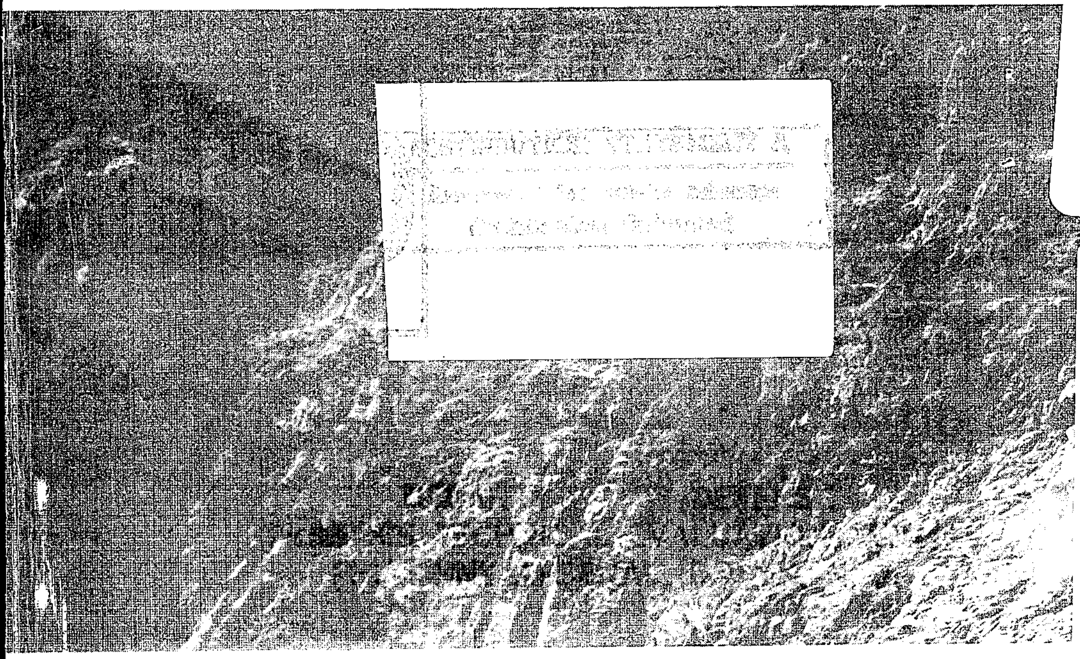
Weatherability of Plastic Materials

Editor:
Musa R. Kamal



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Weatherability of Plastic Materials

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Editor

Musa R. Kamal, *American Cyanamid Company*

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Preface

The growth of the plastics industry in recent years has been accompanied with a significant expansion in the outdoor application of plastic materials. Along with this expansion, it became necessary to develop standard tests for the evaluation of the weathering characteristics of candidate materials in comparison with established specifications. Moreover, dependable techniques were needed for the systematic development of weatherable plastics in the laboratory, and for the study of the effect of variations in basic composition, additives, and manufacturing procedure on weatherability.

In the course of developing or evaluating a material for prolonged outdoor application, it is difficult, if not impossible, to rely on outdoor exposure as the only method of evaluation. Also, the variability of weather in time and space, and the effect of this variability on the weathering characteristics of the material suggest the inadequacy of limited, standard outdoor tests. Thus, the development of useful accelerated and predictive techniques has been one of the most important objectives of weatherability work.

Since plastics are relatively new materials, only limited effort has been directed to the solution and characterization of problems associated with weatherability. On the other hand, the rapid expansion of plastics application outdoors coupled with the complexity and urgency of weatherability problems has emphasized the need for cooperative, centralized effort by plastic manufacturers.

In light of the above, it is not surprising that a comprehensive survey, completed by the Manufacturing Chemists' Association in 1964, resulted in a recommendation of a concerted and unified effort on the part of the plastic materials manufacturing members of the Association to develop reliable, accelerated tests to simulate and predict the long-term weathering performance of plastics. The National Bureau of Standards and its Research Associate Program were selected as an outstanding environment for the project which started in April, 1965.

In yet another aspect of their cooperative effort to encourage significant contributions in the field, the Manufacturing Chemists' Association and the National Bureau of Standards cosponsored the Symposium on The Weatherability of Plastic Materials as a forum to "review and highlight significant activities in the evaluation of the weatherability of plastic materials, and provide an opportunity to introduce new developments and approaches toward the prediction of outdoor durability of plastics."

It is hoped that the publication of the Symposium papers in one volume will enhance the utilization of available information on the weatherability of plastics, and contribute to the definition of some of the major unsolved problems in the field. It is also hoped that this symposium represents only the beginning, and that future symposia will contribute to the exposition and ultimate solution of these problems.

The Editor wishes to express his thanks to Messrs. W. F. Bartoe from Rohm and Haas Company, V. E. Gray from the National Bureau of Standards, H. J. Oswald from Allied Chemical Company, and R. C. Neuman from B. F. Goodrich Chemical Company for their help in the selection and review of papers.

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Recent Developments in the Analysis and Prediction of the Weatherability of Plastics

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Synopsis

The term "weatherability," although commonly used in plastics technology, is a poorly defined concept since it refers to long-term service under complex and variable conditions and because different properties of a plastic are affected to different degrees by a given environment. Improvement in the ability to predict weatherability therefore requires careful redefinition of the problem as well as a refinement of experimental technique. A review of the extensive literature on outdoor and artificial exposure of plastics shows that no simple correlation exists between these two modes of testing. Further, because the rates and mechanisms of deterioration are different when produced by visible light, ultraviolet, heat, or moisture, an arbitrary "accelerated" weathering test will distort the balance of responses observed in the slower outdoor exposure of plastics. Analytical approaches to predicting the resistance of plastics to weather degradation are considered. In an ideal procedure, the effects of specific weathering parameters are established for specific properties of a given material using controlled artificial environments; the make-up of the weather at a given outdoor location is analyzed in terms of these parameters; and finally, by suitable mathematical models, the results to be expected on exposure of the material to this given composition of weather can be computed. While this approach is admittedly complex, its feasibility has been demonstrated. For routine studies where the mathematical approach may be impractical, it appears necessary to abandon the goal of a "universal" artificial weathering test unless only qualitative or screening comparisons are desired. Quantitative predictions, using present testing technology, will be most reliable if restricted to a comparison of materials which are fairly similar in composition.

INTRODUCTION

Perhaps the earliest publication on polymer durability was a paper by A. W. Hoffman[1] in 1860 on the deterioration of gutta-percha cables. In the intervening 107 years, a veritable torrent of papers related to polymer degradation, and in particular to polymer weatherability, has appeared. A bibliography compiled by Searle and Hirt[2] for a period of only 40 mo. in 1957–1960 lists over 1000 references. Many other bibliographies and reviews are available.[3–9] Besides the published work, probably everyone active in this complex field has quantities of empirical data on specific polymers which defy correlation. It is the purpose of the present paper to review the most significant developments from the recent literature and to consider whether it is finally becoming possible to place the study of polymer weatherability on a rigorous scientific basis.

A goal of 20 to 30 years is commonly mentioned today for the "durability" of plastics exposed to weather; yet obviously one cannot afford to wait this long period of time to determine whether the goal has been achieved. Faced with this problem, most workers in the field have adopted artificial exposure procedures which are often erroneously called accelerated weathering tests. Now it should be apparent that since weather goes on 24 hr. a day, every day, it cannot be accelerated. Furthermore, weather resistance itself is a poorly defined property, since it refers to long-term service under complex conditions which fluctuate with time, geographic location, and the particular application or performance criterion which is desired. More reliable predictions of the weathering behavior of plastics will demand a rigorous redefinition of the problem as well as a refinement of experimental technique.

The definition of the plastics weatherability problem, as it has been studied experimentally heretofore, is a very limited one. It is to determine changes in appearance or in mechanical properties (usually not both) which a small sample will undergo after x years of exposure out of doors, facing south, at 45° to the horizontal, at three locations in the United States: Miami, Phoenix, and the experimenter's own laboratory. It must, of course, be recognized that even if satisfactory results are obtained in such exposures, the same plastic may not perform as well when placed in service in larger sizes, random locations and orientations, and under unspecified stresses. To put it another way, *every outdoor exposure is an artificial weathering test* and may be no more representative of performance in actual service than are exposures carried out in a controlled laboratory environment.

FACTORS IN WEATHERING RESPONSIBLE FOR POLYMER DEGRADATION

The deterioration of plastics may be induced by a number of factors and may be manifested in a number of ways. The features of weather which are generally asserted to be responsible for changes in plastics are light (particularly UV), moisture (whether liquid water or water vapor), temperature, and oxygen. All of these except oxygen are widely and erratically variable with location and season. Microbiological degradation is not a significant problem with most synthetic plastics although many additives, notably plasticizers, are attacked by microorganisms. This subject has been reviewed recently[10] and further discussion will be omitted here.

Additional relevant factors include ozone and atmospheric contaminants which may be solid, liquid, or gaseous (dirt, soot, smog, sulfur dioxide, etc.), as well as a general condition which may be termed "severity of cycling." This is intended to distinguish between relatively steady-state environments and climates in which repeated or severe changes in temperature, humidity, etc., can fatigue a specimen.

Ultraviolet Radiant Energy

Sunlight is a major source of radiant energy. It would be a much more serious factor in degradation of materials at the earth's surface than it actually is except that most of the short wavelengths are screened by nitrogen, oxygen, and ozone in the upper atmosphere. Aerospace applications of plastics must contend with the highly damaging far-UV and vacuum-UV, but this problem is outside the scope of the present review. At ground level, the wavelengths which cause the most degradation of polymers (oxidation, chain scission, crosslinking) are in the near ultraviolet, 3000–4000 A., even though these comprise only about 5% of the total sunlight at the earth's surface.

In order for radiant energy to initiate such chemical reactions, it must first be absorbed. It is well known that photons in the near ultraviolet have energies corresponding to the bond energies of certain chemical structures,[11,12] but it must not be assumed from this fact that such structures will impart low polymer durability. On the one hand, absorption of photons by a polymer may lead only to the innocuous dissipation of energy as heat, fluorescence, etc., rather than bond rupture. And conversely, even the most energetically stable bonds such as $C{=}C$ and $C{=}N$ can undergo electronic rearrangements under relatively mild conditions leading to colored or otherwise undesirable species.

Oxygen

Residual double bonds in some molecules such as polybutadiene and polyethylene are especially susceptible to attack by atmospheric oxygen although most polymers react very slowly with oxygen. However, oxidation is greatly promoted by elevated temperatures and ultraviolet radiation, and the reactions of polymers with oxygen under these conditions can be very complex. Oxygen is not usually regarded as an experimental variable in the study of polymer weatherability since the oxygen concentration in the environment is substantially constant and most weathering phenomena occur at the surface of the plastic which is in equilibrium with the air.

Moisture

Water can have at least three kinds of effects which are important for the degradation of polymers. One is chemical: hydrolysis of labile bonds such as those of polyesters or polyamides; a second is physical, destroying the bond between a polymer and a filler like glass fiber or pigment and resulting in chalking or fiber bloom; and a third is photochemical, involving the generation of hydroxyl radicals or other reactive species which can then promote a host of free radical reactions.

Thermal Energy

Under extreme outdoor exposure conditions, a plastic sample may reach 170°F. (about 77°C.).[13] This is not sufficient to promote bond cleavage of any structures likely to be found in commercial plastics. For this reason, the many studies on the pyrolysis of polymers (see reference 5 for one review) are not very relevant to the weatherability problem. The principal role of heat in the outdoor degradation of plastics is in accelerating processes otherwise induced, such as hydrolysis,[14] secondary photochemical reactions,[15] or the oxidation of trace contaminants like hydroquinone.[16]

A single form of response of a given material to weathering, as we actually observe it, may often be produced by any of several factors. Thus if a plastic becomes brittle, it may be caused by photooxidation (polyolefins), carbon chain cleavage (methacrylates), hydrolysis (superpolyesters), or loss of plasticizer [plasticized poly(vinyl chloride)]. In other cases, the observed change is a discoloration which may be associated with actual photochemical reaction (e.g., phthalic moieties in polyesters[17] or in plasticizers,[18] residual monomer (e.g., in polystyrene),[19] or traces of contaminants (e.g., iron in polyesters[20]). Other changes (loss of gloss, chalking, crazing) are often observed in fabricated or compounded plastics which are not strictly chemical effects at all. In view of the complexity of weather and weathering responses, studies of weatherability have historically been based on exposure to actual weather, or some imitation thereof, and only very recently has a rigorous analytical approach to the problem met with any degree of success. We shall therefore review the weathering process by first considering natural weather and then proceed to systems which are simpler in operation but more difficult to relate to natural phenomena.

THE WEATHERING PROCESS

Conventional Outdoor Exposure Procedures

Most outdoor exposure tests in this country are carried out in substantial accordance with ASTM[21] recommended practice D1435. As mentioned above, this specifies mounting the sample at a 45° angle to the horizontal, facing south, and unrestrained. The recommended practice suggests that records be kept of the weather at the test site: average daily temperature, average daily relative humidity, daily rainfall, and total daily solar radiation in langleys (cal./cm.^{2}) in the plane of the samples. The procedure in other countries, at least in the northern hemisphere, is much the same (cf. USSR[22] All-Union Standard No. 10226-62).

These tests, like all performance tests, must of necessity make an arbitrary choice of test conditions; therefore they cannot be expected to serve as simulated service tests with respect to and particular use. Proper interpretation of such tests involves comparison with selected control samples rather than an absolute end-use criterion.

Some of the variables in exposure testing are of particular interest:

Mounting Angle. The effect of sample mounting angle has been studied for a few materials, notably paints and plasticized poly(vinyl chloride). Newland and co-workers[23] measured the UV intensity of sunlight over a

9-yr. period and calculated the relative annual UV exposure of samples mounted at various angles at Kingsport, Tenn. (lat. 36°5′ N). The maximum intensity was calculated to be at about 30°. Nevertheless, there was no evidence that samples at this angle deteriorate faster. Darby and Graham[24] found that plasticized PVC lost elongation fastest in Florida when exposed horizontally with 45° and vertical mountings being successively less severe, even though by analogy with Newland's work, the maximum UV intensity should occur at about a 45° angle. The test results were explained by the greater leaching of plasticizer by rain in a horizontal mounting. On the other hand, metal panels painted with air-drying enamels were found to degrade faster (in terms of gloss, color, and chalking) when exposed in Florida at 85° to the horizontal than at 45°, despite the relatively higher solar altitude in Florida.[25] Recently several plastics were exposed in Florida and Arizona by an ASTM task force[26] on equatorial mounts, at 45° south, and at angles corresponding to station latitude (Arizona 33°, Florida 26°). Surprisingly, after one year, no significant difference in color development was observed between 45° and latitude angle exposures and at most, a very slight acceleration on equatorial exposure. When this study is completed, it should provide a definitive answer to the question of mounting angle effects.

Restraint. For plastics which are stress-sensitive (this is particularly true for polyolefins), exposure under strain will markedly accelerate the rate of deterioration. Newland and Tamblyn[27] have discussed this problem in some detail for both polyethylene and polypropylene, but it is well known that stress sensitivity occurs in many plastics besides the polyolefins.[28,29] It should therefore be understood that unrestrained exposures according to the recommended procedure are likely to be *decelerated* relative to actual service conditions if stress cracking and crazing are important criteria of performance.

Season at Start of Test. Does it make a difference, in an outdoor exposure test which is to last more than a year, at which season the test is started? The literature contains very few references to this question.[30,31] But there is evidence from artificial testing that the *order* in which parameters such as heat and light are supplied to a plastic can be significant, other things being equal. For example, when a film of poly(vinylidene chloride) was irradiated for a few minutes with a mercury arc lamp at 2537 A. and then heated for 24 hr. at 100°C., it turned brown, while if the order was first heating and then illumination, there was no color change.[32] In natural weathering, the balance and the intensity of weather components changes with the season, so this may well be a point for further study.

Environment. Apart from the obvious effects of different climates at various exposure sites, the immediate environment of a test fence can impose different kinds of test conditions. Thus grass, bare earth, cement, and asphalt beneath the mounting stand have different radiative properties and can affect the panel temperature as well as humidity and moisture concentration. Panels exposed close to the ground and atop a building are likewise in different environments. Opinions differ as to the significance of these factors; it would be desirable to have definite experimental evidence.

Intensified Outdoor Exposure Procedures

In an attempt to shorten the exposure time required for degradation, while hopefully avoiding extraneous effects or unnatural spectral distributions (as are observed with artificial light sources), schemes have been devised to concentrate natural sunlight on test samples; that is, to use sunlight intensified by mirrors as a light source in a kind of outdoor weathering device. In conjunction with an equatorial mount, such a system is known as EMMA,[33,34] (Fig. 1). Forced air cooling minimizes overheating of samples. The EMMAQUA is similar but adds an intermittent water spray to simulate rain.[35]

The energy distribution of sunlight which is incident upon samples on the EMMA varies throughout the day and throughout the year, as does natural sunlight, although the energy distributions at any one moment are similar (Fig. 2).

The EMMA and EMMAQUA devices are apparently taking on commercial significance with test results being reported in the technical literature on a fairly routine basis.[36] A detailed study of the EMMA as an accelerated test has been published,[13] using glass-reinforced polyesters and rigid poly(vinyl chloride) as test materials. It was found that the EMMA provided about ten times as much radiation (expressed in langleys, or cal./cm.^{2}) as ordinary 45° South exposure at the same location, but that

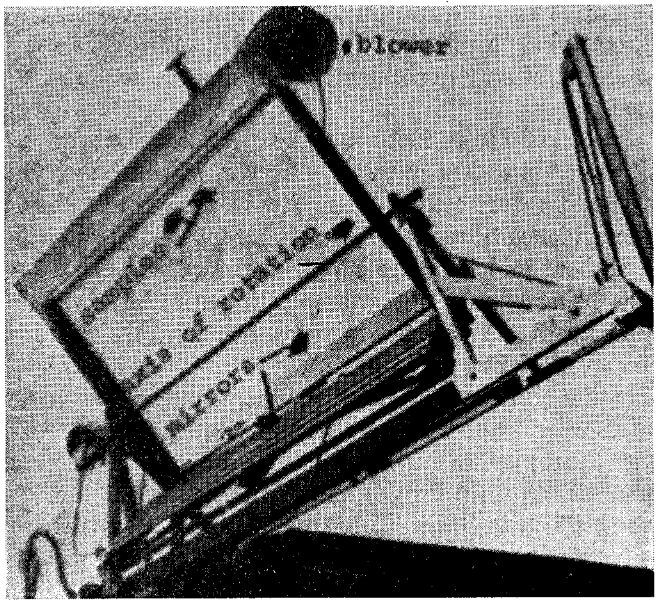

Fig. 1. EMMA exposure device.[13] Reproduced by permission of American Chemical Society.

the efficiency of the EMMA in terms of induced yellowing per 1000 langleys was variable, usually between 50 and 100% of the efficiency of normal sunlight, depending on the formulation of the plastic as well as the duration of exposure. Thus, in terms of actual elapsed time, there is an acceleration of yellowing, but the acceleration factor is not a constant any more than it is in a purely artificial weathering machine. Recent results with poly(vinyl chloride)[36b] and polypropylene[36c] lead to the same conclusion. Despite its careful and ingenious design, therefore, this solar intensifier appears to have no unique advantage as a predictive tool.

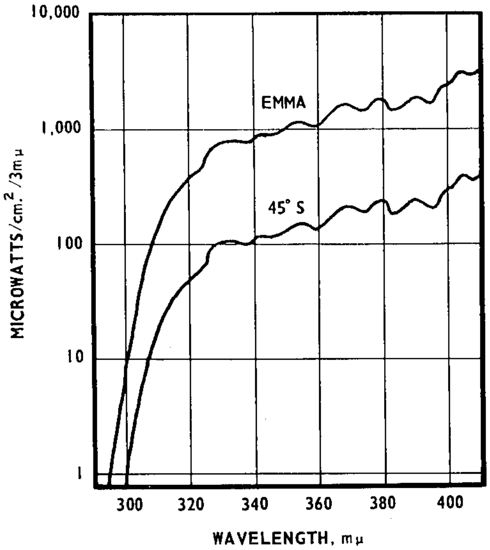

Fig. 2. Comparison of ultraviolet energy spectra of direct sunlight at 45° south and in the EMMA device.[13] Reproduced by permission of American Chemical Society.

Natural Weather, Short Term but Using Highly Sensitive Measures of Change

One use of natural weathering which may be regarded as an accelerated test is to expose samples for brief periods and to use criteria of change which are sensitive enough to anticipate gross changes such as visual discoloration or embrittlement. The success of this approach depends on the ability to develop these sensitive methods of assessing change, and for this reason discussion is deferred to part IV of this paper, where such sensitive detection methods are considered.

Artificial Weather

Laboratory weathering, or, more strictly, exposure of test samples to one or two arbitrary combinations of radiant energy, thermal energy, and moisture, is generally recognized by now as having very limited value in predicting outdoor performance of plastics.[9,37] The deficiencies in laboratory weathering which lead to poor or inconsistent correlations between such tests and outdoor exposures are due to a number of factors: the variability in natural weather; a lack of precise information on the microenvironment of an outdoor sample (for example, what percentage of the time is such a sample covered with a film of water?); the inherent impossibility of accelerating weather without distorting it; and finally, mechanical problems (such as the poor match of the solar spectrum with most artificial light sources,[38] or the variability on aging of light sources such as the xenon arc[39] which are better matches[9,40]). Numerous papers[41–45] describe light sources intended to simulate natural sunlight.

Conventional equipment for artificial weather testing both in the United States[9] and abroad[46] usually comprises a cylindrical sample holder rotating about a high-intensity carbon arc or xenon arc, a means of spraying the samples with water from time to time, and in some instruments a means of controlling the temperature and humidity when the samples are not being sprayed. Recommended practices published by ASTM[47] are intended primarily to promote uniformity between different laboratories and not to evaluate the results or predict any particular correlation with natural exposure. Kinmonth[9] has pointed out many variables in the operation of such test equipment which are still not standardized.

A method for instrument-to-instrument standardization of carbon arc devices has been published[48] which involves exposure of a yellow acrylic coupon with each batch of test specimens and correcting exposure times to periods of equal fading of the coupon. It must be emphasized that this procedure is not intended as a general substitute for precise actinometry or to compare the effects of different exposure environments but only to verify the operational characteristics of the carbon arc.

A monitoring device constructed by Allen[40] serves a similar purpose with xenon arc weathering machines. Since the output of the xenon arc changes with age of the lamp and the accumulation of deposits on the filter jacket, monitoring is particularly important in these instruments if reproducibility is to be achieved.

Conditions for the operation of weathering devices are the subject of constant experimentation.[31,49,50] In view of the broad range of materials (notably paints and plastics) involved in these tests and the fluctuations in weather itself, it is doubtful that any particular choice of conditions can be generally recommended over any other.

Studies of this kind have extended not only to different operating cycles but also to instrument modification or even to new types of testing machines. Descriptions have been given for four of these in U.S. literature:

(*1*) Twin-arc (carbon arc) Weather-Ometer[51] modified by addition of eight Westinghouse fluorescent sunlamps to increase the deficient output in the 3000–3500 A. range. Improved rank correlation with outdoor (Tennessee) exposure for cellulose acetate butyrate plastics was reported relative to the unmodified instrument.[52]

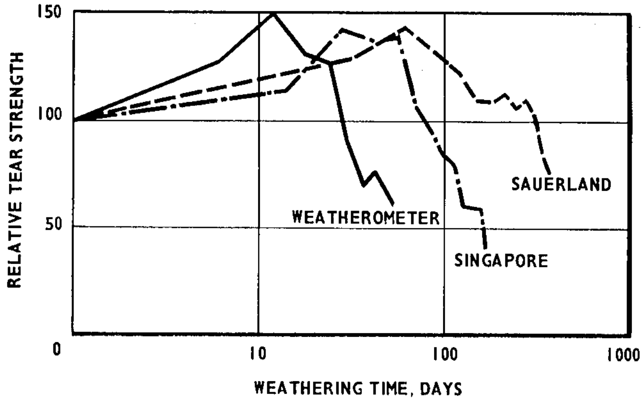

Fig. 3. Changes in tear strength of polyethylene, relative to initial value, as a function of duration of weathering in an Atlas DMC Weather-Ometer, in Singapore, and in Sauerland (Germany).[59] Reproduced by permission of Carl Hanser Zeitschriftenverlag.

(*2*) Combinations of fluorescent sunlamps and blacklights with or without water spray.[53] While the light output is almost entirely in the near-UV range, 3000–3600 A., this equipment has been found to give extremely realistic results, compared with Arizona and Florida exposures, particularly on visually transparent plastics.[16] A very satisfactory degree of correlation was obtained between irradiation with this lamp combination (without spray) and Arizona exposure of rigid PVC.[54] The fact that the fluorescent system is easily operated at temperatures somewhat lower than arc sources undoubtedly helps to minimize the heat-promoted discoloration of this particular plastic.

(*3*) The UV Accelerometer,[55–57] which uses a GE UA-11B mercury arc source with Corex filter and forced air cooling but no water spray. The behavior of plastics in this device is considered by its developers to give good rank correlation with certain outdoor exposures, but published data are as yet rather meager. High-resolution spectra for this light system would probably show an appreciable content of very damaging radiation below 3000 A., not present in sunlight at the earth's surface.

(*4*) Increasing the relative humidity inside a standard XW (open carbon arc) Weather-Ometer, with Corex filters removed, while spraying the backs of samples with cold water to induce deposition of dew on the exposed face.[31] This so-called "dew cycle" was found effective in accelerating the chalking of TiO_2 pigmented surface coatings. Some preliminary experiments[58] suggest that many plastics, as well as coatings, degrade very rapidly in Weather-Ometers operated under conditions approaching 100% relative humidity.

However, *acceleration* is not equivalent to *correlation* with any particular natural weathering exposure. It appears intuitively that faster acceleration means greater departure from natural conditions and hence less likelihood of reliable durability predictions. And, as already mentioned, weather is simply too elusive a variable for correlation with any fixed artificial condition. To cite one example among many, a recently published comparison[59] of exposures of PVC and polyethylene in Singapore, Germany, and a twin-arc Weather-Ometer (presumably under typical operating conditions) showed that for most criteria there was about as much variation between the two exterior exposures as between Singapore and the Weather-Ometer (Fig. 3). The present review attempts at least to specify the outdoor location used as a basis for published correlations with artificial environments; obviously a change in the outdoor test site can be expected to alter the correlation.

Representation of Exposure Conditions

The manner in which exposure conditions are described depends to a large extent on the ultimate method of analysis and the duration of exposure. Thus, a quantitative description of these conditions is not necessary when only a qualitative analysis of the test results is desired. Even when a quantitative representation of exposure conditions is needed, average annual values of solar energy, ultraviolet radiation, moisture, and temperature may suffice for the analysis of long-term data or for long-term predictions. On the other hand, detailed quantitative descriptions of the variables will be necessary for short-term analysis and correlations, and annual averages will not be sufficient for predictions relating to 1 yr. or less.

Annual averages of outdoor conditions at many locations are available for most of the significant variables from weather bureaus and exposure stations.[35,60,61] Some of the variables which are not usually reported include ultraviolet energy, ultraviolet energy distribution, and the duration of rain or wetness. It is possible to make rough estimates of these variables, however, if only annual averages are needed. A variety of methods are available for estimating the ultraviolet fraction of the solar energy at different geographical locations and angles.[23,38,62–69] Climatological data can be used to determine the average duration of rain and wetness at different geographical locations.[70] A number of techniques can be employed to estimate the surface temperature of colored or clear samples from a knowledge of the ambient and black panel temperatures at the same location.[7] In addition to conventional data, exposure stations supply information regarding "UV sun hours," cloud cover, temperature under glass, and similar variables. In general, sufficient information is available from a variety of sources to satisfy the requirements of a rough quantitative description of the weather at different locations.

The short-term representation of exposure conditions is somewhat more complex, however. In the case of indoor devices, the description of the variables is easier than in the case of actual weather conditions. The mathematical, numerical, or graphical representation of exposure variables in a variety of weathering devices has been reported.[9,31,38,53,71–73] The description of conditions in these devices becomes more difficult when dark/light cycles are employed or when the conditions are not uniformly distributed at the sample locations. Information is lacking on a variety of aspects of the conditions in indoor devices. Among these are: effect of color on sample temperature, internal stresses generated by variations in moisture and thermal conditions, actual duration of wetness of the sample, actual humidity conditions at the surface of samples, temperature and moisture gradients across the sample, and the effect of sample holder on the above variables. (As already mentioned, many of these variables affect outdoor exposure as well.)

Many problems are encountered with the representation of short-term weather conditions. Some of these problems are listed below.

(*1*) Weather conditions are hardly uniform or consistent although they tend to follow seasonal and daily periodic patterns.[70,71] An example of the degree of complexity and irregularity of one weather variable is shown in the work of Searle and Hirt[62] on factors affecting the short- and long-range variability of ultraviolet energy in sunlight. This irregularity is complicated by factors like wind, sand, snow, and pollution.

(*2*) Cyclic effects of moisture, temperature, and solar energy are as important as those of the actual levels of these variables. Therefore, it is necessary to obtain data on cyclic changes in the weather and the rates at which these cyclic changes occur.[70]

(*3*) The definition of the exact variables controlling the weatherability of plastics has not been completed. Therefore, many of the variables which are needed for an accurate analysis of weatherability are not available from climatological sources.

(*4*) Only a few of the important weather variables like temperature and moisture have been recorded continuously. Ultraviolet and solar energy distribution, duration of rain, total time of wetness, and the distribution of pollutants have not been reported satisfactorily. There is encouraging evidence of recent efforts to fill these gaps.[62,74–76]

(*5*) The exact representation of weather conditions in algebraic form is out of the question. Therefore, much of the data are reported numerically or graphically. Such representations are bulky and difficult to analyze.

Many efforts to alleviate the above problems are in progress. Current and future efforts in this area, combined with modern computer techniques, should lead to increased availability and usefulness of data on exposure conditions.

RESPONSE OF MATERIALS TO A WEATHERING PROCESS

Apart from the variability in *weathering processes* as such, we must also contend with the fact that the *criterion of change* in a material during such a process will be different for different users. Changes may be judged subjectively—this is most often true of surface effects such as chalking or crazing—or objectively, as in the case of color change, strength deterioration, or other measurable alteration which can affect performance. If one is concerned with the chemical mechanism of polymer breakdown, the criterion is most likely to be a change in the absorption or reflection spectrum, or in the generation of chemically analyzable groups such as carboxyl or peroxide. The fact that different materials may show greatly different modes of failure adds to the complexity of the problem. This is perhaps an obvious point, but it is surprising how often test results are reported in "hours (or months) to failure" without careful specification of the criterion by which failure is judged.

Visual Ratings and Physical Measurements

Plastics users for the most part are concerned either with changes in appearance or with changes in a mechanical property. Physical measurements—such as tensile strength, color difference[77,78] relative to unweathered controls, and fiber bloom in glass-reinforced polyesters as measured by transmission losses for white light[79]—are preferable, of course, to purely visual inspection since they provide a permanent and objective record of results. This is true even though the eye is extremely sensitive to color difference and to intensity difference for light of a given color. Unfortunately, some characteristics do not lend themselves to objective measurement; these include blistering, crazing, and color changes in patterned samples. In addition, whether subjective or objective performance tests are used, outdoor and artificial exposure of plastics generate vast compilations of empirical data. Since batch-to-batch differences frequently exist even for "pure" polymers and tests are often conducted on compounded resins, laminates, and the like, these compilations are of value principally for the compiler himself, his customers, or his suppliers. A monumental production of this type, intended as an aid in military procurement, has been issued by Picatinny Arsenal and supplemented at intervals.[80–82] Similar publications are a part of the world-wide technological literature (East Germany[83] and USSR,[84] for example). To repeat, such information may be useful for specification or sales purposes but is too unwieldy and too highly dependent on individual sample history to be of great help in prediction and analysis of weatherability for broader classes of plastics.

Anticipatory Methods for Assessing Charge

Gross changes in visual appearance or mechanical or optical properties are not very helpful in predicting weatherability since by the time such changes have occurred to a statistically significant degree, the polymer may well have reached a commercially unacceptable condition. If more subtle criteria of change could be developed, they could be used predictively in connection with short-term exposures under realistic conditions. It is surprising that so much less has been done to refine methods for the *detection* of change in weathered polymers than to devise new weathering conditions which intensify the *causes* of change. A few examples of this approach may be cited, however.

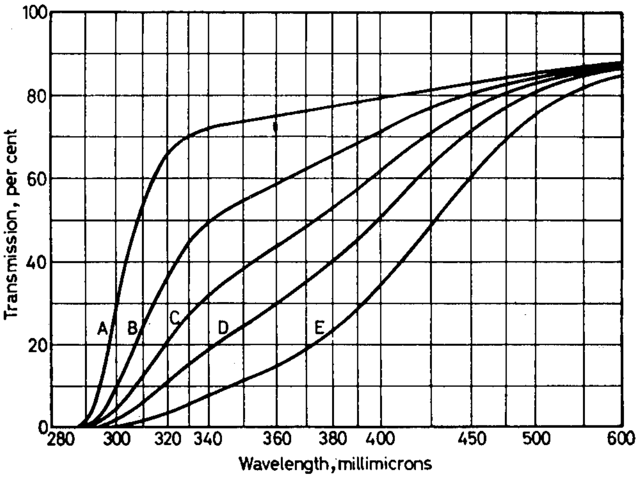

Fig. 4. Change in per cent transmission in the ultraviolet and visible regions of the spectrum of poly(isophthaloyl-*trans*-2,5-dimethylpiperazine) as a function of time of ultraviolet irradiation. A denotes zero time, B 2 hr., C 6 hr., D 12 hr., and E 30 hr. of irradiation.[89] Reproduced by permission of Butterworths Publishers.

Alterations in infrared spectra have been used as criteria of chemical changes in polymers.[85,86] Most spectral studies on degraded polymers are concerned with chemical mechanisms qualitatively rather than with assessing weatherability quantitatively. The mere fact of spectral change, even if it can be associated with a specific chemical transformation, does not constitute a prediction of failure. However, correlations have been made in a few cases. Thus, with polyolefins, the increase in carbonyl absorption in the infrared at about 5.8 μ is associated with ultimate embrittlement or crazing of the polymer and can be detected before the mechanical properties are greatly impaired.[87,88]

Changes in ultraviolet absorbance or reflectance should be a reliable prediction of discoloration. Typically, exposure of a plastic to sunlight or other sources of energy does not affect the location, or even the intensity, of the observed absorption maxima in the ultraviolet; the absorption band simply broadens until the specimen starts to absorb in the blue–violet region of the visible and the characteristic muddy yellow appearance results. If one measured the absorption (or reflectance) in the near-ultraviolet, say at 3600 A., after relatively mild outdoor exposure, it might well be possible to predict in a short time at least the relative ranking of a series of plastics with respect to discoloration (i.e., visible color change) tendencies. While this is a simple enough procedure, no published studies have been found which describe changes in the UV spectrum of the naturally weathered plastics. Figure 4, from the work of Bruck,[89] represents a similar experiment wherein a polyamide is irradiated with 2537 A. UV light, and the ultraviolet and visible spectra are measured at intervals. After short periods of irradiation, the increase in UV absorption is much

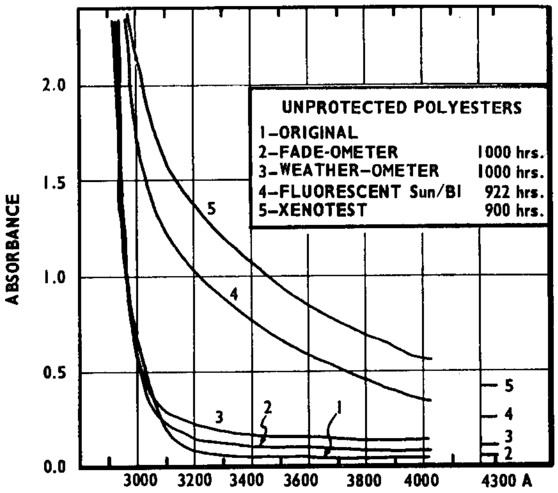

Fig. 5. Ultraviolet absorption curves of polyester films irradiated with various light sources.[90]

more pronounced than the increase above 4000 A. which produces visible discoloration. Hirt and Searle[90] present some data on the UV spectrum of a crosslinked polyester irradiated with other artificial UV sources (Fig. 5). The changes in the ultraviolet after xenon and fluorescent sunlamp/blacklight exposure are again considerably greater than those in the visible region. Analogous results would be expected after brief exposure to natural weather. Hence the prediction of *long-term visible* color change from *short-term* changes the *ultraviolet* spectrum of weathered samples is judged to be a method worthy of investigation. The fluorescence spectrum is another sensitive property of polymers which has not yet been evaluated as a predictive tool.

An interesting method for monitoring the degradation of glass-reinforced polyesters has been described by Gray and Wright.[91] They found that a sample exposed to weather, or to an artificial weathering machine, became colored when treated with a diamine, particularly *N*,*N*-dimethyl-*p*-phenylenediamine, while no color developed when the reagent was applied to unexposed specimens. This color was attributed tentatively to the oxidation of the amine by peroxides generated photochemically on the surface of the specimen. Figure 6 shows typical results after outdoor exposure at Washington, D. C. and after exposure to a carbon arc source. No degradation was detectable in many of these exposed samples by visual inspection prior to the amine treatment. Specific techniques of this type are thus of value in anticipating undesirable chemical changes in weathered plastics. It remains to be seen whether staining procedures can be correlated with other criteria of deterioration and whether similar tests will be applicable to additional classes of plastics besides crosslinked polyesters.

If the weatherability problem is precisely enough defined, it is sometimes

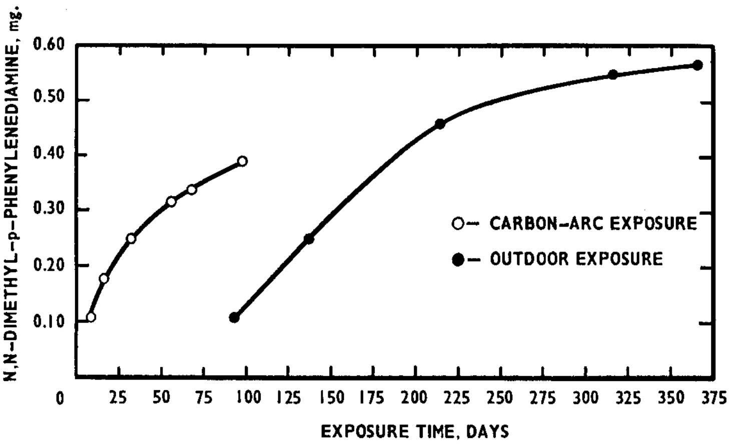

Fig. 6. Amount of *N,N*-dimethyl-*p*-phenylenediamine reacted with outdoor and carbon-arc exposed specimens vs. exposure time for a glass-reinforced polyester.[91] (○) carbon arc exposure; (●) outdoor exposure.

possible to make predictions based on the spectral or chemical properties of individual compounds. For example, the NMR spectrum of UV absorbers was shown[92] to relate to their effectiveness as stabilizers for cellulose acetate butyrate, as judged by embrittlement after outdoor exposure or in a modified carbon-arc Weather-Ometer.[52] Again, the ionization constants of amines correlate moderately well with their effectiveness in reducing the yellowing of polystyrene in a carbon-arc exposure.[19] Similar correlations may well be possible for antioxidants, inhibitors, and other additives.

ANALYTICAL APPROACH TO THE PREDICTION OF WEATHERABILITY

It should be apparent from the above discussion that all methods which are presently employed for the determination of the weatherability of plastics tend to be predictive and extrapolatory. Even outdoor exposure at one or more locations is not sufficient to supply all the necessary information about the actual durability of the material under all weathering conditions.

In the course of predicting and extrapolating weatherability data, it is necessary to employ a number of generalizations and assumptions. Such generalizations are usually intuitive and empirical. Despite the frequent success of some of these predictions, the problem of extrapolation and correlation between short-term studies and actual long-term outdoor exposure remains as the most important and persistent of the weathering problems. Since this is an analytical problem, any serious attempts at obtaining a solution should deal with the physical–chemical representation of the interactions between the properties of the plastic materials and the variables of exposure.

The following discussion summarizes some of the analytical techniques which have been employed for the prediction of plastic weatherability.

Ideal Analytical Approach

Ideally, the weatherability problem should be reduced to a kinetic analysis of the variations in properties of a plastic as a function of exposure time. In such an analysis, all plastic properties would correspond to time functions. Therefore, the study of structure–property interactions and the mathematical representation of significant weather conditions become integral parts of weatherability analysis. The complexity of these objectives and the results of some efforts towards a solution have been reported.[3–5,7,36,93–95]

In the ideal analysis, rate constants and kinetic parameters are obtained either experimentally or by analytical physical–chemical methods. These constants and parameters are then applied to standard kinetic equations showing the relationship between exposure time and conditions on one hand and the responses to exposure on the other hand. Since the rate constants and kinetic parameters are independent of the exposure medium, the kinetic equations should serve as the basis for correlations between the effects of different exposure media on one plastic.

In a generalized algebraic representation of the above, the initial step in the ideal analysis is to describe the value of a plastic property P_j, as a function of composition variables C_i. Thus,

$$P_j = f_j(C_1, C_2, \ldots, C_n) \tag{1}$$

where P_j and C_i are measured at the same time.

But C_i can be kinetically related to the initial concentrations before exposure and the time and variables of exposure. Thus,

$$C_i = g(C_1^\circ, C_2^\circ, \ldots, C_n^\circ, V_1, V_2, \ldots, V_m, K_i, t) \tag{2}$$

where superscript zero denotes the values of the variables at the beginning of exposure; V_i represents weather variables; t is the time of exposure; and K_i is an abbreviation of significant kinetic parameters.

Equation (2) can be simplified further by replacing the exposure variables V_i with the time functions corresponding to these variables.

$$V_i = V_i(t) \tag{3}$$

Therefore,

$$C_i = G(C_1^\circ, C_2^\circ, \ldots, C_n^\circ, K_i, t) \tag{4}$$

and

$$P_j = F_j(C_1^\circ, C_2^\circ, \ldots, C_n^\circ, K_i, t) \tag{5}$$

Equation (5) is in qualitative agreement with weathering experience. Graphical representation of exposure data for the same material in different media usually yields a set of non-identical curves[50,61] due to variations in F_j.

Graphical representation of the results of exposure of different materials in the same medium at the same time reflects differences in $C_i°$, and K_i for the two materials.[50,61] It is also obvious from the above equations that the responses of different properties of the same material in the same medium are not necessarily similar.[61,93]

It should be emphasized that although eq. (5) is simple in form, the functional relationships can be very complex. In fact, the simplified analysis presented here tends to rule out simple, linear relationships between P_j and t for most practical exposures. Therefore, attempts to define constant acceleration factors for different exposure media have been unsuccessful.[31,52,59,96]

Needless to say, the ideal approach described above has not been employed in the analysis and correlation of weatherability data. Some of the reasons for this are related to the difficulty in determining changes in composition upon exposure and the absence of explicit relationships between plastic properties and compositional variables. The lack of meaningful weather information and the complexity of the treatment are other major factors. Thus, at the present stage of development in this area and in the general field of polymer science, it has been necessary to rely on a degree of empiricism and intuition.

The remaining approaches in this discussion may be considered as modifications, remote as they may be, of the above ideal approach. These modifications involve variations in assumptions and emphasis regarding different aspects of the ideal approach.

Chemical Approach

This is a commonly used qualitative technique which emphasizes the relation between chemical composition and weatherability. In essence, it represents an attempt to obtain a correlation between the durability of a plastic material and its composition before exposure. Thus it can be described by the following simplified algebraic equation:

$$P_t = F(C_1°, C_2°, \ldots, C_n°) \tag{6}$$

where P_t is the value of the property after exposure time t.

The effects of exposure time and kinetic parameters are deemphasized in this approach. In fact, the study of the effect of time within the framework of this approach tends to be confusing. Thus, whereas the weatherability of one material may be superior to that of another at the end of 1 yr. of exposure, the order of weatherability may be reversed at the end of 2 yr. of exposure.

The evaluation of the effects of additives and common modifiers on the weatherability of an individual plastic is the most common application of the chemical approach.[24,36,53,97–99] This application has proved to be of great value for purposes of product development. Studies comparing the changes in the properties of different classes of plastic materials which have been exposed to the same environmental conditions are common in the literature.[100–102] In many cases, weathering profiles are obtained which show simultaneously the sensitivity of a number of materials to a variety of exposure conditions.[97,98]

A variety of experimental techniques have been employed in conjunction with the chemical approach. Reference specimens of known durability under the conditions of exposure are sometimes used for purposes of standardization.[46,50] In addition to standard outdoor and indoor weathering media, a variety of controlled tests are conducted to test the sensitivity of the material to isolated exposure variables.[70] In many cases, selected exposure variables are magnified in either magnitude or intensity in order to accelerate the effects of exposure.[31,84,103]

The chemical approach is not without shortcomings even in its qualitative conclusions. In the study of the effects of additives, it should be recognized that, sometimes, slight modifications in composition can lead to significant changes in the mechanism of degradation and the nature of correlation between indoor and outdoor tests.[27] The use of extremely intense conditions of temperature, moisture, and ultraviolet energy, individually or in combination, may lead to unrealistic results.[3,4,84,103] Since the term "durability" is generally poorly defined, comparison to a standard of known "durability" has its drawbacks.[50,59] Even when one property and one exposure medium are employed for both the standard and the test specimen, extrapolations to longer times or other media based on the use of standards can be misleading.

In general, the chemical approach has been most successful in the areas of product development and the study of the effects of additives and modifiers on the weatherability of plastics.

The Longevity Function

Langshaw[7] proposed a general equation for the rate of weathering W.

$$W = A(\mathrm{H})^z + B(\mathrm{L})^y + C(\mathrm{O_2})^x + D(\mathrm{OX}) + E(\mathrm{H_2O})^v + E(\mathrm{S})^u + G(\mathrm{H})^t \times (\mathrm{L})^s + H(\mathrm{H})^r(\mathrm{O_2})^q \ldots \text{etc.} + Z(\mathrm{H})^a(\mathrm{L})^b(\mathrm{O_2})^c(\mathrm{OX})^d(\mathrm{H_2O})^e(\mathrm{S}) \quad (7)$$

where A, B, C, etc., and x, y, z, etc., are constants, and (H), (L), (O_2), (OX), (H_2O), and (S) are the concentrations of heat, light, oxygen, oxidants, water, and stress, respectively.

By measurements of exposure variables and the resulting changes in properties at short intervals, the values of the constants can be determined. The effects of weathering at other sites can be assessed by substituting the calculated constants and the new exposure conditions in eq. (7).

It can be seen that this equation is empirical and does not necessarily reflect the true mathematical relationship between exposure conditions and the resulting changes in plastic properties. Unfortunately, and probably because of complexities in calculation and measurements, Langshaw did not attempt to test the applicability of the proposed equation. Langshaw's model, however, is typical of other longevity functions which represent empirical correlations between changes in plastic properties and exposure variables.

A similar, but less complicated, longevity function was proposed by Moder and Stucky[104] in their evaluation of weatherability of cotton fabrics. They employed the following linear model:

$$Y = a + bX_l + cX_r + dX_t + eX_h \tag{8}$$

where Y represents the breaking strength retention after outdoor exposure. X_l and X_r represent cumulative actinic exposure and cumulative rainfall, respectively, while X_t and X_h represent weighted average temperature and humidity, respectively. $a, b, c, d,$ and e are constants.

Moder and Stucky found that eq. (8) and even a simpler linear representation utilizing only X_e and X_h yield a good representation of actual outdoor results. They warn, however, against the use of this equation for extrapolation purposes since the model was not based on theoretical considerations. This is one of the main shortcomings of the longevity function approach. Moreover, the weighted averages of temperature and humidity proposed by Moder and Stucky seem somewhat unrealistic.

$$X_t = \frac{\sum_{i=1}^{N} t_i l_i}{\sum_{i=1}^{N} l_i} \tag{9}$$

where t_i = high temperature during ith day of exposure; l_i = total langleys during ith day of exposure; and N = total number of days exposure. A similar relation was proposed for X_h.

Both of the above longevity functions conform to the general expression

$$P_t = f(C_1{}^\circ, V_i, K_i, t) \tag{10}$$

They are only slightly different in form from the general analytical eq. (5). The main difference between the two representations is in the nature of the functional relationships. The two longevity functions (7) and (8) assume empirical, mathematically expedient, but theoretically unjustifiable relationships between the change in plastic properties and the independent variables. It should be noted, however, that generalized empirical forms of the type proposed by Langshaw may be satisfactory for correlations between the results of exposure for one material in different media. Such correlations should be possible if the exposure variables in the different media are not radically different and if the mechanisms and degrees of degradation of the material in the different media are comparable. It is obvious, however, that a different correlation will be applicable to each material.

The two longevity functions described so far stress the effect of a multiplicity of exposure variables at the expense of detailed kinetic analysis.

Another group of longevity functions shifts the emphasis from exposure variables to kinetic analysis. Thus, it is assumed that the degree of degradation is controlled by one or two variables of exposure; then, the interactions between the properties of the material and these variables are described in kinetic terms.

In an application of the latter approach, McMahon et al.[14] showed that hydrolytic effects controlled the degradation of the mechanical properties of poly(ethylene terephthalate). Therefore, they employed detailed kinetic analysis to show the interactions between strength retention on the one hand, and temperature and relative humidity on the other hand. The analysis yielded good correlations with the results of outdoor exposure mainly because the outdoor exposures under study were free of the effects of solar energy. Since poly(ethylene terephthalate) is sensitive to the effects of ultraviolet energy,[105] it is expected that the hydrolytic model will not be sufficient for weatherability correlations under "standard" outdoor conditions.

Raphael[106] recommends longevity functions based on the Arrhenius equation relating the logarithm of the property to the inverse of the absolute temperature. Ratner et al.[107] propose equations relating the long-term strength under load to the applied stress. Both of these relations apply to the long-term service life of plastics under specialized exposure conditions.

A variety of correlations emphasize the effects of solar energy. Caryl et al.[35,60] show correlations based on total langleys as the controlling exposure variable. Other workers propose correlations on the basis of total "sun hours" of exposure.[24,84,108,109] Correlations based on integrated solar energy are not very dependable, however. It has been shown that the exposure of polyethylene in Arizona in the summer caused more degradation than exposure to the same amount of langleys in the winter apparently due to the low UV content of solar energy in winter.[9]

Recent studies suggest that the UV portion of solar energy is a significant factor in the outdoor degradation of plastic properties. Singleton, Kunkel, and Sprague[110] report that good correlations could be obtained between outdoor and indoor exposure effects on the basis of integrated ultraviolet energy. Wright[108] and Maxim and Kuist[55,111] present detailed kinetic analysis of the effects of UV energy on plastic materials. Hirt et al.[112] and Chaudet et al.[92] developed mathematical expressions to evaluate the effectiveness of UV absorbers in improving the light stability of plastics.

Ideally, the analysis of ultraviolet energy effects should be based on the interactions at all significant wavelength values instead of the integrated ultraviolet energy because of the complexities of these effects and the dissimilarity of interactions at different wavelengths for the same material.[90,112] Even when ultraviolet effects are of primary importance with regard to degradation, care should be taken to include the effects of other exposure variables which may serve as catalysts for UV degradation.[114]

Exposure Parameters

The general analytical eq. (5) can be written as follows:

$$P = f(C_i^\circ, K_i, V_1, V_2, \ldots, V_m, t) \qquad (11)$$

In turn, it may be possible to rewrite eq. (11) as follows:

$$P_j = F_j(C_i^\circ, b_j, t) \qquad (12)$$

where

$$b_j = f_j(k_i, V_1, V_2, \ldots, V_m) \qquad (13)$$

Equations (12) and (13) represent the basis for the Exposure Parameter Technique which was recently proposed by Kamal.[72] The constants b_j, are termed "exposure parameters." They differ from the kinetic parameters K_i in that they reflect the combined effects of both the kinetic parameters and the exposure variables.

On the basis of an extensive program relating to the changes of 13 different properties of 10 plastic materials in the 25WR Atlas xenon Weather-Ometer, it was shown that changes in properties could be described as follows:

$$\ln P = B_0 + B_1(t - 250) + B_2(I - I^\circ) \qquad (14)$$

where P represents either a plastic property (e.g., tensile strength) or the magnitude of change in a plastic property (e.g., color change); t represents the time of exposure in hours; and I and I° represent the instantaneous and average ultraviolet intensities of the light source, respectively. The constants B_0, B_1, and B_2 are modified exposure parameters.

Equation (14) was reduced further by making corrections for variations in ultraviolet energy intensity, thus leading to the simple relationship

$$\ln P = b_0 + b_1(t - 250) \qquad (15)$$

where b_0 and b_1 are exposure parameters.

Further analysis of the data has shown that the dependence of the exposure parameters on exposure variables can be expressed in the complete quadratic form as follows:

$$\begin{aligned} b_0 \text{ or } b_1 = C_0 &+ C_1X_1 + C_2X_2 + C_3X_3 + C_{12}X_1X_2 + C_{13}X_1X_3 \\ &+ C_{23}X_2X_3 + C_{11}X_1^2 + C_{22}X_2^2 + C_{22}X_3^2 \qquad (16) \end{aligned}$$

where

$$X_1 = \frac{1/T - 0.03194 \times 10^{-2}}{0.7073 \times 10^{-4}}$$

$$X_2 = \frac{W - 0.975}{6}$$

$$X_3 = \frac{F - 24.5}{10}$$

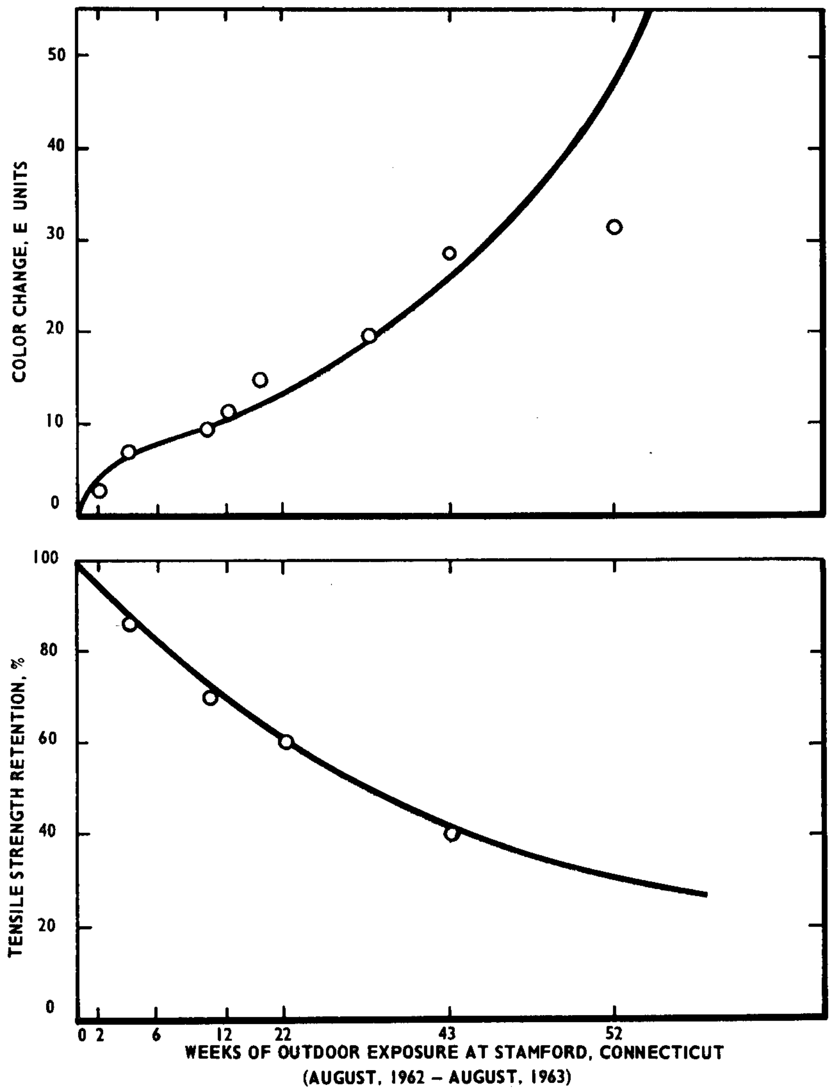

Fig. 7. Correlation of Weather-Ometer and outdoor exposure data on polystyrene using the exposure parameter method: (—) outdoor results predicted from Weather-Ometer tests; (O) observed outdoor results. The abscissa has been normalized for intervals of equal solar energy incidence during the test period (Aug. 1962–Aug. 1963 at Stamford, Conn.).

In the above equations, T is the absolute temperature in °K., W is the duration of the wet portion of the exposure cycle in minutes, and F is the per cent of the time in each cycle during which the sample is wet. X_1, X_2, and X_3 represent normalized exposure variables based on the average conditions during the 16 schedules of the exposure program. The normalization was found helpful in simplifying the calculations.

Exposure parameters were combined with data on outdoor weather conditions in Stamford, Connecticut, to predict the changes in the same properties upon outdoor exposure at that location. The predicted values were in excellent agreement with those actually obtained outdoors. A typical comparison of calculated and actual results is shown in Figure 7 for the color and tensile strength of polystyrene.

In addition to obtaining good correlations, this technique has the advantage of adaptability to more fundamental and theoretical concepts. Thus, the quadratic form and the number or form of exposure variables can be changed to conform more closely with kinetic arguments. The same applies to eq. (15). Similarly, the technique could be extended to permit the analysis of weatherability effects when variables like contaminants and mechanical stress are important.

In the application of this technique to long-term predictions, the indoor studies should be extended to cover the total range of expected degradation. Better correlations should be obtainable by employing a variety of light sources or by effecting changes in the exposure procedure which would yield different levels of light intensity.[115] Stepwise calculations which take into consideration the intermediate variations in outdoor and artificial weathering conditions should yield further improvements in the degree of correlation.

CONCLUSIONS

The study and prediction of the weatherability of plastics materials present a variety of complex problems. Many of these problems derive from the nature of outdoor exposure conditions and the interactions between these conditions and the compositional variables of the materials.

The literature presents voluminous data on the results of outdoor and indoor exposure of a multitude of plastics. However, these data have failed to contribute significantly to the analysis or prediction of outdoor weatherability under generalized conditions. It appears at the moment that the most reliable method of estimating the weatherability of a plastic material under selected outdoor conditions would be based on the actual outdoor exposure of the material for the duration under consideration. In fact, such information will apply only to the same configuration of the material as that employed in the exposure test.

The failure of present weatherability studies can be attributed to many factors. In most cases, the exposure procedure is arbitrary and lacks scientific justification. Data on exposure variables are sketchy, incomplete, and generally unreliable. The representation of these data is inadequate with regard to utility for mathematical and kinetic analysis. Undue emphasis is placed on the changes in the macroscopic properties of the plastic material instead of some of the microscopic and spectral properties which can be related to basic changes in composition. Finally, a large number of the correlative and predictive procedures are empirical and without strong scientific foundation.

A variety of techniques has been developed for the analysis and prediction of weatherability on the basis of scientific principles. These techniques represent modifications in the generalized ideal analysis of weatherability, differing in emphasis and assumptions. The qualitative chemical technique has been successful in product development applications. Longevity functions serve the double purpose of algebraic representation of available exposure data and the estimation of weatherability when one or two exposure variables control the mechanism of degradation. A new approach based on the concept of "exposure parameters" shows encouraging potential for predicting long-term outdoor weatherability at any desired location on the basis of accelerated indoor studies, provided that the appropriate factors in the local weather at the outdoor station have been measured.

An overall review of the status of weatherability studies shows that the problem is still far from a satisfactory solution. On the other hand, recent developments in exposure techniques and methods of analysis represent concrete steps toward such a solution.

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Résumé

Le terme vieillissement, bien que communément utilisé dans la technologie des plastiques est un concept pauvrement défini puisqu'il se réfère à un service à longue durée dans des conditions complexes variables et parce que diverses propriétés du plastique sont affectées à des degrés divers par un environnement donné. L'amélioration dans la possibilité de prédice le vieillissement nécessite dès lors une redéfinition soignée du problème aussi bien qu'un rafinement de la technique expérimentale. Une revue de littérature étendue concernant l'exposition à l'extérieur artificielle des plastiques montre qu'il n'y a pas de corrélations simples entre ces deux modes d'essais. En outre, par suite des vitesses et des mécanismes de détérioration différents quand ils sont produits par la lumière visible, ultraviolette ou la chaleur ou l'humidité, un vieillissement arbitraire accéléré provoquera un déséquilibre dans les réponses observées par rapport à l'exposition des plastiques à des agents extérieurs agissant plus lentement. L'approche analytique en vue de prédire la résistance de plastiques aux dégradations à l'extérieur sont considérées. Dans ce procédé idéal, les effets des paramètres de vieillissement spécifique ont été établis sur des propriétés spécifiques des matériaux déterminés utilisant l'environnement artificiel contrôlé; la composition de l'atmosphère lors de l'exposition à l'extérieur est analysée en termes de ces paramètres; et finalement par des modèles mathématiques adaptés, les résultats attendus à une exposition du matériau dans cette composition déterminée de vieillissement sont analysées. Bien que cette approche est complexe son utilisation a été démontrée. Pour des études de routine, où l'approche mathématique peut être peu pratique, il semble nécessaire d'abandonné le but de test de vieillissement artificiel universel, sauf si des comparaisons qualitatives sont désirées. Des prédictions quantitatives utilisant la technologie d'essais sera la plus rentable, si elle est limitée à une comparaison de matériaux qui sont semblables de composition.

Zusammenfassung

Der Ausdruck "Witterungsbeständigkeit" ist, obwohl in der Kunststofftechnologie allgemein benützt, ein schlecht definierter Begriff, da er sich auf Langzeit-Verwendung unter komplexen und variablen Bedingungen bezieht und weil verschiedene Eigenschaften eines Kunststoffes durch ein gegebenes Milieu in verschiedenem Grade beeinflusst werden. Eine Verbesserung der Möglichkeit die Witterungsbeständigkeitvorherzusagen, erfordert daher eine sorgfältige Neudefinition des Problems sowie eine verfeinerung der experimentellen Methode. Ein Überblick über die ausgedehnte Literatur über Aussen- und künstliche Exponierung von Kunststoffen zeigt, dass zwischen diesen beiden Testmethoden keine einfache Korrelation besteht. Ausserdem wird ein willkürlich "beschleunigter" Bewitterungstest wegen der Verschiedenheit der Schädigungsgeschwindigkeiten und -mechanismen bei Einwirkung von sichtbarem Licht, Ultraviolett, Wärme oder Feuchtigkeit die bei der langsameren Aussen-Exponierung von Kunststoffen beobachtete Verhaltensbilanz verschieben. Analytische Methoden zur Vorhersage der Beständigkeit von Plastomeren gegen Bewitterungsabbau werden geprüft. Bei einem idealen Verfahren werden die Einflüsse spezifischer Bewitterungsparameter auf spezifische Eigenschaften eines gegebenen Materials unter Verwendung kontrollierter Milieube-

dingungen festgestellt; eine Analyse des Wetteraufbaues an einer gegebenen Aussenstelle anhand dieser Parameter wird durchgeführt und schliesslich können mit geeigneten mathematischen Modellen die bei der Exponierung des Materials an diese gegebene Wetterzusammensetzung zu erwartenden Ergebnisse berechnet werden. Diese Methode ist zugegebenermassen kompliziert, ihre Durchführbarkeit konnte aber gezeigt werden. Bei Routine-untersuchungen, wo die mathematische Methode unpraktisch sein kann, muss man, ausser zur Erlangung qualitativer oder auswählender Vergleiche, das Ziel eines "universellen" künstlichen Bewitterungstests aufgeben. Quantitative Vorhersagen sind mit der gegenwärtigen Testtechnologie am verlässlichsten, wenn sie sich auf einen Vergleich von Materialien mit recht ähnlicher Zusammensetzung beschränken.

02

APPLIED POLYMER SYMPOSIA NO. 4, 29–39 (1967)

Some Weathering Characteristics of Plastics

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Synopsis

Outdoor aging of plastics is largely a photo-oxidation process leading ultimately to discoloration and a loss in dielectric and mechanical strength. Embrittlement results from molecular and/or morphological changes caused by chain scission and crosslinking reactions which are mostly a function of specimen thickness and type of polymer. Discoloration indicates the formation of polyene chromophores while dielectric loss is proportional to polar group concentration. For the most part, weathering resistance of a plastic depends on the extent to which ultraviolet radiation is absorbed and harmlessly dissipated. Minute quantities of molecular defects or impurities which absorb ultraviolet radiation greatly reduce the photostability of the polyolefins and other plastics. See p. 30

Superficial effects of outdoor exposure on the physical properties of plastics have been described recently[1–3] and chemical mechanisms have been proposed for several of the different deterioration processes observed. It is clear that oxygen is the preponderant chemical degradant in the weathering of plastics; ozone, water, and other reactants have only minor importance. Although ozone readily cracks gutta percha, the *trans* form of polyisoprene, it seldom damages polymers with saturated main chains. Moisture may function as both a plasticizer and a hydrolytic agent, but, as a rule, condensation polymers with aromatic groups or bulky substituents adjacent to hydrolyzable links in the main chain are relatively stable in neutral media. Under some conditions, rain may accelerate surface erosion of plastics by washing away a protective layer of soluble or friable degradation products. On the other hand, atmospheric oxygen freely penetrates disordered regions in polymers where it reacts with chain segments activated by absorption of ultraviolet radiation. The degradation rate[4] in hydrocarbon polymers depends on the intensity and energy distribution of the solar spectrum in the ultraviolet region, both of which vary somewhat with the seasons as shown in Figure 1.

