountered illuminants of sunlight or xenon-arc emission through Pyrex or soda-lime glass.

Determination of the activation spectrum is by far the easiest experimental procedure—simply employing a given source and a series of sharp cut-off filters without regard to the amount of radiant energy present at each wavelength. Nonetheless, many authors have taken the trouble to measure the action spectrum, that is, taking into account the microwatts of energy at each wavelength. This point of view has been particularly stressed by Krochmann (1986, 1988), his associates (Aydinli et al. 1983; Hilbert et al. 1991), and Kämpf et al. (1991). An excellent example and discussion of the information revealed by a comparison between activation spectra and action spectra is provided by Andrady et al. (1992). The authors warn the experimenter that when test samples are covered by a filter, they may reach a higher temperature than an uncovered control sample or one arranged otherwise so that air can circulate freely.

Effects Observed over an Extensive Range of Wavelengths

When the range of wavelengths considered is extensive—from 254 nm or lower to 450 nm or greater—it is expected that differences in photodegradative behavior will be observed. The gases emitted by wool, studied over a wide range of wavelengths by Launer and Black (1971), provide an example. Distinctly different combinations of gases were generated by 254, 365, or 436 nm radiation (Table 6.1). Bousquet and Foussier (1984) have referred to differences induced by wavelengths as far apart as 254 and 313 nm as a "macroscopic" wavelength effect.

Wavelength mμ	**Mass Spectrum, Percent Gaseous Products**						
	CO_2	**CO**	**H_2**	**H_2O**	**COS**	**H_2S**	**CH_4**
254	34	28	23	11	4	trace	–
365	75	–	–	–	–	–	–
436	100	–	–	–	–	–	–
546	–	–	–	–	–	–	–
(160 °C dark)	22	2	–	63	1	2	8

Table 6.1. Gases produced from wool in vacuo by the light of various wavelengths and by heat (data of Launer and Black 1971).

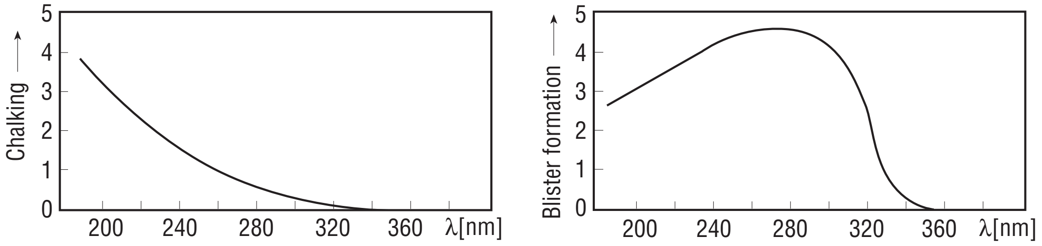
The Laboratoire de Photochemie-UER Recherche Scientifique et Technique et Ecole Nationale Supèrieure de Chemie, Université de Clermont II, has developed a series of light-exposure apparatuses (SEPAP) that utilize, in each separate instrument, lamps that emit radiation in a limited wavelength range (Lemaire et al. 1981). Using various SEPAP exposure devices that emitted 254, 365, 260 to 360 nm, or polychromatic radiation, the authors were able to show that 254 nm radiation produced primarily chlorocarboxylic acids in poly(vinylchloride) and short sequences of double bonds (polyenes). Under near-ultraviolet radiation, on the other hand, chloroketones and longer sequences of polyenes accumulated (Gardette and Lemaire 1986).

Relatively Broad Regions of Sensitivity in the Ultraviolet

Hirt and Searle have published numerous examples of activation spectra that show a general rise in degradation as wavelength is decreased below 400 nm, gradually reaching a peak of activity that is then followed by a decline (Andrady and Searle 1989; Andrady et al. 1992). An example of variations in principal activity to be found over a reasonably broad range of wavelengths can be seen in Renz et al. (1974), Figure 6.1. Their activation spectra are particularly interesting because gross physical changes were observed rather than precisely measured chemical changes. (Johnson et al. 1969 reported the loss of tensile strength versus wavelength in their study, finding major activity between about 330 to 390 nm.) Renz et al. (1974) used a series of sharp cut-off filters and a xenon-arc source (quartz envelope) to investigate the effect of wavelengths between 200 and 360 nm on a variety of coatings. During the tests, panels were alternately sprayed with water and exposed to radiation.

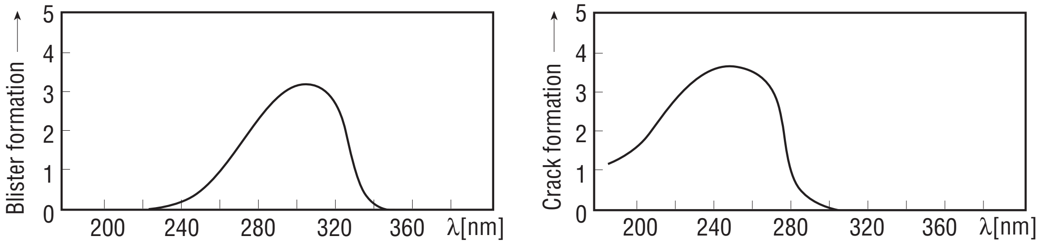
One result demonstrated that the chalking of an alkyd-melamine automobile paint was increasingly dependent upon wavelengths below 340 nm. The degree of chalking, probably based on a visual rating scale, seemed to increase logarithmically with decreasing wavelength (Fig. 6.1a). This type of response is described in “Apparently Nonspecific Response to Decreasing Wavelength,” this chapter.

In contrast, the formation of blisters in a multicoat system involving a layer of unstabilized poly(vinylchloride) (PVC) and acrylic melamine exhibited a more typical activation spectrum; activity extended from 220 to 350 nm with a peak at 300 nm (Fig. 6.1b). Similar curves, but with the maximum effect at 280 and 250 nm, were observed when an acrylic-melamine thermosetting paint was tested and when cracking rather than blisters were observed (Fig. 6.1c and d). Pigmented coatings provided almost complete protection.



a. Chalking of alkyd-melamine (AM) automobile paint

b. Blister formation in poly(vinyl chloride) - AM system



c. Blister formation in AM coating

d. Formation of cracks in AM system

Figure 6.1 a–d. Examples of activation spectra for subjectively rated changes in physical properties (Renz, Töpfel, and Vesper 1974). Reproduced with permission of the publisher.

The authors suggest adjusting the ultraviolet emission of a quartz-enclosed xenon-arc lamp by using a set of six filters placed around the arc, varying in cut-off from 332 to 280 nm. It is possible that ozone will be generated in an unfiltered blank in the set of six (see "Formation of Ozone by Ultraviolet-Emitting Lamps," page 108). However, in their tests, the cut-off filters were placed immediately over the samples; this may have minimized the contact samples may have had with generated ozone.

The details of a technique using information from sharp cut-off filters to isolate the effects of narrow wavelength regions is described in Appendix D (Martin and Tilley 1971). Andrady and Searle (1989), investigating the yellowing of poly(vinyl-chloride), pointed out that the use of sharp cut-off filters exposes subject to both long and short wavelengths and that long wavelengths have been known to induce bleaching. Nonetheless, in the practical world, most exposures subject materials similarly to all wavelengths above a certain lower limit (Andrady et al. 1992). As mentioned in "Activation Spectra" (page 63), the authors include a discussion of differences between activation spectra and action spectra.

Sharp Dependence on Wavelength

In order to gain information on the effect of nearly specific wavelengths, it is usually advisable to employ essentially monochromatic radiation. This can be done experimentally in several ways. In earlier times, many investigators used a low-pressure mercury-vapor source that emitted *multiline spectra.* An experimental set-up was arranged in which individual lines (wavelengths) could be isolated. A major drawback of this method is that one does not have an unrestricted choice of wavelengths. The principal wavelengths for low- and medium-pressure mercury-vapor lamps are 578, 546, 436, 405, 365, 313, 302, 280, 265, and 254 nm.

Discoloration of Groundwood

There are not many examples that can be cited in which striking variations can be shown in the rate or mechanism of photochemical deterioration of materials in the solid state as a function of wavelength in the visible and near- or middle-ultraviolet region. One of the earliest and most dramatic examples demonstrated more than forty years ago by Nolan et al. (1945) and Van den Akker et al. (1949) is the discoloration of lignin-containing paper. With the use of a monochromator, a decided peak of discoloration was observed at about 285 nm (Fig. 6.2). Discoloration increased sharply as wavelengths declined from 400 nm to this point. Thereafter discoloration fell off to about half the peak sensitivity at 265 nm, rising again at shorter wavelengths. These sharply defined variations in sensitivity were found to match closely the absorption curve of lignin and certain lignin-derivative substances (Fig. 6.2). The conclusion drawn was that photochemically induced darkening of groundwood pulp is initiated by the absorption of lignin-based substances.

Deterioration of Rubber

An example of an effective use of interference (narrow-band pass) filters is provided by a study of the degradation of rubber carried out by J. Morand of the Institut Francais du Cautchouc (1966). A 1,600-watt xenon lamp emitting 20 watts in the ultraviolet was used as the source. The filters had a half-band width of 20 nm in the ultraviolet and 12.5 nm in the visible. A heat filter was also used and the samples were cooled to 30 ± 0.05 °C by a temperature-controlled water bath. The irradiance striking the samples under each filter combination was adjusted to a constant 5 milliwatts/cm^2.

The rate of chain scission was determined from measurements of stress-relaxation of stretched rubber samples. The principal results in the case of a purified cumyl-peroxide vulcanizate, shown in Figure 6.3, provide a clear example of non-monatonic changes in quantum yield as a function of wavelength.

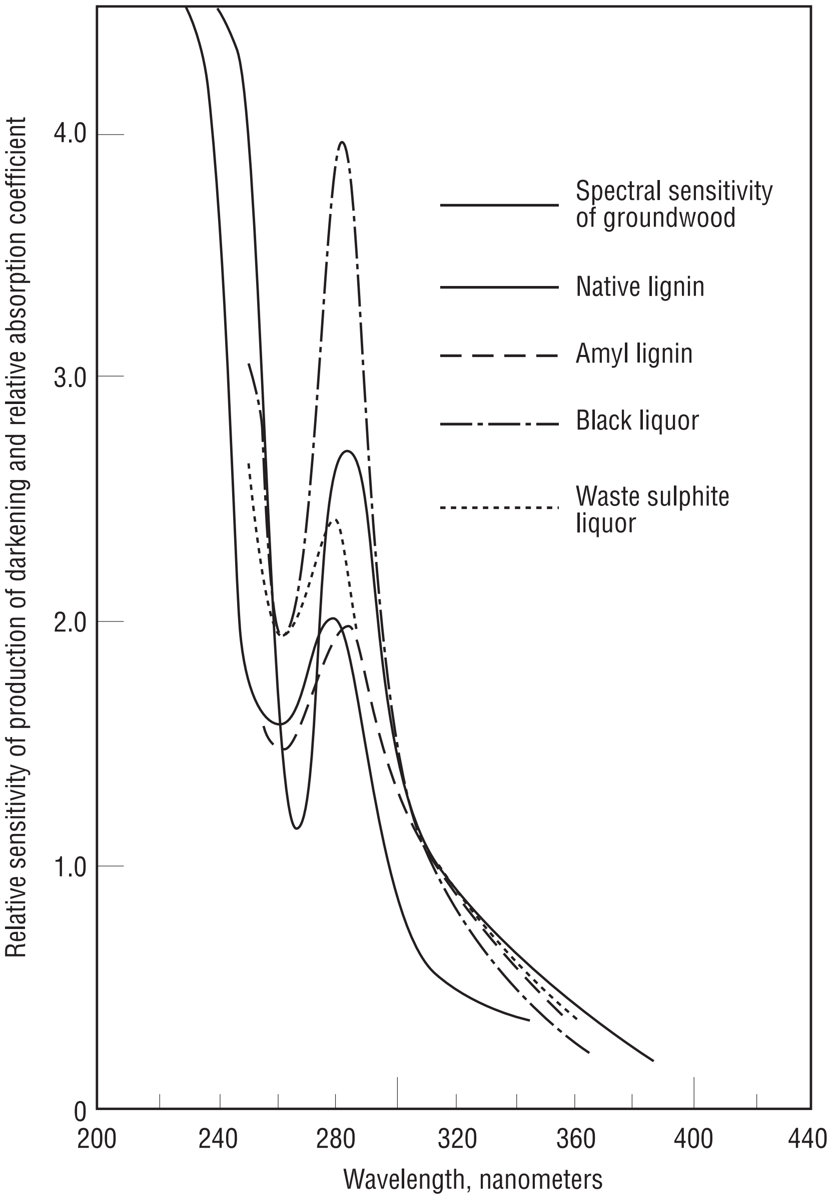


Figure 6.2. Spectral sensitivity of groundwood in comparison with absorption of lignin-containing components of pulp (After Nolan et al. 1945). Reproduced with permission of the publisher.

The author's extensive explanation for the observed wavelength sensitivity is instructive. (A further similar discussion is offered by Yano [1981].) Bar graphs below the curves indicate the region of the spectrum that is theoretically capable of breaking specific bonds in the isoprene (rubber) structure. Upon absorption of wavelengths below 320 nm, photolysis of the C1-C2 and C3-C4 bonds is possible. This leads directly to scission of the main chain. Under the influence of these wavelengths, however, the process is not autocatalytic. The minimum in the curve in the region of 340 nm is considered to be due to the fact that photolysis of the side-chain C2-C5 and C5-H7 bonds, affected by these wavelengths, does not lead to scission of the main polymer chain.

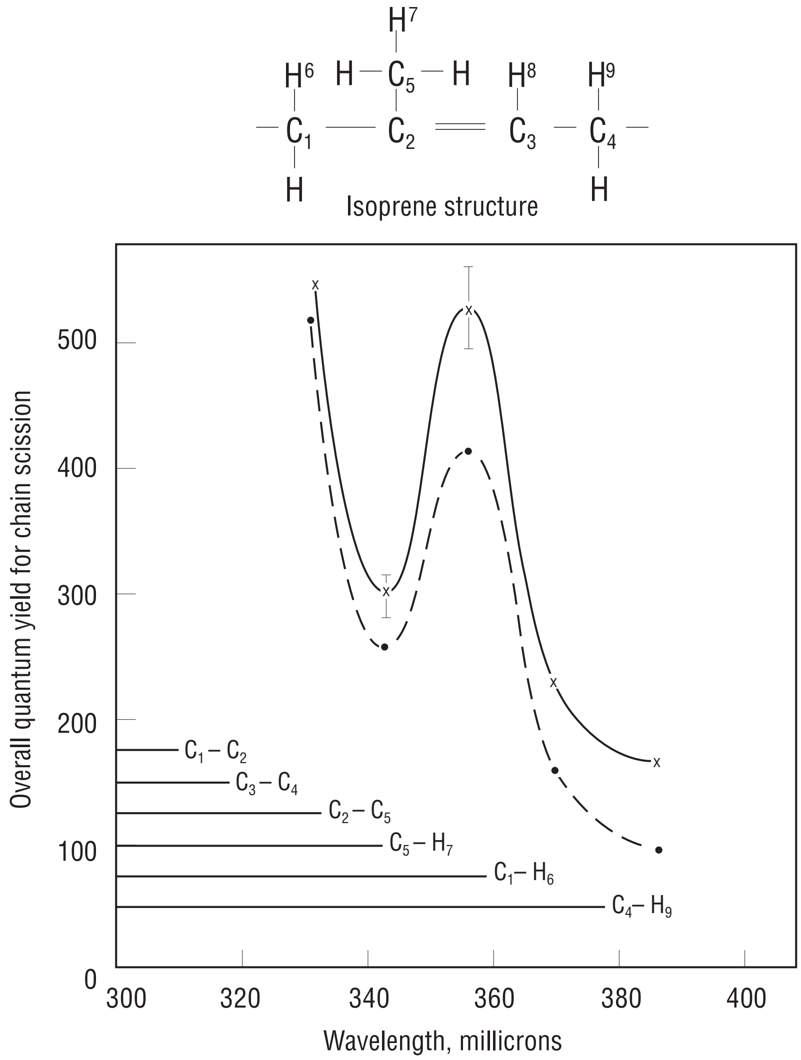


Figure 6.3. Overall quantum yield for chain scissions in a purified isoprene vulcanizate. Bars show wavelength region in which photodissociation of a particular bond is energetically possible. Data at • corrected for reflection, data at × corrected for diffusion and reflection of irradiance (Morand 1966). Reproduced with permission of the publisher.

The optimum quantum efficiency located at about 355 nm may arise owing to the dissociation of the α-methylenic C-H bonds, particularly the C1-H6 bond.

Three observations support this hypothesis: Large amounts of hydrogen gas (H_2) are formed when exposure takes place in a vacuum, peroxides are formed when irradiation takes place in air, and a relaxation of stress is observed (evidence that bonds being broken relieve stress). When zinc oxide, which filters out the shorter wavelengths of ultraviolet, is present, the greatest initial rate of chain scission is shifted to the longer wavelengths, peaking at about 400 nm.

This detailed explanation of the types of bonds that are being affected by different wavelengths provides an excellent example of an *action spectrum* as well as *wavelength specificity* as defined by Searle (see “Activation Spectra,” page 63).

Nylon

The work of Yano and Murayama (1980) serves as an additional example of the precise determination of the influence of wavelength. Films of nylon 30-micrometers thick were exposed to the radiation of a 2-kW xenon lamp dispersed in a grating spectrometer (Nihonbunko Co., model CRM-FA). The change in the density of the film as well as the dynamic modulus of elasticity was measured as a function of wavelength (Fig. 6.4). The authors point out that the decrease in the response below the apparent peak at 250 nm is due in part to the increased absorption of the shorter wavelengths of ultraviolet by the polymer.

Acrylate Polymers

An example of a change in mechanism with wavelength (wavelength specificity) is found in the work of Allen et al. (1985) concerning the stability of electron-beam-cured di- and tri-acrylate resins. The authors observed that greater oxidation took place in a Microscal unit (see Fig. 7.2) than under a 365 nm ultraviolet source. The explanation given was that the shorter wavelengths in the emission from the high-pressure mercury-vapor/tungsten lamp of the Microscal unit were absorbed by carbonyl groups, the principal initiators of oxidation in this type of resin. In contrast, the 365 nm radiation would have been absorbed primarily by peroxide groups and these had been shown not to be major initiators of photo-oxidation in this resin. In the case of a type of resin having traces of benzophenone, cured by ultraviolet radiation, there was little difference in the extent of oxidation. Here the short wavelength radiation from both sources was strongly absorbed by the benzophenone component.

In this example, one type of resin (electron cured) was seriously affected by the source of radiation employed, whereas another (UV cured) was not.

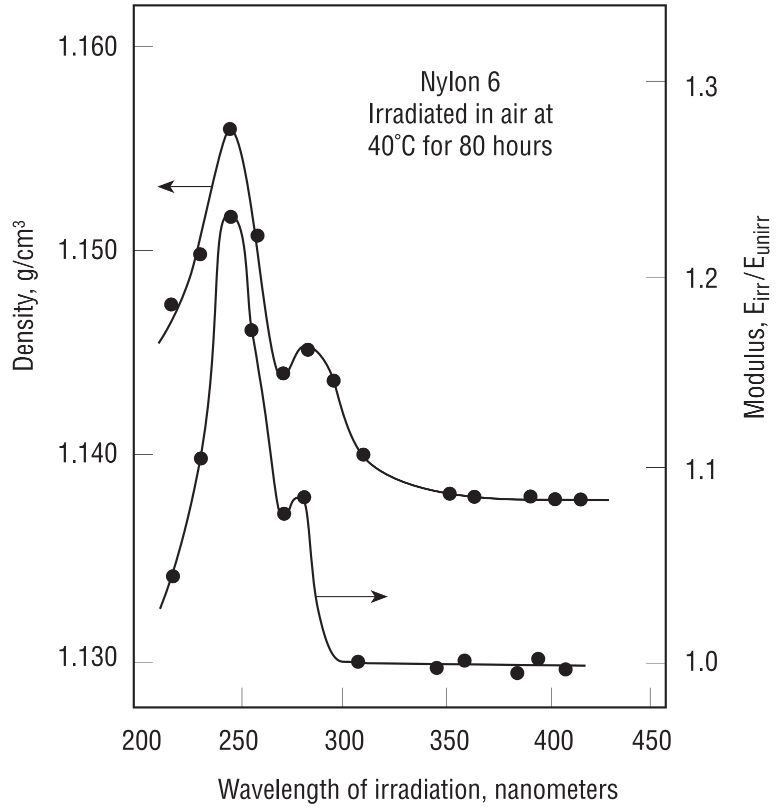


Figure 6.4. Change in density and dynamic modulus of nylon 6 versus wavelength (Yano and Murayama 1980). Reproduced with permission of the publisher.

Depolymerization of Poly(methylmethacrylate) and Other Acrylic Polymers

When investigating the photochemical stability of acrylate and methacrylate homopolymers, it has often been observed that they degrade very rapidly when subjected to 254 nm radiation. Rapid loss of weight occurs, possibly due to volatilization of monomer, and bubble-like blisters result (see Fig. 6.5). In the past, this behavior has led to erroneous initial conclusions regarding the potential long-term stability of acrylic polymers.

A question arises concerning the shortest wavelength that will fail to induce this apparently photolytic, rather than photochemical, deterioration. The author is not sure of the answer to this very important practical question. McKellar and Allen (1979:91–92) state that when poly(methylmethacrylate) is above its second-order transition temperature "high yields of monomer by . . . (an) unzipping mechanism" occurs. The same is noted for poly(ethylmethacrylate) and poly(n-butylmethacrylate). In the latter case, it is noted that photothermal degradation at 170 °C "results in 100% monomer formation." Thus, unzipping (depolymerization) of methacrylate polymers is a familiar phenomenon.

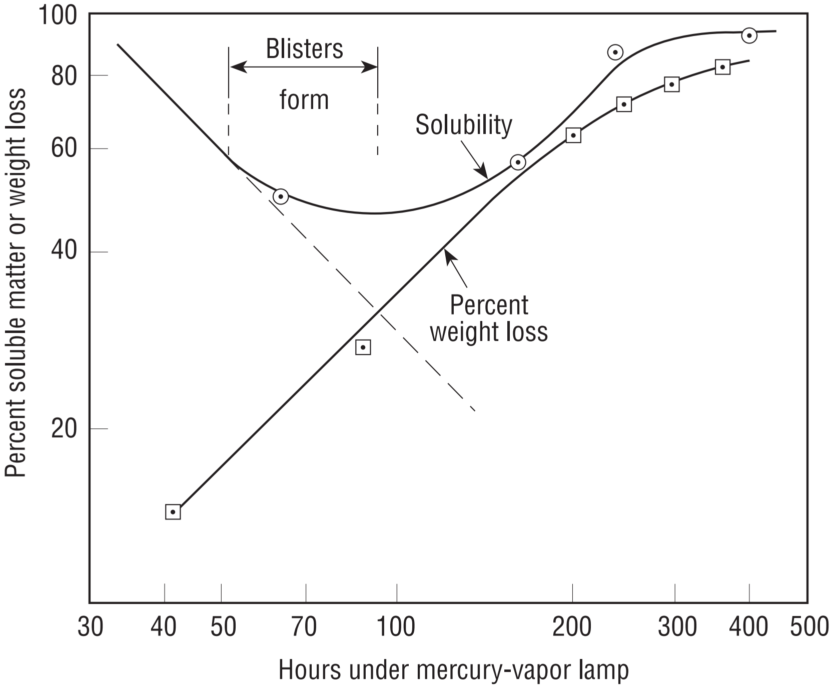


Figure 6.5. Weight loss and changes in solubility of Elvacite 2046 n-butyl/isobutyl methacrylate copolymer exposed to 254 nm radiation (Feller 1975). Reproduced with permission of the publisher.

Hennig (1981) went to some length to show that the increased loss of molecular weight in poly(methylmethacrylate) with decreasing wavelength was simply due to increased absorption by the polymer. However, the loss of molecular weight in bulk polymer may be by random chainbreaking and not necessarily by unzipping (depolymerization). At the lowest wavelength Hennig employed, 265 nm, the loss of molecular weight was not particularly sensitive to film thickness and the extent of loss in molecular weight was rapidly approaching completeness.

One can suggest that the photolytic unzipping, so to speak, of methacrylate polymers apparently poses a problem when wavelengths of 265 nm or less are present. The 254 nm emission of mercury vapor lamps can induce particularly rapid volatilization.

Influence on Induction Time

Exposure to light can often reduce the apparent induction time. One reason for this effect is the fact that exposure to activating radiation leads to a reduction in the chain length of degradation processes, that is, the length of time before the maximum rate of oxidative deterioration occurs (see Appendix B). This is based on the relationship:

$$\text{chain length} = \frac{\text{rate of oxidation}}{\text{rate of initiation}}$$

Examples can be cited. Anton (1965) provides data that show that wavelengths between 270 and 300 nm all but eliminate induction time with respect to loss of tenacity in nylon. At wavelengths between 300 and 415 nm, there is a modest induction time; at wavelengths above 415 nm, the period is longer still. In the formation of carbonyl groups in rubber, elimination of the ultraviolet radiation from a high-pressure mercury-vapor lamp will extend the induction time more than ten-fold (Tkáč et al. 1955).

Derbyshire and Miller (1981) used a series of cut-off filters to study the loss of strength of pine and lime wood. Samples that had been protected by filters with a cut-off at 390 nm almost always showed an apparent induction time before the strength of the samples began to suffer. In contrast, the authors regarded the data for samples exposed under filters that transmitted wavelengths as low as 310 nm as though loss of strength began immediately, giving no indication of an induction period. With filters that cut off at 355 nm, an apparent induction period sometimes took place (four out of six tests). The test data are not precise, yet the evidence suggests an influence of wavelength on physically observed induction time.

Apparently Nonspecific Response to Decreasing Wavelength

National Bureau of Standards / L. S. Harrison Factors of Damage

As noted earlier, as the wavelengths of radiation decrease through blue, violet, and into the ultraviolet, the energy of the photons increases. Thus, a basic point of view regarding the damaging effect of exposure to visible and ultraviolet radiation would be to state simply that the shorter the wavelength, the more energetic the photons, and therefore the more potentially damaging the radiation. Examples of such a general response to wavelength is seen in Figures 6.1a and 6.6.

Perhaps the best-known example of this behavior is the concept of damage factors at each wavelength proposed by the U. S. National Bureau of Standards (1951) working in consultation with the National Archives and, later, with the Metropolitan Museum of Art (Judd 1953, 1954; Harrison 1954a, b). Using data regarding the effect of light on low-grade paper—data that have never been described much more elaborately than this simple statement—the National Bureau of Standards developed a set of arbitrary numbers (factors of damage) that describe the "increasing effect" as the wavelength decreases. These factors were later employed in developing a practically colorless Plexiglas ultraviolet filter used to protect works at the Metropolitan Museum of Art. Lawrence S. Harrison was the lighting consultant for the Metropolitan and these factors of damage have become closely associated with his report on the project (Harrison 1954a, b). The report from the Metropolitan Museum of Art (Harrison 1954a), bearing no date, has long been out of print. The technical development of the concept, however, came from the Bureau. The development of a filter cutting off some blue wavelengths, now known as Plexiglas UF-3, has also been described by Harrison (1963).

In a series of tables, Harrison gave detailed examples showing how the factors of damage for a given wavelength could be used in conjunction with numbers related to the spectral distribution of emission from various light sources and the spectral transmission of various filters, in order to estimate the relative damage that might occur under various combinations of sources and filters. Harrison's way of estimating potential damage by different light sources has apparently not been widely used in the field, possibly because it was understood that the original data only applied rather vaguely to the action on low-grade paper. Yet, as the data in Figure 6.6 and that of Krochmann cited below indicate, the suggestion is not without merit.

Logarithmic Relationship

L. S. Harrison. Harrison did not point out that, when the damage factors (D_λ) were plotted versus wavelength on semilog paper, a straight-line relationship developed between log D_λ and wavelength (Fig. 6.6). One can, nonetheless, believe that the National Bureau of Standards was well aware that this was the case. In 1964, attention was drawn to the fact that the (a) degradation of rubber (Bateman 1947), (b) erosion of paint (Miller 1958), and (c) tendency of certain methacrylate polymers to cross-link (Feller 1963) all responded in a similar way to decreasing wavelengths. Later, it was found that the development of carbonyl groups in poly(vinylchloride) (Martin and Tilley 1971) exhibited much the same behavior (Feller et al. 1981). Figure 6.7 is taken from the latter publication; the response curves represent activation spectra.

Krochmann and Colleagues. In a recent extensive consideration of the problem of minimum tolerable exposure, Aydinli, Hilbert, and Krochmann (Aydinli et al. 1983;

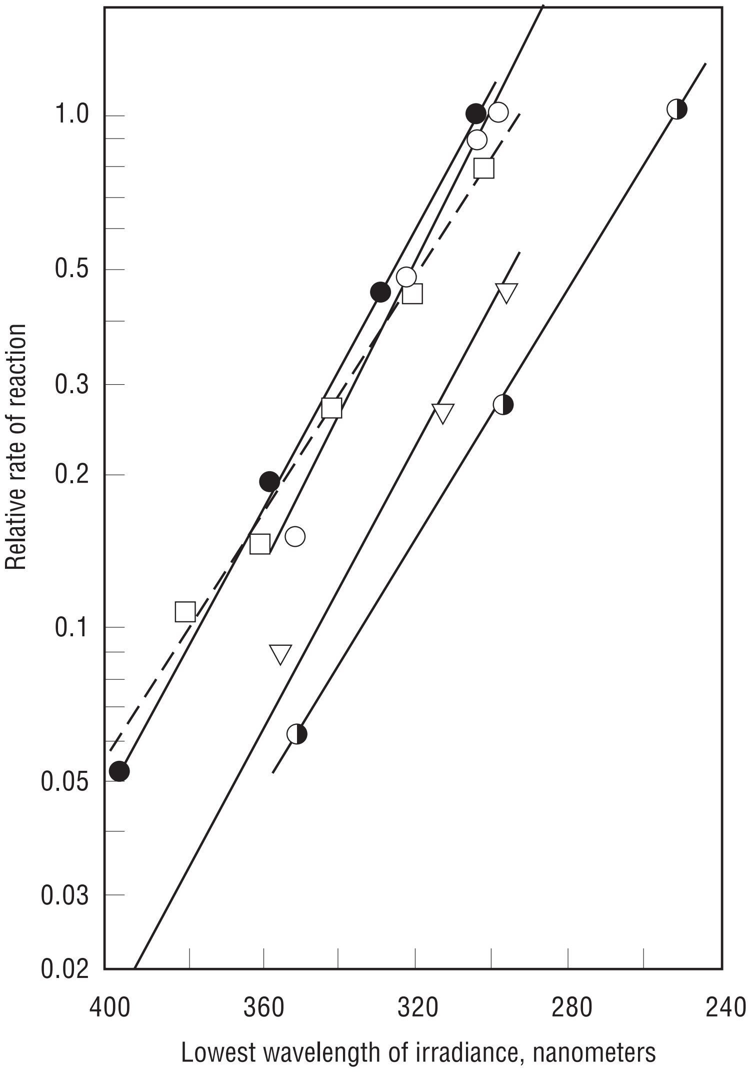


Figure 6.6. Data of various investigators concerning the influence of the lowest wavelength of irradiance on a variety of deterioration reactions. ● *Feller (1963);* ◑ *Miller (1958);* □ *Harrison (1954a);* ○ *Bateman (1947); and* ▽ *Martin and Tilley (1971). After Feller, Curran, and Bailie (1981). Reproduced with permission of the publisher.*

Krochmann 1986, 1988; Hilbert et al. 1991) took particular note of a logarithmic relationship. This was based on their equation:

$$S(\lambda)_{\text{dm rel.}} = ae^{-b\lambda}$$

or

$$ln\ S(\lambda)_{\text{dm rel.}} = lna - b\lambda$$

Here λ is the wavelength in nanometers and $S(\lambda)_{\text{dm rel.}}$ is the relative spectral damage or responsivity of the material, comparable to the NBS/Harrison, D_λ. The logarithm to the base *e* is designated as *ln*. The intercept, *a*, is $1/e^{-300b}$, chosen to make $S(\lambda) = 1$ at 300 nm.

In the case of specific materials and specific photochemical changes, the intercept and slope become important specifications. Using these principles, Krochmann and his associates have determined the slopes, *b*, for a series of watercolors, oil paints, paper, newsprint papers, and textiles. The slopes, based on the amount of exposure necessary to achieve a degree of color change of $\Delta E^* = 1$ at each wavelength (ΔE based on CIE L*a*b* equation), were found to be similar, generally ranging from 0.0100 to 0.0125. The exception was for newspapers, 0.038, which they note is higher than the slope of 2.303 log D_λ values (NBS/Harrison) versus wavelength, 0.026.

Krochmann and his coworkers have used this approach to estimate the minimum exposure under various lamps that will cause a just perceptible color change, considered to be a ΔE^* of 1 based on the CIE L*a*b* color-difference formula. Their studies on these important concepts are extensive.

The Idea of a Threshold of Photochemical Activity

Intensity. Museums have long hoped that a technical advisor could tell them that, below a certain level of *intensity*, no photochemical damage would occur. Unfortunately, it is a basic tenet of photochemistry that there is no threshold of intensity below which deterioration will not occur. (This subject was initially referred to in "The Primary Process," page 49.) If the intensity is reduced to one-thousandth of what it had been and if the reciprocity principle holds, then the rate of photochemical damage would be expected to be reduced to one-thousandth. For all practical intents, perhaps such a low level can be considered to represent completely arrested photoactivity. Nonetheless, from the point of view of establishing principles of deterioration, one must realize that no threshold of intensity is considered to exist below which photoactivity ceases.

This statement, of course, involves the concept of *exposure:* intensity times time. Thus, there is in principle no minimum level of exposure, in terms of footcandle hours, lux hours, or milliwatts per square centimeter, below which a photochemical process will altogether cease. From the museum curator's point of view, the particularly unforgiving factor here is the matter of time. Thus, even at very low intensity of illumination, if a susceptible material is exposed for a sufficiently long time, measurable photochemical changes can be expected. Specifications have been drawn up by a number of museums stating that certain materials may not be exposed to more than a fixed number of lux hours of daylight or fluorescent lamplight per year. The *Illuminating Engineering Society's Handbook, Application Volume* (USA) is one source where such specifications can be found. It must not be forgotten, however, that such specifications are not established in order to *avoid* damage. They are based instead on some minimum acceptable or tolerable damage that would result from extended exposure. The exposure limit set by Krochmann's work, for example, is one that would result in a color change of $\Delta E = 1$ (a "just perceptible" change). A wider discussion of acceptable limits of exposure is needed in the field.

Years ago there was an idea put forth that very little fading of paints and textiles would occur upon outdoor exposure if the level of sunlight intensity fell below 0.823 gram calories/cm^2/min. Although this suggestion has been associated with Clark (1952), the idea apparently came from DeNoon of the South Florida Test Service. A possible reason why this specification may have proven to be reasonably correct is that, as the intensity of sunlight outdoors increases, the temperature of samples on exposure also increases. Below a certain level of sunlight illumination, therefore, the temperature of the specimens may not have been sufficiently high so that serious physical deterioration occurred. (The same factor, of course, must be recognized in exposures to artificial light sources: at increasingly high intensities of illumination the temperature of the samples will increase unless special precautions are taken.) Moderate temperatures, attained when very low intensities of illumination are used, may sometimes lead observers to gain the impression that reactions have been dramatically reduced, if not completely arrested.

Clark's particular "threshold" has long since been abandoned. Instead, following the observation that the degradation of specimens during outdoor aging tests was far greater in summer than in winter, workers today now focus their attention on the net exposure to the ultraviolet component in daylight (Singleton et al. 1965; Zerlaut and Ellinger 1981).

Wavelength. There are many research reports that cite a wavelength above which certain photochemical processes do not occur. For example, Andrady et al. (1989), point out that dehydrochloridation of poly(vinylchloride) does not occur above 300 to 340 nm, depending primarily on the purity of the polymer. The photosensitivity of polypropylene is said to occur chiefly at wavelengths below 330 nm (Melchore 1962). Recall also Figure 6.4, in which marked deterioration of nylon 6 only began at wavelengths below about 300 to 320 nm.

The reason for a *critical wavelength* before specific photodegradation processes will be observed can usually be explained by the need for radiation to be absorbed by a particular chromophoric group before degradation can be initiated. Thus, in discussing the photodegradation of poly(n-butylacrylate), Liang et al. (1982) proposed that 313 nm would not be able to excite the carbonyl group in the polymer but would instead cause hydroperoxide groups to dissociate. Concerning the photodeterioration of alkyd resins, Miller (1958) considered that the aromatic (phthalate) groups principally would be affected below 250 nm; above 295 nm, an attack on the aliphatic portion would predominate. These are examples of what Searle has called wavelength specificity.

There is an aspect, related to intensity, that must not be overlooked when considering the possibility of a limiting wavelength below which there is no photoinduced degradation. Consider Figure 6.6, in which the logarithm of the rate is plotted against wavelength. Note that the relative rate at the longer wavelengths may readily fall to one-hundredth the rate at the shorter wavelengths. As mentioned earlier, if such a very low rate is observed at a relatively long wavelength, then one might consider that a limiting wavelength had been reached.

Perhaps, at one-hundredth or one-thousandth of the rate induced by short wavelengths, one can consider, for all practical purposes, that the reaction has ceased. Apparently, this was the case with the data of Stephenson et al. (1961). In a study of the degradation of polyethylene, Mylar, and Teflon, the authors provided graphs showing that an intrinsic damage index, plotted on a linear scale versus the photon energy level, reached zero at about 3.2 electron volts in each case. However, when the photon energy is plotted against the logarithm of the authors' intrinsic damage index, one finds that their experimental data falls very much in the manner of Figure 6.6. Rather than reaching zero, the intrinsic damage simply is found to have decreased logarithmically with wavelength.

Action of 280–315 nm Wavelengths

Wavelengths lower than those that pass through window glass (lower than about 315 nm) have often been employed in an effort to speed up photochemical deterioration. Of particular interest are wavelengths in the UVB region, 280–315 nm, just below those transmitted by window glass. Fluorescent lamps emitting primarily in this region were introduced some years ago in equipment (QUV) manufactured by the Q-Panel Company. In part because of their reasonable cost relative to the xenon-arc lamps, the use of fluorescent lamps has gained considerable popularity, particularly in testing carried out by automobile manufacturers. (This is discussed further in "UV-

Emitting Fluorescent Lamps," page 80.)

A basic question presents itself: Does the photochemical degradation induced by these shorter radiations duplicate that experienced under natural con ditions? By the "natural conditions," many authors have "outdoors" in mind. However, a conservation scientist must ask if the same photo reactions occur under 280 to 315 nm radiation as occur indoors under normal conditions in a museum. The answer to both questions, regarding the correspondence with outdoor or indoor exposures, is that in many instances the results will *not* correspond (Knowles 1973).

Although it is necessary to check each case, the wisest procedure for those interested in the behavior of materials under museum conditions is to rarely if ever use radiation that does not pass through ordinary window glass, nominally below 310 to 315 nm. In the subsections that follow, evidence will be reviewed that indicates that wavelengths much below 315 nm can indeed lead to "unnatural" photochemical deterioration reactions, a term used by Bauer, Peck, and Carter (1987).

Effects of Unfiltered and Filtered Xenon-Arc Emissions

Literature on the Atlas Electric Devices Ci35 instrument presents data regarding the irradiance ranges under the various filter systems in the xenon-arc equipment, information summarized in Table 6.2. The filter combinations refer to the inner/outer filter system surrounding the xenon lamp. Borosilicate is the type of glass found in Pyrex.

	250–300 nm	**300–400 nm**	**340 nm**
B/B Borosilicate/Borosilicate	0.1–0.2	25–65	0.2–0.55
B/S Borosilicate/Soda Lime	0	25–60	0.2–0.45
B/Q Borosilicate/Quartz	0.4–1.0	30–75	0.25–0.65
Q/Q Quartz/Quartz	6.8–13.0	45–80	0.40–0.75
Natural Daylight	-2.0	-66	

Table 6.2. Xenon-arc irradiance, watts/m^2 *under various filter combinations (Atlas Electric Devices Co. Data, Bulletin No. 1360).*

In an article discussing the effect of slightly different spectral distributions upon the aging of synthetic resins, Nyitrai et al. (1983) used xenon-arc Xenotest 450 and 1200 equipment to show that, in the case of poly(vinylchloride), the concentration of polyene groups having 1 to 7 double bonds in a sequence in the degraded polymer differed when one rather than the other apparatus was involved. The difference in the cut-off wavelength in their equipment was 315 versus 270 nm, the shorter wavelengths occurring in the Xenotest 1200 apparatus. A greater number of long polyene sequences occurred during the Xenotest 1200 exposure, that is, when the shorter wavelengths were involved. Hennig and Horn (1978) reported that filtering out the radiation between 280 and 300 nm in Xenotest equipment sometimes influenced the rate of fading of poly(methylmethacrylate) coatings. Schaaf (1983) stressed that elimination of these wavelengths could prove to be particularly significant when evaluating systems containing ultraviolet absorbers and inhibitors.

Yano and Murayama (1980) found that the dynamic modulus of nylon was only affected by wavelengths below 300 nm. The tendency of poly(methylmethacrylate) to undergo chain scission also becomes particularly important at wavelengths below 300 nm (Torikai et al. 1990).

When evaluating the photochemical activity of TiO_2, Blakey (1985) reported that a radiation source rich in the short wavelengths of ultraviolet (ca. 290 nm) exaggerated the photochemical deterioration of the binder and minimized the effect of the photoactivity of the pigment. This became particularly important when the behavior of different TiO_2 pigments was first tested in an air-drying alkyd and later compared to the behavior of the same pigments in a more durable binder based on a thermosetting acrylic.