Maximum absorption of radiant energy occurs at the surface of plastics containing a uniform distribution of absorbing groups. Thus, thin films are especially vulnerable to photo-oxidation but the surface regions of thicker specimens also crack, chalk and discolor during prolonged exposure. It is possible to extend the service life of polyolefins and poly(vinyl chloride) several fold by addition of 1% or less by weight of a relatively stable light absorber such as a benzophenone or benzotriazole derivative which dissipates most detrimental radiation. But addition of about 2% by weight of a light screen such as a channel black is recommended for adequate outdoor protection of most plastics for time intervals greater than 5 yr.

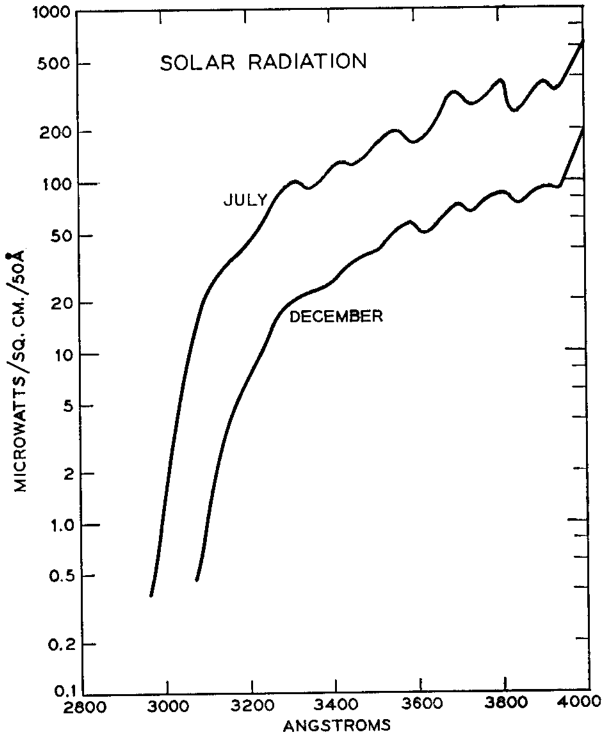

Fig. 1. Seasonal shift of the solar spectrum in the ultraviolet region.[4]

This report reviews the more significant effects of climatic conditions on the physicochemical properties of familiar plastics such as polyethylene, polystyrene, and poly(vinyl chloride).

Polyolefins

Unprotected polyolefins react readily with oxygen during weathering, often becoming brittle long before visual evidence of breakdown appears. Since pure paraffins are transparent to ultraviolet radiation which penetrates the atmosphere, Burgess[5] has proposed that occasional carbonyl groups or other defects in molecular structure absorb the energy required for the photoreaction. Burgess also ascribed the absence of autocatalysis and the ineffectiveness of chain terminators, such as phenolic-type antioxidants, to a degradative mechanism with a high initiation rate and a short kinetic chain length.

Photo-oxidation may proceed by the same free-radical chain mechanism commonly used to explain thermal oxidation of hydrocarbons,

1. Initiation: Polymer $\rightarrow$ $R\cdot$
(*a*) Autocatalysis: $ROOH \rightarrow RO\cdot + \cdot OH$
2. Propagation: $R\cdot + O_2 \rightarrow RO_2\cdot$
$RO_2\cdot + R'H \rightarrow ROOH + R'\cdot$
3. Termination: $RO_2\cdot \rightarrow$ unreactive products
(*a*) inhibition: $RO_2\cdot + HA \rightarrow ROOH + A\cdot$

However, there are distinct differences between the thermal and photoreactions. The propagation step evidently involves many cycles in the thermal reaction because radical chain terminators such as hindered phenols act as effective inhibitors. After the phenol has been consumed the reaction accelerates as homolytic breakdown of accumulated hydroperoxide increases. But phenols and other thermal antioxidants have very little effect on the photo-oxidation of hydrocarbons, indicating that the propagation step, if present, is severely suppressed. It has been proposed[5] that phenols may even function as sensitizers which accelerate rather than inhibit photo-oxidation.

There is general agreement that chain scission and crosslinking reactions occurring during oxidation are the direct cause of mechanical failure. However, recent studies have disclosed that marked morphological changes also accompany polyethylene embrittlement.[6] According to current concepts, polyethylene crystallized from the melt consists of a skeletal structure of crystalline lamellae interlaced with tie chains in a disordered arrangement.[7] Since the tie chain concentration rises with molecular weight, thermal annealing under the most favorable conditions proceeds exceedingly slowly in an ultrahigh molecular weight linear polymer. Yet, exposure of such a polymer to oxygen at elevated temperatures or under ultraviolet radiation[6] produces a rapid rise in crystallinity which has been observed by x-ray[8] and heat of fusion[9] measurements as well as by density

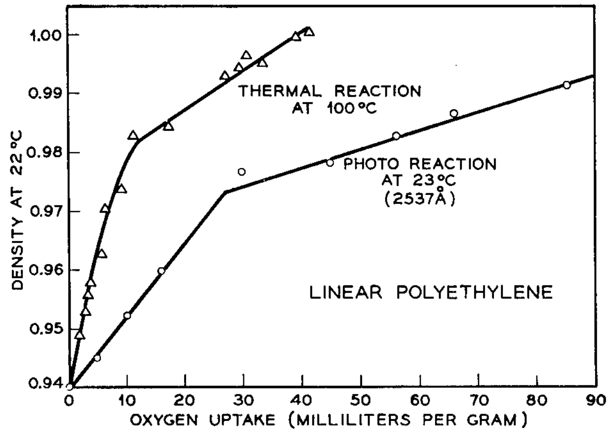

Fig. 2. Change in density of a linear polyethylene during thermal and photo-oxidation.

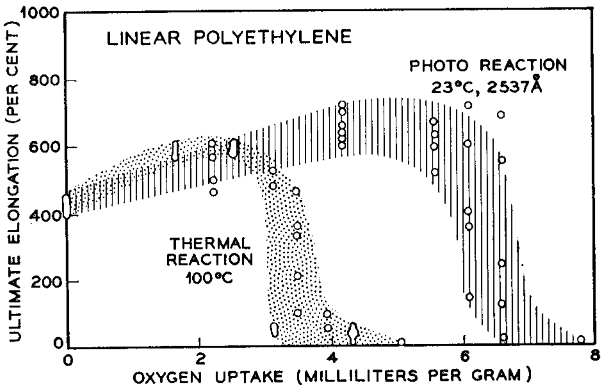

Fig. 3. Variation in ultimate elongation during thermal and photo-oxidation of a linear polyethylene.

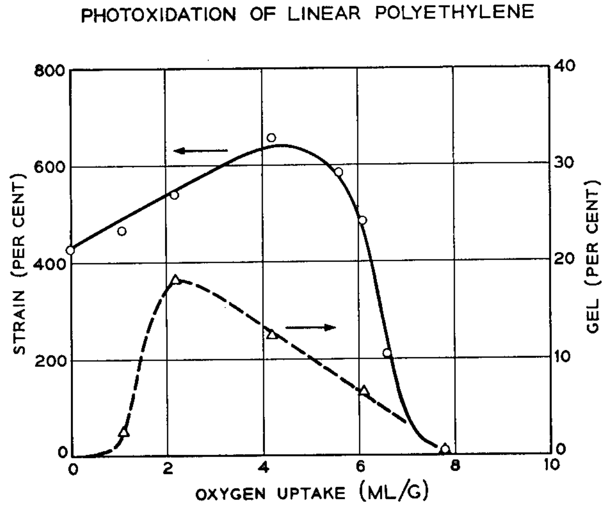

Fig. 4. Change in gel content and ultimate elongation of a linear polyethylene during photo-oxidation of a linear polyethylene.

determinations such as those in Figure 2. The density of polyethylene increases with oxygen uptake in two steps. The abrupt initial rise results from the combined effects of oxidative crystallization and an increase in oxygen content. After chemicrystallization ceases, density rises less rapidly as the chemical reaction gradually levels off in regions of the polymer bulk still accessible to oxygen.

The chemicrystallization process results from oxidative chain scission reactions. As chains break in amorphous regions, the freed fragments relax into a more compact arrangement. The relaxation process is inhibited by branching or crosslinking, and is therefore a function of polymer structure and reaction conditions. For example, the differences in polyethylene

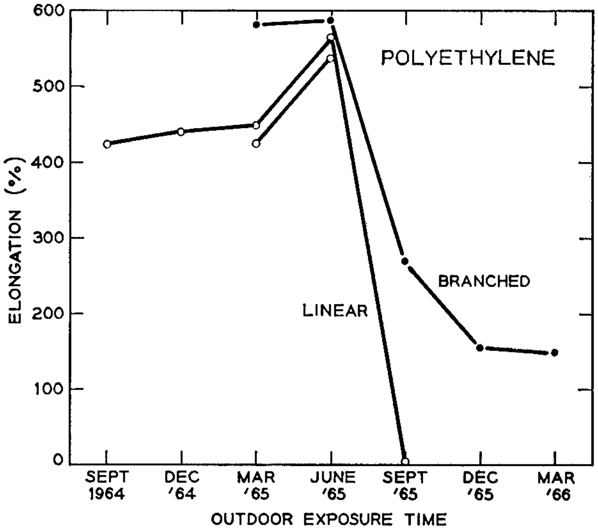

Fig. 5. Seasonal variation in the degradation rate of linear and branched polyethylene during outdoor exposure.

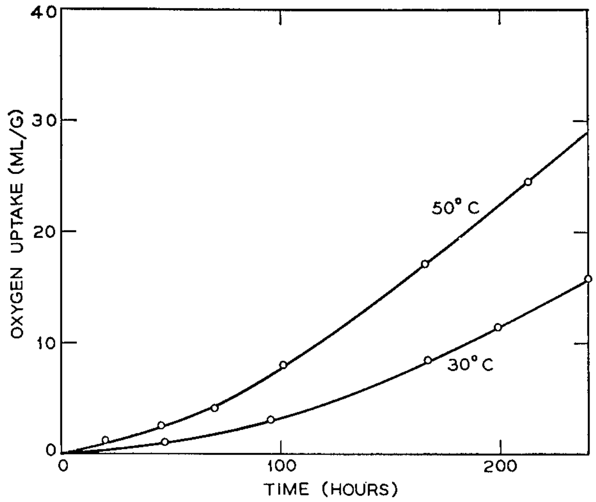

Fig. 6. The effect of temperature on the photo-oxidation of linear polyethylene exposed to 2537 A. radiation.

degradation behavior shown in Figures 2 and 3 are attributable to gel formation occurring during the photoreaction[10] but not during the thermal reaction.[11] Inhibition of crystallization by crosslinks formed during photooxidation increases the fraction of polymer ultimately accessible to oxygen, thereby increasing the level of oxygen consumption associated with embrittlement, as indicated in Figures 3 and 4. Cotten and Sacks[10] have further concluded from their studies that the ratio of scission to crosslinking during photo-oxidation depends on oxygen concentration at the reaction site and therefore varies with both crystallinity (formed from the melt) and specimen thickness.

Similar changes were noted in the mechanical properties of polyethylene during outdoor weathering and during irradiation under a germicidal lamp. Losses in elongation of unprotected linear and branched polymers during outdoor aging are shown in Figure 5. The initial rise in elongation of the linear polymer ($\bar{M}_w > 10^6$) was typical of an ultrahigh molecular weight material drawn at a rate of 2 in./min. Elongation changes in the polymers in Figure 5 were much greater during the summer months since there was a slight shift in the solar spectrum to shorter wavelengths and greater intensities at that time of year.[4] Evidently, higher summer temperatures also enhance the degradation rate of polyolefins[12] during outdoor exposure. The effect is demonstrated clearly in Figure 6 as a distinct difference between the photo-oxidation rates of the linear polymer at 30 and 50°C. during irradiation under a germicidal lamp. On the other hand, there was no detectable sign of deterioration after treatment in oxygen for 300 hr. at 50°C. in the dark. The greater oxygen consumption associated with embrittlement of the branched polymer ($\bar{M}_w$, 10^5) resulted from a lower initial degree of crystallinity and from less extensive chemicrystallization.

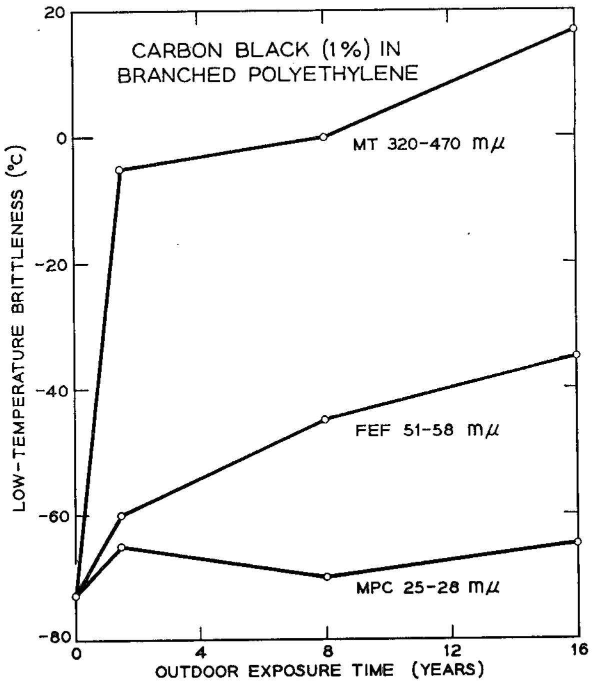

Fig. 7. The relationship of particle size to the effectiveness of carbon blacks as light screens in branched polyethylene. (H. M. Gilroy, unpublished results.)

Crosslinking the branched polymer with a peroxide before irradiation had no noticeable effect on the rate of embrittlement (not shown).

Water, carbon dioxide, and oxidized polymer are the principal products of polyethylene aging. Surface cracks and discoloration usually appear in the advanced stage of breakdown after embrittlement has occurred. Sensitizers such as transition metal ions and some aromatic sulfur compounds promote photo-oxidation, whereas ultraviolet light absorbers and light screens extend the outdoor service life of polyolefins. Minute quantities of impurities undoubtedly account for the non-uniform degradation often observed in different regions of a polymer specimen. Well-dispersed channel blacks provide far more outdoor protection for polymers than the most effective UV absorbers. The relative effectiveness of various classes and concentrations of carbon black as an outdoor protectant for branched polyethylene is shown in Figures 7 and 8. After outdoor exposure for more than 25 yr. in Florida, a polyethylene specimen containing 1% channel black had a brittle temperature that was still below −20°C.

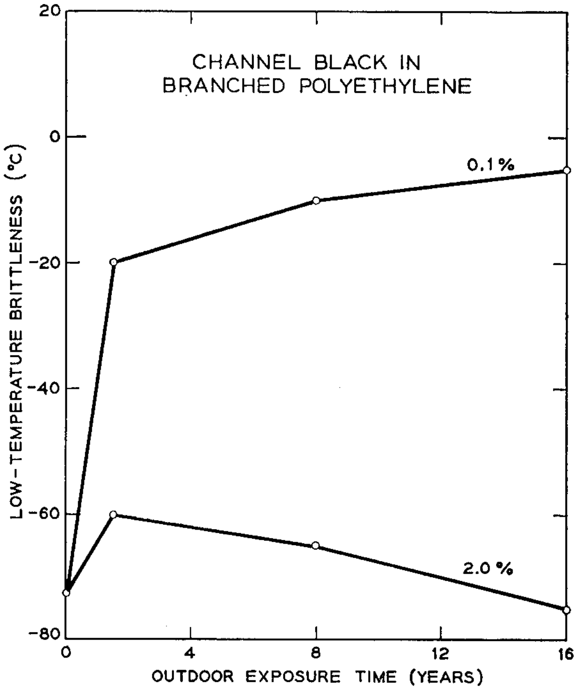

Fig. 8. Variation in low-temperature brittleness during outdoor exposure of branched polyethylene specimens containing 0.1 and 2.0% channel black. (H. M. Gilroy, unpublished results.)

Other polyolefins, such as polypropylene, with numerous hydrogen atoms attached to tertiary carbons, are more susceptible to oxidative degradation than polyethylene. Poly(4-methyl pentene-1) is particularly vulnerable since the amorphous and crystalline regions in the polymer have about the same low density and therefore are nearly equally accessible to oxygen.

Polystyrene

Polystyrene turns yellow and eventually forms surface crazes in sunlight. Achhamer and co-workers[13] proposed that the color change was associated with gradual conversion of phenyl groups to quinoid structures but Grassie and Weir[14] concluded instead that conjugated unsaturation developed along the polymer backbone. The latter workers noted that the rate of yellowing under 2537 A. radiation was unaffected by the presence or absence of oxygen. Since the color intensified while the hue remained unchanged, and since the irradiated polymer darkened rapidly on melting, Grassie and Weir suggested that the immobility of molecular chains in the "rigid polymer film" prevented formation of coplanar sequences of double bonds.

Another study[15] revealed that ultraviolet irradiation of polystyrene in air at 60°C. formed a yellow color which later intensified during post-irradiation storage in the dark. The rate of color intensification in the dark rose rapidly with temperature in the range between 25 and 80°C., suggesting that the degradation mechanism depended on permeability and, in turn, on chain mobility. Some crosslinking[16] also occurred along with color development at the outset of photo-oxidation.

Poly(vinyl Chloride)

Although some doubt still exists about the structural basis for color development in irradiated polystyrene, there is general agreement that color in degraded poly(vinyl chloride) results from development of conjugated unsaturation in the polymer chain.

Poly(vinyl chloride) is essentially transparent to solar radiation, but the unprotected polymer darkens rapidly during weathering. It has therefore been assumed that molecular defects or small quantities of impurities are responsible for the absorption of ultraviolet radiation which initiates degradation. Discoloration results from a zip reaction eliminating successive hydrogen chloride units to form a polyene chain structure[17] represented by the following general reaction,

$$-\!(\mathrm{CH_2{-}CHl})\!-_n \xrightarrow{h\nu} -\!(\mathrm{CH{=}CH})\!-_n$$

Polymer specimens darken long before HCl loss reaches 0.1% by weight and well before embrittlement is detectable. Ultraviolet irradiation at room temperature forms an average polyene sequence of about five conjugated double bonds.[18] Further loss of HCl on heating the irradiated polymer above the glass transition temperature increases the average polyene sequence length to more than fifteen double bonds.

Guyot and his co-workers[19] have synthesized poly(vinyl chloride) by an ionic procedure in order to minimize molecular defects such as terminal unsaturation and chlorine attached to tertiary carbon atoms. Their polymer was much more crystalline than a typical commercial product prepared by the free-radical method. When the polymer was fractionated by precipitation from tetrahydrofuran solution with methanol, it was found that the least soluble fraction had the fewest molecular defects and also had the highest thermal stability.

DeCoste and Hansen[20] found that wavelengths as high as 455 mμ caused degradation of poly(vinyl chloride), but that plasticized compositions of the polymer with an outdoor life of 10 yr. could be prepared in a limited range of colors. The effect of oxygen on hydrogen chloride elimination is uncertain,[21] but oxidative bleaching of the partially degraded polymer has been reported.[22] Since radical species promote HCl evolution it has been proposed[23] that degradation proceeds by a free-radical mechanism and that HCl loss in air is autocatalytic.[24] But it is still not clear that optimum protection requires radical chain terminators as well as the more common additives which neutralize hydrogen chloride, deactivate metallic contaminants, and dissipate harmful ultraviolet radiation.

Miscellaneous Polymers

Polyacetals oxidize readily and have especially low resistance to weathering as illustrated by the telephone pushbutton in Figure 9. After

Fig. 9. Polyacetal specimen after outdoor exposure for two summers. (P. G. Kelleher, unpublished results.)

exposure outdoors-under-glass for 18 mo. (two summers) in New Jersey, the acetal cap chalked and crazed badly, whereas the ABS resin number and letters had darkened but were only slightly eroded.

The outdoor service life of nylons and cellulosic polymers is somewhat better than that of the acetals but is still less than 3 yr. Sunlight generally discolors nylons,[25] bleaches cellulose,[26] and destroys the mechanical properties of both types of polymers. Poly(ethylene terephthalate) and the polycarbonates derived from bisphenols are much more durable outdoors than nylon. As a rule, the replacement of polymethylene segments with aromatic rings in the polymer backbone increases the weather resistance of polyamides and polyesters. Although polycarbonates, polysulfones, and poly(phenylene oxides) are phenolic derivatives, the poly(phenylene oxides) appear to be considerably more susceptible to photo-oxidation.

Poly(methyl methacrylate) and the fluorine-containing polymers have outstanding outdoor durability. Both types of polymers are transparent to UV radiation. The α-methyl groups shielding adjacent methylene units from oxidation make polymethacrylates more stable than polyacrylates. Other factors contribute to the remarkable stability of poly(vinyl fluoride) in comparison with that of poly(vinyl chloride) or of polyethylene. For example, bond dissociation energies are relatively high in fluorine-containing polymers. But it is doubtful that bond dissociation energies account entirely for the fact that unprotected polytetrafluoroethylene specimens have survived continuous outdoor exposure in Florida for more than 25 yr. without detectable change in physical properties.

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Résumé

Le vieillissement à l'extérieur de plastiques est en grande partie un processus de photooxydation amenant finalement à la décoloration et à une perte de force diélectrique et mécanique. Les résultats obtenus au départ des modifications moléculaires et morphologiques causées par les scissions de chaînes et par les réactions de pontage sont une fonction de l'épaisseur de l'échantillon et du type de polymère. La décoloration indique la formation de chromophores polyéniques, tandis que la perte diélectrique est proportionnelle à la concentration en groupe polaire. Pour la plus grande part, la résistance au vieillissement des plastiques dépend du degré auquel la radiation ultraviolette est absorbée et est dissipée. Des quantités petites de défauts moléculaires ou d'impuretés qui absorbent la radiation ultraviolette réduisent grandement la stabilité à la lumière des polyoléfines et autres plastiques.

Zusammenfassung

Die Aussen-Alterung von Plastomeren ist zum grossen Teil ein Photooxydationsprozess, der im Endeffekt zur Verfärbung und zu einem Verlust an dielektrischer und mechanischer Stärke führt. Die Versprödung ist eine Folge molekularer und morphologischer Veränderungen, bedingt durch Kettenspaltungsund Vernetzungsreaktionen, die meist von der Probendicke und dem Polymertyp abhängen. Die Verfärbung weist auf die Bildung von Polyenchromophoren hin, während der dielektrische Verlust der Konzentration an polaren Gruppen proportional ist. Grösstenteils ist die Witterungsbeständigkeit eines Plastomeren von dem Ausmass abhängig, in welchem Ultraviolettstrahlung absorbiert und in unschädlicher Form dissipiert wird. Winzige Mengen an Moleküldefekten oder Verunreinigungen, die Ultraviolettstrahlung absorbieren, setzen die Lichtbeständigkeit der Polyolefine und anderer Plastomerer stark herab.

03

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Fundamental Degradation Processes Relevant to Outdoor Exposure of Polymers

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Synopsis

A survey is presented of the fundamental reactions which can take place when polymers are exposed, separately, to light and oxygen. The kinetics of chain scissioning and crosslinking is presented in some detail. Oxidation is discussed on the basis of Bolland's mechanism. A number of examples in order to illustrate the discussion are given. The simultaneous effect of light and oxygen is illustrated by considering poly(ethyl acrylate). Lastly, the effect of ozone and air pollutants is briefly discussed.

INTRODUCTION

It is well known that sunlight, oxygen, various gases in the atmosphere such as ozone, NO_2, SO_2, etc., contribute to the deterioration of polymers. Many purely empirical tests are performed to determine the amount of this degradation; however, it is difficult to interpret these results from a fundamental point of view, as so many factors are involved simultaneously.

The ~~following~~ discussion ~~will be~~ is confined mainly to polymers of the linear type, especially vinyl polymers. It will be attempted to describe the fundamental processes, which in principle can take place. For this purpose, one factor at a time will be considered. Only in this way, is there a chance of eventually understanding the combined action of all factors.

Sunlight is a powerful source of deterioration for polymers. However, it will not be attempted to describe what happens if the composition of this light is imitated, but monochromatic light will be considered, preferentially of wavelength 2537 A. Light of wavelength 2800 A. corresponds to about 100 kcal./m.—this is the wavelength where carbonyl groups absorb—but the carbon–carbon single bond strength is only about 80 kcal./mole. Hence, it is not surprising that sunlight (3000–4000 A. corresponding to 90–70 kcal./mole) can have such a profound effect on polymers. Most polymers have groups or impurities which absorb in this range.

For our present purpose, we shall also exclude the atmosphere and work in vacuum; this means that we shall consider, first, the pure photolysis of polymers.

If one works with polymer films, one has first to find out at which film thickness the photolysis becomes independent of this thickness; in other words, it is preferable to work with films where diffusion of small molecules out of the film and other diffusion-controlled reactions no longer play a role.

Two processes which can take place during photolysis are of prime importance. These are chain scission and crosslinking. In addition, of course, changes in the spectra take place, indicating that reactions in addition to those mentioned above are proceeding. Chain scissioning and crosslinking are negligible from a chemical point of view, but as far as the mechanical properties of the polymers are concerned, they have a profound effect, due to the threadlike nature of the molecules. Thus a very small number of main bond ruptures or crosslinks will alter these properties profoundly.

Subsequently, we shall consider the effect of oxygen on its own. In addition, photooxidation will be discussed briefly. Last, the effect of ozone and other chemicals on polymers will be briefly indicated.

KINETIC CONSIDERATIONS[1]

Main Chain Rupture

Most photolyses show random main chain rupture, provided crosslinking does not take place. An initially monodisperse sample will be considered first. The assumptions are that all main chain links are of equal strength, independent of their location in the chain molecule, and that the rate of breaking links is proportional to the number of main chain links left in the system at time *t*.

Only cases where a small number of links are broken—about 0.1% or so—will be considered. Then, the total number of links in the system remains practically constant and equal to $[n_0]$, the initial concentration of main chain links. Hence,

$$-d[n]/dt = k_{ir}[n] \cong k_{ir}[n_0] \tag{1}$$

or integrated

$$[n_0] - [n] = k_{ir}[n_0]t$$

Here $[n_0]$ and $[n]$ are the concentrations of main chain links at time $t = 0$ and t, respectively, and k_{ir} is a rate constant. Further, $[n_0] - [n] = [N_0]s$, where $[N_0]$ is the initial concentration of polymer chains and s the average number of breaks in each original chain molecule. Further, $\mathrm{DP}_0/\overline{\mathrm{DP}}_t = s + 1$; hence

$$[N_0]s = k_{ir}[n_0]t$$

or

$$[N_0]\left(\frac{\mathrm{DP}_{n,0}}{\mathrm{DP}_{n,t}} - 1\right) = k_{ir}[n_0]t$$

As $[N_0] = [n_0]/\text{DP}_{n,0}$, one obtains finally the well-known expression for random degradation for moderate degrees of degradation, $\alpha = s/\text{DP}_{n,0}$,

$$\frac{1}{\overline{\text{DP}}_{n,t}} - \frac{1}{\overline{\text{DP}}_{n,0}} = k_{ir}\, t \qquad (2)$$

For larger degrees of degradation, eq. (2) becomes,

$$\ln (1 - 1/\overline{\text{DP}}_{n,0}) - \ln (1 - 1/\overline{\text{DP}}_{n,t}) = k_{ir}\, t \qquad (3)$$

After more than about five breaks per original chain ($s > 5$), the distribution of chain fragments becomes the so-called random distribution,

$$n_{\text{DP}} = \alpha^2(1 - \alpha)^{\text{DP}-1} \qquad (4)$$

which is quite similar to the most probable distribution (chain length 1 to ∞),

$$n_{\text{DP}} = q^2\, e^{-q\text{DP}} \qquad (5)$$

where n_{DP} is the number or moles of chains of length DP and q is a constant equal to $1/\overline{\text{DP}}_{n,0}$. Starting with a sample having a distribution according to eq. (4) or (5), one obtains again eq. (2), with the difference that the initial degree of polymerization is a number-*average* value.

Equation (2) not only holds for photodegradation, but for any type of degradation, which is of a random nature. In the case of photodegradation, the rate constant is given by

$$k_{ir} = \phi_s I'_{\text{abs}}/[n_0] \qquad (6)$$

where ϕ_s is the quantum yield for main chain scission (number of main chain links broken for each quantum absorbed), I'_{abs} is the average number of quanta absorbed by each volume unit/sec. (solution or film, the latter absorbing weakly), and $[n_0]$ is the initial concentration of main chain links.

If Beer-Lambert's law holds, one obtains for small light absorption, and moderate degrees of degradation,

$$k_{ir} = \phi_s k' I_0 \qquad (7)$$

k' is a constant depending on the geometry of the reaction cell or of the film and I_0 is the incident light intensity.

If one works with films having appreciable light absorption, the relationships become more complicated. This case may be considered in some detail. The film is divided into a number of thin layers. The first layer, facing the incident light, will suffer maximum degradation; the degree of degradation is a maximum at the surface and a certain molecular size distribution has been reached. The second and following layers have progressively smaller degrees of degradation and the size distributions correspond to smaller values of α. Thus, there will not be just one degree of degradation throughout the film, but a whole series. However, one can elaborate an average degree of degradation, which is given by the following equation,

$$\bar{\alpha} = \frac{\bar{s}}{\mathrm{DP}_{n,0} - 1} = \frac{1}{\overline{\mathrm{DP}}_{n,t}} - \frac{1}{\mathrm{DP}_{n,0}} = \frac{ktI_0}{m_1x_1}(1 - e^{-ax_1}) \tag{8}$$

where $\bar{s}$ is the overall average number of chain scissions for each original chain molecule, m_1, the number of monomers in each volume unit of the film, a, an optical constant, k a constant of proportionality, and x_1 the thickness of the film. It must be emphasized that $\bar{\alpha}$ must not be confused with α for a film (weak absorption), which has been degraded homogeneously (practically one size distribution throughout); but the overall size distribution corresponding to $\bar{\alpha}$ is one, obtained by considering the size distribution in each layer. For small light absorption, eq. (8) reduces to eq. (2) with k_{ir} given by eq. (7). The size distribution in any one layer can also be obtained.

As already pointed out, the degree of degradation at the incident light surface, α_0, is a maximum,

$$\alpha_0 = k_t I_0 a/m_1 \tag{9}$$

At a distance x from this surface, the degree of degradation becomes,

$$\alpha_x = s_x/\overline{\mathrm{DP}}_0 = \alpha_0\, e^{-ax} \tag{10}$$

As already pointed out above, the UV and IR absorption spectra also change during photolysis. However, this change is independent of the main chain scission reaction. This latter reaction is of such a small extent, that it could not be observed by spectroscopy. The change in spectra is due to independent reactions, leading to changes in the side groups or, for instance, double bond formation in the main chain.

Crosslinking[1]

The other sensitive change, which can take place on photolysis, is crosslinking. This can be followed by separating the gel from the sol fraction or by swelling measurements. In certain cases, IR or NMR spectra may be useful.

There are a number of parameters which have to be defined in this connection. The crosslinking density q is given by the fraction of the total amount of monomer, which is crosslinked. The number of crosslinked monomer in the whole sample is then given by qm_0, where m_0 is the total amount of monomer in the sample. The number of crosslinks is half of qm_0. The condition for reaching the gel point is given by the probability, $p_{c(\mathrm{crit})}$, that one monomer is crosslinked in each original chain. For a monodisperse sample, this leads to:

$$p_{c(\mathrm{crit})} = 1/(\mathrm{DP}_{n,0} - 1) = 1/\mathrm{DP}_{n,0} \tag{11}$$

For any type of heterodisperse polymer, the condition for the gel point is given by,

$$p_{c(\mathrm{crit})} = 1/(\overline{\mathrm{DP}}_w - 1) \cong 1/\overline{\mathrm{DP}}_w \qquad (12)$$

where $\overline{\mathrm{DP}}_w$ is the weight-average chain length. The crosslinking coefficient ϑ, is defined by

$$p_c\,\overline{\mathrm{DP}}_w = \vartheta$$

At the gel point $p_c = p_{c(\mathrm{crit})}$ and

$$p_{c(\mathrm{crit})}\overline{\mathrm{DP}}_w = \vartheta = 1 \qquad (14)$$

For a monodisperse sample $\overline{\mathrm{DP}}_w = \overline{\mathrm{DP}}_n$, hence $\vartheta = \gamma$, and for a random distribution $\overline{\mathrm{DP}}_w = 2\,\overline{\mathrm{DP}}_n$ and $\vartheta = 2\gamma \cdot \gamma$, is the crosslinking index and is defined by,

$$p_c\,\mathrm{DP}_0 = \gamma \qquad (15)$$

Hence, if $\vartheta = 0.5$, there is one crosslinked unit for two chain molecules. The broader the distribution, the fewer crosslinks are needed to reach the gel point.

As already pointed out above, crosslinked polymers can be investigated by separating the sol (soluble) from the gel (insoluble) fraction. For a polymer sample which has initially a random distribution of chain lengths, the sol fraction data are given by the following expression (Charlesby-Pinner),[2]

$$S + S^{1/2} = 2/\vartheta \qquad (16)$$

where S is the amount of sol fraction.

Since $\vartheta = p_c\,\overline{\mathrm{DP}}_w$ and $p_c = \alpha D$ (the probability of crosslinking is proportional to the irradiation dose D), eq. (7) gives,

$$S + S^{1/2} = 2/(\overline{\mathrm{DP}}_w \alpha D) = 1/(\mathrm{DP}_n \alpha D) \qquad (17)$$

Hence, a plot of $S + S^{1/2}$ against $1/D$ should give a straight line, whose slope is $2/(\alpha\overline{\mathrm{DP}}_n)$ or $1/(\alpha\overline{\mathrm{DP}}_n)$. This has been shown to be the case for crosslinking by high energy irradiation. There is no apparent reason why it should not also hold for ultraviolet irradiation. If chain degradation and crosslinking take place simultaneously, the above relationship becomes,

$$S + S^{1/2} = \beta/\alpha + 1/(\alpha\overline{\mathrm{DP}}_n D) \qquad (18)$$

β/α is the ratio of degradation to crosslinking, which is constant for constant D. Thus, a straight line is again obtained by plotting $(S + S^{1/2})$ against $1/D$; however, the intercept is now β/α. If the distribution is not random, then this plot is only linear over part of the range. This Charlesly-Pinner plot can be used to determine the relative efficiency of crosslinking and degradation. Equations (17) and (18) are only valid after the gel point has been reached.

The pre-gel reaction follows the kinetics of a polycondensation polymerization as formulated by Flory.[3] It is based on a statistical treatment. The following assumptions are made: (*a*) the polymer is initially monodisperse; (*b*) crosslinking occurs at random, that is, each monomer in a chain is equally likely to become crosslinked; (*c*) crosslinking takes place only between different chain molecules. Crosslinking in one molecule does not occur.

The theory is given in several textbooks of polymer physical chemistry,[4] and will not be outlined here.

It is interesting to note that if degradation does not take place ($\beta = 0$), the intrinsic viscosity of the polymer sample steadily increases and suddenly starts to drop at a certain critical radiation dose, when the polymer nears the gel point. If the chain scission to crosslinking ratio is high, the intrinsic viscosity decreases continuously with irradiation, but the actual weight-average molecular weight increases while the polymer approaches the gel point. Thus, viscosity measurements may become quite misleading.

Charlesby[5] has elaborated size distributions for sol fractions starting with an arbitrary initial distribution for a case where crosslinking only takes place. In a range prior to gelation, the ratio of the weight-average molecular weight at a definite stage of irradiation to the original weight-average molecular weight is:

$$\bar{M}_w/\bar{M}_{w,0} = 1/(1 - \vartheta) \tag{19}$$

For $\vartheta = 0.5$, this ratio becomes 2.

At the gel point, the ratio of the number-average molecular weight to the initial number-average molecular weight is given by,

$$\bar{M}_{n,g}/\bar{M}_{n,0} = 1/(1 - \bar{M}_{n,0}/2\bar{M}_{w,0}) \tag{20}$$

For a monodisperse sample, this ratio becomes 2 and for a random distribution 1.33.

Highly crosslinked polymers are investigated by swelling or by stress relaxation experiments (Chemorheology).

Miscellaneous

In addition to pure chain scission, one can also have cases where for each chain scission a few monomers are evolved. For the simplest case, one has then, random initiation, followed by depropagation (monomer formation) and termination by disproportionation. If the number of monomers produced per cut is very small, the process can still be treated as a pure random degradation, giving eq. (2). The rate of monomer formation can be measured directly and is given by,[1]

$$\frac{dm_{1,\,\text{total}}}{dt} = k_d \left(\frac{k_i}{k_t}\right)^{1/2} (m_0 - m_{1,\text{total}}) \tag{21}$$

$$= K(m_0 - m_{1,\text{total}})$$

where k_i, k_d, and k_t are rate constant for initiation, depropagation, and termination, respectively, m_0 is the amount of monomer initially contained in the polymer, and $m_{1,\,\mathrm{total}}$ is the monomer formed at time t from the whole sample.

There are also other interesting cases. Thus, random degradation can take place with simultaneous repolymerization of some of the fragments. The physical state of the polymer (crystalline, amorphous, or molten) has also an influence on the secondary reactions following the photolysis.

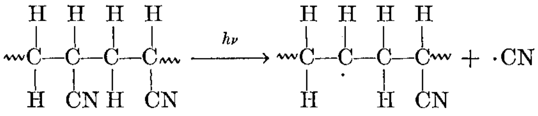
Some Photolysis Reactions

Photodegradation has been reviewed by the author in 1961 and will not be repeated here. However, it will be instructive to give a few examples in order to illustrate the relationships given in the previous section.

Jellinek and Bastien[6] studied the photodegradation of polyacrylonitrile in solution with light of wavelength 2537 A. A random degradation took place, which could be represented by eq. (2) in conjunction with eq. (6). The degradation was found to be independent of polymer concentration in a range of 0.1% w/v to 0.4% w/v. That this must be so can be shown as follows. In a cylindrical cell of length l, one has, provided the Beer-Lambert law is obeyed,

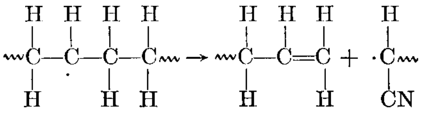
$$\frac{1}{\mathrm{DP}_{n,t}} - \frac{1}{\mathrm{DP}_{n,0}} = \phi_s \frac{2.303E}{[n_0]l} \qquad (22)$$

Here E is the optical extinction of the polymer solution and $[n_0]$ the concentration of main chain links, which is proportional to the polymer concentration. Since E is proportional to $[n_0]$, the degradation is independent of polymer concentration. The quantum yield for chain scission was about 10^{-4} main chain scissions for each quantum absorbed. All photolyses having random initiation have quantum yields of similar magnitude. In addition to chain scissioning, changes in absorption spectra take place. These changes indicate reactions independent of chain scission. Glutaronitrile, a model substance, showed similar changes in its absorption spectrum on exposure to ultraviolet light. A mechanism as follows was proposed by the authors:



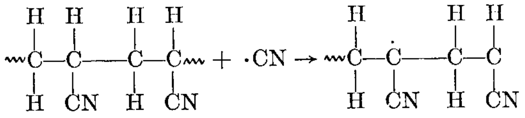
$$\sim CH_2-CH(CN)-CH_2-CH(CN)\sim \xrightarrow{h\nu} \sim CH_2-\dot{C}H-CH_2-CH(CN)\sim + \cdot CN$$

This reaction leads to random breaking of links,



$$\sim CH_2-\dot{C}H-CH_2-CH_2\sim \rightarrow \sim CH_2-CH=CH + \cdot CH(CN)\sim$$

The ·CN radical may react with a tertiary hydrogen atom



$$\sim\!CH_2-CH(CN)-CH_2-CH(CN)\!\sim + \cdot CN \rightarrow \sim\!CH_2-\dot{C}(CN)-CH_2-CH(CN)$$

This may lead to an additional chain scission.

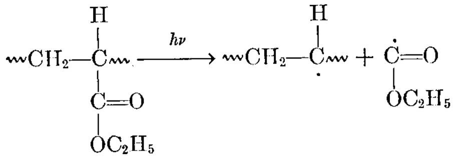
The reaction, which changes the spectra, may consist in stripping off either H_2 or HCN and forming conjugated double bonds in the chain. Internal cyclization is also a possibility to account for the change in spectra. Photolysis of polyacrylonitrile in the form of films leads to crosslinking whether degradation also takes place has not been ascertained with any certainty.

A good example for random degradation, with monomer formation for each cut is poly(α-methyl styrene) studied by Stokes and Fox[7] in the form of films. The photolysis was investigated at 27 and 115°C. At the lower temperature, seven monomers are produced for each cut and at 115°C., 25 units. The photolysis obeys the following reaction scheme,

Initiation	$P_0 \xrightarrow{h\nu} R_i + R_{n-i}$	k_{ir}
Depropagation	$R_i \longrightarrow R_{i-1} + m_1$	k_d
Termination	$R_i \longrightarrow P_i$	k_t

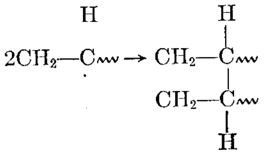
The termination is of the first order, as the intensity exponent for monomer formation is one at either temperature. The quantum yields for chain scission were 1×10^{-3} at 27°C. and 2×10^{-2} at 115°C. In addition, various volatiles were formed.

An example of a simultaneous crosslinking and chain rupture reaction is the photolysis of poly(ethyl acrylate) investigated by Jacobs and Steele.[8] Charlesby's theory (later improved by Pinner), solubility data, swelling ratios, intrinsic viscosities of sol fraction and moles of crosslinked units per unit volume were studied as a function of irradiation time. The experimental results could be accounted for by the following reaction scheme,



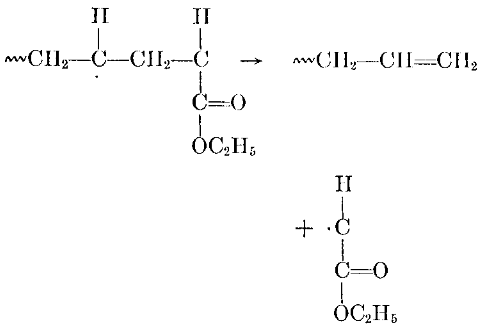
$$\sim\!CH_2-CH(C(=O)OC_2H_5)\!\sim \xrightarrow{h\nu} \sim\!CH_2-\dot{C}H\!\sim + \dot{C}(=O)OC_2H_5$$

Crosslinking can take place when two polymer radicals combine,



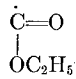
$$2CH_2-\dot{C}H\!\sim \rightarrow CH_2-CH\!\sim\,|\,CH_2-CH\!\sim$$

Chain scissioning can be accounted for by the following reaction,



$$\sim\!\!\sim CH_2-\underset{\cdot}{\overset{H}{C}}-CH_2-\underset{\underset{OC_2H_5}{C=O}}{\overset{H}{C}} \rightarrow \sim\!\!\sim CH_2-CH=CH_2 + \cdot\underset{\underset{OC_2H_5}{C=O}}{\overset{H}{C}}$$

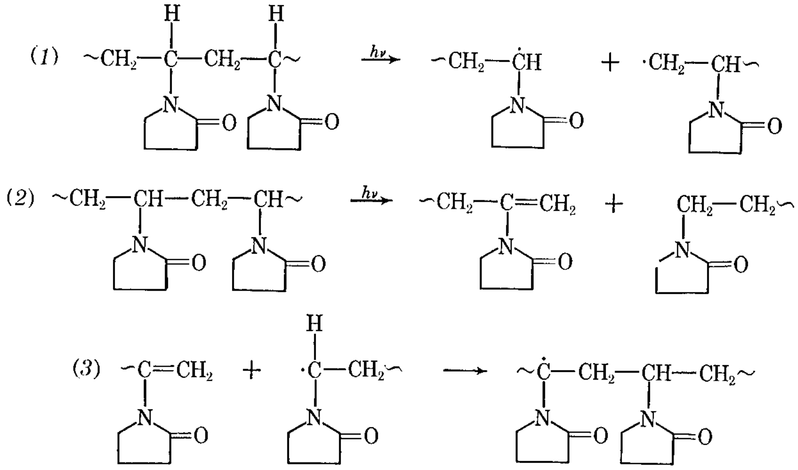
The possibility of transfer through the tertiary hydrogen atom has also to be considered or that instead of



$$\underset{OC_2H_5}{\dot{C}=O}$$

H comes off the chain. The photolysis is quite different from that for poly(methyl methacrylate). This polymer has no tertiary hydrogen atoms and chain scissioning rather than crosslinking takes place.

Last, the photolysis of poly(vinyl pyrrolidone) in aqueous solution will be considered briefly.[9] This reaction follows a chain scission reaction with double bond formation. The latter give rise to repolymerization. The reaction sequence can be formulated as follows,



(or any other radical)
(Chain recombination)

This mechanism leads to an equation as follows,

$$\frac{1}{\overline{\mathrm{DP}}_t} - \frac{1}{\overline{\mathrm{DP}}_0} = k_1 t - \frac{k_2}{k'}\left(e^{-k't} - 1\right) \tag{23}$$

Plotting $(1/\overline{\mathrm{DP}}_t) - (1/\overline{\mathrm{DP}}_0)$ against t gives a curve which at the beginning is a straight line but at later stages decreases considerably in slope.

OXIDATIVE DEGRADATION

The effect of oxygen is of great importance in this connection, although not much damage will be done at room temperature, as far as saturated polymers are concerned, if ultraviolet light is absent. However, it is essential to know the fundamental mechanism of oxidative degradation in absence of UV light in order to understand what is happening in presence of ultraviolet radiation and oxygen.

There is quite a large difference in the rate of oxidation for polymers with and without double bonds. However, the general mechanism for oxidation is based on a scheme by Bolland and other workers,[10] which has to be modified somewhat to suit each particular case. The first products of oxidation are hydroperoxide groups, which decompose leading to chain scission or react with various species and polymer groups. Branching chain reactions are produced, which under certain conditions can become degenerate (unsteady). Termination reactions are usually of the second order. Also, diffusion phenomena have to be considered, as they can become rate controlling; oxygen may have to diffuse through an oxidized surface layer into the polymer, which may either be amorphous or crystalline or both. Further, termination reactions are always diffusion-controlled.

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, crosslinking, 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. Main chain rupture is only a minor, though important, side reaction caused by decomposition of hydroperoxide groups.

The general oxidation mechanism can be formulated as follows:

$$(1)\quad \mathrm{RH} \rightarrow \mathrm{R}\cdot + (\mathrm{H}\cdot) \qquad \text{rate} = v_i$$

Initiation may be brought about thermally by ultraviolet light, catalysts, etc.

Propagation

$$(2)\quad \mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{RO_2}\cdot \qquad k_2$$
$$(3)\quad \mathrm{RO_2}\cdot + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}\cdot \qquad k_3$$
$$(4)\quad \mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{HO}\cdot \qquad k_4$$

Chain Branching

$$(5)\quad \mathrm{RO}\cdot + \mathrm{RH} \rightarrow \mathrm{ROH} + \mathrm{R}\cdot \qquad k_5$$
$$(6)\quad \mathrm{HO}\cdot + \mathrm{RH} \rightarrow \mathrm{HOH} + \mathrm{R}\cdot \qquad k_6$$

Termination

$$\left.\begin{array}{ll} (7) & RO_2\cdot + RO_2\cdot \\ (8) & RO_2\cdot + R\cdot \\ (9) & R\cdot + R\cdot \end{array}\right\} \rightarrow \text{usually small inert products} \qquad \begin{array}{l} k_7 \\ k_8 \\ k_9 \end{array}$$

Inhibition

(10) $ROO\cdot + AH \rightarrow ROOH + A\cdot$ k_{10}
(11) $RO\cdot + AH \rightarrow ROH + A\cdot$ k_{11}
(12) $HO\cdot + AH \rightarrow HOH + A\cdot$ k_{12}

RH represents a polymer molecule and AH an inhibitor molecule.

If steps (*1*)–(*3*) and (*7*)–(*9*) only are operative and steady-state conditions prevail, the rate of oxygen uptake or hydroperoxide formation is given by,

$$-\frac{d[O_2]}{dt} = \frac{d[ROOH]}{dt} = \frac{k_2k_3[RH][O_2]v_i^{1/2}}{2k_2^2k_7[O_2]^2 + k_2k_3k_8[O_2][RH] + 2\,k_3^2k_9[RH]^2} \tag{24}$$

If the oxygen concentration is high, eq. (24) leads to:

$$-\frac{d[O_2]}{dt} = \frac{d[ROOH]}{dt} = k_3[RH]\left(\frac{v_i}{2k_7}\right)^{1/2} \tag{25}$$

At low oxygen concentrations one has,

$$-\frac{d[O_2]}{dt} = \frac{d[ROOH]}{dt} = v_i^{1/2}\,k_2k_9^{-1/2}\,[O_2] \tag{26}$$

If step (*10*) replaces steps (*7*)–(*9*) the inhibited rate of oxygen consumption at high oxygen concentrations becomes,

$$-\frac{d[O_2]}{dt} = v_ik_3[RH]/nk_{10}[AH] \tag{27}$$

n is the number of chains stopped by one inhibitor molecule. Combination of eqs. (25) and (27) gives,

$$\frac{(d[O_2]/dt)\text{ inhibited}}{(d[O_2]/dt)\text{ uninhibited}} = 2k_7/(nk_3k_{10}[RH][AH]) \tag{28}$$

If the termination reactions are replaced by step (*11*), one obtains for large concentrations of oxygen,

$$\frac{(d[O_2]/dt)\text{ inhibited}}{(d[O_2]/dt)\text{ unhibited}} = 2k_1k_7[O_2]/(nk_3^2k_{11}[AH][RH]^2) \tag{29}$$

As an example, the oxidation of polypropylene may be discussed briefly. Oxidation in the absence of ultraviolet light only takes place, to a measurable extent, at elevated temperatures. Pudov, Gromov, Neiman, and Sklyorova,[11] for instance, studied polymer films 40 μ thick over a temperature range from 90 to 140°C. Volatiles were found (H_2O, formaldehyde, acetaldehyde, acetone, hydroperoxides, and carbon monoxide and dioxide.) $C{=}O$ groups and OH groups were followed by infrared spectra.

The experimental rate for oxygen absorption v_{O_2}, obeyed the following relationship,

$$v_{O_2} = a[\mathrm{ROOH}]^{1/2} + b[\mathrm{ROOH}] \qquad (30)$$

a and b are rate constants and ROOH is the concentration of hydroperoxide groups at time t. Hydroperoxides were identified as the primary oxidation products, whereas the other products were dependent on the rate of hydroperoxide formation and are produced by the decomposition of these groups, e.g.

$$\mathrm{ROOH} + \mathrm{RH} \rightarrow \mathrm{RO}\cdot + \mathrm{H_2O} + \mathrm{R}\cdot$$

The energy of activation for hydroperoxide decomposition was found to be 25 kcal./mole.

The mechanism proposed for the overall reaction is a variation of Bolland's scheme:

Initiation	$\mathrm{RH} + \mathrm{O_2} \rightarrow \mathrm{R}\cdot + \mathrm{HO_2}\cdot$	v_i
Propagation	$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{ROO}\cdot$	k_1
	$\mathrm{ROO}\cdot + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}\cdot$	k_2
Branching chain	$\mathrm{ROOH} + \mathrm{RH} \rightarrow \mathrm{RO}\cdot + \mathrm{H_2O} + \mathrm{R}\cdot$	
Termination	$\mathrm{ROO}\cdot + \mathrm{ROO}\cdot \rightarrow$ Inactive products	k_3

The steady-state method for oxygen consumption, considering that $v_{O_2} = k_1[\mathrm{O_2}][\mathrm{R}\cdot]$, gives,

$$v_{O_2} = k_2 \frac{(2k_4)^{1/2}}{k_3^{1/2}} [\mathrm{RH}]^{3/2}[\mathrm{ROOH}]^{1/2} + 2k_4[\mathrm{RH}][\mathrm{ROOH}]$$

or

$$\frac{v_{O_2}}{[\mathrm{RH}][\mathrm{ROOH}]} = 2k_4 + k_2 \frac{2k_4[\mathrm{RH}]^{1/2}}{k_3[\mathrm{ROOH}]^{1/2}}$$

Good straight lines were obtained by plotting $v_{O_2}/[\mathrm{ROOH}]$ versus $[\mathrm{ROOH}]^{1/2}$ and $v_{O_2}/[\mathrm{ROOH}]^{1/2}$ versus $[\mathrm{ROOH}]^{1/2}$.

The same reaction was also studied by Stivala, Reich, and Kellerher,[12] but in this case, the change in area under the infrared carbonyl band (5.6–5.8 μ) was observed over a range of temperatures from 125 to 150°C. Very thin films (2.5 μ) were oxidized. A small amount of volatiles were obtained under these conditions. The experimental results could be accounted for by a mechanism first given by Cullis and Hinshelwood[13] for the low temperature oxidation of higher paraffins,

Initiation	
$\mathrm{RH} + \mathrm{O_2} \rightarrow \mathrm{R}\cdot + \mathrm{HO_2}$	v_i
Propagation	
$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{RO_2}\cdot$	k_2
$\mathrm{RO_2}\cdot + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{H}\cdot$	k_3
$\mathrm{ROOH} + \mathrm{R}\cdot$	
Chain Branching	
$\mathrm{ROOR} \rightarrow 2\,\mathrm{RO}\cdot$	k_5
$\mathrm{R'}\cdot + \mathrm{RH} \rightarrow \mathrm{R}\cdot + \mathrm{R'H}$	k_8

Various reactions

ROOR → Inactive nonvolatile products (chain rupture)	k_6
$RO\cdot \rightarrow R'\cdot$ + volatile products	k_7

Termination

$RO_2 + RH \rightarrow$ Inactive products	k_4
$R\cdot' + O_2 \rightarrow$ Less reactive products	k_9

The reaction scheme proposed by the Russians is similar. The initiation and propagation reactions are the same. Also, the same chain carriers are produced in steps (*5*) and (*8*) as in the Russian scheme.

The maximum rate of carbonyl formation obtained by the steady-state method is,

$$\rho_m = \frac{c_1 v_i}{1 - C_2[\mathrm{RH}]/(\mathrm{C}_2[\mathrm{RH}] + \mathrm{C}_3[\mathrm{O}_2])} = \frac{K_1[\mathrm{O}_2]}{1 - K_2/(K_3 + [\mathrm{O}_2])} \tag{32}$$

Equation (32) is in very good agreement with the experimental results. These authors also found that the rate of formation of the hydroperoxide bond is in good agreement with the mechanism outlined above.

The chain scission reaction, though important, is usually only a minor oxidative side reaction. Thus for polystyrene one can formulate the following mechanism.[14]

(*1*) Polystyrene + $O_2 \leftrightarrows$ Polystyrene hydroperoxide

The peroxide is formed at the position of the tertiary hydrogen atom.

(*2*) Polystyrene hydroperoxide → Chain scission
(*3*) Chain scission → Inhibitions

$$\downarrow$$

Decay of inhibitors

Hence,

(*1*) $d[\mathrm{OOH}]/dt = k_1[\mathrm{O}_2][n]$

where n is the number of non-oxidized tertiary carbon atoms in the system at time t.

(*2a*) $-d[\mathrm{OOH}]/dt = k_2[\mathrm{OOH}]$	Peroxide decomposition
(2*b*) $-d[\mathrm{OOH}]/dt = k_3[\mathrm{OOH}]$	Chain scission
(*2c*) $-d[\mathrm{OOH}]/dt = k_4[\mathrm{OOH}][i]$	Inhibition
(*3a*) $+ d[i]/dt = k_5[\mathrm{OOH}]$	Formation of inhibitors
(*3b*) $-d[i]/dt = k_6[\mathrm{x}][i]$	Decay of inhibitors

For the initial stages of the degradation process, this scheme leads to

$$\frac{s}{P_0} = \alpha = \frac{k_3 k_1}{k_2 + k_4}[\mathrm{O}_2]\, t \tag{33}$$

For the later stages of the process, one has,

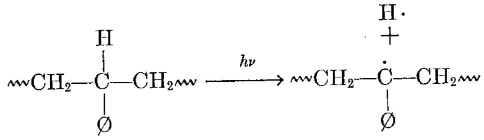
$$\frac{s}{P_0} = \alpha = \left(\frac{k_3k_1}{k_2 + k_4}\right)[O_2]\left(\frac{1}{1 + b}\right)t \tag{34}$$

and for the intermediate stages, the rate of breaking links is given by,

$$\frac{ds}{dt} = \left(\frac{k_3k_1}{k_2 + k_3}\right)[O_2]\frac{P_0}{1 + f(i)} \tag{34}$$

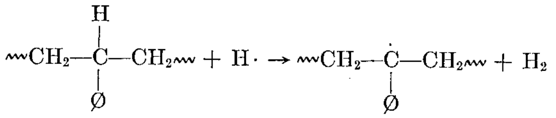
This mechanism is obeyed quite well by the experimental results.

A very instructive investigation has been carried out by Grassie and Weir.[15] They studied, systematically, the photolysis of polystyrene in vacuum and, subsequently, the photolysis in presence of oxygen. Very thin films (0.004 mm.) were taken to exclude diffusion effects. Above 3650 A., no effect was observed even after hundreds of hours of exposure in vacuum. Light of wavelength 2537 A. was effective. Lambert's law was obeyed up to 8×10^{-4} cm. thickness. Polystyrene without catalyst was prepared thermally. The only reaction product obtained by photolysis in vacuum was hydrogen gas. The quantum yield with respect to this gas was 4.3×10^{-2} and the light intensity exponent practically unity. The rates were independent of molecular weight in a range of about 1×10^5 and 15×10^5 and of initiator fragments. H_2 evolution was a linear function of exposure time. The overall energy of activation for the photolysis reaction was 2.9 kcal./mole. The mechanism for this reaction consisted in the primary fission of a C—H bond, most probably that of a tertiary hydrogen atom. The dissociation energies for C—H bonds are as follows: 104 kcal./mole for a C—H bond on the benzene ring, 76 kcal./mole for secondary hydrogens, and 71 kcal./mole for tertiary hydrogens. The bond strength of the latter will be further reduced by resonance. The energy of the radiation of wavelength 2537 A. is 112 kcal./mole and is sufficient to break all these bonds. The radiation will be absorbed by the benzene ring and has to redistribute itself until it is localized in the tertiary C—H bond, which then dissociates. There was no evidence for main chain rupture. The low quantum yield is due to the dissipation of energy by quenching, recombination (cage effect), and collisional deactivation reactions. The neighboring hydrogen atom of the one which dissociates is affected and either dissociates more easily or is abstracted by the first dissociated hydrogen atom. In this way conjugated systems can be formed, which account for discoloration of the polymer. The reaction scheme can then be formulated as a nonchain reaction as follows,

(1) 

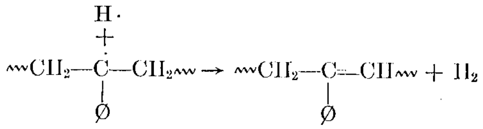
$$\sim\!CH_2\!-\!\overset{H}{\underset{\phi}{C}}\!-\!CH_2\!\sim \xrightarrow{h\nu} \sim\!CH_2\!-\!\overset{H\cdot\;+}{\underset{\phi}{\dot{C}}}\!-\!CH_2\!\sim$$

The hydrogen atom can either recombine with the C-atom (cage effect) or can abstract a neighboring hydrogen atom,

(2) 

$$\sim\!\!\sim CH_2-\overset{\displaystyle H}{\underset{\displaystyle \varnothing}{C}}-CH_2\sim\!\!\sim + H\cdot \rightarrow \sim\!\!\sim CH_2-\underset{\displaystyle \varnothing}{\dot{C}}-CH_2\sim\!\!\sim + H_2$$

or

(3) 

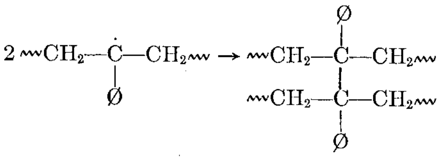
$$\sim\!\!\sim CH_2-\overset{\displaystyle H\cdot\atop +}{\underset{\displaystyle \varnothing}{\dot{C}}}-CH_2\sim\!\!\sim \rightarrow \sim\!\!\sim CH_2-\underset{\displaystyle \varnothing}{C}=CH\sim\!\!\sim + H_2$$

Conjugation takes place with the double bond in the benzene ring or occasionally, it may happen that several neighboring H-atoms react.

There also is the possibility that the primary abstracted hydrogen atom combines with another dissociated one,

$$(4)\ H\cdot + H\cdot \rightarrow H_2$$

It was found that the polymer becomes quickly insoluble and embrittled; this means that crosslinking takes place,

(5) 

$$2\sim\!\!\sim CH_2-\underset{\displaystyle \varnothing}{\dot{C}}-CH_2\sim\!\!\sim \rightarrow \begin{array}{c} \sim\!\!\sim CH_2-\overset{\displaystyle \varnothing}{C}-CH_2\sim\!\!\sim \\ | \\ \sim\!\!\sim CH_2-\underset{\displaystyle \varnothing}{C}-CH_2\sim\!\!\sim \end{array}$$

The absorption spectra also change during photolysis. A shoulder at 825 $cm.^{-1}$ appears in the IR spectrum, which is consistent with a double bond in the chain conjugated with one in the benzene ring. The UV spectra increase in the range of 2300–3500 A. and faster in the range 2400 and 2500–3000 A. The absorption in the 2400 A. region is characteristic of compounds having a C—C double bond. The increase in optical density is linear with time.

Reactions (*2*)–(*4*) depend on the mobility of the hydrogen atom; if this is suppressed, reaction (*4*) will become less important and (*3*) will become accelerated. This is the case, when the photolysis is carried out in the presence of nitrogen gas.

Next, the photolysis was studied in the presence of oxygen. CO_2 and H_2O were formed in approximately equal amounts during the photooxidation; they act as inhibitors and have to be removed continuously. The intensity exponent is again unity. At low oxygen pressure, the rate of oxygen consumption is independent of light intensity. The oxidation rates give an energy of activation of 6 kcal./mole in the range of 28–51 °C. The quantum yield is 8.73×10^{-4} with respect to oxygen consumption. The rates of oxygen uptake are linearly proportional to oxygen pressure, even in mixtures with N_2. The rate is also proportional to radiation dose.

Absorption of light is almost complete for a film thickness of 0.01 mm.; this means that photooxidation of polystyrene in bulk will only take place in a very thin surface layer. In the case of the photooxidation, light above 3650 A. is effective; after an induction period, the reaction proceeds at about 1/40 of the rate of that at wavelength 2537 A.

The mechanism can be formulated as follows,

(*1*) $R + h\nu \rightarrow R\cdot + H\cdot$
(*1a*) $R\cdot + H\cdot \rightarrow RH$ (cage effect)
(*2*) $H\cdot + O_2 \rightarrow HO_2\cdot$
(*2a*) $H\cdot + H\cdot \rightarrow H_2$
(*3*) $R\cdot + O_2 \rightarrow RO\cdot_2$
(*4*) $RO\cdot_2 + RH \rightarrow ROOH + R\cdot$

The mechanism is reminiscent of the Bolland scheme; subsequent ROOH decomposition takes place, but a chain reaction is effectively suppressed by the dominance of diffusion in this condensed system.

Final reactions may consist of,

(*5*) $R\cdot + R\cdot \rightarrow$ crosslinking

The formation of H_2O and CO_2 cannot be explained easily, they may be produced by ROOH decomposition, but other products should also be formed. It is likely that they are the only two products which can diffuse out of the film.

A tentative reaction producing water can be formulated as follows,

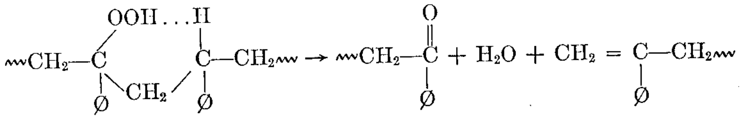
(*6*) $HO_2\cdot + RH \rightarrow R\cdot + H_2O_2$
(*7*) $HO_2\cdot + HO_2\cdot \rightarrow O_2 + H_2O_2$
(*8*) $2H_2O_2 \rightarrow 2H_2O + O_2$

At high oxygen concentrations, reaction (*2a*) is suppressed and there is competition between (*1a*) and (*3*). Thus, as the concentration of the radicals R· is directly proportional to the light intensity and as the overall reaction is given by (*3*), the latter must be a linear function of the light intensity and oxygen pressure.

At low oxygen pressures, (*2*) or (*2a*) can take place more easily, hence reaction (*1a*) is suppressed and the reaction depends only on the O_2 availability. The reaction at wavelengths above 3650 A., must have a different mechanism.