In summary then, there is ample evidence that UVB wavelengths, those from 315 to 280 nm, can occasionally induce differences in degradation chemistry as opposed to the same source filtered by borosilicate or soda-lime glass. Additional evidence will be cited in the following section.

UV-Emitting Fluorescent Lamps

Beginning in the early 1970s, a fluorescent lamp emitting a limited range of radiation peaked at 313 nm, known as the Westinghouse FS-40 fluorescent sunlamp or F40 UVB lamp, was introduced for accelerated aging tests. The Q-Panel Company (26200 First Street, Cleveland, Ohio 44145) soon began to market accelerated exposure equipment using such lamps, known as the QUV instrument. Its use has been formalized in the ASTM G-53 test procedure. In 1984, a UVB-313 lamp, which emitted the same wavelengths but at greater power output, was developed. In 1987, the UVA-340 lamp was introduced and later the UVA-351 (Birchenough 1982; Brennan and Fedor 1987).

The output of these four lamps is shown in Figure 6.7. The UVA-340 emission contains short wavelengths comparable to those found in sunlight. The UVA-351 lamp, on the other hand, emits slightly longer wavelengths similar to the lowest wavelengths that pass through window glass. Whenever one reads the results of exposures carried out in "a QUV" apparatus, the dates of introduction of these lamps must be kept in mind. Unfortunately many authors refer only to the QUV and do not specify the type of lamp involved. Early studies were certainly carried out with the FS-40 lamp.

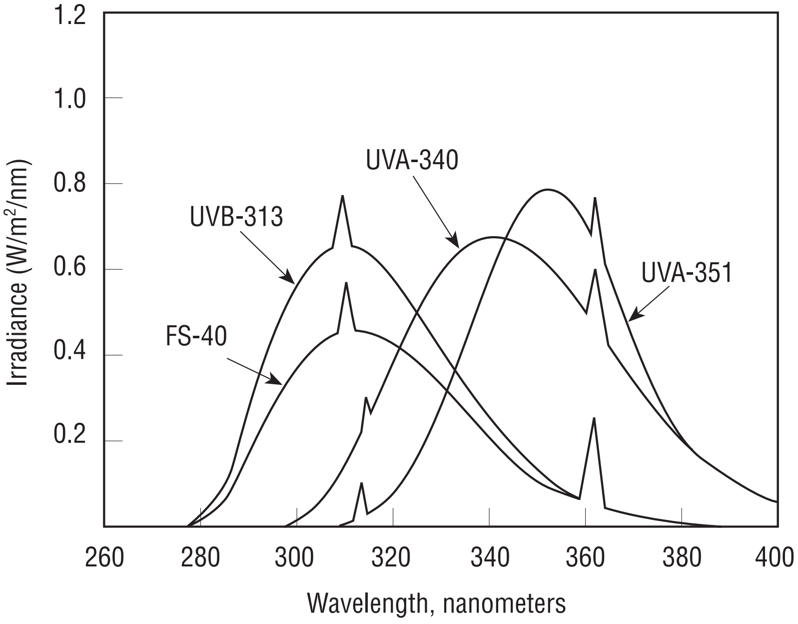


Figure 6.7. Spectral distribution of irradiance from various fluorescent lamps emitting primarily in the ultraviolet (from Brennan and Fedor 1987). Reproduced with permission of the Q-Panel Company.

Those who wish to test materials related to conservation practice may wish to choose primarily the UVA-351 type lamp among those illustrated in Figure 6.7. Admittedly, there is always the possibility that exposures under the other types of lamps will speed up deterioration and at the same time yield results that correlate well with the results of exposures under so-called ordinary conditions. However, one cannot be certain that exposure to wavelengths shorter than those which pass through window glass will yield results similar to those which occur in museums and archives unless tests on the specific materials are made and specific behavior (cracking, yellowing, fading) confirmed.

As mentioned, it is well recognized that the wavelengths between 280 and

315 nm—rarely, if ever, encountered under glass indoors—can give rise to different reactions than those induced by the near ultraviolet and visible. Brennan (1987a) has reviewed a number of references to this problem, some of which will be cited below.

Comparison of Aging in Xenon-Arc Fade-ometer and QUV. Epps has published a number of articles on textile degradation. In one publication (Epps 1983) results in the Atlas Fade-ometer 25-F having a borosilicate inner and soda-lime outer filter were compared with those attained in a QUV Accelerated Weathering Tester (FS-40 lamps). Tests were carried out for a period of 140 standard fading hours (a standard based on the AATCC XRF-1 standard fading cloth). An Orlon acrylic fabric and a nylon 6,6 yellowed considerably in the QUV apparatus. The QUV also caused greater loss of tensile strength.

A comparison of the ultraviolet radiation below 320 nm emitted by various accelerated-aging devices has been made by Davis and Gardner (1982). They report that the QUV with FS-40 lamps emitted almost as much in the wavelength below 320 nm as the Xenotest 1200 with no filter. Table 6.2 indicates that in the Fade-ometer with the borosilicate/soda-lime (B/S) filters there would be little energy present in the wavelengths below 300 nm.

Bauer, Peck, and Carter (1987) of the Ford Motor Company discussed the accelerated weathering of a polyester-urethane coating, monitoring the changes of the amide and isophthalate bands and the loss of gloss under Florida exposure and under four sources: high intensity sunlight (EMMA apparatus), xenon arc, carbon arc, and the FS-40 lamps. An acceleration factor was calculated using the rate of first-order decay kinetics of the amide band in the infrared. Loss of the isophthalate band was taken as indicative of an acceleration chemistry different from that which occurred in Florida. Their research concluded that the "unnatural" chemical reactions (their word for the loss of isophthalate) occurred to the greatest extent with the FS-40 lamps, followed by the carbon arc and then the xenon arc (with borosilicate inner and outer filters; i.e., B/B, Pyrex/Pyrex).

The authors attribute these results to the relative amount of radiant energy below 290 nm in each source. The authors present a curve showing greatly increased absorbance of the coating at wavelengths below about 310 nm. Their study provides a particularly clear-cut example of a change in the ratio of two degradation reactions caused by an increase in the radiation below 290 nm.

Neidlinger and Schissel (1987), reporting on the degradation of poly(methylmethacrylate) after 1,000 hours of exposure, found that 22.2 chain scissions occurred in the QUV instrument versus 1.2 in an Atlas Weatherometer (xenon-arc) equipped with suitable cut-off filters to simulate sunlight. Evidently the shorter wavelengths, present in the QUV, caused increased chainbreaking. Greater loss of transmission, leading to noticeable yellowing, was also observed during QUV exposure of clear films. In films containing ultraviolet stabilizer-inhibitors, greater loss of stabilizer was also observed in the QUV.

Florida Exposure versus QUV. Hartshorn (1987) investigated the degradation of a melamine-aromatic polyester enamel both in Florida and in the QUV apparatus. In the QUV apparatus the aromatic ester band disappeared more rapidly than hydrolysis of the melamine cross-link; in contrast, the two processes proceeded at similar rates in Florida.

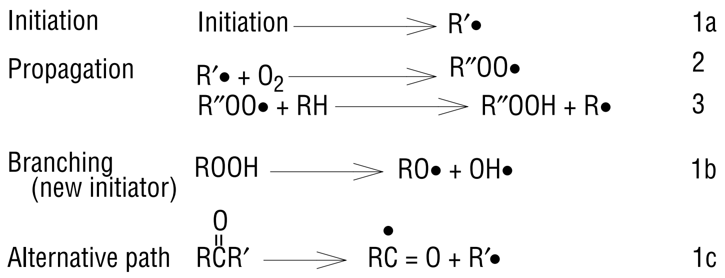
The loss of certain bands in the infrared proceeded according to a first-order decay law. One of the principal points of the article was that, by following the loss of the ether band, the author demonstrated that one could predict the point of failure during outdoor exposure well in advance of any outward signs of physical deterioration.

Gatechair and Evers (1986) have also reported poor correlation between the yellowing of a particular ultraviolet-curable coating in the QUV apparatus compared with the yellowing experienced in six months outdoors in Florida. The emission spectra of the lamps and data in their experimental section showed that the lamp employed in the QUV equipment was the FS-40 type.

This discussion of the characteristics of fluorescent lamps that emit principally in the ultraviolet region is presented in order to make the reader aware of the history and variations in this type of ultraviolet source (Brennan and Fedor 1987). The references to the QUV apparatus when it involved the FS-40 and the more recent UVB 313 lamps are not intended to criticize this equipment but to provide further documentation for the fact that wavelengths just below those transmitted by window glass are well known to be capable of inducing chemical transformations that are different from that induced by higher wavelengths. The manufacturers of QUV equipment and the limited-range ultraviolet-emitting fluorescent lamps well recognize this potential difference in performance and regularly suggest appropriate lamps and filters to take this factor into account.

Wavelength Sensitivity in the Buildup and Dissociation of Peroxides

Thermally induced deterioration at moderate temperatures usually takes place through the formation of hydroperoxides. A subsequent reaction pathway is frequently called a *branching* or *degenerate branching* mechanism. This designation is applied because, after sufficient peroxides have been built up, the main cause of



Initiation $\text{Initiation} \longrightarrow R'\bullet$ 1a

Propagation $R'\bullet + O_2 \longrightarrow R''OO\bullet$ 2

$R''OO\bullet + RH \longrightarrow R''OOH + R\bullet$ 3

Branching (new initiator) $ROOH \longrightarrow RO\bullet + OH\bullet$ 1b

Alternative path $R\overset{\overset{O}{\|}}{C}R' \longrightarrow R\overset{\bullet}{C}=O + R'\bullet$ 1c

Figure 6.8. Elementary steps in the free-radical oxidative chain process leading to the formation of hydroperoxides (ROOH) and potential branching or alternative paths leading to formation of further free radicals.

"initiation" of free radicals changes from the original, usually poorly defined, substances (Fig. 6.8:step 1a), to the breakdown of the hydroperoxides (Fig. 6.8:step 1b).

Two important characteristics of thermally induced "auto-oxidation" are the buildup of the concentration of ROOH to a maximum and subsequent decline in the ever-increasing (autocatalytic) rate of consumption of oxygen (Fig. 6.8:step 2). In contrast, in sensitized *photo-oxidation,* the rate of consumption of oxygen and the buildup of peroxides usually proceeds at a steady pace; a maximum is not often observed. Geuskens et al. (1987) and Vichutinskaya et al. (1982) suggest a reason for a constant rate arising in photo-oxidation; they propose the generation of a sensitizing substance that exists at a relatively small but constant concentration.

It is of considerable interest to confirm whether near-ultraviolet radiation is able to facilitate step 1b in Figure 6.8, the photolytic dissociation of hydroperoxides. The absorption spectra of a representative peroxide, t-butyl peroxide, tapers off rather rapidly at 360 to 380 nm. Nonetheless, such absorption, or that of related hydroperoxide groups, ROOH, might be sufficient to absorb enough near-ultraviolet radiation to give rise to photolysis. The evidence will be reviewed.

Behavior of Polypropylene

Carbonyl-containing oxidation products, those bearing RCOR or RCOH groups, can be responsible for absorption in the near ultraviolet. Carlsson and Wiles (1969) have concluded that ketone groups in polypropylene absorb radiation and undergo what is called Norrish type I photolytic dissociation (Fig. 6.8:step 1c) at wavelengths of 330, 331.3, and 375 nm. The Norrish type I reaction generates free radicals; Norrish type II does not. One important consequence of the Norrish type I deterioration, similar to step 1c, is that it is able to generate radicals which in turn lead to the formation of further amounts of ROOH. The buildup of ketone groups thus represents the intermediate such as proposed by Geuskens and the Russian authors. The primary objective of Carlsson and Wiles's article II (1969) was to point to ketone groups as the principal source of initiation in the early stages of photo-oxidative deterioration.

Article III (1969) considers the action of ROOH and ROOR peroxide structures; these tend to initiate deterioration in later stages. In order to test the importance of step 1b in the photolytic sensitivity of hydroperoxidized polypropylene, Carlsson and Wiles irradiated the films in a vacuum at 370 ± 5 nm. They noted a complete loss of peroxide under the vacuum and also a loss of weight until a point of constant weight was reached. This provided convincing evidence that the ROOH and ROOR structures in the polymer were indeed being photolyzed by the near ultraviolet of 370 nm and even 360 nm radiation (Carlsson and Wiles 1974), action similar to step 1b. After decomposition of the peroxides by the irradiation under vacuum, the authors found important infrared absorption bands at 1726 and 1718 cm^{-1}; these were attributed to ketone groups resulting from the decomposition of tertiary RO• radicals. They stressed that the development of RO• radicals within the polymer would play an important role in scission of the main chain through a process known as beta-scission.

The authors concluded article III with the statement: "Since the hydroperoxide concentration increases continuously during photo-oxidation, some alkyl radicals . . . must combine with O_2 to give peroxy radicals and then fresh peroxide [hydroperoxides] to sustain the auto-oxidation. Peroxy radical formation will probably be favored by low rates of photolysis (i.e., low light intensity and low hydroperoxide concentration) when radical-radical reactions will be relatively infrequent."

It is of interest to note that the authors state (Carlsson and Wiles 1969:591) that *thermally* oxidized films showed no detectable absorption at 3400 cm^{-1} in the infrared, the absorption region of peroxide OH groups. This reinforces the concept that it is the exposure to near-ultraviolet radiation rather than thermal aging that tends to build up the highest concentrations of peroxide.

Nylon

Anton (1965) noted that peroxides build up in nylon when exposed to wavelengths from 270 to somewhere between 340 and 400 nm. No serious diminution in the rate of buildup of peroxides occurred when three different systems filtering this region of the spectrum were used. On the other hand, practically no buildup of peroxide was observed when the films were irradiated with wavelengths above 400 nm; this implies that reaction 1b was not taking place. Similar results have been observed with ethylhydroxyethylcellulose (Feller and Wilt 1990).

Anton also presented data to show that, if the yarn had been thermally degraded so that it absorbed more ultraviolet than an unaged sample, it would build up peroxides and degrade more rapidly than a sample that had a lower ultraviolet absorption.

Polyamides

Vichutinskaya et al. (1982:fig. 4) provide much the same information. Irradiating polyamides at wavelengths between 365 and 436 nm, Vichutinskaya and his associates found that the rate of oxidation often started out rapidly but eventually attained a constant rate. They used thermally aged polymers to generate varying amounts of initial peroxide content before their irradiation experiments. Nonetheless, the steady-state rate of oxygen uptake (recall Fig. 3.4) was found to be independent of the original amount of peroxide present. During irradiation the concentration of peroxide increased in time but the buildup slowed down. Concentrations of .016 meq./g were attained. Similar to Carlsson and Wiles, they projected the idea of an intermediate sensitizer, not ROOH, building up to a constant concentration. They pointed out that the steady-state rate would not be dependent on the light intensity but that the ultimate concentration of the proposed intermediate would. They further found (Vichutinskaya et al. 1982:fig. 5) that in initial stages of oxidation the consumption of oxygen decreased to a steady-state rate at high values of intensity; at low values of intensity oxygen consumption increased up to a steady state (see Appendix C, Fig. C.2). The steady-state rate was found to be proportional to the square root of the light intensity.

Inactive Hydroperoxides

Bousquet and Foussier (1984) discuss the different effects of 313 and 254 nm radiation on the photosensitized reactions that occurred during the photo-oxidation of a rubber-like elastomer that contained an intentionally low content of aromatic groups. A lower quantum efficiency of carbonyl group and cross-link formation was induced by 313 nm radiation compared to 254 nm.

The authors discussed the formation of two types of hydroperoxide groups (OOH) depending in part on their location in the polymer structure. *Active* POOH groups (P standing for the polymer), formed near the phenyl groups, led to the production of two radical species, PO• and •OH. The free radicals arising from this dissociation could initiate oxidation reactions. *Inactive* POOH groups were not affected by photosensitized decomposition in contrast to the active. Their concentration increased steadily during irradiation. When irradiation was carried out at 254 nm, the authors were able to show that a greater fraction of the total POOH formed (as measured iodometrically) was in the active form. The fraction was lower, however, under irradiation by 313 nm ultraviolet (0.93 vs. 0.60). Gardette and Lemaire (1982) also discuss different types of peroxide groups and their different sensitivities towards further reaction.

The authors conclude their presentation with the general statement that their results “warrant the assumption that irradiation of a photosensitized polymer results in the formation of new chromophore groups, which—on further excitation—can also take part in the photo-oxidation process through hydroperoxidic reactivity.”

These four examples provide evidence that near-ultraviolet radiation can induce the photolytic scission of hydroperoxides and also that ketone structures (impurities?) can result in free-radical initiation under the influence of the near ultraviolet.

Fundamental Difference Between Thermally Induced Auto-oxidation and Photo-oxidation

Geuskens et al. (1987) make the general statement that thermally induced auto-oxidation is “autocatalytic and from a certain stage, hydroperoxides are decomposed more quickly than they are formed. On the other hand, photo-oxidation proceeds at a constant rate and the hydroperoxides accumulate.” The authors also point out that a very short induction time is often observed in photo-initiated reactions; an induction time is necessary in order to build up sufficient concentrations of ROOH so there will be increased efficiency of energy transfer from the sensitizing light-absorbing groups to the hydroperoxides. The authors suggest, as noted earlier, that it is the deterioration of peroxides sensitized by neighboring groups that accounts for the steady-state rate of photo-oxidation by near-ultraviolet radiation. Others have suggested that there may also be a dark reaction taking place during which some of the intermediate, sensitizing compounds would gradually decay away.

Although perhaps not often observed, it is nonetheless possible for photochemical deterioration that proceeds through the intermediate of hydroperoxides to occasionally go through a maximum concentration of ROOH similar to the behavior expected in thermally induced hydroperoxide buildup. Iranov et al. (1978) have reported that polyisoprene rubber, exposed to wavelengths above 300 nm, exhibits a maximum in peroxide buildup.

The two apparently different tendencies in the buildup of hydroperoxides (going through a maximum versus increasing monotonically) may not be as different as may first appear. Many studies show that, in thermally activated circumstances, the maximum concentration of hydroperoxide increases as temperature decreases. (This can be seen in Koz'mina's study [1968] of the thermal deterioration of ethylcellulose at 110, 120, and 130 °C.) At lower temperatures, the time that it takes to reach the maximum in hydroperoxide concentration would also increase. From this point of view, it can be appreciated that, since the temperature is often moderate under photochemically initiated conditions, the buildup of hydroperoxide concentration can be expected to tend towards very high concentrations and to take a long time to reach the maximum. Therefore, under normal photochemical exposures at moderate temperatures, one may observe only the progressive buildup of hydroperoxide concentration, the study never extending to the point where a maximum has been reached. This is in contrast to thermal deterioration studies at temperatures of 100 °C or more in which a maximum in concentration of hydroperoxide is nearly always observed. Nonetheless, under photochemical conditions, a maximum buildup of hydroperoxides can indeed sometimes be observed. A plateau, steady-state, concentration can also sometimes be encountered (Adam et al. 1989; Iranov et al. 1978).

Summary

Interest is widely expressed concerning the influence of wavelength on photochemical deterioration. The subject is such a broad one that it seems advisable to summarize the principal points that have been made in this section.

The term *activation spectrum* refers to the influence of wavelength on photochemical response regardless of the spectral distribution of radiant power in the illuminating source. *Action spectrum* refers to the influence of an equal number of photons (or equal radiant power) of exposure at each narrowly defined set of wavelengths across the spectrum. *Wavelength specificity* refers to the specific chemical response induced by specific wavelengths. Examples of each of these aspects have been cited. The wide selection of experimental techniques that can be used to obtain the desired information concerning each of these aspects has also been noted along with certain of their limitations.

Besides specific responses that may be elicited at different wavelengths, a type of general response to wavelength is often cited: The shorter the wavelength, the more potentially damaging. This generalized statement has found formal expression in a relation in which the logarithm of the damage induced is inversely related to the wavelength. The suggestion of this type of response to wavelength came in the 1950s through the efforts of the U.S. National Bureau of Standards, perhaps best known through the 1954 report prepared by L. S. Harrison, a consultant to the Metropolitan Museum of Art. Today, Krochmann and his associates in Germany have greatly enlarged upon the potential applications of this nonspecific, logarithmic response to decreasing wavelength.

Concerning the long-held interest in a threshold below which photochemical damage will not occur, there are indeed many examples of the fact that various reactions will not be induced above a certain wavelength. In contrast, there is theoretically no limit of *intensity* (more properly, *exposure,* intensity times time) of an activating irradiance below which a photochemical process will cease.

Evidence has been provided to document the fact that UVB ultraviolet radiation, 280 to 315 nm (that which is not significantly transmitted by ordinary window glass) is capable of inducing deterioration reactions that are different from those that tend to occur under ordinary museum circumstances. Hence, it is recommended that such wavelengths be avoided in most accelerated photochemical testing that is related to conservation problems. The use of an even shorter wavelength, 254 nm, in tests of potential aging characteristics, is definitely to be discouraged. Research reports in which this wavelength or lower have been used will rarely have relevance to conservation matters.

Hydroperoxides and peroxides can be photolyzed, either directly or by sensitization, to yield free radicals. This can lead to the formation of further peroxide and free-radical reactions. Evidence that near-ultraviolet radiation can initiate such a potentially degradative process has been reviewed.

7 Practical Aspects of Testing

The previous two chapters reviewed general principles concerning how photochemical processes take place. A number of practical aspects of accelerated photochemical testing will next be discussed.

Light Sources

Extensive descriptions of the emission characteristics of various light sources can be found in authoritative texts such as that of Rabek (1982). A few comments are in order concerning the appropriateness of some and the limitations of others.

Lowest Wavelength to Be Used

To speed up the results of exposure to light in a controlled manner, one commonly uses an artificial source in the laboratory rather than sunlight or diffuse daylight. However, many sources emit radiation that does not have the same range or distribution of wavelengths as that found in daylight (Hirt et al. 1960). The visible and ultraviolet radiation in the sunlight that reaches the earth has little energy in wavelengths shorter than about 290 nm; when this passes through ordinary window glass, little below 315 nm is present (Brennan 1987b). Hence, in studies related to museum problems, wavelengths below 315 nm are generally inappropriate. The CIE specification of the relative proportions of ultraviolet, visible, and infrared in sunlight and the comparison with the emission of a 6500-W xenon-arc with borosilicate (Pyrex) filters is in Table 7.1 (Metzinger and Kinmouth 1975; Kinmouth and Norton 1979). Xenon-arc radiation, filtered to resemble sunlight or daylight through window glass, has become the most widely accepted source in tests of general photochemical stability.

Note that about 6% of the total irradiance is often in the ultraviolet (Table 7.1). Many years ago Garry Thomson (pers. comm.) pointed out that ordinary fluorescent lamps frequently emit 2–6% ultraviolet, a fact most recently confirmed by Lull (1992). Thomson suggested that a bank of fluorescent lamps would make a good source for accelerated-aging tests, particularly in tests regarding museum-oriented problems. Currently the field of accelerated testing is experiencing increased acceptance in the use of fluorescent lamps in photochemical testing through the introduction of equipment far more moderately priced than the xenon-arc machines (as mentioned in "UV-Emitting Fluorescent Lamps," page 80). There is even commercial equipment and a proposed ASTM standard being considered in which ordinary (*daylight*?) fluorescent lamps will be employed to evaluate the color stability of equipment and metal furniture intended for offices.

92	Wavelength Range, nm	Sunlight, CIE	Percentage	6500-W Xenon through Pyrex filter	Percentage
Ultraviolet	280–400	68	6.1	73	6.3
Visible	400–750	539	48.1	587	51.3
Infrared	750+	513	45.8	484	42.3
		1120	100.0	1144	92

Table 7.1. Irradiance in xenon-arc Fade-ometer with Pyrex filters compared with CIE reference sunlight (W/m^2; Metzinger and Kinmouth 1975).

In a recent survey of accelerated test methods, Brown (1991) notes that "the selection and use of lamps remains a very open topic."

There have been many studies that attempt to determine whether wavelengths between 290 and 315 nm induce significantly different reactions than those that take place at wavelengths above 315 to 320 nm. As discussed in "Action of 280–315 nm Wavelengths" (page 78), the evidence is that, in tests that attempt to speed up the types of photochemical deterioration that might occur indoors in museums, wavelengths below 310 to 315 nm should rarely be involved. Either window glass (soda-lime) or Pyrex (borosilicate) glass can be interposed to ensure this objective. Admittedly, there is a slight difference in the short wavelengths transmitted by these two types of glasses (Fig. 7.1) and one may wish to verify whether a difference in deterioration will result. It is known, for example, that slight differences in the fading of some of the AATCC and ISO blue-wool fading cloths occur under the different filter systems described in Table 6.2 (Wagner et al. 1985:fig. 1). For this reason, the particular filter system that has been used in photochemical testing should always be described.

Under no circumstances should potential museum conservation problems be evaluated on the basis of studies made with 254 nm radiation or the unfiltered radiation from a low- or medium-pressure mercury-vapor lamp. Over twenty years ago the conclusion was drawn that "the mercury-vapor lamp is not recommended for general use" in the testing of dyed textiles (Giles et al. 1969). If quartz alone is used with common mercury-vapor sources, it must be remembered that quartz will transmit radiation of much lower wavelength than window glass, as low as 250 nm. Conservation scientists usually must disregard reports of research in which such a radiation source has been employed (de la Rie 1992).

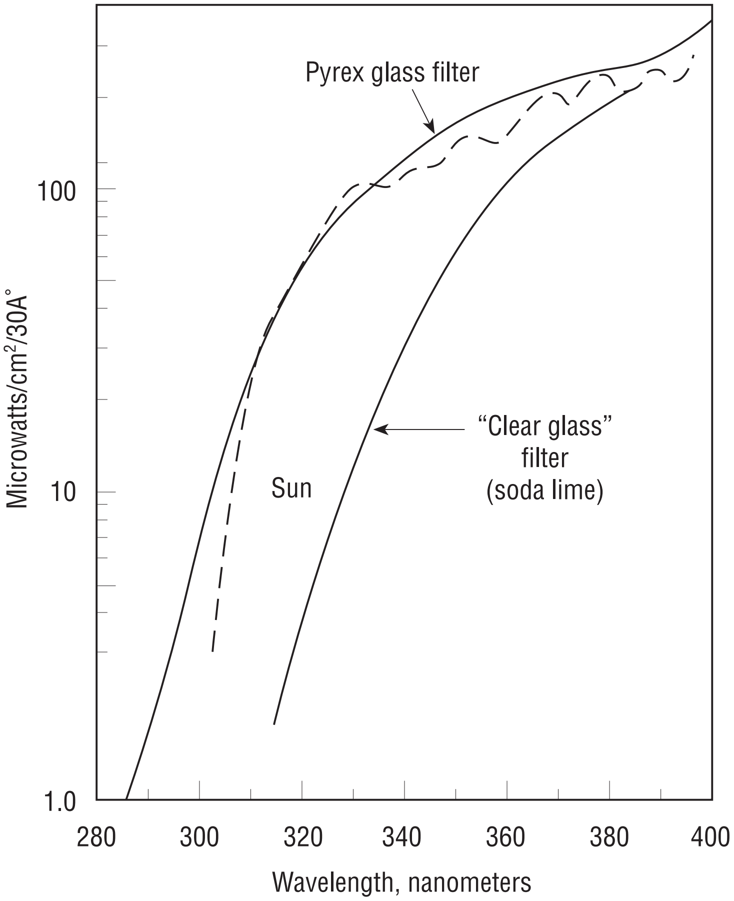


Figure 7.1. Spectral energy distribution of xenon-arc irradiance through soda-lime (clear glass) and borosilicate glass (Pyrex) compared to sunlight at earth's surface (Hirt and Searle 1967). Reproduced with permission of the publisher.

Sources of Polychromatic Radiation

Currently the most widely accepted source of high intensity polychromatic radiation is the xenon-arc lamp with soda-lime or borosilicate (Pyrex) filters interposed. In an early practice used by Giles in England, the so-called mercury-incandescent (MBFT, now ML) lamps are also widely employed, readily available in a commercial device known as the Microscal unit (manufactured by Microscal Ltd., 76 Southern Row, London W10 5AL). The spectral emission is seen in Figure 7.2. A similar lamp is available from General Electric as an EZMERC self-ballasted mercury lamp (M. B. Gotti, General Electric, Nela Park, pers. comm. 1992). A number of studies have led to the conclusion that this type of lamp "gives results in excellent agreement with those obtained in exposure to daylight or the xenon arc" (Giles et al. 1969; Park and Smith 1974; Adelman et al. 1977).

As mentioned, a convenient source of continuous radiation with about 1 to 6% in the near ultraviolet is an ordinary household fluorescent lamp, usually the "daylight" type. Such lamps were used in the 1950s by Garry Thomson at the National Gallery, London (Feller 1975), and have since been used extensively by the author and others. Ordinary fluorescent lamps have an added advantage in that they emit very little infrared and thus tend not to heat up the test samples to temperatures much above 25–28 °C.

Occasionally one may wish to determine the rate of photochemical deterioration under an incandescent light source. A major problem in doing so is the heat generated by such lamps, although suitable filters can be found. The principles associated with the heating effects caused by incandescent lamps have been reviewed elsewhere (Feller 1967).

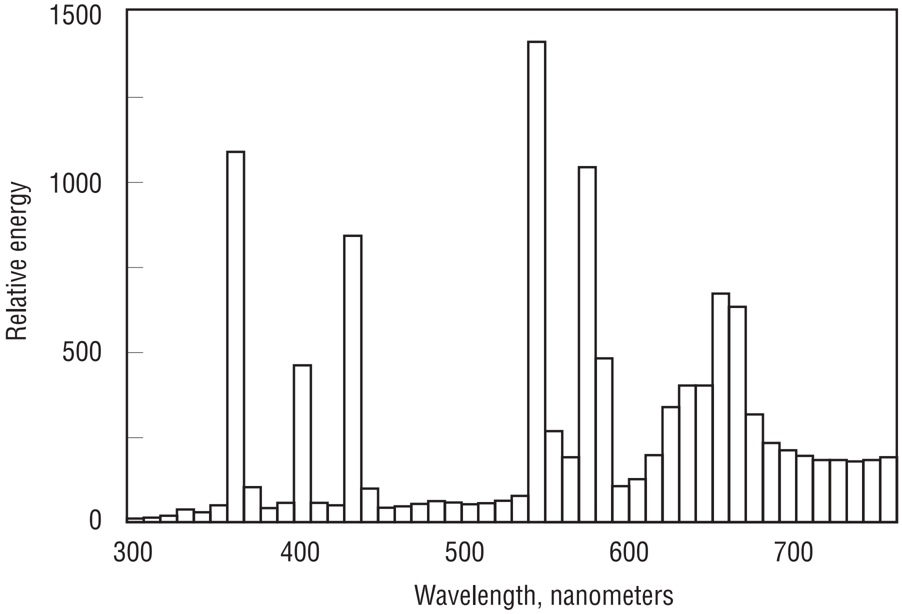


Figure 7.2. Emission spectrum of mercury-tungsten fluorescent (MBTF) lamp (Giles et al. 1969). Reproduced with permission of the publisher.

Quartz-halogen tungsten lamps emit radiation similar to that of the common incandescent tungsten lamps, but because of the quartz envelope and the high intensity, these lamps emit a significant portion of ultraviolet radiation. Conservators may occasionally be called upon to evaluate the relative potential photochemical damage that could be caused by such lamps and hence the emission of ultraviolet radiation is mentioned. In general, quartz-halogen lamps are avoided in the illumination of photochemically sensitive materials in museums or archives unless a glass filter or envelope is interposed and the intensity of illumination on sensitive materials kept at a suitably low level.

Sources of Monochromatic Irradiance

Mercury-Vapor Lamps. Historically, low-pressure mercury-vapor lamps have been used to provide a source in which distinct wavelengths could be isolated by dispersion or suitable filters. As noted in Chapter 6, "Sharp Dependence on Wavelength," a principal drawback is that only a limited number of wavelengths are available and the radiant energy at some wavelengths tends to be lower than is convenient to induce a practical rate of chemical change. Medium- and high-pressure mercury-vapor lamps produce more nearly continuous radiation at wavelengths from the ultraviolet up to nearly 600 nm. These have also been used in accelerated testing with the use of appropriate filters particularly to eliminate the shortest wavelengths of ultraviolet (Lemaire et al. 1981, 1991). Textbooks on photochemistry regularly present details regarding the emission characteristics of mercury-vapor lamps (Rabek 1982; McKellar and Allen 1979).

The 365 nm radiation from a mercury-vapor source, called the long-wave ultraviolet, has been used in many studies in the past. Today, in its place one often finds a fluorescent blacklight or UVA-type lamp used with emission peaked at 365 nm (Fig. 6.7).

Photochemical studies often report studies using the 313 nm radiation from mercury-vapor lamps (not the UVB-type lamp shown in Fig. 6.7). Such a wavelength is not expected to be of major importance indoors under window glass. Nonetheless, many, although perhaps not all, of the reactions induced by this wavelength will be similar to those caused by 315 to 325 in the near ultraviolet.

Spectral Dispersion. A very practical way to study the effects of wavelength is to spread the emission of a continuous radiation source into a spectrum by means of a quartz prism or a diffraction grading. Hirt and Searle did this with sunlight in their original studies (Hirt et al. 1959). The Japanese have used a similar approach in which the sample is placed in a spectrograph so that the dispersed wavelengths strike across the sample (Shimada and Kabuki 1968b; Johnson et al. 1969; Yano and Murayama 1980; Kenjo 1985). In Australia, Holt and Waters (1985) similarly exposed wool to various narrow wavelength regions using a Jasco CRM-FA Spectroirradiator. The Japanese have more recently developed a very large spectrograph facility in which studies of this type can be carried out with rather large samples (Andrady et al. 1989; Torikai et al. 1990). The effect of narrow bands close to a specific wavelength can, of course, be determined if the specimen is placed at the outlet port of a monochromator (Lennox 1969; Kämpf et al. 1991).

To summarize, when reading reports in technical journals one must pay close attention to the wavelengths involved, particularly if 254 nm radiation is specifically cited or if low- and medium-pressure mercury-vapor lamps are used without an effort to filter out the wavelengths lower than one expects to encounter in a museum. The author considers that the conservator should not place practical significance upon the conclusions of studies with 254 nm radiation, for this wavelength has little to do with the radiation encountered in museums and the chemistry is usually not the same as that caused by near ultraviolet. This wavelength tends to cause photolytic deterioration.

When conducting a literature search on ultraviolet degradation studies, it is necessary to check the source of radiation used and the filters employed. If wavelengths much below 315 nm have been present, the research findings may not apply to the conservator's problems. Unfortunately, many authors in the past did not clearly describe the ultraviolet wavelengths involved in their experiments.

Selection of Limited Spectral Ranges

SEPAP Exposure Equipment. The desire to test the deterioration processes induced by particular regions of wavelength led to the development in France of the SEPAP exposure devices (Lemaire et al. 1981). Omya SA (35 Quai Andre Citroen, 75015 Paris) markets a line of apparatus for accelerated photoaging tests under this designation (noted in "Effects Observed over an Extensive Range of Wavelengths," page 64). Their special feature is that each table-top-sized apparatus uses a set of four lamps (located in the four corners of the chamber) that emit radiation in different wavelength regions. The SEPAP 12/24 and 12/24H (water-cooled) use four 400W medium-pressure mercury-vapor lamps. The SEPAP 310 uses a fluorescent lamp that emits 260–360 nm using a phosphor peaked at 310 nm. There is also a SEPAP 254 apparatus and a SEPAP 365, involving 254 and 365 nm radiation respectively. The equipment was developed by the Laboratoire de Photochemie Moleculaire et Macromoleculaire de l'Universite de Clermont II (63170, Aubiere, France), a laboratory affiliated with the CNRS in France. In their research programs the effect of various wavelengths is regularly investigated by carrying out exposures under the different types of lamps. The director of the laboratory is Jacques Lemaire (Lemaire et al. 1981).

Limited Emission Fluorescent Lamps. As discussed in "UV-Emitting Fluorescent

Lamps" (page 80), fluorescent lamps that emit a band of continuous radiation in a limited range of wavelengths in the ultraviolet have now been adapted to accelerated-aging studies. The emission of common types are peaked at wavelengths of 313, 340, and 365 nm, as shown in Figure 6.7. The first two, particularly the 313 nm, were commonly called fluorescent sunlamps. Lamps peaked at 365 nm come in two forms of so-called fluorescent black lamps: BL and BLB. Each emits much the same range of wavelengths but the glass in the latter is a deep blue in color and the lamp emits lower total radiant power. As discussed in Chapter 6, when some of the 313 nm types were first offered in commercial accelerated-aging devices in 1984, they were found to emit sufficiently low wavelengths that the induced aging chemistry was noticeably different from aging under outdoor weathering or the usual xenon-arc testing procedures. This led to the development of the lamps peaked at slightly higher wavelengths, such as the 340 nm lamp introduced in 1987 (Brennan and Fedor 1987).

Speed-up Factors. The question regularly arises concerning just how much the rate of photochemical deterioration can be speeded up by various light sources while at the same time satisfactorily reflecting the behavior that occurs under normal conditions of use. Successful achievement of the latter goal is a challenging task, so much so that authorities have often taken the position that "the degree of correlation between natural and artificial aging seems to be inversely related to the degree of acceleration" (Brown 1991). This situation has led some to suggest that an acceleration factor of five to ten times would represent an acceptable level (Kockott 1989) and that the ultraviolet intensity should "not exceed more than three times the standard solar intensity in a given climatic zone" (Minsker et al. 1982). The author has also suggested, arbitrarily, that the near ultraviolet, if intentionally enhanced, should not constitute more than 20% of the total radiant power in the visible plus near ultraviolet (Feller 1975).

Recognizing that the measured acceleration factor will depend more on the materials involved, as well as temperature and humidity, rather than intensity of irradiance alone, it may be of interest, nonetheless, to review some speed-up factors that have been cited in the past. The EMMA apparatus that uses mirrors to concentrate sunlight on samples is said to provide eight to ten times the normal rate of deterioration under direct sunlight (Kamal 1967:203; Kockott 1989). The irradiance between 300 and 800 nm of vertically impinging direct sunlight has been specified to be about 580 watts/m^2, with a mean radiant exposure in this wavelength range per year in south Florida of 3480 MJ/m^2. Kockott (1989) suggests that the typical xenon-arc Fade-ometer, achieving the intensity of sunlight, would produce an acceleration factor versus Florida of five times; seven and a half times compared to outdoors in central Europe. Tweedie et al. (1971) employed a hypothetical equivalence of five hours in xenon-arc machines to one day of summer sunlight.

Lastly, one may recall that Thomson (1967) noted that the approximate annual exposure on a horizontal surface outdoors in Rome, New York, and Madrid was about 160 ± 10 million lux hours (Mlxh) and that the average annual exposure on a gallery wall amounted to 1.55% of the exterior exposure. For an average gallery wall in London, Thomson estimated 1.5 Mlxh. With an average intensity of illumination of about 320 lux, an annual exposure of 1.1 Mlxh is not unreasonable (Feller 1964).

Numerous authorities have stressed the fact that it is not feasible to establish a fixed factor of acceleration for a given accelerated-aging exposure device. As well as with the light source and physical design of the exposure apparatus, speed-up factors differ with the specific materials being tested (Ketola et al. 1988), particularly when inhibitor systems are involved (Schaaf 1983). Nonetheless, figures such as these may be helpful in making rough estimates of potential speed-up factors.

Sharp Cut-off and Narrow-Band-Pass Filters

When a source of continuous radiation is employed, the effect of wavelength is perhaps most commonly studied by using a series of sharp cut-off glass filters. Major glass companies worldwide offer convenient series of such filters. The chief difference between an investigation using isolated (monochromatic) wavelengths and sharp cut-off filters is that the samples in the latter are essentially exposed to polychromatic radiation, that is, to all wavelengths above the cut-off. As mentioned in “Relatively Broad Regions of Sensitivity in the Ultraviolet” (page 65), this circumstance is close to the “real-life” situation in which protection is usually provided by ultraviolet-absorbing filters or additives. Andrady and Searle (1989) and Andrady et al. (1992) discuss some of the differences in the action effects that are observed when sharp cut-off filters are used instead of those induced by nearly monochromatic radiation. There is also another slight problem some cut-off filters can fluoresce (Mori 1961); examples are Corning glasses 3-71 (3385) and 3-72 (3387).

When one reads a technical report discussing “the effects of wavelength,” it is useful to check if the results reflect the use of monochromatic radiation or a series of cut-off filters. Appendix D describes in detail one way in which the effects of narrow wavelength regions can be determined when cut-off filters are used.

Narrow-band-pass filters, principally those of the interference type, have also been used to select particular wavelengths (Warner and Gruber 1966; Morand 1966; Kämpf et al. 1989). However, these generally result in low radiant power impinging on the samples. Some also may suffer from degradation by the ultraviolet (see "Photochemical Stability of Interference Filters," page 106).

Stress

Thus far, relatively little attention has been given in conservation science to the effects of physical stress in materials as a factor that can speed up deterioration. In his recent review, Crighton (1992:89) drew attention to the subject. Industry has long used stress to hasten deterioration and to aid in the prediction of useful life under conditions different from those used in test situations (Dubois and Hennicker 1960:474; Nguyen and Rogers 1987; Nelson 1990:71–75). Russian publications have dealt extensively with the subject (Regel and Vershinina 1973; Blank et al. 1981; Yusupova 1984; Popov and Zaikov 1987–1988; Rudakova and Zaikov 1988; Vettergren et al. 1989). Korsukov et al. (1973), for example, have reported that aldehyde groups are produced in polyethylene and polypropylene at an increased rate when stress is applied. The effect of stress may become important in the case of materials on exhibition, perhaps a textile hung or draped over a frame; the greatest rate of deterioration should occur where the textile, basket, or leather work experiences the greatest stress of bending or tension.

The reason applied stress leads to a more rapid rate of reaction is that mechanical tension contributes to chemical bond scission. The thermal energy of activation, E, is lowered by the potential energy of the stress, $\delta\ \sigma$. Thus, the familiar Arrhenius equation becomes:

$$k = k_0 \exp\ [-(\mathrm{E} - \delta\sigma) / \mathrm{RT}] \tag{7.1}$$

The durability time of the material, τ_p, is equal to the inverse of the rate, $1/k$, from which the Zhurkov equation is obtained:

$$\tau_p = \tau_0 \exp\ [(\mathrm{E} - \delta\sigma) / \mathrm{RT}] \tag{7.2}$$

$$\log \tau_p = \log \tau_0 + (\mathrm{E} - \delta\sigma)\mathrm{RT} \tag{7.3}$$

Thus, there is a linear relationship between the logarithm of the durability time and the stress, valid for the action of any mechanical force on any elementary chemical transformation, independent of its nature. This linear relationship usually holds, however, only over a limited range of stress, where the kinetics of the process is determined largely by a single elementary event (Emanuel 1980; Emanuel and Buchachenko 1987). It also does not hold at very low levels of stress (Rudakova and Zaikov 1988). Figure 7.3 shows such a relationship for nylon under ultraviolet radiation (Regel and Vershinina 1973). The Russian workers have extended these concepts to include the fast reactions with water and chemically reactive gases such as NO_2 on materials under stress.

Stabilizers sometimes have been found not to be effective when materials are used under stress (Regel and Vershinina 1973). If stress increases the orientation of polymer molecules, oxidation may also be retarded (Peeva and Evtimora 1984).

Experimental Strategies

Use of Several Levels of Severity

It is sometimes advantageous to place test materials at once under several levels of severity of exposure. For example, one can initiate testing in a xenon-arc Fade-ometer or on an exposure rack outdoors. If sufficient funds are available, an EMMAQUA apparatus can be used, affording eight to nine times as much irradiance as ordinary 45° south exposure. Such practice allows one to obtain a rough classification of materials quickly according to whether they are fugitive, excellent, or potentially intermediate in their stability. At the same time, testing can begin under ordinary or UVA fluorescent lamps. On the basis of the highly severe tests, it would be possible to estimate the time that will be required under the milder conditions in order to make a judgment concerning the most promising as well as the questionable intermediate materials.

If control specimens accompany sets of exposures under each condition of severity, they can also serve to indicate whether the different conditions of exposure yield a seriously different ranking of the test materials. "If more than one test is found to be valid, the harshest should be selected, since it will yield . . . the most rapid prediction of service life" (Bauer, Gerlock, and Dickie 1987:213).

One must not forget a matter of basic logic in a testing program: If a material succeeds in withstanding very severe test conditions, far better than a control of proven durability, it is highly probable that it will also behave better than the control under milder conditions. On the other hand, if a substance fails to meet an acceptable limit of durability under very severe conditions of test, this need not mean that the material would fail a test under milder conditions.

One must also not forget that the heating of samples under intense sources of light tends to reduce the moisture content of the samples to such a low level that the test is effectively not as severe as it would be if the light level were slightly lower and the moisture content higher (see Chapter 8).

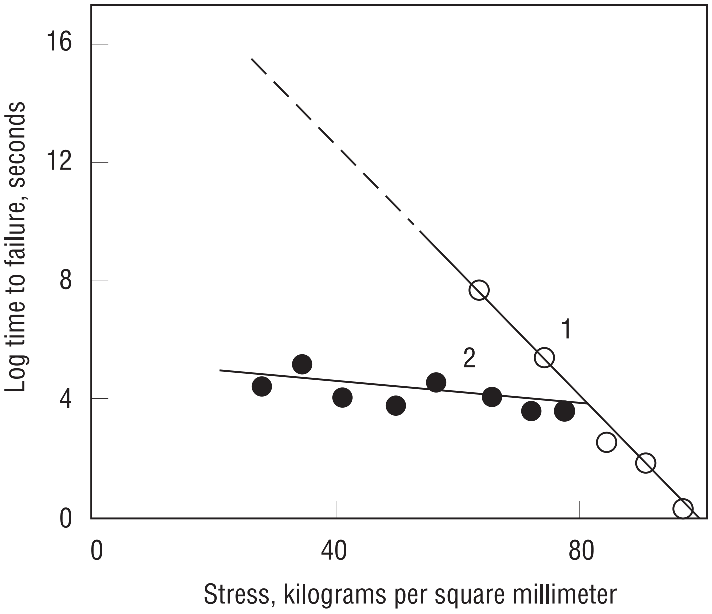


Figure 7.3. Influence of applied stress on the logarithm of the lifetime of nylon fibers under thermal aging. Curve 1 without irradiation. Curve 2 under the influence of ultraviolet irradiation (Regel and Vershinina 1973). Reproduced with permission of the publisher.

Turnaround Time

In carrying out evaluations of performance, if one waits until all the samples have failed before designing a new set of tests, it will take a long time to develop a successful formulation of materials or a satisfactory explanation of their behavior. If, on the other hand, it is possible to see in advance how the experiment is going to turn out, a new set of tests can be prepared and placed on exposure. Turnaround time refers to the time before one can initiate the next set of experiments to verify, modify, or confirm the results of the previous set. An efficient research program thoroughly recognizes this situation. The use of two or three levels of severity can shorten the turnaround time by eliminating the poorest performing samples and indicating those likely to exhibit intermediate stability.

Workers who have introduced the concept of probability of failure have addressed this important practical problem: Not all the samples need to fail if a curve for the probable instance of failure can be employed (Martin and McKnight 1985; Nelson 1990). Application of the Weibull probable-distribution function was discussed in Chapter 4 and shown in Figure 4.2.

Comparison of Property Changes Relative to One Another

One way to estimate whether one accelerated-aging procedure produces much the same effect as another, or whether much the same change occurs under natural aging as artificial aging, is to compare the rate of change of one aspect of the aging process, not with time, but with some other process going on in the material under test. Figure 7.4 presents early data, in which Egerton (1949) demonstrated that the relation of fluidity rise in silk (reflecting the decrease in molecular weight) to loss of tensile strength remained the same regardless of the presence of three different dyes. By comparing the change of hydroperoxide content with the amount of absorbed oxygen, Iring et al. (1978) demonstrated that raising the temperature from 130 to 140 °C did not change the relative rates of these two processes in polypropylene. Stransky et al. (1983) used this approach to show that temperatures above 270 °C caused a change in the mechanism of deterioration of phenolic molding compounds. Comparison of the rate of generation of alkali matter in cellulose with the number of bonds broken allowed Lee et al. (1985) to show that the ratio of the two processes during thermal aging differed considerably from that induced photochemically.

A variation of this approach would be to measure the changes in a given property with time and then use a computer-based matching program to see if the curve of change under one condition matched that under the other condition. This is similar to the procedure used by Simms (1987) in developing an accelerated shift factor (see "Arrhenius-Based Shift Factor," page 152).

Another interesting way to consider the similarity of degradation behavior under two different aging conditions is to plot the percentage change in original property against the *percent elapsed lifetime* (Barnett and Slater 1987). This, of course, puts a premium on determining the lifetime under each test condition.

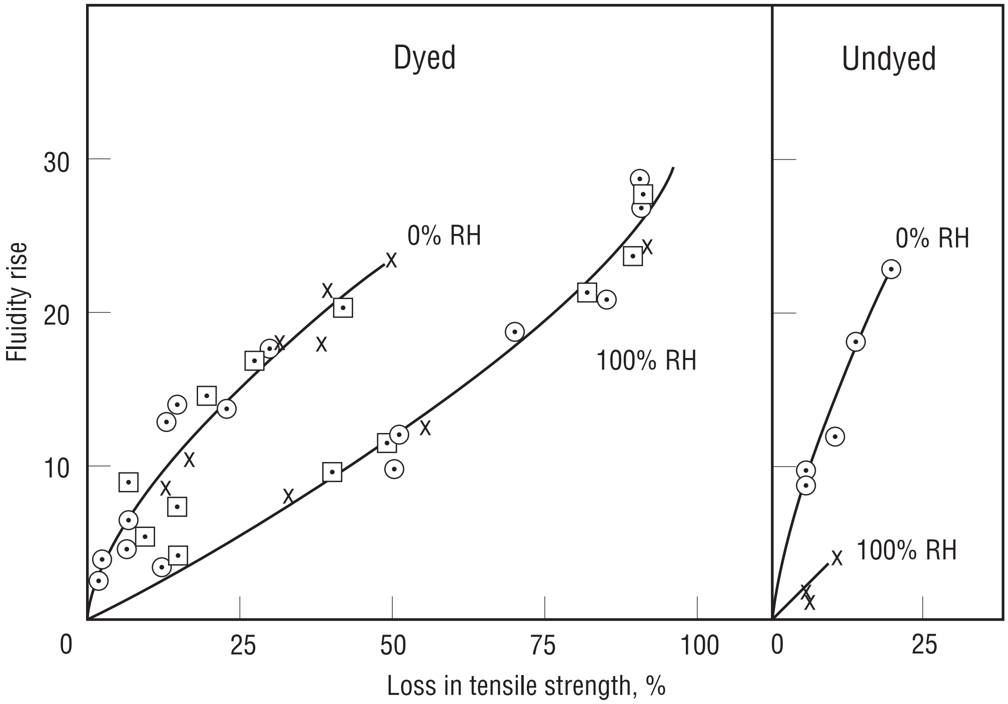


Figure 7.4. Comparison of the relative changes in two properties as a result of exposure to sunlight. After different periods of exposure, the fluidity rise of dyed silk, a measure of the decrease in degree of polymerization, is compared to the loss of tensile strength. The results indicate that the mechanism of failure was not seriously effected by the three dyes involved (Egerton 1949). Reproduced with permission of the publisher.

Special Considerations

Solarization of Glass Filters

When glass filters are exposed to the ultraviolet radiation emitted by xenon-arc radiation through quartz, the absorption in the 340 to 290 nm region decreases rapidly. The effect of 521 hours on the Pyrex glass outer filter in a 6000-W device, reported by Searle et al. (1964) is shown in Figure 7.5. Similar data have been published by Coblentz and Stair (1929, 1934) and by Capron and Crowder (1975).

Solarization affects the shortest (usually the most damaging) wavelengths, seriously altering their intensity during the normal lifetime of lamps. The change in intensity of wavelengths between 290 and 340 nm may require more careful monitoring than is often done.

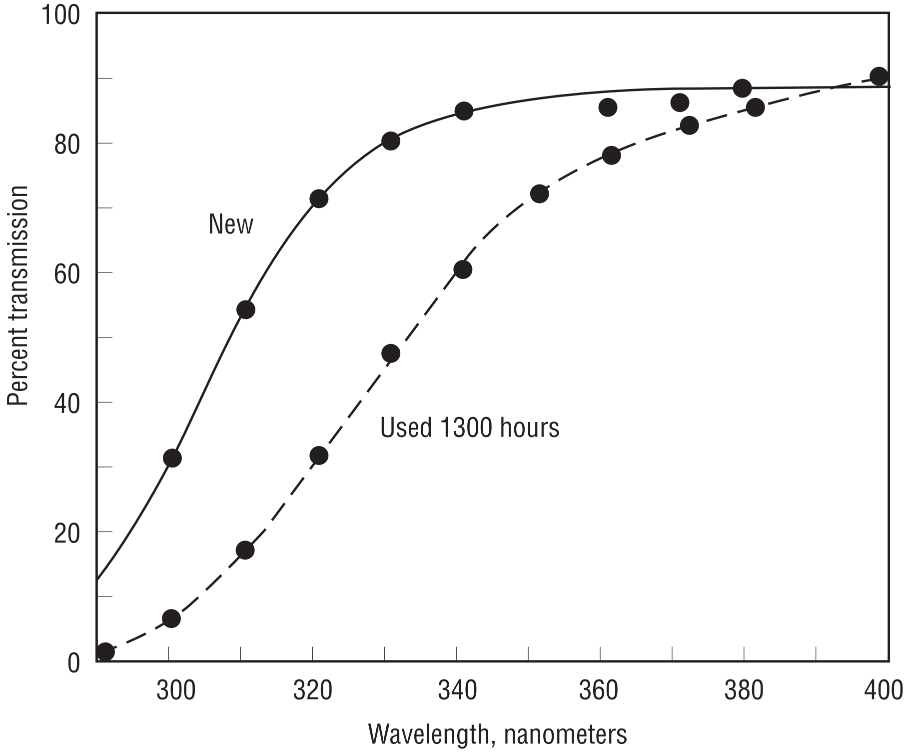


Figure 7.5. Solarization of glass. Transmission curves of new and exposed borosilicate glass outer filters. Xenon-arc source. Hirt and Searle (1967). Reproduced with permission of the publisher.

Fall-off in Emitted Intensity and Short Wavelengths

The intensity of xenon-arc lamps falls off with age. Data documenting this was cited in Feller's review paper of 1975. Commercial instruments now largely circumvent this problem by monitoring the intensity of radiation usually at some specific wavelength such as 340 or 420 nm. Thus, rather than in terms of clock hours, exposure in xenon-arc devices is regulated to a given number of milliwatt hours of irradiance at the monitored wavelength.

Because the intensity of the very shortest wavelengths also decreases, it is generally recommended that xenon-arc lamps be burned for at least 100 hours before they are used in an accelerated-aging experiment. The importance of these two factors is regularly referred to in reviews such as that of Kockott (1989).

If ordinary daylight-fluorescent lamps are used for accelerated tests, the modest percentage of ultraviolet radiation usually present in the radiation from such lamps is likely to decline with use as well as the general intensity and therefore should be monitored. However, few if any hard facts are available concerning this aspect of fluorescent lamp emission.

Thick versus Thin Samples

If the rate of deterioration is dependent upon the presence of oxygen, it is logical to find that the principal deterioration of specimens of yarn (McTigue and Blumberg 1967) and plastic (Adam et al. 1989; Minsker et al. 1982:461) takes place on the outer surface. In order to eliminate the situation in which the rate of deterioration is governed principally by the diffusion of oxygen, preliminary studies are regularly carried out on samples of decreasing thickness until a point is reached at which the measured rate of degradation is no longer affected by thickness.

The effect of sample thickness becomes of some importance when the course of deterioration is followed by measurements of infrared absorption bands by transmission. One cannot assume that the concentration of various absorbing groups is homogeneously distributed throughout a sample of greater, let us say, than 210 micrometers thickness (see Adam et al. 1989). Thickness and the role of oxygen diffusion are discussed further in Chapter 9.

Reversible Color Changes

Occasionally the discoloration of specimens apparently will be reversed following removal of specimens from exposure. This can pose a problem if samples are not measured either immediately or after precisely the same period of time following their exposure to heat or light. Perhaps the most frequently encountered problem occurs in the testing of paper products. It is well known that low levels of illumination in the laboratory can cause thermally discolored paper to bleach to a certain degree; exposed paper can also exhibit post-irradiation darkening (Lee et al. 1989). The same is true of thermally discolored drying oils (Tahk 1980). On the other hand, lignin-containing papers that have been exposed to light can darken when taken off exposure (Lee et al. 1989). It has also long been known that the fading of Prussian blue can be reversible.

An experimenter should check to see if the system under examination poses a significant problem in reversal, for this can influence the answer to the question of how much darkening or bleaching is the result of a given amount of exposure to heat or light (Morris et al. 1985).

In the darkening or intentional bleaching of oils and paper, both changes can go on at the same time. This would be particularly true if certain components reacted in one fashion and other components in another. The situation might also arise if the light source emitted both visible and ultraviolet radiation and these two wavelength regions induced opposite reactions. This happens in paper (Leary 1968) and, as a consequence, different aging results would be obtained if a narrow wavelength source or a polychromatic one (see also Fig. A.2) were used. If two essentially opposing reactions go on at the same time, the result after a period of accelerated aging will be the net effect of the equilibrium state between the two processes.

Photochemical Stability of Interference Filters

A problem that can be anticipated if one wishes to use narrow-band-pass interference filters is that the low wavelengths of ultraviolet radiation which one might wish to isolate by means of such a filter may be capable of degrading the adhesive used to adhere the two plates of the interference filter. To demonstrate this problem, Barr Associates of Westford, Massachusetts, kindly supplied several colorless quartz disks adhered together with two different types of epoxy resins. The 1-inch-diameter disks were exposed by being placed on a sheet of aluminum foil under a bank consisting of an equal number of UVA and UVB fluorescent lamps in a constant-temperature-and-humidity room (23 °C and 65% RH). The wavelengths involved are shown in Figure 6.7.

As especially prepared, one adhesive, type B, was designed to be used only for wavelengths above 320 nm. The results of exposing this type under window glass for a total of 300 clock hours is seen in Figure 7.6a. The most advanced exposure was estimated to be equivalent to about 600 mw/hrs/cm^2 of near-ultraviolet radiation. During this time the filter-system did not decrease in percent transmission by more than about 5 or 6% at wavelengths 320 nm and above. The cut-off wavelength of the adhesive in this system remained close to 290 nm.

In contrast, Figure 7.6b shows the decided change in the transmission characteristics of the quartz plate and adhesive type A during the 300 hours (about 1650 mw/hrs/cm^2) of exposure to the mixed radiation from UVA and UVB lamps. The loss in transmission is not a general one across the spectrum, but occurs principally in a band peaked at about 320 nm. Here the fall in transmission was about 55% at 320 nm and 37% at 280 nm. The cut-off point of the filter also changed during this time, from about 220 to 240 nm.

There are a number of sharp cut-off filters available that can enable one to study the effects of wavelengths in the region 315 to 400 nm. However, if one is particularly interested in investigating the effects of wavelengths lower than 315 nm, this may be the wavelength region that is precisely the most difficult to investigate with the use of interference filters. The adhesives used in fabrication may be deteriorated by the short-wavelength ultraviolet.

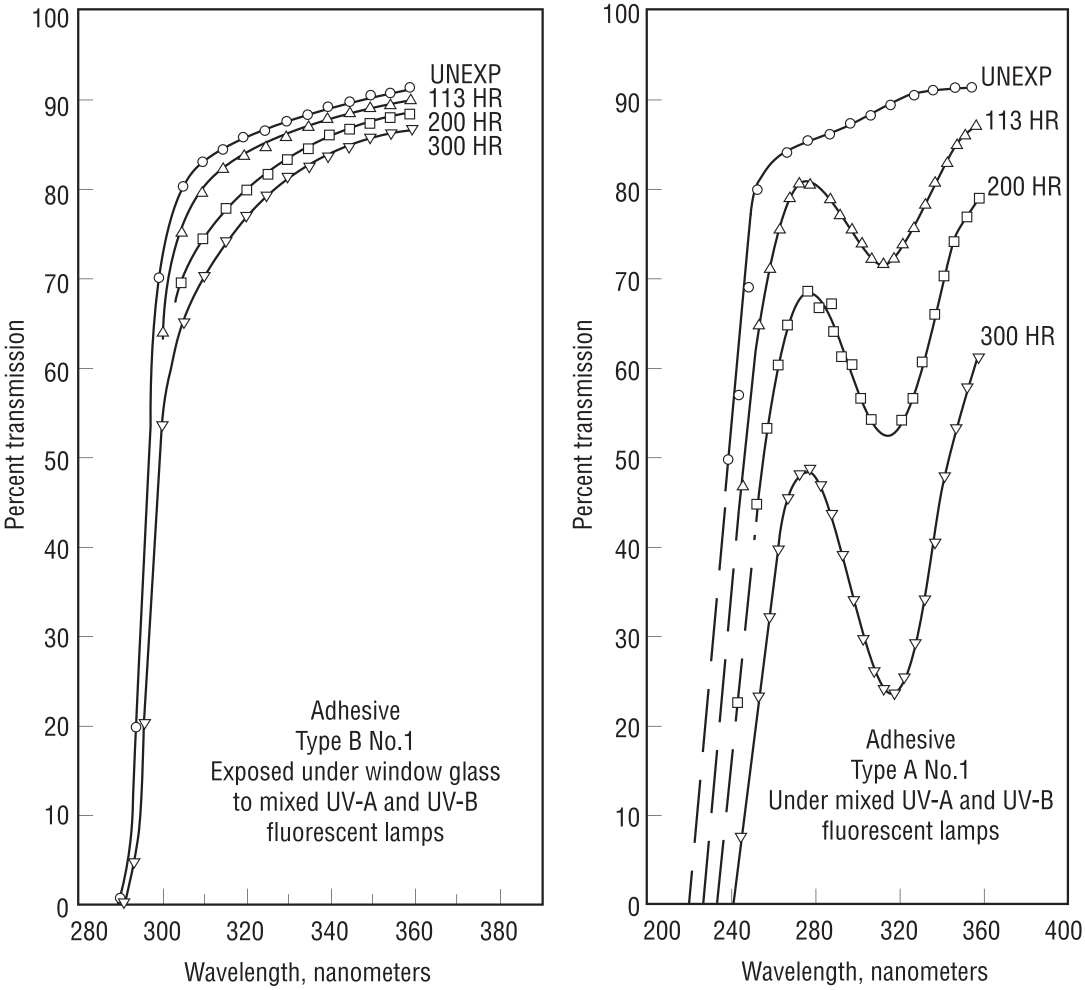


Figure 7.6a, b. Test of transmittance stability in two types of adhesives that might be used in fabricating interference filters. Quartz test wafers and adhesives courtesy of Barr Associates, Westford, Massachusetts.

The results were not surprising or unexpected. The test wafers, supplied by Barr Associates, were not interference filters but were special preparations involving two different adhesives that might be used in fabricating an interference filter, sandwiched between plain quartz plates.

Heat Effects During Light Exposure Tests

Sources of intense illumination commonly cause the temperature of test samples to rise. Therefore an experiment intended to study the effect of light nearly always introduces unwanted heat effects. Besides the obvious effects of heat (the Arrhenius relationship or the effects of second-order-transition temperature discussed in Chapter 10, there is usually a decrease in moisture content of the specimens. A simple method to demonstrate the gross effects of heat as opposed to light during exposure outdoors (as well as under an intense artificial light source) is simply to place a covered control sample either alongside (preferable) or behind an exposed sample. This is particularly useful in estimating the degree of protection of textiles provided by ultraviolet filters, for silk and linen can suffer loss of strength during accelerated exposure tests simply by thermal effects alone. Typical results are illustrated in Figure 7.7.

Experimentally, this potential problem has been circumvented in various ways:

1. Fluorescent lamps emit very little radiation in the infrared. The mild heating of the samples that results can be further diminished by blowing the air of an air-conditioned room or chamber across the samples. This can readily result in moderate sample temperatures of no more than 24 to 28° C.
2. For further cooling, samples on metal panchets can be fastened tightly (for good thermal contact) to the surface of a water-cooled block of metal. Another approach is to use a thermoelectrically cooled device (Padfield et al. 1984).
3. For testing paper, Launer (1940) built a water-cooled surface that had air holes passing through the device. By gently reduced air pressure, the test paper was drawn tightly against a water-cooled surface. When the paper was not cooled in this way during exposure in the Fade-ometer, it discolored. In contrast, when the paper was maintained at a temperature of 30 °C in this device, it bleached (Launer and Wilson 1949).
4. A simple way to expose samples at various values of relative humidity at a fixed low temperature is to expose them in a water- jacketed glass container having various humidity-controlling solutions in the bottom of the container (Cunliffe 1956, shown in Fig. 8.5).

Formation of Ozone by Ultraviolet-Emitting Lamps

As one prepares to evaluate the effect of particularly short wavelengths of ultraviolet radiation, the possibility of generating ozone must be considered. This chemically active gas, if generated, will seriously attack many organic materials, masking the purely photochemical effects (Cass et al. 1990).

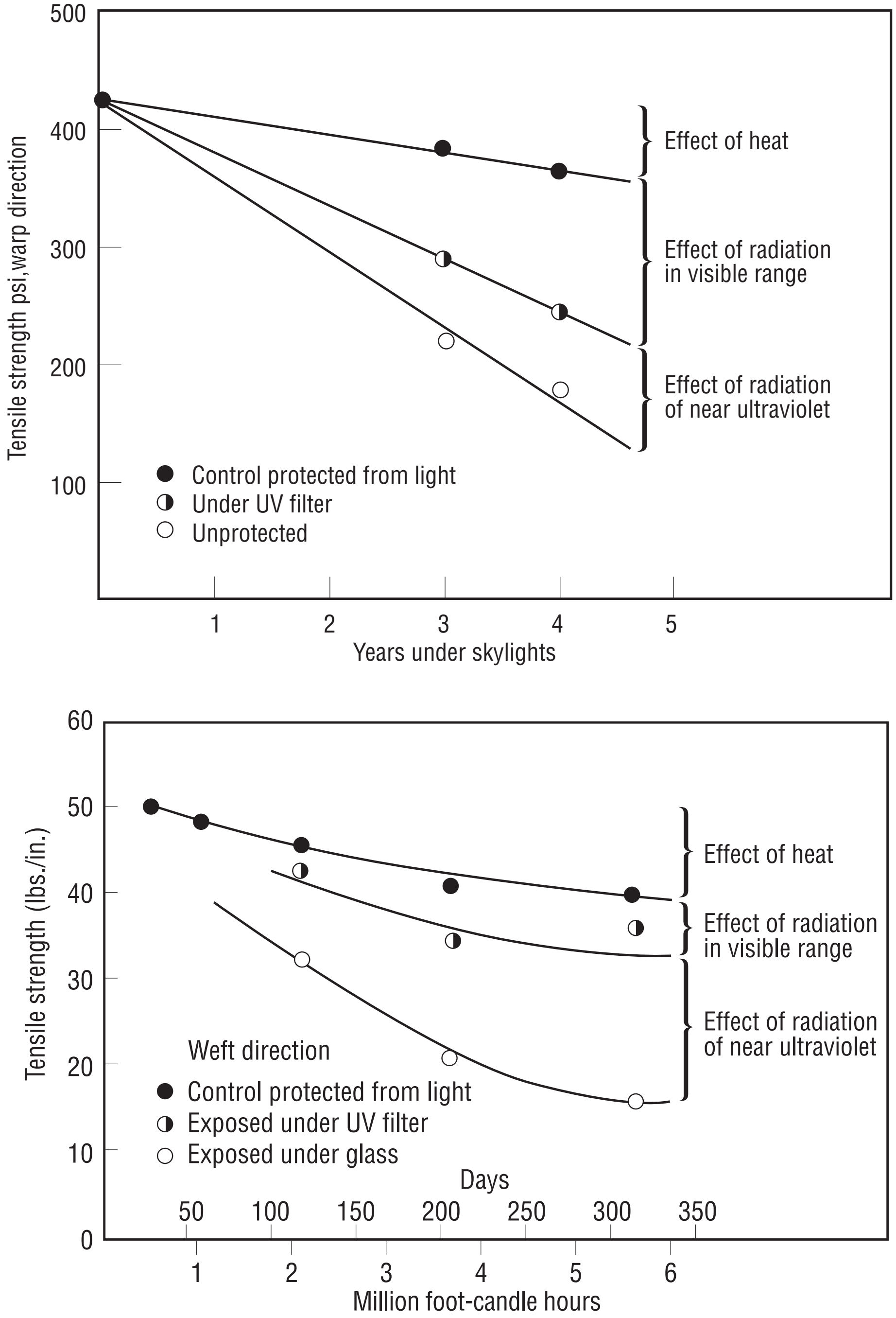


Figure 7.7a, b. Experiments regarding the loss of tensile strength of fabrics during exposure. The loss incurred owing to heat is shown for samples under identical exposure but protected from the light; (a) Raw linen canvas exposed to daylight under museum skylights; (b) Silk exposed to high output "daylight" fluorescent lamps at 85 °F and 30% RH.

Below what wavelength is ozone generated? Two different mechanisms for ozone formation have been proposed, one for radiation below 175 nm and another for radiation from 175 to about 210 nm. At the lower wavelength, dissociation of O_2 occurs. At the higher wavelengths, the reaction may be

$$(O_2)_2 \longrightarrow O_3 + O$$

$$O + O_2 \longrightarrow O_3$$

In a short course given by the Paint Research Institute at Battelle, Columbus (Ohio) Laboratories in May 1987, considerable discussion was given to radiation curing. An illustration in the syllabus (Fig. 7.8) showed the emission of an ozone-free Hanovia lamp. No wavelengths below 246 nm seem to be present, whereas a tail-off to about 210 nm appears in the so-called standard lamp. Freeman et al. (1990) state that 242.4 nm is the conventionally accepted threshold for the photodissociation of the ground state of oxygen, although a recent paper had reported that 248 nm laser radiation was able to produce ozone. Apparently wavelengths below about 242 to 248 nm should not be present if one is to avoid the generation of ozone.

Erythemal and Germicidal Effects of Ultraviolet Radiation

If one contemplates using wavelengths in the range of 313 to 270 nm for photodegradation studies, the *middle ultraviolet,* it is useful to review the wavelengths that cause germicidal effects and erythema (sunburn). The data in Figure 7.9 are taken from a brochure for ultraviolet absorbers published thirty years ago by Antara Chemicals Division of the General Aniline and Film Corporation. Superimposed are the emission curves for UVA and UVB fluorescent lamps. In the IES Lighting Handbook (Application, vol. 1981) there is a curve of erythemal effects which shows a very small efficiency in the wavelength region 325 to 410 nm (1 thousandth at 300 nm).

The germicidal, indicated by the shaded area, and the erythemal effects of UVB emission are peaked at about 300 to 290 nm. For this reason, radiation from UVB lamps should always be shielded from the room in which the experiments are being carried out and the lamps generally turned off when samples are to be added or removed. A pair of sunglasses should be placed next to the equipment, and a warning sign posted nearby.

It is evident that particular attention and protection should be given when UVB lamps are used, although the ordinary glass in eyeglasses apparently will provide some protection.

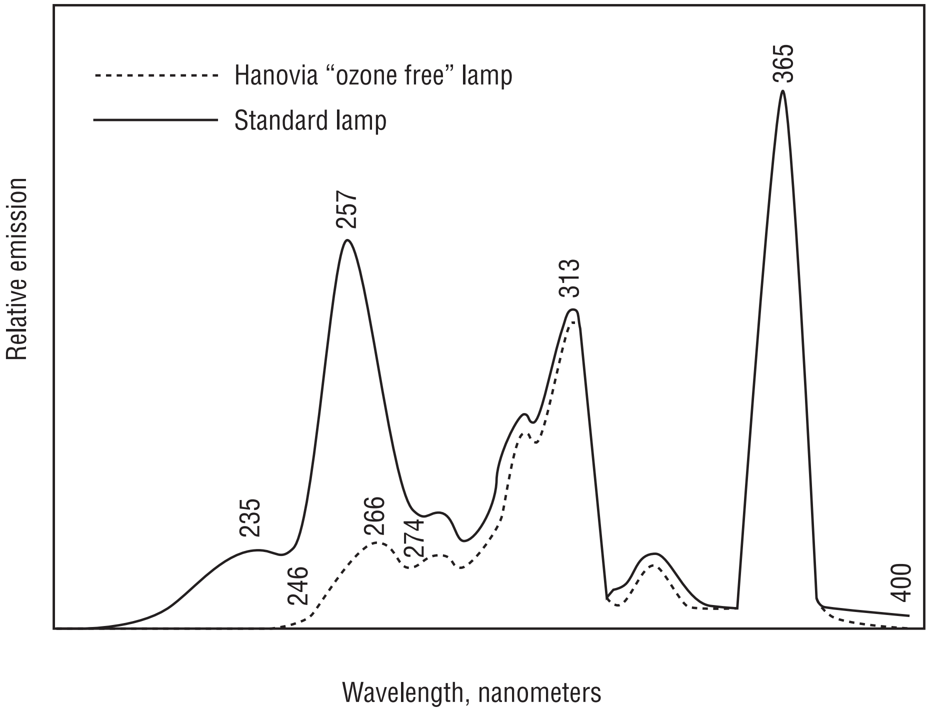


Figure 7.8. Emission of lamps used in UV-curing of coatings, showing characteristics of “ozone-free” emission. From syllabus from the Paint Research Institute Symposium on Photochemical Processes in Film Formation and Degradation, 1978.

Alternate Periods of Light and Dark

Many accelerated-aging tests expose samples continuously to lamp emission, whereas under natural conditions exposure takes place under alternate periods of daylight and darkness. Could the conditions of continuous exposure produce different results from those observable under alternating conditions? The answer is yes. Nonetheless, this aspect of testing under artificial sources of illumination has not been extensively investigated (see Wilhelm 1993:67).

There are several situations in which different results may clearly result. The first arises from the fact that an increase in sample temperature caused by intense illumination tends to lower the moisture content of samples. If the lamps are turned off periodically, there will be an opportunity for a regain in moisture. The result would be that, for a given number of milliwatt hours of exposure to alternating light and dark, the average moisture content of the samples would be higher than under conditions of constant illumination. Fading or other photochemical damage is often

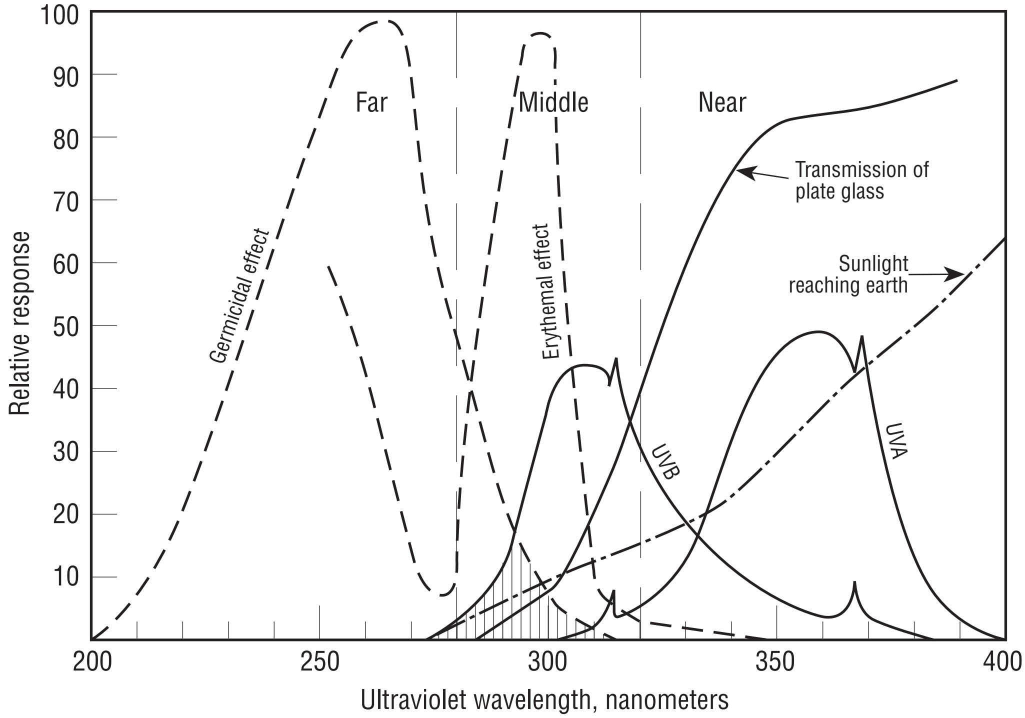


Figure 7.9. Wavelength response with respect to erythemal and germicidal effects in comparison to radiation emitted by UVA and UVB fluorescent lamps. Health hazard data from Antara Chemicals literature on Univul ultraviolet absorbers.

dependent upon moisture content. Henry Levison of the Permanent Pigments Company tested this possibility (pers. comm. 1975) and found, when alternate periods of light and darkness were employed, that the fading of alizarin lake and other artists' oil paints was indeed greater for a given number of footcandle hours of exposure to daylight fluorescent lamps. For routine tests, he settled on a schedule of eight hours on and four hours off (Levison 1976:38). Egerton (1947b) gives one of the earliest discussions of this problem.

If there is a "dark reaction" in any system then it should be obvious that alternating conditions will result in a different net degree of change. Another way in which alternating conditions can seriously affect the results is if expansion and contraction play an important part in the ultimate failure of specimens. As a very simple example, suppose one would wish to rate the durability of a reasonably tough coating such as a 50/50 copolymer of normal and isobutylmethacrylate in comparison to that of damar varnish. During continuous exposure in a carbon-arc Fade-ometer, the damar would remain plastic. Cracks that might form would tend to remain fused together under the heat of the arc lamp. If samples were removed after several hundred hours of continuous exposure, the acrylic and the damar might still appear rather glossy; microcracks in the damar might scarcely be noticeable. On the other hand, if the two coatings were evaluated side by side under glass outdoors, then in contrast to the acrylic the damar would soon become opaque due to extensive fracturing. Following a period of continuous exposure in the Fade-ometer, the marked increase in the brittleness of the damar with exposure would not be so strikingly revealed.

Simple Test for Ultraviolet Emissions

Often the question arises as to whether an ordinary fluorescent lamp emits significant ultraviolet radiation. A simple test to check this possibility, of course, would be to use a commonly available filter, Plexiglas UF-4. One can expose samples of textiles, resins, or colorants to a given lamp or lamp-filter combination both with and without being covered by the UF-4 filter. If less photochemical damage occurs under the ultraviolet filter then there must have been significant ultraviolet radiation in the illuminant. Prussian blue and alizarin lake in dilute mixture with titanium white can serve as convenient controls; their fading is influenced by the amount of ultraviolet. Care must be taken to have sufficient space between the surface of the sample and the UF-4 filter, one-quarter inch or more, to ensure that air and moisture can easily reach the material being tested so that the temperature of the covered samples will not be significantly higher than the uncovered. As mentioned earlier, this precaution needs to be taken when the effects of cut-off filters are being studied (Andrady et al. 1992).

A readily available filter for a related test would be ordinary window glass which cuts off radiation below about 315 nm. If there is any question as to whether significant radiation below 315 nm is present in an experiment, a filter of window glass can always be interposed. This was done by Dilks and Clark (1981) in studies of natural weathering.

Recently Prepared versus Aged Samples

A common practice is to test specially prepared samples rather than materials that have come down to us from the past (naturally aged). “Surrogate” samples are employed, partially because they are expendable and because they can be made with well-defined ingredients. However, it is well known that recently prepared coatings, for example, often increase in strength at first before their strength begins to decline with age. Initial behavior of many products can also be influenced by retained solvent or the presence of unreacted monomer. If an investigator is concerned that recently prepared and “aged” materials will behave much differently under accelerated-aging conditions, surrogate materials can be “pre-aged” in some manner to have reached a particular stage of deterioration before measurement of their rate or manner of aging begins. Recall that Vichutinskaya et al. (1982) thermally aged samples of polyamides to generate varying amounts of peroxide content before irradiation tests began (mentioned in “Polyamides,” page 86).

Summary

This chapter reviews a miscellaneous collection of matters that may concern someone about to undertake a program of accelerated photochemical aging. In answer to the perennial question concerning the shortest wavelengths of ultraviolet radiation regularly to be used to evaluate the aging characteristics that would occur under normal conditions encountered in a museum, archive, or library, the lowest wavelengths significantly transmitted by ordinary window glass are suggested, about 310 to 315 nm. Shorter wavelengths often speed up photodegradation, and may be appropriate to use in certain situations. Nonetheless, care must always be taken to learn whether the chemical processes induced by shorter wavelengths differ significantly from those that occur under normal conditions of exposure. Similar considerations must be given to exposures carried out under the increasingly popular fluorescent test lamps that emit only a limited range of wavelengths in the ultraviolet. As to the maximum speed-up ordinarily achieved by the use of xenon arcs or a system of mirrors designed to increase the intensity of sunlight, figures of seven to nine times above that of normal outdoor exposure to sunlight have been cited.

The behavior of materials under accelerated-aging conditions can be compared objectively to that which takes place under moderate conditions of aging by comparing a chemical or physical change that occurs under the severe conditions of exposure to another change taking place within the material, plotting the loss of molecular weight, for example, versus discoloration or oxygen uptake. The objective sought is to have the rates of the two processes occur in the same relationship relative to one another under both the mild and the more severe conditions. Owing to retained solvent or the under-curing of polymerizable materials, recently prepared surrogate samples may not age in exactly the same manner as those that have reached an advanced age under normal conditions of exposure. To minimize such problems, surrogate specimens are often preaged in some manner before testing.

8 The Effect of Moisture in Oxidative Degradation

Water plays such a major role in degradation chemistry that a separate section must be devoted to the subject. It is generally agreed that degradation will be speeded up by the presence of moisture. Nonetheless, Lemaire et al. (1991) take the position that "the chemical role of water in weathering is far from being understood."

Kamal and Saxon (1967) point out that water can have at least three kinds of effects important in the degradation of polymers. One is chemical: hydrolysis of the ester or amide bonds. The second is physical: loss of the bond between the vehicle and a substrate or pigment. The third is photochemical: generation of hydroxyl radicals or other chemical species (as per Eq. 5.5). A fourth influence could be the facilitation of ionization and the mobility of ionic entities, an important aspect of corrosion chemistry. Polymer formation by condensation reactions with loss of water can be reversed. Ester groups in cellulose acetate-butyrate polymers hydrolzye, yielding destructive acidity (Allen et al. 1987, 1988).

The effect of moisture should always be checked in conducting accelerated-aging tests because its significance can easily be overlooked. As mentioned many times already, the elevated temperatures traditionally employed in thermal-aging tests and achieved in samples exposed to high-intensity light sources tend to reduce the moisture content of samples to levels far less than would be present under usual conditions of aging. As a consequence, erroneous conclusions may be drawn concerning the predicted stability under normal conditions (Padfield et al. 1990). Graminski et al. (1979) note that, when the atmosphere was desiccated, little if any change in physical properties of paper occurred at temperatures between 60 and 90 °C. There are nonetheless notable examples in which increased levels of moisture have a negligible effect on the rate of deterioration; some of these will be cited in this chapter and in Appendix B.