The most adverse effect, industrially, is the discoloration of polystyrene. For the pure photolysis, mainly conjugation with the double bond in the benzene ring, is responsible for this defect. The neighboring tertiary hydrogen atom may be activated by this process and will be abstracted; in this way, conjugated double bonds are formed.

For photo-oxidation, conjugation can be brought about by hydroperoxide decomposition,

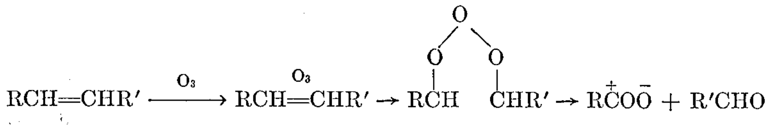


This process can occur by decomposition of OOH-groups at neighboring tertiary C-atoms. The neighboring α-methylene hydrogens are then activated leading to conjugation. Thus, this example shows that by systematic studies, varying one factor at a time, useful results can be obtained.

OZONE AND OTHER CHEMICALS

Polymers are very sensitive even to very small concentrations of ozone. The atmospheric concentration of O_3 varies from zero to a few parts in 10^7 parts of air. Chain scissioning and crosslinking take place in polymers exposed to ozone.

Thus, main-chain scission, for instance, can be brought about as follows,



$$RCH{=}CHR' \xrightarrow{O_3} RCH\overset{O_3}{=}CHR' \rightarrow \underset{RCH\quad CHR'}{\overset{O\quad O}{\overset{O}{\wedge}}} \rightarrow R\overset{+}{C}O\overset{-}{O} + R'CHO$$

Further reactions can then take place. Cracking and rupture usually occur when a polymer is exposed to ozone while held under stress, which must have a definite minimum value. In absence of stress, a thick ozonized layer forms which prevents further deterioration. The stress insures that a fresh surface area is continuously exposed. The work by Braden and Gent[16] is of interest in this connection. These authors made a study of the rate of growth of a single incision in a thin sheet of rubber. They found a number of points, which are especially of importance for the growth of the cut: (*a*) a well-defined value of tensile load has to be exceeded before propagation can take place; (*b*) the cut grows linearly across the rubber sheet; (*c*) the cut grows at a uniform rate except for a short induction period; (*d*) the rate of cut growth is unaffected by the magnitude of the stress except for very large stresses (minimum stress 70 g./cm.^{2}); (*e*) the cut growth increased appreciably for high stresses (>2000 g./cm.^{2}). Solomon and Bloois[17] come to the following conclusion: Ozone is adsorbed by solid surfaces forming a thin oxidized layer (0.01–0.05 μ), which makes certain polymer surfaces resistant to further attack. If such a surface is stretched while exposed to ozone, narrow and deep capillaries are formed at the edges of foreign particles embedded in the polymers. The adsorbed film, being highly mobile, concentrates in the capillaries and cracking takes place.

Crabtree and Biggs[18] observed that stretched rubbers which are irradiated by ultraviolet light show cracks in the presence of peroxides. This cracking takes place whether oxygen is present or not. The process is catalyzed by nitrogen peroxides. The latter reaction proceeds as follows,

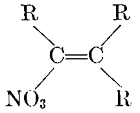
$$NO_2 \xrightarrow{h\nu} NO\cdot + O\cdot$$

$$O\cdot + O_2 + M \rightarrow O_3 + M\cdot$$

$$NO\cdot + O_3 \rightarrow NO_2 + O_2$$

There is no work of a fundamental nature on the effect of air pollutants on polymer surfaces. There are only investigations of the effect of such chemicals on low molecular olefins and saturated hydrocarbons.[19]

NO_2, for instance, reacts in presence of oxygen, but absence of light, with unsaturated hydrocarbons, such as cyclohexene, 1,3-butadiene and 1-hexene. It is suspected that amongst the reaction products there are very small amounts of powerful eye irritants of the type



These compounds are effective when present only in a few parts per million.

The reaction of SO_2 in the presence of UV light with saturated and unsaturated hydrocarbons leads to sulfinic acids. The reaction scheme proposed by Dainton and Ivin[20] is as follows,

$$\begin{gathered} SO_2 \rightarrow SO_2^* \\ SO_2^* \rightarrow SO_2 \\ SO_2^* + SO_2^* \rightarrow SO_2 + SO_2 \\ SO_2^* + RH \rightarrow SO_2 + RH \\ SO_2^* + RH \rightarrow RSO_3H \end{gathered}$$

Recently, we have started a fundamental investigation on the effect of various air pollutants on polymer surfaces.[21] The study is carried out in a high vacuum system with various pressures of NO_2 over a range of temperatures. The reactions are first studied from the point of view of main chain rupture of polystyrene, which actually takes place. At later stages, it will be attempted to identify the various reaction products.

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Résumé

Une revue est présentée en ce qui concerne les réactions fondamentales qui ont lieu lorsque des polymères sont exposés séparément à la lumière et à l'oxygène. Les cinétiques de rupture de chaîne et de pontage sont présentées avec certains détails. L'oxydation est discutée sur la base du mécanisme de Bolland. Un certain nombre d'exemples sont soumis à discussion en vue d'illustrer le problème. L'effet simultané de lumière et d'oxygène a été illustré en considérant le polyméthacrylate d'éthyle. Les effets de l'ozone et des polluants de l'air sont brièvement discutés.

Zusammenfassung

Ein Überblick über die fundamentalen, bei der getrennten Einwirkung von Licht und Sauerstoff auf Polymere möglichen Reaktionen wird gegeben. Die Kinetik der Kettenspaltung und Vernetzung wird in einigen Details behandelt. Die Oxydation wird auf Grundlage des Mechanismus von Bolland diskutiert. Eine Anzahl von Beispielen wird zur Erläuterung der Diskussion angeführt. Die gleichzeitige Wirkung von Licht und Sauerstoff wird an Polyäthylacrylat gezeigt. Schliesslich wird die Wirkung von Ozon und von Luftverunreinigungen kurz diskutiert.

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APPLIED POLYMER SYMPOSIA NO. 4, 61–83 (1967)

Energy Characteristics of Outdoor and Indoor Exposure Sources and Their Relation to the Weatherability of Plastics

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Synopsis

Knowledge and simulation of average weather conditions are a necessary requirement for reproducing and accelerating outdoor exposure by indoor tests. The emission characteristics of sun and sky radiation and of different types of laboratory devices are ~~have been~~ reviewed. The varying actinic effects of the accelerated test sources can be related to their specific emission characteristics through information on the activation spectra of the plastics. Xenon arc emission bears the closest similarity to solar energy in the ultraviolet region. However, acceleration of only one weathering factor can distort the results.

INTRODUCTION

The weathering of plastics is dependent on many atmospheric factors. Ultraviolet radiation promotes the primary photochemical process in clear plastics and plays the major role in degradation. For many types of polymers, heat is a dominant factor influencing the secondary reactions. Other influencing agents are oxygen, humidity, and wetness. The weather is so variable from time to time and from place to place that even comparisons among outdoor tests obtained at different seasons, years, or locations have been inadequate. It is thus not surprising that attempts to provide accelerated weathering tests by various means have failed to give adequate correlations with natural weathering.

While the relative stability of a polymer formulation for use out-of-doors is best demonstrated by actual outdoor testing, this is not always practical. Accelerated tests are required in order to realize the greatest value from experimental formulating work of the laboratory and for predicting results of long-term exposures out of doors. Often the cause of discrepancies between the outdoor and indoor tests is that the indoor ultraviolet sources do not duplicate the spectral energy distribution of natural sunlight. Further, the photochemically active portion of sunlight represents only a small fraction of the total terrestrial solar radiation and is not adequately monitored during outdoor exposure tests. For consideration of the weather-

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* Deceased November 12, 1966.

ability of colorless plastics under terrestrial sunlight, the spectral region of interest is 3000–4000 A.

The total integrated intensity of sunlight expressed in units such as langleys or "ultraviolet sun hours" does not truly measure the actinic ultraviolet radiation. For successful correlations of exposure test data, continuous monitoring and integrating of the photochemically active band intensities is desirable. A means of determining the photochemically effective, or actinic, energy is the measurement of photodegradation as a function of incident wavelength. This is termed the "activation spectrum" of the material. A knowledge of the wavelength sensitivity of the plastic formulations being tested is also important in order to evaluate the relative effect of different test sources.

ACTIVATION SPECTRA

Table I[1] shows the wavelength regions of sunlight which have the greatest effect on various polymers. The peak sensitivity falls between 3000 and 3500 A. for most of the polymers. A Pyrex glass-filtered xenon arc, which has approximately the same ultraviolet spectral energy distribution as sunlight, was used for many of the measurements. The experimental technique for determining the activation spectra has been described previously.[1,2] Briefly, the ultraviolet energy is dispersed across a plastic sample by means of a fast quartz spectrograph (about *f*/2). The extent of photodegradation in the areas of the plastic sample irradiated by the

TABLE I
Activation Spectra Maxima (Wavelength Region of Sunlight Causing Maximum Increase in Absorption or Fluorescence)

Polymer	Activation spectrum maximum, A.	Means of measurement
Polyesters (various formulations)	3250	Visible light[a]
Polystyrene	3185	Visible light, fluorescence
Polyethylene	3000	Infrared (carbonyl)
Polypropylene (non-heat stabilized)	3700	Infrared (carbonyl)
Poly(vinyl chloride), homopolymer	3200	Visible light, fluorescence
Poly(vinyl chloride), copolymer with vinyl acetate	3270 and 3640	Visible and ultraviolet[b] light
Poly(vinyl acetate) film	<2800	Visible and ultraviolet[b] light
Polycarbonate film	2850–3050[c] and 3300–3600[d]	Visible and ultraviolet light, fluorescence
Cellulose acetate butyrate film	2950–2980	Visible and ultraviolet[b] light
Styrene acrylonitrile film	2900 and 3250	Visible and ultraviolet[b] light

[a] 4000 or 4300 A.

[b] 2750–3000 A.

[c] Includes several formulations and film thicknesses.

[d] Longer wavelength maxima were detected by the ultraviolet technique only. Fluorescence intensity decreased under the long wavelength irradiation.

dispersed ultraviolet energy is determined by one or more optical methods. Yellowing and changes in ultraviolet absorption are measured with a Cary Model 14 spectrophotometer using an adapter to convert it into a scanning microdensitometer. A Beckman IR-4 infrared spectrophotometer, similarly adapted for microdensitometry of samples, is used to measure the increase in carbonyl content with exposure. Another method utilizes measurement of the destruction of the natural fluorescence or creation of new fluorescent species due to the photodecomposition reaction. The different techniques usually give comparable results, but the ultraviolet and fluorescence techniques are appreciably more sensitive.

Figure 1 compares the activation spectrum of a polyester casting by the visible and ultraviolet techniques. Both curves show the different effects of the short and long ultraviolet wavelength regions. The region below about 3500 A. causes an increase in absorption, i.e., yellowing, while the longer wavelength ultraviolet energy appears to destroy the absorbing species originally present and causes a decrease in absorption, particularly to ultraviolet light. Investigation has shown that the longer wavelength radiation also destroys the yellow species produced by the shorter wavelengths. The "bleaching" effect of the longer wavelengths is also observed when the fluorescence technique is used. In this case, the original blue-white fluorescence of the plastic decreases in intensity under the long wavelength radiation. Because of the diverse effects of the different wavelength regions, it is important to match the test source at all actinic wavelengths to the one to which the material will be subjected in actual use. Consideration of only the region causing increase in absorption is not sufficient.

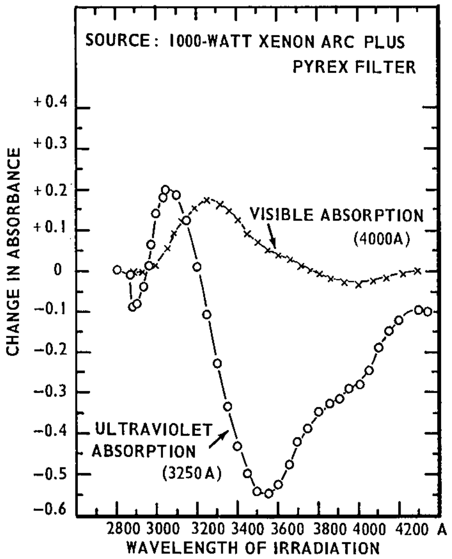

Fig. 1. Visible and ultraviolet activation spectra of a polyester casting.

The activation spectra reported are uncorrected for the energy distribution of the light source and should vary with the source used. However, Melchore[3] has shown by the use of filters that for polyethylene the maximum actinic region of the fluorescent sunlamp/Blacklamp source (FS/Bl) is also at about 3000 A. Estes[4] determined that both the sun and Fade-Ometer emissions between 3500 and 3800 A. have maximum effect on polystyrene. His measurements were also made with the use of filters and gave a different result than shown in Table I for polystyrene.

ULTRAVIOLET SPECTRAL CHARACTERISTICS OF SUN AND SKY

The ultraviolet portion of sunlight from 3000 to 4000 A. which reaches the surface of the earth in the northern parts of the United States constitutes less than 6% of the total radiation of the sun.[5] The daily and seasonal cycles in altitude and azimuth of the sun result in varying distances traversed by the sunlight through the earth's atmosphere. Because of the ultraviolet absorption and scattering by atmospheric constituents, there is a considerably larger effect on the ultraviolet portion than on the total radiation. The varying concentration of ozone in the upper atmosphere has been suggested[6] as the main cause for ultraviolet seasonal variability. In addition to the hourly and seasonal variations, the local weather conditions play a large role with effects due to smoke, dust, fog, and clouds.

Measurements made in Stamford, Connecticut[5] show variations in the ratio of ultraviolet to total sunlight intensity from less than 1% to about 6%. The differences appear to depend more on atmospheric conditions than on daily or seasonal factors. The ultraviolet below 3400 A. shows an

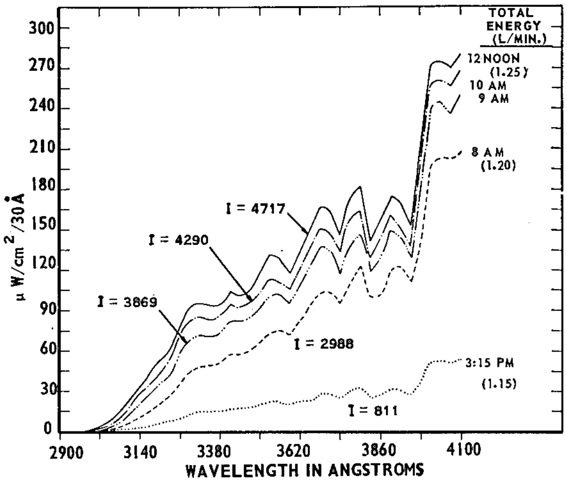

Fig. 2. Daily variation in spectral energy distribution of sunlight on August 19, 1958. Solar altitude at noon about 64°. (Clear sky, some scattered clouds at noon.) (*I*) integrated ultraviolet energy in microwatts.

even larger variation with seasonal and atmospheric conditions than does the total ultraviolet. Figure 2 shows the spectral energy distribution curves of the sun obtained at different times of the day in August, 1958. There were no clouds in the path of the sunlight during any of the measurements. Comparison of the integrated ultraviolet intensity (μw./cm.^{2}) with the total intensity (langleys/min.) shows the disproportionately large change in the ultraviolet intensity with time of day. Figure 3 compares the integrated ultraviolet energy below 3500 A. with the total radiation as a function of the time of day. The total radiation shows relatively little variation compared with the large changes in the actinic ultraviolet. The sudden drop in intensity in the early afternoon was due to the formation of haze.

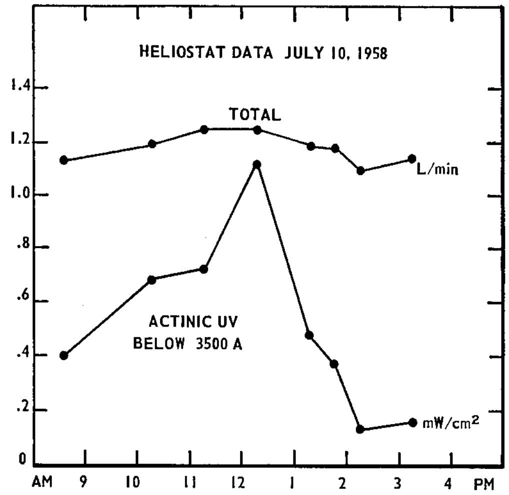

Fig. 3. Comparison of total energy and ultraviolet energy for different hours of the day.

The data given above were obtained for normal incidence of the sun measured at a narrow angle which included only a small portion of skylight. On a clear day the amount of ultraviolet from the sky is comparable to that from the sun[7] and may be greater in the early morning and late afternoon hours, especially in the short wavelength region. This is due to preferential scattering of the short wavelength radiation by small particles in the atmosphere.[8] The spectral quality of skylight and its relation to sunlight varies with the season as well, being similarly determined by the solar elevation. The proportion of short/long wavelength ultraviolet in skylight is higher in the winter when the solar elevation is low and scattered radiation takes on more importance. The ratio of sky/sun radiation in the ultraviolet region is also higher in the winter when the absolute ultraviolet intensity of both sun and sky is lowest. Local conditions of light clouds and fog likewise decrease the direct solar radiation but increase the proportion of scattered radiation. Measurements have shown that the intensity of ultraviolet in skylight does not decrease as much as the visible radiation on a cloudy day.

Because skylight is different from sunlight and varies more with daily, seasonal, and local conditions, the spectral distribution of incident solar energy depends on the amount of skylight included and thus on the angle and plane at which measurements are obtained. A number of investigators have measured and compared daylight radiation of skylight with that of the direct rays of the sun in the ultraviolet and visible regions.[9–12] Experimental and theoretical studies on absorption and scattering of solar energy by the atmosphere have been made in order to predict the spectral, geographical, and seasonal distribution of the energy that reaches the earth's surface.[13–18] Based on measurements of solar radiation on planes of different orientations,[19,20] Heywood developed a method for calculating the probable intensity of total (sun plus sky) solar radiation on a surface inclined to the horizontal at any attitude or azimuth relative to the sun's meridian. This requires measurement of the total radiation received on a horizontal surface only. The optimum mounting angle for outdoor weathering of plastics to obtain maximum intensity at a given location has been discussed by Newland.[21]

Due to seasonal and local variations in the intensity of the actinic portion of sunlight, it is recognized that "time of exposure" is not a good basis on which to assess outdoor exposures of samples. Presently the intensity of sunlight is measured in many locations with a pyrheliometer and reported in either langleys (g.-cal./cm.^{2}) or "ultraviolet sun hours."[22] The latter measures the number of hours during which the intensity exceeds a value of

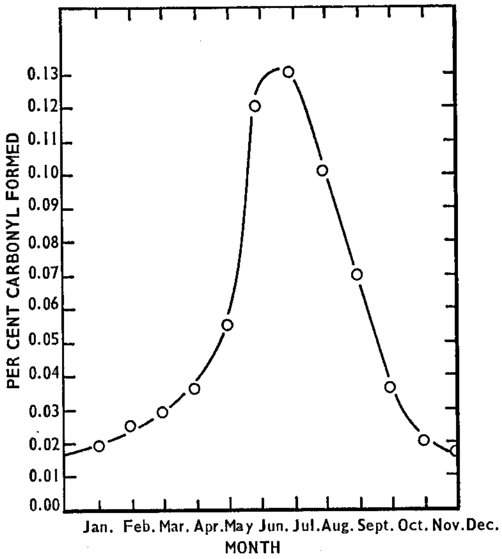

Fig. 4. Amount of carbonyl formed by solar irradiation of polyethylene with 15,000 langleys at different months of the year.

0.823 langleys/min. on the samples. Both of these methods measure total radiation rather than the actinic ultraviolet portion. Large changes in the latter portion, which constitute only a small fraction of the total radiation, may go unnoticed in such measurements.

In an attempt to monitor and integrate the actinic ultraviolet energy during outdoor exposure tests, a five-channel photometric monitoring unit was built.[23] This measured two regions in both the ultraviolet and visible portions of the sun's spectrum as well as the duration of rain and dew. A uranium fluorescent glass filter was used behind an ultraviolet transmitting cobalt filter to isolate the ultraviolet in the presence of red radiation. A spectroheliometer measuring the ultraviolet in five wavelength intervals was built[24] over ten years ago and used to obtain data in Miami, Florida and in Detroit, Michigan. The instrument continuously measured the amount and spectral distribution of direct solar radiation and integrated the energy in each channel by means of watt-hour meters. It has also been reported[13] that measurements are obtained in Washington, D. C. with a photocell and viscor filter combination responsive to energy in the region of maxium eye sensitivity.

A striking experimental verification of the inadequacy of evaluating exposure in langleys is given in Figure 4 and Table II. Every month from April 1960 to March 1961, films of the same batch of polyethylene were sent to Arizona for exposure to 15,000 langleys. The extent of degradation of each sample was based on the amount of carbonyl groups formed and the elongation retained. Even at constant level of total incident radiation, degradation proceeds faster in summer than in winter. In order to estimate the amount of incident actinic ultraviolet radiation as shown in the last column of the table, the data of Coblentz[25] were used. Although the ultraviolet data were for a different location and time, the estimated

TABLE II
Degradation of Polyethylene Exposed to 15,000 langleys in Arizona, 1960

Month	Carbonyl formed, %	Elongation retained, %	Est. UV exposure[a]
January	0.019	100	345
February	0.025	100	435
March	0.029	100	615
April	0.036	91	795
May	0.055	79	945
June	0.120	43	1020
July	0.130	19	1035
August	0.102	25	1020
September	0.070	43	975
October	0.036	88	690
November	0.020	100	435
December	0.017	96	285

[a] Total langleys in the region of 2900–3150 A., obtained by multiplying 15,000 langleys by the fraction of energy in this region, from Koller.[8]

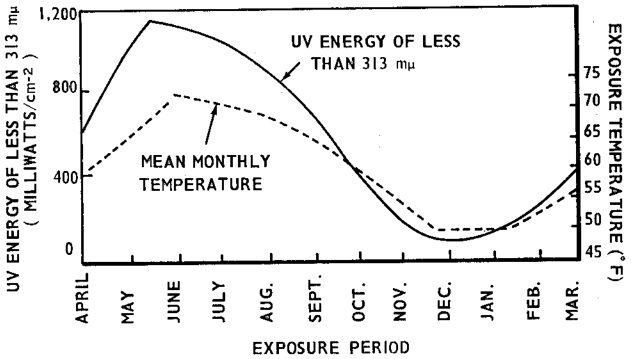

Fig. 5. Seasonal fluctuations of temperature and distribution of ultraviolet energy.

ultraviolet energy correlates much better than the total radiation with the degradation found. Data in the 2900–3150 A. region had been obtained because of the interest in the erythemal (sunburn) region of the ultraviolet. Coincidentally, this is also the region of sunlight which has the greatest effect on polyethylene. Singleton[6] similarly showed that the divergent data on strength loss of fibers for winter and summer exposures fall on a single curve when ultraviolet radiation rather than total radiation is used as the criterion of exposure.

Considering that temperature has a large influence on the photodegradation reaction of many polymers, it is of interest to note the temperature variation with season in Figure 5.[3] The temperature and ultraviolet radiation both increase and decrease with altitude of the sun. The increased degradation in the summer months is probably due to the higher temperature as well as to the increased ultraviolet intensity. For exposures of polyester in which the ultraviolet energy was monitored, the higher ambient temperatures of the summer season were obviously a significant factor in the degradation.

INDOOR ACCELERATED TEST SOURCES

The uncontrollable large variations and inadequate monitoring of outdoor exposure parameters pertaining to weathering effects are some of the factors that have caused investigators to turn to indoor accelerated testing units. Laboratory testing devices are much more amenable to standardization and control of variables. Two major purposes should be served by these indoor test sources: (*1*) the determination of relative photochemical stability and weather resistance of different materials, and (*2*) the prediction of the life expectancy of samples from relatively short-term exposure testing. It seems obvious that any meaningful correlation with the effects of outdoor exposure would require simulation of as many as possible of the outdoor parameters to which the material will be subjected. Yet, many of the testing devices employ light sources which give very poor simulation to the ultraviolet energy of sunlight.

Carbon Arcs

The carbon arc type instruments have served as the standard for laboratory weathering for many years. They were developed originally for the paint and dye industries and later were adopted by the plastics manufacturers. Although these devices may be adequate for simulating outdoor exposures on materials sensitive to the visible region, they fall short in their ability to simulate the ultraviolet portion of sunlight which is the actinic region for clear plastics. The ultraviolet spectral energy distribution of two types of carbon arcs[26] are compared with sunlight in Figure 6. Most of the ultraviolet energy is concentrated in the cyanogen bands. These impart intensity far in excess of that of sunlight in the region above 3500 A. At shorter wavelengths the intensity of the enclosed carbon arc is considerably less than that present in sunlight. The sunshine carbon arc has relatively weaker cyanogen bands because of the free flow of air around it. It also gives a closer approximation to sunlight at the short wavelength end of the spectrum. The spectral distribution of the radiation can be varied somewhat by the core type of the carbon rod. Generally the core contains salts of metals of the cerium group along with other metals. The short wavelength radiation is modified by Corex "D" filters in the sunshine arc and by Pyrex glass globes in the enclosed arc. The spectral distribution of the radiation is affected somewhat by changes in the transmission characteristics of the globes and filters with use.

The carbon arcs will rate as more stable those clear plastics which undergo reversal of degradation under long wavelength ultraviolet radiation. Better correlations with sunlight exposures of enamels have been obtained

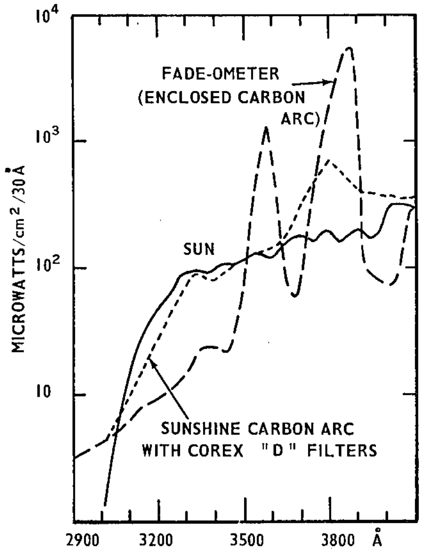

Fig. 6. Ultraviolet spectral distributions of the enclosed carbon arc Fade-Ometer, and sunshine carbon arc compared with sunlight.

using the sunshine arc rather than the enclosed arc.[27] Most of the indoor weathering devices are presently available with temperature and humidity controls and water spray. The latter can be used during the dark cycles to provide contact moisture in the manner that samples are usually wet out-of-doors.

Fluorescent Lamps

The fluorescent sunlamp has been used for accelerated testing of light fastness for many years in the manner recommended by the ASTM Committee D-20 on plastics.[28] A bank of five Type FS-20-T12 Westinghouse 20-w. fluorescent lamps are mounted 7 cm. above a turntable on which the samples are placed. The ultraviolet energy emitted by this lamp shows little resemblance to that of sunlight. The spectral distribution is shown in Figure 7. The peak intensity is at 3130 A. At this wavelength the intensities of the fluorescent sunlamp at the sample distance and of sunlight are approximately equal. In contrast to the carbon arc, the fluorescent sunlamp has considerably less intensity than sunlight in the long wavelength region and much more intensity below 3130 A. In addition, the emission extends to shorter wavelengths than in sunlight. Since the ultraviolet absorption of clear plastics increases gradually with decreasing wavelength, the degradation should increase as the short wavelength energy in the source increases. Thus, the fluorescent sunlamp should have a harsher effect on clear plastics than either sunlight or the carbon arc.

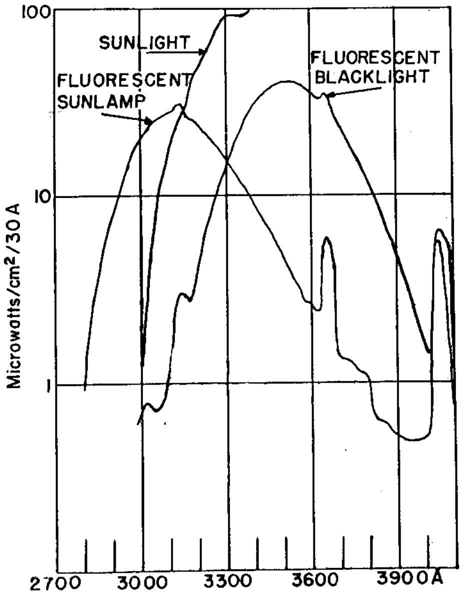

Fig. 7. Ultraviolet spectral distributions of the fluorescent sunlamp and fluorescent blacklight.

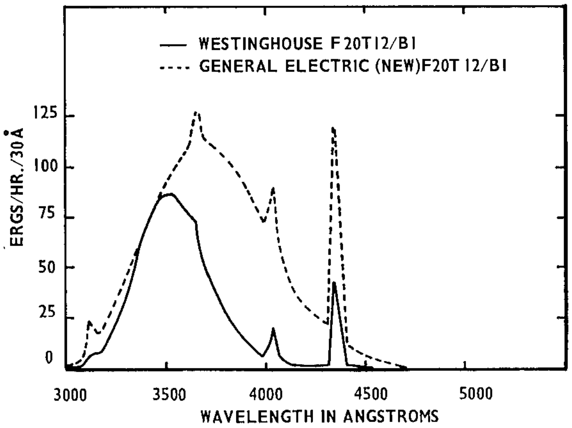

Fig. 8. Comparison of Westinghouse and General Electric fluorescent blacklamps.

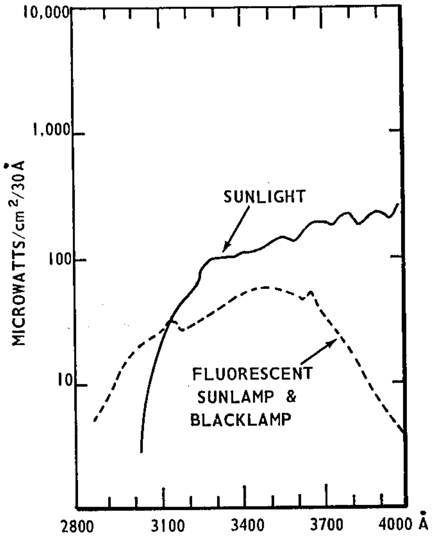

Fig. 9. Combination of Westinghouse fluorescent sunlamp and blacklamp compared with sunlight.

The use of the fluorescent blacklamp in conjunction with the fluorescent sunlamp was recommended by Hirt[29] in an attempt to improve the deficiency in the long wavelength ultraviolet region compared with sunlight. The spectral energy distribution of a 20-w. Westinghouse F20T12/Bl fluorescent blacklamp is also shown in Figure 7. The emission of this lamp peaks at 3520 A. and in combination with the sunlamp provides closer approximation to sunlight. The new type 20-w. General Electric F20T12/Bl fluorescent blacklamp has considerably different emission characteristics. As shown in Figure 8, the peak emission of the phosphor is shifted to 3650 A. coincident with the mercury emission line. In addition, the peak intensity and long wavelength energy are considerably increased. Figure 9 shows the emission curve of the combination of the two Westinghouse fluorescent lamps, the sunlamp and the blacklamp, compared with sunlight. Although the energy distribution is still different from that of sunlight, considerable improvement is achieved over the sunlamp alone. The new General Electric blacklamp would provide a better match to sunlight. Cipriani[30] has shown that the data on relative stabilities of polyester, polyolefins, rigid poly(vinyl chloride), and ABS polymer exposed to the fluorescent sunlamp/blacklamp (FS/Bl) source correlate well with sunlight data.

The exposure units incorporating the fluorescent lamps are generally laboratory modifications of one of the weathering units built for either the carbon or xenon arc light sources. An instrument is also available commercially.[31] This type of device is one of the most conveniently operated and least expensive indoor test sources. An equal number of fluorescent sunlamps and blacklamps are alternately mounted inside the circular rotating sample drum. The energy output can be maintained relatively constant by a program of staggered replacement of the tubes. The uniform illumination over the entire height of the sample rack is a major advantage over other types of weathering devices in which the radiation emanates from a small central area of the light source.

Fluorescent sunlamps have also been used in conjunction with the carbon arc. More than 20 years ago Tamblyn[32] reported on a modification of the twin-arc Weather-Ometer by the addition of eight Westinghouse 20-w. fluorescent sunlamps to increase the intensity at the short wavelength end in order to match the distribution of sunlight more closely. While the short wavelength intensity is raised over that of the carbon arcs alone, the total distribution falls short of a similarity to sunlight. Nevertheless, in the case of cellulose acetate butyrate, the correlation of accelerated weathering with natural weathering was claimed[32] to be better with the modified than with the unmodified Weather-Ometer.

Xenon Arcs

The quartz-jacketed high-pressure xenon arc is a relatively recent innovation in indoor weathering. Figure 10 shows several types of xenon arcs. The 6000-w. Osram arc requires water cooling. The cylinders shown alongside the arc are used for this purpose. The 1500-w. Quarzlampen arc is cooled by forced air. The cylinders used with the arc in the W.P.L. Xenotest instrument allow for additional water cooling of the air surrounding the samples. The water merely circulates between the two cylinders and does not come into contact with the arc. The cylinders used with both arcs also serve as filters to reduce the short wavelength emission of the arc in order to provide radiation simulating terrestrial sunlight. Figure 11 compares the filtered xenon emission with sunlight and shows the effect of several types of filters on the radiation of the 6000-w. Osram arc. The optimum simulation was obtained with Pyrex (Corning 7740) glass inner and outer cylinders of 1.94 and 2.39 mm. thickness, respectively.[5]

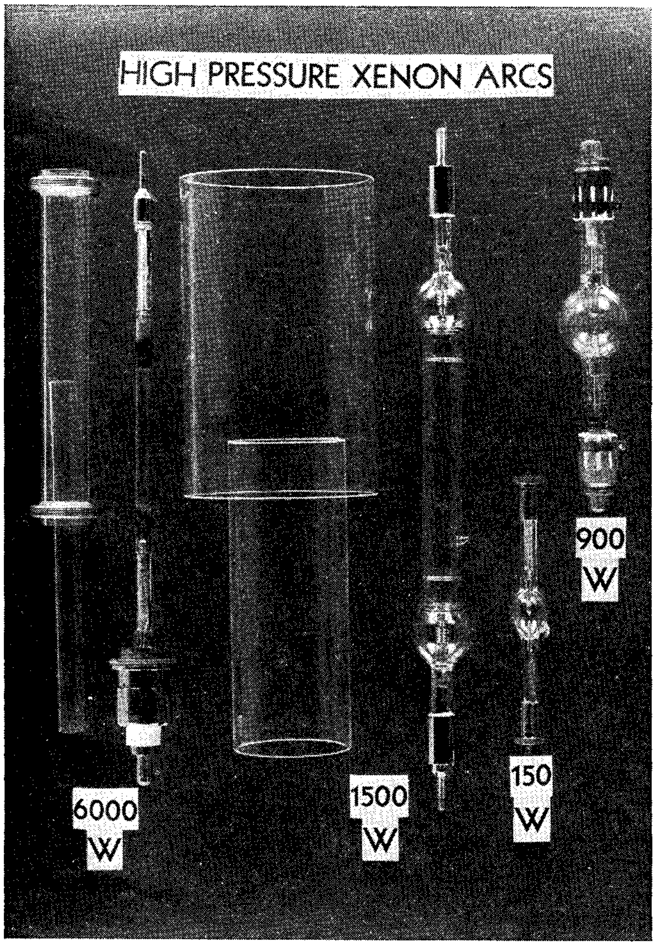

Fig. 10. High-pressure xenon arcs plus their filters; 150-w. Osram (XBO 150 w.) and 900-w. Hanovia (538C9) are air-cooled compact arcs, 1500-w. Quarzlampen and 6000-w. Osram (XBF 6000 w.) are water-cooled long arc types.

In addition to screening out the short wavelengths, these filters also reduce the strong xenon radiation in the near infrared region between 0.8 and 1.0 μ. The cylinders of the Quarzlampen arc have similar transmission characteristics.

The ultraviolet intensity of the 6000-w. arc at the sample distance (18 in.) in the Atlas Model 60 WR Weather-Ometer[26] is about 90% of the intensity of direct sunlight as measured on a clear day in June in Stamford, Connecticut. The intensity of the smaller instrument, which uses a 2500-w. Osram arc at 10 in. from the sample rack, is approximately the same.[33] The absolute intensity of the 1500-w. Quarzlampen arc at the sample distance of about 3 in. in the Xenotest weathering unit is 25% greater than noon summer sunlight. However, the samples are generally not continually exposed to the radiation. When the instrument is operated either on a

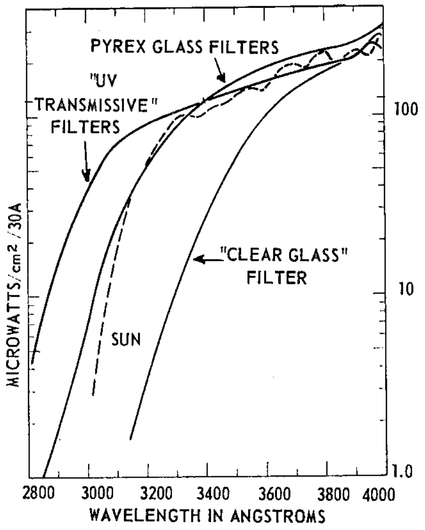

Fig. 11. Spectral energy distribution of 6000-w. Osram xenon arc through various types of filters compared with sunlight at the earth's surface.

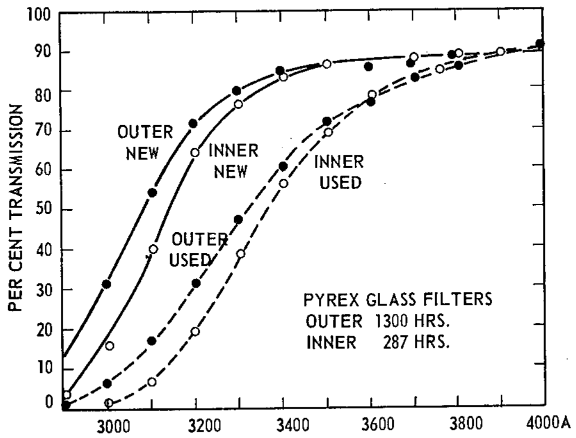

Fig. 12. Transmission curves of new and used inner and outer Pyrex glass cylinders of 6000-w. Osram xenon arc.

light–dark cycle or with the water spray in use, the sample carrier is periodically turned 180° on its own axis. Therefore, the total energy received by the samples will be somewhat less than in the Atlas unit for an equal period of weathering. The intensity of a larger, 4500-w. unit is reported by the manufacturer to be equal to that of the smaller unit. An inner quartz cylinder and outer "special" UV glass cylinder with seven sections of an infrared filter in between, all cooled by a strong current of air, constitute the filter system of the larger instrument.[34] The new 1500-w. model (Xenotest 150) also uses these filters instead of the older system. Since the infrared filters screen out more of the short wavelength ultraviolet energy than is required for adequate simulation of sunlight, one of the seven filters is replaced by an ultraviolet transmitting filter except for simulation of sunlight behind window glass. In view of the diverse effects of different regions of the ultraviolet on plastics, it is questionable whether a small amount of the very short wavelength energy transmitted by the ultraviolet filter can compensate for loss of a greater intensity of longer wavelength ultraviolet energy.

Loss in intensity and change in spectral characteristics with use results mainly from solarization of the filters and metallic deposits on the arc. Both of these factors are more severe in the Osram arcs than in the Quarzlampen arcs. "Solarization" is the term used for the decrease in transmission of the filters on exposure to ultraviolet radiation. The filters of the Osram arc solarize more rapidly because of their greater proximity to the arc. In fact, the inner filter solarizes considerably faster than the outer filter. Figure 12 shows the transmission curves of the filters before and after use with the 6000-w. arc. Although Pyrex glass is relatively more stable than other types of filters, the transmission characteristics change rapidly during the first 20 hr. use of the inner cylinder and the first 100 hr. use of the outer cylinder. Fortunately, subsequent irradiation has a less drastic effect. In order to maintain nearly constant spectral distribution conditions, it is recommended that the filters as well as the arcs be pre-aged and used only for a specified length of time. The period of use suggested is 20–250 hr. for the inner cylinder and 100–1000 hr. for the outer cylinder and the arc (ASTM Designation: D2565–66T).

The circulating water in contact with the outside of the Osram arc causes formation of metallic deposits under the influence of ultraviolet radiation unless extreme precautions are taken to maintain a metal-free circulating system. Metallic deposits form on the inside of both arcs due to sputtering of the tungsten electrodes. In the Quarzlampen arc the deposit is caught in the expanded sections of the arc below and above the central portion to which the samples are exposed. Thus, it has relatively little effect on the main portion of the arc.

Mercury Arcs

The General Electric S-1 400-w. mercury vapor lamp has been used for many years as an accelerated test source for plastics with or without apparatus for allowing periodic exposure of the samples to fog.[35] The lamp is mounted above a turntable at a distance of 18 cm. between the bottom of the lamp and the top of the samples. The spectral curve of the S-1 sunlamp is compared in Figure 13 with sunlight. Most of the energy is concentrated in the mercury emission lines. The background is very weak as it is in all low-pressure mercury vapor sources. The very short wavelength mercury emission is filtered out by the glass used for the bulb. There is probably as much short wavelength energy below 3200 A. as in the fluores-

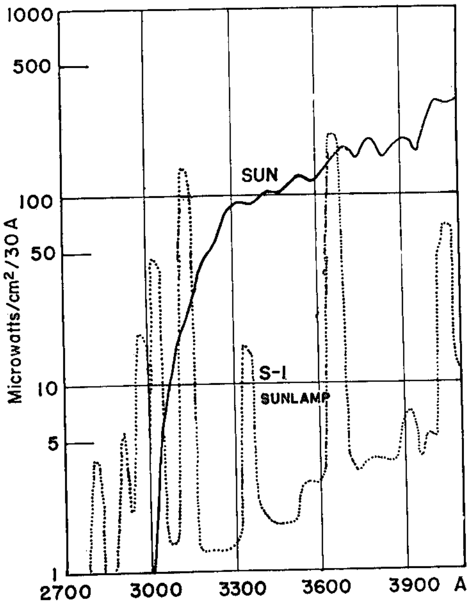

Fig. 13. Spectral energy distribution of S-1 sunlamp compared with sunlight.

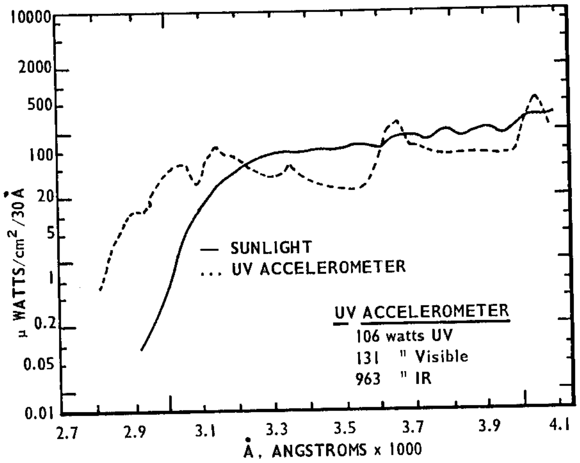

Fig. 14. Spectral energy distribution of UV accelerometer compared with sunlight.

cent sunlamp. In the longer wavelength region the background is weaker and the mercury emission lines stronger than in the fluorescent sunlamp.

The high-pressure mercury arc is another ultraviolet radiation source used in some laboratories for determining relative photochemical stability of materials. The UViarc described by McCarthy[36] incorporates a Hanovia #74A-10 700-w. mercury vapor lamp with a Corning No. 9700 Corex D glass filter to reduce the emission intensity in the short wavelength region. Other designations have been given to the UViarc and it is often used without a filter. A recently available commercial instrument called the UV accelerometer[31] incorporates a General Electric Type UA-11B quartz high-pressure 1200-w. mercury arc and a Corex filter as an outer jacket. Figure 14 shows the spectral distribution compared with sunlight.[37] The increased pressure causes a large increase in the background continuum but has relatively little effect on the mercury emission lines. However, the intensity at 3000 A. is 100-fold greater than in sunlight and the short wavelength emission extends considerably beyond that of sunlight. The large acceleration in degradation, relative to sunlight exposures of plastics, is due to the additional high-energy short wavelength radiation not present in sunlight. This will often result in a different type of degradation mechanism. Good rank correlation has been claimed between this instrument and sunlight in New Jersey and Florida for vinyl type polymers and copolymers.[38] However, further testing is required on materials which are more photochemically stable so that differences among them can be more readily evaluated.

Comparative Intensities of Sources

Table III compares the ultraviolet intensities of some of the more commonly used sources. The absolute intensities were determined by means of the ferrioxalate actinometer[39] at the normal sample distance for each source. The integrated intensities of total and short wavelength ultraviolet were obtained from the spectral distribution measurements.[29] Although the total ultraviolet intensity of the enclosed carbon arc source is at least four times as great as the other sources, its short wavelength intensity is relatively negligible compared to the long wavelength emission. The ratios, shown in the last column, are probably more significant than the intensities, particularly for materials in which the long wavelength radiation reverses

TABLE III
Absolute Ultraviolet Intensities of Weathering Sources at Sample Distance

Source	Total UV, μw./cm.^{2}	UV below 3500 A., μw./cm.^{2}	Ratio $\frac{\text{3500 A.}}{\text{total UV}}$
Sunlight, June 1957, noon, Stamford, Conn.	4243	1177	0.278
Sunlight, Dec. 1957, noon, Stamford, Conn.	1389	257	0.185
Xenon (Xenotest 1500W)	5474	1340	0.245
Xenon (Atlas Weather-Ometer 6000W)	3735	960	0.258
Carbon arc (Fade-Ometer)	19,531	309	0.016
Sunshine carbon arc	8486	1386	0.163
Fluorescent sunlamp/blacklamp (3.5-in.)	1543	908	0.588
S-1 Sunlamp (8.5-in.)	666	328	0.492

the effects produced by the shorter wavelengths. The enclosed carbon arc source shows the largest divergence from sunlight. The sunshine carbon arc source is considerably better, having nearly the same ratio as December sunlight. The S-1 sunlamp and combination of fluorescent lamps have a high proportion of short-wavelength energy. The xenon arcs show the closest similarity to summer sunlight.

ACCELERATED SUNSHINE

Except for the xenon arcs, laboratory light sources have different ultraviolet radiation characteristics than sunlight. Many of the indoor test sources accelerate exposure testing by virtue of their high-intensity short-wavelength radiation. Because results of such tests frequently fail to correlate with long term outdoor exposures, Caryl and Helmick[40] developed a method to accelerate exposures under natural sunlight. Ten highly polished Alzak-treated aluminum mirrors are used to intensify the energy of sunlight on the test materials in a device known as the EMMA (Equatorial Mount with Mirrors for Acceleration). Forced air cooling minimizes overheating of the samples although the sample temperature is somewhat higher than under normal exposure conditions. An equatorial mount keeps samples perpendicular to the sun's rays all day so that even without additional mirrors the amount of total radiation received exceeds that on exposure racks facing south at a 45° angle. It is estimated that with ten mirrors, the samples receive about 8 times as much radiation as on an equatorial mount without mirrors and about 10 times as much as on exposure at 45°S. The amount of radiation received on a clear day is estimated to be greater than for a 24-hr. exposure in the carbon arc weathering devices.[41]

Although the sunlight intensity is increased by a factor of ten, acceleration of degradation ranges from twofold to elevenfold[42] depending on the polymer and formulation under test. The dependence of acceleration on type of material exposed thus limits extrapolation of the data to 45°S. It appears, therefore, that acceleration effected through increased intensity alone may fail to give good correlation with natural exposures. Secondary processes promoted by temperature, oxygen, and moisture play a major role in polymer degradation and vary with polymer formulation. For this reason, acceleration of only the primary process by increase in intensity can distort the results even if the spectral distribution is maintained constant.

COMPARATIVE WEATHERING UNDER DIFFERENT LIGHT SOURCES

The majority of comparative studies made under different weathering conditions are concerned with modifications of a particular polymer, usually by the use of additives. Although many factors contribute to weathering, frequently the discrepancies among weathering tests can be related solely to the varying emissions of the different light sources. The diverse effects

TABLE IV
Increase in Absorbance of Polyester Films at 4300 A.

Protective absorber	Carbon arc Weather-Ometer, 1000-hr.	Xenotest, 900 hr.	FS/Bl, 922 hr.
Unprotected polyester	0.06	0.35	0.22
1-Hydroxy-4-methoxybenzophenone	0.05	0.27	0.08
2,2′-Dihydroxy-4-methoxybenzophenone	0.02	0.19	0.12
Precision = 0.01			

of different wavelength regions on certain materials are a major cause of the discrepancies under different light sources.

Table IV[1] compares an unprotected polyester with two samples containing different ultraviolet absorbers exposed to three different light sources; the carbon arc Weather-Ometer; the Xenotest, and the FS/Bl unit. The polyester films were exposed to the three light sources for approximately the same length of time. The xenon source, having the highest intensity of energy below 3500 A., yellows the protected and unprotected samples at the fastest rate. It is of interest to note that the dihydroxybenzophenone offers better protection than the monohydroxy compound against the xenon and carbon arc sources but is not as efficient against the fluorescent lamps. Experiments have shown that the photochemical stability of these additives in polyester is not a factor affecting the relative stability of the materials under the different light sources. Rather, the explanation lies in the interrelationship between the screening ability of the additive and the emission of the light source. In polyester the longest wavelength absorption band of the dihydroxy compound is at 3420 A. while that of the monohydroxy compound is at 3280 A. The latter is closer to the emission peak of the fluorescent sunlamp. The minimum, or "window," in the absorption of the dihydroxy compound occurs in the region where the fluorescent sunlamp has its strongest emission. The dihydroxy compound thus has poorer screening ability for this source. In contrast, the carbon arc and xenon sources have the major portion of their ultraviolet intensity in the region most strongly absorbed by the dihydroxy compound. In a separate study,[30] when polyester with and without light stabilizers was exposed to the FS/Bl and carbon arc sources, it was found that the former gave results which were in better agreement with natural weathering in Florida and Arizona.

The discrepancies among weathering tests can frequently be due to the varying ratios of short/long wavelength ultraviolet emission of the different light sources. This becomes an important consideration for materials, such as polyester, which are subject to diverse effects by different wavelength regions. The film thickness of such materials is also a factor in determining the relative effect of the light sources. For example, studies under different light sources have shown that the FS/Bl exposure unit has a greater yellowing effect than the xenon source on thick castings of polyester whereas the reverse situation was found for thin films of polyester.[1] Because of the logarithmic nature of the absorption process, increasing the thickness of the sample will have a far greater influence on the weak absorption in the long wavelength region than it will on the strong absorption in the short wavelength region. In the case of the thick samples, the yellowing can be more readily offset by the bleaching under the long wavelength radiation in the xenon source. In the case of the thin films, bleaching under either source is negligible and the shorter wavelength emission of the FS/Bl becomes the determining factor.

Several comparative studies under different light sources have been reported for polyolefins. The FS/Bl was shown[30] to be superior to the sunshine carbon arc and the enclosed carbon arc in predicting the relative stabilities to sunlight of polypropylene containing various protective ultraviolet absorbers. [Melchore[3] has pointed out that the resistance of unstabilized polypropylene is so poor that differences among weathering units cannot be detected.] It should be noted that the temperature differences of the weathering units could contribute significantly to the results. The samples were exposed outdoors during the fall and winter months when the temperature ranged between 5° and 33°C. The FS/Bl unit operated at 30°C. while the carbon arc source gave a black panel temperature of 55°C. Cipriani[30] showed that the FS/Bl accurately predicts ultimate outdoor aging of polyethylene. In other studies on polyethylene, Tatevos'yan[43] showed that the enclosed carbon arc lamps are superior to quartz mercury vapor lamps for predicting outdoor aging. His conclusions were based on the similarities in the types of photochemical degradation produced.

Plasticized PVC generally shows such poor resistivity to ultraviolet light that because of the rapid discoloration, valid conclusions cannot be drawn among different light sources. Darby and Graham[44] reported that there was no correlation in results when plasticized PVC was exposed to natural weathering, the Fade-Ometer, and the Weather-Ometer. However, Tatevos'yan[43] has shown that carbon arc sources and sunlight promote the same type of photodegradation, i.e., chain scission, whereas the quartz mercury vapor lamp causes crosslinking predominantly. Cipriani[30] pointed out that while the FS/Bl does not provide useful data for plasticized PVC, it is very effective in predicting outdoor aging of rigid PVC. Unprotected rigid PVC was compared with protected PVC containing four ultraviolet absorbers at two different concentration levels. The carbon arc source gave completely erroneous results by imparting the highest stability rating to the control (unprotected PVC) in contrast to natural weathering results.

Applications of polystyrene are mainly in connection with indoor lighting fixtures containing cool white or warm white fluorescent lamps. Therefore, accelerated exposure tests should predict aging under these light sources. Estes et al.[4] suggested that the Fade-Ometer would be better than the fluorescent sunlamp, the high-pressure mercury arc, or natural sunlight for this purpose since it has minimal radiation in the short-wavelength ultraviolet region in which the fluorescent cool white lamp is deficient. However, McCarthy[36] showed that the UViarc (high pressure mercury arc) with a Corex D filter cutting off radiation below 3000 A. causes discoloration in polystyrene which most closely duplicates that caused by cool white fluorescent lamps. The relationship between unstabilized and stabilized polystyrene was determined with the Fade-Ometer, S-1 Sunlamp, sunlight, and UViarc with Corex filter.

One of the few studies, other than on paints and colored materials,[45,46] comparing various materials under several light sources was carried out by Singleton et al.[6] on fibers of polyester, nylon, cellulose triacetate, acrylic, and many other types. Evaluations were made of 17 yarns in the sunshine carbon arc Weather-Ometer with Corex D filter, the 2500-w. xenon Fade-Ometer with clear glass filter operated on a light-dark cycle and outdoors in Arizona. Samples were exposed until they showed a predetermined strength loss. The hours of exposure in the accelerated unit were then plotted against the radiation received outdoors to give this strength loss. Only when the sun's radiation was based on incident ultraviolet rather than on total langleys did the accelerated tests correlate with outdoor exposure, i.e., put the yarns in the same order of resistance to weathering.

CONCLUSIONS

Accurate knowledge of the ultimate outdoor exposure conditions of any material is an impractical expectation. Weathering factors such as heat, moisture, and humidity as well as the amount and quality of ultraviolet radiation vary with location, time of day and year, and even orientation of material. In order to realize optimum results from indoor test sources, it is best to simulate certain average weather conditions. A necessary requirement in attempting to duplicate natural weathering is complete simulation of the radiation characteristics of sunlight in all critical actinic regions. For clear plastics, this is generally the entire ultraviolet region of sunlight, i.e., 3000–4000 A. It is known that one actinic region will promote chain scission or depolymerization while another will promote crosslinking. It has been shown that radiation effects by one energy region can be reversed by another region in some materials. Xenon arc emission bears the closest relationship to the solar spectrum in the ultraviolet region.

It must be assumed that any attempt at acceleration may produce different effects than the natural course of weathering. Because of the complex nature of the weathering process, and its variation with type of material, acceleration of one factor alone can distort the results. Even acceleration on the basis of time only, eliminating the light–dark cycle, may interfere with an accurate correlation with natural conditions. However, by extensive studies of the effects of various parameters and their interaction, it should be possible to vary these in a manner such that meaningful interpretations can be made on accelerated exposure tests.[33] Better correlations can be obtained between indoor and outdoor exposures by monitoring the actinic energy under both conditions.[47]

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Résumé

La connaissance et la simulation des conditions de vieillissement sont une condition nécessaire pour reproduire et accélérer l'exposition à l'extérieur au moyen de tests *in vitro*. Les caractéristiques d'émission du soleil et de radiation des nuages et des différents types d'appareils de laboratoire ont été revues. Les effets actiniques variables des sources de tests accélérés peuvent être reliés à leurs émissions spécifiques caractéristiques au moyen d'une information des spectres d'activation des plastiques. Un arc d'émission de Xénon fournit la similitude la plus proche de l'énergie solaire dans la région ultraviolette. Toutefois, l'accélération d'un seul facteur de vieillissement peut déformer les résultats.

Zusammenfassung

Kenntnis und Simulierung der mittleren Wetterbedingungen sind ein notwendiges Erfordernis für die Reproduzierung und Beschleunigung der Aussen-Exponierung durch Laboratoriumtests. Ein Überblick über die Emissionscharakteristik der Sonnen-und Himmelsstrahlung sowie von verschiedenen Labortiumsvorrichtungen wurde gegeben. Die variierenden aktinischen Effekte der Lichtquellen beim beschleunigten Test können durch eine Information über die Aktivierungsspektren der Kunststoffe zu ihrer spezifischen Emissionscharakteristik in Beziehung gebracht werden. Die Emission eines Xenonbogens hat im Ultraviolettbereich die grösste Ähnlichkeit mit der Sonnenenergie. Die Beschleunigung eines einzigen Bewitterungsfaktors kann aber die Ergebnisse verfälschen.

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Survey of Techniques for Evaluating Effects of Weathering on Plastics

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Synopsis

This paper surveys those physical and chemical test methods that could be applied in the prediction of the performance of plastics under outdoor exposure. Techniques to measure appearance, strength, and flexibility are reviewed. Color changes alone, although widely used, are shown to be an insufficient measure of weathering. The more sensitive spectroscopic and chemical test methods that have been found to measure oxidation and hydrolysis products in polymeric materials are examined for usefulness in quantitatively measuring plastic degradation. The methods reviewed are used to determine carbonyl, carboxyl, peroxidic, and hydroxyl groups.

INTRODUCTION

One of the goals of experimental techniques for measuring the effects of weathering is to predict performance. This objective will eventually be attained once the critical properties can be quantitatively measured and the rate curves for these properties established. This goal, which has not been achieved to any great extent, must be borne in mind in any consideration of the measurement and prediction of weathering effects.

A brief review is presented of some of the methods now being used to measure changes in the chemical and physical properties of plastics, and other closely related materials such as paints and asphalt. The references chosen reflect the interests of the authors.

The first section is devoted to the discussion of appearance and mechanical property measurements now used to evaluate the weatherability of plastics. These are discussed as to their use in providing a coherent picture of weatherability.

The second section is devoted to a discussion of methods to assess chemical changes in plastics. The methods herein cited are specifically selected for their use as tools to measure quantitatively the chemical changes produced in weathered plastics.

Finally, it is shown that some recent investigations have correlated these chemical changes with the changes in appearance and physical properties.

EVALUATION OF APPEARANCE AND MECHANICAL PROPERTIES

The two characteristics that determine the ultimate usefulness of a plastic are its retention of appearance and its retention of mechanical properties. Therefore, measurements of these properties are used to assess the effects of weather and exposure. Several techniques used to measure appearance and mechanical properties will be reviewed.

Many tests have been devised to measure changes in reflected color, transmitted color, and surface features such as gloss and microscopic topography. These measurements of appearance can be made with great precision and thus are commonly used to evaluate the changes caused by exposure of plastics. The main problem, however, is that although these measurements can give an accurate monitoring of short-term aging effects, it is not usually possible to extrapolate these results for the prediction of long-term service life.

Smith and Lowry[1] made extensive use of three appearance factors in their evaluation of several formulations of polyesters. Color and gloss measurements along with photomicrographs were used to follow the weathering of glass-reinforced polyester panels. Loss of gloss and change of color were found to occur along with the stress-cracking as observed by microscopy. However, many studies have shown that color changes of plastics are not always directly related to weathering or exposure; very few studies of gloss changes have been made.

During studies of the solarization of polyester resins, Hirt and others[2] discovered that the yellowing produced during exposure was subject to

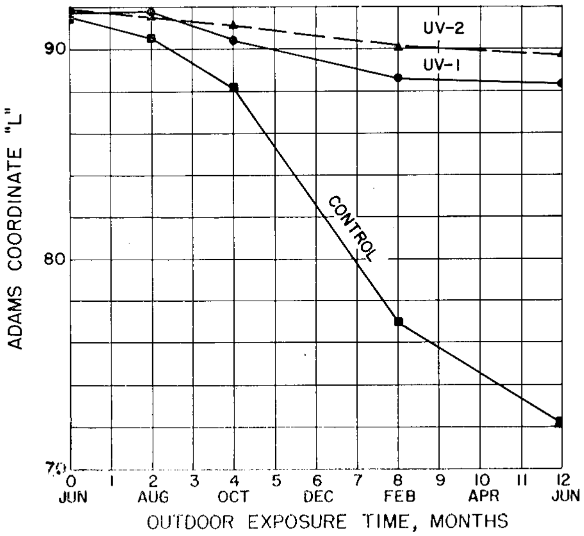

Fig. 1. Color changes produced by outdoor exposure of rigid PVC, without and with ultraviolet absorbing materials, UV-1 and UV-2.

fading. Controlled atmosphere tests, using in one case pure oxygen and in the other pure nitrogen, proved that oxidation during exposure was responsible for the fading in color.[3] This was also shown in the studies by Havens[4] and by Scarbrough and others,[5] who found that color changes produced in poly(vinyl chloride) (PVC) during photodecomposition were greater in nitrogen atmosphere than in oxygen. Later, the outdoor weathering studies of PVC by Gray and Wright[6] showed that the rate of color formation is greater in winter than in summer (Fig. 1), but that the proportions of oxidation products formed are greatest in the summer months (Fig. 2). Frey[7] demonstrated a relationship between the color changes occurring during the natural and artificial weathering of PVC, but found no direct relationship between color and impact strength.

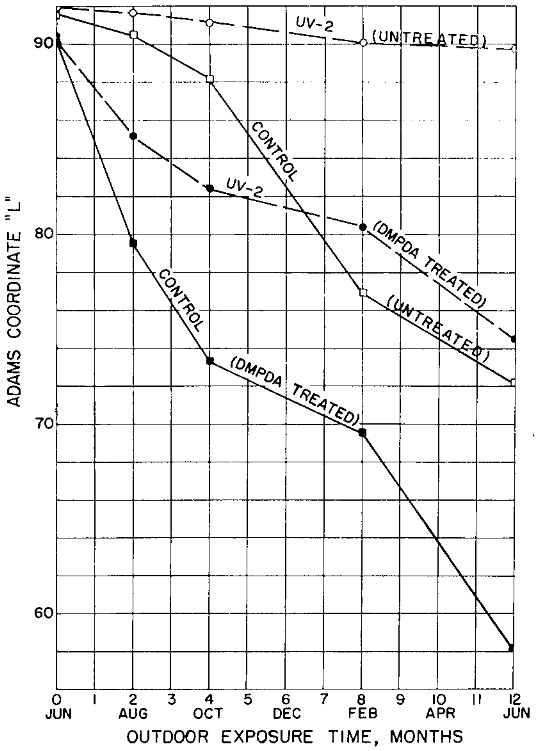

Fig. 2. Color changes of rigid PVC produced by outdoor exposure and by chemical treatment to detect oxidation products.

Color changes of many other organic materials have been shown to be unrelated to their exposure to ultraviolet radiation. In the studies of Launer and Wilson,[8] the "yellowing" reaction of paper was found to be caused by heat, whereas, ultraviolet radiation caused bleaching. Recently, Wengert[9] found that ultraviolet exposure produced a similar bleaching effect on wood in the presence of oxygen.

The surfaces of rubber, paints, and plastics crack and develop flaws during aging or weathering. Microscopy was used by Lindquist and others[10] to observe the different defects of surface coatings. No quantitative method was developed for assessing the extent of these microscopic defects. Harding and McNulty[11] found that embrittlement of nylon specimens is due to a thin film of surface material. Removal of this surface restored the physical properties to approximately the original values. Smith and Lowry[1] showed the importance of formulation in preventing surface cracking of polyesters. Photomicrographs of surface cracking were made, but no quantitative assessment of stress-cracking was reported.

To accelerate stress-cracking during weathering, Tamblyn et al.[12] exposed stressed, U-shaped specimens to outdoor and laboratory exposure. They reported that the technique is acceptable for estimating minimum and maximum life of stressed polyolefins.[13]

Gouza and Bartoe[14] reported a technique that permits a more realistic measurement of the stressing of plastic specimens. They subjected specimens to a constant load during exposure, and measured creep and time to develop stress-crazing under various loads. Time to failure was found to be directly related to stress. This type of test appears to be most adaptable to all sheet plastics—reinforced and unreinforced alike. Weathering tests using this technique could provide data to predict stress limits.

Recently, high-speed tensile tests (8000 in./min.) were found to show effects of shelf-aging on the elastic response of nylon; however, no effects were shown by ordinary tensile-strength measurements.[15] It remains to be seen whether this tool can be applied to the measurement of changes produced by weathering, and whether such changes can then be validly extrapolated to predict weatherability.

Two interesting techniques have recently been applied to measurement of changes of film properties during exposure. Gutfreund[16] reported on creep measurements of unsupported paint-films during ozone exposure. An ozone atmosphere was used to accelerate the changes in the physical properties of paint films. Good agreement was reported between results from this technique and the outdoor performance of the paints tested. This is similar to the use of ozone in cracktesting of rubber compounds. A simple stiffness test developed by Newton and Wake[17] was recently used by Warner and Gruber[18] to evaluate physical property changes caused by light aging.