Normal Response

Testing programs customarily consider the relationship of the rate of deterioration in relation to relative humidity (RH), the moisture content of air relative to the maximum possible content of water vapor in the air at the particular temperature and pressure. It is to be expected that the actual moisture content of a paper, textile, or plastic is the controlling factor, and that this would be controlled by the partial pressure of water vapor in the atmosphere. Some workers, therefore, consider their results to be more fundamentally significant if expressed in terms of the moisture content of the material under test.

The effective moisture content of materials rather than RH has long been recognized in terms of the perhaps inappropriately named "object humidity." This refers to the situation in which an object is exhibited under higher-than-normal intensity of illumination and, therefore, the materials are at a higher temperature than that of the ambient air in the immediate vicinity of the instrument used to measure the RH. In other words, it is the temperature of the object and the air in immediate contact with its surface that directly influences the moisture content of the object rather than the relative humidity, as one might normally measure the ambient conditions in the room or exhibit case in which the object is located. Martin and Gardner (1981) point out, nonetheless, that the inherent water absorption of materials is not in itself a good indicator of their potential long-term durability in moist environments.

Because moisture content is generally the result of an absorption process, the commonly encountered deterioration response to relative humidity is an S-shaped curve such as seen in Figures 8.1–8.3. The underlying reason for this behavior is the *absorption isotherm* as seen in Figure 8.4 (see also Cardamone et al. 1992:fig. 7). A mathematical expression for this response is known as the Freundlich absorption isotherm:

$$\frac{x}{m} = kp^{1/n}$$

where x is the mass of gas such as water vapor absorbed at pressure p by m grams of absorbing material; k and n are constants. Langmuir's absorption equation, based on theoretical considerations, is

$$\frac{x}{m} = \frac{k_1 k_2 p}{1 + k_2 p}$$

or

$$\frac{p}{x/m} = \frac{1}{k_1 k_2} + \frac{p}{k_2}$$

At intermediate pressures, Langmuir's equation gives much the same results as the Freundlich (Glasstone 1946).

Irregular Response

The response of cellulose to decreasing moisture content does not diminish monotonically but instead goes through a minimum at about 0.8% moisture content (DuPlooy 1981). At this point the absorbed moisture is zero and the only water remaining is the so-called *bound water*. Further reduction of water content begins to eliminate the bound water and this generally leads to an increased rate of deterioration. Graminski et al. (1979) also state that the minimum occurs because a portion of the water in cellulose is chemically inactive—the bound water fraction. Hon (1975) has pointed out that below a water content of 5–7%, the opportunity to form free radicals is reduced.

This correlates with the minimum point for the loss of molecular weight in cotton exposed in a carbon-arc Fade-ometer (Daruwalla et al. 1967).

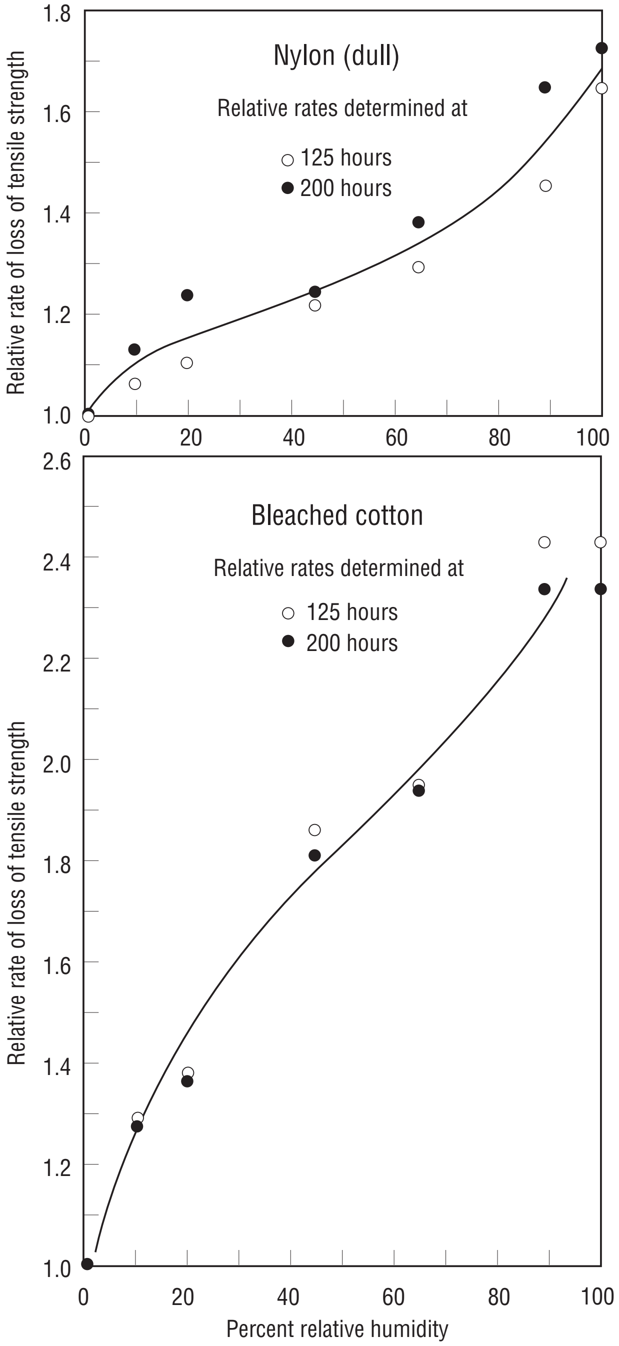


Figure 8-1a, b. Loss of tensile strength of (a) nylon and (b) bleached cotton yarns in relation to relative humidity upon exposure to MBTF (mercury-tungsten fluorescent) lamps. Based on the data of Shah and Srinivasan (1978).

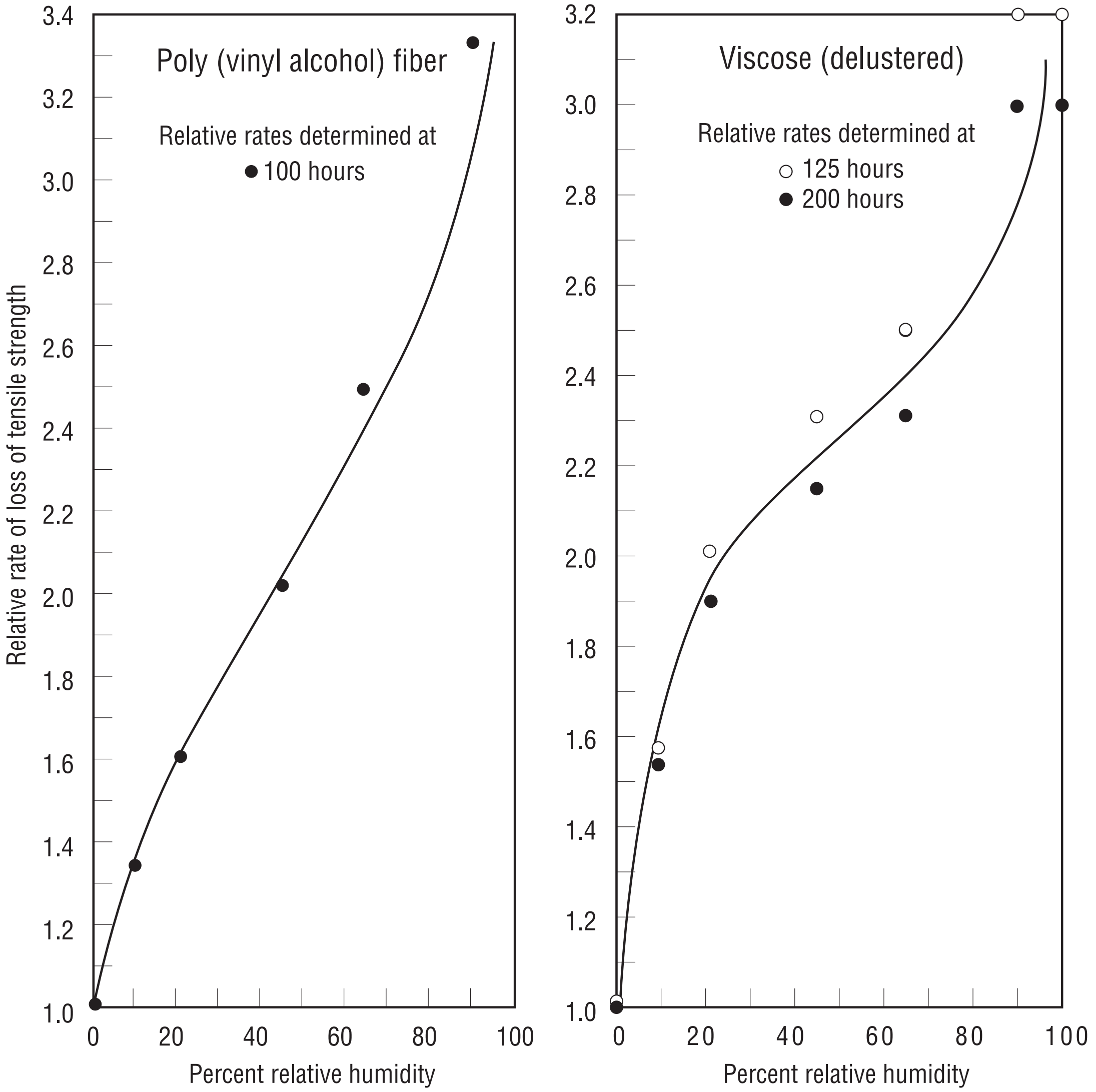


Figure 8.2a, b. Loss of tensile strength of (a) poly(vinylalcohol) and (b) viscose yarns in relation to relative humidity upon exposure to MBTF (mercury-tungsten fluorescent) lamps. Based on the data of Shah and Srinivasan (1978).

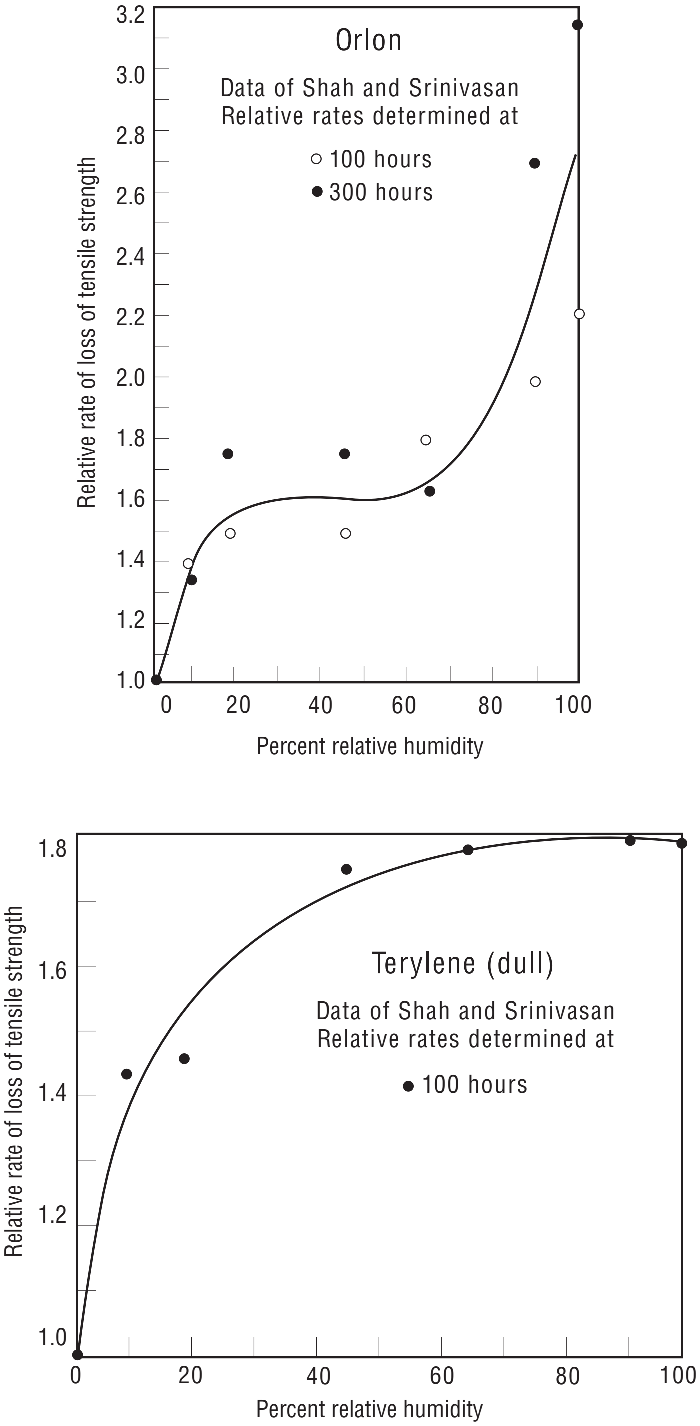


Figure 8.3. Loss of tensile strength of Orlon and Terylene yarns in relation to relative humidity upon exposure to MBTF (mercury-tungsten fluorescent) lamps. Based on the data of Shah and Srinivasan (1978).

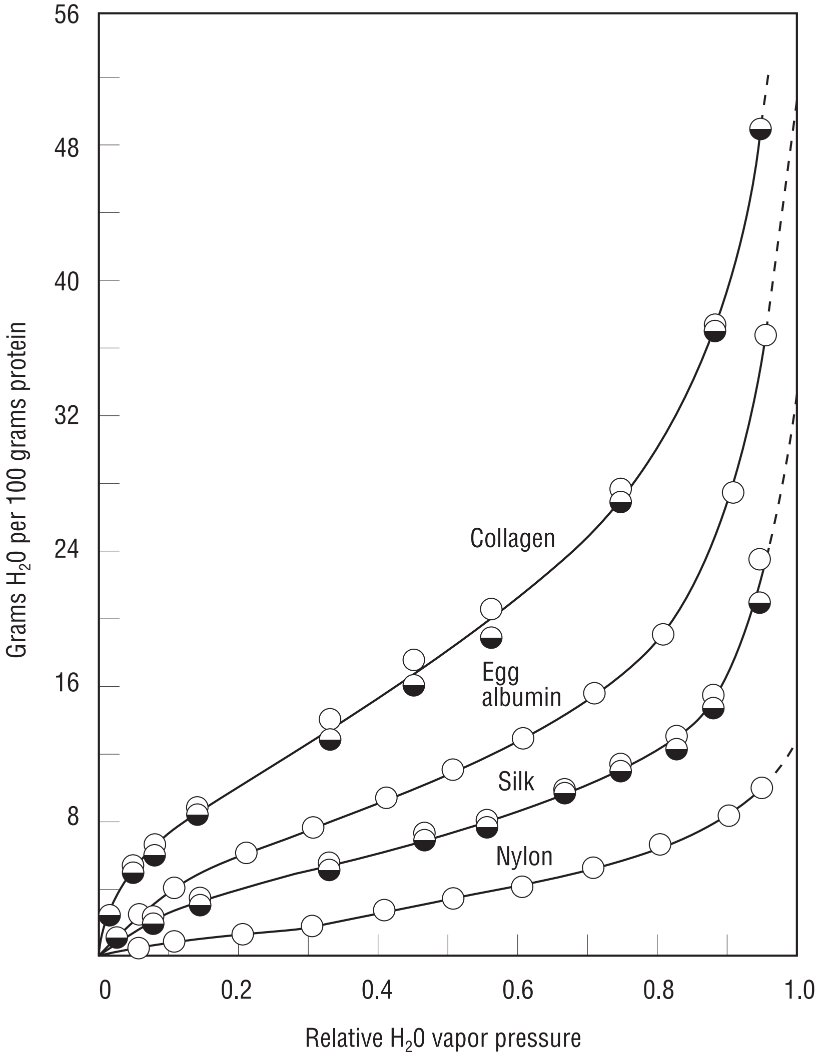


Figure 8.4. Adsorption isotherms of several materials, showing typical S-shaped response (Bull 1944). Reproduced with permission of the publisher.

Discontinuities relative to RH may also be encountered in certain situations where salts that form hydrates are present, perhaps in testing certain cements.

Negligible Influence of RH

Instances in which one would expect hydrolysis to be a major mechanism of degradation have sometimes proven otherwise. For example, immersion of nylon 6,6 in water at 40–60 °C for 30 to 60 days results in considerable loss in strength. Yet, at 100 °C, little loss is observed, possibly because of the diminution of oxygen in the boiling water. Supplemental tests have confirmed that the degradation is not purely hydrolytic since it does not occur in the absence of oxygen (Mikolazcuski et al. 1964).

The photo-oxidation of acrylic coatings cross-linked with urethane has been found to be relatively independent of humidity in contrast to acrylics linked with melamine (Bauer 1987; Bauer et al. 1986). "In the photodegradation of wool humidity is a relatively unimportant parameter" (Holt and Waters 1985). The fading of disperse dyes in poly(ethylene terephthalate) has been reported to be relatively insensitive to relative humidity (Giles et al. 1974); also the fading of gamboge in poly(vinylacetate) (Bailie et al. 1988).

References can be cited in which moisture appears to have little effect or even a retarding effect in photodegradation. However, in many such instances, it will be found that the exposure involves the very short wavelengths emitted by mercury-vapor lamps. Reference to two such examples appear in Tweedie et al. (1971). Essentially, short wavelengths induce photolytic processes, initiating free-radical reactions that need not involve an H_2O molecule. Perhaps the best-known example is the historically important study of Launer and Wilson (1949) on the deterioration of paper by 254 nm as compared to that by near-ultraviolet radiation.

Behavior at 0%, 100%, and Intermediate Values of Relative Humidity

The traditional way to test the effect of water vapor has been to place samples in sealed tubes in which either a drying agent such as phosphorous pentoxide or a few milliliters of water were placed in the bottom to achieve conditions of 0% or 100% RH, respectively. This was the procedure used in some of the earliest studies of dye fading (Chevruel 1847). The assumption is generally made that 0% RH has been achieved. Nonetheless, a question will remain as to whether all of the absorbed moisture has been removed or whether, as pointed out in "Irregular Response" (page 116), 0% RH results in the rate that would not be the same as that extrapolated from behavior at higher values of relative humidity.

On the question of 100% RH, Calvini (1987) has emphasized the fact that there can be differences in behavior between situations that principally involve absorbed water vapor, and situations that involve water in the condensed (liquid) phase. If the latter occurs, contact with water may cause leaching and cracking effects that lead to distinctly different results than that which would occur when only the absorption of water vapor were affecting behavior (Abeysinghe et al. 1982). The desire to test objects under the two extremes, 0% and 100% RH, can thus pose certain practical problems that are often not controlled or defined unambiguously.

Maximum Increase in Photochemical Deterioration, 0–100% RH

It may be useful to suggest, in a qualitative manner, some maximum changes in rate of degradation that have been observed between 0 and 100% RH. The extensive information developed by Shah and Srinivasan (1978) on the effects of relative humidity on the phototendering (embrittlement) of undyed fibers (Figs. 8.1–8.3) are summarized in Table 8.1. Seven yarns were exposed to the mercury-tungsten fluorescent (MBTF) lamps in a Microscal light-fastness tester. The percent loss of tensile strength after various exposure times and at various values of RH were reported. To prepare the data for Figures 8.1 to 8.3, the losses were calculated relative to the loss of strength at 0% RH. The results are much as expected: an S-shaped curve similar to the isotherm for the absorption of water by many substances. The response of terylene is the exception.

The typical S-shaped data illustrate key aspects in the attempt to answer the question, How significant is RH in accelerated photochemical aging? One can ask: What is the maximum effect? There is also a second question: How significant to photochemical damage are slight variations in RH under experimental or typical room conditions at moderate temperatures and humidities?

Yarn	Approximate "Maximum Increase": Increase in relative rate of TS loss 0% vs. 100% RH	Aproximate rate increase 0% to 20%	"Humidity Sensitivity Index": Approximate rate increase for a change of 10% (in range of 20–80%RH)[a]
Orlon	270%	56%	4.4%
Terylene (dull)	180% (2.7X)	55%	2.5%
Nylon (bright)	220%	20%	6.0%
Nylon (dull)	170%	15%	4.1%
Cotton (bleached)	240%	40%	8.8%
Viscose (delustered)	300%	92%	5.7%
Poly(vinylalcohol) fiber	300%	60%	11.7%

a.
$$\frac{\text{Rel. Rate at 80\% RH} - \text{Rel. Rate at 20\% RH}}{\text{Rel. Rate at 20\% RH}} \times 100 = \text{Change (from 20 – 80\% RH)}$$

$$\frac{\text{\% change}}{6} = \text{average increase for 10\% rise in RH in the range 20 – 80\% RH (Humidity Sensitivity)}$$

Table 8.1. Rates of tensile strength (TS) loss of various yarns exposed in Microscal Tester (summary of data from Shah and Srinivasan 1978).

The answer to the first question is to consider some differences in rates observed between 0 and 100% RH as reported in the literature. The numbers depend, of course, on the change being measured (dye fading, fiber tensile strength loss, or loss of polymer molecular weight) as well as the specific dye or polymer and its physical form. (As noted, the fading of many dyes on wool is not particularly sensitive to humidity.) Cunliffe (1956) reported that the average ratio of rates of fading of twenty-nine dyings on wool between 32 and 100% RH amounted to 1.6 at 25 °C and 2.5 at 60 °C. Experiments on the fading of six traditional fugitive colorants were carried out by Kühn (1968); between 25 and 65% RH, the rates of fading increased 3.1 ± 0.2 times at 20 °C and 2.7 ± 0.4 times at 30 °C as summarized in Table 8.2. The loss of tensile strength of silk dyed with Cibanone Orange R when exposed to sunlight for eight days was 4.1 times greater at 100% than at 0% RH (Egerton 1948); dyed cellulose acetate yarns lost tensile strength four to seven times faster (Egerton 1949). Dyed nylon yarns proved to be less sensitive to loss of tensile strength at high RH than dyed silk yarns (Egerton 1947a).

An increase in the rate of deterioration between 0 and 100% RH as high as 11.6 times was predicted for loss of DP in cellulose triacetate films at 21°C on aluminum (Allen et al. 1988); an increase of sixteen times for cotton containing the photosensitizing pigment zinc sulfide (Egerton 1949) and ten times for viscose delustered with titanium dioxide (Egerton 1947a). These high values, however, may be exceptional.

To obtain 100% RH, a few cubic centimeters of water are customarily placed in the bottom of a container in which the samples are sealed. The Oddy (1973) test is a valuable, simple procedure of this type, particularly for detecting the corrosive action of materials on metals (Blackshaw and Daniels 1978; Hnatiuk 1981). There are, however, questions that can arise concerning the relevance of information gained from such a procedure regarding the behavior of organic materials. In attempts to attain 100% RH using sealed tubes, as Calvini (1987) pointed out, one may have condensed water present rather than saturated vapor. An indication of the difficulty in being certain of measurements made at very high values of RH can be seen in the Shah and Srinivasan data for bleached cotton and delustered viscose (Figs. 8.1b and 8.2b): The experimentally measured changes at 90 and 100% RH are reported to be the same. It is difficult to control and to measure relative humidity in this range. Nonetheless, if not too much stress is placed on the test conditions having been precisely 0 and 100%, a useful indication of the possible maximum effect of RH is perhaps in the range of three- to ten-fold.

	From 25 to 45%	From 45 to 65% RH	From 25 to 65%
at 20 °C	2.78 ± 0.20	1.11 ± 0.04	3.09 ± 0.21
at 30 °C	2.33 ± 0.27	1.16 ± 0.07	2.70 ± 0.40

Colorants cast as water colors in gum arabic: magenta (rosaniline, fuchsine), archil, Brazil wood, saffron, yellow Persian berries lake, green Persian berries lake.

Table 8.2. Increase in fading rates with RH six fugitive watercolors under OSRAM Universal-white fluorescent lamps (data from Kühn 1968).

If one examines this question from the point of view of someone carrying out accelerated photochemical aging tests, it can be seen that the major increase in rate occurs in the transition between 0% RH to some modest level of moisture (Table 8.1). This is particularly significant in the case of materials that are notably hygroscopic. It would appear logical to recommend that "some moisture should be present" in all accelerated photochemical aging tests. There are, after all, some processes that fail to take place at all unless moisture is present. The photochemical activity of titanium white is a familiar example (Kämpf et al. 1978). Bansa and Hofer (1989) suggest 65% RH and 80 °C for the testing of paper (further discussed in "Relative Humidity in Accelerated Aging of Paper," page 126). Tentatively one can suggest at least 20–25% RH.

Behavior under moderate conditions may be considered as that occurring in the region from 20 to 80% RH. Here, the increase in absorption and the rates of many photochemical processes may be nearly linear with increases in RH. The last column in Table 8.1 shows that, for the six most sensitive yarns, the response generally amounts to an increase in the rate of photochemical damage of between 2.5 and 11.7% for an increase in 10% RH; the average is 6%. This aspect concerning the effect of relative humidity on the fading of the traditional pigments, carmine lake, gamboge, alizarin lake, and Vandyke brown, has been discussed by Bailie et al. (1988). The authors defined a humidity sensitivity index (HSI) as the increase in rate of fading for an increase of 10% RH in the range 40–60% RH. For the four pigments in a poly(vinylacetate) vehicle, these values were 11, 0, 22, and 11%, respectively.

Information about the behavior in this central region of the isotherms is useful in estimating the effects of small changes in the humidity level in a museum environment, or in an accelerated-aging test situation in which the relative humidity is poorly controlled (Wilhelm 1993:89, fig. 2.26).

Reactions Proportional to the Concentration of Water

If the presence of water is so important in many processes of deterioration, examples of rate equations of the character

$$k = k_1 + k_2 [H_2O]$$

or

$$k = A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT} [H_2O]$$

should be known. This is exactly the equation proposed by Auerbach (1989) for the combined thermo-oxidative and thermo-hydrolytic loss of tensile strength of nylon and Kevlar. Similar equations were suggested by Golovoy and Zinbo (1990) for the hydrolytic breakdown of polyarylate resins and by Martin and Gardner (1981) for poly(butylene terephthalate). The equations of Auerbach and the latter authors are in one sense "general," useful for predicting the effects of both temperature and humidity on the rate of deterioration. Using similar equations, Sebera (1988) has suggested the development of a series of "isoperm" (isopermanent) curves in which temperature could be plotted versus relative humidity along lines calculated to represent equal rates of deterioration.

Since the equilibrium moisture content can be shown in many cases to be related to relative humidity (RH), we find the relationship often expressed in terms of either RH or moisture content such as in Golovoy and Zinbo's graph showing

$$k = 1.02 \log \text{(equilibrium water concentration)}$$

where k is the specific rate constant for polyacrylate molecular weight degradation. Martin and Gardner's equation for predicting quarter lifetimes is similar. Graminski et al. (1979) used both RH and the partial pressure of water vapor in plotting their degradation data. Borman (1982) plotted half lifetimes against the partial pressure of water vapor, deriving an equation that related partial pressure to relative humidity and temperature in degrees Kelvin:

$$\log p_{H_2O} = 8.951 - \frac{2259}{T} + \log \text{(RH)}$$

Because the general absorption isotherms tend to be S-shaped, there will usually only be a limited range of humidity, generally the middle, over which a linear relation with RH may hold. Thus, if one looks carefully at Borman's figures 1 and 2, the data, which extend over more than a decade of partial pressures, appear to be slightly curved rather than linear as the authors suggest.

Relative Humidity in Accelerated Aging of Paper

There has long been an argument as to whether a moderate level of moisture is necessary in the accelerated thermal aging of paper. One of the most extensive investigations into this question has been carried out by Bansa and Hofer (1989). In evaluating the behavior of a wide variety of papers, the authors clearly demonstrated that aging, being the net result of many overlapping and mutually influencing chemical processes, was not uniformly accelerated with increasing temperature and humidity. Their findings led to the recommendation to employ conditions of 80 °C and 65% RH. Twenty-two naturally aged papers of various types and dates of manufacture were tested and their moisture content measured at temperatures between 50 and 95 °C and 50 to 75% RH. The moisture content over the range of 50–80 °C and 50–65% RH was about 6 ± 1%. At 95 °C the level was not quite one percent lower.

Lee et al. (1988) suggested that the many conflicting reports on the effect of beating upon the subsequent stability of pulps could be accounted for by the different results of thermal aging under dry versus moist conditions.

There have been even fewer studies made on the influence of humidity in photochemical aging of paper. However, some basic data have recently been provided by Jeon and Block (1990). They were able to show that humidity had little effect on the photochemical loss of tear strength at room temperature. As the temperature increased in the range 50–56 °C, however, humidity became increasingly important. The thermal energy of activation for photochemically initiated loss of strength was determined to be between 12.8 and 10.9 Kcal/mole, far below the energy of 26 to 28 Kcal/mole reported for thermally induced loss. The rate of photochemical aging thus proved to be much as theory would suggest: relatively insensitive to the effects of temperature.

Past research on the role of moisture in the natural and accelerated thermal aging of paper could be reviewed at length. The problem is still being actively investigated (Shahani et al. 1989). The present consensus is that a moderate level of moisture is advisable in accelerated photochemical or thermal aging tests.

Regulation of RH During Experiments

A time-honored way of obtaining different levels of RH under which to conduct experiments is to use various saturated salt solutions. The concentration of water vapor in equilibrium with such solutions is constant, dependent upon the temperature. The apparatus used by Cunliffe (1956), shown in Figure 8.5, is typical of this experimental procedure. Golovoy and Zinbo (1990) used saturated solutions of KI, NaCl, $CaSO_4$, and K_2SO_4 to obtain values of 56, 73, 87, and 95% RH, respectively, at 100 °C. The International Critical Tables provide data from which such information can be obtained [see also ASTM (1992) standard E 104-85].

A more refined technique is to pass the air through chambers filled with water at a constant temperature. Gray (1977) gives the temperature of the water and the temperature of an oven from 90 to 40 °C that will result in approximately a 5% moisture content of paper under test. The approximate RH of the air in the oven when it has been thus saturated is also given.

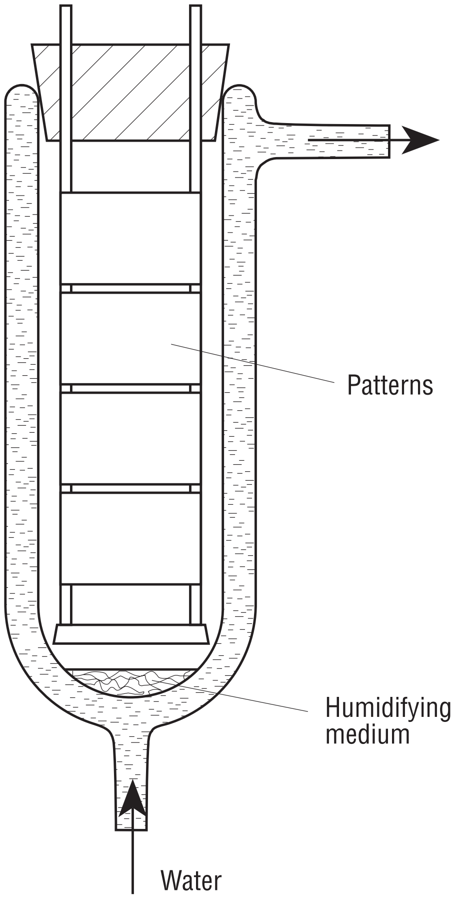


Figure 8.5. Simple apparatus for exposing samples to different levels of relative humidity and temperature (Cunliffe 1956). Reproduced with permission of the publisher.

If the volume of air surrounding the specimens is rather large, and there is no forced circulation within the sealed vessels, care must be taken that the level of humidity throughout the chamber has reached its equilibrium value before photochemical exposure is done. Care must also be taken that substances emitted during exposure and confined by the enclosed chamber do not affect the rate of deterioration. The latter is discussed further in Chapter 10.

Permeability to Water Vapor

This extensive and intriguing subject will not be considered here. Remarks regarding the permeability of protective coatings have recently been made by de la Rie (1992). Kimball and Munir (1978) report a study of the change in permeability of three types of polymers as they age during exposure to xenon-arc radiation filtered by Pyrex glass.

Influence of Temperature and Humidity on Corrosion of Protected Metals

Although the primary focus here is on organic materials, also of concern is the search for general principles regarding the influence of temperature and humidity on deterioration. In 1980 an empirical correlation had been noted between the rate of corrosion of protective-coated metals and the *sum* of RH plus the Centigrade temperature: RH + t. A theoretical explanation of the reason for this relationship has since been published (Cuddihy 1987). The basic equations are well known and the mathematics simple.

The importance of this general principle governing corrosion time in metals is that, once the relationship has been determined for a particular system, accelerated-aging tests can be carried out at any temperature and RH and the behavior under those conditions predicted.

Summary

The chemical substance water can participate in the processes of deterioration in a number of ways: physical, photochemical, and hydrolytic. The presence of water facilitates ionization, an important aspect in the corrosion of metals. Examples can be found in which the rate of deterioration is directly proportional to the equilibrium concentration of water. In other cases, moisture has little effect. Instances are also known in which the hydrolysis of bonds, thought to be the principal process of degradation in a polymer, did not take place in the absence of oxygen. The diversity of these possible modes of action has led authorities to assert that the role of water in weathering remains far from being understood. The action of moisture in deterioration, difficult to predict, must be verified in each specific situation.

9 The Role of Oxygen

Jellinek (1967) had this to say in introducing the subject of oxidative degradation:

> Oxidation has to be studied from various angles before a probable mechanism can be formulated. Thus oxygen uptake, peroxide formation or formation of other groups such as carbonyl groups, production of volatiles, main chain rupture, cross-linking, reactions of polymer side groups, action of inhibitors, etc., have to be investigated. The physical state of the polymer is also of importance: thus different results are obtained whether the polymer is crystalline or amorphous, or below or above its softening point . . . it is essential to know the fundamental mechanism of oxidative degradation in the absence of u.v. light in order to understand what is happening in the presence of ultraviolet radiation and oxygen.

The abundant supply of oxygen in the air, amounting to approximately 21% by volume, is involved ubiquitously in the oxidative deterioration of organic materials. When a deterioration experiment involving thin films is carried out in the open air, the concentration of oxygen available to the reactants effectively remains constant. As a consequence, its role may not be apparent. There are, however, three principal ways in which the role played by oxygen can be disclosed. The first is simply by exposing the samples under an atmosphere of pure oxygen and then comparing the behavior under this circumstance to that in a vacuum or an inert atmosphere such as nitrogen. Early workers, Chevruel (1847) and Russell and Abney (1888), investigated the fading of pigments and dyes in this manner. In a slightly more elaborate variation, samples can be exposed to known mixtures of oxygen and nitrogen or other gases of interest. The second approach would be to follow the consumption of oxygen either by its change in volume or pressure. The third involves the use of pressures of oxygen higher than normal. These three modes of investigation will be discussed at some length below.

Deterioration in the Presence or Absence of Oxygen

By exposing samples in an inert atmosphere or vacuum to high temperatures or to ultraviolet and visible radiation, one can learn if changes occur under these circumstances and of what type. If certain bands in the infrared disappear or at least are diminished upon exposure to visible or near ultraviolet in a vacuum, this is evidence that photolytic changes are taking place, reactions that do not involve oxygen. In this manner, irradiating ethylene-propylene polymers at 313 nm under nitrogen, Li and Guillet (1984) were able to show that this wavelength led to photo-induced decomposition of peroxide groups in the polymer and that this in turn led to the breaking of chains. Geuskens (1982) showed earlier that, under vacuum, 365 nm radiation would not photolyze the hydroperoxide groups. In another application, Tahk (1980), by carrying out an experiment under helium, was able to demonstrate that the bleaching of scorched paint by ultraviolet light is enhanced by the presence of oxygen. In recent years, Lemaire and his associates have exploited to great advantage the technique of exposing samples both in a vacuum and in air in the analysis of mechanisms of deterioration (Lemaire et al. 1991).

Should the investigator be concerned primarily with thermal degradation, marked changes that occur in an inert atmosphere provide evidence of *pyrolytic* deterioration, thermal processes that do not involve oxygen. It is often useful to be able to state, in conducting an accelerated-aging test, that "none of the changes observed [under the particular conditions of temperature or irradiation] were due to pyrolytic or photolytic processes."

If slight changes are noted in the earliest stages of exposure in an inert atmosphere or vacuum, these can be due to traces of oxygen that may still be present. However, when the changes persist beyond an initial period, continuing practically throughout a course of exposure, then the evidence for photolytic or pyrolytic changes becomes rather convincing.

Varying Ratio of Oxygen to Inert Gas

As mentioned, an elaboration of the above approach would be to follow the rate of deterioration while varying the ratio of oxygen to nitrogen or other gases of interest. An example of what can be learned from this is seen in Appendix C Figure C.4. Here the relative significance of the key step is demonstrated, the step in which hydroperoxide radicals attack the principal organic compound undergoing deterioration. As discussed in Appendix C, if this key reaction is very fast, lowering the amount of oxygen in the atmosphere will lower the rate of deterioration significantly (Bateman and Morris 1953). However, if this reaction is slow, the concentration of oxygen would have to be reduced to extremely low levels in order to reduce the rate of deterioration effectively.

Arney et al. (1979) demonstrated that similar responses take place in the fading of artists' colorants. A measurable rate at 0% oxygen indicated the existence of a purely thermal process of fading, separate from the role of oxidation. Their analysis of degradation into two aspects, oxidative and purely thermal, was also applied to the discoloration and loss of tensile strength of paper (Arney and Jacobs 1979, 1980).

Kenjo (1980) reports an interesting situation in which a trace of oxygen (5%) is useful to prevent cinnabar, litharge, and sienna from being reduced if storage under an inert atmosphere is contemplated.

To follow changes in the infrared spectra of polypropylene during thermal degradation, Stivala et al. (1963) passed nitrogen and oxygen through U-tube bubblers at different flow rates in order to obtain the required mixtures of the two gases. Kämpf et al. (1978) developed equipment in which the atmosphere surrounding samples could be precisely controlled as well as the character of the illumination. This device was used to great advantage in their studies on the nature of chalking of paint vehicles by titanium white pigments. They found that chalking did not occur in the absence of either oxygen or moisture. Webb et al. (1982) describe a much smaller controlled environmental chamber in which the atmosphere surrounding a sample coated on an attenuated total infrared reflectance surface could be varied during exposure to ultraviolet.

Measurement of the Consumption of Oxygen

The consumption or uptake of oxygen can be measured directly by connecting the reaction chamber to a calibrated-buret-type manometer. One of the simplest of this type of apparatus was used extensively by Shelton and his coworkers (1946, 1953, 1954) in their investigations of the thermal oxidation of rubber. Hawkins et al. (1959a, b), at Bell Laboratories, also made extensive use of similar equipment (Fig. 9.1). In the same basic apparatus, Shelton and Cox (1954) used mixtures of oxygen and nitrogen to study the effect of decreasing the partial pressure of oxygen. Mesrobian and Tobolsky (1947) initially employed much the same system to measure the consumption of oxygen during photochemical degradation. An equally simple apparatus is described by Vachon et al. (1968) in their study of the effect of pH on the thermal degradation of nylon in solution. More sophisticated systems, such as that described by Tabankia et al. (1985), are now regularly employed.

Measurement of the consumption of oxygen is particularly successful in systems that exhibit a marked induction time followed by an abrupt increase in oxygen uptake as in the Bell Laboratories' testing of polyethylene insulation containing carbon black (Hawkins et al. 1959a, b; 1971). The end of the induction time frequently marks the end of the useful properties of a polymer system (Grieveson et al. 1961). A sharp increase in the rate of oxygen consumption often is also an indication that the concentration of an inhibitor has fallen to an ineffective level (Vink and van Veen 1978).

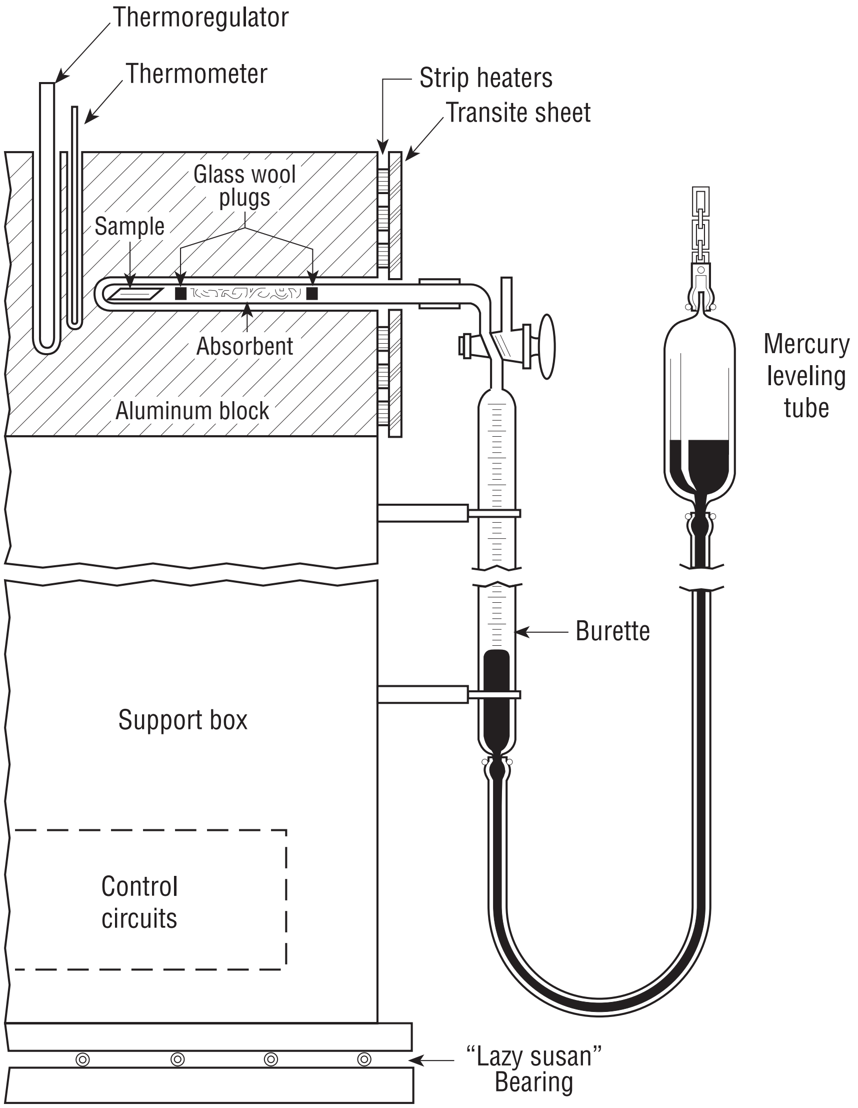


Figure 9.1. Simple type of apparatus used for measurement of oxygen uptake during thermal aging (after Shelton and Winn 1946; Hawkins, Matreyek, and Winslow 1959).

Less abrupt changes also yield valuable information. Shelton and Winn (1946) detected three stages in the uptake of oxygen by GR-S rubber. After the absorption of just 10 ml of oxygen per gram of hevea gum stock heated at 90 °C, Shelton et al. (1953) found the tensile strength of rubber had been reduced to a minimum. Grattan, in studying the consumption of oxygen in various modern artifacts made of poly(vinylchloride) and acrylonitrile-butadiene-styrene, observed uptakes of about 4 to 40 cc per gram (David Grattan, pers. comm. 1992; Grattan 1993). The consumption of as much as 80 ml of oxygen per gram of polymer was monitored in the Bell Laboratory studies as well as in the earlier investigations of Mesrobian and Tobolsky (1947).

Rose and Mayo (1982) point out that oxygen absorption can have certain limitations. They found it unsuitable for making lifetime predictions for polypropylenes, and one may assume other polymers, when they contained different types of stabilizer systems; loss of physical properties could occur at widely different levels of oxygen uptake. For example, an efficient peroxide decomposer might permit considerable absorption of oxygen before embrittlement of the polymer. The effectiveness of inhibitor systems can also vary with the intensity of illumination and the thickness of the samples (Faulkner 1985).

A key practical problem to be taken care of in using oxygen-uptake equipment is the absorption of gases such as CO_2 and water vapor. These frequently are given off during degradation with the result that the decrease in the volume of oxygen will appear less than is actually the case. Shelton and Winn (1946) used calcium oxide for this purpose; Hawkins, Hansen, Matreyek, and Winslow (1959) and Boss and Chien (1966) used a Linde Molecular Sieve. Major (1958) employed an elaborate absorption system in which the quantities of H_2O, CO_2, and CO evolved were measured during the heating of paper at 170–200 °C.

Arrangements can also be made to circulate the oxygen within the apparatus through an absorbing column. In this manner, CO_2, CO, H_2O, and other components emitted during degradation can continually be removed from the oxygen. To accomplish this, Mesrobian and Tobolsky (1947) modified their original apparatus. Hernandi (1976) has described commercial equipment available in eastern Europe that circulated the oxygen through absorbents while also monitoring the decrease in its volume.

With a buret filled with mercury or other suitable fluid, as in Figure 9.1, there is the need to adjust the level of the reservoir periodically in order to measure the volume accurately and to maintain the degradation under reasonably constant pressure. A simple hand-cranked windlass to raise the leveling bulb is illustrated by Osawa et al. (1978). It was not long, however, before adjustment of the level in the buret was automated; Mesrobian and Tobolsky (1947) did so in the second version of their apparatus. The Goodrich Research Center developed a computer-programmed controller capable of monitoring the consumption of oxygen in a set of four burets (Krueger 1973). A twenty-eight-station device was eventually automated. Grieveson et al. (1961) took an interesting approach. They measured the increased voltage across a nichrome wire partially immersed in a column of mercury. The consumption of oxygen caused the level of the mercury to fall, exposing an increasing length of the nichrome wire, whereupon the increased resistance was measured.

In an early paper, Horrobin et al. (1946) describe a device in which the temperature of the sample being exposed to light was controlled by a surrounding volume of water, the light beam travelling down a tube, much as in a telescope, striking the exposure chamber located near the bottom. The tube and exposure chamber were thoroughly jacketed with water except for the surface upon which the sample was placed, facing the light. As noted, highly sophisticated systems in which sample temperature and surrounding atmosphere can be changed at will have been described by Kämpf et al. (1978) and by Tabankia et al. (1985).

When short wavelength ultraviolet radiation is used in such experiments, a manometric fluid other than mercury is often substituted. This guards against the possibility that traces of mercury vapor may be photoactivated and initiate unwanted reactions (Grassie and Weir 1965). Horrobin's group used tetralin; Grassie and Weir, dioctylsebacate.

The decrease in pressure can also be monitored. Rasti and Scott (1980) used a change in pressure to follow the thermal and photochemical oxidation of linseed oil as influenced by verdigris and vermilion. Grassie and Weir (1965) describe a sensitive differential pressure device that could measure the absorption of 1.9×10^{-5} millimoles of oxygen, approximately one molecule of oxygen per molecule of the styrene polymer under study; the sample size was only 5 mg. Working on a volume of only 0.04 cm^3, Bigger and Delatycki (1987) devised an adaptation of this apparatus which relied on a differential pressure transducer.

One of the fundamental drawbacks of measuring the change in pressure is that the rate of deterioration often varies with the partial pressure of oxygen (Wilson 1955). Moreover, trapped decomposition products can influence the course of reaction. As a result, measurements of the change in pressure have not been extensively employed. Rose and Mayo (1982) found that their apparatus was not reliable over long periods of time.

One can also monitor the change in the concentration of oxygen, particularly in mixtures with argon or nitrogen, by determining the two components by gas chromatography. This procedure was employed by Rose and Mayo (1982) and most recently by Grattan (1993). A wide variety of atmospheres and degradation products can be so monitored (Wlodarezak 1988).

Higher Than Normal Pressure of Oxygen

Scientists have long been fascinated by the possibility that a useful increase in the rate of deterioration can be obtained by higher-than-normal partial pressures of oxygen. Shelton and Cox (1954) found that the consumption of oxygen by vulcanized Hevea and GR-S rubbers containing oxidation inhibitors obeyed the following empirical equation with respect to the partial pressure of oxygen, P:

$$k_2 = \alpha\,(1 + \quad 1 + \beta p) + \sigma p \tag{9.1}$$

Here α, β, and σ are constants and k_2 the steady-state rate of oxygen consumption. The authors proposed a mechanism and kinetic scheme that explained the derivation of this relationship. Stivala et al. (1963) made a similar detailed kinetic analysis regarding the thermal oxidation of polypropylene. In contrast to Equation 9.1, Grieveson et al. (1961) found that the induction time in their study of Ziegler polyethylenes was related to the reciprocal square root of the partial pressure of oxygen.

To carry out thermal degradation under pressures above one atmosphere, use has long been made of stainless steel pressurized containers, the so-called Parr bombs that have customarily been employed in the destructive oxidation of materials for the purpose of elemental analysis. However, as mentioned, problems caused by acidic and other degradation products can be encountered under such “sealed tube” conditions. Nonetheless, Faulkner (1982) reported that an oxygen pressure of 4.4 atmospheres successfully speeded up the deterioration of polypropylene 3.6 times faster than aging in air at 60–90 °C. The energy of activation in air and at high partial pressures of oxygen proved to be the same, thus suggesting that the same reactions took place under either condition.

Shlyapnikov et al. (1987) use heating times to failure at high oxygen pressure to predict the failure at normal oxygen pressures of polymer systems that exhibit decided induction times.

Influence of Sample Thickness and Oxygen Diffusion

In thick samples, the rate of oxygen consumption may not be related to its nominal concentration in the surrounding atmosphere. Instead, consumption may be limited by diffusion of oxygen into the interior of the test material (Fukushima 1983). It is a regular practice, therefore, to run tests on a series of samples of decreasing thickness until the measured rate per gram of sample—in terms of oxygen absorbed or any other property observed—is no longer influenced by sample thickness (or weight of sample if the length and width are held constant); Shelton and Winn (1946) provide an example of this practice. The limiting thickness is governed by the rate of reaction with oxygen relative to the rate of its diffusion to the reaction site (Boss and Chien 1966; Furneaux et al. 1980–81).

Because reactions initiated by ultraviolet and short wavelength visible radiation are likely to be more rapid than thermally initiated reactions, it is usually the case that samples need to be much thinner for photochemical aging tests than for thermal (Cunliffe and Davis 1982). This general circumstance is further supported by the fact that the diffusion of oxygen is likely to be greater at the higher temperatures customarily employed in the thermal degradation studies; hence, thicker samples can be tolerated at higher temperatures.

The energy of activation for diffusion is on the order of 10 Kcal/mole while that of thermally induced chemical reactions is likely to be 20 Kcal/mole or higher. The result is that the critical thickness will not remain the same as experiments are carried out at increasingly higher temperatures (Wilson 1955). Blum et al. (1951), for example, developed Arrhenius plots showing the effect of temperature on both the limiting diffusion rate and the overall rate of oxygen uptake in rubber, using a set of samples that varied in thickness from 0.01 to .08 inches. Over this range, the sample thickness at which the rate became free of the diffusion limitation differed, depending upon the temperature as well as the type of rubber.

Partially because light is absorbed as it passes into a material and because of the diffusion problem under discussion, photochemical damage is largely confined to the outer surfaces of moderately thick samples (recall Fig. 5.2) (Schoolenberg and Vink 1991). For such reasons, Singleton et al. (1965) suggest that the surface-to-volume ratio of fibers and yarns and the yarn twist should be similar when different chemical types of fibers are to be compared. A number of authors have developed data such as seen in Figure 9.2 that show the changes in the concentration of photodegradation products with depth within the sample. The results of Furneaux et al. (1980–81) regarding both naturally and artificially aged polyethylene particularly come to mind. Lemaire and his colleagues have used microspectrophotometry to develop such profiles based on thin slices taken from exposed materials (Adam et al. 1989; Jouan et al. 1989; Fromageot and Lemaire 1991).

Cunliffe and Davis (1982) present theoretical calculations of the depth profile of deterioration across the thickness of samples, showing the zone in the interior in which deterioration proceeded at a much lower rate owing to "oxygen starvation" (Thomson 1978). In other words, the potential rate of deterioration under the particular conditions of temperature and irradiation is greater than the rate at which oxygen can diffuse into the interior. Cunliffe and Davis especially discuss the implications during outdoor exposure. Billingham and Calvert (1980) provide a detailed discussion of the conditions under which the effects of oxygen diffusion become important in the thermal oxidation of polymers. In a reference already cited, Müller (1983) discussed in detail how the depth of deterioration in high-density polyethylene differed between xenon-arc and outdoor exposure.

Giles et al. (1972b) describe a simple set up and experimental design that permitted comparisons to be made between the rate of fading of dyes and the permeability of various vehicles. Differences in apparent fastness of the dyes was attributed in many cases to a lower rate of diffusion of oxygen in the more crystalline textile fibers.

Oxidative Induction Time Analysis

The induction time or the time-to-failure of materials that have been on exposure is often noticeably shortened over that of an unexposed control sample. This observation can be used to monitor the progressive extent of aging of many materials. Shlyapnikov et al. (1987) refers to this procedure as a "combined test": determining the time-to-failure of unexposed material upon accelerated thermal aging and monitoring the properties of the naturally aged material under the same accelerated thermal aging. Kramer and Koppelmann (1987) call the procedure a "residual lifetime" test; Cope and Revirand (1982–83) call it "residual thermal stability."

Because thermal aging has principally been used to monitor residual lifetime, further discussion of the concept is taken up in the following chapter.

Otey (1986), studying the weight loss of poly(vinylchloride) at 185 °C under both nitrogen and oxygen, defines an "oxidative induction period" as the time when the loss of weight under oxygen becomes 1% greater than the loss under an inert atmosphere, nitrogen. The thermo-oxidative induction time is thus defined as the point at which the rate of thermally induced weight loss under oxygen significantly differs, as just defined, from that under nitrogen. By measuring the decrease in induction time that resulted from changes in formulation or in length of exposure outdoors, Otey was able to establish the relative stability of 10 mg samples of coatings taken from electrical cables. As well as monitoring the deterioration that took place during exposure outdoors in this manner, Otey also demonstrated that significant deterioration had taken place during a year and a half of storage.

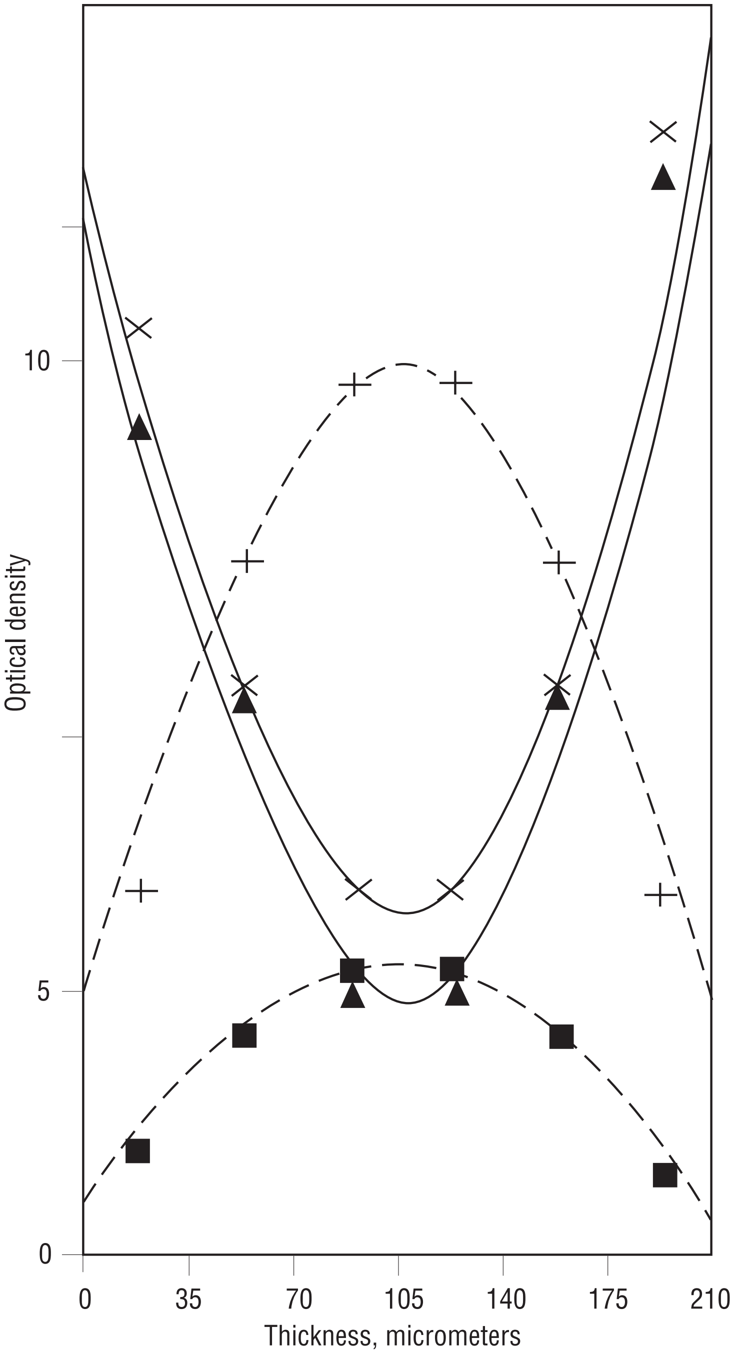


Figure 9.2. Concentration profile through butyl rubber exposed to wavelengths above 300 nm at 60 °C (SEPAP 12/24 apparatus):× hydroxyl photoproducts (absorption at 3440 cm-1);▲ carbonyl photoproducts (at 1716 cm-1);■ 1-4 cis double bond structure (at 740 cm-1);+1-4 trans double bond structure (at 968 cm-1). Jouan et al. (1989). Reproduced with permission of the publisher.

Hydroperoxides

The presence of oxygen commonly, although not invariably, leads to the formation of hydroperoxides (ROOH) through a reaction with hydrocarbon free radicals. (An excellent discussion of the role of peroxides in deterioration can be found in Grattan [1978].) This process is usually represented by the following equations:

$$R\bullet + O_2 \longrightarrow ROO\bullet \quad (9.2)$$

$$ROO\bullet + RH \longrightarrow ROOH + R\bullet \quad (9.3)$$

This sequence of reactions requires no light. The resultant hydroperoxides (ROOH) have a role either as initiators of further reactions or as intermediates (Allen et al. 1985). Hydroperoxides (sometimes simply referred to as peroxides) play a significant role as deterioration initiators through the reaction

$$ROOH \longrightarrow RO\bullet + \bullet OH \quad (9.4)$$

A second possible reaction,

$$RO\bullet + RO\bullet \longrightarrow ROOR \quad (9.5)$$

leads to the formation of true peroxides but these are usually present in lesser concentrations than ROOH. (An exception, at low partial pressures of oxygen, is discussed in Appendix C.)

The dissociation of ROOH into the two radicals, reaction 9.4, can be induced both thermally and photochemically. Adam et al. (1989) have reported hydroperoxides in polybutadiene, for example, to be unstable at 100 °C and reasonably stable at 60 °C. However, Kelen (1983: 111) has stated that saturated alkylperoxy radicals are quite stable below 300–400 °C. Transition-state metals, such as cobalt and iron, can also promote the dissociation of hydroperoxides into ROO• and RO• radicals at moderate temperatures. This process is briefly reviewed by Mills and White (1987) in their discussion of the drying process in linseed oil paints. It has been said that hydroperoxides absorb weakly up to 350 nm (Scott 1984). Carlsson and Wiles (1974) found that they can be photolyzed (Eq. 9.4) in polypropylene even at 360 nm, leading to the formation of "reactive radicals capable of cleaving the polymer backbone." The scission of hydroperoxides can also be induced through photosensitization by the presence of neighboring aromatic groups or carbonyls (Bousquet and Fouassier 1984; Ng and Guillet 1987).

Hydroperoxide groups form at many locations in a hydrocarbon, for example, at sites where a tertiary or a secondary hydrogen had been. The result produces hydroperoxide groups having varying degrees of stability (Allen et al. 1985). The consequence is that the maximum concentration of hydroperoxide attainable in thermal oxidation will vary in different polymers as will the steady-state concentration often observed in photo-oxidation. Lemaire et al. (1991) observed concentrations of 11 mmol per kg in one polyamide structure and as much as 60 mmols/kg in another. Wilt measured values as high as 800 mmols per kg in ethylhydroxyethylcellulose (Feller and Wilt 1990) but much lower amounts in ethylcellulose.

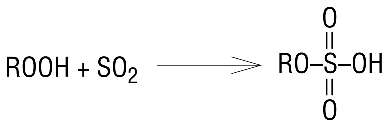
Detection of Hydroperoxides

At times the absorption at approximately 3400 cm^{-1} (hydrogen bonded peroxide OH) or at 3550 cm^{-1} (free hydroperoxides) in the infrared has been used as a measure of peroxide development (for example, Yano 1981), but, without experience, this practice is subject to ambiguities in interpretation.

Stoichiometric reactions with the ROOH groups provide a much more precise measure. The time-honored method of analysis of macromolecular hydroperoxide content in organic polymers is to dissolve the material in isopropyl alcohol or in a chlorinated hydrocarbon solvent and to then add sodium iodide and acetic acid. The liberated iodine can then be titrated with sodium thiosulfate (method used by Feller and Enke 1982; Feller and Wilt 1990). The intensity of the color of I_3^- can also be measured spectrophotometrically at 420 nm. Another approach is to put the materials into solution or cause the substance to be extensively swollen in 1,2-dichloroethane and to treat afterwards with ferrous ammonium thiocyanate solution (Adam et al. 1989). The ferric ammonium thiocyanate complex can then be analyzed spectrophotometrically [λ (max) = 512.5 nm, ε = 21000 mol^{-1} liter cm^{-1}]. The hydroperoxide concentration is calculated on the basis of the equation

$$\mathrm{ROOH} + 2\mathrm{Fe}^{2+} + 2\mathrm{H}^{+} \longrightarrow \mathrm{ROH} + 2\mathrm{Fe}^{3+} + \mathrm{H_2O} \qquad (9.6)$$

An interesting additional technique for peroxide analysis is to treat an oxidized polymer with SO_2. This reacts specifically with hydroperoxides as follows (Rånby and Rabek 1975):



$$\mathrm{ROOH} + \mathrm{SO_2} \longrightarrow \mathrm{RO{-}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}OH} \qquad (9.7)$$

The sulfate groups formed can be detected by infrared (Mitchel and Perkins 1967).

Exposure to SO_2 gas has also been used to completely eliminate hydroperoxides prior to other analyses of aged coatings (Dilks and Clark 1981; Allen et al. 1985). Richters (1970) heated polypropylene films treated with SO_2. The resultant decomposition of the alkyl sulfates yielded conjugated-double bond systems; the intensity of the color so developed served to indicate the extent of oxidative damage.

A method which warrants further study and development before its utility is fully understood is the "Russell effect" (Daniels 1984, 1986, 1987). This involves exposure of surfaces, exposed to light or abrasion, to especially sensitized photographic film that reacts as a very sensitive detector of peroxides and possibly other free-radical initiators that tend to produce peroxides. Another sensitive technique for detection of peroxides and free radicals is chemiluminescence (Monaco et al. 1982; Mendenhall 1990; Gromeck and Derrick 1993).

Summary

The direct breaking of chemical bonds in materials upon exposure to ultraviolet and visible light in the absence of oxygen is termed *photolysis*. This process is most commonly induced by wavelengths of ultraviolet radiation much shorter than those normally encountered under museum or archival conditions. There are also *pyrolytic* chemical changes that can be induced by high temperatures in the absence of oxygen. However, the type of change of principal interest with respect to the long-term stability of organic materials involves thermally or photochemically induced *oxidation*. Ways of detecting all three types of chemical changes have been noted. The role of oxygen can be disclosed by experiments carried out in its absence, by measurement of its consumption, or by observation of the effect of varying amounts of oxygen relative to an inert gas. In thick samples, the rate of diffusion of oxygen into the specimen can control the rate of deterioration in the interior of the material relative to the exterior. For this reason, precise studies of the influence of oxygen on rates of deterioration are regularly initiated by testing specimens of decreasing thickness until a dimension is achieved at which the rate is no longer dependent on the thickness of the sample.

10 Thermally Induced Oxidative Deterioration

Kamal (1970) states that "the highest temperatures to which a plastic material may be exposed outdoors (170 °F, 76 °C) do not supply sufficient thermal energy (70–90 Kcal per mole) to cause bond cleavage in commercial polymers. Thus, although temperature is important as a rate-controlling parameter in many of the degradative processes (e.g., oxidation and hydrolysis), polymer degradation by pure thermal energy is not a critical factor in weatherability studies." Purely thermal degradation is often called *thermolysis*, *thermolytic*, or *pyrolytic* degradation; oxygen is not involved. However, in speaking of thermal aging tests, rather than such reactions, one usually has in mind thermo-oxidative deterioration; that is, reactions induced by thermal energy in the presence of and with the participation of oxygen but in the absence of visible and near-ultraviolet radiation.

In such tests there is always a question concerning whether water partakes in the process, whether water is absolutely necessary for a particular reaction to take place. Unfortunately, in the practical world of thermal accelerated-aging testing, it has often been the case that the concentration of water in the system is not monitored. Instead it is usually allowed to seek some ill-defined level dependent upon the temperature of the sample or physical system and upon the condition of humidity in the ambient atmosphere. The role of water has been discussed in Chapter 8.

In precise studies, a distinction has been made between three processes: purely thermal (pyrolytic), thermo-oxidative, and thermohydrolytic degradation (for example, Philipp et al. 1969). These aspects of deterioration can be isolated by carrying out studies under a vacuum (or inert gas), in oxygen (or air), and in the presence or absence of water vapor. Such practice can lead to valuable insights. For example, Vachon et al. (1968) were led to the conclusion that the degradation of nylon was not a purely hydrolytic process as might be expected. They found instead that the scission of the amide linkages did not occur in the absence of oxygen. Measurement of the rate of deterioration of nylon and Kevlar versus relative humidity allowed Auerbach (1989) to conclude that at 150–170 °C there was a purely thermal reaction that took place in the absence of moisture. Through extrapolation of an Arrhenius plot (see "The Arrhenius Equation," page 144) Auerbach further demonstrated that moisture-induced reactions would contribute only in a minor way to deterioration at ambient temperatures. In their studies of photochemically induced fading of colorants and deterioration of paper under decreasing concentrations of oxygen, Arney and coworkers (1979, 1980) reported that there were thermally induced changes occurring that apparently did not involve oxygen.

The Arrhenius Equation

It has long been known that the effect of temperature on the rate of chemical reactions can usually be expressed by a relationship proposed by Arrhenius in 1889. Mills and White (1987:134) provide an excellent introduction to the subject of the Arrhenius equation and its integrated form as it is commonly employed:

$$\ln k_{rate} = -E / RT + Z \tag{10.1}$$

Here, *k* is the rate of reaction, *E* the energy of activation of the reaction, *R* the gas constant (1.986 calories per mole), *T* the temperature in degrees Kelvin (273 plus the degrees Centigrade), and *Z* a constant. The symbol ln refers to the natural logarithm of *k*, the logarithm to the base *e*.

The ratio of the specific rates of reaction, k_2/k_1, at two temperatures, T_2 and T_1, is customarily calculated by the following form of the Arrhenius equation using logarithms to the base 10:

$$2.303 \log k_1 / k_2 = \frac{-E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{10.2}$$

How does such a relationship come about? It can be related to the Maxwell distribution law, which expresses the distribution of kinetic energies of molecules. Thus, in the equation

$$n_E = ne^{-E/RT} \tag{10.3}$$

n_E is the number of molecules at a particular absolute (Kelvin) temperature, *T*, that possess a kinetic energy greater than *E* among the total number of molecules present, *n* (Glasstone 1946:264). Stated in other terms, the above equation expresses the probability of a molecule having an energy in excess of *E*. The ratio of the number having energy *E* at two different temperatures is

$$\frac{n_1}{n_2} = \frac{e^{-E/RT_1}}{e^{-E/RT_2}} \tag{10.4}$$

or

$$\ln n_1 / n_2 = 2.303 \log n_1 / n_2 = \frac{-E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{10.5}$$

The same relationship holds for the thermal distribution of electronic, vibrational, and rotational energies. If, in order to react, molecules need to have an energy above a certain level (the *activation energy*), as Arrhenius proposed, then it comes about that a change in reaction rates with increased temperature will be expressed by the equations cited above, either 10.1 or 10.2.

The Arrhenius equation has been traditionally used in accelerated thermal aging tests in the following manner: Some measure of the *rate of reaction* is determined at several temperatures (at least three, preferably more) and the logarithm of those *rates* is plotted versus $1/T$, the inverse of the absolute temperature (degrees Kelvin). A typical plot is shown in Figure 10.1 (Gray 1977). Grattan (1978) also provides examples in his discussion of the subject. The data can be used to estimate the rate that would be experienced at other temperatures. Perhaps most often the slope is extrapolated to predict the rate at room temperature, as is done in Figure 10.1, or extrapolated to some temperature at which a material will be used or stored. According to Equation 10.1, the slope of the curve is $-E/R$ and thus is used to calculate the energy of activation, R being a constant. Nelson (1990), who has an extensive discussion of applications of the Arrhenius equation, points out that if a failure mechanism is dependent upon diffusion, this, too, will follow the Arrhenius relationship.

Limitations

Gray (1977) pointed out two key limitations to the use of the Arrhenius equation. First, linear specific rates of change must be obtained at all temperatures used. By this it is meant that the rate of reaction, however this is measured or represented, must be constant over the period of time at which the aging process is measured. If the apparent rate should vary over the time of the test, then one would not be able to identify a specific rate that is assignable to a specific temperature.

If the mechanism of the reaction at higher or lower temperatures should differ, this, too, would alter the slope of the curve. Numerous examples of non-linear Arrhenius plots, the consequence of a change in mechanism, can be found in the literature (Hawkins, Matreyek, and Winslow 1959; Hartley and Guillet 1968; Chodak and Zimanyova 1984; Kramer and Koppelmann 1987). Below about 40 °C, Richters (1970) found that the deterioration of polypropylene was initiated by contaminating iron particles; above this temperature, oxidation tended to take place throughout the bulk of the sample. Another source of error would be that the mode of physical failure of an adhesive system would differ at the two temperature extremes. Nelson (1990:31) specifically warns that the temperatures should not be so high that the mode of physical failure changes from that exhibited at the temperatures of normal usage. River (1984) lists five reasons why errors may be introduced in the extrapolation of Arrhenius data from high temperatures to low.

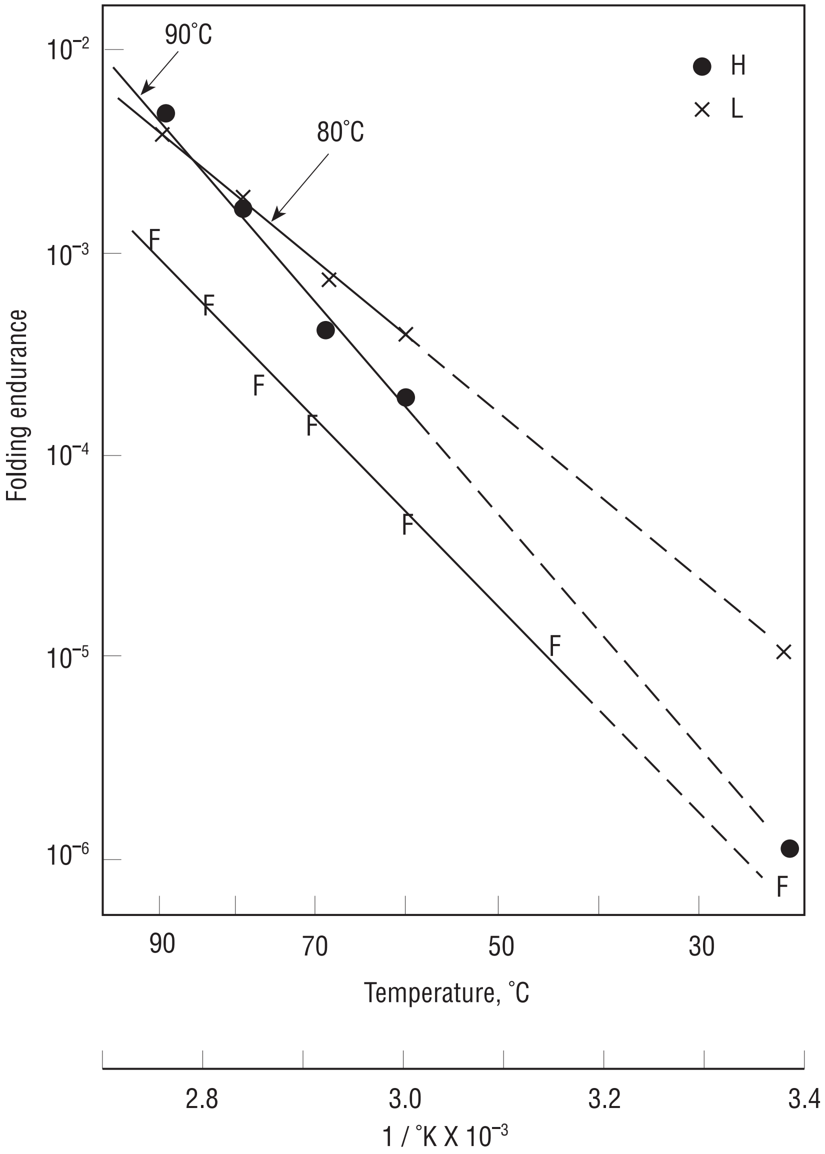


Figure 10.1. Arrhenius type plot with • representing paper H and × representing paper L. Logarithm of folding endurance of several paper samples versus 1/T, the inverse of temperature in degrees Kelvin. Note that paper H would be ranked more stable than L if tested at 90 °C. If tested at 80 °C, the relative ranking would be in the same order as the values extrapolated to 25 °C. In contrast, paper F would not change its rank relative to L regardless of the test temperature (Gray 1977). Reproduced with permission of the publisher.

As a second fundamental limitation, it is necessary that the energy of activation be independent of temperature, that is constant over the range of temperatures of interest. However, the apparent energy of activation is not always constant, particularly when there is more than one process going on (Chornet and Roy 1980). Partially for this reason, it has been widely recommended that the rates of reaction in a plot such as Figure 10.1 not be extrapolated to a temperature markedly greater or lower than that of the last experimental data point. One can be more specific concerning this matter, as discussed in the next section. Note that Gray's lowest experimental temperature was 60 °C; extrapolation to room temperature amounted to just thirty-five degrees lower.

Agrawal (1985) has pointed out a key limitation: The Arrhenius equation applies to homogeneous reaction conditions and has little significance in solid-state reactions. He cites two easily understood reasons for nonlinearity between $\log k$ and $1/T$: a change in reaction mechanism, as just mentioned, and also possibly the existence of a temperature gradient within the sample due to heat and mass transfer effects. Day et al. (1989) describe an example where the rate of oxidation became diffusion-controlled at lower temperatures. Kelly et al. (1982) report nonlinear Arrhenius plots for the fading of certain dyes on acrylic and poly(vinylalcohol) substrates. Agrawal's 1985 paper rebuts the arguments of Brown (1982) who questioned the appropriateness of the Arrhenius equation in the pyrolysis of wood and paper.

There are two clear situations in which a change in mechanism can occur: (1) when, at higher temperatures, an inhibitor begins to take part in reactions that lead to the formation of a new free-radical entity and thereby a new source of initiation and (2) when a polymer rises above its melting point or its second-order transition temperature (Grieveson et al. 1961). The latter is discussed in the next section.

It is well to keep these various limitations in mind. Moreover, it is recognized that the generation of rate data at several temperatures is a time-consuming task, making Arrhenius studies somewhat "impractical" for repetitive (routine?) testing (Edge et al. 1992).

If one wishes to predict the rate of deterioration at room temperature on the basis of the slope of the Arrhenius equation (representing the energy of activation), it is well understood that the energy of activation measured depends upon the property change measured. Reilly et al. (1991) present a table showing that, on the basis of six different properties studied—properties such as the retention of tensile strength or intrinsic viscosity, increase in acidity, and decrease in emulsion melting point—the predicted useful lifetime of cellulose triacetate film at 20 °C varied from 40 to as much as 1,000 years. In earlier studies, Adelstein and McCrea (1981) found the range to be 100 to better than 2,000 years depending on the property measured. Allen et al. (1988) report marked differences in the apparent energy of activation depending on the type of container in which the films were heated: glass, polyethylene, tin-plate, or aluminum.

Reactions Above and Below the Second-Order Transition Temperature, *Tg*

If one attempts to extend a plot of log *k* vs. $1/T$ to ever higher temperatures, the polymer system may change its physical state at some point, either by melting, as in the case of crystalline or partially crystalline substances (Fig. 10.2; Shlyapnikov et al. 1987), or by passing from a glassy state to that of a highly viscous liquid at the second-order transition temperature or glass temperature (*Tg*). This is a major limitation that can be cited regarding the use of the Arrhenius relationship, limiting how far one may extrapolate the experimental data to very much higher or lower temperatures. In reading accelerated-aging literature, one will note that authors often will state carefully that the polymer was being tested only at temperatures either above or below the *Tg* (Schoolenberg and Meijer 1991, for example).

At temperatures below *Tg,* the motion of polymers is highly restricted; Baková and Lazár (1969) speak of the molecular conformation as being “frozen.” Under these conditions, when a free radical is generated by heat or light, it may not be able to move very far from the original site (called the *cage* effect). With acrylic polymers, for example, Baková and Lazár found that the rate of decay of radicals became very much faster as temperatures approached *Tg* (Fig. 10.3). Increased molecular mobility at temperatures above *Tg* may induce cross-linking to predominate over chainbreaking (Theberge and Cloud 1978; Chodak and Zimanyova 1984). It has been suggested that this is the reason that cross-linking predominates when poly(isobutylmethacrylate) is tested in the usual xenon-arc Fade-ometer; here, the sample temperature may reach as high as 62 °C. In contrast, significant chainbreaking occurs when the temperature of the sample is kept at 32 °C (Feller et al. 1981). Chapiro (1975) provides an interesting discussion of the effect of temperatures below *Tg* in increasing the graft copolymerization of various polymers.

A striking example of the effect of *Tg* is seen in Figure 10.4 (Guillet 1973); a sharp jump in the quantum yield of chain scission of poly(styrene-phenyl vinyl ketone) copolymers (PS-PVK films) occurs when the temperature of the specimens is above *Tg* (around 102 °C). Even subtle forms of motion within the polymer structure can effect deterioration. The data of Wandelt (1986) illustrates this possibility (Fig. 10.5). Below the gamma transition, 256 °K, very little molecular motion exists in the polystyrene polymer Wandelt was studying. Above this temperature, phenyl group rotation set in. At the beta transition, 318 °K, skeletal motion of the polymer chain becomes significant; at this point, chain scission increased.

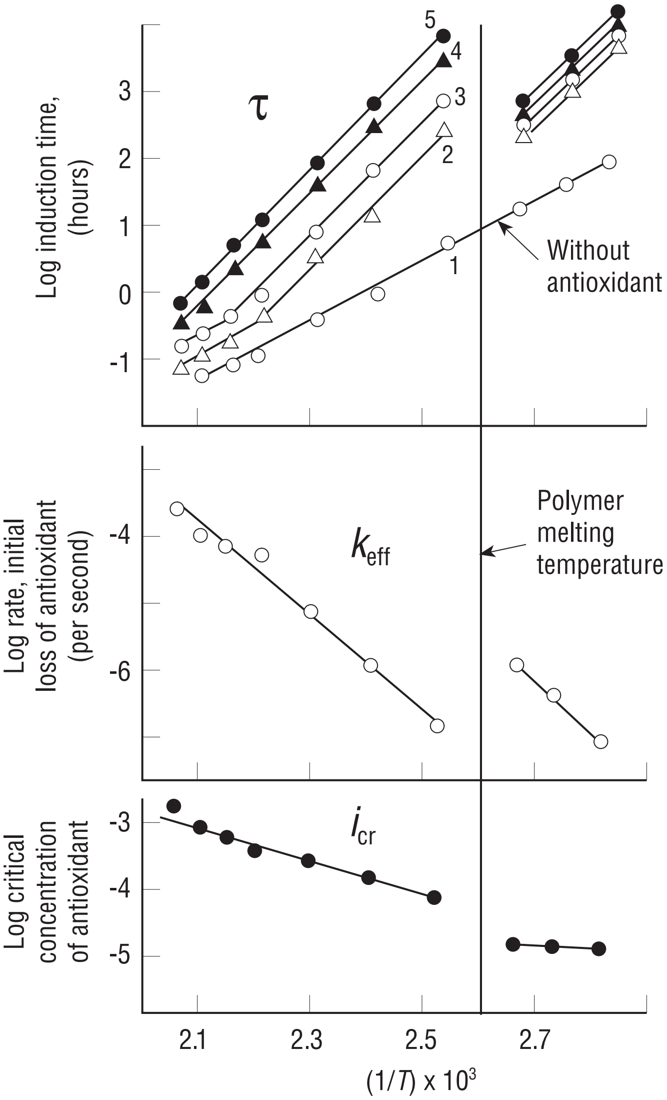


Figure 10.2. Discontinuity in Arrhenius-type plots owing to change of state of polyethylene polymer (melting). Curves 2 to 5 refer to increasing concentrations of antioxidant (Shlyapnikov et al. 1987). Reproduced with permission of the publisher.

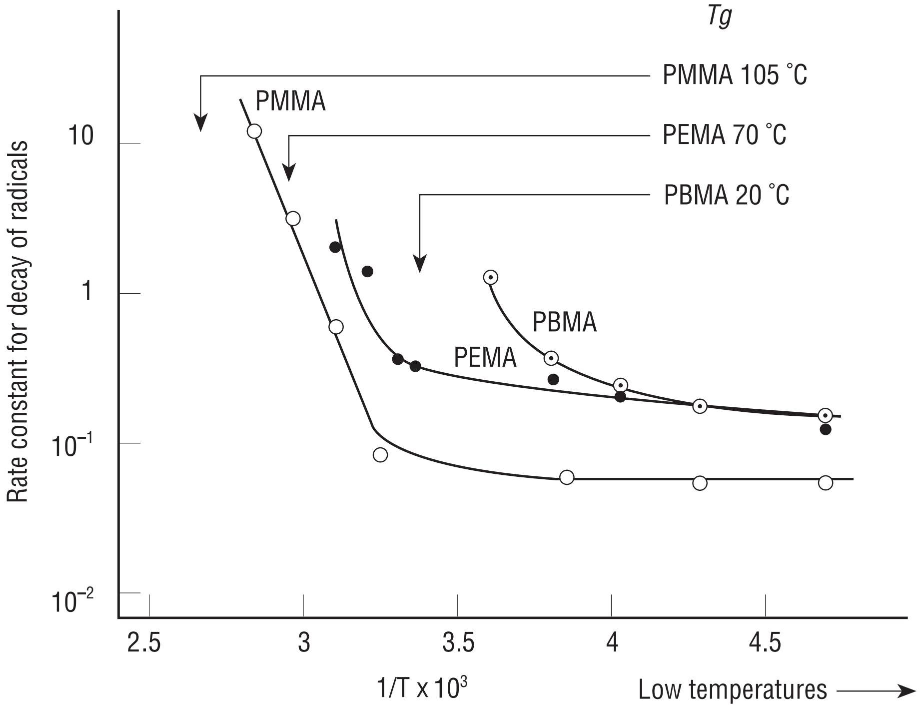


Figure 10.3. Discontinuity in Arrhenius-type plots. Decay of radicals, generated by mechanical destruction, in poly(methylmethacrylate, PMMA), poly(ethyl-methacrylate, PEMA), and poly(n-butylmethacrylate, PBMA) as function of inverse of temperature in degrees Kelvin. Rapid increases in rate as the second-order transition temperature (Tg) *is approached (Baková and Lazár 1969). Reproduced with permission of the publisher.*

In summary, if accelerated-aging tests are carried out solely at temperatures above the second-order transition temperature, the rate of certain key reactions may be sufficiently altered that Arrhenius-based extrapolations of possible behavior down to room temperature (specifically to temperatures below *Tg*) can be in error. Theberge and Cloud (1978), Chodak and Zimanyova (1984), and River (1984) cite examples where predictions of stability would have been in error if the fact that tests have been carried out at temperatures above Tg were not considered. The effect of a wide range in test temperature can become particularly troublesome in the case of systems that contain inhibitors (Shelton et al. 1953; Hawkins et al. 1959a; Shlyapnikov et al. 1987). Scott (1969) goes so far as to warn us that "stabilizers which are effective at low temperatures are not necessarily effective at high temperatures, and vice versa."