EVALUATION OF CHEMICAL CHANGES

General Discussion

The measurement of the chemical changes occurring in plastics during exposure to weather has been a neglected area until recently. Many elegant techniques have been used for the characterization of "pure" polymers, but most have not been adapted to studies of plastic degradation. Most degradation products have certain functional groups in common, and therefore quantitative analysis of these groups is possible by measurement of their common spectral absorptions and chemical reactions.

This discussion will be concerned with those methods that have been applied or show promise of being applicable to many classes of plastics. They are presented in two subsections: (*1*) spectroscopic methods, and (*2*) chemical methods. These methods measure specific chemical structures formed or destroyed during weathering of plastics.

Spectroscopic Methods

Luongo published two papers in 1960 on the analysis of chemical groups formed during the oxidation of polyethylene and polypropylene.[19,20] The kinetics of polyethylene oxidation were studied by Baum[21] and Beachell and Tarbet.[22] They used infrared absorption techniques to measure rate of hydroperoxide and carbonyl formation. Other examples that may be cited of the use of infrared absorption were studies of the thermal oxidation of formaldehyde resins and polybenzyl.[23,24]

Campbell and Wright[25] adapted the infrared absorption method for rate studies of the weathering of asphalt thin films. This work provided the best analysis of the many factors important in the weathering of asphalt films. The effects of temperature and humidity,[26] ozone,[27] nitrogen dioxide,[28] and irradiation sources[29] have been evaluated by infrared absorption techniques.

The materials studied by the above-mentioned workers were of predominantly hydrocarbon composition. Thus, there were usually few interfering infrared absorption bands to confuse the degradation studies. Plastics or polymers containing large proportions of oxygenated compounds, and therefore, interfering infrared absorption bands, have not been studied so successfully. Achhammer et al.[30] found that infrared absorption techniques were too insensitive to measure photodegradation of polyamides. Another study[31] recently showed that very little qualitative and quantitative information was gained from infrared absorption studies of weathered polyurethane.

There has been some interest in the use of infrared reflectance techniques for measuring chemical structure. In 1960, Dannenberg[32] published a paper on the use of a reflectance accessory to analyze thin films of clear coatings on specularly reflective metals. This was proposed as a method to study surface coatings for metals.

The introduction of "attenuated total reflectance" optical devices has brought the measurement of chemical structure of surfaces nearer to practicality. The photodegradation of organic coatings by exposure to mercury and xenon lamps has been studied by this means.[33] The significant results are that the protective effects of pigments vary with radiation source and that mercury lamps cause much greater surface degradation.

Both infrared reflectance techniques suffer from the great loss of energy caused by variations in the reflecting surfaces. Therefore, neither of these methods shows promise for quantitative evaluation of commercial materials.

One method has appeared that offers hope for infrared techniques to study surface degradation of many complex materials. Johnson[34] developed a technique for abrading paint and plastic surfaces and determining the chemical composition of the removed material by infrared analysis. By use of this technique, he showed that the surfaces have a different chemical composition from the bulk material. Thus, for a paint film containing silicone oil as a surface-active agent, the silicone oil collected at the surface; for a polyethylene film, a slip-agent was detected on the surface. The limitations of this method are those that apply to all infrared techniques, such as interference caused by pigment masking of the spectrum. Effects such as leaching of additives could be studied by this method, as well as changes caused by weathering.

The use of ultraviolet spectroscopy to follow chemical changes caused by exposure dates back as far as the work of Coblentz and Stair.[35] They evaluated the effect of strong ultraviolet radiation on the transmission of cellulose, cellulose acetate, and cellulose butyrate.

The main use of ultraviolet spectroscopy has been with plastics to which infrared studies are not applicable or for which ultraviolet studies may be much more sensitive to the chemical changes. Exposure studies[36] of polystyrene (using an S-1 sunlamp) showed that ultraviolet spectra were much more sensitive to chemical changes than were infrared absorption spectra. Also, ultraviolet absorption of nylon was shown to increase during accelerated weathering, although infrared spectra were unchanged.[30] The photodegradation of vinylidene chloride–vinyl chloride copolymer was also found to produce ultraviolet-absorbing products.[37] The measurement of the ultraviolet spectrum provided a more sensitive means for evaluating early changes during these studies than did the infrared spectrum. Similar conclusions were drawn from a study of the weathering of an elastomeric polyurethane using both ultraviolet and infrared spectra.[31]

Overall, the use of ultraviolet spectroscopy appears to be confined to pure polymeric systems or the study of separate components (i.e., the change of ultraviolet absorber concentration with time). The presence of ultraviolet absorbers, pigments, heat stabilizers, and other additives in commercial plastic formulations makes the ultraviolet absorption data far less useful.

CHEMICAL METHODS

Carboxyl Tests

Palit and Ghosh[38] developed a very sensitive dye–polymer interaction test for measurement of carboxyl groups in polymers. Their interest was the analysis of polymer endgroups. They discovered that the absorbance of certain acid-indicating dyes was directly proportional to carboxyl group concentration and that many types of endgroups can be converted into carboxyl groups and analyzed. Campbell and Wright[39] have adapted this chemical technique to measure carboxyl groups formed in photodegraded asphalt.

This technique shows great possibilities for the measurement of degradation during early stages of weathering for most plastics—many of which can form carboxyl groups during oxidation or hydrolysis. The dye reacts with sulfonic acid groups and is also absorbed into many plastics; therefore, this method may have to be adapted to each polymer system.

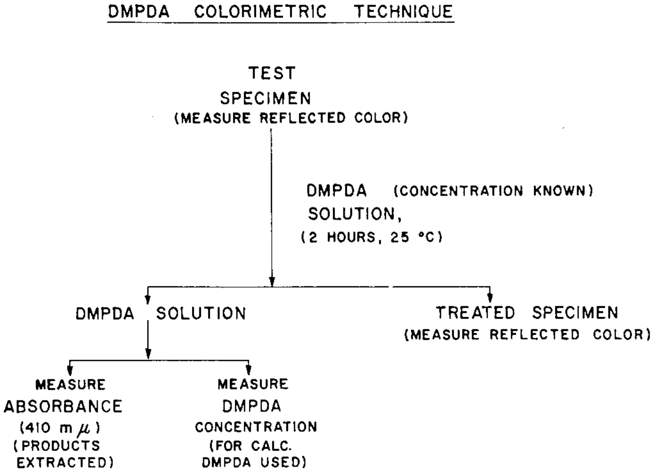

Fig. 3. Diagram of colorimetric technique used to measure carbonyl degradation products.

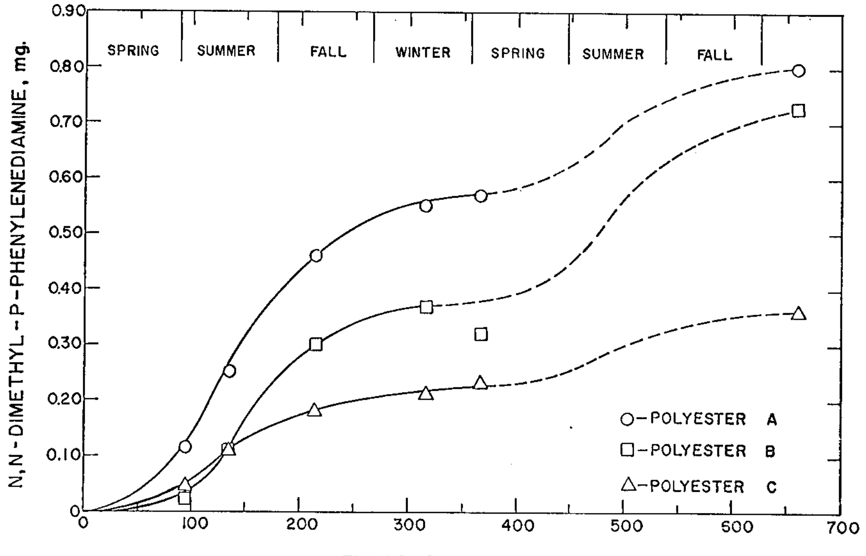

Fig. 4. Comparison of degradation rates for three polyesters as measured by *N,N*-dimethyl-*p*-phenylenediamine (DMPDA) technique.

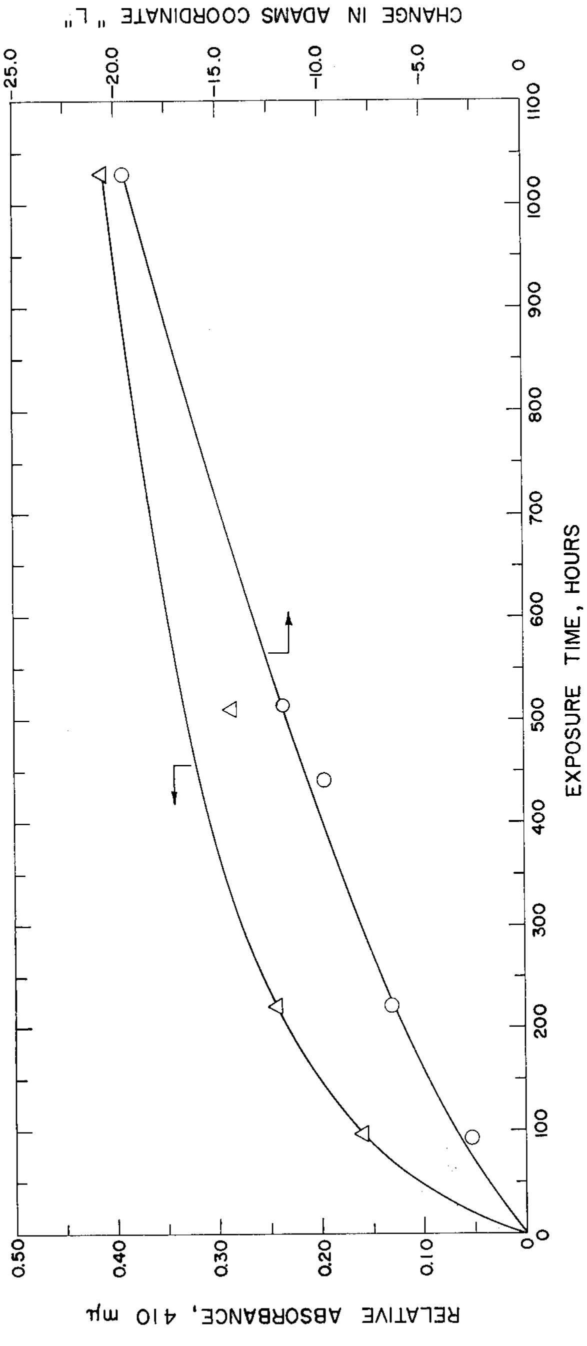

Fig. 5. Color of PVC photodegradation products treated with DMPDA colorimetric reagent.

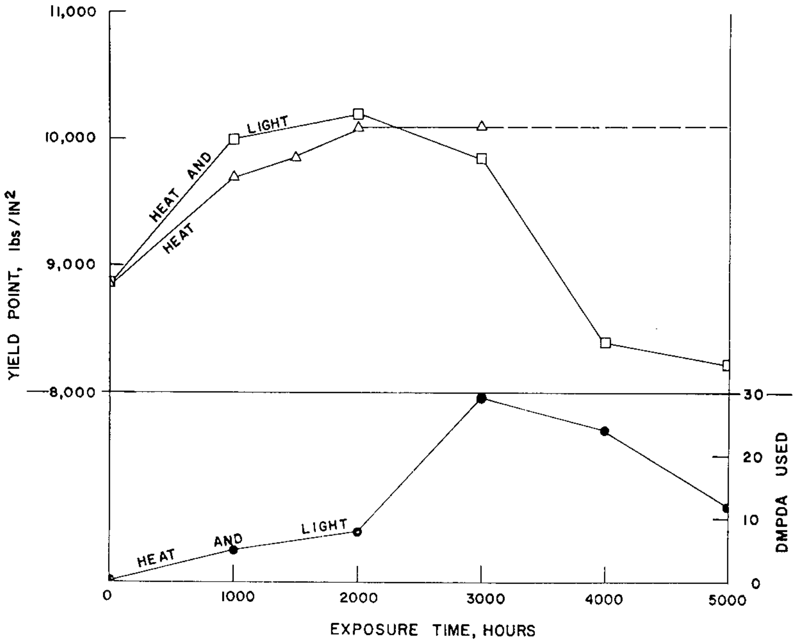

Fig. 6. Changes of tensile strength and proportions of oxidation products during exposure to heat and both heat and light.

Another chemical method for determining carboxyl groups was first reported by Heacock.[40] His technique involves the reaction of sulfur tetrafluoride with the carboxyl groups in oxidized polyethylene and polypropylene. The plastic was subsequently analyzed for acid fluoride content by infrared absorption techniques. This technique permits carboxyl groups to be analyzed in the presence of carbonyl compounds such as aldehydes and ketones.

Carbonyl Tests

In 1961, Gray and Wright[41] developed a chemical method for measuring the proportion of carbonyl groups formed during the weathering of commercial, glass-reinforced polyesters. This same colorimetric technique was later found to be applicable to poly(vinyl chloride), poly(methyl methacrylate) and cellulose acetate–butyrate plastics.[3]

This technique consists of reacting a phenylenediamine with exposed plastics and determining the amounts of diamine reacting with the carbonyl groups in the plastic (Fig. 3). Some colored products are formed on the plastic surface and some in the solution. The main products appear to be condensation products of the carbonyl compounds and the phenylenediamine. The amount of the diamine reacting provides a direct means of measuring carbonyl products, and the color of the plastic surface provides an indirect means. This chemical technique has been used to show that the exposure of polyesters (Fig. 4) and poly(vinyl chloride) (Fig. 5) outdoors and in weathering devices leads to increased carbonyl products on the plastic surfaces. Studies of heat-stabilized poly(vinyl chloride) have shown that the variables of heat history and stabilizers can be evaluated by this simple technique. Campbell and Wright[39] have also shown that carbonyl compounds and peroxidic compounds formed during oxidation of asphalts can both be measured by use of the diamine colorimetric technique. They made use of the difference in reactivity in basic and acid solution, and measured both peroxide and carbonyl compounds formed during asphalt oxidations.

The diamine technique is very sensitive and therefore subject to some secondary interferences. The reagent will react with peroxide catalysts and any carbonyl-containing compounds in plastics additives.

TRENDS IN WEATHERABILITY TESTS

Weatherability testing of plastics has shown new trends with the development of new techniques. The most hopeful sign has been the combination of physical and chemical tests to follow the degradation of plastics during weathering tests. Schollenberger and Dinbergs[31] did a comprehensive study of polyurethane weathering by use of infrared and ultraviolet spectroscopy, oxygen absorption, and stress–strain measurements.

Oxidation and stress–strain studies of poly(vinyl chloride) showed that physical properties can be related to heat history as well as to ultraviolet exposure[6] (Fig. 6).

The future of plastics testing will most surely involve a more closely integrated program that makes use of (*a*) those chemical techniques that explain the underlying degradation reactions and (*b*) those physical measurements that most sensitively monitor the important mechanical properties. The acceleration of chemical and physical changes will be accomplished by simultaneous stressing and exposure.

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Résumé

On passe en revue les méthodes d'essais physiques et chimiques qui pourraient être appliquées en vue de prédire les qualités de certains plastiques exposés à l'action d'agents atmosphériques. On considère les techniques de mesure de l'apparence, la force et la flexibilité. Une modification de couleur, bien que fort utilisée, n'est à elle seule qu'une mesure insuffisante du vieillissement. On examine les méthodes d'essais spectroscopiques et chimiques les plus sensibles afin de mesurer les produits d'oxydation et d'hydrolyse au sein de matériaux polymériques du point de vue de leur utilité pour mesurer quantitativement la dégradation de plastiques. Les méthodes considérées permettent la détermination des groupes carbonyles, carboxyles, peroxydes et hydroxyles.

Zusammenfassung

Diese Mitteilung gibt einen Überblick über diejenigen physikalischen und chemischen Testmethoden, die zur Vorhersage des Verhaltens von Plastomeren bei der Verwendung im Freien verwendet werden können. Verfahren zur Messung des Aussehens, der Festigkeit und der Biegsamkeit werden besprochen. Farbänderungen allein, obwohl

weitgehend verwendet, bilden ein ungenügendes Mass für das Bewitterungsverhalten. Die empfindlicheren spektroskopischen und chemischen Testmethoden, mit welchen die Oxydations- und Hydrolysenprodukte in polymeren Materialien bestimmt werden können, werden auf ihre Brauchbarkeit zur quantitativen Messung des Plastomerabbaus untersucht. Die besprochenen Methoden werden zur Bestimmung von Carbonyl-, Carboxyl-, Peroxyd- und Hydroxylgruppen verwendet.

06

APPLIED POLYMER SYMPOSIA NO. 4, 97–110 (1967)

Accelerated Weathering of Polymers: Radiation

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Synopsis

The objective of this work was to study the radiation characteristics in three artificial weathering devices and to do a preliminary survey of the effects of high-intensity irradiation on plastics. An absolute radiometer was used to measure radiation characteristics in the xenon arc and sunshine carbon and enclosed carbon arc Weather-Ometers. The irradiance from the xenon arc was stable over 1 hr., but the irradiance from the carbon arcs fluctuated. Irradiance received in 1 hr. at the sample drum for sunshine and enclosed carbon arcs ranged from 315 to 1020 w./m.^{2} and 297 to 679 w./m.^{2}, respectively, while the xenon arc showed a relatively constant irradiance of 910 w./m.^{2}. All three devices had a maximum irradiance near the center of the sample drum with intensities at top and bottom being 15–40% less. Seven plastic films were exposed to a xenon arc over a 200-fold intensity range by decreasing the arc-to-sample distance. At up to 6.1 times earth-level sunlight, no significant changes resulted within 100 hr. At 81 times earth-level sunlight, white-pigmented film decomposed within 30 hr. and clear films showed changes in ultraviolet and infrared spectra within 69 hr. At 379 times earth-level sunlight, five clear plastics decomposed within 12 hr. or less.

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Degradation of polymers on exposure to weather is caused primarily by solar radiation (ultraviolet, visible, infrared), water (dew, rain, humidity, snow), heat, and other atmospheric constituents (e.g., oxygen, ozone, oxides of nitrogen). Duplicating these environmental causes of degradation should allow the effects of weathering to be reproduced in the laboratory.

The objectives of the present work were (*a*) to study the radiation characteristics in the most widely used artificial weathering devices and (*b*) to do a preliminary survey of the effects of high-intensity irradiation on plastics, in a search for faster methods of evaluating weatherability. These two topics will be treated as Parts A and B, respectively.

BACKGROUND

There is a lack of general correlation of results between exposure of materials to natural and artificial weather;[1] a major cause of this is the scarcity of significant data defining both the natural and artificial exposure conditions.

Standard methods of accelerated weathering[2] use exposure to artificial light, along with control of temperature, water, and/or other atmospheric constituents. Radiant flux at the sample is usually less than or nearly equal to the intensity of sunlight at the earth's surface (about 740 w./m.^{2}).[3]

The intensity of sunlight is often described in terms of a "solar constant," which is the solar irradiation at normal incidence outside the atmosphere (air mass = 0) at the mean solar distance. At sea-level, a reasonable standard for solar intensity can be calculated using air mass = 2, i.e., sunlight passes through a daily average of two optical thicknesses of atmosphere before reaching the earth's surface. One solar constant at air mass = 0 is 1400 w./m.^{2}, and one solar constant at air mass = 2 is 740 w./m.^{2}.[3]

Shorter evaluation times were sought in this study; irradiation at high intensity should yield short time of evaluation, according to the fundamental Bunsen-Roscoe law of photochemistry: "The amount of material transformed in a photochemical change is proportional to the product of the light intensity and the time of illumination."[4]

PART A: RADIOMETRY

Apparatus

Radiant Energy Sources. Measurements were made in three Atlas Weather-Ometers:*[5] (*1*) Xenon arc, Model 60 WR; (*2*) Enclosed carbon arc, Model SMCR; (*3*) Sunshine carbon arc, Model XWR.

The xenon arc device uses a 6000-w., high pressure, water-cooled lamp (Osram XBF-6000 W-X/1) of the long-arc configuration. The lamp has an overall length of 14 in. and is $1^1/_{32}$ in. in diameter, with an arc gap between the electrode tips of about $4^1/_2$ in. The lamp consists of a burner tube surrounded by a water jacket assembly of inner and outer pyrex (or quartz, when specified) cylinders. The lamp had been operated about 500 hr. before this study. The xenon arc device was operated at 5800 w. and a black-panel temperature of 55°C. Humidity control and water spray were not used in this device or either of the carbon arc devices. A cylindrical sample drum of 94-cm. diameter surrounds the xenon arc.

The enclosed carbon arc device uses three No. 20 cored carbons, one $^1/_2$ in. × 12 in. carbon rod as the upper electrode and two $^1/_2$ in. × 4 in. carbon rods as the lower electrodes. The single solenoid-actuated arc was operated at a potential of 120–145 v. at 15–17 amp. This is enclosed in a bell-shaped pyrex globe. Black-panel temperature was 55°C. The cylindrical sample drum surrounding the arc has a diameter of 86 cm.

The Sunshine carbon arc device uses three No. 22 ($^7/_8$ × 2 in.) carbons as the upper electrodes and three No. 13 ($^1/_2$ × 12 in.), carbons as the lower electrodes. The arc burns between only one pair of carbons at a time and automatically shifts from one pair to another as the carbons are consumed. It operates at 60 amp. with 50 v. across the arc. A constant-current arc regulator unit actuates the carbon feeding mechanism. The

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* Certain commercial instruments and materials are identified in this paper in order to specify the experimental procedure adequately. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment identified is necessarily the best available for the purpose.

arc is behind a frame of Corex D filters. Black-panel temperature was 55°C. A circular sample drum of 96-cm. diameter surrounds the carbon arcs.

The fourth light source whose irradiance was measured as a check on the monitoring equipment was the NBS standard-type 1000-w. coiled-coil, tungsten-filament quartz–iodine lamp (General Electric DXW-1000). This supplementary standard of spectral irradiance was operated under the recommended conditions at 8.30 amp. with a potential of 120 v.[6]

Monitoring Equipment. A radiometer, Model DR-2, manufactured by Thompson-Ramo-Wooldridge Space Technology Labs, was used to monitor total radiation intensity received. The sensor of the DR-2 radiometer consists of a split disk of blackened thin metal foil behind a quartz window, one-half of which is densely aluminized. Therefore, on irradiation, a temperature difference will exist between the half-disks, and this temperature difference is proportional to the radiant flux striking the sensor. The radiometer is temperature compensated from −107 to +82°C. The time required by the radiometer to reach 63% of full output in response to a step function input is 0.7 sec.; thus total response is achieved in about 2 sec. It has a uniform flat response from 0.25–2.5 μ, and was calibrated at 10.0 mv. output per 1400 w./m.^{2} input.[7]

A Sargent multi-range recorder (Model MR) was used to obtain a running recording of irradiation received by the sensor.

Results

The curves for irradiance at the sample drum normal to the center of the arc are presented in Figure 1 for typical 1-hr. periods for the three artificial weathering devices studied—xenon arc, enclosed carbon arc, and Sunshine carbon arc. The flat curve of irradiance from the xenon arc for this period contrasts sharply with the irregular curves obtained for the carbon arcs.

The intensities of the three individual carbons in the Sunshine carbon arc device remain fairly steady, but vary widely with respect to each other. The intensity for each carbon, its burning time before switching to a new carbon, and the firing sequence did not appear predictable.

The overall average intensity recorded in 9 hr. was 667 w./m.^{2}; average maximum, and average minimum were 740 and 618 w./m.^{2}, respectively. Lowest flux recorded was 315 w./m.^{2} and the highest was 1020 w./m.^{2}.

Average burning time per carbon was 22 min. although times as short as 5 min. and as long as 38 min. were recorded.

The irregular series of frequent peaks and valleys composing the curve of irradiance from the enclosed carbon arc shows as much as 100% increase from minimum to maximum value in any given hour. The average irradiance, computed from the instantaneous values at 20-sec. intervals, (Fig. 2) is relatively stable after the first hour of operation, falling off very slightly about the twentieth hour of burning time. Overall average was computed to be 440 w./m.^{2}. The spread between the maximum and minimum intensities increases with time of operation; maximum and minimum irradiances recorded were 679 and 297 w./m.^{2}.

The irradiance from the xenon arc is seen to be constant for the representative hour of operation shown in Figure 1, with a value of 910 w./m.^{2}. This lamp had been operated about 500 hr., so the initially rapid decrease of intensity in the first few hundred hours had already taken place.

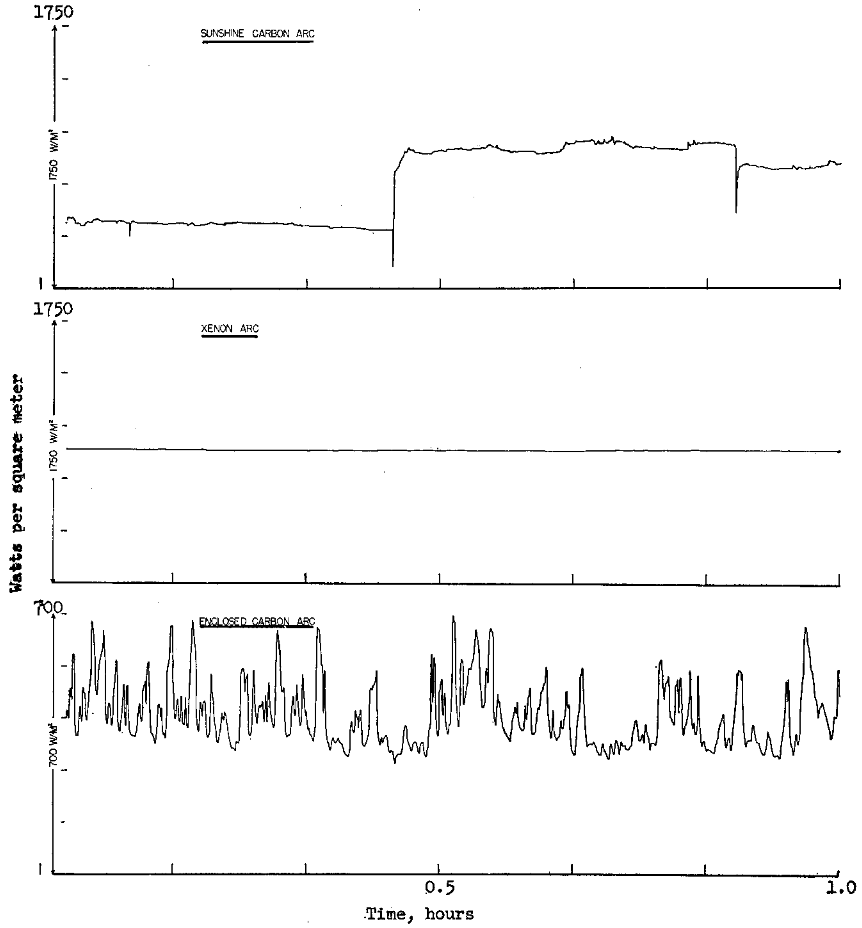

Fig. 1. Typical irradiance at the drum in 1 hr. for enclosed- and Sunshine carbon arcs and xenon arc.

The dependence of irradiance on height is shown in Figure 3 for the carbon and xenon arcs, with the sensor height being varied in the plane of the sample drum parallel to the arc. All three show maximum irradiance near the center of the drum, with intensities at top and bottom of the drum being 15–40% less. The xenon and Sunshine carbon arcs exhibited smooth parabolic curves with extrapolated intensities at the top and bottom of the drum falling off to 60–65% of the maximum intensity.

Irradiance at the drum for the enclosed carbon arc is generally parabolic with a slight dip at the center; its two maxima occur about 3 cm. above and 5 cm. below the center line. This can presumably be attributed to the characteristics of the carbon arc, i.e., the bright core tips are spaced a few

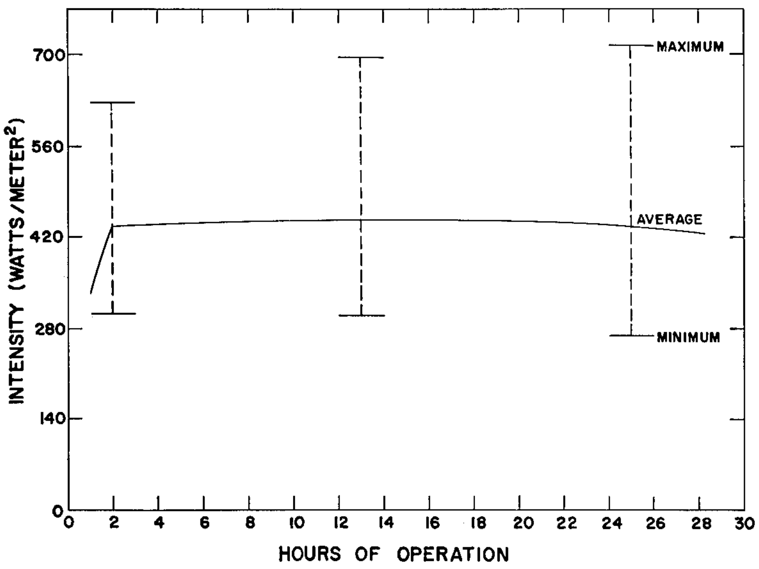

Fig. 2. Intensity vs. hours of operation for enclosed-carbon arc.

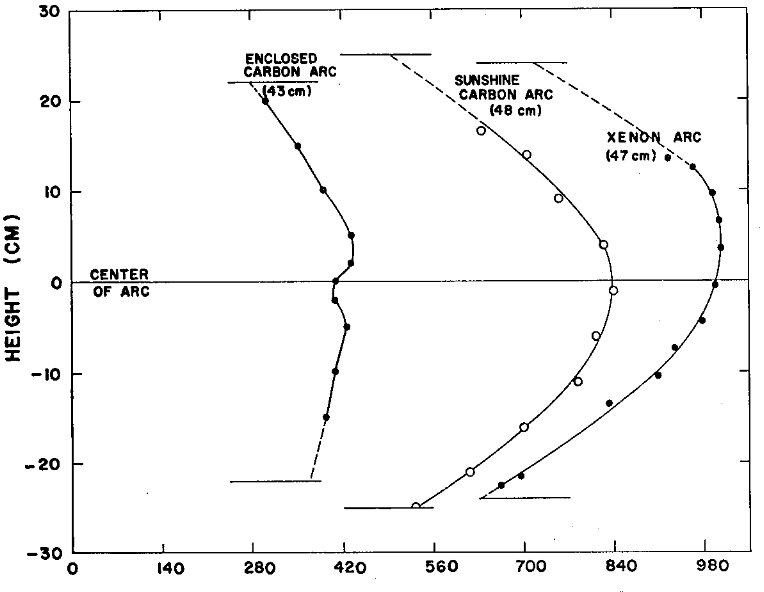

Fig. 3. Height vs. intensity for xenon and carbon arcs at drum distance.

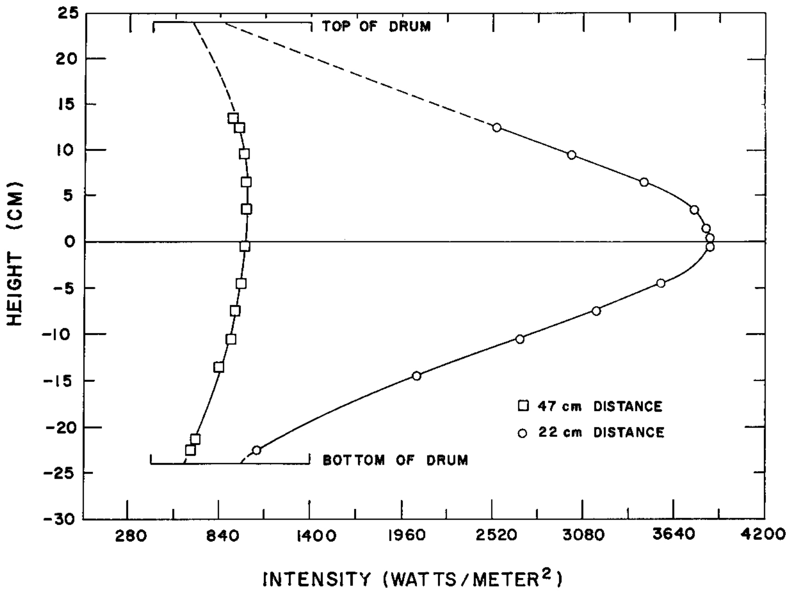

Fig. 4. Height vs. intensity for xenon arc at 47 cm. (drum) and 22 cm. distance.

centimeters apart. (A similar dip was not observed at the center of the Sunshine carbon arc curve because the rippled surface of the Corex D filter diffuses radiation.) Intensities at the top and bottom of the drum are 65 and 85% of the maximum intensity, respectively.

The maximum irradiance for the xenon arc is about 2.1 times the maximum irradiance for the enclosed carbon arc. This intensity factor can be important in the acceleration of degradation of plastics.

The dependence of irradiance on height is shown in Figure 4 at 47 cm. (drum distance) and 22 cm. for the xenon arc Weather-Ometer. The steep parabolic curve at 22 cm. drops off rapidly so that top and bottom received only 25% of the irradiation found at the center.

It can be seen that the intensity at 22 cm. is about 4 times that at 47 cm. but that the area of nearly uniform irradiance is severely reduced, as expected.

Figure 5 shows the variation of center-line intensity vs. distance from the NBS standard-type, 1000-w. quartz–iodine lamp, and the xenon arc with quartz jackets, and xenon arc with pyrex jackets and Corning 1–69 infrared filter.

If intensity is plotted against the square of the distance from the source according to the inverse square law:[8]

$$I = P/r_2$$

(where I = intensity of illumination, P = illuminating power, r = distance, for a point source), nearly linear plots result. Small deviations can be attributed to the nonpoint sources and to reflections from the 1–69 filter.

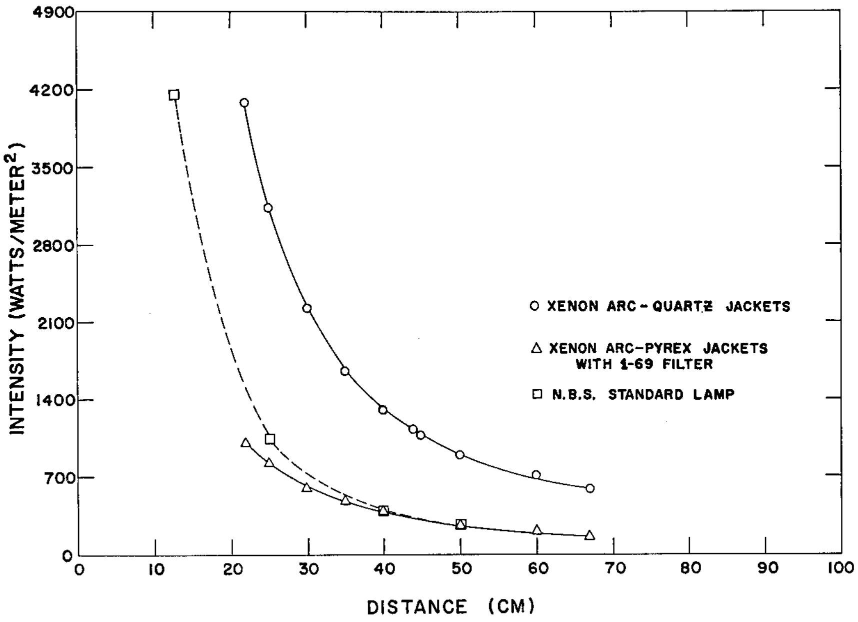

Fig. 5. Intensity vs. distance for NBS standard lamp and xenon arc.

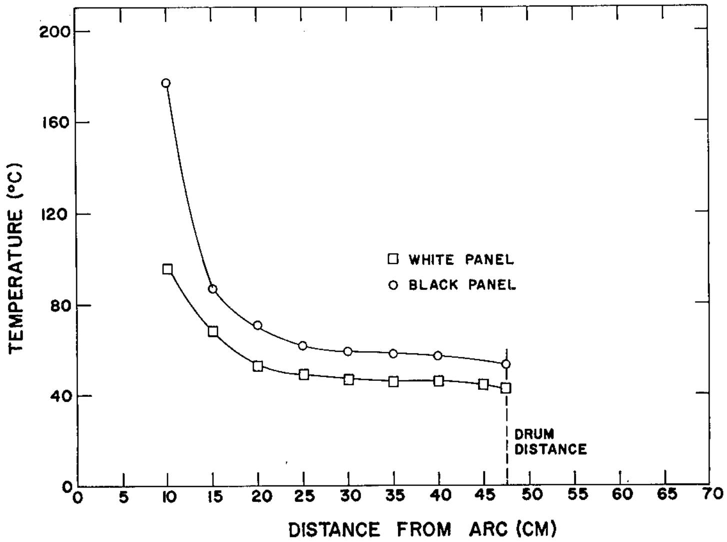

Fig. 6. Black- and white-panel temperatures vs. distance from xenon arc.

Conformance to the inverse square law was checked with measurements through the infrared heat-absorbing transmission filter (1–69), in order to be certain that there was no effect of heat on the radiometer. At all distances, transmitted intensity was reduced to about 25–30% of the unfiltered intensity.

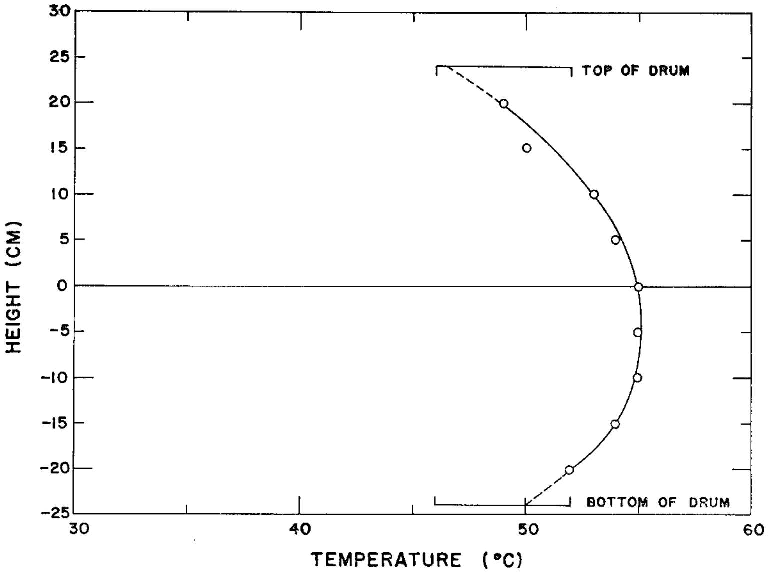

Fig. 7. Height vs. temperature of black-panel exposed to xenon arc.

To describe the distribution of temperature inside the xenon arc Weather-Ometer, standard black-panel[5] temperature measurements were made at various drum heights. Temperatures of a similar white panel were also measured. The panels were placed parallel to the xenon arc for all measurements. Temperatures were measured with copper–constantan thermocouples and recorded on a Sargent recorder.

Figure 6 shows the black- and white-panel temperatures versus distance (panels normal to the xenon arc axis). Both temperatures begin to rise sharply as the panels are moved closer than 20 cm. from the arc.

The panel temperatures deviate slightly from the inverse square law but should give reasonable approximations of the temperature of exposed opaque materials.

Figure 7 shows a parabolic curve for the plot of height versus black-panel temperature. Once again, irradiation diminishes at the top and bottom of the drum as evidenced by the temperature decrease. Black-panel temperatures in the drum plane vary no more than ±4°C. from the average, in this xenon arc device.

Summary and Conclusions

Radiation characteristics of carbon and xenon arc weathering devices were measured with a radiometer to characterize accelerated light exposures. The results are probably influenced by the geometry of the sensor, the radiation sources, and the enclosure. The irradiance from the xenon arc was found to be very steady in sharp contrast to the irregular irradiance from the carbon arcs over 1-hr. periods. Average, maximum, and minimum, irradiances from the Sunshine carbon arc at the sample drum

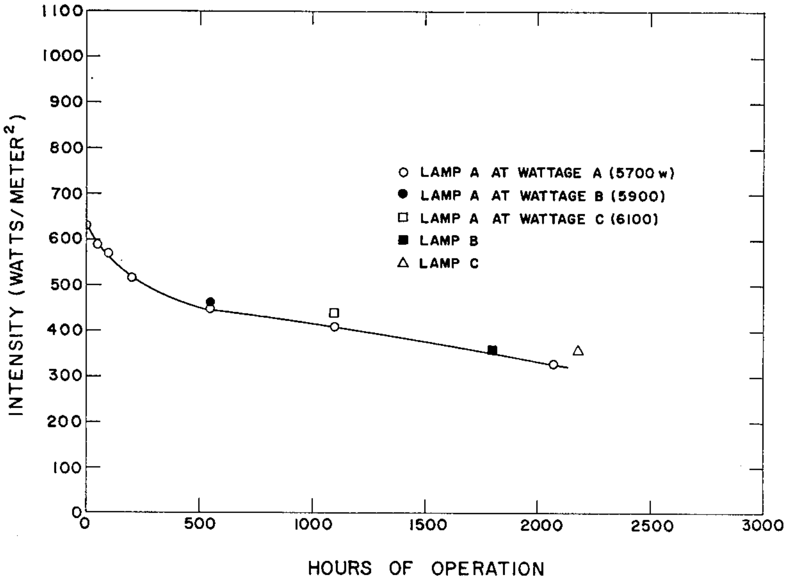

Fig. 8. Intensity vs. hours of operation for xenon arc with pyrex jackets at 60 cm.

were 667, 1020, and 315 w./m.², respectively. Average, maximum, and minimum from the enclosed carbon arc at the sample drum were 440, 679, and 279 w./m.², respectively. The xenon arc with Pyrex jackets showed a relatively constant irradiance at the sample drum of 910 w./m.² over a 1-hr. period.

It should be noted that xenon arc intensity is known to decrease significantly in the first few hundred hours of break-in; thereafter, the rate of decrease is much less. Figure 8 shows Gray's measurements[9] of this long-term change using a Model 65 radiometer made by Yellow Springs Instrument Company. The small effect of increasing operating wattage of the arc as recommended by Atlas is illustrated. Data for two additional lamps are also given. These results are in good agreement with the chemical dosimetry results of Martin et al.,[10] who measured decrease of radiant flux (below 500 nm.) with time.

All three devices had a maximum irradiance near the center of the drum with intensities at top and bottom of sample drum being 15–40% less.

For exposures at 22 cm. from the xenon arc the variation of intensity with height was much greater than at the usual sample distance of 47 cm.

Measurements of intensity versus distance were in reasonable agreement with the inverse square law for the carbon and xenon arcs and NBS standard-type lamp.

Black- and white-panel temperatures measured at the center of the xenon arc sample drum were 53 and 43°C., respectively. Temperatures rose rapidly closer than 20 cm. from the arc, reaching 178°C. for the black-panel and 96°C. for the white-panel, at 10 cm.

Black-panel temperatures decreased parabolically from the center of the vertical drum plane.

PART B: EXPOSURE OF POLYMERS

Apparatus

Plastics were exposed to radiation in the Atlas xenon arc Weather-Ometer mentioned in Part A. This lamp had been operated about 500 hr. prior to these exposures. It can be seen from Figure 8 that the intensity of the arc may have gradually decreased a few per cent during this study.

Figure 5 shows measured irradiance versus distance normal to the center of the xenon arc. Table I gives intensities at all the test distances used.

TABLE I
Irradiance at Exposure Distances

Distance from arc, cm.	Intensity, w./m.^{2}	Solar constants at AM = 2
1.3	280,000	379
5	60,000	81
20	4,900	6.6
36	1,650	2.2
46 (drum)	1,060	1.45

Irradiances at 46, 36, and 20 cm. were measured with the radiometer; irradiances at 5 and 1.3 cm. were calculated from the equation of Walsh,[8] for illumination from a line source. The actual radiance of the lamp at 500 hr. was calculated from measured irradiance. Radiance was then substituted in Walsh's equation to calculate irradiance at the closer distances.

A reasonable standard for earth-level (air mass = 2) intensity and distribution is 740 w./m.^{2}; the best available match to this distribution in the ultraviolet-visible region (where photochemical initiation is probable) is filtered irradiation from a xenon arc.[11,12]

Exposure of Plastics

Seven plastic films were exposed to five intensities of irradiation from the xenon arc with pyrex filters. The samples were: colorless transparent films (1–4 mil) of polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC), poly(vinyl fluoride) (PVF), poly(ethylene terephthalate) (PETP), and a white-pigmented (2 mil) poly(vinyl chloride).

These samples were exposed directly opposite the central 9 cm. portion of the xenon arc. The films were mounted unbacked at 46, 36, and 20 cm. from the arc in aluminum frames affixed to spacers extending from the sample drum. No cooling of these samples was needed because white-panel temperature as close as 20 cm. measured only 50°C.

Samples (strips of plastic 2 cm. wide) were also exposed at 5 cm. from the arc. For cooling, they were wrapped around the outside of an Allihn condenser with an effluent cooling water temperature of 23°C.

The exposures at 1.3 cm. were performed by wrapping 2-cm. widths of the samples directly around the outer water jacket of the xenon arc. This was done in an attempt to keep the samples cool, but it was not completely effective since most samples ignited at this distance.

The *pigmented* sample, PVC-A was exposed at 46 cm. on the sample drum for 97 hr.; there was no visible change, and its infrared spectrum was unchanged. Similar results were obtained after 97 hr. at 36 cm. and 20 cm. At 5 cm., a dark gray streak developed by 30 hr. and this darkened and became wider until the sample was removed at 69 hr. At 1.3 cm. the plastic ignited immediately when the arc was turned on.

Clear samples of PVC-B and polypropylene were used to survey the effect of increasing intensity on unpigmented films. PVC-B showed no significant changes in appearance or infrared spectrum after 178 hr. at 46, 36, and 20 cm. Similarly, polypropylene showed no changes at 46 and 36 cm. but at 20 cm. it did give a very small increase in intensity of carbonyl (1710 cm.$^{-1}$) and hydroxyl (3450 cm.$^{-1}$) bands in the infrared.

At 5 cm. all six clear plastic samples showed changes in their ultraviolet spectra after 69 hr. Infrared spectral changes were seen only in the polyolefins and poly(vinyl fluoride). No changes in appearance were obvious.

At 1.3 cm. five of the six clear plastics charred or embrittled extensively within 12 hr. or less; only the polyethylene remained visibly unchanged at 12 hr., but it did show changes in the infrared and ultraviolet spectra within 2.5 hr.

Thermal effects on the samples are probable at the two closest exposure distances. Future high-irradiance tests may be improved by filtering out the excess infrared of the xenon arc and/or more efficient cooling of samples.

Correlation studies on results of such exposures to artificial radiation with exposure to natural sunlight is in progress.

APPENDIX A

Table II is a tabulated comparison of the major light sources used in commercial artificial weathering devices. This summary has been useful in considering their relative technical merits: simulation of actinic radiation of sunlight, total intensity including its variations with time and over the test plane, general correlation with typical outdoor exposures, and size of exposure area. Estimates of efficiency of the devices are also included: maintenance requirements, "down-time," and frequency of lamp replacement.

The term "Suns" in column 4 refers to the intensity of irradiation at the center of the test drum. One "sun" is approximately equal to the suggested standard intensity of sunlight at the earth's surface, 740 w./m.^{2}.

TABLE II
Comparison of Light Sources for Artificial Weathering

	Type	Solar simulation	Intensity uniformity		"Suns"	Correlation	Exposure area, in.^{2}	Maintenance, hr.	"Down time"	Lamp replacement, hr.
			Spatial	Temporal						
Carbon arc	Single enclosed	Poor in UV (high 360/380 $m\mu$ UV peaks)	±20%	Very variable	$^1/_2$	Poor to good	1000	High-ea. 20	Weekends + 1 hr./day	20
	Sunshine	"	±20%	Variable	1	Fair to good	1500	High-ea. 20	"	20
Fluorescent sunlamp/blacklamp (FS/BL)		Poor in visible/IR (low energy in visible/IR above 350 $m\mu$)	±20%	"Relatively constant"	1 (UV only)	Good for colorless or unplasticized plastics	1500	Low-ea. 100	Negligible	100
Xenon arc	Atlas	Poor in IR (high 800–1000 $m\mu$ IR peaks)	±20%	Decreases about 30%/1000 hr.	1	Good	1500	Low-ea. 100	1 hr./week (1%)	2000
	Xenotest	Good (excess IR filtered out)	±10%	Decreases about 15%/1000 hr.	2	Good	650	Low	Negligible	1500
	Spectrolab	Best available	±5%	Constant (±1%)	1–20	Not available	200 (at 1 sun)	Low	Negligible	1500

The data were gathered from published and manufacturers' literature as well as from our own measurements. Figures are rounded off for ease of comparison.

We are grateful to the many staff members of the National Bureau of Standards, particularly those of the Building Research Division, who aided us technically and personally. Outstanding help has been received from Dr. W. W. Walton and V. E. Gray.

We appreciate the contribution of each representative on our Steering Committee of the Manufacturing Chemists' Association, especially F. H. Carman, W. F. Busse, and W. F. Bartoe.

Finally, thanks are given to our supervisor, Dr. W. F. Brucksch, for being a source of inspiration.

The TRW radiometer used in this work was on loan through the courtesy of Spectrolab Division of Textron Electronics Company.

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Résumé

L'objectif du présent travail était l'étude des caractéristiques de radiations de trois méthodes de vieillissement artificiel et d'obtenir une revue préliminaire des effets des irradiations de hautes intensités sur des plastiques. Un radiomètre absolu a été utilisé pour mesurer les caractéristiques de radiation dans un arc de xénon, dans un arc solaire au charbon et dans un arc au charbon Weather-Ometers. L'irradiance au départ de l'arc de xénon était stable durant une heure mais les radiations au départ des arcs de carbone variaient. L'irradiance reçue en une heure sur un tambour à la lumière solaire et à des arcs de carbone incorporés s'élevait de 315 à 1020 watts/m^2 et de 297 à 679 watts/m^2, respectivement. Alors que l'arc de xénon montrait une irradiance constante de 910 watts/m^2. Ces trois méthodes avaient un maximum d'irradiance au voisinage du centre du tambour de l'échantillon avec des intensités au sommet et à la base de 15–40% inférieures. Sept films plastiques ont été exposés à l'arc au xénon avec un domaine d'intensité de 1 à 200 fois en décroissant la distance de l'arc à l'échantillon. A des durées d'irradiation solaire de 6.1 fois plus élevées, aucune variation significative n'a été observée après 100 heures. A éclairement solaire 81 fois celle du niveau du sol, le film à

pigments blancs se décomposáit endéans 30 heures et le film clair montrait des variations dans les spectres ultraviolets et infrarouges endéans les 69 heures. A un éclairement solaire 379 fois celui du niveau de la terre, cinq plastiques clairs décomposaient endéans 12 heures ou moins.

Zusammenfassung

Der Gegenstand der vorliegenden Arbeit war die Untersuchung der Strahlungscharakteristik bei drei künstlichen Bewitterungsvorrichtungen und die Gewinnung eines ersten Überblicks über die Wirkung der Bestrahlung hoher Intensität auf Plastomere. Ein Absolutradiometer wurde zur Messung der Strahlungscharakteristik in Weather-Ometern mit Xenonbogen sowie "Sunshine"- und eingeschlossenem Kohlebogen verwendet. Die Einstrahlung vom Xenonbogen war während einer Stunde konstant, diejenige von den Kohlebögen dagegen zeigte Schwankungen. Die an der Probentrommel während einer Stunde auffallende Bestrahlung lag beim "Sunshine"-Kohlebogen zwischen 315 und 1020 Watt/cm^2, beim eingeschlossenen Kohlebogen zwischen 297 und 979 Watt/cm^2, während der Xenonbogen eine verhältnismässig konstante Bestrahlung von 910 Watt/cm^2 zeigte. Bei allen drei Apparaten lag das Bestrahlungs maximum in der Nähe der Mitte der Probentrommel und die Intensität an der Spitze und am Boden war 15–40% niedriger. Sieben Plastomerfilme wurden der Bestrahlung eines Xenonbogens bei Variierung der Intensität in einem 200-fachen Bereich durch Verringerung des Abstandes Bogen-Probe ausgesetzt. Beim bis zu 6,1-fachen des Sonnenlichts an der Erdoberfläche traten innerhalb 100 Stunden keine signifikanten Änderungen auf. Beim 81-fachen des Erdoberflächen-Sonnenlichts zersetzten sich weisspigmentierte Filme innerhalb 30 Stunden und klare Filme zeigten innerhalb 69 Stunden Veränderungen in den Ultraviolett- und Infrarotspektren. Beim 379-fachen des Erdoberflächen-Sonnenlichts zersetzten sich fünf klare Plastomere innerhalb von 12 Stunden oder weniger.

07

APPLIED POLYMER SYMPOSIA NO. 4, 111–118 (1967)

Accelerated Light Exposure in the Xenotest: Results, Limits, and Comparison with Conventional Equipment

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Synopsis

It is shown that accelerated artificial exposure of plastics to light and humidity in an apparatus (Xenotest) produces results which correspond to a large degree with those obtained in nature. Particularly, it is made evident that the high irradiance of 1600 w./m.^{2} on the sample in the apparatus does not cause any incorrect estimation of the results because a direct inverse relationship exists between exposure time and irradiance. It is indispensable, however, that the spectral energy distribution of the light source in the apparatus correspond to that of the global radiation.

The examination of the light and weather fastness of plastics presents manifold difficulties. The reason is first that long periods of time must pass until results are obtained that can be evaluated and on the basis of which the test parameters can be modified. Second, one will discover that various properties of the plastics change in the course of the weathering process. It will be shown later that they do not change in the same degree. Thus one must attempt to utilize the changes of characteristic properties that are easy to measure for the evaluation of the test results.

Further, it is highly important if the samples are exposed only to light, without the application of rain and humidity, or if they are also exposed to weathering at certain degrees of humidity and with periods of rain.

The accelerated test, as dealt with in this paper, means acceleration only with regard to exposure to light. The irradiance on the samples can be exactly controlled and measured. As concerns the application of humidity and rain, an aging test cannot easily be accelerated within a measurable scope.

First of all, let us define the accelerated light exposure test. In this paper it means an irradiance of about 1600 w./m.^{2} (or 20,000 foot-candles) on the sample. It will be demonstrated that with such intensities results can be expected to correspond to those obtained in nature. Further, it will be proved that with the product of intensity and exposure time being constant, results can be achieved that are equal within certain tolerances.

This brings up the question which properties of the lighting unit are particularly critical with regard to an accelerated test of exposure to light.

The Spectral Energy Distribution of the Light Source

If the results of the light exposure test in the apparatus are to correspond to those attained in nature, the spectral energy distribution of the light source in the unit must correspond as closely as possible to global radiation. This applies especially to samples that absorb selectively or if the absorption spectra of the samples are not known at all. It is evident that the effect of spectral deviations may be greater the higher the irradiance on the samples.

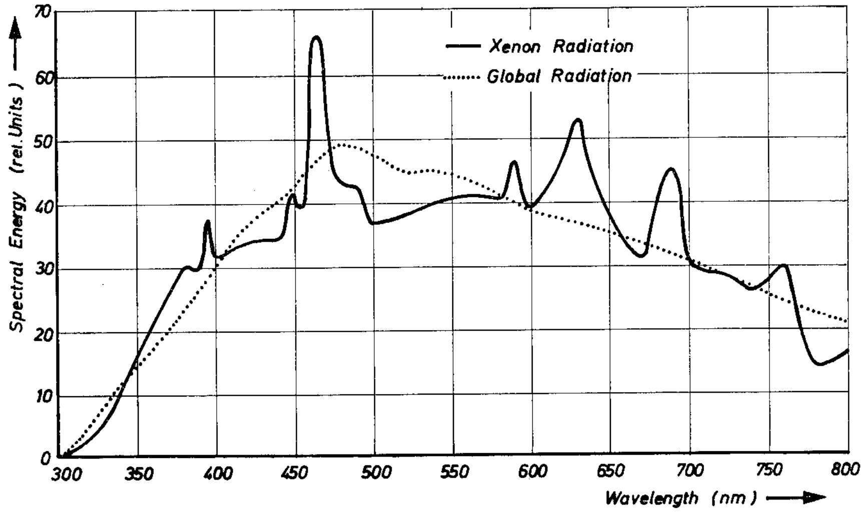

Fig. 1. Spectral energy distribution: global and filtered xenon radiation.

Figure 1 shows the radiation of the light source in the Xenotest as compared with global radiation. The source is an air-cooled xenon lamp whose light is filtered with pre-aged filter glasses. The global radiation indicated in the graph is the standard value as recommended in Germany by a standards committee. It is based on very accurate measurements. Of course, there are variations in the spectral energy distribution of global radiation. Up to a certain degree these variations can be imitated, as long as this seems sensible, by changing the system of the filters.

The Temperature on the Samples

An accelerated light exposure test may involve the danger that, owing to the high luminous intensity, the temperature on the samples (i.e., the black panel temperature) is raised to such a high level that plastics are deteriorated and consequently the results are falsified. Figure 2 shows the effect of the filter system in the infrared range of the spectrum. The filters absorb such a great portion of the infrared radiation of the xenon light that the black panel temperature is below 50°C. The relatively low sample tem-

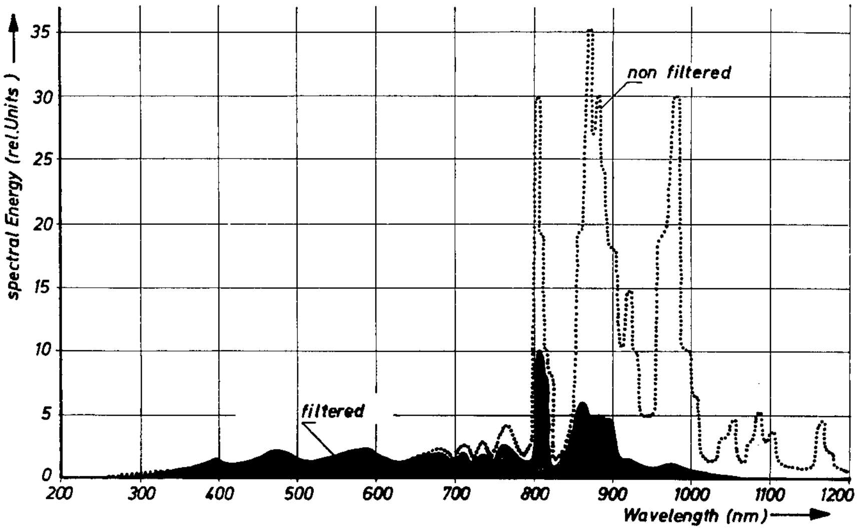

Fig. 2. Energy distribution of a xenon burner.

peratures thus attained offer the additional advantage that, if necessary, they allow high degrees of humidity without any expensive special arrangements.

The Change of the Relative Spectral Energy Distribution of the Light Source

Figure 3 shows the spectrum of the filtered xenon radiation after the burner has been in use for 0, 800, and 1500 hr. The total intensity de-

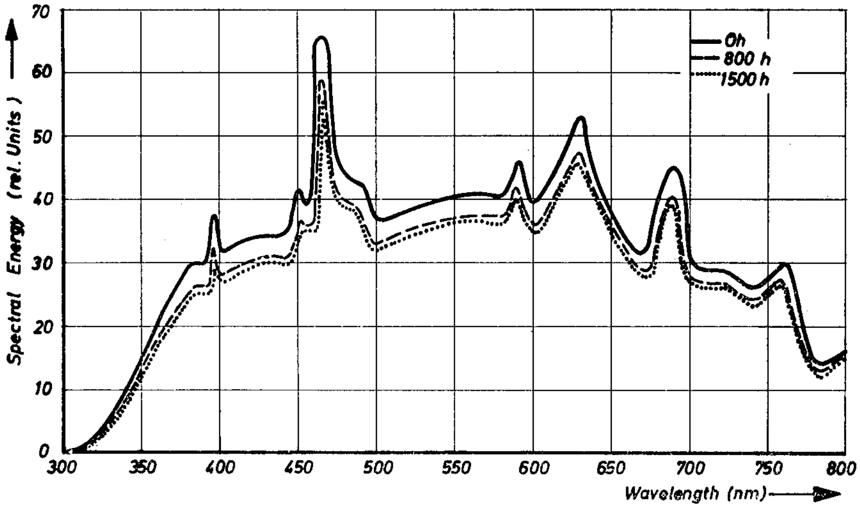

Fig. 3. Spectral energy distribution of xenon radiation as function of burner age.

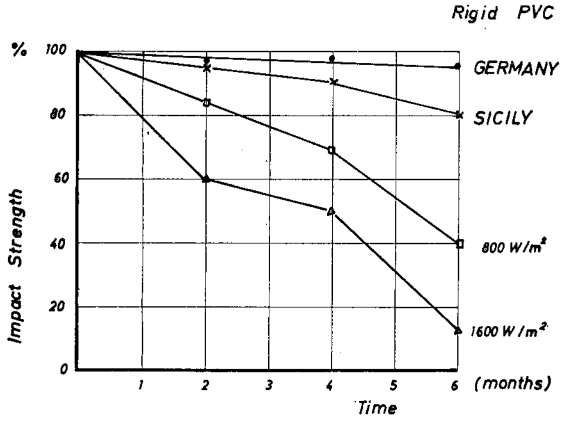

Fig. 4. Soft PVC. Impact strength as function of exposure time.

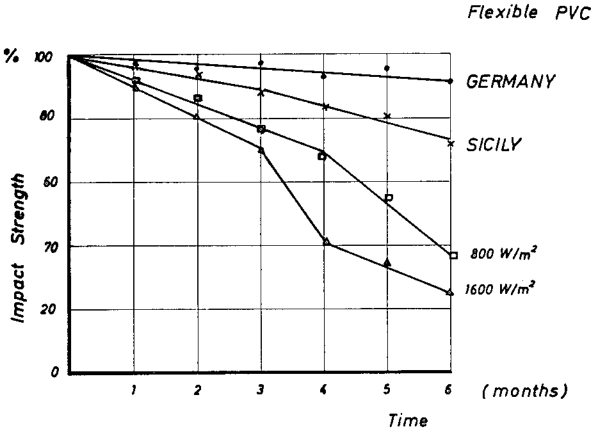

Fig. 5. Hard PVC. Impact strength as function of exposure time.

creases of course, as the life of the lamp advances. The change of the spectral energy distribution is, up to a service life of 1500 hr., not so substantial that falsifications of the test result might result.

The description of some exposure tests will show the results and limits of the accelerated test.

The decrease of impact strength serves as a measure for the aging of soft PVC (Fig. 4). The exposure tests were carried out with the same material in Germany, Sicily, and in the Xenotest machine with irradiances of 800 and 1600 w./m.². During the artificial exposure test the relative air humidity was set at 40–50%. There was a 5-min. rain interval after every 3 hr. It is evident from the curves that the test periods approximately decreased inversely proportional to the irradiances.

Similar tests with hard PVC under the same conditions provided similar results, as can be seen from Figure 5.

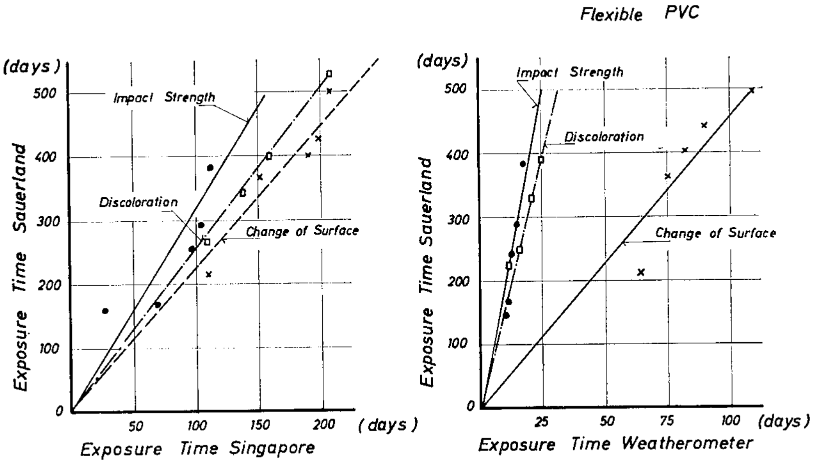

Fig. 6. Soft PVC. Correlation between exposure times.

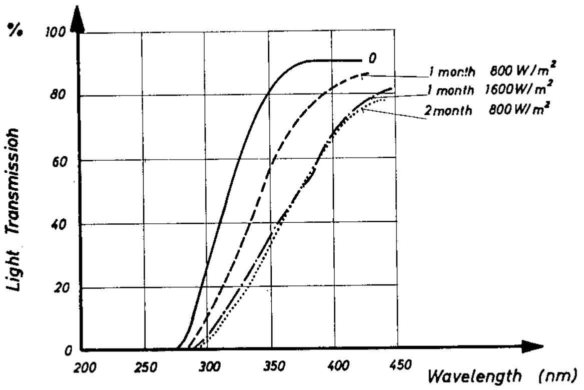

Fig. 7. Polystyrene. Light transmission as function of exposure time.

Unfortunately, it is not possible to give a constant factor that indicates the actual time acceleration of the exposure effects in the machine as compared with exposures in nature. The values shown in Figure 6 were taken from a publication by Simon[1] and interpreted by us. They reveal that with a single plastic material (soft PVC) various characteristic properties are modified to a different extent and consequently their acceleration factors are different. Comparisons were made between exposures in Sauerland (Germany), Singapore, and in the Weather-Ometer. These tests make evident that there is a non-uniformity of the time-accelerating factors not only with tests made in an apparatus and outdoors but also with tests made at places of different climates.

This phenomenon is even more striking if various types of plastics are compared. In the case of soft PVC, the acceleration factor regarding the decrease of impact strength measured in the exposure tests on the Xenotest was about 10 whereas it was about 20 in the case of hard PVC.

Figures 4 and 5 have already given an indication that with the irradiance used in this case the result of the exposure tests depends on the product of exposure time and irradiance on the samples. In Figure 7 the spectral transmission of a transparent polystyrene film is shown. The absorption edge of the unexposed film is about 300–450 nm. After 1 mo. of exposure (irradiance on the samples 800 w./m.^{2}), this edge shifted about 25 nm. and after 2 mo. about 50 nm. If the film was exposed to an irradiance twice as strong (1600 w./m.^{2}) for 1 mo., its transmission curve almost exactly coincided with that obtained with 800 w./m.^{2} after 2 mo. exposure. These results show again that the accelerated exposure test with doubled irradiance leads to the same degree of degradation within half the time.

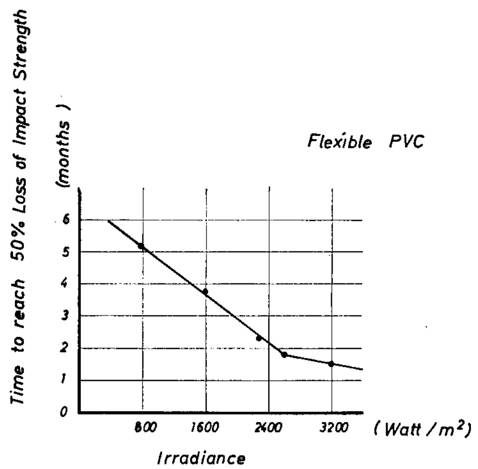

Fig. 8. Soft PVC. Time required to reach 50% loss of impact strength as function of irradiance.

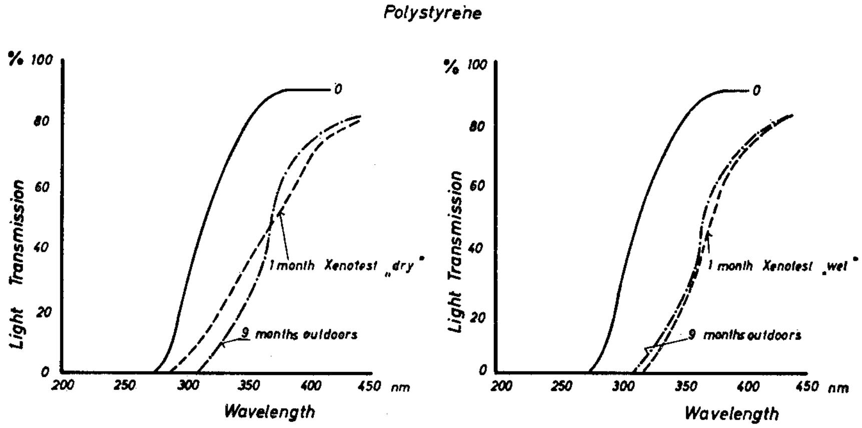

Fig. 9. Polystyrene. Effect of weathering.

This raises the question of how high the values can be for a proportionality between irradiance and exposure time to be expected. To find an answer to this, tests were carried out the results of which are shown in Figure 8. On the x axis the values of the irradiance are indicated, and on the y axis, those of the time that is required to reduce the impact strength of the exposed soft PVC samples to 50% of their original value. Up to the amount of 2600 w./m.^{2} proportionality between irradiance and exposure time exists. During these tests the samples were constantly maintained at an equal temperature by means of additional cooling to avoid any aging effects that might be caused by the influence of temperature.

The limit of 2600 w./m.^{2} for the zone of proportionality between exposure time and irradiance established in this case does not equally apply to all kinds of material. For most substances it is higher.

While all tests described so far were made without or with only little use of humidity and rain, an example will now be quoted where accelerated exposure to light is coupled with rain periods.

The left-hand side of Figure 9 shows the exposure result of a polystyrene film, as seen in Figure 8. The additionally drawn transmission on curve of a sample weathered outdoors reveals some characteristic deviations. As soon as the exposure in the apparatus was accompanied by a period of rain (20 min. rain, 60 min. dry, relative air humidity 75%), an approximation of the outdoor weathering curve and that obtained in the Xenotest was brought about (right). This effect is doubtless due to the influence of the humidity on the surface of the polystyrene film.

The purpose of this paper was to make a qualitative and as far as possible a quantitative comparison between the results of "normal" and "accelerated" exposure tests by means of a few arbitrarily selected examples ~~and to show by this the justification of accelerated exposure to light.~~ We deliberately confined ourselves to a few materials only and to the examination of several characteristic properties, since this matter, by nature, is very complex anyhow and, as pointed out above presents manifold problems.

The samples used were PVC and polystyrene.

The test results were obtained and compiled by a number of factories of the chemical industry in Germany in cooperation with Quarzlampen Gesellschaft mbH of Hanau.

Although differences in the materials due to production caused certain inaccuracies in the test results, we hope that nevertheless we have shown the justification of the accelerated light exposure test.

Reference

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Résumé

On a montré que l'exposition artificielle accélérée de plastique à la lumière et l'humidité dans un appareil (Xenotest) produit des résultats qui, pour une grande partie, correspondent avec ceux obtenus dans la nature. Particulièrement, on montre que l'irradiation à 1600 W/m^2 de l'échantillon dans l'appareil ne cause pas d'estimation faussée des ré-

sultats par suite du rapport inverse direct qui existe entre le temps d'exposition et l'irradiant. Il est toutefois indispensable que la distribution de l'énergie spectrale de la source lumineuse dans l'appareil corresponde à celle de la radiation globale.

Zusammenfassung

Es wird gezeigt, dass beschleunigte künstliche Exposition von Kunststoffen gegen Licht und Feuchtigkeit in einem Apparat (Xenotest) Ergebnisse liefert, welche in einem hohen Ausmass den unter natürlichen Bedingungen erhaltenen entsprechen. Besonders wird klargemacht, dass die hohe Einstrahlung von 1600 W/m^2 auf die Probe im Apparat keine unkorrekte Bewertung der Ergebnisse verursacht, da eine umgekehrte Proportionalität zwischen Expositionsdauer und Einstrahlungsintensität besteht. Es ist aber unerlässlich, dass die spektrale Energieverteilung der Lichtquelle im Apparat derjenigen der Globalstrahlung entspricht.

08

APPLIED POLYMER SYMPOSIA NO. 4, 119–129 (1967)

Actinometry of Sunlight at Kingsport, Tennessee

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Synopsis

Daily and seasonal variations in the actinic portion of sunlight make it desirable to develop a precise method for integrating actinic radiation in outdoor weathering tests. Data collected at Kingsport, Tennessee, over a 16 yr. period by using a uranyl oxalate actinometer are reported. A comparison of the results obtained with this actinometer, a pyrheliometer, and a photoelectric integrator with those obtained by integration based on carbonyl formation in polyethylene was made which indicated the varying degrees of utility of these methods for monitoring sunlight. The last method was found to have some distinct advantages.

Introduction

Many factors affect the quantity and spectral distribution of sunlight reaching the earth's surface at any given geographical location.[1,2] Not the least of these are the atmospheric contaminants present at the location. These factors, along with the natural variance in radiation due to seasons, make it desirable to integrate accurately the actinic radiation which is responsible for the weathering of materials exposed outdoors. Several methods of integrating sunlight have been evaluated during the 16 yr. we have been operating a weathering station at Kingsport, Tennessee. One of these methods, the uranyl oxalate actinometer, has been used continuously. The data accumulated with this actinometer during this period will be presented, and the various other methods of integrating the actinic radiation, such as the pyrheliometer, a photoelectric integrator, and carbonyl formation in polyethylene, will be compared.

Experimental

The actinometer solution used was identical to that described by Forbes and co-workers.[3,4] This is an aqueous solution $0.01M$ in uranyl acetate and $0.05M$ in oxalic acid. The solution was catalyzed with sulfuric acid. 100 ml. of the solution was placed in a 300-ml. quartz bottle enclosed in an aluminum can which had a semicircle of evenly spaced holes, 0.0625 in. in diameter, drilled at a height of 1.25 in. above the bottom of the can.[5] This assembly was mounted on the weathering racks at the same angle as the test specimens (36.5°) with the holes to the south. The actinometer is shown disassembled in Figure 1.

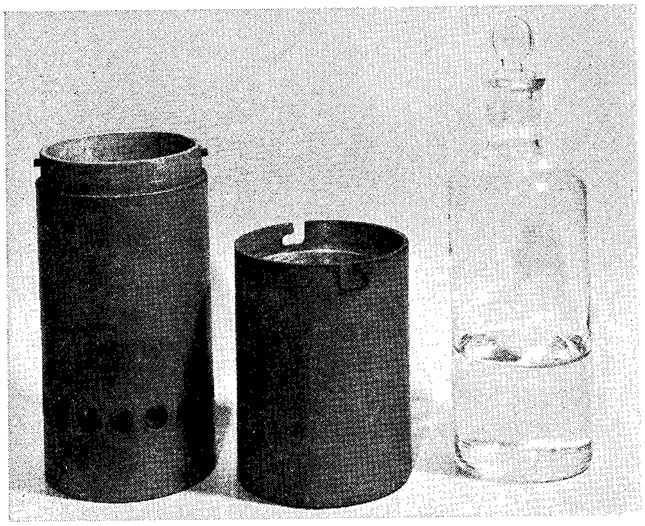

Fig. 1. Uranyl oxalate actinometer container at Kingsport, Tenn.

The actinometer design limited the decomposition of the oxalate to about 15% of the total for an exposure period of 3 wk. during the summer and about 2 mo. in the winter. At the end of each period of exposure, an analysis to determine the amount of residual oxalate was made by titration with permanganate; the spent solution was replaced with fresh. Integration was made in terms of milliequivalents of oxalate decomposed which were plotted against time (e.g., Fig. 2).

The quantum yield for the decomposition of oxalate has been reported to be about 0.5–0.6 from wavelengths below 300–470 mμ and then to drop rapidly to zero at 490 mμ.[3,4] The assumption was made that the part of sunlight which damages plastics lies within this 300–490 mμ band. Sunlight of this region has been monitored continuously in Kingsport, Tennessee, since May 1, 1950. Yearly variations are shown in Figure 3, and the average monthly accumulation for the period of 1951 through 1965 is shown in Figure 4. The cumulative curve for the period of 1950–1966 is shown in Figure 2.

A weather bureau-type pyrheliometer similar to that described by Kimball and Hobbs[6] (manufactured by Eppley Laboratories Inc.) was also used to monitor sunlight. It was a 10-junction instrument having a resistance of 40 ohm, and was calibrated against a reference standard to develop an emf of 2.44 mv. (g. cal.)$^{-1}$ cm.^{2} min. The instrument was mounted in a glass-covered cabinet facing south at a 45° angle. The millivolt output was fed to a single-point Leeds and Northrup recorder which had a range of 0–2 (g. cal.) min.$^{-1}$ (cm.^{2})$^{-1}$ and was equipped with an integrator.

Integration of sunlight with the Eppley pyrheliometer is shown in Figure 5 for 1960. Comparative data are also shown for the integration of actinic radiation with the uranyl oxalate and polyethylene actinometers.

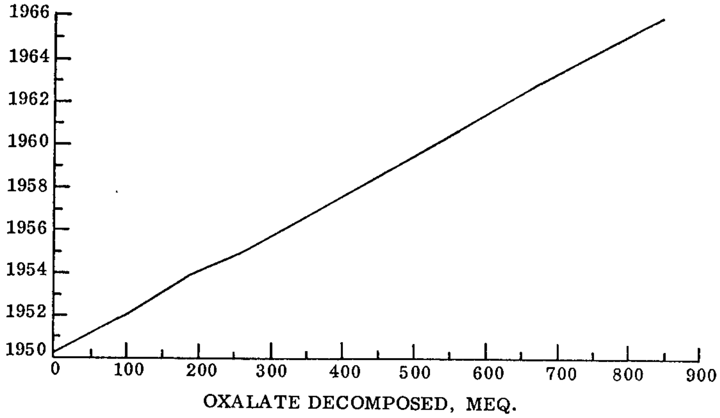

Fig. 2. Integration of actinic radiation in sunlight at Kingsport, Tenn., by oxalate decomposition from 1950 to 1966.

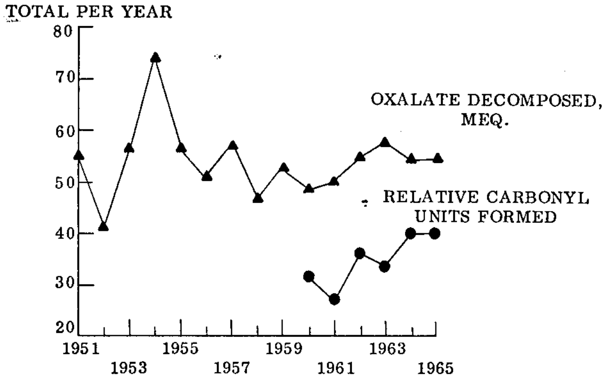

Fig. 3. Integration of actinic radiation in sunlight at Kingsport, Tenn., from 1951 to 1965.

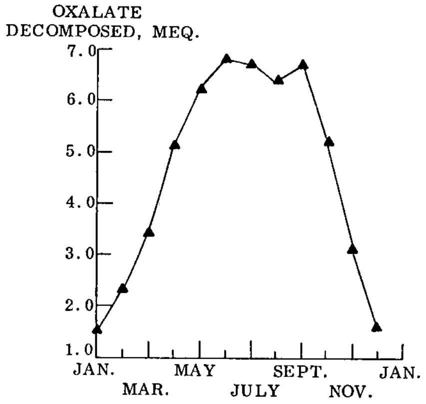

Fig. 4. Average integration of actinic radiation in sunlight at Kingsport, Tenn., by months from 1951 to 1965.

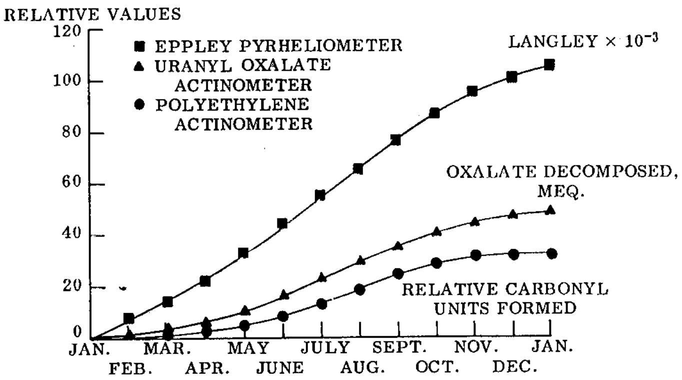

Fig. 5. Integration of actinic radiation in sunlight at Kingsport, Tenn., with actinometers in 1960.

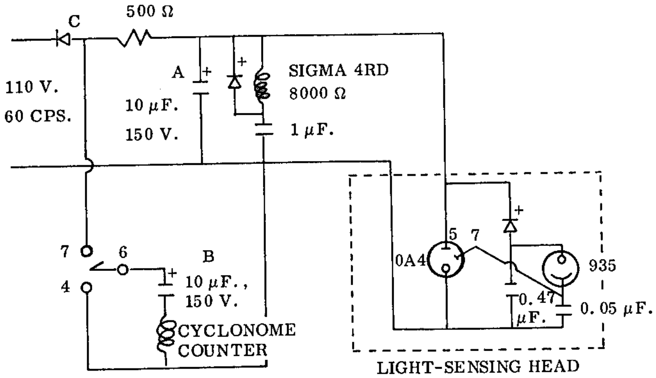

Fig. 6. Wiring diagram for photoelectric integrator.

The wiring diagram for the photoelectric integrator used in the experiments is shown in Figure 6. This instrument employs a photoemissive-type sensing tube (No. 935) as its primary measuring element. This tube is connected in a circuit so that the resistance of the tube acts as a throttling device on the current supplied to charge a condenser (0.05 μf.). When the charge on the condenser has reached an intensity sufficient to ionize the control electrodes of a cold cathode relay tube (OA4), the relay tube conducts, and by its conductance causes current to flow from a condenser (1 μf.) through a coil and close the relay (4RD). The charge is placed on this condenser from a conventional half-wave rectifier circuit by means of a diode which is polarized so that the relay coil is short-circuited during the charging of the condenser. This effectively disables the relay and prevents it from closing during the charging process. The contacts (No. 4, 6, and 7) of the relay are connected to a cyclonome motor and counter assembly in such a way that they cause the motor coil, working with the condenser *B*, to actuate the motor properly. The function of the diode and condenser (0.47 μf.) in the light-sensing head is to provide a stabilization of the direct voltage applied to the photocell circuit. The direct current required to operate the complete integrator is supplied by the diode rectifier *C*, and is filtered by the 500 ohm resistor and 10 μf. capacitor *A*, associated with the rectifier. This type of integrator permits remote recording of the pulses. A count is obtained which can be considered as a measure of ultraviolet langleys received by the specimens being weathered.

The light-sensing head was mounted in a screw-cap aluminum can, 4 in. in diameter, in which a 1.5 in. × 1 in. window had been fabricated. The photocell was screened by a 2.98-mm. thick Corex glass (Corning Glass Works, No. 9863) which transmits light in the range of 250–400 mμ. The light striking the photocell was further screened by a 0.003-in. thick stainless steel sheet in which a pattern of nine holes, 0.04 in. in diameter, had been drilled. The stainless steel sheet was supported by a quartz plate. The light-sensing head was mounted on the same plane as the specimens being exposed. The arrangement of the light-sensing head and the resistance bulb thermometer, (Leeds and Northrup type H with a range of -10 to $+120$°F.) used to monitor temperature is shown in Figure 7.

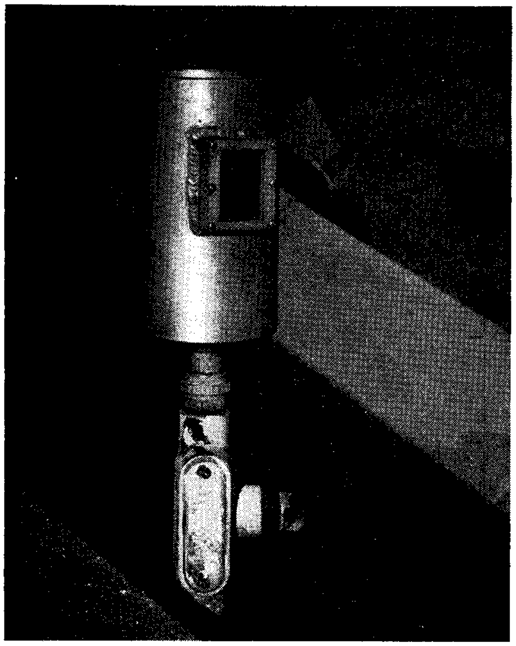

Fig. 7. Photoelectric sensing head at Kingsport, Tenn.

Tenite Polyethylene 800 molded plates, 50 mils thick, were used as the medium for the formation of carbonyl groups. The absorption by the carbonyl groups at 5.82 μ was measured before and after the plates were exposed. The increase in carbonyl content, expressed in relative units, was used as a measure of the actinic radiation. The carbonyl content of the exposed specimens was calculated relative to that of a 70-mil thick sheet as follows:

$$\text{Relative Carbonyl Units} = \frac{\begin{array}{c}\text{Absorbance of exposed 50-mil thick plate}\\ \text{(corrected to a thickness of 70 mils)}\end{array}}{\begin{array}{c}\text{Absorbance of 70-mil thick unexposed}\\ \text{standard}\end{array}}$$

$$= 1346 \times \frac{\text{Absorbance of exposed plate}}{\text{Thickness of plate in mils}}$$

Polyethylene plates 0.5 in. wide × 2.5 in. long were mounted on the sample racks alongside the test specimens being weathered. The increase in relative carbonyl units formed in these plates was plotted versus exposure time. The development of the carbonyl groups was found to be relatively linear for times up to 20–40 days during the summer and up to 2 mo. during the winter. Carbonyl development curves for plates the

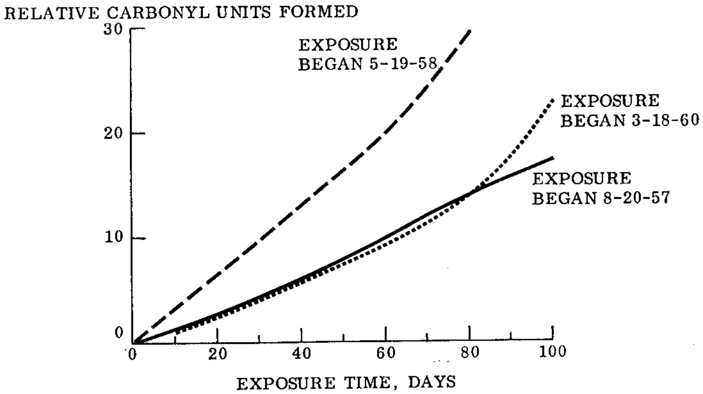

Fig. 8. Formation of relative carbonyl units in polyethylene.

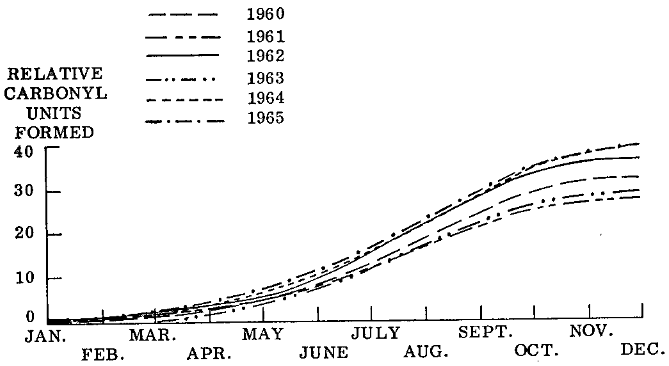

Fig. 9. Integration of actinic radiation in sunlight at Kingsport, Tenn., with polyethylene actinometer from 1960 through 1965.

exposure of which began in the spring, summer, and fall are shown in Figure 8. As shown by the figure, the development of carbonyl during exposure beyond the 20–40 days in summer and 2 mo. in winter accelerated autocatalytically. Exposures on the plates used for actinometry were held within the time period in which the carbonyl development curve was linear. The cumulative curves obtained in this way for the years 1960–65 are shown in Figure 9. Yearly totals are also plotted in Figure 3 for comparison with the uranyl oxalate actinometer integration.

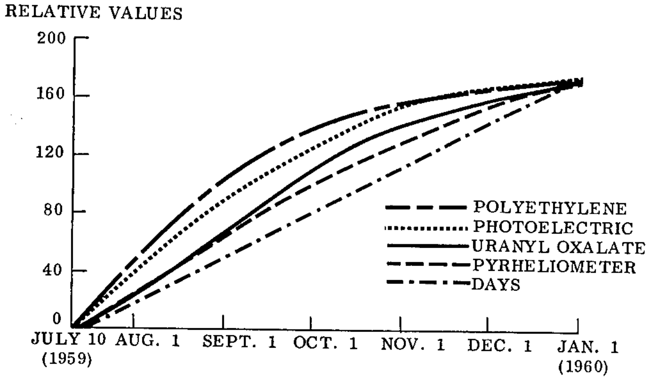

Fig. 10. Comparison of actinometers.

Data were collected concurrently over a period of 6 mo. by all four integrating methods: uranyl oxalate actinometer, pyrheliometer, photoelectric integrator, and determination of relative carbonyl units formed in Tenite Polyethylene 800 molded plates. These data are shown, normalized to days in Figure 10.

Discussion

The actinic radiation as measured by the decomposition of oxalate in the uranyl oxalate actinometer averaged 54 meq./yr. over the period recorded. The maximum (74 meq.) and minimum (41 meq.) amounts of actinic radiation were recorded during the years 1954 and 1952, respectively. The milliequivalents decomposed per month (averaged over a 15 yr. period) indicate that a relatively constant amount of radiation is received during the months of June to September; the average amount is about 6.6 meq./mo. A ratio of 2.1 was found between the decomposition of oxalate during the summer months of July and August and that during the winter months of November and December.

The uranyl oxalate actinometer has been used successfully to integrate the exposure of Tenite Butyrate plastic.[5] It has proved to be very helpful in smoothing out seasonal variations in actinic radiation during the years of use in Kingsport. It has also been applied to the integration of exposures of polyethylene with a similar degree of success.[7]

A disadvantage inherent in the uranyl oxalate actinometer is the cumbersomeness of the preparation and subsequent analysis of the solution. The solution often freezes in winter and the oxalate comes out of solution. This causes a small error in the measurements. The influence of temperature on the rate of reaction is included in the uranyl oxalate actinometer although the temperature coefficient for the decomposition of uranyl oxalate is probably less than that for the degradation of plastics by sunlight.

The Eppley pyrheliometer was at a decided disadvantage in the integration of actinic radiation in sunlight because it was situated under glass which screened a large portion of the ultraviolet light. The major objection to using a pyrheliometer to integrate actinic radiation in the weathering of plastics is the fact that the pyrheliometer integrates the entire sunlight spectrum, and since the ultraviolet radiation is such a small percentage of the total, the variations in ultraviolet integration are smothered by the larger amounts of visible and infrared radiation.

As shown in Figure 10, the curve obtained from integration with the pyrheliometer more nearly follows the linear integration by days than the curves obtained by any of the other methods evaluated. The ratio of summer to winter irradiation is 1.4 for the pyrheliometer. This system might be improved if a suitable filter could be utilized to restrict the integration to the ultraviolet and visible regions of sunlight or to the ultraviolet region alone.

Several serious disadvantages were encountered with the photoelectric integrator. The phototube was so sensitive that full sunlight completely swamped the counter. Some means of reducing the radiation striking the photocell was required. The method described previously in the experimental section was developed after much experimentation. The phototube was found to have a satisfactory lifetime. However, the OA4 tube was very troublesome. It gradually weakened and failed and thus created errors. The integrator required recalibration after each tube replacement. The ratio of ultraviolet light integrated from July 10 to September 1, 1959 to that integrated from November 1 to December 31, 1959 was found to be 4.5. As shown in Figure 10, there is a large difference in the slopes of the summer and winter sections of the curve for the photoelectric integrator.

When all aspects of the integration with the photoelectric integrator were considered, this integrator was found to be more troublesome than the uranyl oxalate actinometer. The high summer to winter ratio (4.5) indicates that the results obtained with the photoelectric integrator should agree with the observed weathering rates in plastics.

The highest ratio of summer to winter integration was found for the polyethylene actinometer. In this case the ratio was 6.7. As shown in Figure 9, the actinic radiation capable of generating carbonyl groups was prominent during the months of July, August, and September where the rate of increase was high. The rate of carbonyl formation was much decreased during the winter months of October through January. A comparison of the curves shown in Figure 8 where the rates of carbonyl formation are shown for samples of polyethylene exposed during the spring, summer, and fall indicates that the rates are approximately the same for spring and fall and that the rate of carbonyl formation during the summer was twice that during the spring and fall. The section of the curve prior to the onset of autocatalysis is linear at all times of the year. The initial rate of carbonyl formation, however, is dependent upon the initial carbonyl content of the polyethylene.

The plot of the cumulative total of relative carbonyl units formed in polyethylene (Fig. 9) during the years 1960 through 1965 shows the yearly variation in total actinic effect and indicates the usefulness of the carbonyl formation method. It is interesting to note the year 1963 where no carbonyl formation was recorded for the months of January and February. This is typical of the weathering rate in Tennessee. We have found that our plastic compositions suffer very little damage during the winter months.

A comparison of the total actinic radiation as integrated by the uranyl oxalate actinometer and the polyethylene actinometer (Fig. 3) indicated that the two methods do not always agree. For example, the total milliequivalents of oxalate decomposed during 1961 and 1963 indicated that each of these two years were more intense than the respective preceding year. The opposite relation is indicated when the total number of carbonyl units are compared.

The polyethylene actinometer has some distinct practical advantages over the other methods described. It is comparatively easy to use and requires only an absorption curve in the 5.82 μ region for analysis. It can be mounted at an angle identical to that of the specimens being tested and only a small strip of polyethylene, sufficient for an infrared curve, is required. A disadvantage is that the rate of carbonyl formation is influenced by the prior oxidative history of the polyethylene, and thus different lots of polyethylene have different rates of carbonyl formation. It is therefore necessary to calibrate each polyethylene with regard to others used as actinometers.

We have found it desirable to use polyethylene which has a very low initial carbonyl content, i.e., 0.3 relative units or less. The different lots of polyethylene can be satisfactorily calibrated by determining the relative rates of carbonyl formation in each during the same exposure interval. It might be possible and even desirable to select polyethylene having a rate most suitable to the plastic being weathered.

Conclusions

Many factors, such as ultraviolet intensity, temperature of the material, relative humidity of surrounding atmosphere, and rainfall, influence the rate at which organic materials degrade when exposed to the weather. Ultraviolet radiation is perhaps the largest factor involved in degrading plastics and in fading dyes. Considerable variation is present in the total energy received as ultraviolet radiation on the earth's surface. Summer to winter variations of the order of 600% were recorded. Some method of integrating the actinic portion of sunlight other than exposure time is desirable in conducting weathering tests outdoors. Of the methods used in collecting the data presented, it is possible that each may have an advantage depending upon the type of material being tested.

In the case of the exposure of plastics in which the degradation is by photo-oxidation, some photochemical method may be best employed. The actinic decomposition of oxalate is such a reaction. In this instance, the influence of temperature on the rate of reaction is included in the actinometer, although the coefficient for the decomposition of uranyl oxalate is probably less than that of the degradation of most plastics by sunlight. A disadvantage inherent in this method is the cumbersomeness of the preparation and analysis of the solutions.

In cases where light fastness of dyes is the major concern, the Eppley pyrheliometer may be best suited as an integrator of actinic radiation since it integrates the entire sunlight spectrum. Many dyes are known to be faded not only by ultraviolet radiation but also by the visible portion of sunlight.[8] The pyrheliometer also has the advantage of giving immediate readings without chemical analyses.

The photoelectric integrator offers the advantage of freedom from analyical procedures. With the proper selection of photocell and screening techniques, any desired portion of the spectrum can be measured. The photoelectric integrator is unlike the chemical actinometers in that the effect of temperature on the photochemical reactions occurring in the materials being studied is neglected. The use of temperature measurements to adjust the count recorded with a properly screened photoelectric integrator could offset this disadvantage.

The increase in carbonyl content of polyethylene upon exposure to natural weathering gives a measure of the photooxidation which occurred. This measure of photooxidation in polyethylene was found to correlate with the degree of loss in physical properties during weathering. Integration with polyethylene might be expected to be the best method for monitoring tests on polyolefins. In this case, the temperature coefficient more closely approaches that for plastics than the temperature coefficients in the other methods and it is included in the system. The analysis is relatively simple; it requires only an infrared curve and a calculation. The polyethylene actinometer was found to have the highest ratio of summer to winter intensity of any of the methods evaluated. The method was found to be applicable to polyethylene and Tenite Butyrate. Further experimentation is needed to determine the applicability to other materials.

The choice of a method for integrating sunlight depends upon the type of material being studied, and it is possible that any of the methods discussed has applications wherein it is best suited. The data presented render it possible to transfer estimates of relative values from one system to another.

The authors acknowledge the assistance of J. W. Henry for the design and construction of the photoelectric integrator and A. L. Stone for the Eppley pyrheliometer data.

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Résumé

Des variations quotidiennes et saisonnières de la partie actinique de la lumière solaire rendaient désirables de développer une méthode précise pour intégrer la radiation actinique des tests de vieillissement à l'extérieur. Les résultats rapportés à Kingsport, Tennessee, sur une période de six ans en utilisant l'oxalate d'uranyle comme actinomètre sont discutés. La comparaison des résultats étudiés avec cet actinomètre, un pyrhéliomètre et un intégrateur photoélectrique, avec ceux obtenus par intégration basée sur la formation de groupes carbonyles au sein de polyéthylène a été faite et indique des degrés variables d'utilité de cette méthode pour contrôler l'intensité de lumière solaire. Cette dernière méthode présente certains avantages marqués.

Zusammenfassung

Tägliche und jahreszeitliche Schwankungen im actinischen Teil des Sonnenlichtes lassen die Entwicklung einer Präzisionsmethode zur Integrierung der actinischen Strahlung bei Aussen-Bewitterungsversuchen wünschenswert erscheinen. In Kingsport, Tennessee, mit einem Uranyloxalatactinometer über einen Zeitraum von sechs Jahren gesammelte Daten werden mitgeteilt. Ein Vergleich der mit diesem Actinometer, einem Pyrheliometer und einem lichtelektrischen Integrator erhaltenen Ergebnisse mit denjenigeneiner auf der Karbonylbildung in Polyäthylen beruhenden Integrierung wurde durchgeführt und zeigte den verschiedenen Brauchbarkeistgrad dieser Methoden für die Kontrolle des Sonnenlichts. Die letzte Methode besass einige deutliche Vorteile.

APPLIED POLYMER SYMPOSIA NO. 4, 131–139 (1967)

A New Technique for Evaluating Outdoor Weathering Properties of High Density Polyethylene

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Synopsis

This paper describes a new test method using highly stressed specimens of high density polyethylene as a means of accelerating the failure of plastics subjected to long-term outdoor exposure. The use of various artificial light sources to accelerate the weathering of plastics has been the subject of many previous studies. However, most of these accelerated studies have not resulted in a completely reliable correlation with data obtained during actual long-term exposure to natural ultraviolet light. The test method described uses natural sunlight as the ultraviolet light source but accelerates failures by inducing artificially high stresses in the test specimens. The technique utilizes the Bell Telephone Laboratories bent strip type specimen which is commonly used for determination of environmental stress crack resistance. The specimens are mounted outdoors and the time to 50% failure is reported. A failure occurs when a crack appears in the stressed area. This outdoor weathering test has been useful in predicting the relative long-term outdoor exposure performance of various high density polyethylene homopolymers and copolymers by evaluating such variables as resin density and melt index as well as pigment and stabilizer systems. These polyethylenes are of the type being used today to manufacture a number of commercial items. While it is beyond the scope of this paper to attempt to predict the actual outdoor service life of any particular plastic piece, the method has been extremely useful as a screening test to optimize the selection of polymers and various stabilizer and pigment systems. Bent strip failures are presented on materials which have been exposed outdoors near Pittsburgh, Pennsylvania, as well as the East Texas Gulf Coast. In both exposure locations, certain pigment systems were observed to prolong the specimen failure time. Likewise, certain ultraviolet light absorber systems were more effective than others evaluated. Paralleling the evaluation of the bent strips was the outside exposure of standard tensile bars. These "unstressed" specimens took considerably longer before exhibiting signs of ultraviolet light degradation. This is further proof of the accelerating effect of applied stress on the degradation of high density polyethylene.

INTRODUCTION

This paper describes a new test method using highly stressed specimens of high density polyethylene as a means of accelerating the failure of plastics subjected to long-term outdoor exposure.

The use of various artificial light sources to accelerate the weathering of plastics has been the subject of many previous studies. However, most of these accelerated studies have not resulted in a completely reliable correlation with data obtained during actual long-term exposure to natural ultraviolet light.

None of the artificial weathering units, such as the Weather-Ometer, Fade-Ometer, Xenon-Arc, or fluorescent sun lamps[1] is capable of exactly duplicating the wavelength of light found in natural sunlight. Admittedly these units produce accelerated failures; however, it is quite common to have specimens which fail early in this type of test perform comparatively well in an outdoor environment and vice versa.

TEST METHOD

The test method described uses natural sunlight as the ultraviolet light source but accelerates failures by inducing artificially high stresses in the test specimens. The technique utilizes the Bell Telephone Laboratories[2] bent strip type specimen which is commonly used for determination of environmental stress crack resistance of ethylene plastics under ASTM D1693-60T. Ten 1.5 × 0.5 × 0.125 in. specimens are cut from a compression-molded plaque which has been prepared under prescribed conditions. A controlled 0.020-in. deep longitudinal slit is cut into the center of each specimen. Then each specimen is bent into a U shape with the stress-inducing slit on the outside and inserted into a channel. The specimens are mounted outdoors and the time to 50% failure is reported. A failure occurs when a crack, or hole which later forms a crack, appears in the stressed area. In reality, this technique evaluates the summation effect of various phenomena such as ultraviolet light degradation, thermal oxidation, and stress crack resistance. Failures are not a result of ultraviolet light degradation alone. As in the case of a chain breaking at its weakest link, a specimen may undergo failure because of an inherent weakness in stress crack or oxidative resistance, ultraviolet light degradation, or any combination of these factors.

In fact one means we have used to accelerate the test method is to purposely choose polymers which are susceptible to stress crack resistance, presuming that the sunlight will degrade these specimens even faster. Other means we have used to accelerate failures include drastically reducing the cooling cycle of the molded specimens to induce additional "molded-in" stresses. Another means of accelerating failures is by the proper choice of geographic location or season of the year in order to increase the amount and intensity of ultraviolet light radiation.

Significance

This outdoor weathering test has been useful in predicting the relative long-term outdoor exposure performance of various high density polyethylene materials by evaluating such variables as:

(*1*) 0.96 density homopolymers versus 0.95 density copolymers of high density polyethylene.

(*2*) average molecular weight or melt index.

(*3*) pigmentation systems.

(*4*) ultraviolet light absorbers, antioxidants, and other additives.

These polyethylenes are of the type being used commercially to manufacture outdoor service items such as beverage cases, produce tote boxes, outdoor stadium seats, lawn furniture, ropes, and protective coatings for steel pipe. While some of these items may be subjected to continuous outdoor exposure, others are exposed to the weather during only a portion of their life span. It is beyond the scope of this paper to attempt to predict the actual outdoor service life of any particular plastic item. There are too many variations in product design, fabrication process, internally or externally applied stresses, service abuse, degree of outdoor exposure, geographical location, etc., to achieve this. However, the method has been extremely useful as an accelerated screening test to optimize the selection of polymers, and various stabilizer and pigment systems.

Quite obviously the use of natural sunlight makes this a relative test, necessitating that suitable controls be established within each test program. Failure times were reported in days, or weeks, but in each case care was exercised to record the exposure location and the date the exposure was started. In order to eliminate the relative nature of this type of test, Messrs. Newland and Tamblyn,[3] in a similar study, used an actinometer and expressed their failure times in milliequivalents of oxalic acid decomposed in a uranyl oxalate actinometer. However, we did not use this type of instrument in our studies.

Experimental Results

Bent strip failures are presented on materials which have been exposed outdoors along the Southeast Gulf Coast (Port Arthur, Texas), as well as 35 mi. west of Pittsburgh (Monaca, Pennsylvania). This evaluation technique was developed during the preparation of a number of customer-oriented laboratory service projects and as such was not designed specifically for the presentation of a technical paper. However, it was felt our findings were interesting enough to submit at this time and could provide a useful basis for future work in this area.

Figure 1 illustrates the effect of polymer melt index, or average molecular weight, on two 0.95 density polyethylene copolymers, both resins being pigmented a dark brown and stabilized with the same antioxidant and the same ultraviolet light absorber. The 50% failure levels during the Texas exposure occurred in 8 wk. for the 3.0 melt index polymer, and 40 wk. for the 1.5 melt index polymer. Failure of the Pennsylvania-exposed specimens occurred in 27 and 88 wk., respectively, for the 3.0 and 1.5 melt index polymers. Thus, a three- to fivefold increase in life was obtained by using a lower melt index polymer. Also shown is the two- to threefold acceleration obtained by exposing the specimens in the more southerly environment.

Figure 2 illustrates a 0.96 density, 0.5 melt index polymer of relatively poor stress crack resistance, failing in 8–9 wk. in Texas whether pigmented with a cadmium yellow system or an "outdoor black" pigment system.

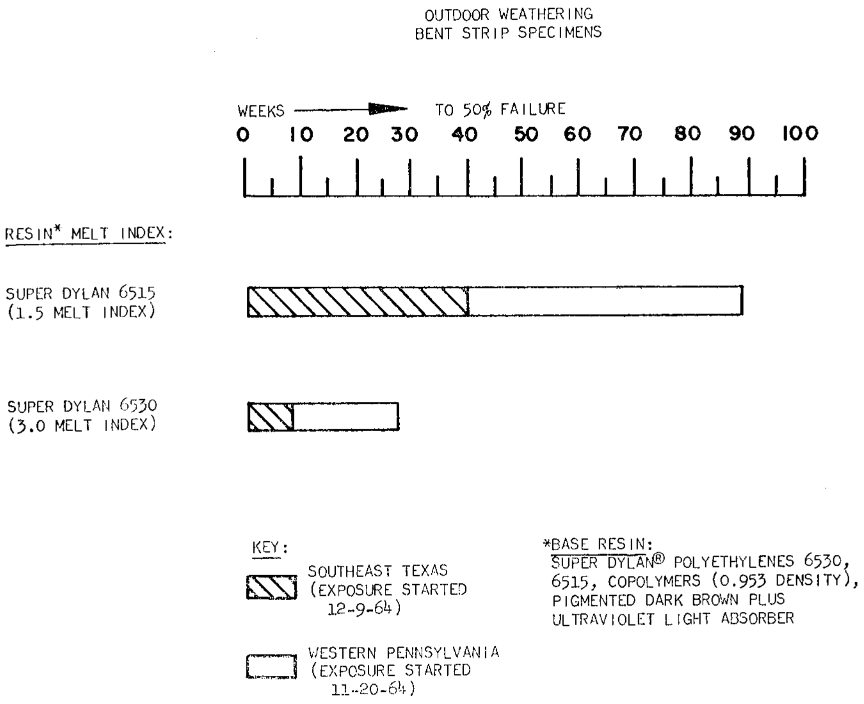

Fig. 1. Outdoor weathering bent strip specimens. Effect of polymer melt index.

In contrast, a natural 0.95 density, 0.25 melt index, high density polyethylene copolymer, with good stress crack resistance and without any pigment or ultraviolet light absorber, lasted 10 wk. However, this copolymer, when evaluated with the same cadmium yellow pigmentation system, lasted over 2 yr. in Texas (111 wk.) before reaching the 50% failure level.

Figure 3 depicts eight different pigment systems evaluated in a 0.95 density, 3 melt index, injection-molding grade, copolymer, each with the same antioxidant and ultraviolet light absorber system. The colors used were a dark blue, dark green, dark brown, terra cotta, beige, red, orange, and yellow. Exposures were carried out simultaneously in Texas and Pennsylvania. The dark blue specimens failed within 3 wk. in Texas and 24 wk. in Pennsylvania; in both cases blue was the first color to fail. The color which afforded the best protection was the orange pigment system. The orange specimens failed after 18 wk. in Texas and 36 wk. in Pennsylvania. The yellow and red colors were almost as effective as the orange. However, it must be pointed out that the pigment concentration levels between colors were not held constant as these colors were formulated to meet a particular customer's marketing requirements.

Thus, in the case of the blue, failure occurred eight times faster in Texas than Pennsylvania, and for the orange only twice as fast. Standard $^1/_8$-in.

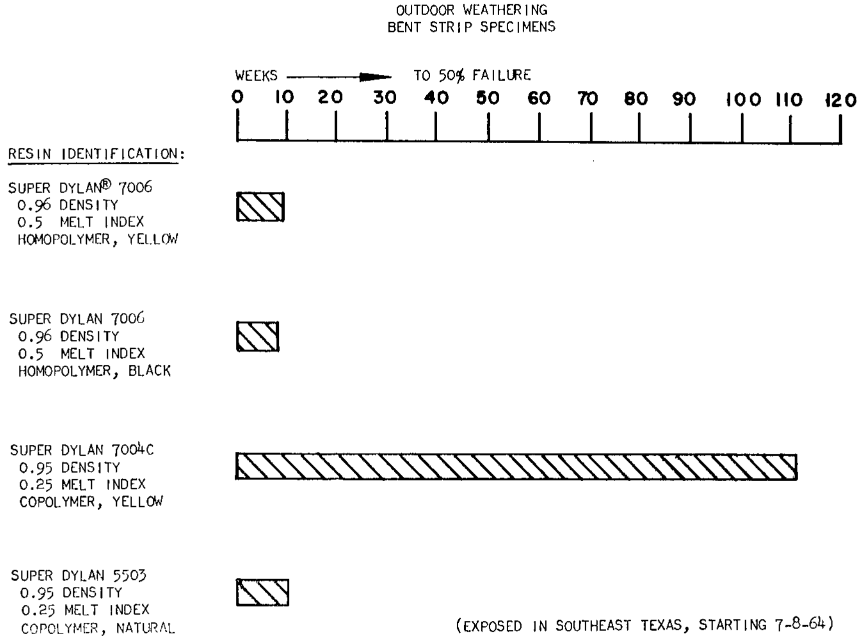

Fig. 2. Outdoor weathering, bent strip specimens. Effect of density, melt index, and pigmentation.

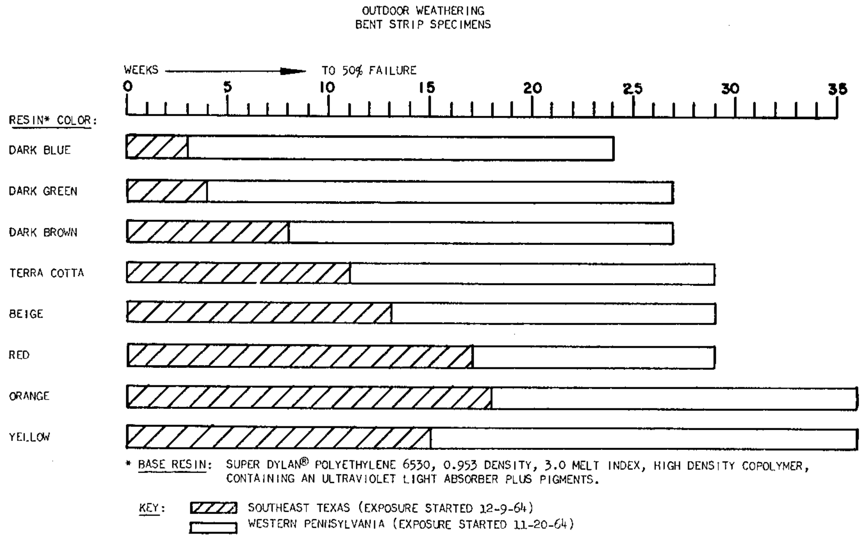

Fig. 3. Outdoor weathering, bent strip specimens. Screening ability of various pigment systems.

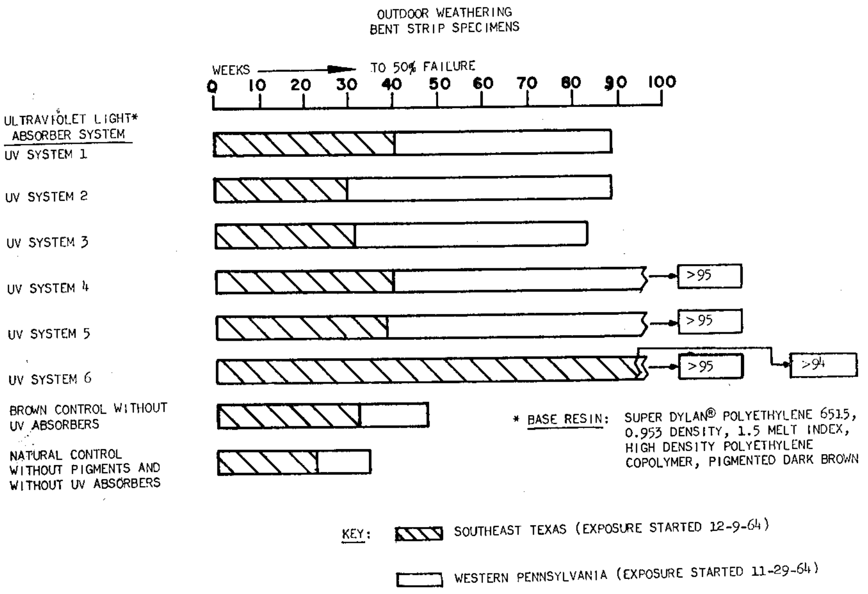

Fig. 4. Outdoor weathering, bent strip specimens. Screening ability of various ultraviolet light absorbers.

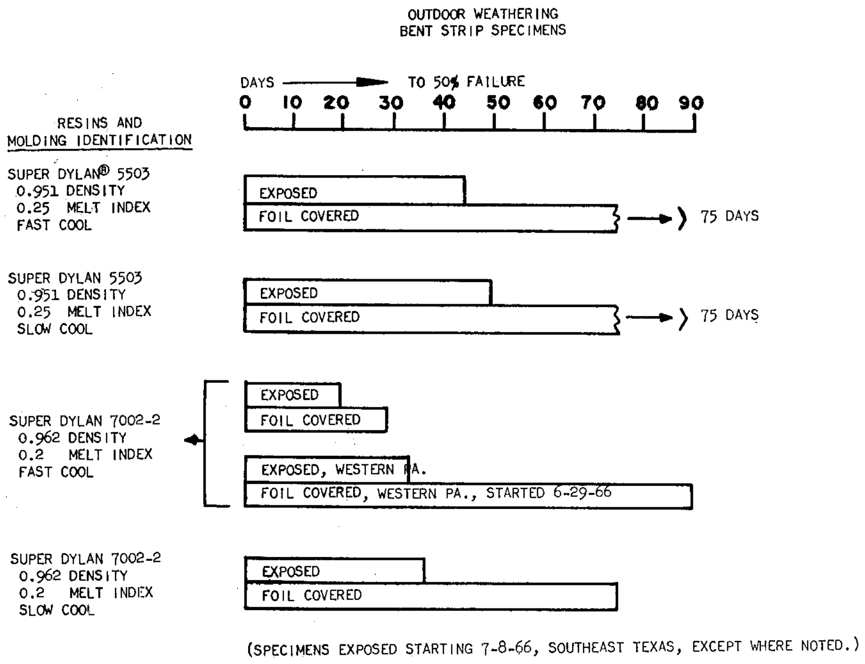

Fig. 5. Outdoor weathering, bent strip specimens. Effect of sunlight.

thick injection-molded tensile bars molded from the same eight batches of colored polyethylenes were exposed simultaneously at the two outdoor locations as well as in a Fade-Ometer. It is interesting to note that after 52 wk. outdoor exposure, and 2000 Fade-Ometer hours, none of the eight colors has exhibited any significant deterioration in tensile properties. These tensile specimens mounted outdoors will be evaluated at 1-yr. intervals for 5 yr. We will be interested to learn if the relative tensile property deterioration of the eight colors, as noted by a greater than 50% loss in elongation, parallels the bent strip data presented in Figure 3. Fade-Ometer data on the tensile bars will be obtained up to 5000 hr.

Figure 4 compares the weathering properties of several ultraviolet light absorber systems, all compounded in a dark brown 0.95 density, 1.5 melt index, high density polyethylene copolymer. Two controls were used; the same dark brown polymer without any ultraviolet light absorber, as well as the same polymer unpigmented, also without an ultraviolet light absorber. Again exposures were carried out simultaneously at the Texas and Pennsylvania locations. By studying Figure 4 one can see the moderate benefits afforded by the brown pigment system and most of the ultraviolet light absorber systems. However, of special interest to us was the vastly superior protection afforded by UV System Number 6. Once again, simultaneously exposed tensile bars have shown no loss of properties after 52 wk. outdoors, or 2000 Fade-Ometer hours.

The data presented in Figure 5 were designed specifically to separate the factors of ultraviolet light degradation from those failures due to stress cracking and thermal embrittlement in this test method. Duplicate specimens were mounted outdoors. but in each case one set was covered with a hood of aluminum foil to screen out all direct sunlight. Natural polymers, without ultraviolet light absorbers, were used in this study. Also used were two sets of molding conditions to determine the effect of the added internal molding stresses caused by rapid cooling of the plaques. The prolonged times to failure of specimens mounted under the aluminum foil hood is vivid proof of the deterioration effect of natural sunlight. Also evident is the slight acceleration effect of the more rapidly cooled specimens.

CONCLUSION

The exposure of highly stressed specimens of high density polyethylene in natural sunlight is an effective means of obtaining accelerated outdoor weathering data. Though results are relative in nature, the technique serves as an extremely useful tool in rating the effects of weathering on such variables as polymer types, pigment systems, ultraviolet light absorbers, and other additives.

Thanks are given to Messrs. E. Chappel, N. Richey, L. T. Smith, and H. L. Zimmerman of the Sinclair-Koppers Company, Product Development Laboratory and Port Arthur, Texas, Polyethylene Plant Control Laboratory, for their specimen preparation and compilation of data through heat waves and hurricanes alike.

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Résumé

Ce manuscrit décrit une nouvelle méthode d'essai utilisant des échantillons hautement étirés de polyéthylène de haute densité comme moyen d'accélérer la cassure des plastiques sujets à des expositions à l'extérieur de longue durée. L'utilisation de diverses sources de lumière artificielle en vue d'accélérer le vieillissement des plastiques a été l'objet de nombreuses études antérieures; toutefois, la plupart de ces études avec accélération n'ont pas donné une corrélation claire avec les résultats obtenus par des expositions actuelles à long terme pour la lumière ultraviolette et naturelle. La méthode d'essai décrite utilise la lumière naturelle comme source de lumière ultraviolette, mais accélère le défaut en incluant des tensions élevées dans les échantillons. La technique utilise des échantillons sous forme de bandelettes suivant le procédé des 'Bell Telephone Laboratories' qui sont communément utilisés pour la détermination de la résistance à la failure sous la tension environnante. Les échantillons sont montés à l'extérieur et on note le temps pour un défaut atteignant 50%. On note comme défaut l'apparition d'une failure dans la région soumise à tension. Ce temps de vieillissement extérieur à été utile pour prédire la performance au cours de l'exposition à durée relativement longue de homopolymères et de copolymères de polyéthylène de haute densité en évaluant de telles variables, à savoir la densité de la résine, l'indice de fusion, de même que des systèmes de pigments et de stabilisateurs utilisés. Ces polyéthylènes sont du type utilisé actuellement dans la manufacture d'objets commerciaux. Bien que cela dépasse l'objet du présent manuscrit d'essayer de prédire la durée de service à l'extérieur d'un objet en plastique déterminé, la méthode a été extrêmement utile comme test de sélection pour assurer la meilleure sélection des polymères, et les différents systèmes stabilisateurs et pigments. On montre des défauts qui se présentent dans des bandelettes soumises à tension et exposées à l'extérieure près de Pittsburgh, Pa., aussi bien qu'à la côte Est du Golfe du Texas. Dans les deux cas, certains systèmes de pigments prolongèrent la durée de vie avant l'apparition de défauts. De même certains systèmes absorbants de la lumière ultraviolette étaient plus efficaces que d'autres. Parallèlement à cet examen sur des bandalettes tendues, on a également considéré l'exposition à l'extérieur de barres de tension étalon. Ces échantillons non-étirés nécessitaient des durées beaucoup plus longues avant de manifester une dégradation à la lumière ultraviolette. Ceci est une preuve supplémentaire de l'effet accélérateur de l'application d'une tension à la dégradation de polyéthylène à densité élevée.

Zusammenfassung

Eine neue Testmethode wird beschrieben, bei welcher Proben von Polyäthylen hoher-Dichte unter starker Spannung als Mittel zur Beschleunigung der Zerstörung von Plasto meren bei langzeitiger Exponierung im Freien verwendet werden. Die Anwendung verschiedener künstlicher Lichtquellen zur Beschleunigung der Bewitterung von Plastomeren wurde in vielen früheren Arbeiten untersucht. Die meisten dieser Beschleunigungsversuche brachten aber keine völlig verlässliche Korrelation zu den bei einer richtigen langdauernden Exponierung gegen natürliches, ultraviolettes Licht erhaltenen Daten. Die beschriebene Testmethode verwendet natürliches Sonnenlicht als Ultraviolettquelle, beschleunigt aber die Schädigungen durch künstliche Induzierung hoher Spannungen in den Testproben. Es werden Proben vom Biegestreifen-Typ der Bell Telephone Laboratories verwendet, wie sie gewöhnlich zur Bestimmung der milieubedingten Spannungs-

Rissbeständigkeit dienen. Die Proben werden im Freien eingespannt und die Zeit bis zum 50% igen Versagen wird ermittelt. Als Versagen wird das Erscheinen eines Risses in der gespannten Fläche betrachtet. Dieser Bewitterungstest im Freien war zur Vorhersage des relativen Verhaltens verschiedener Polyäthylenhomopolymere hoher Dichte und vom Copolymeren bei langzeitiger Exponierung im Freien brauchbar, wobei Variable, wie Dichte und Schmelzindex des Harzes sowie Pigment- und Stabilisator-systeme in Betracht gezogen wurden. Diese Polyäthylene gehören zu dem heute zur Erzeugung einer Reihe handelsüblicher Produkte verwendeten Typ. Die Voraussage der tatsächlichen Gebrauchs-Lebensdauer irgend eines Plastik-Gegenstandes im Freien geht über den Rahmen der vorliegenden Mitteilung hinaus; die Methode hat sich aber als Test zur optimalen Auswahl von Polymeren sowie verschiedener Stabilisator- und Pigmentsysteme erwiesen. Die Zerstörung von Biegestreifen von Stoffen durch Bewitterung bei Pittsburgh, Pennsylvanien, und an der Ostküste des Golfes von Texas wird beschrieben. An beiden Orten verlängern gewisse Pigmentsysteme die Lebendauer der Probe. In gleicher Weise waren gewisse Absorbentien für Ultraviolettlicht wirksamer als andere. Parallel zu den Biegestreifen wurden Standard-Zugstäbe bewittert. Diese "nicht verspannten" Proben brauchten viel länger, bevor Anzeichen eines Ultraviolettlicht-Abbaues auftraten. Das bildet einen weiteren Beweis für die beschleunigende Wirkung einer angelegten Spannung auf den Abbau von Polyäthylen hoher Dichte.

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Practical Approach to the Study of Polyolefin Weatherability

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Synopsis

Six test methods for monitoring UV degradation were evaluated. They included surface crazing, tensile properties, flex tests, brittleness temperature, melt index, and aging of stressed specimens. Of these methods, there is a reasonable correlation between flex tests, tensile properties, and aging of stressed specimens. However, aging of flexed specimens and tensile strength compare very closely and for this reason a decrease to one-third the original tensile strength was the criterion used to indicate failure of aged specimens for this study. Aging at 45° south at three different locations indicated that 1 yr. in Phoenix, Arizona, is approximately equivalent to at least 2 yr. in Bartlesville, Oklahoma, and to greater than $3^1/_2$ yr. in Akron, Ohio. While there is scattering of data, Weather-Ometer results indicated that 1000–2000 hr. exposure are approximately equivalent to 12–24 mo. in Arizona at 45° south, 3000–4000 hr. compare to 24–36 mo., and over 5000 hr. compare to greater than 42 mo. with the same relationship holding for Arizona and the other two locations. The comparison of EMMA (Equatorial Mount with Mirrors) and Weather-Ometer aging indicates some contradictory data even though EMMA has some value for accelerated aging. Comparison of Weather-Ometer aging and outdoor service of several commercial polyethylene items indicates that predictions based on Weather-Ometer data from correlations shown in this paper are conservative. None of the weathering devices studied correlate too closely with actual outdoor service, but are effective for screening and for establishing guidelines for estimating outdoor service life.

Introduction

It would certainly be desirable to have a weathering device which would accurately and rapidly predict the outdoor service life of a plastic formulation. The use of such an instrument would ultimately result in improved stabilization systems for polyolefin resins. However, in the absence of such equipment, it is often necessary to make use of the Edisonian approach to developing suitable outdoor resin formulations. There is little doubt that this "trial and error" method is a very costly as well as a time-consuming procedure to follow. However, if the use of plastics in outdoor applications is ever to be promoted, it is a path which must be traveled.

In the following presentation, general, practical approaches that can be employed in the evaluation, formulation, and prediction of long weathering polyolefin compositions will be reported. This will include a discussion of the significance and limitations of the various test methods which can be used to monitor UV-induced degradation in polyolefins. In addition, the effects of polyolefin structure, the type and concentration of pigments and UV absorbers, and the geographic location and type of exposure on the ultimate weatherability of polyolefin formulations will be discussed. Finally, a number of application areas will be discussed in which polyolefin resin formulations have been successfully used for greater than 7 yr. Wherever possible, the long weathering formulation used in these application areas will be related to accelerated weathering data to indicate the type of correlation that is possible.

History of Test Methods

The rapid technological advances in ultraviolet stabilization of polyolefins has generated a great interest in test methods for monitoring UV degradation. A literature search discloses a variety of techniques which have been or still are being employed as criteria for resin degradation resulting from ultraviolet exposure. Some of the methods encountered include determination of tensile properties,[1–5,7–9] carbonyl absorption,[2,6–8,10] flex tests,[6–8] brittleness temperature,[1] UV absorber concentration,[7] flexural strength,[2,11] power factor,[1,12] dielectric constant,[1] melt index,[13] surface crazing,[4] and aging of stressed specimens.[2,4,11] In order to determine which of these procedures provides a realistic indication of UV-induced degradation, each method was carefully reviewed with the intention of selecting several methods for further study. Since tensile properties are the most commonly used criteria for determining weatherability of plastics, it is interesting and beneficial to compare this method with others less commonly employed. On this basis, the techniques chosen in addition to tensile properties included surface crazing, melt index, flex tests, brittleness temperature, and aging of stressed specimens.

For this study, both natural and UV-stabilized (0.1% UV-531, a substituted benzophenone) ethylene–butene-1 copolymer in the appropriate form were exposed for varying lengths of time in an Atlas XW Weather-Ometer, and subsequently evaluated by these six techniques. Since most of these test methods can be found in the literature, no attempt will be made in this report to record the details of the individual procedures except in instances where more than one method of evaluation may be possible.

On the basis of this preliminary evaluation, the following generalizations were drawn:

(*1*) Surface crazing does indicate specimen or sample failure and correlates very well with tensile properties as long as the same individual evaluates all samples. The disadvantage to this test is that the failure point is a matter of personal opinion which makes it difficult for two laboratories or even two individuals to obtain comparable results on the same sample.

(*2*) There does not appear to be any correlation between melt index and the other test methods employed. No abrupt change in the slope of the melt index versus exposure time curve was evident. The curve served only to indicate a rapid decrease in melt index initially and then a very gradual increase with increasing exposure. Theoretically, if the mechanism involved is chain scission, there should be a rapid increase in the melt index at the time at which the resin is degraded as indicated by other test methods. In this particular study, the melt index increase was relatively small after the initial drop.

(*3*) The flex life test, in which tensile specimens (ASTM D412-61T, Die C), are slowly bent 180° with the exposed surface on the outside, appeared to indicate some correlation with absolute elongation. For the most part, when absolute elongation was less than 10%, the specimen would break when subjected to these conditions. Sample breaks were very few when elongation values were greater than 10%. Although there were some exceptions to this generalization, they were believed to be due to the test error in measuring tensile properties.

(*4*) Brittleness temperature results indicated that failure time was obtained in only one-half of the exposure hours required to reduce elongation an absolute value of 10%. It should be noted that the failure point was arbitrarily selected as −50°F. since the slope of the curve at that point is almost perpendicular. This is not unexpected for high density polyethylene since the surface crazing would decrease the impact strength due to its notch sensitivity. The failure point used in this study would have significance only with resins having less than −100°F. initial brittleness temperature since some resins would be brittle at −50°F. before any exposure.

(*5*) The bent strip test in which 0.060-in. thick specimens, $1^1/_2$ in. in length and $^1/_2$ in. in width were bent 180°, inserted in a metal channel and aged, became brittle at almost the same point at which tensile strength had been decreased by one-third.

Table I summarizes the relationship between these various test parameters with Weather-Ometer exposure hours. It was concluded from these data that UV degradation of weathered specimens could be followed by tensile strength, elongation or embrittlement of a bent strip. Be-

TABLE I

A Comparison of Hours to Failure for Various Test Methods

Test procedure	Hours to failure: With UV absorber, hr.	Hours to failure: Without UV absorber, hr.
Tensile strength to $^2/_3$ original value	1050	250
Elongation to absolute value of 10%	800	225
Brittleness temperature, −50°F.	400	125
Bent strip, F_{50}	1000	260

cause of the equipment available and ease of testing, tensile strength was chosen. For the purposes of this paper, the point at which the tensile strength was two-thirds of its original value was chosen as the failure point.

Effects of Geographic Location

It is well known that the geographic location of exposure can play an important part in the outdoor life expectancy of a plastic item. However, very little information is available concerning the differences in weathering effects that can be expected from various locations. In this study, three different locations were employed: Phoenix, Arizona; Bartlesville, Oklahoma; and Akron, Ohio. Unbacked tensile specimens were exposed at 45° south in all three locations and tensile strength was determined at periodic time intervals. Table II illustrates the results of this study.