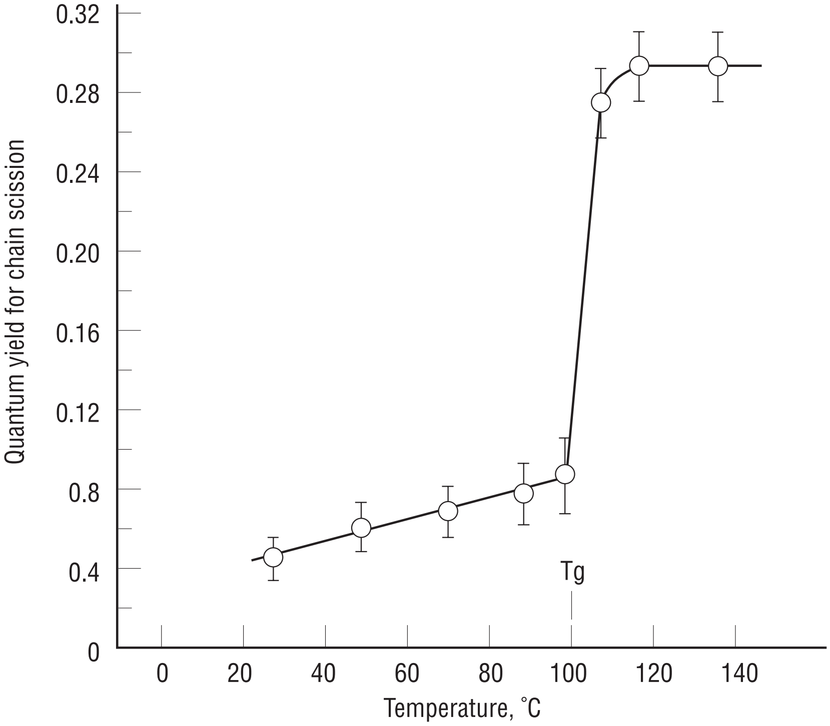


Figure 10.4. Discontinuity in Arrhenius-type plots. Influence of second-order transition temperature (Tg) *on quantum yield of styrene-phenylvinylketone copolymer (Guillet 1973). Reproduced with permission of the publisher.*

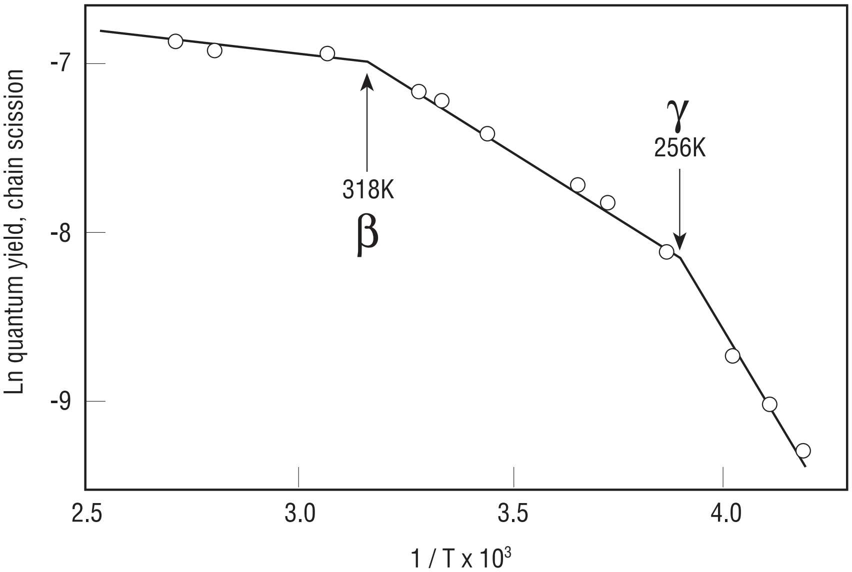


Figure 10.5. Discontinuity in Arrhenius-type plots. Quantum yield of chain scission of polystyrene exposed to 254 nm radiation. At γ *transition phenyl group rotation begins. At* β *transition skeletal motion becomes significant (Wandelt 1986). Reproduced with permission of the publisher.*

Arrhenius-Based Shift Factor

Should one wish to compare the course of deterioration processes at various temperatures and to demonstrate that essentially the same overall kinetic series of events takes place at each temperature, there has long been a custom of plotting data as in Figure 10.6. At each higher temperature, the experimental data are plotted, not against time, but against time multiplied by a shift factor, a_T. The latter is based on the increase in rate above some reference temperature, T_r, calculated from the Arrhenius relationship as follows:

$$\log a_T = \log k_2 / \mathrm{k}_{\mathrm{T}_r} = \frac{E}{2.303R}\left(\frac{1}{T_r} - \frac{1}{T_2}\right) \qquad (10.6)$$

This equation differs from the form in Equation 10.2 in that E is positive; k_2 and k_1 are reversed. The equation so written yields the increased speed of the reaction at the higher temperature over that of the lower.

The data shown in Figure 10.6 (Clough and Gillen 1981) refer to the elongation of poly(vinylchloride) samples after thermal aging in air relative to the elongation of the samples before thermal aging. The samples were initially irradiated with a Co-60 source in order to cause them to be especially sensitive to thermal degradation. The shift-factors, given in the figure, were calculated on the basis of an activation energy of 23.3 Kcal/mole.

The term *shift factor* is a handy one but its meaning may not be universally accepted. One finds, for example, the same term used in comparing outdoor exposures with weatherometer data (Simms 1987). Simms's application, however, more nearly represents an application of the reciprocity principle in what is essentially photochemical deterioration rather than an application of the Arrhenius equation. Regardless, it will probably remain a useful exercise to compare the rate of change under moderate conditions to data obtained under accelerated conditions simply by multiplying the time scale by some fixed number. If the data are not made to coincide simply by multiplying the time to achieve given degrees of change by some constant (shift factor), then one will have convincing evidence that the highly complex factors involved in deterioration were not simply and uniformly speeded up by the conditions chosen to accelerate the degradation.

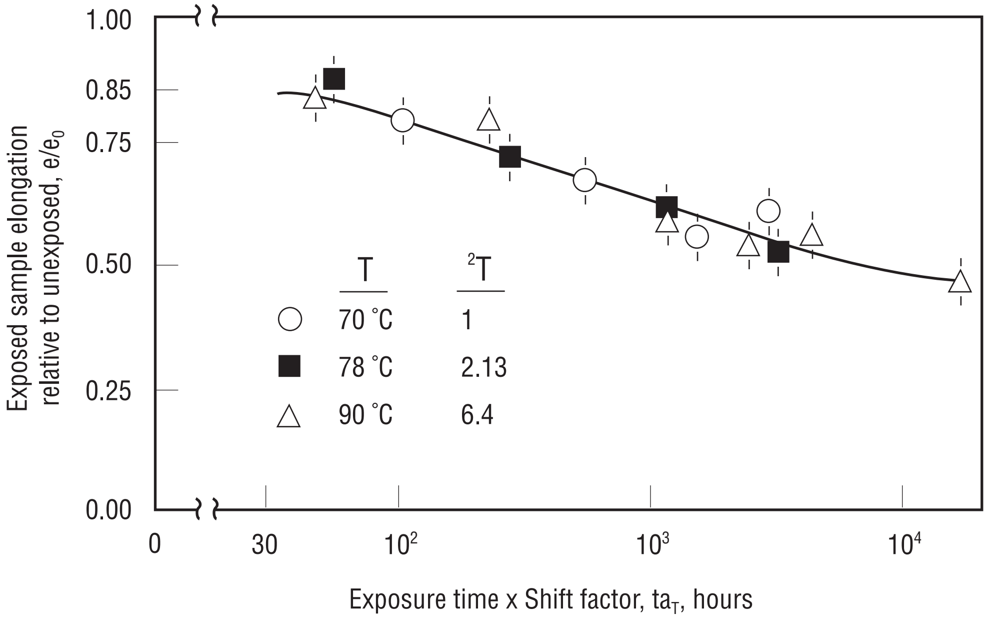


Figure 10.6. Time-temperature superposition of the loss of elongation during thermal aging of polyvinylchloride. Pre-exposed to gamma radiation. To achieve superposition, data at 78 and 90 °C were multiplied by the Arrhenius-based shift factors shown (Clough and Gillan 1981). Reproduced with permission of the publisher.

Indirect Way of Measuring Rates at High Temperatures: Thermogravimetric Methods

Papasian (1972) describes a method of analysis in which the rate of weight loss of a polymer under vacuum (thermolytic degradation) was measured rapidly by a thermogravimetric method of analysis (TGA). The rates fell on an Arrhenius plot in agreement with data obtained at constant temperature (isothermally) but at much lower temperatures. In the thermogravimetric technique the accumulative weight loss is measured as the temperature is raised. The specific rate constant k_r is calculated from the so-called instantaneous first-order loss in weight of a polymer at any given time and temperature, dx/dt, dividing this by the weight of material remaining at that time, x_o-x. Here, x is the weight lost, x_o the initial weight.

$$k_r = \frac{dx/dt}{x_0 - x} \qquad (10.7)$$

Two processes were noted in Papasian's study of silicone deterioration; the first stage represented loss of solvent. To predict the rate of deterioration to lower temperatures, it was necessary to use the rate of weight loss in the second stage. This stage related to thermal decomposition, whereas the first-stage data simply represented solvent loss.

Cardwell and Luner (1977) and Duswalt (1977) have described the use of thermogravimetric analysis in the oxidative degradation of paper (see also ASTM 1992, E 698-79). Crighton (1992) mentions the use of this method to detect degradation in silk. It must not be forgotten, however, that, in the progressive heating at temperatures rising from 260 to 450 °C, one is measuring chemical reactions that take place at these high temperatures, reactions that may not be the same as those that take place at room temperature. Thus, every research worker who wishes to use the results of thermogravimetric measurements to predict behavior at room temperature is forced to carry out extensive experiments to demonstrate that the measurements and the empirical stability indices derived therefrom indeed yield predictions that correlate well with the results under ordinary conditions of exposure. Duswalt closes his paper by saying, “If the oxidation rates observed by TGA are assumed to be a valid measure of paper permanence, the technique can be very useful.” Note the “if” and “assumed.”

In their second paper, Cardwell and Luner (1977:382) compared the ranking of ten papers with respect to mechanical properties, activation energy, mean degradation temperature, and the stability index derived from thermogravimetric measurements. They compared the results of thermogravimetric analysis to those of traditional accelerated-aging tests. In particular, poor correlation was found between the various methods of measuring the stability of papers and their ranking with respect to energy of activation.

Thermogravimetric studies measure loss of weight. This can be measured in vacuum, nitrogen, or air. Many polymeric systems, however, lose their useful physical properties while undergoing only a minimal loss of weight. Day et al. (1989) caution, “Data obtained from fast heating rate experiments in air were found to be misleading . . . Before the weight-loss kinetic technique is used for lifetime predictions, correlation of test results with actual lifetime information is required to establish the viability of the method and the nature of any correlations should they exist.”

Thermogravimetric techniques offer a rapid method of accelerated-aging tests. Nonetheless, the limitations must be appreciated.

Isothermal Differential Calorimetry

Paloniemi (1972) has described the use of a sensitive calorimeter that measures the heat given off as a polymer decomposes at a constant temperature (isothermal circumstances). Temperatures between 110 and 230 °C were used. With this equipment, the author was able to demonstrate in a number of cases that the usual Arrhenius-based approach yielded incorrect lifetimes when extrapolated to normal conditions (Fig. 10.8). This occurred because more than one chemical process was usually involved.

The Equalized-Aging Process

Some time later, Paloniemi and Lindstrom (1977) proposed an accelerated-aging procedure called the *equalized-aging process.* Their approach is designed to alter the humidity and the concentration of oxygen so that the rates of the three principal degradation reactions—thermal, oxidative, and hydrolytic—will take place at the same rates relative to one another at an elevated temperature as they do under the conditions of normal usage. The method is based on a number of assumptions such as the fact (a) that the reactions are of the homogeneous type and (b) that only one chemical reaction of each of the three principal degradation processes is significant (rate determining). Paloniemi (1981) has prepared a detailed theoretical analysis of the principles and limitations of the equalized-aging method, including the situation in which one of the three processes may be diffusion controlled. The rates of reaction are determined by isothermal differential calorimetry; that is, by measuring the heat generated in samples maintained at various constant temperatures under nitrogen and under varying concentrations of oxygen and water vapor (Paloniemi 1972).

In their 1977 article, Paloniemi and Lindstrom explain their equalized-aging procedure in simple though detailed terms. A reference temperature is chosen near to the normal operating condition. In electrical insulation testing, this temperature usually is rather high. The samples are then heated in nitrogen at three or more elevated temperatures; this procedure yields the increase in the rate of purely thermal (pyrolytic) degradation with temperature. Again under nitrogen, the rate of hydrolysis is measured at three levels of water vapor concentration. Following this, a mixture of dry nitrogen and three or more levels of oxygen is used. The results of these three series of tests yield the speed-up factors for the thermal, hydrolytic, and oxidation processes at each of the elevated temperatures. The data can also yield a value for the apparent order of the reaction with respect to water and oxygen, information that can be used to refine the rate calculations if the reactions prove not to be simply first order. Based on the information gained, conditions of oxygen and water vapor concentration are selected at each elevated temperature such that the relative

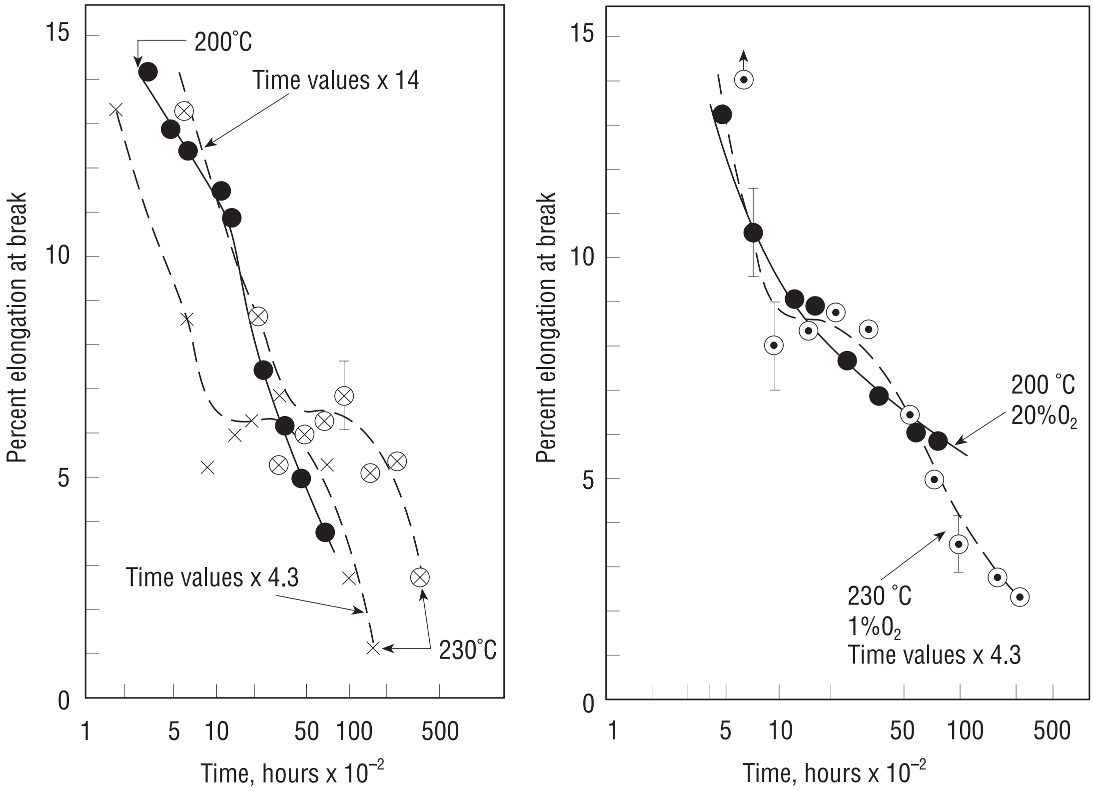


Figure 10.7a, b. Results of conventional thermal-aging tests on polyester-imide enameled copper wire showing (a) elongation-at-break at 200 °C compared to results at 230 °C; early aging data evidently have a higher Arrhenius-based shift-factor than later stages; and (b) results of equalized-aging process (EAP) technique: aging at 230 °C conducted at 1% oxygen concentration rather than 20% (Paloniemi and Lindstrom 1981). Reproduced with permission of the publisher.

rates of the thermal, oxidation, and hydrolysis processes at the higher temperature will be the same as they were at the reference temperature.

To verify the success of the equalized-aging procedure, changes in physical or chemical properties (loss of weight, elongation-at-break, breakdown voltage, time to lose a fixed percentage of strength) with time of heating at the different temperatures were measured. If the speed-up factor over the entire period under each test condition remains reasonably constant, the authors consider this to be evidence that the rates at the higher temperatures, when extrapolated to a lower temperature, will give a far better estimate of the rate at the lower temperature than rates measured under conventional methods of test in which the concentration of oxygen or water vapor at the higher temperatures are not adjusted.

Figure 10.7 illustrates some typical results (Paloniemi 1981). Figure 10.7a shows the results of conventional testing of a polyester-enameled wire at 200 and

230 °C, in which the concentration of oxygen is the same in both cases. One finds that the times to attain a given degree of elongation at 230 °C are about one-fourteenth that at 200 °C at the beginning of deterioration. This corresponds to the speed-up factor determined for thermo-oxidative deterioration. In the later stages of the deterioration, the changes in properties at 230 °C more nearly correspond to 1/4.3 times the changes that occurred at 200 °C. The author considers this stage to correspond to the speed-up factor for a purely thermal rate of deterioration.

In Figure 10.7b the oxygen concentration in the test at 230 °C was lowered to 1% to make the oxidation reactions proceed at the same rate relative to the purely thermal ones. Figure 10.7b compares the results of elongation-at-break measurements of the enameled wire heated at 200 °C with the results at 230 °C and the lower oxygen concentration multiplied by a speed-up factor of 4.3. Measurements of elongation-at-break lack precision, but the authors consider that the equalized-aging-adjusted concentration of oxygen introduced a reasonably constant speed-up factor over a considerable period of test.

Figure 10.8 confirms the advantage of the equalized-aging procedure. Extrapolation of the results of the manufacturers' conventional tests on an epoxy resin conducted at 210 and 180 °C would lead to the predicted life at 160 °C indicated in the figure. The manufacturers' test results at 160 °C turned out to be much shorter than that predicted by the extrapolation. Undoubtedly this came about because the rate of deterioration was too low in the conventional tests at 180 and 210 °C. When the atmosphere in the reference test at 210 °C was adjusted according to EAP principles (oxygen and water vapor concentrations raised), the test results multiplied by 12.7 corresponded closely to the rate that had been observed at 160 °C.

The data in Figure 10.8 demonstrate again that the overall rates of deterioration measured during conventional thermal tests often do not yield a linear Arrhenius-type plot. This is largely owing to the fact that rarely is a single and homogeneous chemical process involved. A colleague has said that the EAP procedure is too complicated to be of much use. The description is included here to show that the objective of "equalization" of the various processes has been met by at least one research group.

Isothermal measurements of the low levels of heat evolved by chemical reactions are being applied with considerable success today as a measure of the onset of rapid deterioration (Kramer and Koppelmann 1987; Hansen et al. 1990).

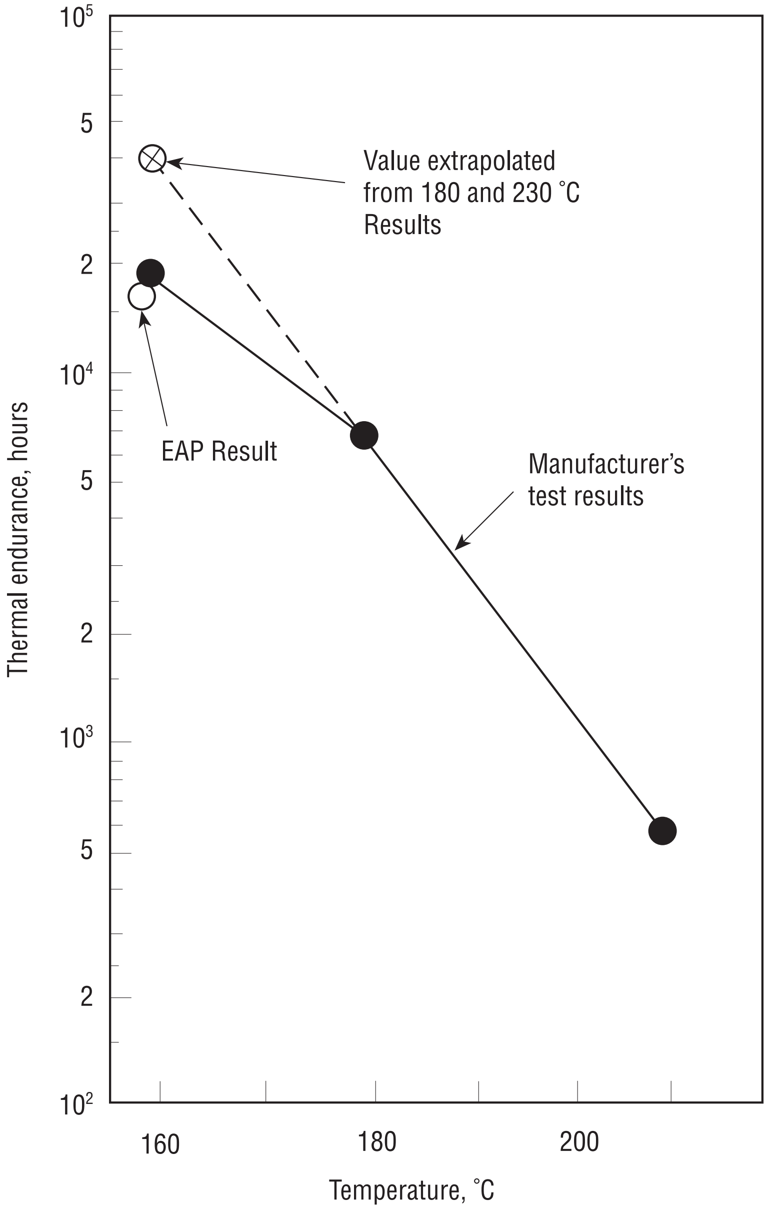


Figure 10.8. Thermal endurance of epoxy resin extrapolated to 160 ℃ on the basis of test results at 180 and 210 ℃. Equalized-aging adjustments to higher concentrations of oxygen and water vapor produces results at 160 ℃ close to the conventionally measured value (Paloniemi and Lindstrom 1981). Reproduced with permission of the publisher.

Problem in Choosing a Single Temperature at Which to Compare Different Systems

Differences in activation energies (the slope of Arrhenius plots) was the key problem that Gray (1977) wished to stress regarding the desire one might have to rank the durability of papers by testing at only one temperature and at one exposure time (72 hours at 105 °C, for example). In Figure 10.1 one can see that, when a test is made at temperatures above about 85 °C, paper H embrittles at a lower rate than L. On the other hand, if the rate were determined at lower temperatures, or the data extrapolated to room temperature, H loses fold strength faster than L. The ranking of the much less durable paper F, relative to H or L, would, however, remain the same regardless of test temperature.

Adelstein and McCrea (1981) and Adelstein et al. (1991) provide examples of problems similar to papers H and L in ranking the durability of cellulose triacetate versus polyester-based film; Kramer and Koppelmann (1987) provide an example of polybutenes versus polyethylene.

Glass and Valange (1988) cite another aspect of thermal testing, in which the temperature selected can affect comparisons of the effectiveness of one antioxidant relative to another. The authors showed that the ratio of embrittlement times for polypropylene involving two different antioxidants varied when behavior was compared at 150, 135, and 120 °C. The relative merit of product 1 versus product 2 "crossed over," reversed its order of merit, at about 125 °C. Authors often attribute such results to differences in the rate of volatilization of inhibitors; Glass and Valange, on the other hand, pointed out that the chemical reactions that different types of inhibitors undergo may respond to temperature increases differently. In other words, different types of inhibition as well as other reactions can have different energies of activation. In the oxidative degradation of acrylonitrile-butadiene-styrene (ABS) resin, Shimada and Kabuki (1968a) determined that the initiation reaction had an activation energy of 10 Kcal/mole, whereas a subsequent step had an activation energy of 10–20 Kcal/mole. In testing polyhydantoin film, Paloniemi and Lindstrom (1977) reported that the ΔE for thermal degradation was 14.5 Kcal/mole, for hydrolysis was 17 Kcal/mole, and for oxidation, 30 Kcal/mole.

Potential Contamination by Volatile Components

When thermal aging tests are carried out in an ordinary circulating air oven, there are many aspects of the procedure that can introduce a lack of reproducibility. If antioxidants, plasticizers, or degradation products are volatile, it is well known that these can be lost at different rates and can migrate to neighboring samples, affecting aging behavior. One may also encounter a problem with dyes that sublimate at the test temperature instead of remaining put.

Control of Humidity

As mentioned, it is a challenge to maintain a near-normal level of relative humidity and moisture content when materials are heated in an oven. A simple but crude way to circumvent this problem is to conduct tests in a pair of closed vessels in which the atmosphere in one is kept perfectly dry and in another, water is left in the bottom in order to ensure a condition of 100% relative humidity. As mentioned earlier, this procedure introduces problems with trapped decomposition products and with the fact that condensed water may be in direct contact with the test materials. Another approach is to equilibrate samples at a normal temperature and humidity, before sealing the container and raising it to the high level employed in testing.

Gray (1977) published a table giving the calculated relative humidity (RH) in an oven having temperatures from 60 to 110 °C when the air of the laboratory, drawn into the oven, was at 23.9 °C and 50% RH. He called these the conditions of an "arid oven"; the relative humidity ranged from 7.45 to 1.04%. In order to maintain a moisture content of about 5% in the paper at oven temperatures from 40 to 90 °C, Gray recommended passing room air through baths of heated water until the air became saturated at the required temperatures before entering the oven. A table gives the recommended bath temperatures and the resulting approximate RH in the ovens, which ranged from 38 to 53% RH. Bansa and Hofer (1989) give a series of graphs showing the range of moisture content of a half dozen papers between the temperatures of 50 and 95 °C, and 45 and 75% RH. The moisture content averaged between about 4 and 7%. Tables giving the relative humidity attainable by salt and sulfuric acid solutions at various temperatures are available (ASTM 1992, standard E 104-85).

Classes of Thermal or Thermo-oxidative Stability

Occasionally one will find industrial products being evaluated by exposure to very high temperatures for brief periods of time (McNeill 1992). For certain engineering applications the strength of plastic composites has been tested at 200 to 260 °C for as long as 1,500 hours (Theberge and Cloud 1978). Wilson and Forshee (1959) specified 40 days at 124 °C in a moist oxygen atmosphere as a test for the acceptability of cellulose-acetate films for the lamination of paper. The Encyclopedia of Chemical Technology (Kirk et al. 1968) mentions a test on ethylcellulose that involves heating at 120 °C for 16 hours. In the Bergmann and Junk test for the stability of cellulose nitrate, samples are heated at 132 °C and the evolved HCl measured (Green and Bradley 1988). What do the results of tests at these elevated temperatures mean in terms of materials that might give poor (less than 20 years' service) or excellent (more than 100 years' service) performance in conservation?

It may be useful to consider a rough classification of materials in terms of the elevated temperature that they are able to withstand. The American Institute for Electrical Engineers, for example, classified insulating materials according to the highest temperature that could be practically tolerated: Class O 90, Class A 105, Class B 130, and Class H 180 °C (Von Fischer and Bobalak 1953). Table 10.1 presents a rough estimate of possible testing times for different classes of thermal stability based on the crude approximation that the rate of deterioration will double for a rise of 10 °C and on the statement that heating paper for 72 hours (3 days) at 100 °C is equivalent to about twenty-five years of aging under normal conditions of aging. Varnish insulation on electric motor stators provides an example of a material whose life doubles for every 10 °C the operating temperature is lowered (Von Fischer and Bobalak 1953).

The figures in Table 10.1 are only the crudest of estimates. They are presented to stimulate further discussion of the high temperatures and short times that might be involved in rapid evaluation of materials in various classes of stability.

The question naturally arises as to how high a temperature might be used to give a valid speed-up of the thermo-oxidation of an organic material which can be used to estimate the rate of deterioration under more moderate temperatures. Stransky et al. (1983) present an interesting approach to answering this question in the case of phenolic molding compounds. They used the method of comparing the relative change of two different properties under aging conditions of increased severity (see "Comparison of Property Changes Relative to One Another," page 102). They plotted weight loss against the loss of flexural strength or flexural modulus at six increasing test temperatures between 190 and 313 °C. At 285 and 313 °C the data no longer obeyed the same relationship as at the lower temperatures, a result that the authors attributed to a change from decomposition by oxidation and scission to one of "thermal shock." They concluded that "the highest temperature at which the aging mechanism is still valid (to be) about 270 °C."

Although the classes of useful lifetimes are specified in much the same terms, a material that would fall in one of the classes of thermal stability (Table 10.1:A, B, and C) need not fall in the same class if evaluated with respect to their photochemical stability (Table 1.1).

Thermo-oxidative class of stability	Approximate years of intended lifetime at room temperature	Times in which desired properties might be retained at:		
	20 °C	100 °C	140 °C	200 °C
Class C, unstable	20 or less	2.4 days	7 hours	
Class B, intermediate	20–100			
Class A2, excellent	100 minimum	12 days	36 hours	0.6 hour
Class A1, excellent	500 minimum	60 days	180 hours	3 hours

Table 10.1. Rough estimates of possible required testing times at high temperatures.

Residual Thermal Stability

There is a technique for evaluating the extent of deterioration of samples that have been on exposure for some time outdoors or under ultraviolet radiation, which Bäck and Kopp (1989) call *residual heat stability* (RHS). This consists of comparing the times for a given change in properties under an accelerated thermal decomposition test between that of an exposed and an unexposed sample. The authors used the time at 200 °C for the sudden emission of HCl from poly(vinylchloride) (PVCl) coatings to decrease to 5% of the time required in an unexposed sample. By periodic RHS tests on coatings that had been on exposure, they were able to monitor decay and to predict a service life of 23 ± 3 years for PVCl plastisols. Tüdos et al. (1985) exposed rubber samples to ultraviolet to measure, in a similar manner, changes in thermal degradation behavior as a function of the time of exposure. The International Standards Organization's procedure for residual thermal stability testing is ISO Standard R182 (Cope and Revirand 1982–83).

A variation of this procedure, worked out by Russian authors (Shlyapnikov et al. 1987), is particularly suitable for studying the thermal deterioration of systems containing inhibitors. The analysis evaluates the effect of pre-aging. It has been found that the thermally induced induction time of inhibited systems often obeys the familiar first-order equation:

$$k_{eff}\tau = ln \frac{i_o}{i_{cr}} \tag{10.8}$$

where τ is the induction time before major deterioration begins (the service life), i_o is the initial concentration of inhibitor and i_{cr} is the critical concentration. The effective specific first-order rate constant (k_{eff}) is the fraction of the inhibitor lost per unit of time. More properly, the equation should include the induction time at the critical concentration of inhibitor:

$$\tau = \tau_{cr} + \frac{1}{k_{eff}} \; ln \frac{i_o}{i_{cr}} \tag{10.9}$$

The authors consider the case where the polymer is heated for a period of time, t_1 at temperature T_1 and then heated at a higher temperature, T_2, until the end of the induction period. This procedure would yield Equations 10.10 and 10.12, since during time t_1 the inhibitor concentration would be reduced from its initial concentration to i_1 (i_o reduced to $i_1 = i_o \exp[-k_1 t]$ or $ln\ i_i = ln\ i_o - k_1 t$).

$$t_2 = \tau_{cr} + \frac{1}{k_2} \; ln \; \frac{i_1}{i_{cr}} \; = \tau_{cr} + \frac{1}{k_2} \left[\frac{ln\, i_0}{in\, i_{cr_2}} - k_1 t \right] \tag{10.10}$$

$$t_2 = \tau_{cr} + \frac{1}{k_2} \; ln \; \frac{i_0}{i_{cr_2}} - \frac{k_1}{k_2} \, t_1 \tag{10.11}$$

$$= \tau_2 - \frac{k_1}{k_2} \, t_1 \tag{10.12}$$

Equation 10.12 states that the induction time at the second (higher) temperature, t_2 (the time until the antioxidant concentration at T_2 reaches the critical concentration) is linearly related to the time of heating (t_1) at the lower temperature. This is illustrated in Figure 10.9. The lower temperature, of course, could be that of the normal condition of exposure, as in the RHS test. Shlyapnikov calls this procedure "the combined test."

The critical concentration of a thermal-oxidation inhibitor is not much influenced by the partial pressure of oxygen. If τ_2 equals zero, then Equation 10.12 becomes:

$$\tau_1 = \frac{\tau_2 k_2}{k_1} \tag{10.13}$$

This means that the induction time (service life) at normal oxygen pressures (τ_1) is related to the induction time that will occur under higher pressure (τ_2). An extrapolation to the point at which there would be no induction time at the higher pressure condition can be used to indicate the predicted induction time under the lower pressure or service condition (Fig. 10.9).

Although the authors do not stress the point, their analysis applies primarily to thermally induced aging. In many cases, photochemically induced induction times may obey similar rules, but one should apply these techniques to photochemically induced changes with caution. Shlyapnikov's work originally attracted the author's attention as a dramatic example of the effect of *Tg* (or in this case, a melting phenomenon; Fig. 10.2). However, the equations and techniques for "extrapolation to normal service conditions" illustrate a number of general principles that have been developed concerning thermal-aging testing.

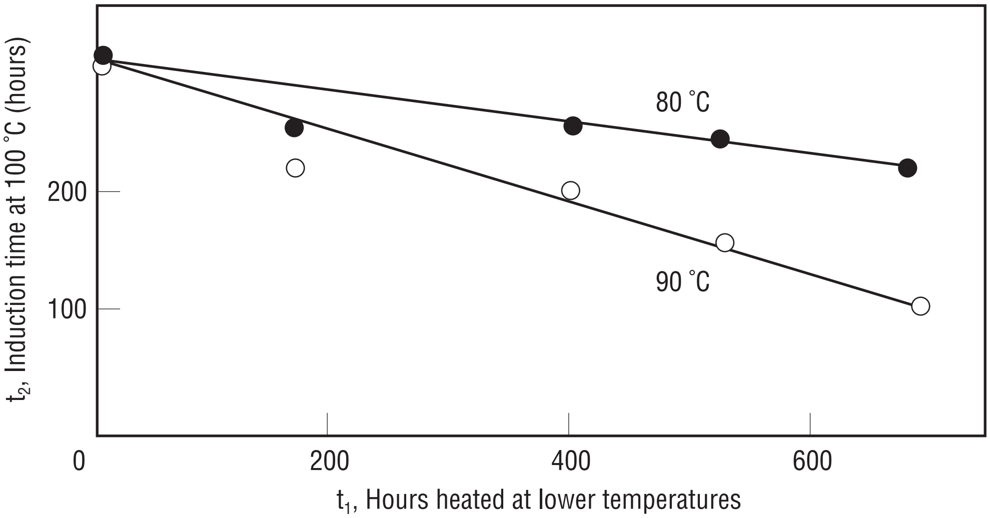


Figure 10.9. Induction period of polyethylene oxidation measured at 100 °C as a function of preliminary oxidation time at 80 and 90 °C.

Summary

Thermally activated processes of deterioration can be profitably studied from the point of view of purely thermal (thermolytic or pyrolytic) reactions—those that take place in the absence of oxygen and water—as well as thermohydrolytic and thermo-oxidative processes. The latter are of chief concern in the usual accelerated thermal-aging test. Higher-than-normal temperatures are commonly used in such tests in order to speed things up. The Arrhenius equation is widely employed in order to extrapolate the so-measured rates of deterioration and to estimate thereby the rate at the moderate temperature of ordinary usage. There are, however, a number of limitations to the use of this procedure to predict rates at normal (low) temperature. Some of these have been pointed out, particularly situations in which the physical state of the substance or the mode of failure of a system differs in the higher or lower temperature range. With increased understanding, it has been possible to develop a number of sophisticated ways of studying thermal effects, such as the equalized-aging process and residual thermal stability testing. The employment of high temperatures admittedly poses many problems, yet, just as in photochemical stability, it is recognized that materials can withstand a wide range of temperatures and that situations arise in which the use of very high temperatures is both practical and appropriate in accelerated-aging tests, particularly in the case of highly stable synthetic polymers such as Kevlar and Tedlar (Auerbach 1989).

11 Toward the Future

The conservator's and conservation scientist's understanding of deterioration mechanisms and techniques of prevention and prediction is but at an early stage. In the future, greater information concerning the chemical mechanisms of deterioration of specific materials must be sought. Additional attention must be given to establishing the pattern of deterioration in specific materials and conservation problems, what might be called the pathogenesis of their deterioration. Which systems tend to deteriorate in an accelerating manner so that the longer they go untreated the faster their deterioration progresses? Cellulose nitrate (Derrick et al. 1993) and linen (Stoll and Fengel 1988) may provide examples. Which materials or systems of materials exhibit an apparent induction time during which practically no change in key physical properties occurs, but after which either a very rapid change or catastrophic failure occurs? The cross-linking of butylmethacrylate polymers (Feller et al. 1985b), the degradation of cellulose triacetate film (Allen et al. 1988; Edge et al. 1992), and corrosion of protected metals provide examples of induction-time behavior. What are the ways in which knowledge of these modes of behavior can be used to advance preventive care and effective treatment?

A continued search is needed for methods to monitor the changes that occur as the materials of artifacts age. Croll (1987) has said that "two approaches exist for measuring degradation." The first is "to determine how far it has progressed." The second is "to measure a parameter that permits a prediction to be made about the eventual lifetime of a coating." Considerable progress is currently being made towards the objective of monitoring deterioration. Kirillov and Mikolajchuk (1990) have used Fourier transform infrared to monitor the ratio of lignin to cellulose in decaying archeological wood. Infrared analysis can also monitor the loss of camphor plasticizer from cellulose nitrate sculptures (Derrick et al. 1993). Edge et al. (1992) propose measurement of the moisture regain of cellulose triacetate film by microwave spectroscopy to monitor the condition of photographic film. Shashoua et al. (1992) suggest following the loss of nitrate groups in cellulose nitrate films by Fourier transform infrared. Perhaps, by change in the degree of polymerization of the cellulose, the age of cotton and linen can be monitored (Stoll and Fengel 1988). A critical review is in order concerning current progress in the development of techniques for monitoring deterioration in specific materials.

The role played by the buildup of peroxides in the materials within museum collections needs further elucidation beyond the fact that their presence has been noted in rubber cement, transparent mending tapes, and certain cellulose ethers (Feller and Enke 1982; Feller and Wilt 1990). The practical usefulness of antioxidants and ultraviolet-absorber additives, already addressed by de la Rie (1988), needs further development. Additional consideration must be given to the question of standards of acceptable and unacceptable durability for materials to be used in long-term conservation practice, both indoors and outdoors. Successful efforts are being made to do so in the case of epoxy resins (Down 1986; Grassie et al. 1985–86) and paper (Bansa and Hofer 1989).

Few, if any, observations have been made to demonstrate the effects of physical stress in hastening the deterioration of textiles, paper, and leather under conditions of storage and display. The utility of "control" materials and "monitors" of exposure needs further consideration. More information needs to be assembled concerning how much damage is likely to occur in specific materials as the result of specified numbers of lux hours of irradiance having spectral distributions comparable to typical light sources encountered in the display of cultural patrimony.

Questions also remain concerning whether significant differences can be encountered when the results of tests under continuous exposure are compared to those of diurnal alterations of light and darkness, and of seasonal differences in temperature and humidity. Further studies are needed regarding the effectiveness of maintenance under inert atmospheres or in the presence of oxygen scavengers.

Elucidation of the processes of deterioration requires sophisticated laboratory techniques. Wider recognition perhaps can be given to a selected number of relatively standard procedures and standard properties to be monitored in accelerated-aging tests. It may also be possible to develop a few relatively simple procedures and controls that will enable those less well endowed with training, equipment, and funding to scan and rank the myriad proprietary materials and systems that the conservator so frequently needs to evaluate. As an illustration of such a method, ASTM Committee D 01.57.10 is currently working on a method for the use of the ISO R105 blue wools by artists as a standard of lightfastness. Last, but not least, greater use must be made of experimental design and statistical principles in accelerated-aging studies (Reedy and Reedy 1992; Bierwagen 1987:192).

Many of these matters have already received and are continuing to receive consideration. Nonetheless, it is hoped that these concluding remarks will provide a convenient summary of a few of the challenging tasks that await attention.