TABLE II
Exposure Result (45° South) at Three Locations

Formulation	Months to failure[a]		
	Arizona	Oklahoma	Ohio
UV-stabilized natural polyethylene homopolymer	<12	12	18
UV-stabilized natural polyethylene homopolymer	<12	18	24
UV-stabilized natural polyethylene homopolymer	12	18	30
UV-stabilized natural ethylene–butene-1 copolymer	<12	18	30
UV-stabilized natural ethylene–butene-1 copolymer	12	30	>42
Green-stabilized ethylene–butene-1 copolymer	12	30	>42
Blue-stabilized polyethylene homopolymer	36	>42	>42
Red-stabilized ethylene–butene-1 copolymer	>42	>42	>42

[a] Reduction of tensile strength by one-third.

These results indicate that 1 yr. exposure in Arizona is approximately equivalent to 2 yr. in Oklahoma and to greater than $3^1/_2$ yr. in Akron, Ohio. It should be noted that this correlation is not, by any means, foolproof since some exceptions are evident. Nevertheless, it should be useful as a "rule of thumb" approximation for obtaining some indication of the effect of weathering in these different geographic locations.

Comparison of Weathering Devices

Another important area investigated was to determine whether a correlation exists between Weather-Ometer and outdoor exposure. For this study, tensile specimens were exposed both in the Weather-Ometer

TABLE III
Correlation of Weather-Ometer Hours to Actual Outdoor Exposure in Months

Hours of exposure,	Months of exposure		
Weather-Ometer hours	Arizona	Oklahoma	Ohio
1000–2000	12–24	24–42	>42
3000–4000	24–36	>42	>42
5000	>42	>42	>42

and in Arizona, Oklahoma, and Ohio at 45° south. The same criterion of failure was used in this study as in the preceding one and the results of this investigation are summarized in Table III. It should be noted that these data are a summary of over 7 yr. correlation between Weather-Ometer results and outdoor exposure in Arizona. Again, it should be used only as a general yardstick for correlating outdoor performance to performance in a Weather-Ometer. It should be noted that these results do not take into account the differences which can exist between Weather-Ometers.

In addition to the program of correlating Weather-Ometer data to outdoor exposure, some limited studies were also conducted comparing Weather-Ometer data to EMMA results. The EMMA is an equatorial mount with mirrors mounted at an angle of 45° that is reported to accelerate outdoor aging by a factor of 6–10-fold. This was the primary interest in exploring this device. When an attempt was made to correlate data obtained from EMMA and the Weather-Ometer, major discrepancies became apparent. For example, Figure 1 shows that an orange formulation is much better in Weather-Ometer aging than the titanium dioxide pigmented formulation. However, as is evident from Figure 2, EMMA results indicate that the white formulation is equal or superior to the orange compound. Although this example is shown for polypropylene monofila-

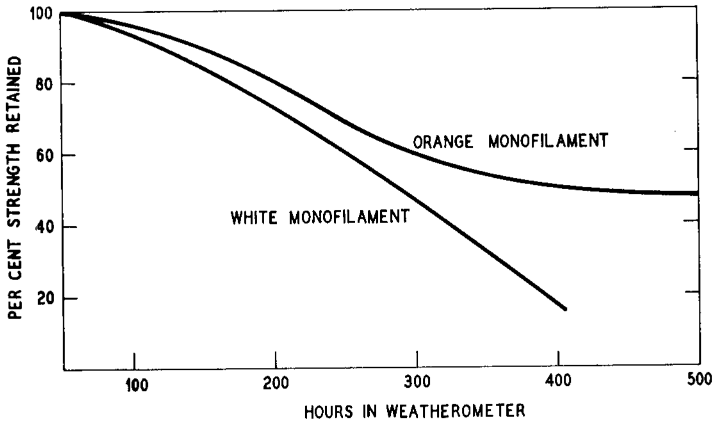

Fig. 1. Weather-Ometer exposure of polypropylene monofilament.

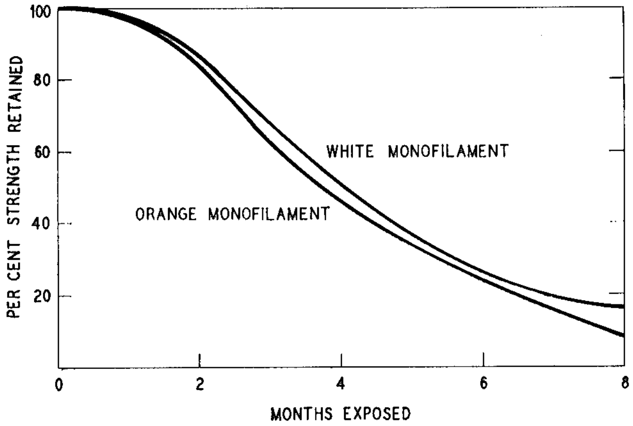

Fig. 2. Results of EMMA exposure of polypropylene monofilament.

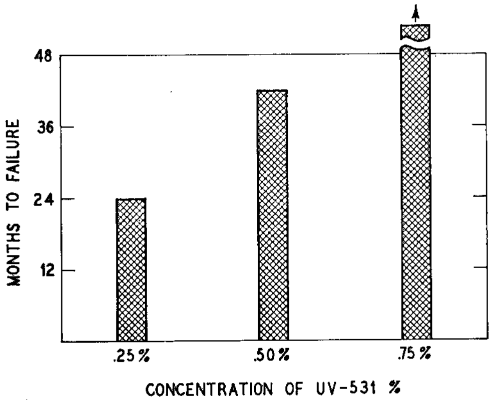

Fig. 3. Exposure of three levels of UV-531 in high-density polyethylene at 45° south (Arizona).

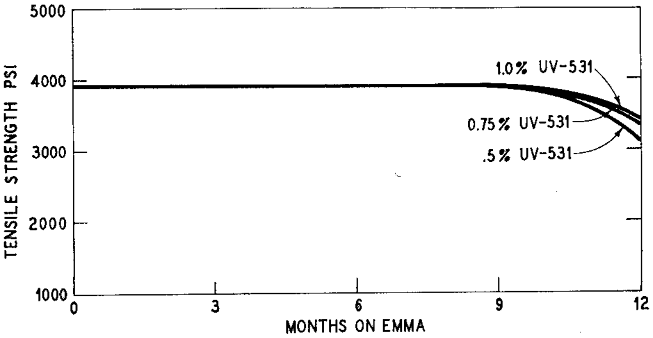

Fig. 4. Effect of UV concentration on weatherability of high-density polyethylene exposed on EMMA.

ment, the same directly conflicting data have been obtained on polyethylene tensile specimens from other tests performed.

There is also some question of whether EMMA may accelerate the process of degradation too rapidly. Figure 3 illustrates the effect of UV-531 concentration on degradation of compounds exposed at 45° south in Arizona. From this data, it is evident that increasing the concentration of UV absorber increases the overall resistance of the formulation of UV-induced degradation. However, when similar samples were exposed on the EMMA for a period of 12 mo. (see Fig. 4), there is indication that the differences noted in Figure 3 are not as obvious.

Effect of Polyethylene Type

Along this same line, it is of interest to compare Type I and Type III polyethylene resins in the Weather-Ometer and on EMMA. Figure 5 indicates that after 2500 hr. exposure in the Weather-Ometer, the Type I resin had retained less than two-thirds of its original tensile strength while the Type III resin was virtually unaffected. Conversely, the Type I material had retained a much higher absolute per cent elongation than the high-density resin. However, if one were to calculate per cent elongation retained, it would more closely correlate with the tensile strength because the low density resin retains a larger per cent absolute elongation by virtue of the fact that the original elongation is much greater.

A comparison of Figures 5 and 6 indicates that EMMA exercises a greater effect on low-density resin and less on high density polyethylene than does the Weather-Ometer. Although tensile strength values in both Figures

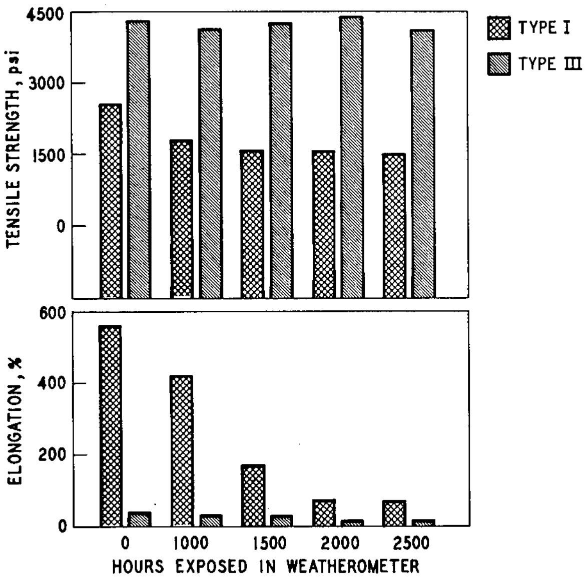

Fig. 5. Effect of density on weathering resistance of polyethylene resins.

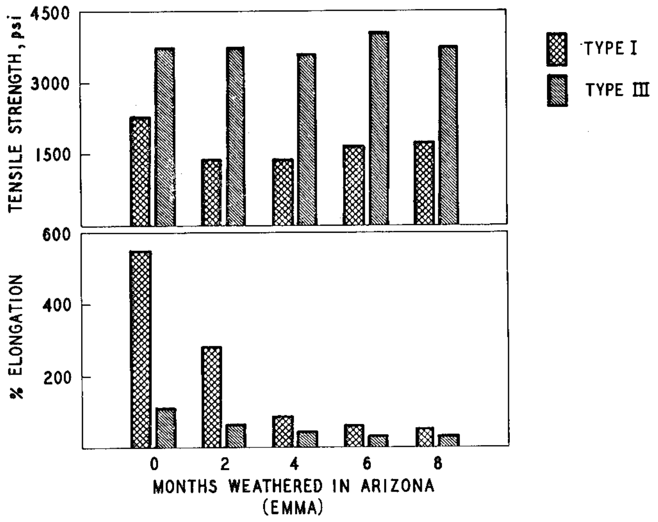

Fig. 6. Effect of density on weathering resistance of polyethylene resins.

5 and 6 are similar, the elongation is quite different. At the end of the test period, the elongation of the Type I resin was closer to the Type III resin in the specimens exposed on EMMA than those exposed in the Weather-Ometer.

Effect of Carbon Black Type

A test to determine the stabilizing effect of two types of carbon black was performed on EMMA. Two ethylene–butene-1 copolymer blends were prepared. One blend contained $2^1/_2\%$ channel black while the other blend

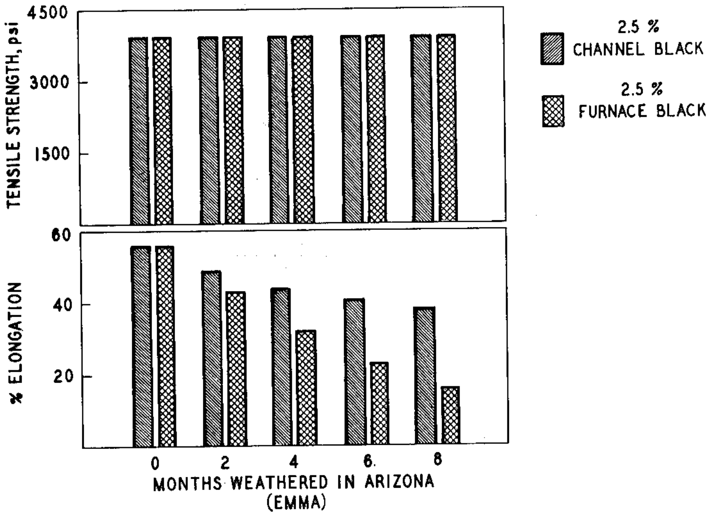

Fig. 7. Effect of carbon black type on weathering of Marlex ethylene–butene-1 copolymer.

was compounded with $2^1/_2\%$ furnace black. The results of the data obtained from 8 mo. exposure on EMMA are shown in Figure 7. Although the tensile properties remained essentially constant during the exposure period, the elongation of the sample containing channel black decreased to approximately 37% and for the resin containing furnace black to about 16%. It is difficult to interpret these data properly in view of the fact that samples containing $2^1/_2\%$ furnace black have been exposed in an Atlas Weather-Ometer for greater than 25,000 hr. without any brittleness or significant loss in tensile properties.

Applications

The Weather-Ometer is the accelerated weathering device most commonly used in the plastics industry. It is interesting to compare Weather-

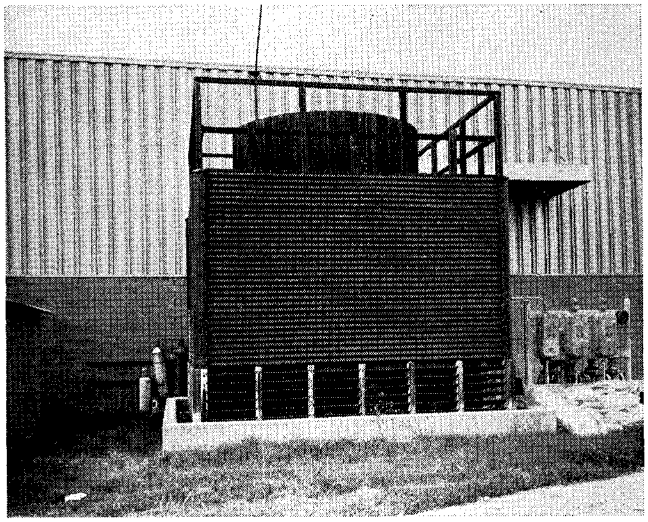

Fig. 8. Cooling tower.

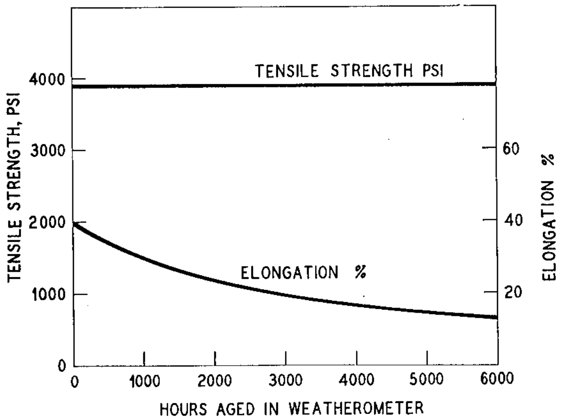

Fig. 9. Effect of weathering of cooling tower side panels.

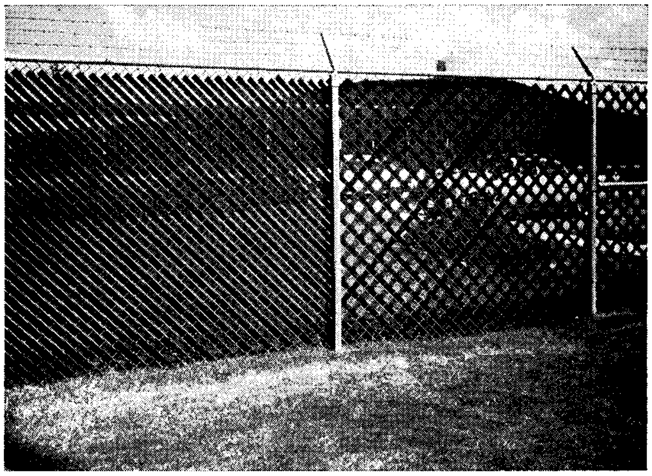

Fig. 10. Fencing strips.

Ometer results with actual service conditions for an item. This can be determined by examining a number of actual applications which have a history as great as 9 hr. The first application is cooling tower side panels which were fabricated from high-density polyethylene (density 0.960, melt index 0.2). This tower, which is shown in Figure 8, has been in service in Bartlesville, Oklahoma, for 9 yr. with no visible indication of failure. Recent tests gave a tensile strength of 3900 psi and an absolute elongation of 13%. Weather-Ometer data obtained on this same color formulation is shown in Figure 9. It should be noted that this particular green formulation has retained its tensile strength after 6000 hr. of exposure in the Weather-Ometer and the elongation has decreased to an absolute value of 16%. One item that should be noted is that the thickness of the cooling tower side panels is in the range of 100–125 mils whereby the specimens

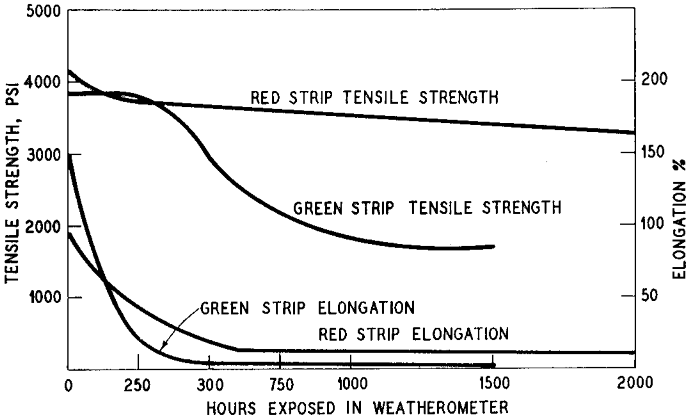

Fig. 11. Effect of the weathering on fence strip exposed in Oklahoma.

aged in the Weather-Ometer were only 60 mils in thickness. As was previously reported,[14] thickness can and does have an effect on weathering resistance. The important fact, however, is that the formulation which has lasted greater than 6000 hr. in the Weather-Ometer has lasted greater than 9 yr. in outdoor service in Oklahoma.

Another interesting application to review is fencing strip material. In this application, strips of polyethylene sheet are interwoven in a chain link fence for decorative purposes. Figure 10 is an illustration of this application. Two colors were employed, a red and a green. Tensile properties versus Weather-Ometer exposure hours for these formulations are shown in Figure 11. It should be noted that the red formulation is still satisfactory after 2000 hr. in the Weather-Ometer, whereas the green formulation failed after only 525 hr. employing the one-third decrease in tensile strength as the criterion for failure. Using the correlation discussed from information given in Table II, this would indicate a life greater than 42 mo. for the red formulation in Oklahoma and less than 24 mo. for the green compound. In actuality, however, the fencing strips are still in service in Bartlesville, Oklahoma, after more than 6 yr. use. Tensile properties determined after 6 yr. of exposure on the actual fence material indicated tensile strengths and elongations of 5000 psi and 14% for the red, as compared to 4800 psi and 13% for the green material.

Another very successful outdoor application for high-density polyethylene is rural delivery newspaper tubes. There are a number of color formulations used for this application, such as black, red, blue, green, and white. With the exception of the black compound, the remaining color formulations when exposed in a Weather-Ometer showed failure times in the range of 800–1500 hr. This would indicate a service life in the Ohio area of approximately 3–3$^1/_2$ years. Actual tubes which were exposed in the Ohio area for approximately 3–3$^1/_2$ years were evaluated for tensile and impact properties and these results are tabulated in Table IV. The tensile strength of specimens cut from the different colored tubes showed little variation. All were acceptable. The only information obtained to compare with the loss of tensile properties as shown by Weather-Ometer data on these colors was obtained from the falling ball impact test on the molded part. For

TABLE IV

Properties of Newspaper Delivery Tubes after 3 yr. Outdoor Service

	Sample designation				
	Black	Red	Blue	Green	White
Tensile strength, psi, tube exposed	4050	3440	4060	3480	3520
Absolute elongation, %, tube exposed	44	47	32	27	43
Impact strength, ft.-lb. to failure, tube exposed	64	56	32	32	24

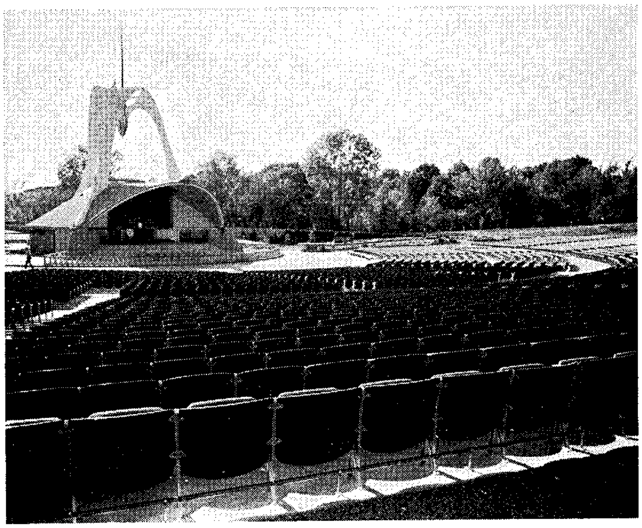

Fig. 12. Stadium seats, Bellville, Illinois.

Fig. 13. Stadium seats, Los Angeles, California, Coliseum.

both this test and the Weather-Ometer data, the black exhibits the best weathering resistance followed by the red, blue, green, and finally the white.

Another example of an excellent outdoor application for high-density polyethylene is outdoor stadium seats. Injection-molded seats with a nominal thickness of 180 mils have been in service at Bellville, Illinois, for $3^1/_2$ yr. with no failures and no visible evidence of degradation. An illustration of these seats is shown in Figure 12. Blow-molded seats also have been in service in the Los Angeles Coliseum for more than 2 years.

These are illustrated in Figure 13. An interpretation of Weather-Ometer data indicated that these formulations should last a minimum of 6 yr.

Another interesting, although small, application for polyethylene was a traffic marker guide. This application originated before the advent of the UV stabilizers normally used for polyolefin resins today. In fact, this particular yellow formulation was stabilized with phenyl salicylate. It was not unexpected, therefore, that Weather-Ometer data indicated complete embrittlement after only 500 hr. of exposure. It is interesting to note that the traffic guide markers have been in service over 7 yr. in Oklahoma and have rendered satisfactory service. Needless to say, however, there was some evidence of surface crazing on the part as well as some loss in the original color.

Conclusions

It is apparent that the interpretation of Weather-Ometer data described in this paper will, with few exceptions, give a very conservative estimate of the outdoor service life of the formulations. Some of the reasons for this have been discussed many times and are well known. However, all of the applications mentioned in this paper clearly indicate a need for an accelerated weathering device which will accurately predict outdoor service life. All of the weathering devices used do serve a useful purpose. They are useful, within limits, for predicting the expected outdoor life of a formulation as well as screening test samples for future outdoor service. However, the best test of a plastic item is still its satisfactory performance in outdoor service.

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Résumé

Si méthodes d'essais pour enrégistrer la dégradation ultraviolette ont été évaluées. Ils comportent le fendillement superficiel, les propriétés de tension, les tests de flexion, la température de fragilité, l'indice de fusion, et le vieillissement de ces échantillons tendus.

De ces méthodes, il y a une corrélation raisonnable entre les tests de flexion et les propriétés de tension et le vieillissement des échantillons étirés. Toutefois, le vieillissement d'échantillons courbés et la force de tension sont très voisins et pour cette raison une diminution d'un tiers de la force de tension initiale a été prise comme critère pour indiquer un défaut des échantillons vieillis pour cette étude-ci. Le vieillissement à 45° sud pour trois localisations différentes indiquent que une année à Phoenix, Arizona, est approximativement équivalente à au moins 2 ans à Bartlesville, Oklahoma et à une durée supérieure à 3 ans $^1/_2$ à Akron, Ohio. Bien qu'il y ait une certaine diffusion des données, des résultats du Weather-Ometer indiquaient que 1000 à 2000 heures d'exposition sont approximativement équivalentes à 12–24 mois en Arizona, à 45° Sud, 3.000 à 4.000 heures comparées à 24–36 mois et au-delà de 5.000 heures comparées à une durée plus grande que 42 mois avec la même relation pour l'Arizona et pour les deux autres localisations. La comparaison de EMMA (Equatorial Mount with Mirrors) et le vieillissement au Weather-Ometer indique certains résultas contradictoires bien que EMMA montre une certaine valeur pour le vieillissement accéléré La comparaison du vieillissement au Weather-Ometer et du service à l'extérieur de nombreux polyéthylènes commerciaux indique que des prédictions basées sur les résultats du Weather-Ometer au départ des corrélations montrées dans ce manuscrit restent intactes. Aucun des appareils de vieillissement étudiés ne se rapprochent très fort du service à l'extérieur mais ils sont effectifs pour sélectionner et pour établir certaines lignes maîtresses pour estimer la durée de vie en service extérieur.

Zusammenfassung

Sechs Testmethoden zur Kontrolle des UV-Abbaues wurden kritisch ausgewertet, nämlich Oberflächenrissbildung, Zugeigenschaften, Biegetests, Sprödigkeitstemeratur, Schmelzindex und Alterung gespannter Proben. Es besteht eine annehmbare Korrelation zwischen Biegetests, Zugeigenschaften und Alterung gespannter Proben. Besonders ähnlich verhalten sich die Alterung gespannter Proben und die Zugfestigkeit und aus diesem Grund wurde die Abnahme der ursprünglichen Zugfestigkeit um eindrittel bei der vorliegenden Untersuchung als Kriterium für das Versagen der gealterten Probe verwendet. Alterung unter 45° nach Süden an drei verschiedenen Orten zeigt, dass ein Jahr in Phoenix, Arizona näherungsweise mindestens zwei Jahren in Bartlesville, Oklahoma und mehr als dreieinhalb Jahren in Akron. Ohio äquivalent ist. Innerhalb der Streuung der Daten zeigten die Weather-Ometer-Daten, dass eine Exponierung durch 1000 bis 2000 Stunden etwa 12–24 Monaten in Arizona unter 45° nach Süden äquivalent ist. 3000–4000 Stunden entsprechen 24–36 Monoten und mehr als 5000 Stunden lassen sich mit einem Zeitraum grösser als 42 Monaten vergleichen. Die gleiche Beziehung wir für Arizona gilt für die beiden anderen Orte. Der Vergleich zwischen EMMA (Aquatormontierung mit Spiegeln) und Weather-Ometer Alterung lässt gewisse Widersprüche erkennen; gleichwohl besitzt EMME einigen Wert für beschleunigte Alterung. Ein Vergleich zwischen Weather-Ometer-Alterung und Aussengebrauch einiger kommerzieller Polyäthylengegenstände zeigt, dass Voraussagen auf Grund von Weather-Ometer-Daten mit den hier gezeigten Korrelationen möglich sind. Keine der untersuchten Bewitterungsvorrichtungen entspricht sehr enge dem tatsächlichen Aussengebrauch; sie sind aber für Zwecke der Auswahl und der Aufstellung von Leitlinien für die Bestimmung der Lebensdauer bei Aussengebrauch geeignet.

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Practical Problems in Predicting Weathering Performance

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Synopsis

Plastics are appearing more frequently in larger parts where good outdoor weathering resistance is essential. Weathering results for polyethylenes are analyzed to establish lifetimes during which a reasonable physical condition is maintained. Unmodified natural resins are not suitable for prolonged outdoor applications. For a well-formulated high-density polyethylene containing either UV stabilizer or nonblack pigment, a life of 5 yr. is possible in a temperate climate. A somewhat longer life may be projected for low-density polyethylene. These estimates are based exclusively on outdoor results because rapid artificial methods are not considered reliable for high-density polyethylene. Means of accelerating outdoor tests are discussed.

INTRODUCTION

Plastics have been appearing more frequently in larger parts where good weathering resistance is essential. This trend is well illustrated by high-density polyethylene. Recent outdoor applications include sleds, buoys, boats, and stadium seats. Problems of fabrication and part design have been met, but the more serious need is to provide for adequate weathering resistance.

In this paper ~~we analyze~~ weathering results are analyzed in terms of their relevance to ~~such~~ practical problems. This analysis leads to suggestions as to how tests can be made more meaningful. The discussion covers polyethylenes, mainly the high-density type, and refers both to published results and to findings from Union Carbide ~~our~~ laboratories.

DISCUSSION

Criteria of Failure

The progress of deterioration in polyethylene has been followed in several ways in past experimental studies. Changes have been noted in (*a*) measurements that relate to chemical structure, (*b*) special properties, (*c*) appearance, and (*d*) mechanical properties.

In the first group are such determinations as intrinsic viscosity,[1] carbonyl content,[1–3] and melt index.[4] These may be useful in elucidating the

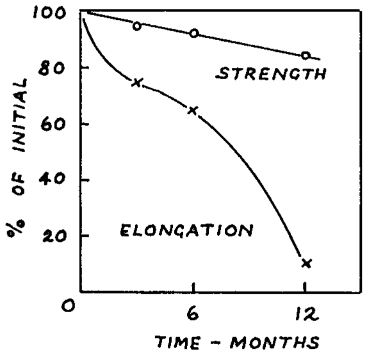

Fig. 1. Decline of tensile properties during weathering of high-density polyethylene in New Jersey. Sample 0.05 in. thick of 0.96 density resin.

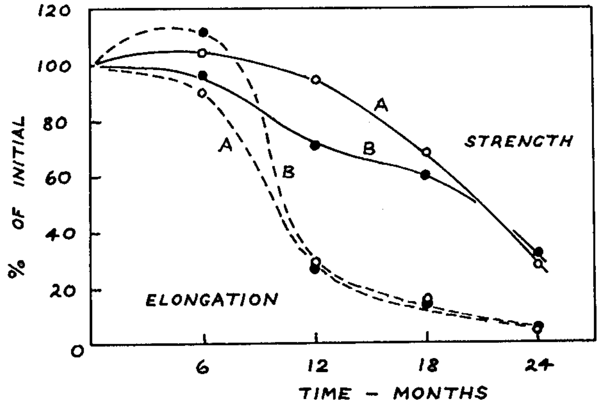

Fig. 2. Decline of tensile properties during weathering of two high-density (0.96) polyethylenes, 0.125 in. thick, in New Jersey.

mechanism of weathering, for example, in identifying crosslinking, oxidation, and chain scission, or in providing a quick indication of deterioration. They are less effective in revealing the mechanical quality of a compound and are therefore not useful to our purpose.

The special properties that have been followed are the dielectric constant and power factor.[5–7] These relate particularly to electrical applications.

Relevant to end performance is a change in appearance as manifested by a change in color or by the onset of surface cracking or crazing. With colored polyethylenes the change in color usually occurs well after a serious decline in mechanical properties and marks a secondary end point. Early discoloration, which can be construed as failure, is more common in natural formulations, but these are not likely to be used for large outdoor parts. Surface cracking coincides with a significant loss in physical properties[2,4,8] but is an indirect and qualitative indicator.

The decline in mechanical properties with outdoor exposure is what really determines the life of a large part. The course of tensile strength and

TABLE I
Detailed Properties of Samples[a]

Fig. or Table	Density	Melt index	UV stabilizer	Pigment	Prepared by	Thickness, in.
1, 4	0.96	0.2	None	None	Extrusion	0.05
2A	0.96	0.7	None	None	Injection molding	0.125
2B	0.96	0.6	None	None	Injection molding	0.125
3	0.92	2	None	None	Injection molding	0.125
5	0.96	?	Yes	None	Comp. molding	Variable
6	0.95	Variable	Yes	None	Comp. molding	0.06
II, 1	0.96	0.7	See II	None	Comp. molding	0.07
2	0.96	0.2	See II	None	Extrusion	0.05
3	0.96	3.5	See II	None	Comp. molding	0.07
4	0.96	0.2	See II	None	Comp. molding	0.06
III, 1	0.96	0.7	None	See III	Comp. molding	0.07
4	0.96	?	None	See III	Comp. molding	0.07

[a] All weathering exposures 45° south.

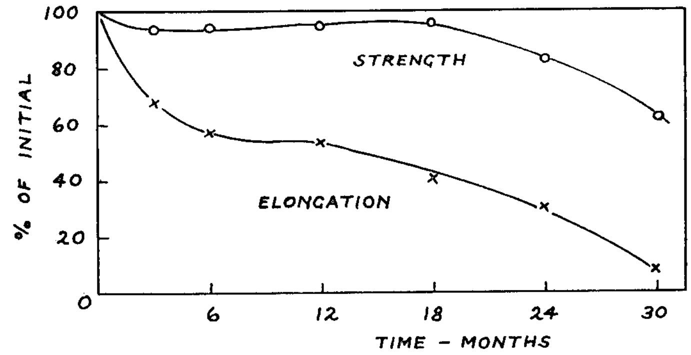

Fig. 3. Decline of tensile properties during weathering of low-density (0.92) polyethylene, 0.125 in., in New Jersey.

elongation during the outdoor weathering of high-density polyethylene is shown in Figure 1 (our studies). McNally's results for similar resins[9] weathered in a nearby location appear in Figure 2. The detailed characteristics of the samples in Figures 1 and 2 may be found in Table I along with similar information for other results in this paper. The principal difference between Figures 1 and 2 is the thickness, and the greater thickness probably explains the slower decline in Figure 2.

At equal thickness a low-density resin (Fig. 3 from Barrett[7]) weathers somewhat more slowly than a high-density one. This comparison for resins containing no UV stabilizers or pigments shows that neither resin in the unmodified form is suitable for prolonged outdoor uses.

Elongation declines much faster than strength in Figures 1–3. The strength is still quite high even when the elongation has almost disappeared and the material has become brittle. Elongation is the more sensitive criterion of deterioration and is the better criterion of failure in a weathered sample.

For satisfactory engineering performance in the end application, a material should retain some of its initial mechanical properties and the weathering life should be defined accordingly. A reasonable definition of life is the time to reach one-third of the initial tensile elongation. With high-density polyethylene (0.96) the initial tensile elongation may be 60% at 20 in./min. testing speed and the end point then corresponds to 20% elongation.

Several other end points have been proposed: (*a*) The time to reach either two-thirds of the tensile strength or 10% of the initial elongation.[10] This is less demanding than our proposal. (*b*) The time at which the sample fails to survive a manual bend test. This is a subjective procedure in which sample thickness may be a variable. Further, the series of readings versus time cannot be used to construct a plot as in Figure 1 that allows interpolation and extrapolation. [For a thickness of 0.06 in., Martinovich[10] has shown that this end point is equivalent to that given under (*a*)]. (*c*) The brittle temperature, particularly after additional oven aging, has been shown as exceedingly sensitive by Wallder et al.,[5] but it is probably better adapted to indicate very early deterioration.

Our own current preference for a plot of elongation versus time, and for the "one-third" end point, cannot yet be applied exclusively. There are several valuable published results based on less demanding criteria and these will be accommodated within our framework.

Although they have not used them as end points, Evans and Lawson[6] and McNally[9] have compiled some interesting information on dimensional changes.

Acceleration

Even with unmodified polyethylenes that have only moderate weatherability, the experimental exposure time may reach 2 yr. in a temperate climate. The most common accelerating device in the U.S.A. is the Weather-Ometer (X1A or XW) which has been designed to have a spectrum of radiation resembling that of sunlight. In the Weather-Ometer the high-density sample that was exposed 1 yr. outdoors (Fig. 1) loses nearly all elongation in 500 hr. (Fig. 4). The degree of acceleration is roughly consistent with a rule-of-thumb that 1 hr. in the X1A is equivalent to 1 sun-hr. outdoors. 500 hr. in the X1A are then equivalent to 6 mo. outdoors in New Jersey and to lesser times in Florida and Arizona where the annual sun hours are about 1500 and 2000, respectively.

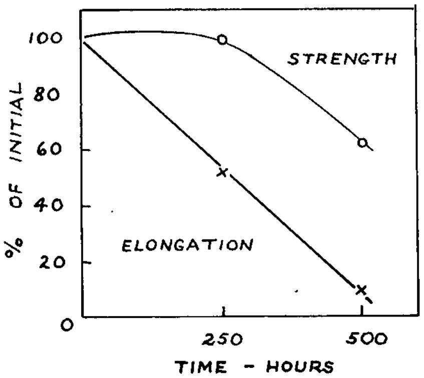

Fig. 4. Decline of tensile properties of high-density (0.96) polyethylene in the XIA Weather-Ometer. Samples are similar to those in Figure 1.

This rule-of-thumb becomes unreliable for polyethylenes modified with pigments or with UV stabilizers. For example, the addition of 1% or more titanium dioxide to high-density polyethylene invariably lengthens its life several fold in the Weather-Ometer but has no effect or a slightly negative one outdoors. Further, in a given series of stabilized or pigmented compounds run by one observer, we have noted that the ratio of Florida hours to X1A hours (both to fail) may vary about threefold.

Other artificial accelerating devices have been proposed, for example, the fluorescent-black light combination of Cipriani et al.[3] This is yet to be thoroughly proven.

At present, we prefer outdoor results for high-density polyethylenes and use the Weather-Ometer only to eliminate the poorest experimental formulations from our outdoor program.

Some acceleration is possible with outdoor weathering in the sense that a plot of elongation versus time can be extrapolated. Unfortunately the course of the plot is not usually regular (Figure 1), and the longest observed time cannot be extrapolated more than 100%. In fact the safe limit is often much less. Much of the irregularity in the plot may arise from seasonal changes. Thus, Melchore[11] has shown that the damaging UV radiation is several times more intense in the northern summer than in the winter.

Design and Formulation Factors

The thickness of the part is a design factor. The formulation variables are the melt index and density of the resin and the use of pigments and UV stabilizers.

In mechanical design, thickness is proportioned to the needs for adequate stiffness and strength. Larger parts of polyethylene may have a thickness ranging from 0.04 to 0.14 in. Now thickness is also known to be related to weathering performance. It is accepted that thin films weather more rapidly than thick sections. A more quantitative relationship observed by Martinovich[10] is given in Figure 5; in conjunction with the decline in elongation of Figure 1, we may calculate that at a thickness of 0.125 in. the weathering life is one-third longer than at 0.06 in. The minimum thickness defined by mechanical needs may then be increased, if necessary, to achieve the required weatherability (at an increase in the weight of the part and in the production expense).

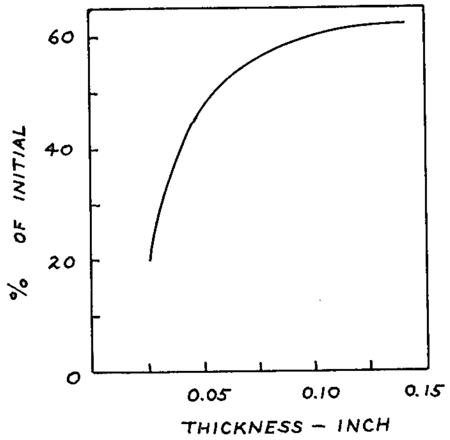

Fig. 5. Effect of thickness on tensile elongation of high-density (0.96) polyethylene after 12 mo. in Arizona. Formulation contains UV stabilizer.

The resin variables have also been investigated by Martinovich.[10] Lower melt index resins weather more slowly than those of higher melt index, as also found earlier by Gottfried and Dutzer.[4] Presumably the improved mechanical properties that go with a lower melt index (and higher molecular weights, either number-average or weight-average) mean that the resin has farther to go before it deteriorates to a given level. There is often no hardship for the fabricator in this situation for he tends to use resins of low-melt index in larger parts for other reasons. He likes the superior end properties, and resins of lower melt index are more amenable to the blow molding or thermoforming methods that are common for the larger parts. Where injection molding is applied, the lowest possible melt index (2–3) is suggested.

The other resin variable is density whether 0.95 or 0.96. Here the recommendation of the higher density by Gottfried and Dutzer[4] flatly contradicts that of Martinovich.[10] The conclusions about density derive principally from Weather-Ometer studies in both papers and are not trustworthy in our view. Martinovich does mention specific outdoor results along the same lines, and for that reason we prefer his conclusion that the lower density is better.

Even when thickness, melt index, and density are adjusted for maximum weatherability, the outdoor life of a natural high-density polyethylene containing only standard antioxidants is inadequate. Either a pigment or a UV stabilizer must be added to reach a good level.

Among two of the better stabilizers are TBS and UV-531 (chemical formulae given in Table II). Life expectancies for natural (uncolored) resins containing these appear in Table II. For only one of the values has there been an extrapolation from a shorter time. Otherwise tests were continued to the time cited. It is interesting that though the results are drawn from four sources there is a fair agreement. Further, the relation-

TABLE II

Life Expectancy of UV-Stabilized High-Density Polyethylene[a]

	Florida		Arizona		New Jersey	
Stabilizer[b]	Life,[c] mo.	Source[d]	Life,[c] mo.	Source[d]	Life,[c] mo.	Source[d]
None	6	1	3	4	12	2
	6	3				
0.25 TBS	11–16	3	10	4	28[e]	2
0.5 TBS			12+	4		
0.5 UV-531	16	3	12+	4	36	3

[a] Thickness range: 0.05–0.07 in.

[b] Stabilizers (UV): TBS: *p-tert*-butyl phenyl salicylate; UV-531: 2-hydroxy-4-octoxy benzophenone.

[c] End point: manual bend, or 10% of tensile elongation retained, or 2/3 of tensile strength retained. Plus (+) indicates that end point not reached when test stopped.

[d] Sources: (1–3) different investigators in this laboratory; (4) Martinovich.[10]

[e] Extrapolated from elongations at 3, 6, 9, and 12 mo.

TABLE III
Life Expectancy of High-Density Polyethylene[a]
Containing 1% Pigment

Pigment type	Florida		Arizona	
	Life,[b] mo.	Source[c]	Life,[b] mo.	Source[c]
Phthalocyanine green	24	1	18	4
Cadmium yellow	12	1	18	4
Cadmium red	12	1	18	4
Titanium dioxide, anatase	4	1	3	4
rutile	6	1	6	4

[a] Thickness: 0.06–0.07 in.

[b] End point: manual bend or equivalent.

[c] Sources: (1) this laboratory; (4) Martinovich.[10]

ship is sustained that life in New Jersey is about double that in Florida or Arizona.

A similar tabulation for the better pigments is given in Table III. 1% of the proper pigment substantially lengthens the life of a high-density polyethylene. 2% may be even better according to Martinovich[10] and Gottfried and Dutzer.[4]

The additional findings of Table IV are offered cautiously because they are not directly comparable with all other results in this paper which are based on plaques. Injection-molded experimental boxes were exposed with the inside bottom surface facing 45° south. Boxes were removed periodically for 3-ft. drop tests on to concrete and tumbling tests. In the drop tests one box was evaluated at several temperatures beginning at room temperature and going to lower temperatures. The box was dropped on each of the eight corners (top and bottom) in turn, and the temperature of 50% break or four breaks was determined. This temperature was usually −60°F. or better for unexposed boxes. Life was determined as the period to reach a point of −20°F. Other boxes were tumbled in a large drum. Original boxes easily lasted 500 revolutions without damage. The life was taken as the period of weathering to bring about failure at 300 revolu-

TABLE IV
Weathering of Experimental Boxes[a]

Pigment type	Per cent	Life, mo.	
		Florida	New Jersey[b]
Cadmium yellow	0.5	18	24+
Titanium dioxide white	1.0	3	9
Cadmium red	0.25	24	24+

[a] Outside dimensions of box are 18 × 12 × 4 in. There is no lid. The box is divided into compartments by dividing walls. Thickness of construction varied from 0.08 to 0.10 in. Resin formulation: 0.96 density, 3.5 melt index, 0.25% UV-stabilizer.

[b] Notation 24+ indicates that end point not reached after 24 mo. exposure.

tions. The two evaluations usually gave similar answers, and an occasional discrepancy was resolved by taking the lower time.

The results of Table IV for formulations containing both stabilizer and pigment are moderately consistent with the preceding results if we assume that the presence of stabilizer and pigment together is no more beneficial than either one alone.

The continuous exposure (Table IV) is much more rigorous than the conditions of only partial exposure that a box would receive in general outdoor use. Hence an expectation of at least 5 yr. exposure for red and yellow items is justified by the results.

Other Variables

There are other variables in weathering performance about which little is yet known: antioxidant type, interaction between UV stabilizer and pigment, and fabrication method. Interactions of practical value may exist here but we know little about them as yet. A further variable is the character of the pigment dispersion in the resin. Such dispersion has been well established as important in the weathering protection afforded by carbon black in low-density polyethylene.[5,12] A similar effect may operate with other pigments and determine the degree of protection, but there is yet no information on this point.

Practical Lives

The results presented suggest that a life of about 3 yr. in a temperate climate may be expected for a high-density polyethylene that contains either 0.5% of a good UV stabilizer, or 1–2% of a suitable pigment. This expectation holds for a thickness of 0.06 in. If the thickness is doubled, we may expect a life of 4 yr. A further increment of 1 yr. may be possible if the melt index is 0.2 and the density is 0.95. (These comments exclude compounds containing 1% or more of carbon black for which a much longer life is expected.[10])

The life of 5 yr. is based on an end point that is not rigorous; manual bend or equivalent. This criterion may be appropriate if the fabricated product bears little or no stress during its existence. If stressing or flexing is expected, as in most larger parts, the "one-third" end point is more appropriate and a life of 4 yr. is more likely. All these figures should be cut about 50% if exposure in Arizona or Florida is being considered. With low-density resin, somewhat longer lives are possible.

When well formulated, the polyethylenes offer a resistance to continued outdoor exposure that justifies broad application in large parts. A favorable factor is that many end uses involve only intermittent outdoor exposure and the projected life can thus be increased.

Remarks on Weathering Tests

In predicting practical confidence we have confined ourselves to results for outdoor weathering. The preferred indicator is a plot of tensile elongation versus time. This allows some extrapolation although it is not safe to exceed double the observed time. When the course of tensile elongation is not available, we have fallen back on end points based on manual bending.

An experimental system based on outdoor weathering has the disadvantage that exposure time may be long. A twofold acceleration may be gained in Arizona or Florida but with the drawback that samples leave the close control of the experimenter. Much greater acceleration might be realized with samples only 0.01 in. thick. The results of Clark and Havens,[13] and Matveeva et al.[1] for such thicknesses suggest that a few months in a temperate zone would be sufficient. The four or six warmer months would be preferred as giving the more intense and probably consistent radiation (see previous remarks under "Acceleration"). This proposal would, of course, need the foundation of a finding that a correlation between life and thickness is reasonably consistent among several typical formulations.

An extrapolation of twofold for elongation and fivefold for thickness, or a total of tenfold might be realizable. (An extrapolation of tenfold is the absolute maximum for any weathering procedure at present. This is the same extrapolation permissible for engineering results with creep and long-term tension.)

A last comment on the weathering of polyethylenes is that future results for natural, unmodified resins may have little interest except as controls or as guides to an elucidation of mechanism.

It is a pleasure to acknowledge the counsel of W. J. Goodwin, drawn from his long experience with weathering. Discussion with F. J. Skiermont has been fruitful. Some of the results quoted here were provided by F. J. Crimi and J. A. Slank, and R. J. Stockman.

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Résumé

Des plastiques sont utilisés en plus grande quantité lorsque la résistance au vieillissement à l'extérieur est essentielle. Les résultats de vieillissement pour le polyéthylène sont analysés en vue d'établir les durées de vie pour lesquelles une condition physique raisonnable est maintenue intacte. Les résines naturelles non modifiées ne sont pas adaptées à des applications à l'extérieur prolongées. Pour un polyéthylène de haute densité déterminée contenant soit un stabilisateur contre la lumière ultraviolette, soit un pigment non-noir, une durée de vie de cinq ans est possible dans un climat tempéré. Une durée de vie quelque peu plus longue peut être projetée pour le polyéthylène à basse densité. Ces estimations sont basées exclusivement sur des résultats à l'extérieur par suite des méthodes artificielles parce que las méthodes artificielles rapides ne peuvent pas etre considérées comme reproductibles pour le polyéthylène de haute densité. Des moyens d'accélérer les tests à l'extérieur sont soumis à discussion.

Zusammenfassung

Plastomere werden immer häufiger in grösseren Teilen verwendet, wo eine gute Aussen-Bewitterungsbeständigkeit wesentlich ist. Bewitterungsergebnisse an Polyäthylenen werden zur Ermittlung der Lebensdauer, während welcher eine annehmbare physikalische Bedingung eingehalten wird, ausgewertet. Unmodifizierte Naturharze sind für längere Aussen-Anwendung nicht geeignet. Für ein gut rezeptiertes Polyäthylen hoher Dichte mit einem Gehalt an UV-Stabilisator oder nicht-schwarzem Pigment ist in gemässigtem Klima eine Lebensdauer von fünf Jahren möglich. Eine etwas grössere Lebensdauer kann für Polyäthylen niedriger Dichte angenommen werden. Diese Abschätzungen beruhen ausschliesslich auf Aussen-Ergebnissen, da küntsliche Schnellalterungsmethoden für Polyäthylen hoher Dichte nicht verlässlich erscheinen. Mittel zur Beschleunigung von Aussen-Tests werden diskutiert.

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APPLIED POLYMER SYMPOSIA NO. 4, 167-173 (1967)

Determination of Hydroperoxide Groups in Oxidized Polyethylene

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Synopsis

A method has been developed for detecting hydroperoxide groups formed during the early stages of oxidation of polyethylene. The oxidized polymer is exposed to sulfur dioxide vapors at room temperature. Sulfate groups are formed fairly rapidly and apparently quantitatively by selective reaction with the hydroperoxide groups. Analysis is based on the strong infrared absorption of the sulfate groups at 1195 cm.$^{-1}$. As little as 0.1 ppm of hydroperoxide should be detectable.

In reviewing the oxidation of polyolefins Hawkins and Winslow[1] suggested that the reaction proceeded via a free-radical chain mechanism much like that proposed by Bolland and Gee[2] for low molecular weight hydrocarbons. Oxidative reaction of a substance such as polyethylene was explained by the following sequence,

Initiation:

$$\mathrm{RH} \xrightarrow{k_1} \mathrm{R}\cdot$$

Propagation:

$$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{k_2} \mathrm{ROO}\cdot$$

$$\mathrm{ROO}\cdot + \mathrm{RH} \xrightarrow{k_3} \mathrm{ROOH} + \mathrm{R}\cdot$$

Chain branching:

$$\mathrm{ROOH} \xrightarrow{k_4} \mathrm{RO}\cdot + \mathrm{HO}\cdot$$

$$\mathrm{RO}\cdot + \mathrm{RH} \xrightarrow{k_5} \mathrm{ROH} + \mathrm{R}\cdot$$

$$\mathrm{HO}\cdot + \mathrm{RH} \xrightarrow{k_6} \mathrm{HOH} + \mathrm{R}\cdot$$

Termination:

$$\left.\begin{array}{l} 2\,\mathrm{R}\cdot \xrightarrow{k_7} \\ 2\,\mathrm{ROO}\cdot \xrightarrow{k_8} \\ \mathrm{R}\cdot + \mathrm{ROO}\cdot \xrightarrow{k_9} \end{array}\right] \rightarrow \text{Inert products}$$

The initiation rate k_1 is quite slow in the absence of light. Under the influence of oxygen, heat, ultraviolet light, high energy radiation, and other

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sources of thermal energy, however, this reaction is accelerated and the peroxy radicals formed provide the basis for a variety of oxidation products, such as aldehydes, ketones, carboxylic acids, and esters.

A number of procedures have been proposed for the determination of peroxide groups. Those based on polarography require a solution, and, therefore, are of little value for analysis of hydrocarbon polymers. Iodometric and colorimetric procedures lack specificity and are subject to interference from dissolved oxygen. For example, *N*,*N*-dimethyl-*p*-phenylenediamine has been used as a reagent for benzoyl peroxide in flour.[3] Gray and Wright[4] applied the reaction in a colorimetric method for measuring polyester degradation due to weathering. Advantage was taken of reactions of the antioxidant, phenathiazine, with hydroperoxide groups in rubber.[5] The resulting oxy-radical was detected by electron spin resonance. Measurement of the infrared absorption band intensity of the unbonded —OOH band at 3550 cm.$^{-1}$ has been used by Rugg and co-workers[6] and Luongo[7] for detecting hydroperoxide groups in early stages of the autooxidation of polyethylene. Although this band is nearly specific for —OOH groups, it is relatively weak and, therefore, appreciable concentrations must be present before they can be detected. Sensitivity was improved by Rugg et al.[6] by scanning the sample at 130°C., but this was not very convenient and the temperature encouraged further reaction.

Hydroperoxides have been found to react selectively with sulfur dioxide to form the corresponding alkyl hydrogen sulfate,[8]

$$ROOH + SO_2 \rightarrow ROSO_2OH$$

The reaction was used by Ashby[9] for removal of low levels of *t*-butyl hydroperoxide in *t*-butyl peracetate. Wirth and Oldham[10] described reaction of sulfur dioxide with peroxidized hydrocarbons containing 12–20 carbon atoms to form alkyl hydrogen sulfates.

We have observed fairly rapid reaction of sulfur dioxide with hydroperoxide groups formed during the early stages of oxidation of polyethylene. Measurement in the infrared of the resulting strongly absorbing sulfate groups forms the basis for a new, specific, sensitive method of analysis. With slight modification the method should be suitable for determination of hydroperoxides in polypropylene and other polyolefins.

Experimental

Samples of polyethylene (1 mil films) were thermally oxidized by heating in air. After various periods of time, portions were scanned in a double-beam infrared spectrophotometer. The same specimens were then placed in a vacuum desiccator, air was evacuated, and gaseous sulfur dioxide introduced to a pressure of 1 atm. After several hours exposure the samples were removed from the desiccator and rescanned. Alternatively, separate portions of the oxidized samples were exposed to sulfur dioxide.

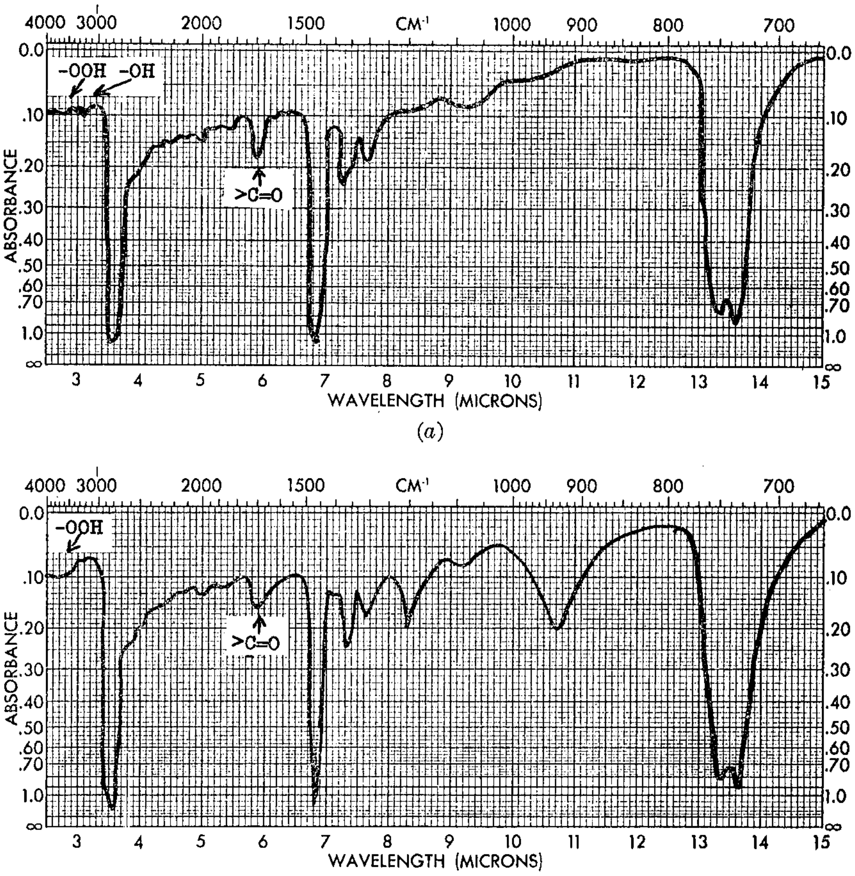
Comparative spectra on samples heated in air for about 2.5 hr. at 150°C. are shown in Figure 1. Differences are quite marked in the 900–1700 cm.$^{-1}$

TABLE I
Correlation of Hydroperoxide and Sulfate Bands

Oxidation conditions	Absorbance values —OOH (3520 cm.$^{-1}$)	 —SO$_4$ (1195 cm.$^{-1}$)	 (920 cm.$^{-1}$)	Absorbance ratios 1195/3520	 920/3520
2 hr., 140°C.	0.00150	0.0213	0.059	14.2	39
1.5 hr., 150°C.	0.00173	0.0237	0.081	13.7	46
2.5 hr., 150°C.	0.00732	0.097	0.204	13.4	28
3.5 hr., 150°C.	0.00600	0.084	0.286	14.0	48

region and are consistent with absorption expected of sulfur–oxygen-containing functions.

A few experiments were made to establish whether the new groups were attached to the polymer chain. Samples of the reacted polyethylene films



(a)

(b)

Fig. 1. Infrared spectra of polyethylene after heating for 2.5 hr. at 150°C.: (a) direct scan; (b) after exposure to SO$_2$.

were soaked overnight in water and then extracted with chloroform at room temperature for 0.5 hr. Infrared spectra after this treatment showed no significant changes.

Film samples of polyethylene were oxidized for varying periods to produce a range of hydroperoxide levels. Infrared scans were made before and after sulfur dioxide treatment. The —OOH region at 3520 cm.$^{-1}$ was scanned using 20 to 1 scale expansion[11] and the —SO_4 region between 1195 and 920 cm.$^{-1}$, using 5 to 1 scale expansion. Absorbance values at these wavelengths are given in Table I.

Discussion

Referring to Figure 1*a*, the presence of unbonded —OOH groups is indicated by the band at 3520 cm.$^{-1}$ and bonded —OOH together with —OH

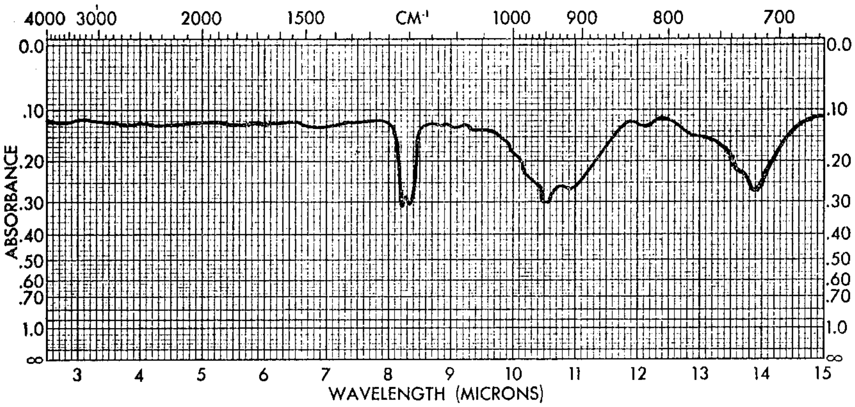


Fig. 2. Infrared spectrum of dilauryl sulfite (5% solution in *n*-hexane vs. *n*-hexane, 0.053 mm. cell).

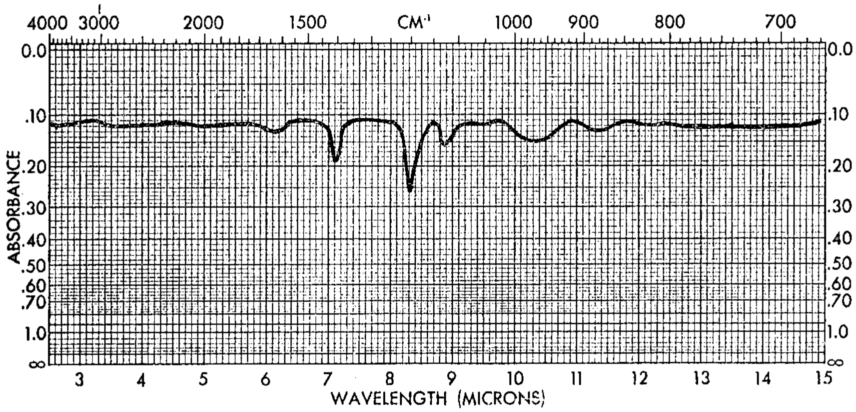


Fig. 3. Infrared spectrum of dilauryl sulfate (8.3% solution in *n*-hexane vs. *n*-hexane, 0.053 mm. cell).

at about 3380 cm.$^{-1}$. In the spectrum following sulfur dioxide treatment, the band at 3520 cm.$^{-1}$ has disappeared and that at 3380 cm.$^{-1}$ has markedly decreased. (Note that the intensity of the carbonyl band at 1720 cm.$^{-1}$ is reduced slightly and broadened after SO_2 treatment, indicating a weak absorption band near 1675 cm.$^{-1}$.) Also new bands of moderate to strong intensity appear at 1415, 1195, and 920 cm.$^{-1}$. There is no evidence for dissolved unreacted sulfur dioxide which would be expected to absorb at 1350 cm.$^{-1}$.

As noted previously, low molecular weight hydroperoxides react with sulfur dioxide to form the alkyl hydrogen sulfates. Similar reaction would be expected, at least to some extent, in the polyethylene. However, there is no evidence for such a group; acid —OH gives strong absorption near 1090 cm.$^{-1}$ with broad general absorption in the 2600–3100 cm.$^{-1}$ region.[12]

Reference to the literature indicates that sulfate esters absorb in the ranges 1350–1440 cm.$^{-1}$ and 1150–1230 cm.$^{-1}$,[12] while a weak band also has been observed near 1675 cm.$^{-1}$.[13] Sulfite esters also have a strong band between about 1135 and 1215 cm.$^{-1}$.[13] In order to verify these results on sulfates having fairly long-chain alkyl groups, dilauryl sulfate and dilauryl sulfite were studied. These compounds were prepared by the method of Barkenbus and Owen[14] using reaction of the alcohol with sulfuryl and thionyl chlorides. The spectrum of dilauryl sulfite, Figure 2, showed bands at 940 and 1220 cm.$^{-1}$. Dilauryl sulfate, on the other hand, showed absorption at 1415 and 1195 cm.$^{-1}$, as shown in Figure 3.

Comparisons with the spectrum in Figure 1*b* show marked similarities between the dialkyl sulfate and the oxidized sulfur dioxide-treated polyethylene. Hence, it appears that the diester is formed in the polyolefin. This diester may well result from reaction of hydroxyl groups present in the polymer after oxidation, with the strongly acidic hydrogen sulfate group. The latter group, therefore, would serve as an intermediate in diester formation. The marked decrease in the —OH band at 3380 cm.$^{-1}$ (Figures 1*a* and 1*b*) tends to support this postulation.

The data of Table I indicate a good correlation between the hydroperoxide band at 3520 cm.$^{-1}$ and the sulfate band at 1195 cm.$^{-1}$, the ratio being about 14. This indicates that use of the sulfate band should provide a sensitive specific method of analysis for hydroperoxide groups. The considerable improvement in sensitivity over direct measurement is further aided by the fact that the region around 1195 cm.$^{-1}$ is reasonably free of other group absorptions, at least for polyethylene. Although the 920-cm.$^{-1}$ band appears highly favorable, it does not correlate well with the 3520 or 1195 cm.$^{-1}$ bands, indicating that absorption in this region is associated either with more than one vibration or with a different type of function than the sulfate group.

Development of the new method of analysis required calibration with a known system. Absorptivity constants were calculated from measurements on an *n*-hexane solution containing 8.31% dilauryl sulfate. Infrared spectra were obtained on this solution in a 0.053-mm. cell using *n*-hexane in an 0.045 mm. cell in the reference beam of the spectrophotometer. The absorbance of the 1195 cm.$^{-1}$ peak was 0.140.

For calculation of hydroperoxide groups per 2000 carbon atoms, the following relation was used,

$$\frac{a}{t \times 4.93}$$

where a is the absorbance of the 1195 cm.$^{-1}$ band, t is the thickness of the sample in centimeters, and 4.93 is the absorptivity coefficient. Alternatively, calculation as milliequivalents of —OOH per gram of sample can be made from the relation:

$$\frac{a}{t \times 138}$$

In order to establish reaction time, samples of oxidized polyethylene film 12.5 mils thick were exposed to sulfur dioxide for periods ranging from 2 to 15 min. at room temperature. Results, given in Table II, indicate that for samples 12.5 mils or less in thickness exposure for 10–15 min. should be adequate.

TABLE II
Effect of Sulfur Dioxide Reaction Time on Absorbance

Exposure to SO_2, min.	—OOH absorbance	SO_4 absorbance	SO_4/—OOH
2	0.015	0.171	11.4
5	0.015	0.180	12.0
10	0.019	0.269	14.2
15	0.022	0.304	13.8

Limit of detection was estimated from analysis of 12.5 mil films of polyethylene exposed to air at 90 or 95°C. for periods ranging from 8 to 24 hr. and then exposed to sulfur dioxide vapor for 20 min. Samples were scanned before and after SO_2 treatment using 20 to 1 scale expansion. In all cases —OOH absorption at 3520 cm.$^{-1}$ was too weak for suitable detection. Intensity of the SO_4 band was quite adequate, as shown in Table III. The

TABLE III
Hydroperoxide Content of Oxidized Polyethylene

Oxidation conditions	Absorbance 1195 cm.$^{-1}$	No. —OOH/ 2000 C	—OOH, ppm, wt. basis
16 hr., 90°C.	0.00104	0.0066	7
20 hr., 90°C.	0.00200	0.0127	15
44 hr., 90°C.	0.0194	0.123	150
8 hr., 95°C.	0.00108	0.0069	7
16 hr., 95°C.	0.00775	0.049	52
24 hr., 95°C.	0.0339	0.214	220

lower limit of detection was calculated at 0.0003 absorbance unit equivalent to about 2 ppm —OOH. There was some problem from interference fringes; otherwise an even lower sensitivity would have been expected. Use of thicker specimens and samples giving no interference fringes would be expected to permit detection of as little as 0.1 ppm hydroperoxide.