Appendix A
Photochemical Effects in the Discoloration of Wool

The behavior of wool provides an excellent example of the complexities when an attempt is made to answer the question: How does wool discolor when exposed to visible and near-ultraviolet radiation? Stray or scattered light within the test equipment can give false results (Fig.A.1). The net degree of discoloration can depend on the length of exposure time chosen (Figs. A.2 and A.5) and on the light source (Fig. A.2) or specific wavelength (Fig. A.4) selected. The behavior is also influenced by the prior treatment as well as the particular sample under test (Fig. A.3).

Use of Monochromator in Australian Studies

Extensive studies have led to considerable knowledge concerning the effect of different wavelengths of radiation on the yellowing and bleaching of wool. The fact that both processes can occur at the same time and that each is chiefly the result of certain regions of the spectrum is strongly reminiscent of the behavior of paper. Lennox and his coworkers at CSIRO in Australia have investigated the problem for a number of years, developing the data given in Fig. A.1, showing that the greatest bleaching effect occurred at around 450 nm and that yellowing was generated primarily by wavelengths below 360 nm (Lennox 1969). This work also demonstrated that significant overall yellowing of the wool samples was generated by temperatures in the range of 40 to 80 °C. A monochromator and 1600-W xenon lamp was used to obtain these data. (The authors state that the yellowing above 560 nm, shown in Figure A.1, apparently was due to stray ultraviolet radiation in the apparatus.)

Effect of Heat and Different Light Sources

Data provided by Lennox and King (1968) on the discoloration of wool clearly illustrate some of the problems one can encounter if more than one major process takes place during exposure to light, particularly when the sources have decidedly different distributions of emitted spectral energy. Figure A.2 shows the result of irradiating five different samples of wool, each with a different initial yellowness index, with four different light sources. The fluorescent sunlamp (emitting primarily 310 nm radiation) caused only increased yellowness, whereas the fluorescent bluelamp, emitting radiation peaked at 420 nm, resulted in bleaching. Sunlight principally caused bleaching but

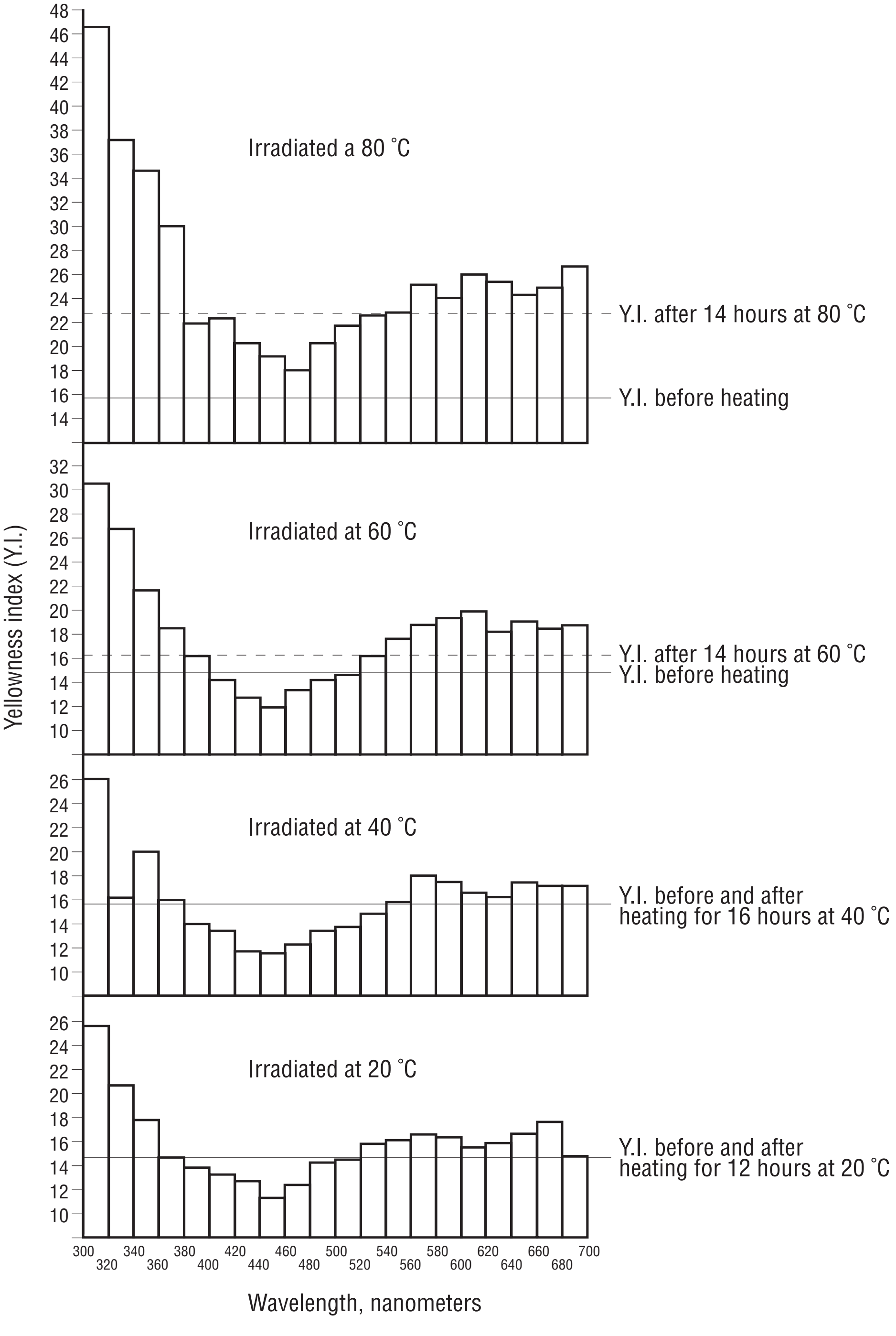


Figure A.1. The effect of irradiation wavelength on the yellowing of moist wool fabric at four different temperatures. The yellowing beyond that is due to temperature alone and at wavelengths above 560 nm is probably due to scattered ultraviolet radiation (data of Lennox 1969).

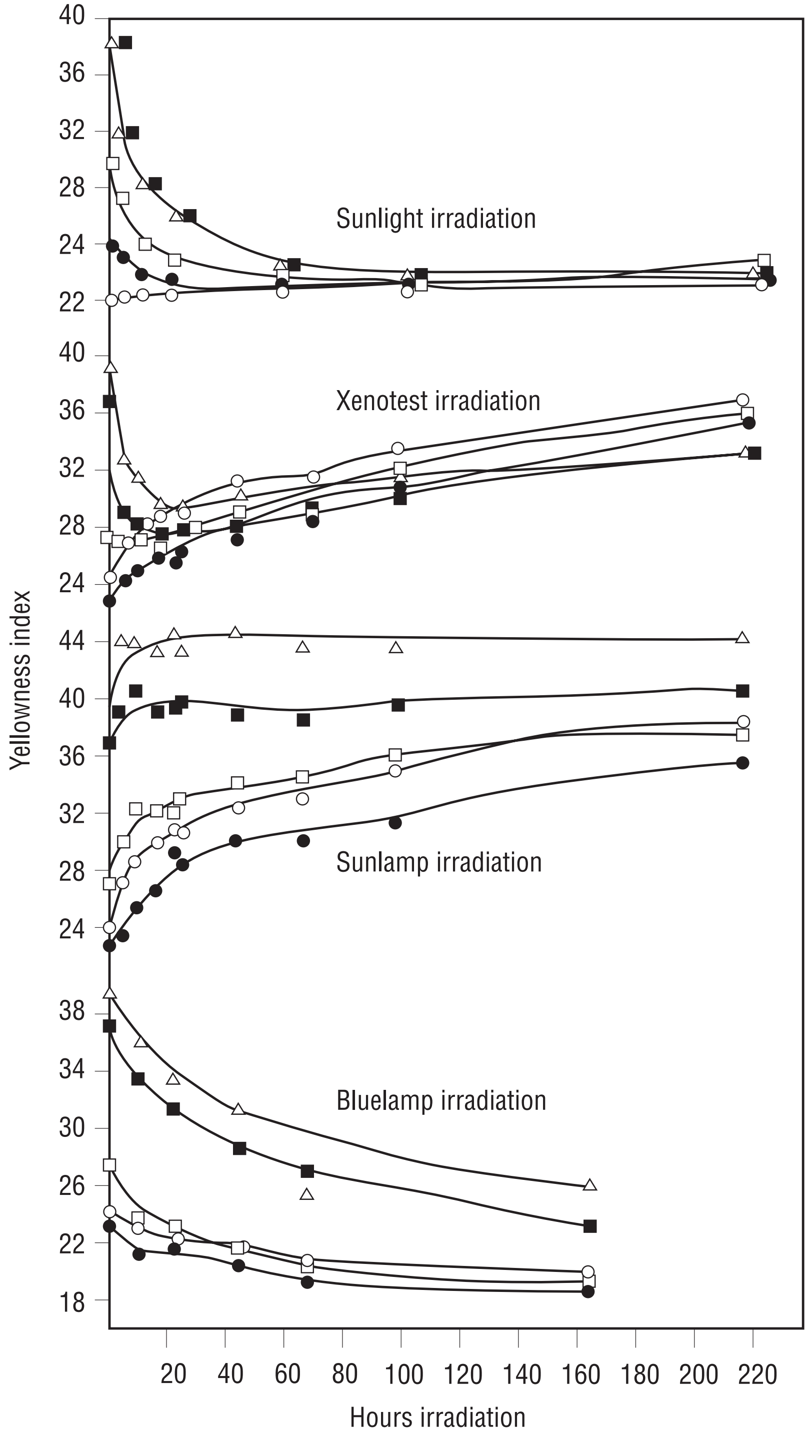


Figure A.2. Exposure of scoured wools from five sheep, covering a range of initial yellowness indexes, to sunlight and to four artificial sources of radiation (data of Lennox and King 1968).

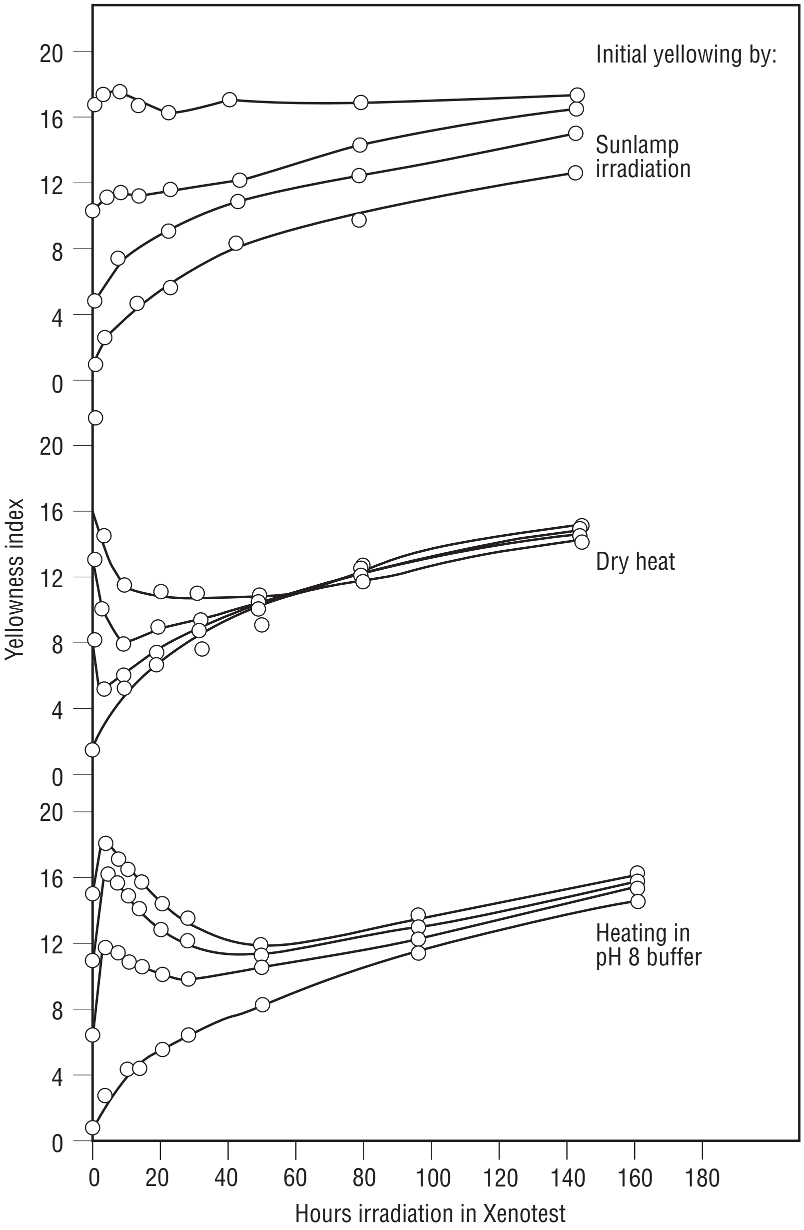
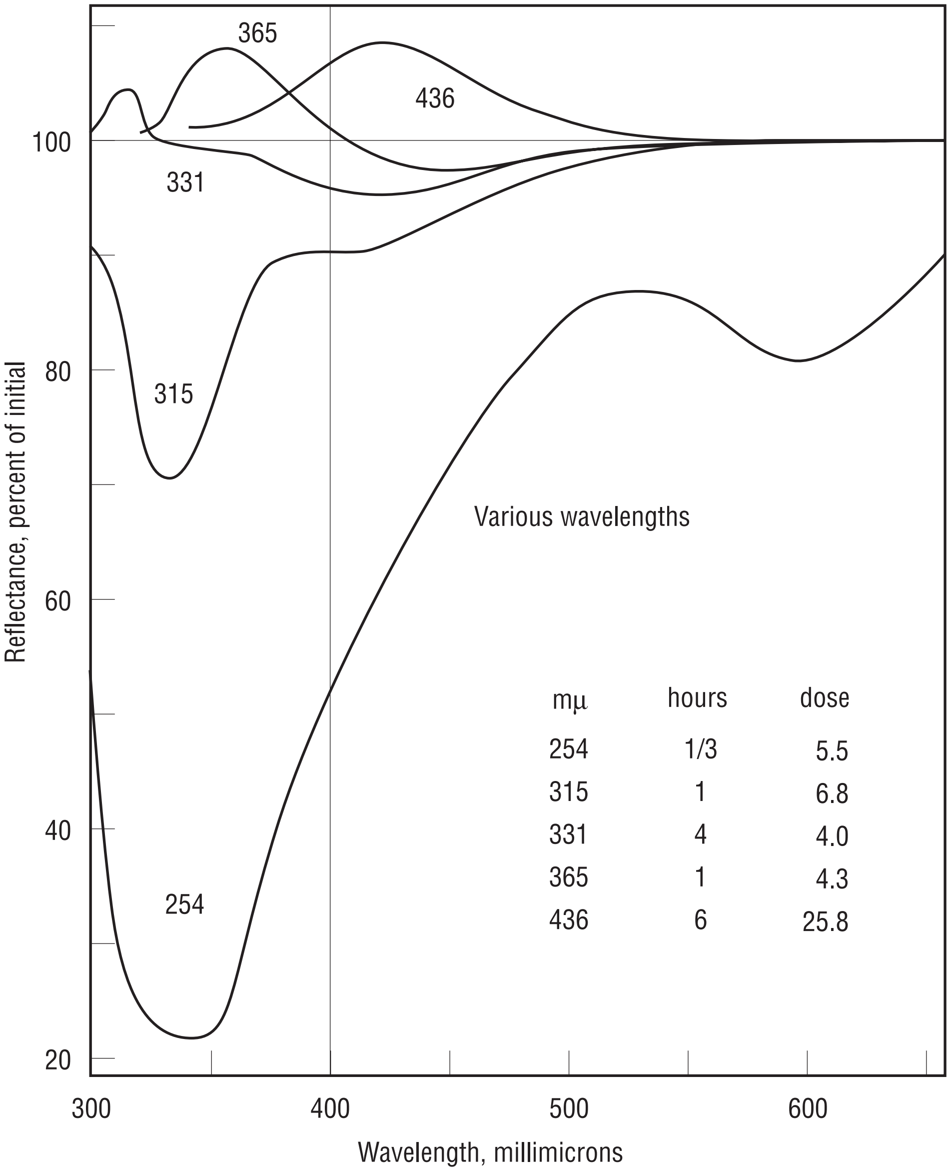


Figure A.3. Exposure of wool fabric in the Xenotest following yellowing in the laboratory by three different methods, each having four different levels of initial yellowness (data of Lennox and King 1968).



mμ	hours	dose
254	1/3	5.5
315	1	6.8
331	4	4.0
365	1	4.3
436	6	25.8

Figure A.4. Effect of wool of various monochromatic wavelengths. Upper right quadrant: bleaching. Lower right quadrant: yellowing or greening. Left of 400 mμ line: invisible increases or decreases of UV reflectance. Various arcs and filters. Dose = hours x *intensity in milliwatt-hrs/cm*^{2}*. Intensity at 254 mμ was 16.5 mw/cm*^{2} *(data of Launer 1965).*

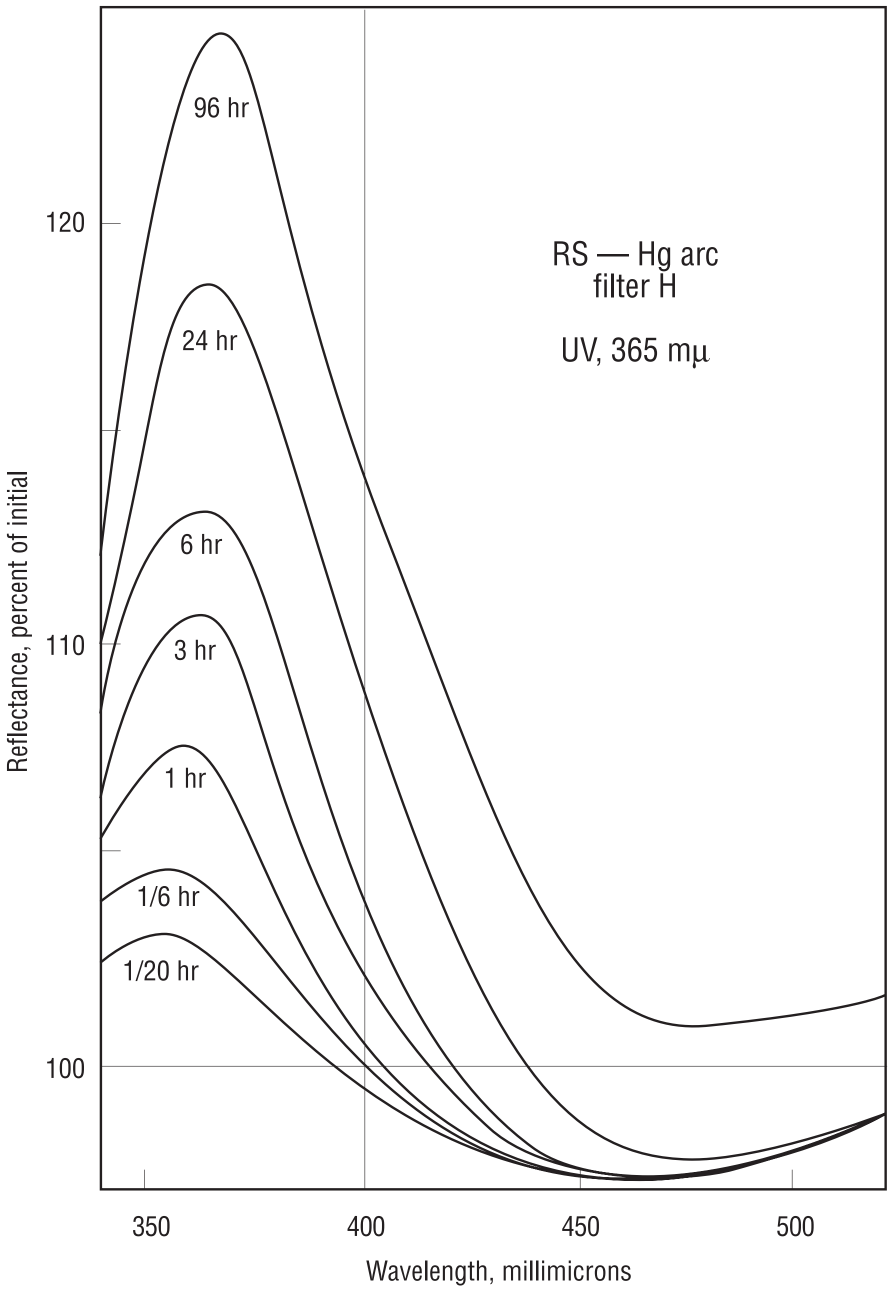


Figure A.5. Yellowing and/or bleaching and invisible ultraviolet reflectance increases by 365-nm UV. Various periods (data of Launer 1965).

the initially palest sample yellowed slightly. Xenotest exposure caused initial bleaching in the three most yellow wools; however, all samples eventually yellowed.

Figure A.3 shows the color changes induced in wools that have been intentionally discolored by various means prior to exposure in the Xenotest equipment. The yellowing induced by exposure to a light source rich in ultraviolet (sunlamp) is not bleached out. The yellow discoloration induced by heat behaves very much like that of the wool's natural yellowness (seen in Fig. A.2): Some samples were bleached initially but the palest wool sample darkened throughout the xenon exposure.

In Figure A.3, the wool darkened by heating in an alkaline buffer exhibited a sharp initial jump in yellowness. A similar phenomenon (a marked initial coloration followed by loss of color) has been observed in the aging of hydroxyethylcellulose (Feller and Wilt 1990). Apparently at least three different processes influence the results: the rapid initial yellowing, the fading of this discoloration, and the buildup of further chromophoric groups.

These results are important in part because they draw attention to the fact that the initial degree of discoloration influences the course of the aging curve; that is, the course of further color change in addition to the basic tendency of the light source to cause either bleaching, yellowing, or a combination of both effects. (Yellowness index in these studies was based on 100(R-B)/G, where the letters stand for the percent reflectance measured with red, blue, and green filters in a Colormaster Differential Colorimeter.)

Influence of Wavelength of Irradiance on Spectral Reflectance of Wool

Launer (recall the name in the landmark publications on paper deterioration by Launer and Wilson) may have provided the clearest demonstration of the effects of specific wavelengths on the spectral reflectance of wool (Launer 1965). The results that he obtained by irradiating wool with various wavelengths is seen in Figure A.4. A wavelength of 365 nm caused increased absorption in the visible region initially and, eventually, bleaching (Figure A.5).

When there is more than one process going on during photochemical exposures, it is likely that different wavelengths will stimulate one process more than another. Thus, Launer states, "yellowing decreases in the order 254, 315, 331, 365, and ceases entirely above 389 nm, and the disruption of bonds could be expected to decrease in the same order." He provides further insight by stating, "In the transition region wherein both yellowing and bleaching can occur, both at 365 and 389 mμ, a steady state is reached in which the rates of formation and elimination of absorbers are equal. This state persisted for 6 hours or more, after which the formation of blue absorbers slowed down, and their elimination prevailed. *The slowing down of bond disruption (and blue absorber formation) is probably due to what must be a depletion of the limited number of sites in the wool molecule that are subject to disruption at these relatively low photon energies. For higher-energy photons no such limitation was observed.*" (And therefore we find only yellowing. Author's italics.)

Launer's statement provides an excellent explanation for a *declining rate* or autoretardant stage in deterioration, attributed to the depletion of a limited number of particularly photosensitive sites (Feller 1977) (Figure 3.1c).

Conclusion

The literature provides excellent information regarding the effects of various wavelengths on the coloration and discoloration of wool. Furthermore, if the ISO R105 or the AATCC blue wool standards are to be used as monitors for photochemical exposure in museum-oriented studies, this information is of value regarding what may be happening to the wool substrate under different sources.

The chemistry of wool deterioration has been most recently reviewed by Crighton (1992).

Appendix B

Dyes

Owing to the great commercial significance of dyed textiles, much has been published and much is known about the fading of dyes. The literature is vast. Studies carried out with the short wavelengths of ultraviolet radiation emitted by unfiltered mercury vapor lamps will frequently turn up in an initial literature search. Unfortunately, as mentioned many times in these pages, the mechanisms that occur at these wavelengths may not be the same as those that will take place under the near ultraviolet and visible wavelengths of chief interest to conservators. Moreover, in searching the literature, one must remember that the extensive studies on dye fading, oxidation, and reduction carried out in solutions do not necessarily yield the same results as those on a fiber (Giles and McKay 1963:544).

The reader who wishes to pursue this extensive subject must be referred to reviews such as the recent one by Allen (1992) or the earlier one (Allen 1987) with its 234 references. There are also equally thorough early reviews by Giles and McKay (1963) as well as books such as that of Allen and McKellar (1980). Van Beek and Heertjes (1966) have presented an authoritative nine-page overview of the fading of organic dyestuffs by light which should be required reading for those who wish a brief introduction to the subject.

It is perhaps fair to say that more is known about the mechanisms, the specific chemical processes, involved in photochemically induced fading than is known about the chemistry of yellowing and embrittlement of paper, varnishes, and coatings. Space is not sufficient to develop the subject of mechanism extensively here; our purpose instead is to discuss the practical aspects of accelerated-aging tests. It is appropriate, therefore, to review factors that can influence the outcome of accelerated photochemical testing of materials to which organic colorants have been applied. The subject chiefly concerns dyes but many of the observations also apply to the behavior of lakes and certain pigments.

Giles and McKay (1963) succinctly summarizes this extensive subject. The rate at which a dye fades is governed by seven factors: (1) the photochemistry of the dye molecule; (2) the physical state of the dye; (3) the chemistry of the substrate; (4) the fine structure of the substrate; (5) the presence of foreign substances; (6) the atmosphere; and (7) the illumination. The last two aspects are discussed extensively in earlier chapters, although not always specifically regarding dyes. The other aspects deserve amplification.

Concerning Mechanisms

It has often been said that oxidation of the dye molecule should be the predominant reaction in fading (Giles and McKay 1963:541). Giles and McKay (1963: 540) briefly cite early investigations that demonstrated that many dyes would not fade in the absence of oxygen. However, the situation must be expressed more generally by saying that fading involves both oxidation and reduction processes. Giles and McKay thus state (1963:549): "The dye molecule is excited by absorbed radiation and then takes part in oxidation-reduction reactions. The dye may be oxidized or reduced, and some other substance, e.g., the fiber, simultaneously reduced or oxidized."

It is now generally considered that oxidation of the dye molecules occurs chiefly on cellulose and reduction takes place chiefly on protein substrates such as wool and gelatin. This problem is of such great significance in the testing of dyes for lightfastness that Irick and Boyd (1974) go so far as to say that "the ranking of a series of dyes depends on the fabric" (substrate). Cumming et al. (1956) sums up the situation in this manner:

> A dye may fade either by oxidation or by reduction. Fading on any non-protein substrate is normally a process of photochemical oxidation involving dye, water, and oxygen. The substrate itself does not necessarily take part in this reaction, though it may do so in special cases, and it may, of course, itself suffer photochemical degradation in a reaction which is independent of the dye fading.
>
> On a protein substrate fading appears to be normally a photochemical reduction process (at least in the early stages of fading), in which some constituent of the protein itself, probably the histidine side-chains, acts as the reducing agent. It is not known whether oxidation occurs in special circumstances on proteins, but this seems likely. It is known that a few particular dyes may be reduced when faded on non-protein fibres and this leads to the general conclusion that reduction and oxidation are alternative photochemical mechanisms of fading on any substrate, but usually reduction occurs on proteins, and oxidation on non-proteins.

Understanding of the different behavior on proteins as opposed to cellulose came about, as explained by Chipalkatti et al. (1954), owing to the pioneering studies of Kienle et al. (1946). In this work, the fading mechanism of a series of phenylazonaphthalene dyes was elucidated by using a series of substituents on the phenyl group. Hammett's σ-values for substituents on the benzene ring indicate whether the active site (here the azo group) is preferentially oxidized (negative values of σ) or reduced (positive values of σ) (Hammett 1970). Thus, the series of dyes in Figure B.1 tend to increase in their rate of fading on cellulose as the Hammett σ values become increasingly negative. In contrast, on silk (protein) faster fading occurred with the dyes having more positive σ values. The principle of using Hammett's concept of sigma and rho values perhaps has not been extensively used in recent years to elucidate mechanisms of dye fading, but at least one reference within the last decade can be cited, a study of the lightfastness of anthraquinone dyes (Allen et al. 1987).

Allen's extensive reviews (1992, 1987) and that of Egerton and Morgan (1970) can serve as an introduction to the subject of the specific mechanisms by which various chemical classes of dyes fade. For example, it has been found that azo dyes can fade by either oxidation or reduction and that the quantum yield is not effected by varying partial pressure of water vapor (Datyner et al. 1977). The fading of triphenylmethane colorants is apparently initiated through the ejection of an electron from the photo-excited dye cation. Anthraquinone dyes are able to sensitize the breakdown of cellulose or nylon fibers. Many studies on the behavior of specific classes of dyes could be cited, such as the contributions of Allen et al. (1981) on reactive and on anthraquinone disperse dyes (1975). Electron spin resonance can also reveal much

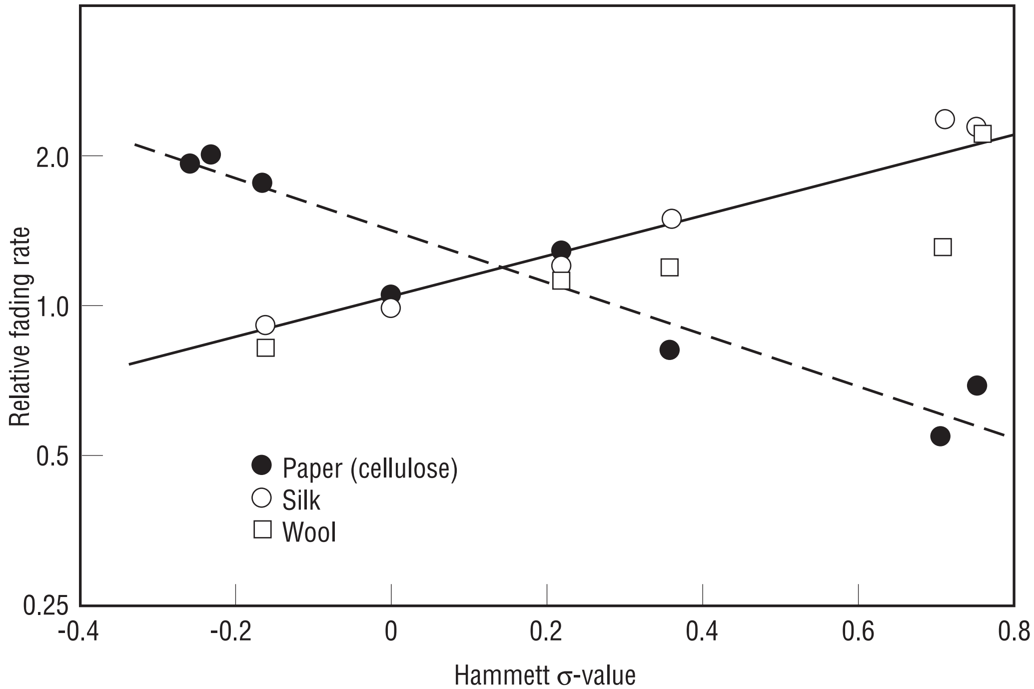


Figure B.1. Fading of phenylazonaphthalene dyes on cellulose and proteinaceous substrates relative to the Hammet σ-value of the substituent groups on the phenyl ring (after Chipalkatti et al. 1954).

concerning the formation of free radicals either in the dye component or the substrate (Coles and Nicholls 1976).

This last remark brings up the important subject of *photo-tendering.* This refers to the situation in which "a dye or pigment sensitizes, accelerates, or catalyzes the breakdown in molecular structure of a polymer substrate or binder material" (Allen 1987:67). The result may be reduction in molecular weight of the substrate molecules or may be cross-linking. As Allen points out, there has been much controversy about various mechanisms of photo-tendering. Nonetheless, it is easy to see how the dye molecule in an excited state can extract hydrogen from a substrate or water molecule, initiating a series of free-radical reactions that can lead to the destruction of the substrate. A series of equations proposed by Egerton (1949) is cited in Chapter 5. This scheme is not necessarily general or accurate in every detail. Nonetheless, such proposed mechanisms are useful in indicating the potential complexity of the photochemical processes. Of interest, for example, is the fact that slightly different pathways and intermediates have been proposed for dry and moist conditions, such as the following scheme cited by Allen (1987), where *D* is the dye and *D** the excited dye molecule:

$$D \longrightarrow {}^1D^* \text{ (singlet)} \longrightarrow {}^3D^* \text{ (triplet state)}$$

$$ {}^3D^* + {}^3O_2 \text{ (ground state)} \longrightarrow D + {}^1O_2 \text{ (singlet)} \qquad \text{dry conditions}$$

$$ {}^1O_2 + P\text{-}H \text{ (polymer)} \longrightarrow \text{oxidation products}$$

$$ {}^1O_2 + 2H_2O \longrightarrow 2H_2O_2 \qquad \text{moist conditions}$$

$$ H_2O_2 + \text{P-H} \longrightarrow \text{oxidation products}$$

Allen also cites the well-known photosensitivity caused by the presence of titanium and zinc white pigments as well as by cadmium sulfide. The presence of these pigments can lead to the formation of hydrogen peroxide (H_2O_2). This fact becomes particularly important in accelerated-testing experiments where undyed or unpigmented fibers can be degraded if placed adjacent to samples either dyed or pigmented that can thus evolve H_2O_2. Egerton (1948, 1949) presents an early discussion of this phenomenon.

Because an excited dye molecule has so many ways in which it can dissipate the energy absorbed, the quantum efficiency of fading and photosensitized deterioration of the substrate tends to be low (Giles et al. 1972a; Datyner et al. 1977; Kelly et al. 1982).

To round out reference to mechanisms of fading, it should be mentioned that studies of the mode of attack of ozone on dye molecules have recently been carried out in an extensive series of investigations sponsored by the Getty Conservation Institute (Cass et al. 1989).

Physical State of Colorant

Giles and his associates systematized the fading behavior of dyestuffs as a function of their degree of dispersion or aggregation (Giles et al. 1961, 1968a, 1977). More than half the pages in Giles and McKay's 1963 review is devoted to a summary of the state of contemporary knowledge of this subject. Lightfastness is effectively greater in the case of the larger particles. One result, as discussed more fully in the next section, is that the lightfastness of many dyed systems has been found to increase with the concentration of the dyestuff applied to the substrate. Large pigment particles also tend to fade more slowly than those finely dispersed (Hafner 1975).

Giles and others have proposed that the degree of association of dye molecules can be judged by the relative absorption of the two principal bands that are often present in the absorption spectra of dyes. The x-band (longer wavelength absorption) represents the monomeric dye; the y-band, the shorter wavelength absorption, is generally characteristic of the associated dye (Giles and McKay 1963:555). By following the change in the y/x band ratio, one can find, for example, indications that fading has taken place in a heterogeneous collection of particles and that the smaller, more fully dispersed particles break down first, and that the average particle size of the residual dye usually increases as fading progresses (Giles et al. 1968a; Tera et al. 1985). Moreover, should the dyes become more well dispersed during the early stage of exposure owing to an increase in the temperature of samples, this can be detected by an initial rapid increase in the y/x ratio. The concept of y/x ratios is still being applied (Tera et al. 1985).

The dependence of fading upon the state of aggregation of the dyestuff is one of the key practical problems in attempts to replicate fading tests. If an intra- or inter-laboratory repeat dyeing is carried out, the state of aggregation may not be duplicated. As a result, even though the same dye is involved, differences in fading behavior may be encountered that are not easily explained. Allen (1987) sums up the subject in this manner:

> Studies have continued to appear demonstrating the fact that aggregated dyes exhibit a much higher lightfastness than mono-disperse dyes. Dyes in more amorphous polymers apparently display a higher lightfastness than

when present in a more crystalline polymer and this was confirmed with experiments altering the porosity of regenerated cellulose film. On a more theoretical basis a new mathematical model has been developed to show that the rate of fading of dyes varies with $1/a^2$ (where a = radius of dye particle) for large dye particles, whereas for smaller dye particles the rate tends towards $1/a$ and for any small dye particles is independent of particle size (Giles et al. 1977). These models were later confirmed in a study on the effect of pigment particle size on the light stability of paint films (Hafner 1975).

Kinetics of Fading

Giles and his coworkers did much to organize the kinetic aspects of fading. The evolution of some of their ideas (Giles et al.) can be seen in the sequence of articles dated 1961, 1963, 1968 (two articles), and 1977. In an excellent summary of his position, Giles proposed that curves of apparent loss of dye concentration with time could be placed in five classifications (Giles et al. 1968a). Class I represented first- or second-order decay, the dye being present as single molecules or very small aggregates. Class II has Class I as an initial stage, followed by zero-order decay. Class III was zero-order fade, the loss of a constant amount of dye per unit of time, the dye in large aggregates or firmly enmeshed in substrate molecules. Class IV showed an apparent initial rise in dye concentration before a decline; Class V showed an increasing rate of fade with time. The last two behaviors occurred when large aggregates were affected by heat.

Giles and others solved the problem of precisely monitoring the change in concentration of dye during fading by measuring the change in absorption when the dyes were cast in thin transparent films, a technique still used (Kelly et al. 1982). By measuring the change in the optical density of the transmitted light, it was relatively easy to demonstrate first- or zero-order decay in the concentration of dye. However, if one wishes to follow the change in concentration of dye in a textile by measurement of the change in reflectance curves rather than transmission, the relationship of reflectance to concentration is much more complex than the Beers Law relationship which is usually obeyed in the case of transmitted light. In the fading in paints, for example, Johnston-Feller et al. (1984; Johnston-Feller 1986) used Kubelka-Munk theory in order to relate reflectance data to concentration of colorant.

In the early studies of the kinetics of fading, dating from about 1929 to the 1950s, Giles and others became aware that the time for a given fraction of the dye to be lost was often related to the initial concentration of dye. This was expressed as a "characteristic fading" curve with the equation

$$\log t_F = a \log D_0 + b$$

where t_F is the time required for a given loss of dye by fading, D_0 is the initial amount of dye present, and a and b are constants (Giles and McKay 1963:548; Giles, Johari, and Shah 1968). The slope, a, provides qualitative information on the state of association of the dye in the substrate. The slope should be zero (the curve horizontal) for pigments and large aggregates of dyes; steeper for systems in which increased aggregation or changes in particle size distribution occurs (Giles et al. 1961). These variations lead to the five classifications of fading behavior noted above.

One may also encounter cases of apparent reversible fading in which the initial shade change is somewhat restored in the dark. True *phototropism* can occur in solution, for instance, owing to a cis-trans change in the azo group observed in yellow and orange azo dyes (Egerton and Morgan 1970). On the other hand, yellow flavanthrone vat dye is reduced to the green leuco form when exposed to light on cellulose; in the dark, oxygen in the air will restore the yellow color. Cases of intensification of color upon exposure and apparent fading in the dark have been reported, attributed to the decreased aggregation of a dye under the heat of the illumination and reaggregation of the particles during cooling in the dark (Giles et al. 1961:840). Thus, when measuring the net change in color after exposure, one must always be alert to the possibility of reactions that may tend to continue or to reverse when samples are taken off exposure.

Whereas the kinetic expressions of fading rates cited above represent the state of the knowledge approximately two decades ago, those who wish to develop new concepts and interpretations will do well to review the various complexities of the problem that these earlier workers drew attention to. Allen (1987), for example, emphasized the fact that "most technological problems that arise in this field are due not only to the photochemical properties of the dye itself but also to the subsequent interactions that the photo-excited molecule may undergo with its environment." The latter refers to secondary reactions, particularly with the substrate. The statement that "no single mathematical expression can define dye-fading rates in textiles" perhaps still fairly represents the current point of view (Giles, Johari, and Shah 1968a).

Influence of Temperature and Humidity

We have earlier pointed out that the primary step in photochemistry is essentially independent of temperature. As a consequence, the rate of fading is often characterized by a low sensitivity to increased temperature (low energy of activation). This subject was reviewed with appropriate examples in Chapter 5. As mentioned elsewhere, the practical verification of this behavior is often confounded by the fact that simply raising the temperature of samples tends to lower the ambient relative humidity and, as a consequence, lower the moisture content of the sample.

In certain cases, the rate of fading of dyed materials may not yield a linear Arrhenius plot over a wide range of temperature. This is particularly true if measurements are made both below and above the second-order transition temperature (*Tg*) of the substrate (Kelly et al. 1982). The research team may also find that at moderate to high temperatures a dye may tend to sublime.

The situation with respect to temperature and humidity can be summarized briefly as follows (Kelly et al. 1982):

> Normally purely photochemical reactions have no activation energy [no thermal activation energy], hence the temperature dependence of fading must be due to the dark [secondary] reactions in the fading sequence subsequent to the initial excitation of the dye molecule. Lightfastness normally decreases with increasing atmospheric humidity, the extent of the effect being dependent on the dye-substrate system, and is very pronounced with cellulosic fibers.

Allen (1987) has elaborated further:

> In textiles, absorbed moisture apparently swells the fibres thus enabling air to penetrate the intermolecular pores more readily. This theory is supported by the fact that a humidity effect was not observed in the fading of dyes on anodised aluminum (Giles and McKay 1963). However, in this same programme of work the lower humidity sensitivity of the fading of dyes on wool does not support this hypothesis since wool actually swells more than cotton when it absorbs moisture. In this latter case some difference in chemical interaction between the dye and the two fibres was proposed. Previous work by the same authors indicates that whilst photoreduction is dominant in protein structures oxidation is dominant in other polymers. This conclusion was confirmed experimentally, to some extent, by the observation that a direct dye in cellulose under sealed conditions was stabilised whereas the same dye in gelatin film faded at the same rate in sealed and unsealed conditions.