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Résumé

Une méthode a été développée pour détecter des groupes hydroperoxydes formés au cours des premières étapes d'oxydation du polyéthylène. Le polymère oxydé est exposé à des vapeurs de dioxyde de soufre à température ordinaire. Des groupes sulfates sont formés rapidement et apparemment quantitativement par réaction sélective àvec les groupes hydroperoxydes. L'analyse est basée sur la forte absorption infrarouge du groupe sulfate à 1195 cm^{-1}. On peut de cette façon détecter jusque 0.1 ppm d'hydroperoxyde.

Zusammenfassung

Eine Methode zur Auffindung von Hydroperoxydgruppen, die während des Frühstadiums der Oxydation von Polyäthylen entstehen, wurde entwickelt. Das oxydierte Polymere wird der Einwirkung von Schwefeldioxyddämpfen bei Raumtemperatur ausgesetzt. Durch selektive Reaktion mit den Hydroperoxydgruppen werden ziemlich rasch und offenbar quantitativ Sulfatgruppen gebildet. Die Analyse beruht auf der starken Infrarotabsorption der Sulfatgruppen bei 1195 $cm.^{-1}$. Es sollten sich noch 0,1 ppm. Hydroperoxyd nachweisen lassen.

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APPLIED POLYMER SYMPOSIA NO. 4, 175–188 (1967)

Factors Affecting Light Resistance of Polypropylene

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Synopsis

The stability of polypropylene on exposure to light and the means for improving its resistance to such exposure have been subjects of concern since this plastic was introduced in 1957. The structure of the polymer makes it susceptible to oxidation. The length of the induction period is decreased and the rate of oxidation increased by heat and light. Three types of additives, antioxidants, hydroperoxide decomposers, and light stabilizers, are most widely used to protect polypropylene. Accelerated laboratory tests of light resistance are not yet capable of predicting durability with precision, and outdoor exposure tests are complicated by seasonal variations in the intensity of sunlight. These variations can be smoothed out by "correcting" the langley values for ultraviolet content or by applying empirically determined equalization factors. Improved correlation with Weather-Ometer tests is obtained by this means. Since oxidative attack starts at the exposed surface of the polymer, thicker test specimens have longer life outdoors. The lifetime of polypropylene varies approximately as the square root of the ultraviolet absorber concentration. Absorbers are relatively more effective in thick specimens than in thin. Pigments are generally beneficial to light resistance of the total polymer compound. Carbon black is the most effective light-absorbing pigment, but even titanium dioxide, which is known to be photocatalytic in some circumstances, is shown to extend the life of polypropylene plastics. The crystalline nature of polypropylene leads to different morphology or fine structure in its fabricated forms. Films which are rapidly cooled from the molten state have a relatively low degree of crystallinity and greater transparency. They tend to degrade more slowly in light than counterparts which have developed higher crystallinity and coarser spherulitic structure. Orientation of polypropylene film leads to some increase in light resistance which may be attributed to increased transparency, more uniform crystalline order, and reduced oxygen permeability. Surface coating provides an alternative to internal additives as a means of protecting polypropylene from light.

The voluminous patent literature and the numerous papers appearing in technical and trade journals on the subject of the stability of polypropylene are testimony to the importance attached to this area of research and development by the plastics industry. This polymer and its related family of copolymers offer an excellent combination of physical properties, chemical resistance, good processability, and low cost. These have made polypropylene attractive for a wide variety of applications in plastics, fibers, and film. But the structure of the polypropylene molecule makes

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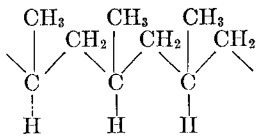
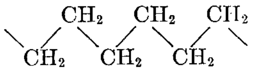


Polypropylene



Linear Polyethylene

Fig. 1. Polyolefin structures.

$$\begin{array}{ll}
\text{Initiation:} & RH \xrightarrow[\text{light}]{\text{heat or}} R\cdot + H\cdot \\
\text{Propagation:} & R\cdot + O_2 \rightarrow ROO\cdot \\
 & ROO\cdot + RH \rightarrow ROOH + R\cdot \\
\text{Termination:} & \left.\begin{array}{r} 2R\cdot \rightarrow \\ R\cdot + ROO\cdot \rightarrow \\ 2\,ROO\cdot \rightarrow \end{array}\right\} \begin{array}{l} \text{Non-initiating or} \\ \text{Nonpropagating} \\ \text{Products.} \end{array}
\end{array}$$

Fig. 2. Mechanism of oxidative degradation.

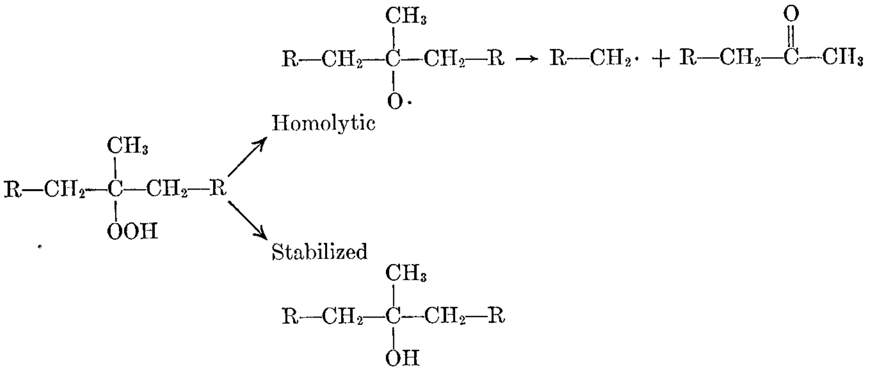


Fig. 3. Decomposition of polypropylene hydroperoxide.

it readily susceptible to oxidative attack. The rate of oxidation, and subsequent degradation of properties, is increased by heat and by exposure to ultraviolet light. If advantage is to be taken of its desirable properties, it must be protected against this attack by the judicious use of additives.

To establish a common basis for discussion of the mode of degradation and the role of stabilizers, it is useful first to have a look at the structure of the polymer (Fig. 1). The most striking feature is the occurrence of alternating tertiary carbon atoms which are the sites of attack by oxygen. The mechanism of the initiation, propagation, and termination of the radical chain reaction which is involved in the oxidation of polypropylene has not yet been worked out to the last detail, but, for our purposes here, the widely accepted scheme of the autoxidation of hydrocarbons put forward by Ingold,[1] Bateman,[2] Uri,[3] Bolland,[4] and others, is sufficient. We show it here (Fig. 2) to aid in our understanding of the role of additives.

Three different types of stabilizers are now usually found in light-resistant grades of polypropylene. First is the antioxidant or radical inhibitor, most commonly a hindered phenolic compound, which acts to interrupt the chain reaction by its ability to form relatively stable free radicals. Second is the hydroperoxide decomposer, often a sulfur-bearing compound or organic phosphite, which is believed to cause the decomposition of OOH groups in a manner which does not lead to chain scission or to free-radical production.[5] In Figure 3 the two alternative routes of decomposition are shown, the homolytic leading to degradation and the stabilized to nonradical products. The third additive is the light stabilizer. This may be an all-organic ultraviolet light absorber which thermalizes the incident radiation. Hydroxybenzophenones and benzotriazole derivatives are prominent in this use. An alternative type is an organometallic compound, such as Ferro AM101 or Cyasorb 1084, which are nickel complexes. Recent work in our laboratories has indicated that this type of stabilizer functions through two different mechanisms: (*1*) by light absorption, and (*2*) by quenching the energy of the excited state of carbonyl groups in the polymer which have absorbed ultraviolet light.[6]

Methods of Evaluation of Light Stability

The assessment of the light resistance of polypropylene and its response to modification of the polymer compound is complicated by many factors, not the least of which is the test method employed. Accelerated tests are not yet capable of predicting service life for polypropylene with precision, but this is not a problem unique to this polymer. We hope that useful guidelines will come out of the work being done on the Plastics Weatherability Project here at the Bureau of Standards under the auspices of the Manufacturing Chemists' Association.

Meanwhile we continue to do most of our testing in Florida, although outdoor exposure is also a very imperfect standard. Seasonal effects and the inadequacy of the langley as a measure of the sun's radiation have been discussed by American Cyanamid workers[7] and, more recently, by Celanese investigators.[8] The magnitude of the seasonal effects on polypropylene is illustrated in Figure 4 which shows the Florida exposure (in langleys) required to produce a 50% loss in strength of monofilaments as a function of the month in which the tests were started. We often use monofilament for light stability studies, partly because this represents a major market for our resins, but also because it provides quantitative, reproducible results in comparing formulations. Three different formulations (A, B, C) were included, and all shows the same cyclical behavior. December tests have about twice the life expectancy of those started in June.

The data represented in Figure 4 were collected about 5–7 yr. ago and should not be taken as representative of the current "state of the art." These data and some from the experiments which we will be discussing later in this paper should be regarded as illustrations of principles, all in the context of the evolutionary improvements which have been taking place as the industry has come to a better understanding of polypropylene.

Various attempts have been made to normalize the seasonal variation in the sun's intensity. Both the Cyanamid and Celanese groups have shown that exposure data can be better rationalized if only that fraction of the total langleys which is attributable to the ultraviolet radiation is applied. Unfortunately, data are not routinely available on the distribution of radiant energy as a function of wavelength. The groups referred to above had some success in applying the data published by Coblentz[9] on ratio of UV (2900–3150 A.) to total langleys measured at Washington over a period of 8 yr. Results were encouraging despite the great difference in location (exposure tests were in Arizona).

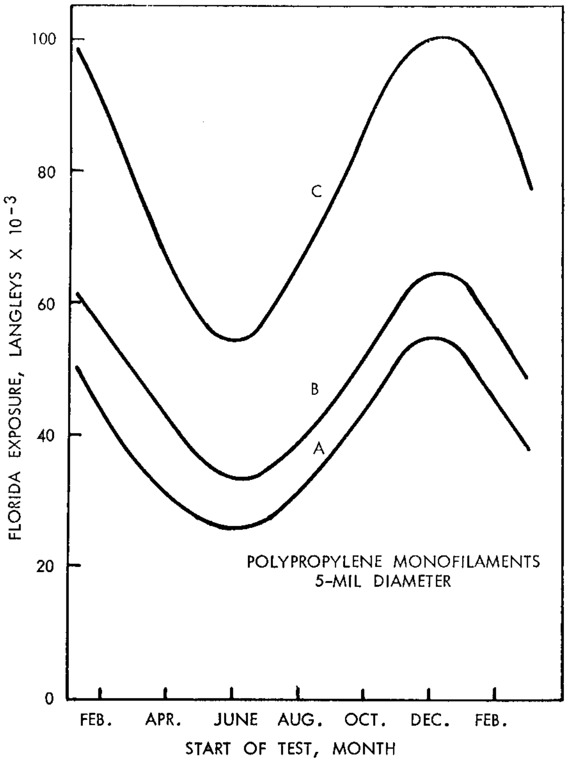


Fig. 4. Seasonal effects on exposure required to produce 50% loss of strength.

Another possibly useful approach to the normalizing of seasonal variations in intensity of radiation is that developed at the General Motors Florida Test Field.[10] These seasonal equalization factors (Table 1) are intended for use in tests of the colorfastness of fabrics but in principle may provide a means of handling data on plastics or filaments. In effect, the table attempts to level out Florida data by adjusting each month's exposure

TABLE I
Seasonal Equalization Factors

	General Motors (from colorfastness)	From UV langleys[a]	
		UV, % (from Coblentz)	Factor
January	1.32	2.3	2.30
February	1.22	2.9	1.83
March	1.10	4.1	1.29
April	1.00	5.3	1.00
May	0.90	6.3	0.84
June	0.85	6.8	0.78
July	0.82	6.9	0.77
August	0.83	6.8	0.78
September	0.87	6.5	0.81
October	1.0	4.6	1.15
November	1.2	2.9	1.83
December	1.3	1.9	2.79

[a] Divide total daily (or monthly) langleys by appropriate factor for that month to get "corrected total langleys."

in langleys to what it would have been in the "average months" of April and October. Analogous factors can be derived from the Coblentz data.

We observed earlier that approximately a 2:1 ratio exists between seasonal extremes in exposure of polypropylene monofilaments. From the General Motors tabulation we obtain a ratio of 1.6 between the most severe and the least severe months, and from use of the ultraviolet fraction approach, this ratio is 3.6. The closer agreement of the experimental data with the GM approach implies that ultraviolet content alone is not a sufficient measure of the total effect of the weather.

To illustrate how such equalization factors may nonetheless be useful in correlation of outdoor exposure data with accelerated laboratory tests, we show in Table II some comparative data on a group of four pigmented monofilaments (15-mil diameter) exposed in Florida and in the Twin-Carbon-Arc Weather-Ometer (standard ASTM D1499 wet–dry cycle). Florida tests

TABLE II
Polypropylene Monofils-Carbon Arc Weather-Ometer versus Florida Exposure

	Exposure till loss of 50% strength			
		Florida (started December)		
Filament	Weather-Ometer, hr.	Total langleys	langleys, GM method	UV, langleys
AW	905	59,000	51,000	2,100
BW	1310	86,000	83,000	3,850
CW	785	49,000	42,000	1,600
CG	1380	96,000	89,000	4,250

were started late in the month of December. Regression analyses on these data show very high coefficients of correlation of Weather-Ometer versus Florida results no matter how the outdoor results are handled. The langley data based on the GM factors show a marginally better correlation than the other two methods of expressing exposure. Although there is a twofold difference in lifetime represented in these filaments, it is not too surprising that the "corrections" have little influence on the correlation since all the exposures were run concurrently. The results have been sufficiently encouraging, however, to lead us to expand these experiments with exposures at different seasons and to include work in the xenon arc Weather-Ometer which provides a better simulation of the sun's spectrum.

Influence of Specimen Thickness and Absorber Concentration

Since the degradation of polypropylene on exposure to light is the result of oxidation and since the attack proceeds from the exposed surface inward, one certainly expects thicker samples to survive longer than their thinner counterparts. In a qualitative sense, this is easily demonstrated. Table III shows a summary of Florida lifetimes (in total langleys and in "normalized" langleys) of injection-molded bars, monofilaments, and multifilament yarns in two formulations—one without ultraviolet absorber, the other containing 0.5% absorber. No pigment was involved. These data probably raise more questions than they answer. It will be difficult to develop rigorous mathematical expressions for the effect of thickness on weathering since "all other things" are seldom equal in this type of work. Different fabrication conditions are required and different crystalline fine structures will develop, resulting in varying degrees of transparency and ratios of "core" to "skin." We are now trying to establish more systematic data in this area.

A factor closely related to the thickness effect is the influence of the concentration of ultraviolet absorber in the polymer. The experiments from which the data on the previous table (Table III) were taken are described more completely in the next two figures. The objective here was to determine the value of increasing levels of ultraviolet absorber in extending the life of the polymer on exposure to the weather. The first graph (Fig. 5)

TABLE III
Florida Lifetime versus Specimen Thickness

			Exposure till loss of 50% strength			
			No UV absorber		0.5% UV absorber	
Specimen	Thickness, in.	Start of exposure	Total langleys	Corr. langleys	Total langleys	Corr. langleys
Molded bars	0.062	Oct.	63,000	52,600	133,000	128,000
Monofil	0.005	Dec.	43,000	33,600	67,000	56,000
Multifil, (210/35)	0.001	Dec.	21,000	16,000	30,000	22,900

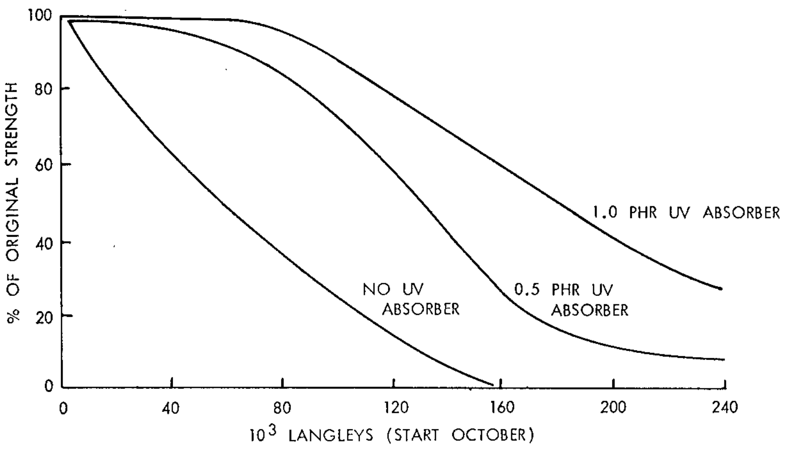


Fig. 5. Weathering of Pro-fax injection-molded dumbbells (1/16 in. thick).

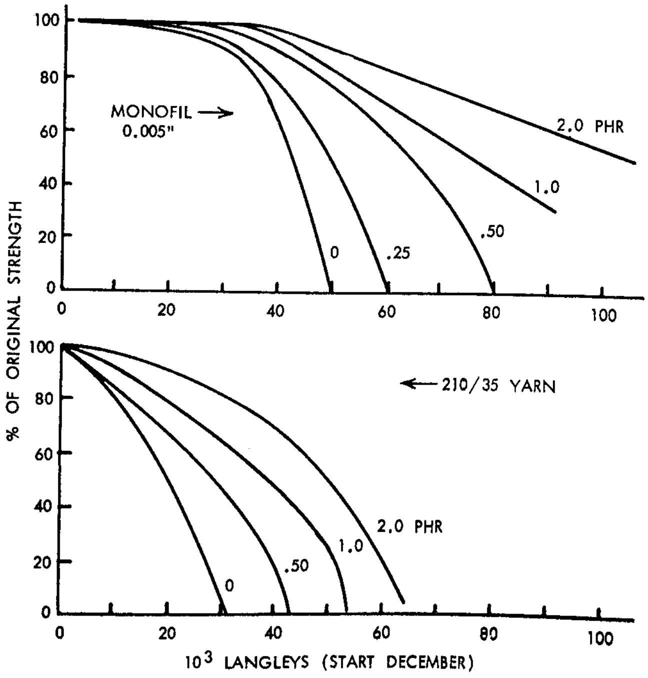


Fig. 6. Influence of UV absorber concentration on fiber weathering in Florida.

shows how the strength of the injection-molded bars falls off on aging with 0, 0.5, and 1.0% of a commercial ultraviolet absorber present. The second set of graphs (Fig. 6) shows similar tests on monofilaments and multifilament yarns with absorber concentration extended to 2%. If we "normalize" the exposures represented in these curves by applying the GM factors which we discussed earlier, we find remarkably good agreement

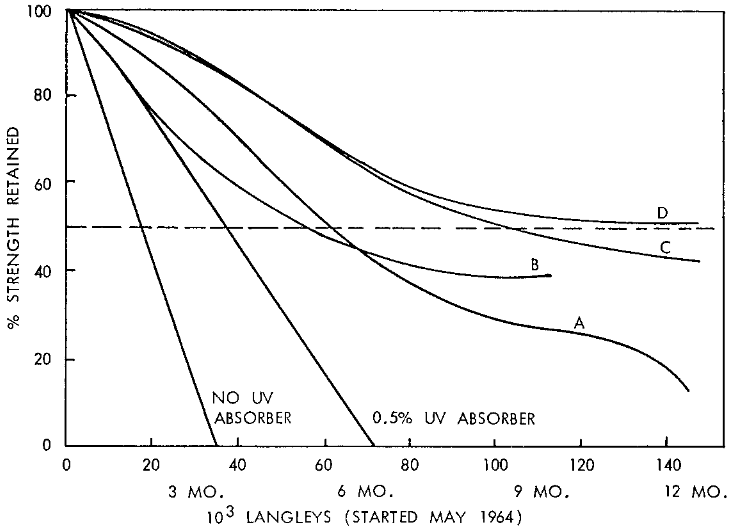


Fig. 7. Florida exposure vs strength of 5-mil monofilaments containing supplementary additives.

with the prediction, derived from the kinetics of the oxidation, that the effectiveness of the absorber should vary as the square root of the change in concentration. Thus, to double the life, it is necessary to quadruple the absorber concentration.

We can also show from these data that our ultraviolet absorber is more effective in heavier cross-sections. The use of 0.5% ultraviolet absorber yields a 140% increase in the life of the 62-mil bars, a 67% increase in the monofilament, and a 43% increase in the yarn. This simply reflects differences in surface to volume ratio and in the depth in which the additive has an opportunity to do its job of absorbing the harmful radiation.

Other stabilizer components (antioxidants and synergists) can add to or detract from light stability, thus raising or lowering the base line from which the absorber starts to work. To show the significance of the total formulation with respect to light stability, we have reproduced (in Fig. 7) the results of the Florida exposure of a group of 5-mil monofilaments, all but one of which (the control) contain the same ultraviolet absorber at the same concentration (0.5%). The upper curves represent resins which contain additional components, of a proprietary nature, which are obviously capable of greatly extending the useful life of the material, supplementing the action of the absorber.

Effect of Pigments

Since most polypropylene materials reach the market place in colored form, it is appropriate to inquire how pigments influence resistance to ultraviolet light. This could be the subject of an entire symposium in itself. We will confine ourselves here to a few remarks about the extremes

TABLE IV
Pigments versus Weathering, ($^1/_{16}$ in. Molded Specimens)

	Strength retained, %, months in Florida (started Sept.)		
	6	12	18
Impact grade			
Natural	49	16	Brittle
White (1% TiO_2)	94	74	50
Black (2.5% channel)	109	108	108
General purpose grade			
Natural	34	7	Brittle
Black	105	103	107
Light-resistant grade			
Natural	96	68	57
Black	112	108	107

of black and white. The final result of the presence of the pigment is a complex interaction of its opacifying or light-absorbing power, its possible photocatalytic influence, its heat-absorbing effect, and its influence on the other additives. Just as it is for polyethylene, finely divided, well-dispersed, channel-type carbon black is unexcelled as a light absorber for polypropylene. We have injection-molded samples on our test fence in Wilmington, Delaware, containing 2.5% Monarch 74 black, which are in excellent condition, with no sign of surface crazing or chalking, after more than 6 yr. of weathering. The primary white pigment, titanium dioxide, also had a protective influence when used at 1–2% concentration in molded material. In thinner sections, as in fibers, its well-known photocatalytic activity tends to overcome its opacifying effect and the final performance is usually no better than, and sometimes slightly poorer than, its natural, unpigmented counterparts. To illustrate the magnitude of these effects in molded specimens, we show in Table IV some Florida data on strength retention. The blacks here contained 2.5% Monarch 74 and

TABLE V
Pigments versus Weathering, $^1/_{16}$ in. Molded Specimens

	Strength retained, %				
	Months in Florida (started July)				
	3	6	9	12	24
General purpose grade					
Natural	43	Brittle			
White (2% TiO_2)	98	62	38	25	4
Black (2% bone black)	—	84	—	77	71
Light-resistant grade					
Natural	98	70	64	58	36
White	95	94	87	90	76
Black	—	97	—	89	86

had lost no strength after 18 mo. The white, containing 1% rutile TiO_2, was down to 50% of its original strength at that time. In another series (Table V), a coloring type bone black, added more to provide a glossy, jet-black color than to provide optimum protection, held up very well for 2 full years in Florida. With this poorer black pigment, a light stabilizer provided some added benefit.

Morphological Effects

The crystalline nature of polypropylene leads to rather complex morphology or microstructure in fabricated articles. Crystallite and spherulite size, degree of orientation, density, ratio of fine-structured skin to coarser-structured core, and other more subtle effects can be greatly influenced by the stock melt temperature, the rate of cooling, the rate of filling the mold, and the rate of nucleation. Quench cooling or use of certain nucleating agents leads to greater transparency. One would expect these factors to have an influence on the light resistance of the finished item. Several years ago in our laboratory, Dr. R. M. Hall made a study of the effect of quench temperature of 25-mil compression-molded, light-stabilized Profax on Fade-Ometer life. The results (Fig. 8) showed a striking dependence on quench temperature. Rapid cooling produced low density, small crystallite size, high transparency, and long Fade-Ometer life. A maximum

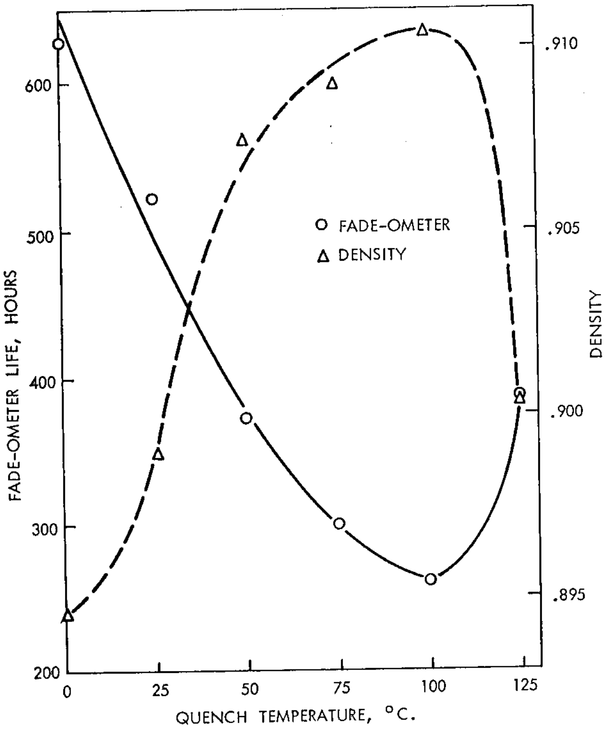


Fig. 8. Effect of quench temperature on Fade-Ometer life and density

TABLE VI
Effect of Cooling Rate on Weathering of General Purpose Polypropylene;
Exposure: Wilmington, Delaware, Started May 20, 1966

Exposure	Density	C=O, %	I.V.	Brittle
	Ice water quench			
Initial	0.8895	0.003	2.21	No
30 days	0.8894	0.011	2.18	No
60 days	0.8932	0.06	1.25	Slight
90 days	0.9024	>0.10	0.35	Yes
	Press-cooled			
Initial	0.9060	0.004	2.23	No
30 days	0.9075	0.014	2.06	No
60 days	0.9087	0.06	1.56	Yes
90 days	>0.91	>0.10	0.43	Yes

density and minimum Fade-Ometer life were obtained at a quench temperature of 100°C. The sheets were pressed at a platen temperature of 215°C. for 15 min. and then plunged directly into the quench bath at the indicated temperatures.

More recently, pressed films of 10-mil thickness were prepared from a general purpose resin containing no light stabilizer and were cooled from the melt in two different ways: (*1*) by quenching rapidly in ice water, and (*2*) by controlled slow cooling in the press. This produced a wide difference in density and transparency. The films were then exposed to the hot, dry Delaware summer weather in 1966, starting on May 20. They were checked monthly for density, carbonyl (5.85 μ band) development, intrinsic viscosity, and flexibility (Table VI). The clear thin films apparently were degraded so rapidly in the absence of light stabilizers that the differences in crystalline structure were overwhelmed and the two types behaved essentially the same.

To determine whether orientation has any influence on outdoor durability, all other things being as nearly equal as possible, a series of films

TABLE VII
Effect of Linear Orientation on Weathering of Thin General Purpose
Polypropylene Film; Exposure: Wilmington, Delaware, Started May 20, 1966

Draw ratio	Initial strength, lb./in.^{2}	Strength retained, %, days exposure				Intrinsic viscosity, days exposure			
		30	45	60	90	0	30	45	60
0	6,400	—	45	0	—	2.0	1.8	0.9	0.3
2×	12,000	47	—	29	0	1.9	1.9	1.4	0.8
3×	19,100	90	64	30	0	2.1	1.8	1.3	0.7
5×	29,700	86	86	17	0	2.2	1.9	1.5	1.0
7.5×	45,200	100	80	46	0	2.0	1.8	1.2	1.1
10×	63,000	80	61	36	0	2.2	1.9	1.4	0.8

was cast from general purpose resin and drawn to various extents both linearly and biaxially. The experiment was designed to yield films all in the 1–1.5-mil thickness range. The linear films were drawn "in line" with the extrusion casting operation. The biaxially oriented films were drawn from cast films using a T. M. Long stretching device.

The effect of weathering on the linear films is shown in Table VII in terms of retained strength and change of intrinsic viscosity through the summer months. There is some evidence here that orientation is beneficial in that all of the oriented films outlasted the unoriented control film. However, drawing beyond 3× appears to have no significant influence on light resistance.

The weathering behavior of the biaxially drawn, balanced film was similar to that obtained with the linearly drawn film, i.e., all of the oriented films retained their properties longer than the control, but there were no real differences among them in their rate of degradation.

The improvement in light resistance brought about by orientation is not yet completely understood, but it may be attributed to a combination of increased transparency, more uniform crystalline order, and reduced oxygen permeability.

Promise in Surface Coating

As a final factor which may be used to influence the light resistance of polypropylene, we would like to call attention to the alternative of using a surface coating on the molded material. Recent developments in surface treatment and/or primer coats now make it possible to adhere a top coat very effectively to polypropylene. We have compared general purpose resin with a lacquered version of the same material in Florida weathering. After 6 mo. of exposure, the natural and white pigmented controls both showed obvious surface crazing and degradation. However, the same materials, when coated with a white pigmented nitrocellulose–acrylic lacquer, showed no evidence of surface damage after a full year of exposure, and the tests are continuing.

Conclusion

In this review of the various factors which exert an influence on the light resistance of polypropylene, we have discussed the nature of the oxidative degradation process and the role of the stabilizing additives which may be used to combat it. Accelerated test methods for the evaluation and prediction of service life outdoors are filled with pitfalls, but progress is being made in understanding seasonal variations in Florida and Arizona exposures, and even the much maligned carbon arc laboratory devices seem capable of yielding meaningful comparative data. The xenon arc Weather-Ometer, whose spectral energy distribution, at least in the ultraviolet and visible regions, closely matches that of natural sunlight, shows great promise. We have confirmed that thicker specimens have longer useful lives and that ultraviolet absorbers have a predictable dependence on concentration. Pigments are generally helpful in adding to light resistance of molded material. The influence of polymer morphology on light resistance is beginning to be better understood, but there are limitations to what can be done to modify these properties since the demands for efficient fabrication processes will probably always dominate. Finally, the potential usefulness of surface coatings as a means of protecting polypropylene from light, as well as providing increased flexibility in decoration and coloring, has been pointed out.

As a result of laboratory and field experience obtained during the first decade of polypropylene's availability, there now exists a substantial understanding of its strengths and weaknesses. Through a greal deal of work on synthesis, formulation, and testing by the resin manufacturers and suppliers of additives, great strides have been made in providing increased light resistance for the polymer in its many useful forms. Although each added increment of life has now become harder to achieve, there is reason to expect that longevity will continue to increase.

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Résumé

La stabilité du polypropylène à l'exposition à la lumière et les moyens pour améliorer sa résistance à une telle exposition ont fait l'objet de réunions depuis que ce plastique a été introduit en 1957. La structure du polymère rend celui-ci oxydable. La longueur de la période d'induction diminue et la vitesse d'oxydation croît par la chaleur et la lumière. Trois types d'additifs, à savoir des antioxydants, des décomposants d'hydroperoxyde et des stabilisants à la lumière, sont le plus souvent utilisés pour protéger le polypropylène. Des tests accélérés de laboratoire de résistance à la lumière ne sont pas encore capables de prédire la durée de vie du matériau avec précision et des tests d'exposition à l'extérieur sont compliqués par des variations saisonnières de l'intensité de lumière solaire. Ces réactions peuvent être diminuées en corrigeant les valeurs pour la teneur en lumière ultraviolette ou en appliquant des facteurs d'égalisation déterminés empiriquement. Une corrélation amméliorée des tests du Weather-Ometer a été obtenue de cette façon. Etant donné que l'attaque oxydante débute à la surface exposée du polymère, des échantillons d'essais plus épais présentent une durée de vie à l'extérieur plus longue. La durée de vie du polypropylène varie approximativement comme la racine carrée de la concentration en absorbant de lumière ultraviolette. Les absorbants sont relativement plus efficaces dans les échantillons épais que dans les échantillons fins. Les pigments sont généralement favorables à la résistance à la lumière du polymère total. Le noir de carbone est le plus efficace absorbant à la lumière mais même le dioxyde de titane qui est connu comme photocatalyseur dans certaines circonstances augmente la durée de vie des plastiques à base de polypropylène. La nature cristalline du polypropylène amène à des morphologies différentes ou structures fines des matériaux frabriqués. Les films qui sont rapidement refroidis au départ de leur état fondu présentent des degrés de cristallinité relativement faibles et une transparence plus grande. Ils tendent à se dégrader plus lentement à la lumière que les autres échantillons qui ont une cristallinité plus élevée et une structure sphérulitique plus compacte. L'orientation du film de polypropylène augmente légèrement la résistance à la lumière qui peut être attribuée à une transparence accrue, un ordre cristallin plus uniforme et une perméabilité à l'oxygène plus réduite. Le recouvrement de surface permet une autre méthode à des additifs internes comme un moyen de protection du polypropylène à la lumière.

Zusammenfassung

Die Stabilität von Polypropylen gegen die Einwirkung von Licht und die Mittel diese Beständigkeit zu verbessern, bildeten einen Gegenstand des Interesses seit der Einführung dieses Plastomeren im Jahre 1957. Die Struktur des Polymeren macht es der Oxydation zugänglich. Durch Wärme und Licht wird die Länge der Induktionsperiode herabgesetzt und die Oxydationsgeschwindigkeit erhöht. Drei Additivtypen, nämlich antioxydantien, Zersetzungsreagentien für Hydroperoxyde und Lichtstabilisatoren, werden am häufigsten zum Schutz des Polypropylenes verwendet. Beschleunigungs-Laboratoriumtests für die Lichtbeständigkeit sind noch nicht in der Lage, Präzisionsangaben für die Dauerhaftigkeit zu liefern und Aussenexponierungstests werden durch die jahreszeitlich bedingten Schwankungen der Intensität des Sonnenlichtes kompliziert. Diese Schwankungen können durch eine "Korrektur" der "langley-" Werte für den Ultraviolettgehalt oder durch Anwendung empirisch bestimmter Ausgleichfaktoren geglättet werden. Auf diese Weise wird eine bessere Korrelation zu Weather-Ometer-Tests erhalten. Da der oxydative Angriff an der exponierten Oberfläche des Polymeren beginnt, besitzen dikkere Testproben eine längere Lebensdauer im Freien. Die Lebensdauer von Polypropylen hängt angenähert von der Quadratwurzel aus der Konzentration des Ultraviolettabsorbers ab. Absorber sind in dicken Proben verhältnismässig besser wirksam als in dünnen. Pigmente sind im allgemeinen für die Lichtbeständigkeit des Gesamtpolymersystems günstig. Russ ist das wirksamste lichtabsorbierende Pigment; aber sogar Titandioxyd, das bekanntlich unter gewissen Umständen photokatalytisch wirkt, zeigt die Fähigkeit, die Lebensdauer von Polypropylen zu verlängern. Die kristalline Natur von Polypropylen führt zu einer verschiedenartigen Morphologie oder Feinstruktur in seiner verarbeiteten Form. Bei rascher Kühlung aus dem geschmolzenen Zustand besitzen Filme einen verhältnismässig niederen Kristallinitätsgrad und grössere Transparenz. Sie zeigen eine Tendenz zum langsameren Abbau unter Licht als die Gegenstücke mit höherer Kristallinität und gröberer Sphärolithstruktur. Orientierung von Polypropylenfilmen führt zu einer gewissen Zunahme der Lichtsbesändigkeit, was auf erhöhte Transparenz, einheitlichere kristalline Ordnung und herabgesetzte Sauerstoffdurchlässigkeit zurückgeführt werden kann. Der Oberflächenüberzug liefert eine Alternative zu den inneren Zustätzen als Mittel zum Lichtschutz von Polypropylen.

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Outdoor Exposure of Organotin-Stabilized Rigid PVC

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Synopsis

Rigid unpigmented PVC sheets containing organotin stabilizers were exposed to several types of outdoor weathering at Phoenix, Arizona. Measurements were made of color and haze development and changes in physical properties of the sheets at intervals during the exposure period. The degradation behavior of translucent PVC sheets placed on an outdoor accelerated exposure device correlated in part with one of the exposure conditions used: 45° southern exposure, unbacked panels. Translucent rigid PVC stabilized with organotin maleate derivatives and containing ultraviolet absorbers appeared to be most resistant to outdoor photodegradation.

INTRODUCTION

The use of rigid PVC is growing for exterior applications such as window sash, extruded siding, and exterior sheeting. The performance of these products, as well as PVC pipe, over the past 10 yr. has shown that the properties of PVC can be exploited commercially in building applications based on opaque rigid PVC formulations designed for the purpose. It is obvious that retention of both appearance and physical properties of the finished articles under service conditions is necessary to its ultimate acceptance by the consumer. Most of this weathering data and practical experience has been gained with opaque, pigmented formulations, largely white or gray. This work deals with the effect of organotin stabilizers and UV absorbers on the behavior, in sunlight, of translucent PVC not formulated with the protective pigments used in the successful opaque products.

Many factors, such as temperature, humidity, mechanical erosion, and of course, light energy can cause degradation of rigid PVC when exposed outdoors. The initial effect noted is surface discoloration with prolonged exposure causing a change in physical properties such as stiffening and a decrease in impact resistance.

A great deal of work has been done in the area of protecting rigid vinyl articles against photodegradation. Ultraviolet absorbers and antioxidants have been recommended as additives to the basic heat-stabilized PVC formulation for this purpose.

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This paper deals specifically with the effect of several organotin stabilizers on the outdoor weathering behavior of translucent rigid PVC. Other components of commercial vinyl formulations such as pigments, lubricants, and impact modifiers were not used. Inclusion of these components would therefore tend to obscure the degradation response of the vinyl sheet to stabilizer composition.

In addition to stabilizer evaluation, the effect of an ultraviolet absorber was measured by adding it to half of the tin-stabilized test samples.

The outdoor exposure data was obtained over a 2-yr. period at Phoenix, Arizona. Three different test conditions were used, one of these being an accelerated outdoor weathering device.

EXPERIMENTAL

Samples were prepared according to the following recipe:

PVC homopolymer (Geon 103 EP B. F. Goodrich)	100 phr
Stabilizer	3.0 phr
Ultraviolet absorber (where used) [Tinuvin PS (a substituted benzotriazole) Geigy Chemical Company]	0.1 phr.

Formulations were milled for 5 min. at 350°F. on a 2-roll differential speed mill, and were then pressed into panels, 2.5 × 5.0 × 0.08 in.

The stabilizers employed were a dibutyltin bismercapto ester derivative and three dibutyltin maleate derivatives.

The panels were exposed in duplicate as follows: one set at 45° southern exposure, unbacked. Samples were mounted on a frame inclined 45° from the vertical and facing south. Only the edges of the panels were fastened. Radiation passed through the panel, and temperature at the surface of the panel was about the same as ambient air temperature.

One set was exposed at 45° southern exposure, backed. Samples were mounted directly onto a backing material, usually plywood, such that a dead air space of about $^1/_{16}$ in. was formed between the panel and the backing. This construction had the effect of increasing panel surface temperatures an average of 10–15°F. higher than ambient air temperatures during the height of the daily solar radiation.

In addition, one set of panels was placed on an accelerated outdoor weathering device called EMMA-10 (equatorial mount with mirrors for acceleration). This unit, which has been previously described,[1] consisted of a follow-the-sun unit which concentrates natural sunlight on a test specimen by a group of 10 mirrors. Heat buildup at the specimen surface was minimized by blowing air over the test specimen during exposure. The advantage of this unit compared to artificial accelerated light sources, such as carbon arc or fluorescent light devices, was that the outdoor unit delivered concentrated light with the same spectral energy distribution as natural sunlight, hopefully leading to better correlation with natural outdoor exposure. (Artificial indoor light devices, however, would be useful for ac-

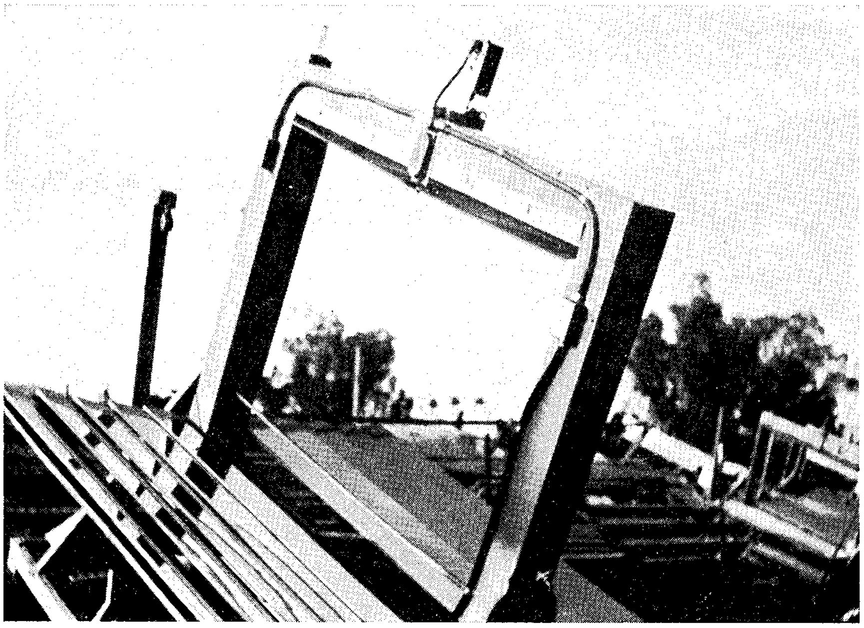

Fig. 1. EMMA-10.

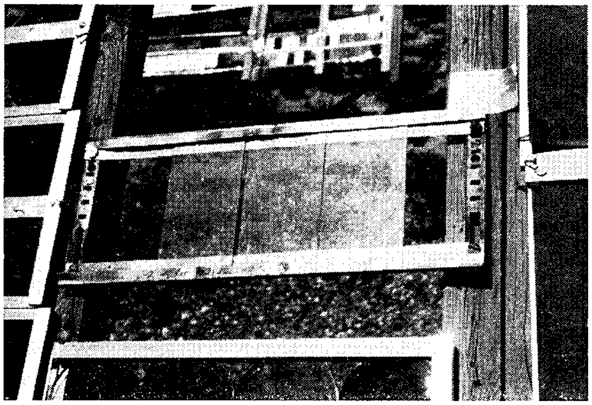

Fig. 2. Arizona exposure, 45°S, unbacked.

celerated testing of materials for indoor use, such as fluorescent light fixtures.)

Figure 1 is a picture of the EMMA device, while Figures 2 and 3 show the 45°S unbacked and backed test racks, respectively.

One complete set of panels was retained in the dark over the entire exposure period to measure any degradative changes due to aging in the absence of light.

All panels were sent to Phoenix in June, 1964 and tests were begun simultaneously on all three exposure racks in order to minimize seasonal variations in both light intensity and spectral distribution energy.

The panels on test on the 45°S exposure racks were returned to our Rahway, N. J. Laboratories at approximately 25-kilolangley intervals (1 kilolangley = 1000 langley, 1 langley = 1 g.-cal. of radiant energy/cm.^{2} of surface), and the accelerated test (EMMA) samples were returned at approximately 50-kilolangley intervals. All samples were measured for color and haze development using a Meeco Colormaster Model 4. Readings were calculated in terms of yellowness index (YI) for color (ASTM D-1925), and contrast ratio (ASTM D-1738-60 T) for haze. Physical measurements were made only at the 0, 25, 50, and 200-kilolangley exposure intervals. The tests performed were hardness (ASTM D-785), impact resistance (ASTM D-256), and tensile strength (ASTM D-638).

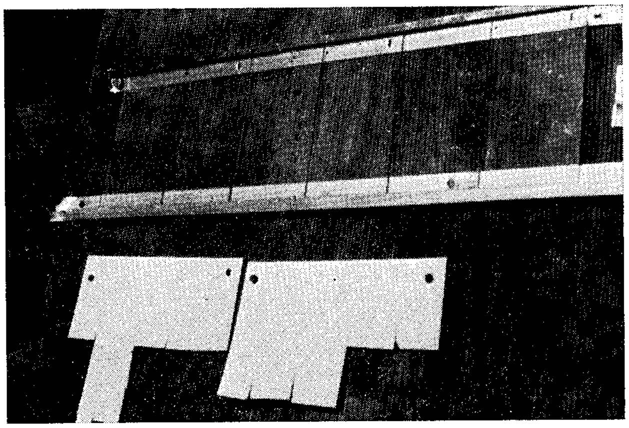

Fig. 3. Arizona exposure, 45°S, backed.

On completion of the measurements, the panels were returned to Arizona and replaced on the exposure racks. About 17 days elapsed between the time the samples were removed from the racks and the time they were replaced. The total radiant energy figures shown on the following graphs include only the amount recorded while the panels were actually on test.

RESULTS AND DISCUSSION

Surface Discoloration

Figure 4 indicates the color development of the panels subjected to accelerated test exposure. All PVC panels containing only resin and tin stabilizer showed noticeable surface discoloration after 60 kilolangleys. This point was taken at the beginning of visual degradation. The panel stabilized with the organotin mercapto derivative appeared to darken at a greater rate than the panels stabilized with the organotin maleate derivatives.

The addition of ultraviolet absorber to any of the resin–organotin maleate formulations had a pronounced effect on the resistance of the PVC panel to

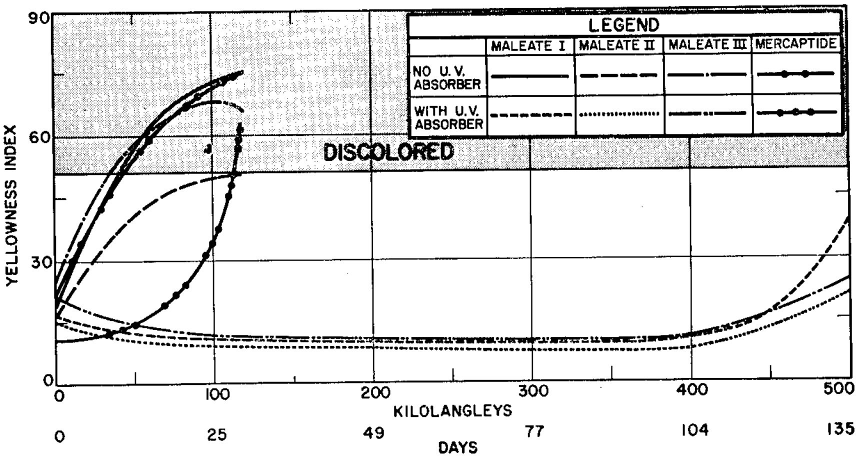

Fig. 4. Arizona test results, PVC color, EMMA 10.

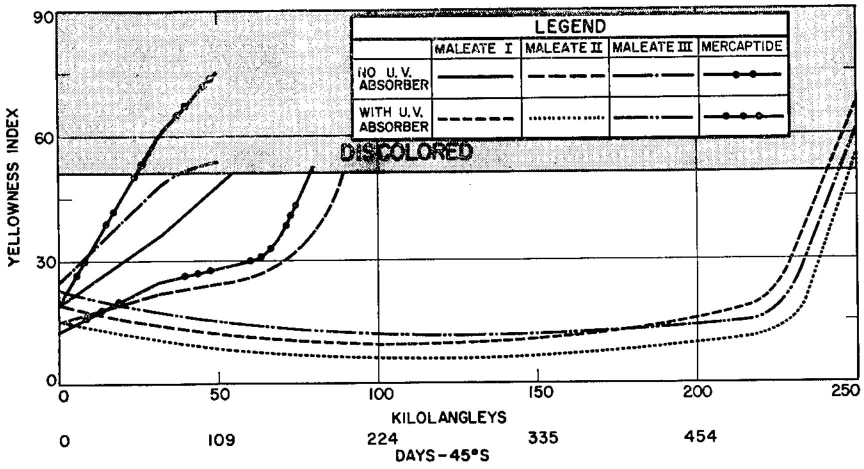

Fig. 5. Arizona test results, PVC color, 45°S, unbacked.

photodegradation. Initially, slight bleaching of the panels was noted up to 100 kilolangleys.

The color curve then remained constant to about 400 kilolangleys. At this point discoloration began and progressed rapidly so that at 530 kilolangleys the panels were completely blackened. This was after 142 days of actual exposure.

The PVC panel containing the organotin mercapto stabilizer and ultraviolet absorber showed discoloration after 100 kilolangleys exposure. The ultraviolet absorber increased only slightly the resistance of the organotin mercapto-stabilized PVC panel to surface discoloration.

Figure 5 shows the exposure measurements obtained for the unbacked, 45°S test rack. The amount of radiant energy impinging on the test panel

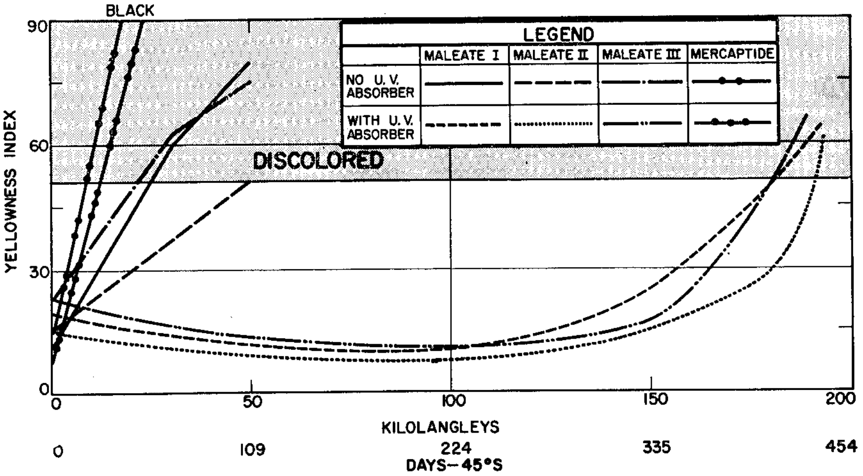

Fig. 6. Arizona test results, PVC color, 45°S, backed.

was again measured in kilolangleys, but the actual exposure time was quite different from that recorded on the accelerated test rack. The total amount of radiant energy measured on the accelerated test rack during the 142 days of actual exposure was 530 kilolangleys, an average of 3.72 kilolangleys per day. The average energy measured on both the 45°S through the backed test racks was 0.441 kilolangleys/day. The average radiation ratio of EMMA exposure to 45°S was therefore 8.4 to 1.

The PVC sheets containing only organotin maleate stabilizer showed less rapid surface discoloration than the sheet stabilized with the organotin mercapto derivative. By 50 kilolangleys exposure, however, all samples were discolored.

As was the case with accelerated exposure, the addition of ultraviolet absorber to the organotin mercapto-stabilized PVC formulation did improve slightly the resistance of test panel to discoloration, but the effect was much more pronounced than when ultraviolet absorber was added to the formulation using organotin maleate stabilizers. A slight bleaching effect was again noted which reached a minimum at 100 kilolangleys. After 215 kilolangleys (488 days), the average color reading of the maleate-stabilized PVC panels containing ultraviolet absorber was the same as the initial unexposed reading. Surface blackening finally occurred at 241 kilolangleys (546 days).

Figure 6 shows comparable data obtained on the 45°S backed test rack. As previously indicated, temperatures at the backed panel surface were higher for this exposure condition than for either 45°S unbacked or accelerated outdoor exposure.

The effect of higher surface temperature was to increase surface discoloration markedly. All formulations containing just resin and stabilizer showed marked discoloration after 25 kilolangleys exposure. There was virtually no difference in the discoloration rate of the mercaptin-stabilized PVC panel when ultraviolet absorber was added to the formulation.

The incorporation of ultraviolet absorber into the formulations employing organotin maleate stabilizers delayed the time-to-severe-discoloration to 190 kilolangleys. Very little difference was noted in the discoloration rate of the panels containing the various organotin maleate stabilizers.

Haze Development

Haze development during service exposure must be considered when designing rigid PVC for such applications as roofing panels and light fixture diffusers. The quantitative measurement of this factor proved difficult due to the fact that duplicate panels gave haze readings which varied as much as ±20%.

Figure 7 shows haze development for the samples on the accelerated exposure rack. Haze development paralleled surface discoloration. By 100 kilolangleys, all panels containing only resin and stabilizer had developed cloudy surfaces. By 110 kilolangleys, the panel containing organotin mercapto stabilizer and ultraviolet absorber showed a noticeable haze.

The PVC panels containing organotin maleate stabilizers and ultraviolet absorber remained visually clear until 400 kilolangleys exposure.

Haze developed gradually thereafter to 530 kiloangleys when the test was discontinued due to the surface blackening of the panel.

The 45°S unbacked exposure data shown in Figure 8 indicate that panels containing only stabilizer appeared cloudy by 50 kilolangleys. When ultraviolet absorber was added to the organotin mercapto-stabilized formulation, the onset of visual haze was delayed to 75 kilolangleys. The PVC panels containing ultraviolet absorber and organotin maleate stabilizers showed no visual haze until 200 kilolangleys exposure.

Figure 9 shows the corresponding haze values for the 45°S backed exposure test panels. The higher panel surface temperature again caused

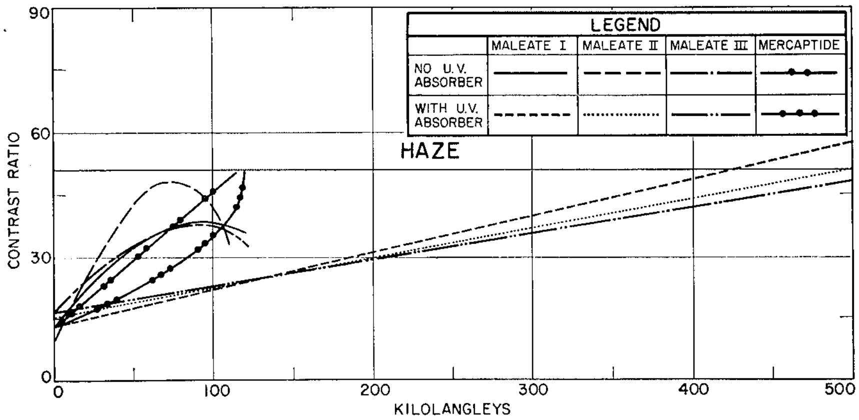

Fig. 7. Haze results, EMMA 10.

cloudiness to appear more rapidly on all samples. All panels containing only tin stabilizer were cloudy by 50 kilolangleys; the panel stabilized with the organotin mercapto derivative clouded very rapidly whether ultraviolet absorber was present or not. Panels containing organotin maleate stabilizer and ultraviolet absorber did not appear visually cloudy until 140 kilolangleys of radiant energy had impinged on the panel.

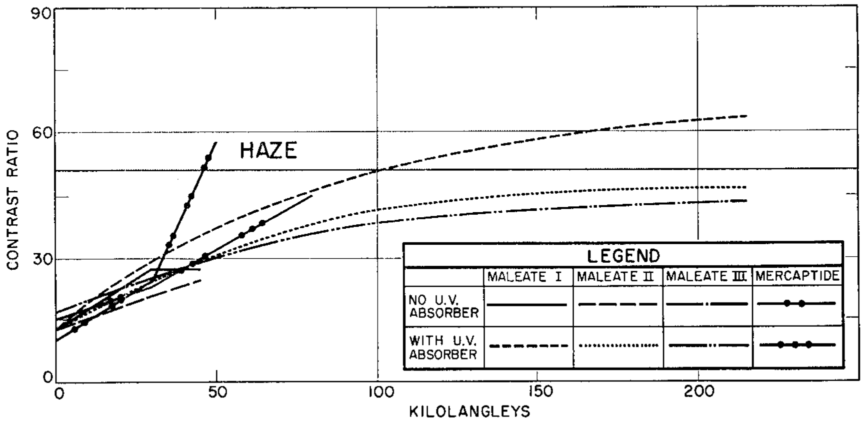

Fig. 8. Haze results, 45°S, unbacked.

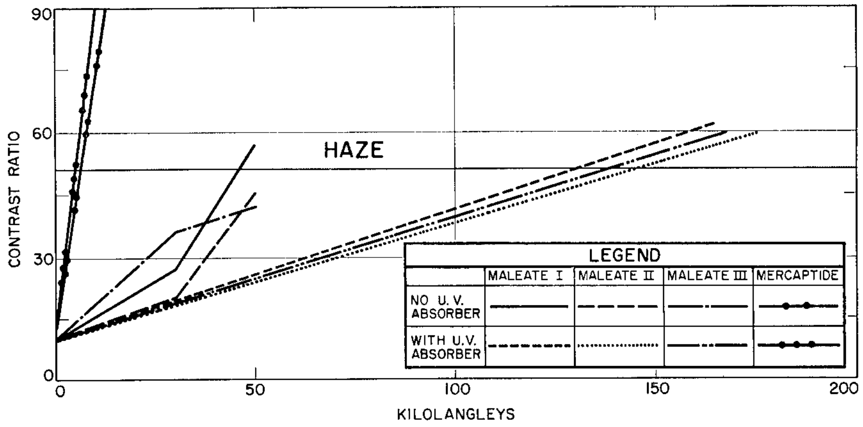

Fig. 9. Haze results, 45°S, backed.

Hardness

Figure 10 shows the surface hardness (Rockwell "M" scale) for the PVC panels on the accelerated exposure rack. The panels containing organotin maleate stabilizers showed little change in hardness up to 83 kilolangleys. Hardness increased sharply after this point, probably due to either volatilization of resin or stabilizer impurities, or actual crosslinking of the polymer.

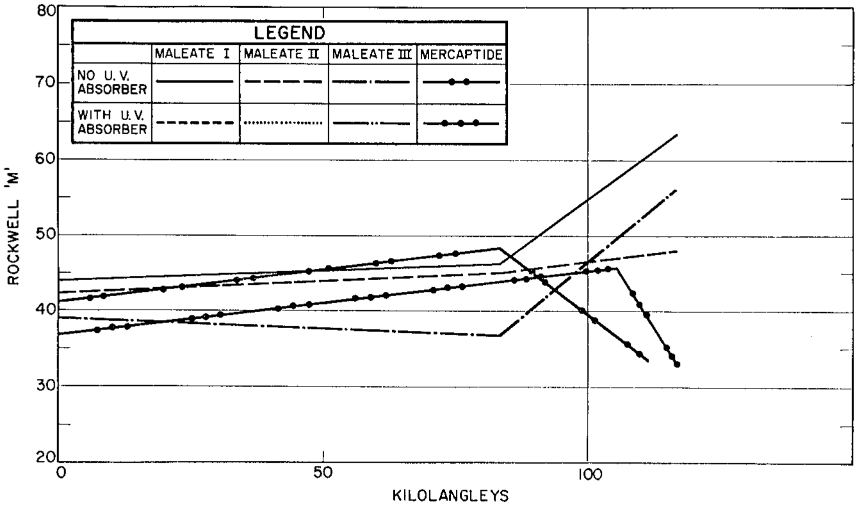

Fig. 10. Hardness results, EMMA 10.

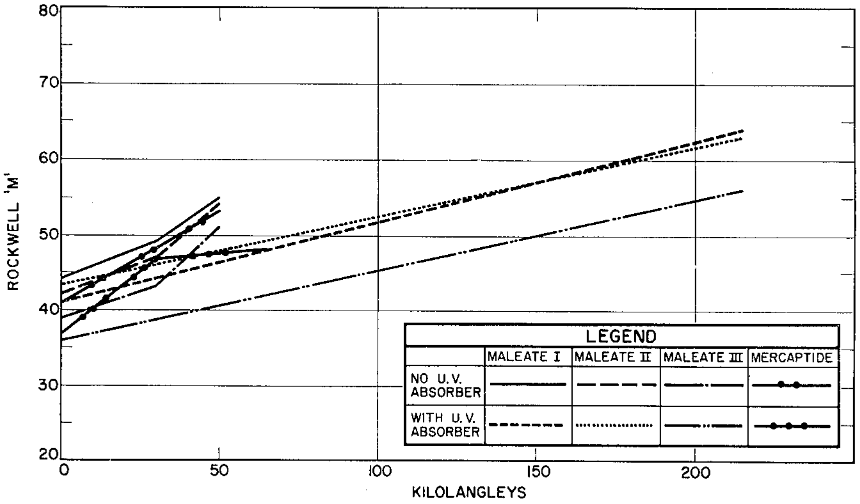

Fig. 11. Hardness results, 45°S, unbacked.

The panel containing the organotin mercapto stabilizer showed about a 22% decrease in hardness over the same exposure period. The reason for the decrease is not clear at present. The addition of ultraviolet absorber to the panels containing organotin maleate stabilizers delayed the rapid increase in hardness previously noted. Up to 100 kilolangleys, a 28% increase in hardness was measured. The addition of ultraviolet absorber to the panel containing the organotin mercapto stabilizer did not cause an appreciable change in the hardness reduction described above.

Figure 11 shows hardness measurements obtained on the 45°S unbacked exposure rack. Panels containing only organotin maleate stabilizer showed

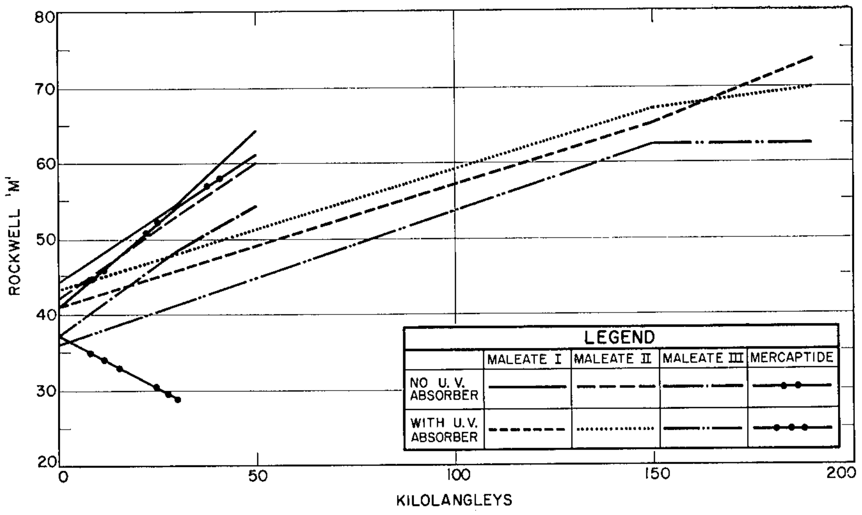

Fig. 12. Hardness results, 45°S, backed.

an average increase of 35% in hardness up to 50 kilolangleys. No additional measurements were made after this point on these panels. When ultraviolet absorber was added to the resin–organotin maleate stabilizer formulation, hardness increased by 50% to 215 kilolangleys but was only 10% higher than the original hardness figure at 50 kilolangleys.

The panels containing the organotin mercapto stabilizer both with and without ultraviolet absorber showed a 35% hardness increase up to 50 kilolangleys. The test was terminated at this point.

Figure 12 presents hardness readings on the PVC panels exposed on the 45°S backed test rack. The effect of backing the panels and thus raising the surface temperature is to accelerate surface hardening. Panels containing only organotin maleate stabilizers showed a 47% increase in hardness up to 50 kilolangleys. The panels containing ultraviolet absorber and organotin maleates showed a 23% hardness increase up to 50 kilolangleys. The behavior of the PVC sheet containing organotin mercapto stabilizer was peculiar. When no ultraviolet absorber was present, a 47% increase in hardness to 35 kilolangleys was measured. The panel containing ultraviolet absorber showed a decrease of 30% over the same exposure period. The measurements may not be meaningful due to the very degraded condition of the sheets at this point.

Tensile Strength

The PVC panels containing only resin and stabilizer showed a 22% average reduction in tensile strength (from 7300 to 5700 psi) up to 100 kilolangleys exposure on the accelerated testing rack. The data is shown in Figure 13.

The panels containing ultraviolet absorber and organotin maleate stabilizers showed either a very small loss in tensile strength or a slight increase

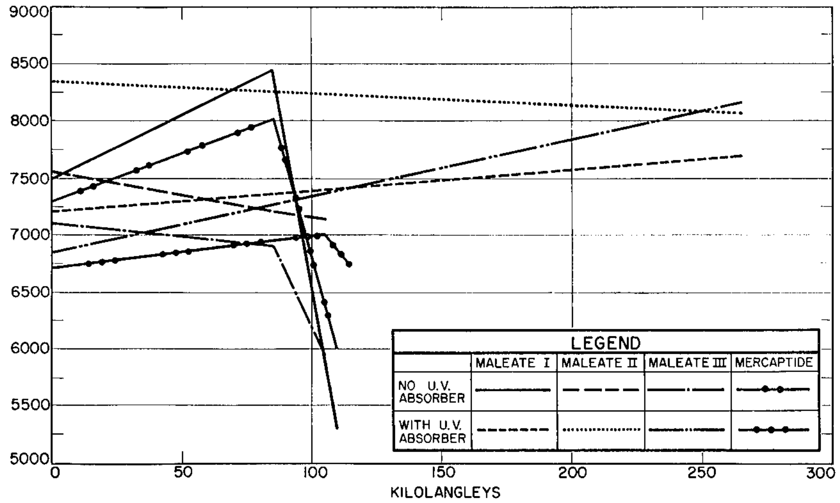

Fig. 13. Tensile strength, EMMA 10.