Conclusion

To all but the most dedicated specialists, the available information concerning the mechanisms by which specific chemical classes of dyestuffs fade under the influence of visible and near-ultraviolet radiation tends to be overwhelming. The conservation scientist can have reasonable confidence that, somewhere in the extensive literature, a problem closely related to the one of principal concern may have already been investigated. The observable lightfastness of a given dyestuff is highly dependent on the particular substrate or vehicle involved, upon the chemical affinity between the two, and upon the degree of physical absorption, dispersion, or aggregation of the dye substance. Without prior information, the effect of temperature and humidity on a specific dye/substrate system is not readily predictable. Because fading can involve both oxidation and reduction, confirmation of the critical mode of action is required in each individual case. Such factors contribute to deviations in the experimental findings between laboratories and between different batches of supposedly duplicate preparations.

Appendix C

Induction Time and the Auto-oxidation of Organic Compounds

Oxidation is perhaps the fundamental cause of the deterioration of organic substances. It is therefore appropriate to consider the basic mechanism of oxidation of organic compounds in detail. As a result of the fundamental investigations by Bolland and Gee (1946) and others beginning in the late 1940s, we are able to make a number of useful generalizations regarding a type of reaction of organic compounds known as auto-oxidation, a process characterized by the fact that the rate of oxygen consumption increases in time up to a point at which a maximum rate is attained, after which it may decrease as the more readily oxidized sites within the molecules become fully reacted.[1]

The type of auto-oxidation of particular interest is that which takes place through the mechanism of organic hydroperoxide formation (compounds of structure ROOH). Equations C.1 provide the chemical equations that explain this process. An *initiation* step generates free radicals—either R•, RO•, or ROO•. In advanced stages of auto-oxidation, these free radicals are considered to arise primarily from the decomposition of the hydroperoxides (ROOH) that are formed.

Propagation of the chain reaction involves two substeps: the fast uptake of oxygen, forming a radical, ROO•, which then attacks another organic molecule in a slower substep 2. The latter—the rate of hydrogen atom abstraction from an organic molecule—is generally considered to be the rate-controlling substep.

Proposed Chemical Reactions:

$$\begin{array}{rll} \text{Step 1: Initiation:} & 2ROOH \rightarrow R\bullet + ROO\bullet + H_2O & (k_1) \\ \text{Step 2: Propagation:} & R\bullet + O_2 \rightarrow ROO\bullet \quad \text{fast} & (k_2) \\ & ROO\bullet + RH \rightarrow ROOH + R\bullet & (k_3) \\ \text{also,} & ROO\bullet + C{=}C \rightarrow ROOC - C\bullet & (k_{3a}) \end{array} \tag{C.1}$$

Termination occurs when two radicals combine, or when a radical decomposes to yield particles that are no longer free radicals.

$$\begin{array}{lll} \text{Step 3: Termination:} & 2R\bullet \rightarrow & (k_4) \\ & ROO\bullet + R\bullet & (k_5) \\ & 2ROO\bullet \rightarrow & (k_6) \end{array}$$

Kinetic Laws of Auto-oxidation

Chemical kinetics is a branch of physical chemistry that deals with the laws that relate to the influence of various factors on the rate of chemical reactions. The mathematical equations used to express these relationships may seem complicated to those unfamiliar with the principles, but the conclusions based on them permit valuable generalizations to be made concerning the influence of heat, light, oxygen, and catalysts on the rate of chemical reactions.

Kinetic Relationships

$$\frac{-d[O_2]}{dt} = \frac{d[ROOH]}{dt} = k_3\,[ROO\bullet][RH] \quad \text{under mild conditions of oxidation} \qquad (a)$$

at high oxygen pressures

$$k_1[ROOH]^2_\infty = k_6[ROO\bullet]^2 \text{ at steady state (max. rate)} \qquad (b)$$

$$\frac{-d[O_2]}{dt} = k_3\left(\frac{k_1}{k_6}\right)^{\frac{1}{2}}[ROOH]_\infty[RH] \quad = \frac{k_3{}^2}{k_6}[RH]^2 \qquad (c)$$

(C.2)

at low oxygen pressures

$$\frac{-d[O_2]}{dt} = k_2[R\bullet][O_2] \qquad (d)$$

$$k_1[ROOH]^2_\infty = k_4[R\bullet\,]^2 \text{ at steady state (max. rate)} \qquad (e)$$

$$\frac{-d[O_2]}{dt} = k_2\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}}[ROOH]_\infty[O_2] \qquad (f)$$

The basic assumption in the proposed mechanism of auto-oxidation in Equations C.1 is that, under mild conditions of oxidation, Equation C.2a will describe the rate of consumption of oxygen, $-d[O_2]/dt$, at least in the early stages of oxidation. The rate will be controlled by substep k_3 because substep k_2 is very fast. At later stages, the maximum rate of oxygen consumption is given by Equation C.2c.

Maximum Rate

For preservation scientists, the first important conclusion to be drawn from consideration of Equation C.2c is that—regardless of how the oxidation of an organic material may be initiated—an organic compound tends to exhibit a characteristic maximum rate of oxidation at any particular temperature. (Humidity, undoubtedly, is also a factor.) The maximum rate is dependent primarily on the temperature because temperature influences k_3, the specific rate constant of substep 2, and k_6, a specific rate constant of termination.

The second conclusion to be drawn from Equation C.2c is that variations in the rate of initiation do not effect the maximum rate (k_1 need not appear in Eq. C.2c). Thus, in Figure C.1, the experimental data clearly demonstrate that increasing the amount of cobalt catalyst, which influences the initiation step, shortens the time required to reach the maximum rate, but does not change the maximum rate, just as the theory predicts (Woodward and Mesrobian 1953).

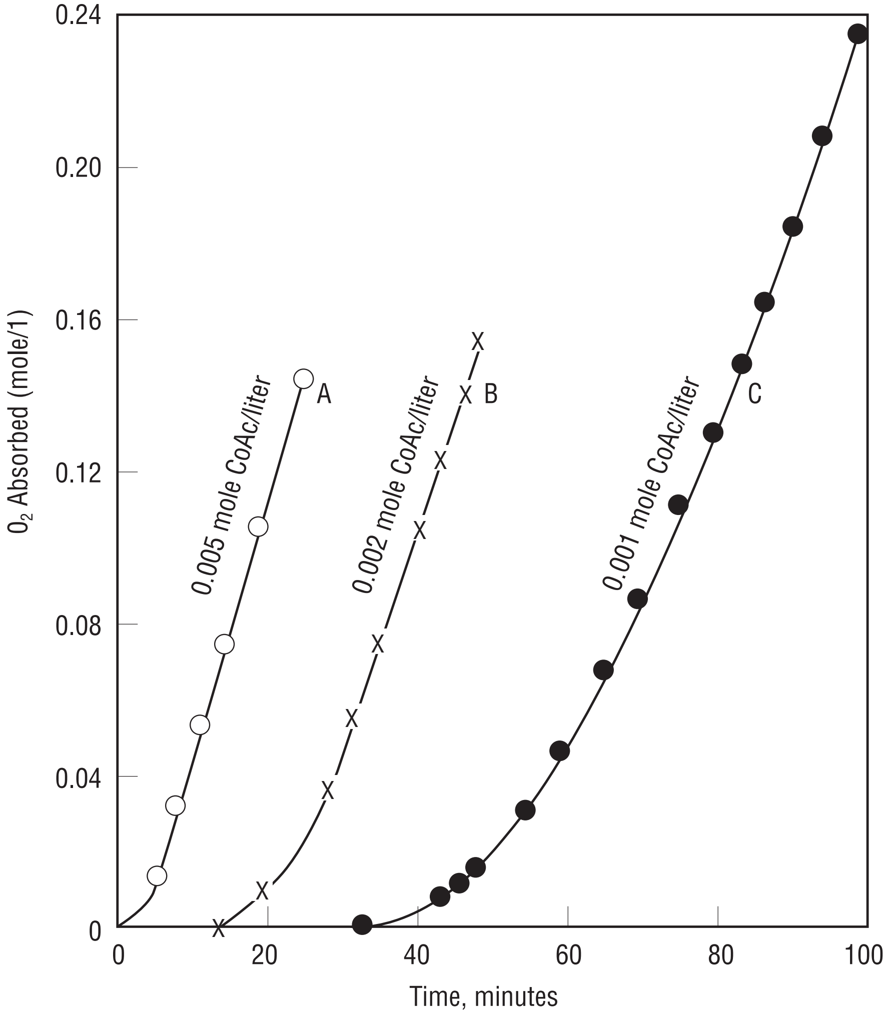


Figure C.1. Auto-oxidation of tetralin in the presence of cobaltous acetate (Woodward and Mesrobian 1953).

Induction Time

More than 40 years ago, Tobolsky et al. elaborated on the basic kinetic equations of Bolland and Gee (1946), starting with the assumption that both the production and disappearance of ROOH should be considered:

$$d\,\mathrm{ROOH}]/dt = k_3(k_1/\,k_6)^{1/2}\,[\mathrm{ROOH}][\mathrm{RH}] - k_1[\mathrm{ROOH}]^2 \tag{C.3}$$

Based on Equation C.3, these authors developed mathematical equations to show how the rate of oxygen consumption would increase in time until a maximum of *steady-state* rate is obtained (Tobolsky et al. 1950). The increase in the oxygen uptake with time was expressed as a function of - $[O_2]/[\mathrm{ROOH}]_\infty$ (the amount of oxygen uptake, relative to the maximum concentration of hydroperoxide) and the ratio $[\mathrm{ROOH}]_\infty/[\mathrm{ROOH}]_0$ (the ratio of the maximum concentration of hydroperoxide, $[\mathrm{ROOH}]_\infty$, to the initial concentration, $[\mathrm{ROOH}]_0$.) The calculated curves, shown in Figure C.2 are similar to the curves observed with many compounds during thermal aging: The rate of oxygen consumption generally starts out very slowly and builds up to a maximum rate (compare Fig. C.1 with Fig. C.2). In some cases (dotted lines), where there is a high initial concentration of peroxide, the rate may start out very high before falling off to the *steady-state* value.

One of the essential characteristics of auto-oxidation is its chain-reaction aspect. As the result of the propagation substeps 1 and 2 in Equation C.1, a great many organic molecules can be converted to ROOH *by a single initiating event.* Such a process is known as a *free-radical chain-reaction* and the *chain length* is given by the following relationship:

$$\text{chain length} = \frac{\text{rate of oxidation}}{\text{rate of initiation}} = \frac{k_3\,[\mathrm{RO_2}\bullet][\mathrm{RH}]}{k_1\,[\mathrm{ROOH}]^2} = \frac{k_3\sqrt{k_1/\,k_6}\,[\mathrm{ROOH}][\mathrm{RH}]}{k_1\,[\mathrm{ROOH}]^2} = \frac{[\mathrm{ROOH}]_\infty}{[\mathrm{ROOH}]} \tag{C.4}$$

Equation C.4 tells us that, when the maximum rate is achieved, that is, when [ROOH] is equal to $[\mathrm{ROOH}]_\infty$, the chain length will be 1. This fact has important consequences when an attempt is made to inhibit reactions occurring at high temperature or to inhibit photochemically initiated reactions, because inhibitors that react with peroxide radicals, thereby interrupting the chain, will have little effect when the chain length is short.

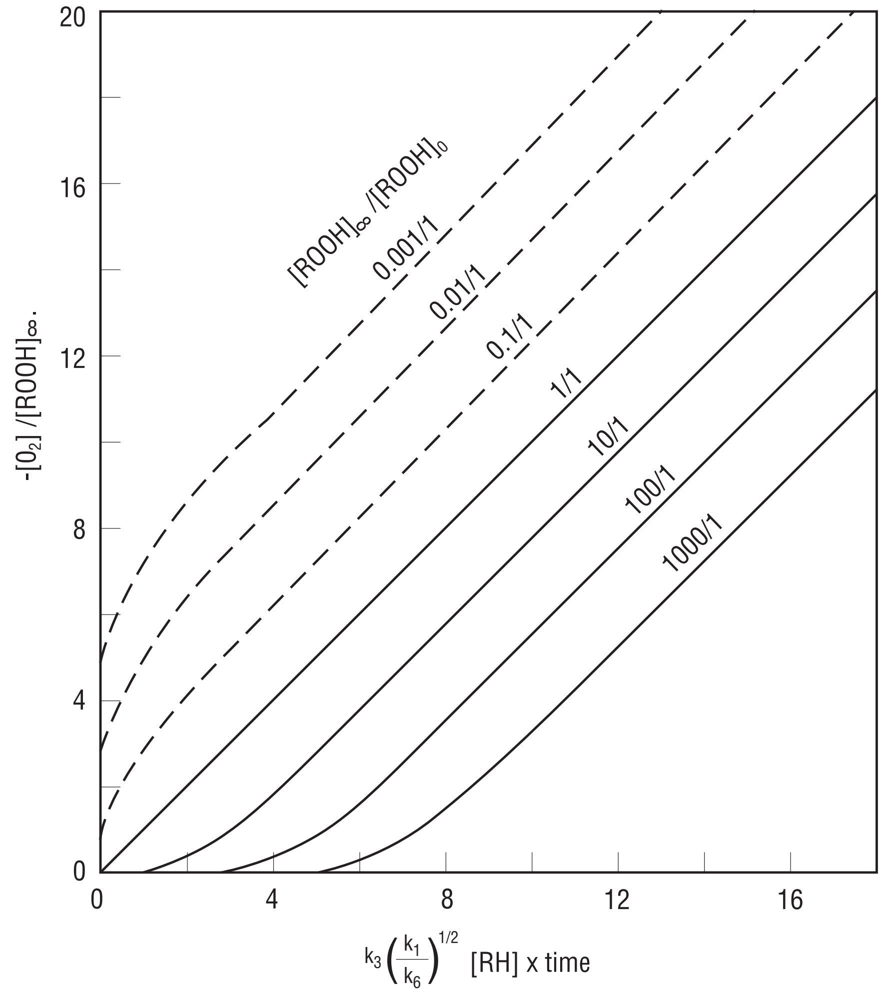


Figure C.2. Theoretical curves of oxygen absorption as a function of time (Tobolsky, Metz, and Mesrobian 1950).

The length of time before the maximum rate of oxygen consumption is obtained may be called the *induction time*. From consideration of Figure C.2 , it can be seen that the induction time is related to the chain length of the propagation step; that is, to $[ROOH]_\infty/[ROOH]_0$. In practice, induction times are observed to vary considerably, from very long times to practically zero, depending on the materials and conditions.

Influence of Light

Analysis of the kinetics of the reactions tells us much about the action of light on auto-oxidation. Careful examination of the chemical products of many oxidation reactions by a number of investigators has confirmed the fact that exposure to light does not alter the character of the propagation substeps. Instead, light influences the initiation step. Because the rate of initiation is speeded up, exposure to light shortens the time required to reach the maximum or *steady-state* rate of oxidation.

These important conclusions are illustrated by the data of Tobolsky et al. (1950) for the oxidation of natural rubber shown in Figure C.3. At 50 °C, the photochemically activated rate proceeds at the maximum rate for that temperature, while the thermal reaction apparently has a long induction time. At 75 °C, the thermally activated rate of oxidation has a measurable induction time before the rate attains the *maximum rate,* which is indicated in Figure C.3 to be equivalent to the photochemically induced rate. Finally, at a sufficiently high temperature, 100 °C, both the thermally and photochemically activated reactions proceed at the same rate.

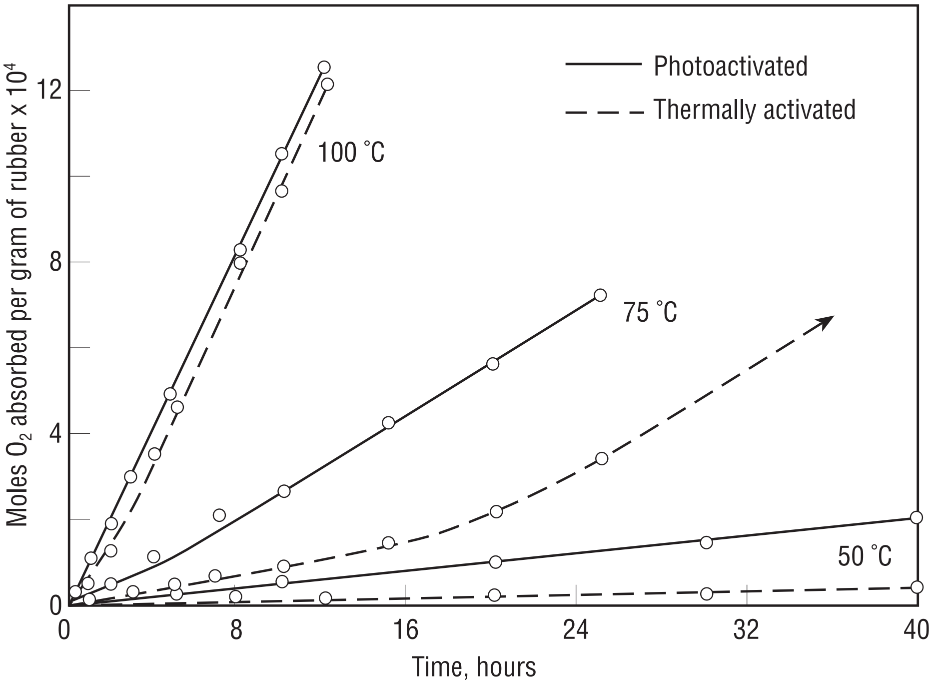


Figure C.3. Oxygen absorption versus time for natural rubber vulcanizate (Tobolsky, Metz, and Mesrobian 1950).

Why is exposure to light so harmful to many museum objects? Part of the answer is that it tends to shorten the time required to reach the maximum possible rate of oxidation at a given temperature. In many cases, such as the examples illustrated in Figure C.3, the induction time is reduced for all practical purposes to zero.

Influence of the Concentration of Oxygen

There has long been an interest in preservation science in the protection of sensitive materials by storing or exhibiting them in an inert atmosphere. Analysis of the kinetic reactions in Equation C.1 suggests that, at low concentrations of oxygen (or, as the chemist might say, "at low partial pressures" of oxygen) propagation substep k_2 would become the rate-controlling step and, therefore, Equation C.2f would account for the maximum rate of consumption of oxygen.

The range of oxygen pressures over which the transition occurs from a rate of oxidation independent of oxygen pressure (governed by Eq. C.2c) to a rate directly related to the concentration of oxygen (Eq. C.2f) is determined by temperature and by the speed of (termination) substep k_3. Thus, Bateman and Morris (1953) have demonstrated that a hydrocarbon of low reactivity in (termination) substep 2, hexadecene-1, is not apparently influenced by the pressure of oxygen down to as low as 1 mm of mercury (one atmosphere of oxygen is equivalent to 760 mm). In comparison, ethyl linoleate (related to one of the important components of linseed oil) begins to be influenced by a decrease in the partial pressure of oxygen below 200 mm and 2,6-dimethylhepta-2,5-diene which reacts still faster, is influenced by the concentration of oxygen even at one atmosphere (Fig. C.4).

Thus, kinetic analyses provide a firm theoretical basis on which to predict the way in which the rate of oxidative deterioration of many materials may be controlled by diminishing the concentration of oxygen in the surrounding atmosphere. The substances that are most sensitive to oxidation are the ones that will most readily benefit from even a partial reduction of the concentration of oxygen.

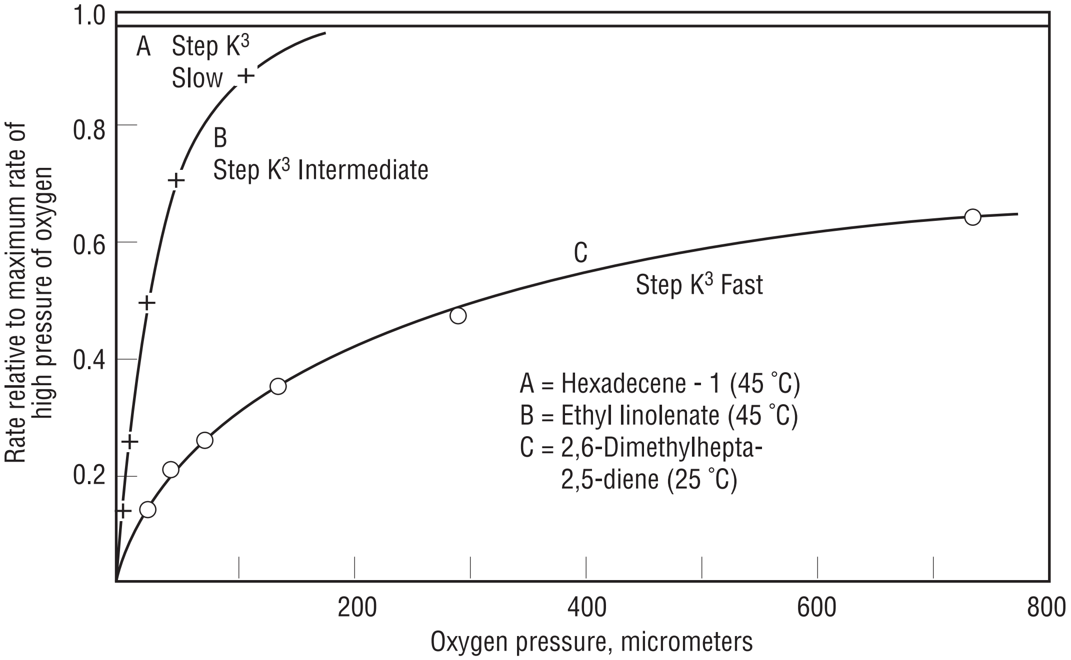


Figure C.4. Effects of oxygen pressure on oxidation rates of unsaturated hydrocarbons (Bateman and Morris 1953).

Influence of Inhibitors

Equations developed by Bolland and Gee (1946) predict that the rate of oxygen consumption will be slowed down in an inverse relationship to the concentration of an inhibitor that terminates the main chain by reactions of the type:

$$AH + R\bullet \text{ (or } ROO\bullet\text{)} \rightarrow A\bullet + RH \text{ (or } ROOH\text{) (AH is the inhibitor)}$$

The induction time has been found to be increased in proportion to the logarithm of the concentration of the inhibitor in many instances.

Conclusion

Not every case of oxidative deterioration or organic substances proceeds by the mechanism of hydroperoxide formation and auto-oxidation. However, in the large number of cases that do, the landmark publication of Tobolsky et al. (1950) provides the essential theory and equations to undergird the development of improved methods and materials for preservation. Thus, as stated by the author in a previous publication, we must set about to determine those materials to be preserved that tend to undergo auto-oxidation and to exhibit an induction time (Feller 1967). Further, we must begin to analyze problems in deterioration and preservation of organic materials in museums by distinguishing those aspects that are associated with the initiation steps (the effect of light and catalysts) from those associated with the propagation steps (the effect of the chemical structure of compounds and the effect of the concentration of oxygen).

Many changes in physical properties that occur during deterioration—changes in brittleness, tensile strength, and color—exhibit a period in which little seems to be taking place, yet following which marked changes occur. Such a period of relative stability may be considered as an apparent induction time with respect to a given physical property or chemical reaction. In 1976, it was pointed out that an apparent induction time could be observed in the deterioration of a variety of materials and could be observed in the changes that occur in a variety of their physical properties.[3]

The induction time in oxidative deterioration that involves the formation of organic hydroperoxides may be precisely defined as the time of exposure before the maximum rate of oxygen consumption occurs under any given set of conditions. Upon consideration of this definition, it appears that most of the measures that are taken, or that should be taken, to conserve organic materials are concerned with processes that occur during the induction time of oxidative deterioration and are measures essentially concerned with prolongation of the period of induction. Certainly, the concepts presented here will give direction to our research on the preservation of organic materials for many years to come.

Notes

The material in this appendix originally appeared in the *Bulletin of the American Institute for Conservation* 14 (2) 1974:142-51, under the title "Fundamentals of Conservation Science: Induction Time and the Auto-oxidation of Organic Compounds."

1. The kinetic expression for the rate at which molecule A is consumed in the reaction $A + B \longrightarrow m$ is expressed as $-d(A)/dt = k(A)(B)$ where (A) stands for "the concentration of A." For the reaction $A + A \longrightarrow m$, the corresponding expression is $-d(A)/dt = k(A)^2$. The first mathematical equation may be stated as follows: "The incremental change in the concentration of A, $d(A)$, with infinitesimally small increments of time, dt (that is, the instantaneous rate of change in the concentration of A) is proportional to the concentration of A multiplied by the concentration of B." The factor or proportionality, k, has been called the "specific reaction rate."

2. Algebraic manipulation of Equation C.2a allows us to derive Equation C.2c on the basis of the assumption that, when the maximum or steady-state rate is reached, the rate of initiation will be equal to the rate of termination (Eq. C.2b). The final simplification of C.2c is obtained by further assuming that, at this stage, -d[ROOH]/dt = 0 in Equation C.3. The equations shown here are all based on a number of assumptions that allow them to be conveniently simplified. The most important qualifying assumption in all the derived equations is that initiation involves the "bimolecular" decomposition of ROOH, although this is not the invariable rule.

3. Long-term studies have shown that the apparent induction time for the formation of insoluble matter in butyl methacrylate polymers exposed on a laboratory wall illuminated by diffuse daylight is about 11 years (Feller, Stolow, and Jones, 1985:159). Chemical reactions that result in deterioration—in the form of chain-breaking or the development of colored substances, for example—involve changes in the structure of R from the original organic compound. These frequently are reactions involving the break up of the radicals R• and ROO• and may or may not lead to termination. On the other hand, the cross-linking of poly(butyl methacrylate) and related polymers is likely to be the result of a termination step.

Appendix D

Sensitivity to Wavelength as Determined by Sharp Cut-off Filters

Narrow-band-pass filters allow one to detect directly the effects at relatively specific wavelength regions. In contrast, sharp cut-off filters permit all wavelengths above a certain minimum to strike the sample, making it somewhat more difficult to isolate the effects of specific wavelengths. Nonetheless, it is the usual case in the practical world that materials are exposed to "all photoactive wavelengths above a certain cut-off wavelength."

Martin and Tilley (1971) describe a method by which the specific effects of the narrow range of wavelengths between each of a series of sharp cut-off filters can be calculated. Table D.1 gives the basic experimental data on the rate of photo-oxidation of poly(vinylchloride) measured by the change in absorption of the carbonyl group and the relative radiant power reaching the sample in various wave bands (represented by the differences in the transmitted radiant power in the wavelengths between each of the filters). The equations given in the appendix of the Martin and Tilley article (shown here on pages 198-99) illustrate the technique of solving a series of equations to determine the factors associated with the photochemical activity of each of these wavelength regions. The calculations yielded the results shown in Figure D.1, indicating that the wavelengths between 355 and 385 nm constituted the region of maximum photochemical activity. Similar figures based on the use of sharp cut-off filters appear in Andrady and Searle (1989) and Andrady et al. (1992).

Relative Energy in Each Wavelength Band

Filter no.	280–312 nm	312–355 nm	355–385 nm	385–415 nm	415–445 nm	445–480 nm	Photo-oxidation rate (R), under each filter $10^{-4}\ \Delta A\ h^{-1}$
None	3.2	17.7	17.9	25.8	29.1	50.7	4.63
A	0.5	14.8	16.1	23.3	26.5	46.5	4.27
B		2.1	14.1	23.0	26.4	46.5	2.68
C			3.5	16.6	22.6	42.0	0.94
D				6.2	24.2	44.7	0.28
E					0.6	36.9	0.08
F						9.2	nil

Table D.1. Energy distributions and photo-oxidation rates for unstabilized poly(vinylchloride) (Martin and Tilley 1971).

Calculations Used by Martin and Tilley (1971)

Estimate of β for Different Wavelength Bands

Using the relation $R = \beta I$, where R is the rate of photo-oxidation and I the intensity of radiation, equations may be stated from the data in the table below for each of the bands of wavelength.

Thus, if β_1, β_2, β_3, β_4, β_5, and β_6 correspond to the bands 280–312, 312–355, 355–385, 385–415, 415–445, and 445–480 nm respectively, and R_{nil}, R_A, R_B, R_C, R_D, R_E, and R_F are the rates of photo-oxidation of the PVC when the radiation passes through no filter, and filters A, B, C, D, E, and F, respectively, the equations are:

$$R_{\mathrm{nil}} = 4.63 \times 10^{-4} = 3.2\,\beta_1 + 17.7\,\beta_2 + 17.9\,\beta_3 + 25.8\,\beta_4 + 29.1\,\beta_5 + 50.7\,\beta_6 \qquad (1)$$

$$R_A = 4.27 \times 10^{-4} = 0.5\,\beta_1 + 14.8\,\beta_2 + 16.1\,\beta_3 + 23.3\,\beta_4 + 26.5\,\beta_5 + 46.5\,\beta_6 \qquad (2)$$

$$R_B = 2.68 \times 10^{-4} = 2.1\,\beta_2 + 14.1\,\beta_3 + 23.0\,\beta_4 + 26.4\,\beta_5 + 46.5\,\beta_6 \qquad (3)$$

$$R_C = 0.94 \times 10^{-4} = 3.5\,\beta_3 + 16.6\,\beta_4 + 22.6\,\beta_5 + 42.0\,\beta_6 \qquad (4)$$

$$R_D = 0.28 \times 10^{-4} = 6.2\,\beta_4 + 24.2\,\beta_5 + 44.7\,\beta_6 \qquad (5)$$

$$R_E = 0.08 \times 10^{-4} = 0.6\,\beta_5 + 36.9\,\beta_6 \qquad (6)$$

$$R_F = 0.00 \times 10^{-4} = 9.2\,\beta_6 \qquad (7)$$

This empirical set of equations cannot be uniquely solved.

However, assuming $\beta_6 = 0$ and β_5 is very small and neglecting β_1 in equation (2), the equations may be approximated to the following:

$$R_A - R_B = (4.27 - 2.68)\,10^{-4} = 12.7\,\beta_2 + 2.0\,\beta_3 \qquad (8)$$

$$R_B - R_C = (2.68 - 0.94)\,10^{-4} = 2.1\,\beta_2 + 10.6\,\beta_3 + 6.4\,\beta_4 \qquad (9)$$

$$R_C - R_D = (0.94 - 0.28)\,10^{-4} = 3.5\,\beta_3 + 10.4\,\beta_4 \qquad (10)$$

$$R_D - R_E = (0.28 - 0.08)\,10^{-4} = 6.2\,\beta_4 + 23.6\,\beta_5 \qquad (11)$$

From (8): $\beta_2 = (0.12 \times 10^{-4}) - 0.16\,\beta_3$ (12)

From (9): $\beta_3 = (0.16 \times 10^{-4}) - 0.2\,\beta_2 - 0.6\,\beta_4$ (13)

Substituting (12) in (13):

$\beta_3 = (0.14 \times 10^{-4}) - 0.6\,\beta_4$ (14)

From (10): $\beta_3 = (0.19 \times 10^{-4}) - 3.0\,\beta_4$ (15)

Substituting (15) in (14):

$$\beta_4 = 0.02 \times 10^{-4} \quad (16)$$

Hence, from (14):

$$\beta_3 = 0.13 \times 10^{-4} \quad (17)$$

From (12): $\beta_2 = 0.09 \times 10^{-4}$ (18)

and from (11): $\beta_5 = 0.003 \times 10^{-4}$ (19)

Substituting these values of β_2, β_3, β_4, and β_5 with $\beta_6 = 0$ in (1) gives:

$$\beta_1 = 0.037 \times 10^{-4} \quad (20)$$

This value of β_1 is considered to be less accurate than the values of β_2 to β_6 because there is much less energy in the 280–312 nm band upon which it has been based.

Substituting the value of β_5 in (6) indicates that $\beta_6 = 0$ but $\beta_6 = 0.002$. Evaluating the R.H.S. (right-hand set [or series]) of equations (1) to (6) with the values

$\beta_1 = 0.037$

$\beta_2 = 0.090$

$\beta_3 = 0.130$

$\beta_4 = 0.020$

$\beta_5 = 0.003$

$\beta_6 = 0.002$, gives:

Calculation for the L.H.S. (left-hand series of numbers):

(1) = 4.74 cf. L.H.S. = 4.63

(2) = 4.08 cf. L.H.S. = 4.27

(3) = 2.65 cf. L.H.S. = 2.68

(4) = 0.94 cf. L.H.S. = 0.94

(5) = 0.28 cf. L.H.S. = 0.28

(6) = 0.08 cf. L.H.S. = 0.08

thus indicating that the estimates are reasonable.

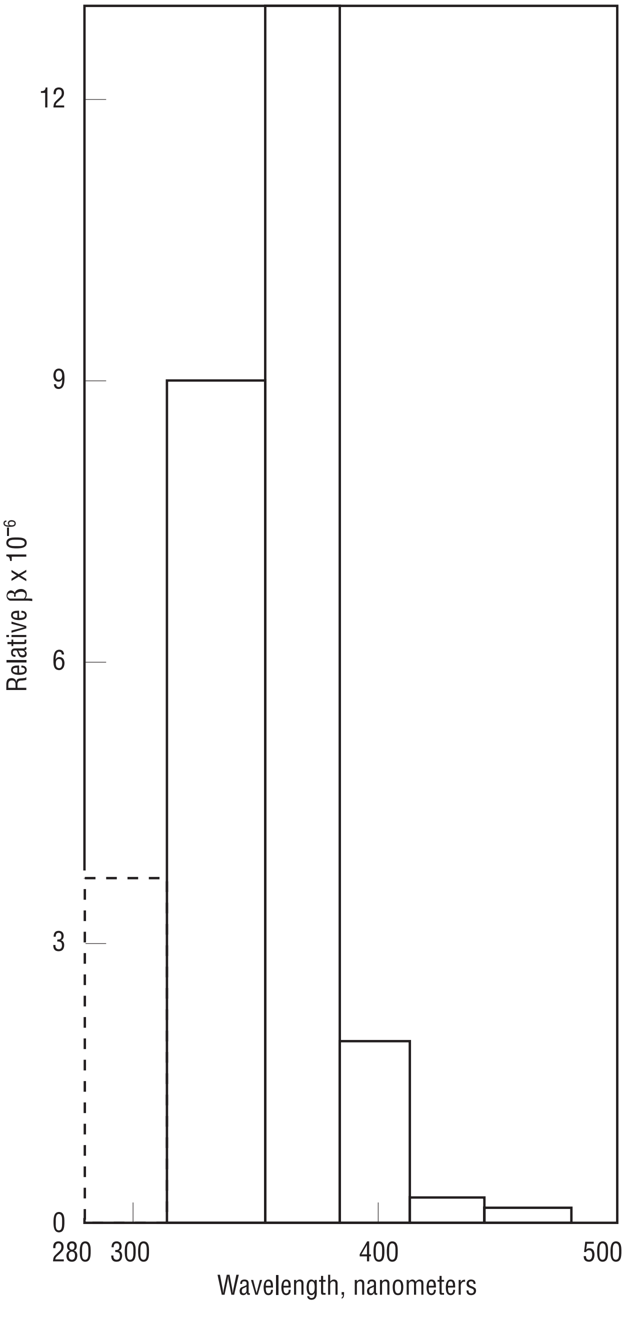


Figure D.1. Wavelength sensitivity of PVC photo-oxidized by xenon-arc or solar radiation (Martin and Tilley 1971).

Appendix E

Determination of Photo-initiation Rates by Measurement of Nitroxide Termination

In the early 1980s workers at the Ford Motor Company research laboratories began developing a technique that enabled one to determine the rate of photo-initiation (Gerlock et al. 1983; Gerlock 1983; Gerlock et al. 1984). The most accessible descriptions of the procedure are perhaps those of Gerlock et al. (1985) or Gerlock et al. (1984). In the presence of a high concentration of a nitroxide compound (>NO•), one can determine the rate at which free radicals are photo-induced by plotting the initial rate of decay of the nitroxide free radical (determined by electron spin resonance, ESR) versus nitroxide concentration and extrapolating to the value at zero nitroxide.

$$d[>NO\bullet]/dt) \quad = \quad -R_i \quad - \quad k[>NO\bullet]_0$$

initial rate of decay of nitroxide radicals = rate of photo-initiation – k (proportionality factor) times initial concentration of nitroxide

The second term simply represents the normal first-order decay of the nitroxide. The intercept at zero nitroxide concentration, -R_i, represents the formation of initiating free radicals (X•) because this process also reduces the concentration of nitroxide through the following series of reactions:

$$A \xrightarrow[\text{light}]{} A^*$$

molecule with sensitizing chromophore — activated molecule

$$A^* \rightarrow 2X\bullet \text{ (two free radicals)}$$

$$X\bullet + >NO\bullet \rightarrow >NOX$$

Figure E.1 shows the authors' data for a number of acrylic-melamine coatings. The intercepts at zero concentration of nitroxide represent the rates of photoinitiation in the different polymers.

This powerful tool was able to determine initial rates of photo-initiation in about an hour's time, whereas the determination of the rates of loss of gloss required about 100 hours of exposure. The technique was able to show precisely that the presence of rutile titanium white did not increase the photo-initiation rate but instead lowered it by shielding the resin from the light. The authors were also able to show that the rate of loss of gloss (empirically a first-order decay) was proportional to the square root of the rate of initiation. Although humidity increased the rate of deterioration of the coatings, it was found that the rate of photo-initiation was not increased, forcing the authors to look for another explanation. The release of formaldehyde during hydrolysis resulted in a further source of oxidation: the formation and subsequent reactivity of peroxyformic acid.

Numerous publications by these authors describe the technique of "doping" coatings with the necessary nitroxide after exposure (Gerlock et al. 1988) and recommend a test protocol for rapid tests of weatherability (Bauer, Gerlock, and Dickie 1987). More recently the authors have described in detail the deterioration of acrylic/melamine and acrylic/urethane coatings containing a hindered amine light stabilizer (Gerlock et al. 1986; Gerlock et al. 1987; Bauer et al. 1990).

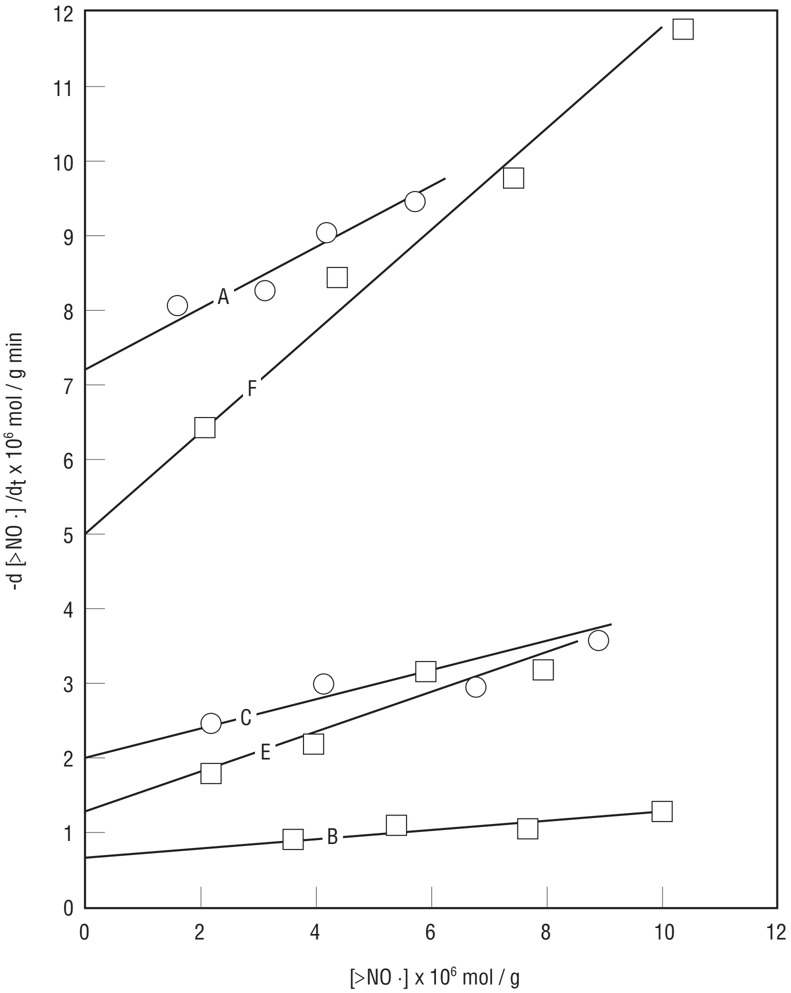


Figure E.1. Initial rate of nitroxide loss versus initial nitroxide concentration for the six coatings. The slope is a measure of the ease of hydrogen abstraction by excited state nitroxide, while the intercept is the rate of free-radical photo-initiation in the coating (Gerlock et al. 1984).

Although this technique is only briefly mentioned here, it is one of the most sensitive and potentially powerful ways of studying the photochemistry of deterioration for it provides a way in which the rate of photo-initiation may be determined with specificity. Rather than employing this time-consuming (although precise) procedure, Sommer et al. (1991) have suggested as an alternative simply measuring the increase in the free-radical concentration within a coating material under exposure by ESR spectroscopy.

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About the Author

Robert L. Feller has made major contributions to scholarship and conservation since first entering the field in the early 1950s. After earning a Ph.D. in physical-organic chemistry from Rutgers University, he joined the Mellon Institute (now Carnegie Mellon Research Institute) in Pittsburgh as senior fellow of the National Gallery of Art Research Project on artists' materials. In 1976 he became director of the Center for Materials of the Artist and Conservator through a grant from the Andrew Mellon Foundation. His principal research interests have concerned the physical properties and long-term stability of thermoplastic resins and the fading of pigments and other deteriorating action of visible and ultraviolet radiation. An Honorary Member of the American Institute for Conservation, he is currently director emeritus of the Research Center on the Materials of the Artist and Conservator at Carnegie Mellon Research Institute.