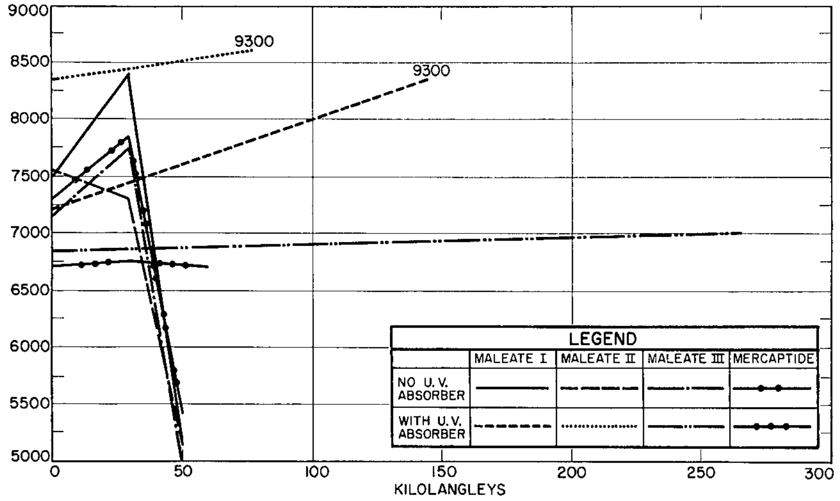

Fig. 14. Tensile strength, 45°S, unbacked.

up to 250 kilolangleys. The increase was not statistically significant. The PVC panel containing the organotin mercapto stabilizer and ultraviolet absorber showed no loss in tensile strength up to 100 kilolangleys and a marked reduction past this figure.

The 45°S unbacked exposure data is shown in Figure 14. Panels containing only resin and tin stabilizer lost 28% of their initial tensile strength after 50 kilolangleys exposure. The presence of the ultraviolet absorber in the formulation prevented significant loss in tensile strength up to 250 kilolangleys. The test was terminated at this point.

The 45°S backed exposure data is presented in Figure 15. Measurements appeared to be more scattered and a detailed analysis of the data was difficult. In general, however, panels containing only resin and stabilizer show an average decrease of 32% in tensile strength after 50 kilolangleys exposure. The panels containing resin, stabilizer, and ultraviolet absorber showed no significant decrease to 190 kilolangleys. The test was terminated at this point.

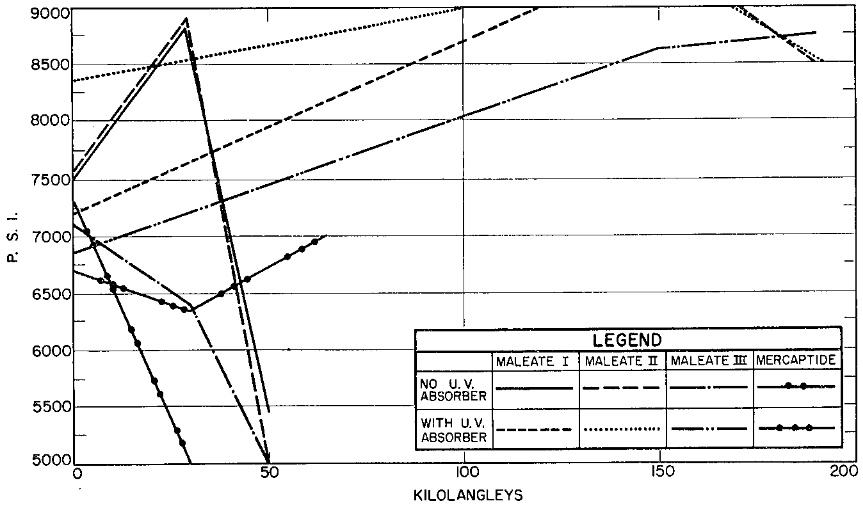

Fig. 15. Tensile strength, 45°S, backed.

Impact Resistance

A rigid PVC sheet mounted on a backing, such as house siding, would not require as high a degree of impact resistance as would a free-standing structural member. Impact modifiers, however, are usually added to vinyl formulations because the end use item must be able to support at least its own weight in both tensile strength and impact during exposure. It was therefore desired to determine if different stabilizers caused differences in impact resistance of unmodified PVC panels during outdoor exposure.

The impact data for the PVC panels on accelerated exposure are shown in Figure 16. The panels containing only resin and organotin maleate stabilizers showed increases in impact strength up to 75 kilolangleys followed by a reduction in impact thereafter. The net effect was an average reduction in impact of 12.5% from the initial value after 110 kilolangleys exposure when the test was terminated. The panels containing resin, organotin maleate stabilizer, and ultraviolet absorber showed an average loss in impact resistance of 17% after 260 kilolangleys exposure.

The data on impact for the PVC panels exposed at 45°S unbacked are shown in Figure 17. The measurements followed no consistent pattern, but in general, the panels containing only resin and organotin maleate stabilizers increased 21% in impact strength up to 50 kilolangleys exposure when the test was terminated. The panel containing only resin and organotin mercapto stabilizer lost 30% of its impact strength over the same exposure period.

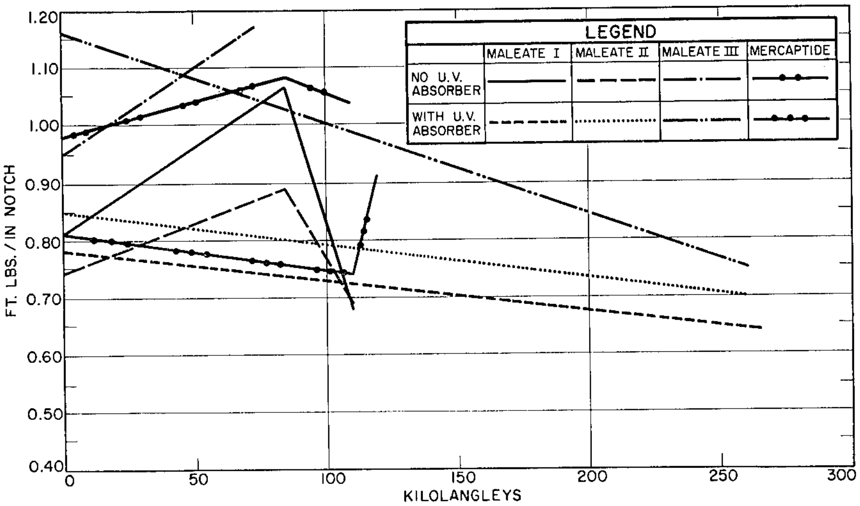

Fig. 16. Impact resistance, EMMA 10.

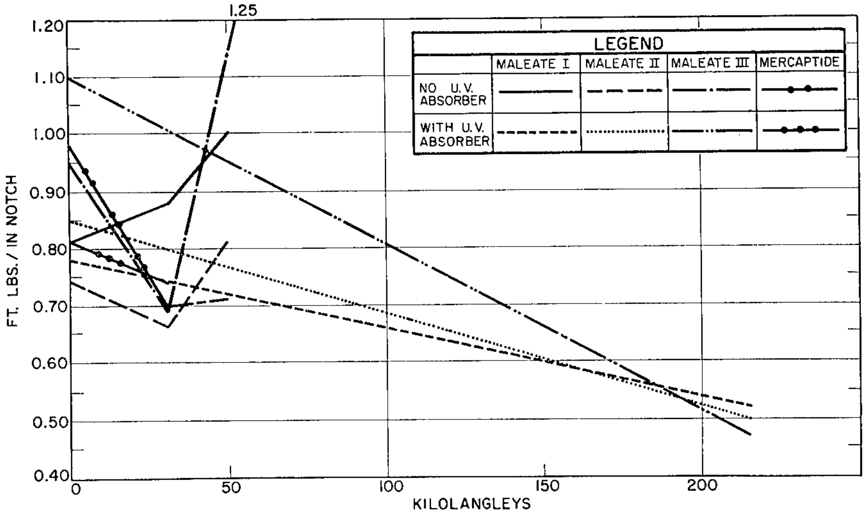

Fig. 17. Impact resistance, 45°S, unbacked.

Where the ultraviolet absorber was part of the formulation, all panels decreased an average of 44% after 225 kilolangleys.

Figure 18 shows the data obtained for panels exposed at 45°S backed. Again, the higher ambient temperature at the surface of the panel during exposure caused more severe degradation than that recorded on 45°S unbacked exposure. The panels containing only resin and organotin stabilizer had an average initial impact resistance of 0.85 ft.-lb. at 25 kilolangleys and 1.0 ft.-lb. and 0.75 ft.-lb. after 50 kilolangleys exposure. The impact resistance of the panels containing organotin maleate stabilizers and an ultraviolet absorber decreased an average of 50% after 195 kilolangleys.

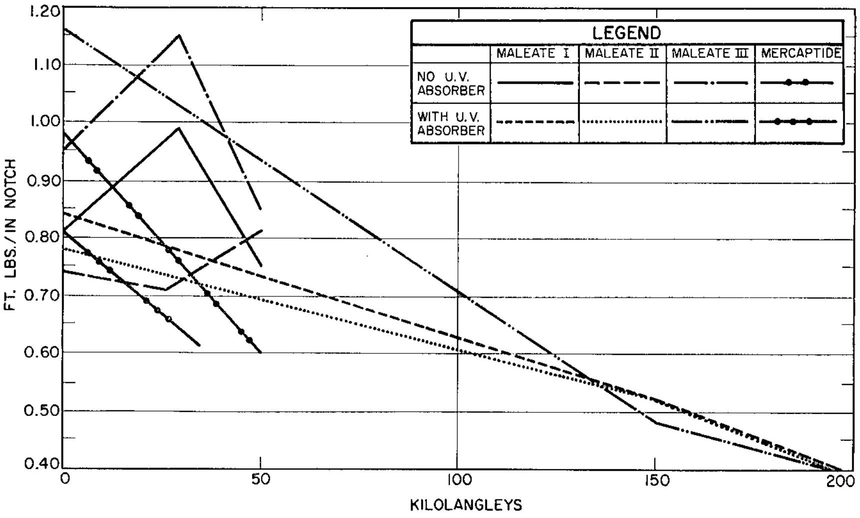

Fig. 18. Impact resistance, 45°S, backed.

Control Samples

All PVC panels kept in the dark for 18 mo. at room temperature showed negligible changes in color, haze, tensile strength, and impact resistance. A slight increase (5%) in hardness was noted. This would indicate that none of the physical and optical changes observed on the panels were the result of the outdoor exposure.

CONCLUSIONS

A comparison of the various exposure conditions indicates that the 45° southern exposure, backed sample, causes the greatest changes in the physical and optical properties of the translucent rigid vinyl sheets during the first 100 kilolangleys of exposure. The higher panel surface temperature associated with this exposure method is probably responsible for the increased amount of degradation compared to the 45°S unbacked exposure test since the same amount of radiant energy was received by the panels on both test racks.

The accelerated outdoor exposure test (EMMA) appears to correlate in part with 45°S unbacked exposure in terms of color and haze development at least up to 150 kilolangleys of exposure. The amount of radiation received on the accelerated exposure rack is about 8.4 times that received on 45°S exposure; one month's exposure on accelerated test would therefore be comparable to about 8 mo. exposure at 45°S, unbacked. Actually, the ratio was closer to 3.9 to 1 over the entire exposure period. The measurements obtained on the changes in the physical properties correlate less well on the two exposure conditions due probably to the fewer number of observations recorded during exposure. In general, however, the panels containing only resin and organotin stabilizers showed increases in hardness and reductions in both tensile strength and impact resistance over the exposure period.

The panels containing organotin maleate stabilizers and ultraviolet absorber showed no loss in tensile strength on either the 45°S backed and unbacked exposure and less change in hardness and impact resistance values compared to the panels containing no ultraviolet absorber.

The mercaptotin derivative used in this test, even when formulated in conjunction with an ultraviolet absorber, does not appear to be well suited for stabilization of clear rigid PVC when exposure to light is anticipated.

Although much more work remains to be done on commercial formulations containing lubricants, pigment, and impact modifier, this series of tests indicates that organotin maleate stabilizers, especially when compounded with an ultraviolet absorber, appear best suited for clear rigid vinyl formulations for outdoor service use.

I wish to acknowledge the assistance of Messrs. J. Gottlieb and W. Mayo in the preparation of the samples and recording of the test results.

Reference

1. B. L. Garner and P. J. Papillo, *Ind. Eng. Chem., Prod. Res. Develop.*, **1**, 249 (1962).

Résumé

Des feuilles de PVC rigides non pigmentées contenant des stabilisants organostaniques ont été exposées à de nombreux types de vieillissement à l'extérieur à Phoenix, Arizona. Des mesures ont été faites sur le développement de la couleur et d'un trouble, et sur les changements de propriétés physiques des feuilles à intervalle régulier au cours de la période d'exposition. Le comportement à la dégradation des feuilles de PVC plascées dans un appareil à exposition accélérée extérieure peut être relié à une des conditions d'exposition utilisées, à savoir 45° par exposition au midi, sous forme de panneaux non recuits. Le PVC rigide stabilisé avec des dérivés maléate organostaniques et contenant des absorbants ultraviolets apparaissait être le plus résistant à la photodégradation à l'extérieur.

Zusammenfassung

Steife, unpigmentierte PVC-Platten mit einem Gehalt an Zinn-organischen Stabilisatoren wurden in Phoenix, Arizona verschiedenen Arten einer Bewitterung im Freien

unterworfen. Während der Exponierung wurden in gewissen Abständen die Entwicklung der Verfärbung und Trübung sowie die Änderung der physikalischen Eigenschaften der Platten gemessen. Das Abvauverhalten von PVC-Platten in einer Vorrichtung für Exponierungsbeschleunigung im Freien zeigte zum Teil eine Korrelation zu einer der verwendeten Exponierungsbedingungen: 45° Exponierung nach Süden, rücken-freie Scheiben. Die beste Beständigkeit gegen Photoabbau im Freien schien starres PVC bei Stabilisierung mit Zinn-organischen Maleinsäurederivaten und einem Gehalt an Ultraviolettabsorbern zu besitzen.

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APPLIED POLYMER SYMPOSIA NO. 4, 205–218 (1967)

Accelerated Aging of Poly(methyl Methacrylate) Copolymers and Homopolymers

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Synopsis

The Twin Carbon-Arc Weather-Ometer has been used to predict the outdoor aging characteristics of commercial poly(methyl methacrylate) and methyl methacrylate-α-methylstyrene copolymer formulations. Results show that the Weather-Ometer, operated under ASTM E-42, Condition D, caused changes in the spectral and mechanical properties of these polymers similar to those obtained during extended outdoor exposure. However, varying Weather-Ometer exposure periods were required to predict the rate and degree of changes during outdoor weathering for these polymeric systems. In conclusion, the Twin Carbon-Arc Weather-Ometer can be used effectively to screen the outdoor performance of these acrylic polymers but cannot be utilized to predict absolute values for long-term outdoor exposure.

INTRODUCTION

The exposure of plastic materials in a Carbon-Arc Weather-Ometer is a widely used technique for estimating long-term outdoor aging performance. As a result of the higher ultraviolet energy and average temperature levels in the Weather-Ometer, polymer degradation is accelerated manyfold as compared with normal outdoor exposure, even in tropical climates. This frequently allows rapid prediction of years of outdoor performance of plastic formulations in a matter of weeks or months. Unfortunately, the type, rate, and degree of degradation by the many mechanisms possible may be altered significantly by the different temperatures and energy distribution of the Weather-Ometer. Degradation reactions which may be insignificant outdoors may, on occasion, predominate under the conditions used in the Weather-Ometer, or the reverse may be true. Therefore, it is generally desirable to determine the relationships between outdoor aging and Weather-Ometer exposures for a number of formulations of a desired polymer system before relying heavily on this or any other accelerated test method.

This article compares the degree and type of degradation obtained in the Atlas Twin Carbon-Arc Weather-Ometer with that obtained outdoors in Southern Florida, Arizona, and New Jersey for two crystal clear plastics and several of their transparent dyed formulations. The plastics include crystal and dyed formulations of (*1*) poly(methyl methacrylate) (PMMA) and (*2*) the copolymer of methyl methacrylate and α-methylstyrene (MMA–α-MS copolymers), a high heat-resistant type of acrylic. The studies involve analyses of changes in spectral transmission, color, and tensile properties during extended outdoor and Weather-Ometer exposure.

EXPERIMENTAL

The plastics studied include (*1*) PMMA formulations as represented by commercial Lucite 140 (crystal), Lucite RD-05 (red) from DuPont, and Plexiglas V-883 (amber) from Rohm and Haas, and (*2*) MMA–α-MS copolymer formulations represented by commercial Bavick-11 UVA (crystal), Bavick-11 Red 203 and Red 204, Bavick-11 Amber 318, and certain experimental colored formulations from J. T. Baker Chemical Company. Each MMA–α-MS formulation contained 0.1% of a commercial ultraviolet stabilizer. The commercial grades of both polymers above are representative of the crystal and colored plastics used by the automotive industry for tail light, turn signal, and other exterior plastic lenses.

Study of Spectral Changes

Three inch diameter disks of 0.125 in. thickness were prepared by injection molding of the desired plastic formulation. The PMMA specimens were annealed for 4 hr. at 180°F., while the MMA–α-MS copolymer specimens were annealed for 4 hr. at 230°F. (following a programmed 1-hr. temperature rise and preceding a 1-hr. temperature decrease to room temperature).

The disks were exposed in duplicate both in the Weather-Ometer and outdoors in southern Florida and Phoenix, Arizona. Weather-Ometer exposure was conducted in a Twin Carbon-Arc unit employing ASTM procedure E-42 Condition D at a temperature of 145 ± 5°F. with a wet cycle (102 min. dry, 18 min. spray). Outdoor exposure was conducted in accordance with the Society of Automotive Engineers test, SAE J-576a. This procedure requires the exposure of 3-in. diameter by various thickness disks on racks, without backing, facing due south and 45° from the horizontal.

Control and exposed specimens were analyzed periodically for spectral transmission and color with a GE spectrophotometer. The transmission curves obtained were translated to the CIE tristimulus values and chromaticity coordinates through use of a Digital Tristimulus Computer. (Davidson and Hemmendinger, Easton, Pa.). The percentage light transmission for a transparent material is defined as the Y tristimulus value times 100. Then the percentage change in light transmission, as used in this article, is (Y exposed $-$ Y control) (100)/Y control.

Study of Mechanical Changes

Tensile bars (ASTM D638 Type I) of crystal PMMA and both a commercial and an experimental grade of MMA–α-MS copolymer were also produced by injection molding and annealed as described above. The commercial MMA–α-MS grade contained 0.1% of an ultraviolet stabilizer while the experimental formulation contained 0.1% of the ultraviolet stabilizer plus 0.2% of an antioxidant. The tensile bars were exposed in the Weather-Ometer and outdoors in New Jersey on racks facing due south 45° from the horizontal. Tensile strength and elongation were determined on an Instron Universal Testing Machine operated at a crosshead speed of 0.2 in./min.

RESULTS AND DISCUSSION

The results of both outdoor aging over a 2 yr. period and Weather-Ometer exposure over a 1500 hr. period illustrate the excellent aging resistance of the basic uncolored PMMA and MMA–α-MS copolymer systems. The changes in light transmission and color during exposure with the dyed systems appear, therefore, to be related to instability of either the dyes or the dye–polymer systems rather than to the polymers themselves.

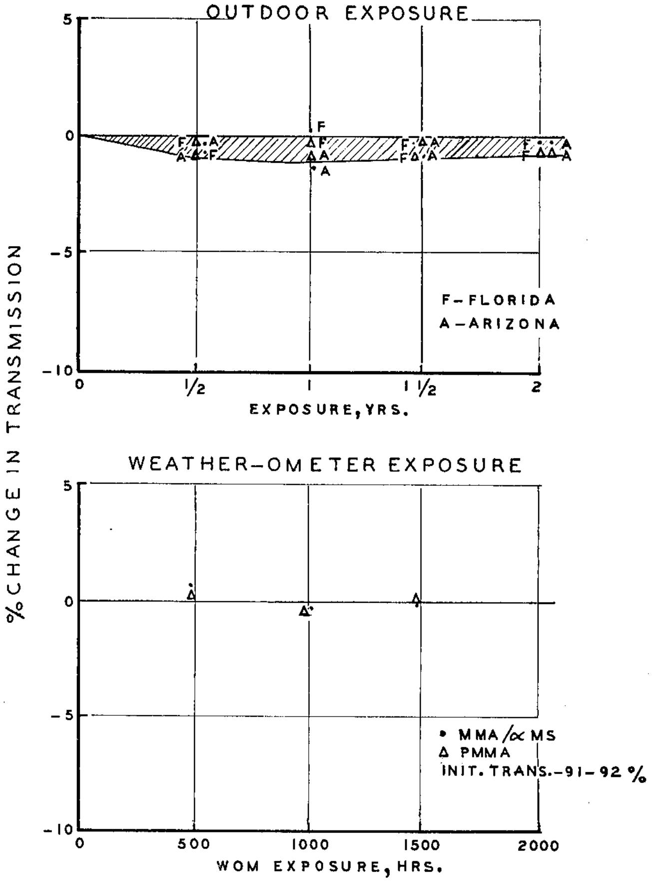

Fig. 1. Changes in light transmission during exposure of crystal specimens.

Crystal Plastics

A comparison of the changes in light transmission during outdoor and Weather-Ometer exposure is given in Figure 1 for both the commercial MMA–α-MS copolymer and PMMA homopolymer systems. The results show that essentially no changes occur during 2 yr. outdoors in either Florida or Arizona or during 1500–hr. of Weather-Ometer exposure except for a trace of yellowing due to ultraviolet degradation on the surface facing either the sun or the carbon arc. This yellowing results in less than a 1% change in light transmission. There was no other visible evidence of any type of surface deterioration during the extended exposure periods. These results attest to the excellent retention of optical properties for both plastic matrices under accelerated and normal outdoor aging.

Transparent Red Specimens

Red plastic specimens evaluated in this study were based on three dye systems. The first dye, used widely in commercial PMMA and MMA–α-MS copolymer for automotive exterior lenses, is an anthraquinone red dye. It is used over a wide concentration range with polymer matrices, but the concentration of major interest to the lens manufacturers, and therefore used in this study in both polymer types, is about 0.18 wt.-%. This concentration produces a transparent red plastic of about 24% light transmission in a specimen 0.125 in. thick. The second dye is a two-component system which produces a darker red and is used therefore to obtain the desired appearance and optical effects in thinner tail light lenses. It is composed of six parts by weight of the anthraquinone red dye mentioned above and one part by weight of a stronger bluish red anthraquinone dye. This system was evaluated only in the MMA–α-MS copolymer at a concentration of 0.144% which results in a light transmission of about 17% in a specimen 0.125 in. thick. The third red dye system was experimental and was only incorporated into the MMA–α-MS copolymer system. It involved both the stronger anthraquinone red dye and an amber dye incorporated in such concentration to produce an automotive red of essentially the same color and transmission as that of the first system.

As shown in Figure 2, plastic specimens utilizing only the one-component anthraquinone red dye darkened significantly (lost transmission) during both outdoor and Weather-Ometer exposure. However, the rate of darkening decreased significantly with exposure time. This was particularly true with the MMA–α-MS copolymer system which darkened more rapidly than the PMMA during the first 6 mo. outdoors but less rapidly thereafter and consequently exhibited essentially the same loss in light transmission after 2 yr. of exposure at both locations.

The second red formulation, containing only 75% as much of the above anthraquinone red dyestuff, in addition to small amount of the stronger anthraquinone red dye also darkened outdoors and in the Weather-Ometer. However, the transmission reduction with this darker system was consider-

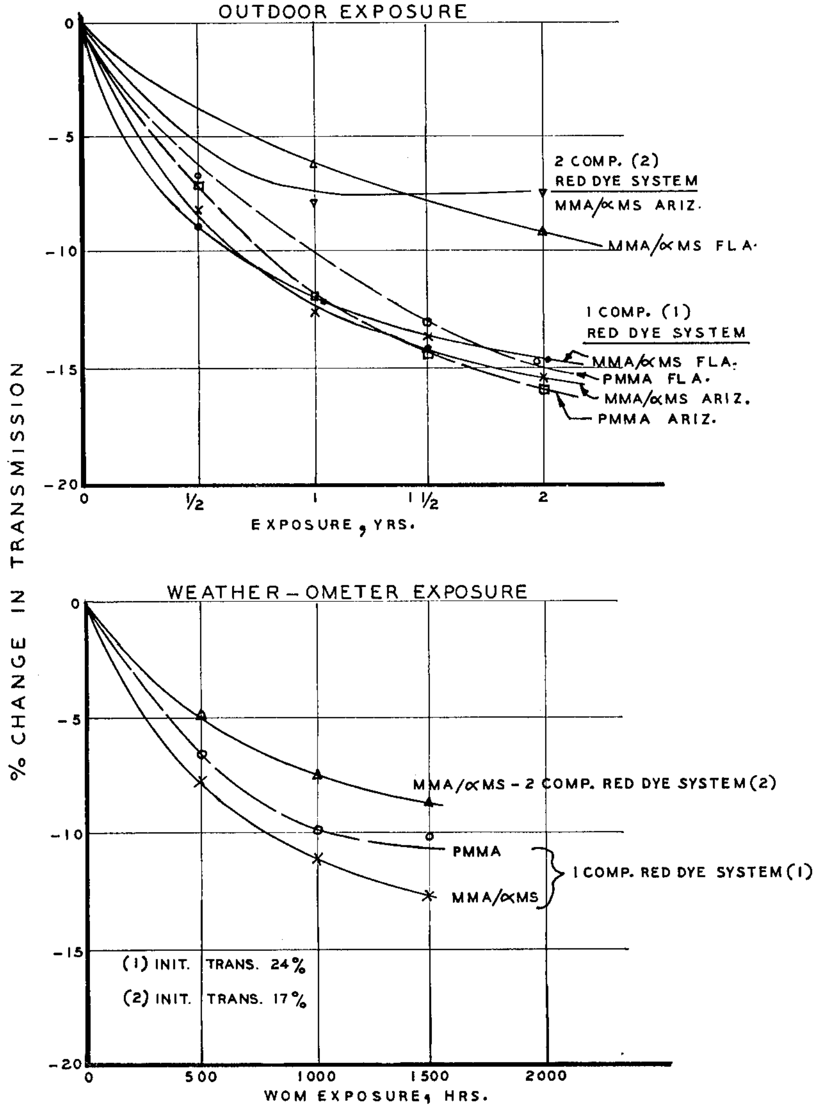

Fig. 2. Changes in light transmission during exposure of commercial red specimens.

ably less than with the previously discussed red formulations. These data, and other work not reported here, suggest that the darkening is directly related to the concentration of the weaker anthraquinone red dye in the formulation.

A comparison between the transmission loss with time for the outdoor and Weather-Ometer exposures with these two red dye systems indicates that a good correlation exists for the first half year outdoors and the first ~500 hr. in the Weather-Ometer. All the spectral transmission changes occurring during the first half year outdoors at both locations can be pre-

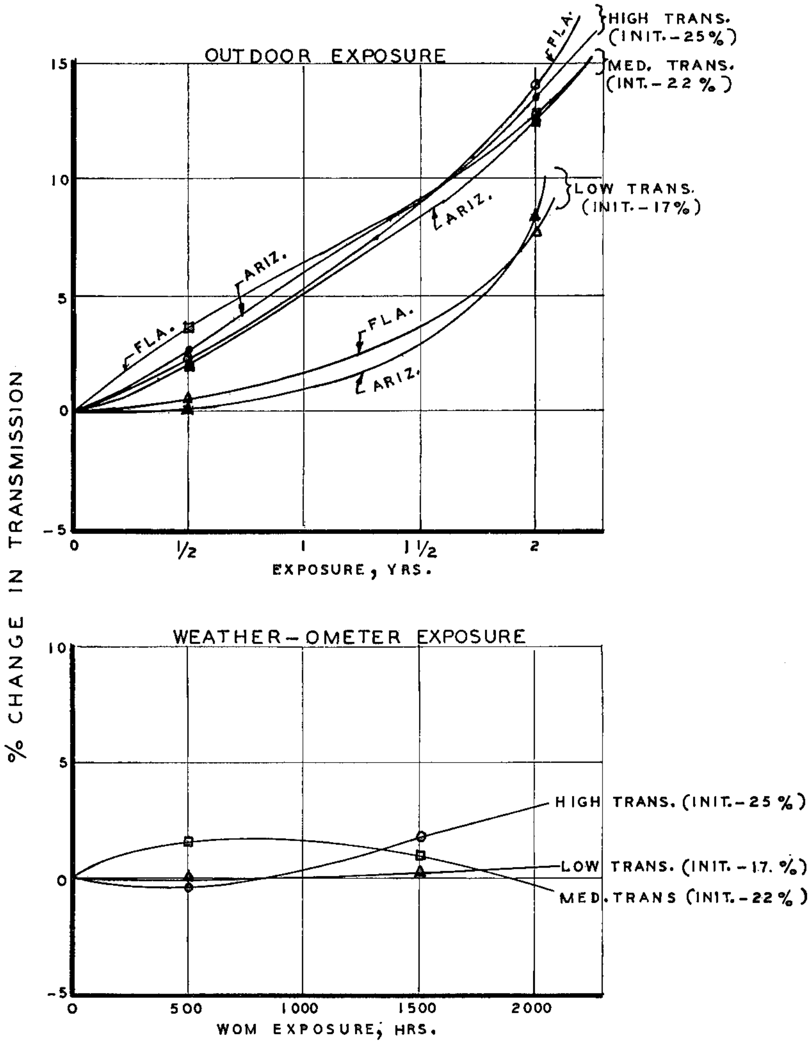

Fig. 3. Changes in light transmission during exposure of experimental red specimens.

dicted accurately by Weather-Ometer exposures between 300 and 600 hr. Beyond this period, however, there is a widening Weather-Ometer exposure period required to predict a given degree of change during outdoor aging. For example, only 670 Weather-Ometer hr. are necessary to predict 1 yr. of outdoor exposure in Florida for the commercial two component MMA–α-MS copolymer system, whereas it is estimated that over 2000 hr. would be required to duplicate the 1 yr. Arizona changes for the commercial PMMA system utilizing the one-component dye. This increasing lack of correlation is a function of at least two phenomena. The first is the decreasing rate of degradation with increased exposure time outdoors and in the Weather-Ometer which markedly reduces the sensitivity of this pre-

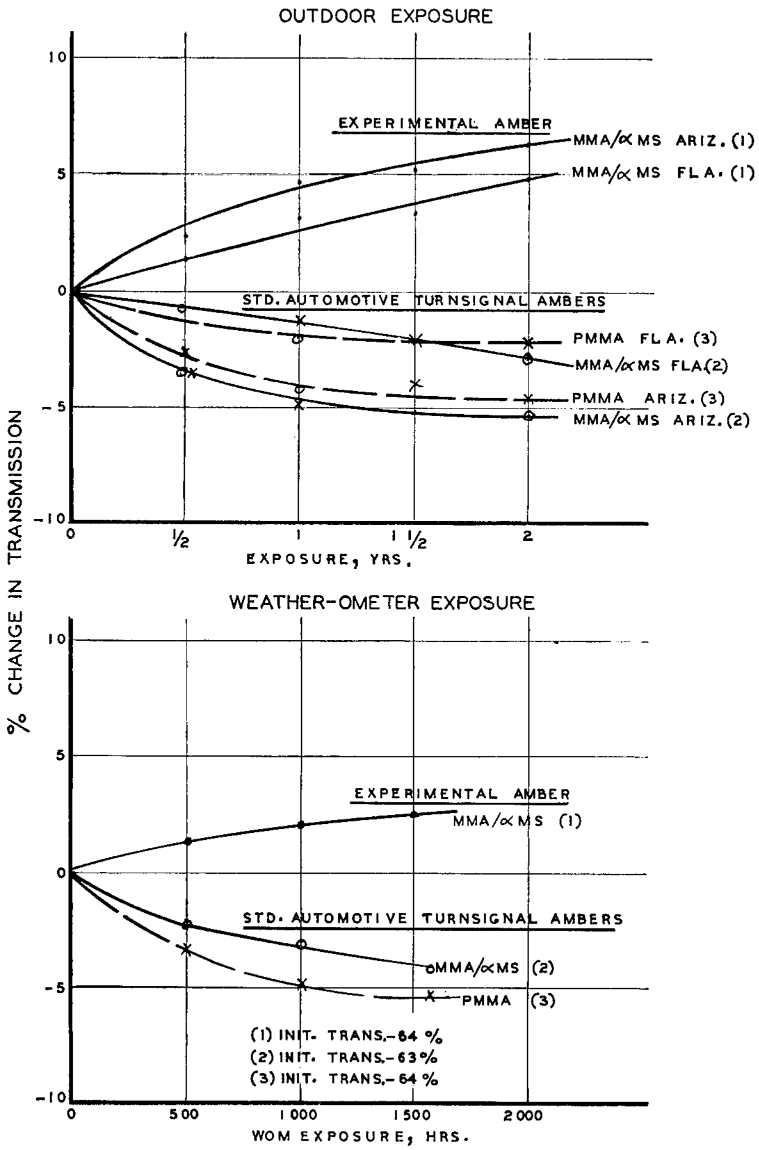

Fig. 4. Changes in light transmission during exposure of amber specimens.

diction method. The second is the fact that the outdoor performance differs between the testing sites such that it is impossible to expect equal correlation with outdoor results at both locations during a given interval.

Analyses of the chromaticity coefficient data during both types of exposure indicate that although the samples darkened noticeably, the color changes were practically insignificant.

The third set of red specimens, produced only in the MMA–α-MS copolymer with the experimental two-component dye system, faded appreciably and equally under outdoor exposure in Arizona and Florida but only slightly in the Weather-Ometer. The data, given in Figure 3, suggest that the fading produced outdoors in 1 yr. cannot be duplicated in the Weather-Ometer within a reasonable test period utilizing the conditions of ASTM E-42 Condition D. With this experimental red system there is also a significant color change toward the yellow during outdoor exposure which is not predicted adequately in the Weather-Ometer. For example, the yellowing of the Florida and Arizona samples after $^1/_2$ yr. exposure is slightly greater than that occurring in the Weather-Ometer specimens after 1500 hr. exposure.

Transparent Amber Specimens

Amber specimens studied were based on two dye systems. The first is that used for the commercial amber grades of both PMMA and the MMA–α-MS copolymer for automotive turn signal lenses. The single component organic dyestuff is generally used at a concentration of 0.06–0.07 wt.-% in each polymer type and produces an amber plastic of approximately 63–64% light transmission at 0.125-in. thickness. The second amber system is based on an experimental dye and was studied only in the copolymer matrix.

The amber polymers containing the commercial dye exhibited slight tendencies toward darkening outdoors and in the Weather-Ometer, as shown in Figure 4. The degree of transmission change was roughly the same for the homopolymer and copolymer when aged outdoors but was slightly greater for the homopolymer when exposed in the Weather-Ometer. There was a considerably greater loss of light transmission during exposure in Arizona than under the milder temperature and radiant energy conditions in Florida. As a result, only short Weather-Ometer exposures are needed to predict the changes observed in southern Florida (approx. 200 WOM hr./yr. Florida), whereas longer periods are necessary to simulate Arizona exposure results (800–1700 hr./yr. Arizona exposure for the PMMA and MMA–α-MS systems, respectively).

Analyses of the changes in the chromaticity coefficients and visual inspection of the specimens indicate that color changes are very slightly toward the red and away from the yellow during exposure under the various test conditions.

The amber MMA–α-MS copolymer system containing the experimental dye exhibited a very pronounced fading (increase in transmission) and yellowing (increase in y chromaticity coefficient). This was particularly evident during outdoor aging in Arizona and considerably less apparent during aging in Florida and in the Weather-Ometer. As a result, 1 yr. of Florida exposure can be predicted acceptably by 1700 Weather-Ometer hr. The Arizona results, on the other hand, can only be predicted by unacceptably long Weather-Ometer exposures, such as an estimated 3000 WOM hr./yr. of Arizona exposure.

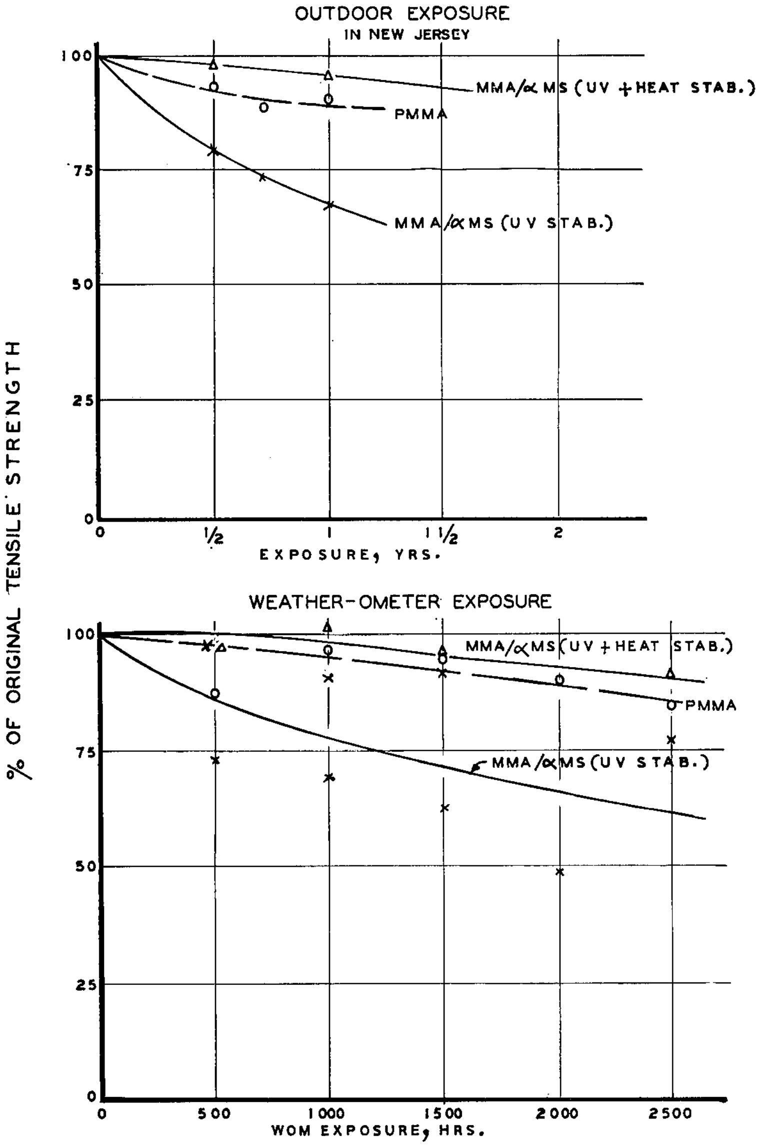

Fig. 5. Changes in tensile strength during exposure.

Study of Tensile Property Changes

Changes in tensile strength and flexibility of crystal tensile bar specimens of PMMA homopolymer and of MMA–α-MS copolymer were studied during exposure in the Weather-Ometer and outdoors in Phillipsburg, New Jersey. The results, given in Figures 5 and 6, show a definite embrittlement of the commercial MMA–α-MS copolymer system containing only 0.1% of an ultraviolet stabilizer in the Weather-Ometer and during outdoor aging.

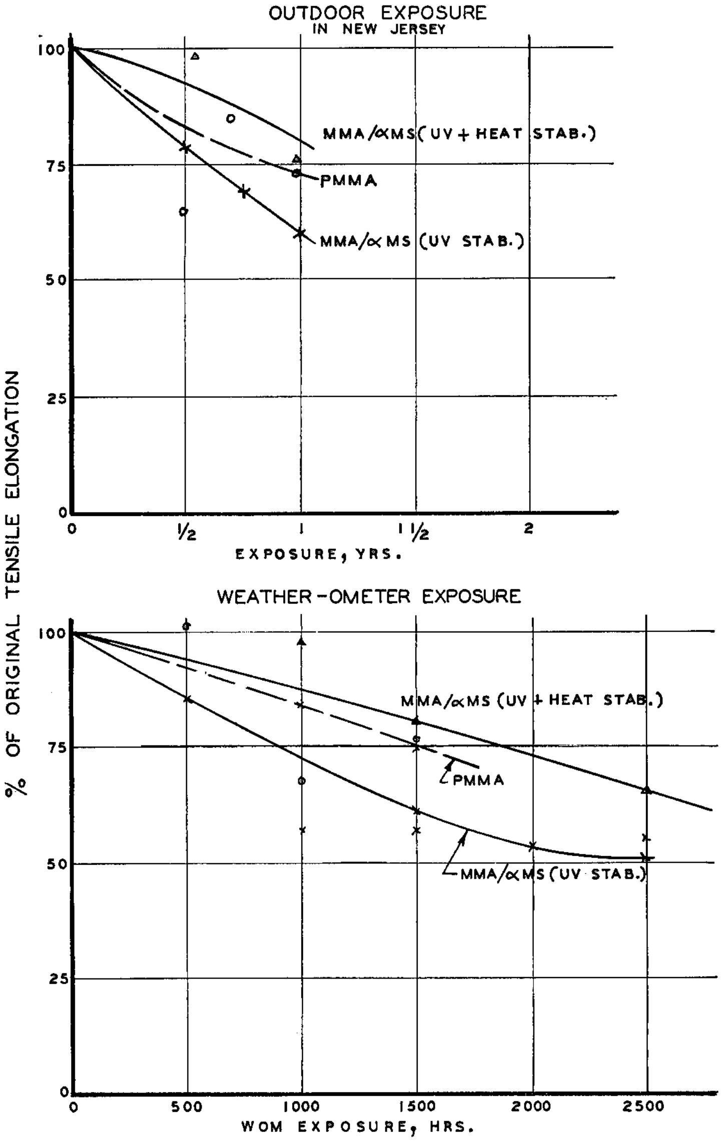

Fig. 6. Changes in tensile elongation during exposure.

The apparent embrittlement with the slightly tougher and softer PMMA homopolymer is somewhat less in both exposure tests. This difference is felt to be due both to the slightly better ultraviolet resistance of the homopolymer and to its somewhat greater flexibility and lower Young's modulus. These latter factors tend to minimize the effects of small degrees of polymer degradation on tensile strength and elongation.

It is interesting to note that stabilization of the MMA–α-MS copolymer system with a combination of 0.1% of an ultraviolet stabilizer and 0.2%

of an antioxidant resulted in a crystal clear polymer system exhibiting much improved resistance to loss in tensile properties during aging both in the Weather-Ometer and outdoors. In fact the performance of this synergistic formulation equalled or exceeded that of the PMMA homopolymer.

Comparison of the Weather-Ometer and outdoor results indicates good agreement between the two. While there is considerable variation in data obtained with different samples in the Weather-Ometer, as shown by the MMA–α-MS (ultraviolet-stabilized) data in Figures 5 and 6, the average curves adequately predict the relative and absolute changes occurring during outdoor exposure in New Jersey. In this case there is a relatively minor time variation required in the Weather-Ometer to predict exactly the changes in tensile properties of the three formulations. This time varies from 1400 hr. to predict the 1-yr. loss in elongation for the heat and ultraviolet stabilized MMA–α-MS copolymer system to about 2100 hr. required for the loss in tensile strength for the PMMA homopolymer.

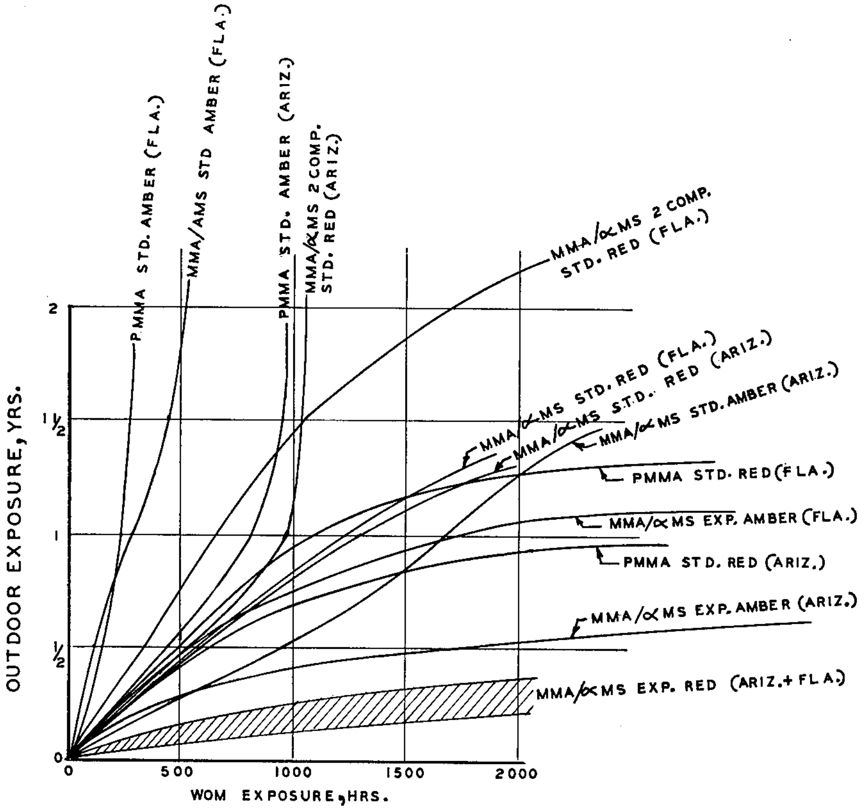

Fig. 7. Comparison of Weather-Ometer and outdoor exposure time for equal changes in light transmission.

Weather-Ometer Prediction of Outdoor Exposure

Figures 7 and 8 provide a correlation between the Weather-Ometer and outdoor exposure results obtained at three locations for all the systems involved in this study. The fact that there are positive correlations between the Weather-Ometer hours and outdoor exposure period to obtain a given change in properties for all systems attests to the ability of the Weather-Ometer to predict adequately the type of changes occurring outdoors. The fact that a considerably varied Weather-Ometer exposure time is required to predict the exact results, even at a single location, indicates that this accelerated weathering apparatus must be used with discretion when attempting to predict absolute outdoor performance for formulations with PMMA and MMA–α-MS copolymers.

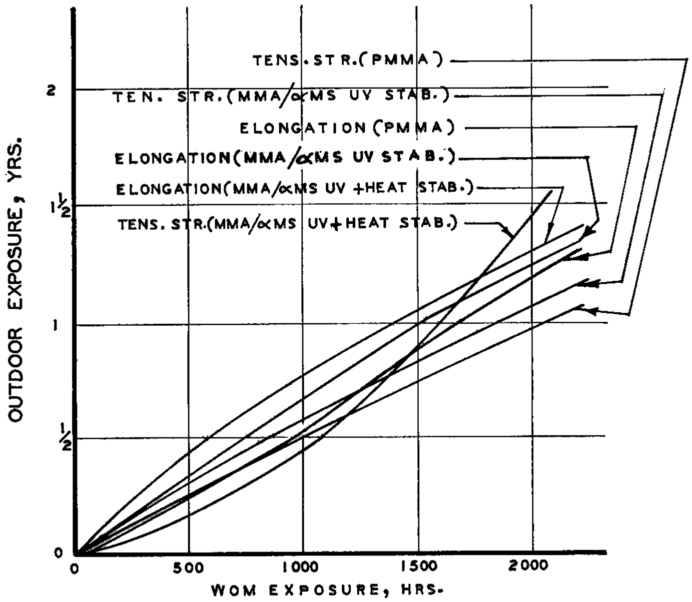

Fig. 8. Comparison of Weather-Ometer and outdoor exposure time for equal changes in tensile properties.

CONCLUSIONS

The Twin Carbon-Arc Weather-Ometer used under ASTM E-42 Condition D appears to simulate accurately and accelerate outdoor exposure for several formulations of the poly(methyl methacrylate) and the methyl methacrylate–α-methylstyrene copolymer systems. Based on this study, it appears that the Weather-Ometer can be used to predict the type but not necessarily the degree of visual or mechanical changes which take place during outdoor exposure of these transparent polymers. For example, Weather-Ometer data was shown to predict (*1*) essentially no visible changes in the crystal PMMA or MMA–α-MS system during 2 yr. of exposure in Arizona or Florida, (*2*) the loss of transmission during exposure for commercial automotive red and amber formulations, (*3*) the fading of experimental red and amber dye systems in the MMA–α-MS copolymer, and (*4*) the relative embrittlement during outdoor exposure in New Jersey for two crystal MMA–α-MS formulations and one PMMA sample.

The Weather-Ometer was less effective in predicting accurately the rates of change during outdoor aging. Weather-Ometer times required to predict outdoor changes appear to be a function of many factors including: (*1*) the mechanisms of degradation under the various conditions for the various polymer/dye systems; (*2*) the outdoor locations under consideration—longer times were required to predict generally larger effects under hotter Arizona conditions; (*3*) the types of changes occurring—reactions causing darkening were generally more rapidly predicted than those causing fading; (*4*) the degradation rate curves themselves—the sensitivity of prediction decreases as the rate of degradation approaches zero either outdoors or in the Weather-Ometer. Consequently, no suitable relationship between Weather-Ometer exposure time and outdoor exposure time could be developed for all types of PMMA and MMA–α-MS copolymer systems under study.

Based on the above considerations, it is felt that the Twin Carbon-Arc Weather-Ometer can be used effectively to screen the relative outdoor performance of the PMMA and MMA–α-MS copolymer formulations but should not be utilized by itself to predict absolute long-term outdoor performance.

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Résumé

Le Twin-Carbon-Arc Weather-Ometer a été utilisé pour prédire les caractéristiques de vieillissement de polyméthacrylate de méthyle commercial et de copolymères à base d' σ-méthyle styrène–méthacrylate de méthyle. Les résultats montrent que le Weather-Ometer travaillant dans des conditions ASTM E-42, condition D, entraîne des changements dans les propriétés spectrales et mécaniques de ces polymères, semblables à ceux obtenus au cours d'une exposition à l'extérieur prolongée. Toutefois, des périodes d'exposition variées au Weather-Ometer étaient nécessaires pour prédire la vitesse et le degré de changement du vieillissement à l'extérieur pour ce système polymérique. En conclusion le Twin-Carbone-Arc Weather-Ometer peut être utilise effectivement pour étudier les performances à l'extérieur des polymères acryliques, mais ne peut pas être utilisé pour prédire les valeurs absolues des expositions à l'extérieur à longues durées.

Zusammenfassung

Das Zwillings-Kohlebogen-Weather-Ometer wurde zur Bestimmung der Alterungscharakteristik von kommerziellen Polymethylmethacrylat- und Methylmethacrylat/α-Methylstyrol-Copolymer-Systemen herangezogen. Die Ergebnisse zeigen, dass das Weather-Ometer bei Betrieb unter ASTM E-42, Bedingung D, zu Änderungen der spektralen und mechanischen Eigenschaften dieser Polymeren führte, die den bei einer längeren Exponierung im Freien erhaltenen ähnlich waren. Es waren aber verschiedene Exponierungszeiten im Weather-Ometer erforderlich, um die Geschwindigkeit und das Ausmass der Änderung während einer Bewitterung dieser Polymersysteme im Freien angeben zu können. Das Zwillings-Kohlebogen-Weather-Ometer ist also ein wirksames Instrument, um eine Auswahl des Verhaltens dieser Acrylpolymeren im Freien zu treffen, kann aber nicht zur Gewinnung von absoluten Werten für langzeitige Exponierung im Freien verwendet werden.

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Factors Affecting the Environmental Stability of Laminates

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Synopsis

Curvature in a warped decorative laminate is mathematically shown to be a function of the strain coefficients, tensile moduli, and thickness of the individual layers comprising the structure. The most important of these functions are the strain coefficients. The interaction of stresses in two directions is discussed, and it is demonstrated that the size and shape of the panel influence the observed curvature. Thus, reducing the width of a sheet increases the warpage developed by the laminate in the long direction. Anisotropy exists to varying degrees in all the components of a typical laminate because of their fiber base. Some components are significantly more anisotropic than others depending upon their total resin content and the state of cure of the resin. The major component of the laminate, the phenolic resin–Kraft paper core, is the most anisotropic, particularly at high humidity where the cellulose fibers are most seriously affected by moisture. This component is shown to be highly unstable. Cyclic exposure to high humidity induces permanent shrinkages in length and width which in turn produce permanent warpage in a laminate under similar conditions. In addition, the phenolic core tends to shrink lengthwise (in the fiber direction) at very high humidity whereas the melamine components do not. The properties of separately molded components are different from those of the comparable materials isolated from a composite laminate. The print layer, in particular, absorbs a considerable amount of moisture produced by the other components during the cure of the laminate. This results in a very high potential shrinkage of this component. The major cause of low humidity warpage is shown to be the high shrinkage of the print relative to that of the phenolic core.

Composite, multicomponent laminates have serious problems of dimensional instability under variable humidity and temperature conditions. This instability manifests itself by a pronounced tendency of the structure to warp, or curl, and under certain conditions by an apparent increase in stiffness.

Superficially, the reasons for environmental warpage seem obvious. Structures such as decorative laminates are composed of at least two, and sometimes three of four layers of different paper bases impregnated with different thermosetting resins. To complicate matters, the resins are used in different concentrations and cured to different degrees, and frequently filled papers are employed in specific components of the laminate. As a result, the various segments of these laminates differ in properties and react differently to changing environmental conditions.

This explanation, while generally correct, does not really get to the heart of the matter. It is a simplified view of a very complex phenomenon. Laminate behavior in reality is governed by a complicated interplay of many variables, some of which are not obvious to casual examination.

Previous investigators of this problem have described the effects of process variables on the warpage of laminates. From a study of the behavior of separately molded laminate components, the major cause of low humidity curvature was attributed to the difference in shrinkage between the melamine components and the phenolic core.[1] In addition, attempts have been made to develop the mathematics of laminate warpage by relating curvature to the physical–mechanical characteristics of the structure.[2]

Effort in this study has been directed toward combining the two approaches. Ideally, of course, it would be desirable to explain laminate behavior in exact quantitative terms. It has been demonstrated that considerable insight into this problem can be gained through separately studying the parts that make up the whole. However, the method has limited application quantitatively. An alternate approach consists of breaking the whole down into its constituent parts (the reverse of the normal procedure). It will be shown that viewing the problem in this light produces much more satisfactory results.

MATHEMATICAL ANALYSIS OF A WARPED LAMINATE

One-Dimensional Curvature

The curvature of a warped laminate can be related to the properties of each individual layer by means of a stress–strain analysis. The basic derivation of this relationship is shown in the Appendix and is similar to that of Norris at the Forest Products Laboratory.[2]

The final equation [eq. (6)] relates the radius of curvature to the tensile modulus and dimensional movement of each layer of the laminate. The dimensional movement m is the movement or total strain the layer would undergo if unrestrained by the other segments of the structure.

The equation can be used for laminates consisting of any number of layers. In this presentation a standard laminate will consist of three layers: a phenolic resin–Kraft paper core having properties m_1, E_1, t_1; a melamine resin–alpha cellulose paper print having properties m_2, E_2, t_2; and a melamine resin–alpha cellulose paper overlay having properties m_3, E_3, t_3. Such treatment is undoubtedly a simplification of a real case since there are transition zones at the interfaces of these layers and also because these layers may not be truly homogeneous in themselves. However, these limitations need not be considered to illustrate the value of this approach.

Two-Dimensional Curvature

The equation just derived is for the relatively simple case of expansion (or shrinkage) of a laminate in one direction. A real laminate, of course, expands or contracts in three directions, one of which, the thickness, is only of limited interest. But because the dimensional changes of the various components are unequal in both length (machine direction) and width (transverse direction), there is real curvature in both these directions. These cannot be treated independently, since there are obvious mechanical interactions between the two. Unfortunately, the mathematics of two-directional curvature is quite complex, and has not been fully developed. Therefore, for analytical purposes we have confined the analysis to the more simple, one-dimensional situation. In doing this, we will recognize that the elastic properties of the materials can differ according to whether they are measured in the machine direction or the transverse direction so that different analyses can be made according to which direction is used in defining the material properties.

Equation (6) indicates that the curvature developed by a laminate depends upon three factors: the relative environmental strain coefficients, the moduli, and the thicknesses of the individual components or layers. It is only necessary to have some idea of the relative magnitude of these factors to determine how important each is in a qualitative sense. Table I lists typical values for each layer of a commercial three-component laminate as determined experimentally. In using these, it is assumed that the laminate is initially flat so that $(1/R)_{\text{calc.}} = (1/R)_{\text{final}}$, and that the panel is cycled from an initially dry condition to an equilibrium at 98% relative humidity. If the panel is not initially flat, it is clear from the derivation of eq. (6) that $(1/R)_{\text{calc.}}$ is actually $(\Delta 1/R)$ and represents the change in curvature resulting from the changed environmental conditions.

The warped panel having the indicated component properties will, in theory, develop a curvature of 0.11 in.$^{-1}$ in the machine direction and 0.049 in.$^{-1}$ in the transverse direction. Using the above values for $(1/R)$, the independent effects of m, E, and t on curvature have been determined.

Effect of Core Thickness. Figure 1 shows the effect of varying the core thickness from about 30 to 80 mils. This is equivalent to varying the total laminate thickness from 40 to 90 mils by increasing the core thickness alone. All other values, such as strain, Young's modulus, etc., for each component were held constant. The results of these calculations are shown in Figure 1. Thinner cores result in greater curvature while thicker

TABLE I
Properties of a Typical Laminate

Component	m (strain), in./in.		E (tensile modulus), psi		t (thickness), in.
	MD	TD	MD	TD	
Core (No. 1)	2.73×10^{-3}	8.55×10^{-3}	3.98×10^{5}	3.03×10^{5}	0.0492
Print (No. 2)	7.87×10^{-3}	10.68×10^{-3}	8.79×10^{5}	8.04×10^{5}	0.0072
Overlay (No. 3)	9.45×10^{-3}	12.1×10^{-3}	7.48×10^{5}	5.72×10^{5}	0.0036

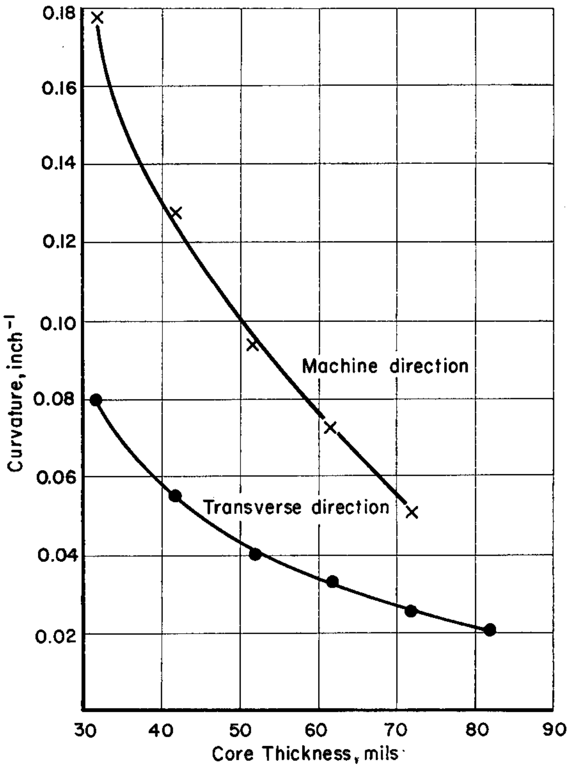


Fig. 1. Effect of core thickness on laminate curvature at 98% R.H. and 73°F.

cores reduce the curvature. At a core thickness of about 80 mils, curvature is very low and the radius of curvature is beginning to approach infinity. This effect is obviously due to the increasing stiffness of the core with increasing thickness.

Effect of Strain Coefficient. Model laminates were analyzed in which the curvature was a function of the strain coefficient for each individual component. For example, the strain coefficient in the print and overlay were held constant, while the core coefficient was varied by ±50%. The effect on laminate curvature was then determined. The same procedure was adopted for variations in strain coefficients in the overlay and print. The results are plotted in Figure 2. They show several points quite clearly:

(*1*) Curvature variation is linear with changes in strain coefficient of a single component.

(*2*) Increasing the strain coefficient of the core or decreasing the strain coefficient of either melamine layer decreases curvature. This results, of course, from the fact that all of these changes reduce the differences between the strain coefficients.

(*3*) The rate of change of curvature with change in strain coefficient is greatest for the core, intermediate for the print, and lowest for the overlay.

(*4*) These slopes are essentially the same in the two principal directions for each component. The amount of change in curvature for a 50% change in strain coefficient is always greater, however, in the transverse direction because the initial transverse strain coefficients are greater.

Effect of Young's Modulus. Warpage is also a function of Young's modulus. The effect of changes in this variable is illustrated in Figure 3.

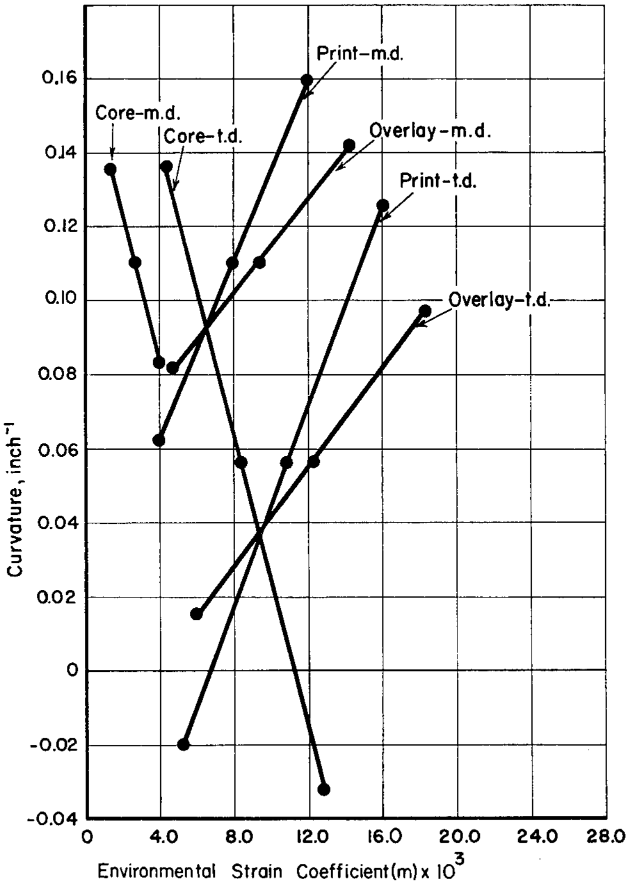


Fig. 2. Dependence of laminate curvature on strain coefficients of individual laminate components.

These again are based upon theoretical calculations, but they reveal certain interesting trends.

(*1*) Curvature is not as responsive to reasonable changes (±50%) in component modulus as it is to the same percentage change in strain.

(*2*) Reducing the core modulus results in very large increases in curvature. In effect, the core then provides less resistance to the pulling action of the melamine layers. The curvature becomes largely dependent on the relative strains and moduli of the melamine layers.

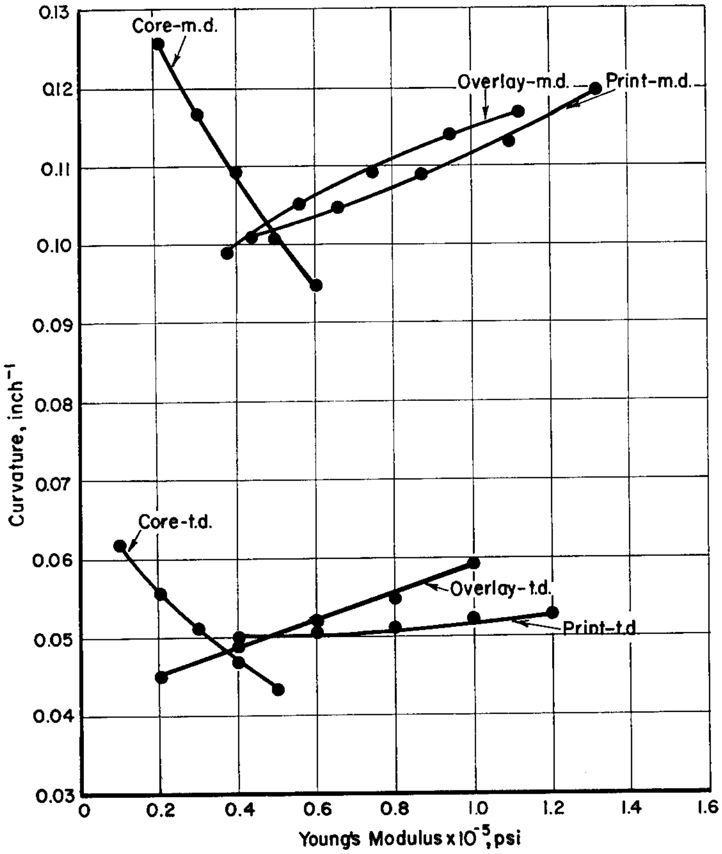


Fig. 3. Effect of component modulus on laminate curvature at 98% R.H. and 73°F.

Stress Distribution

The tensile stress at any point in a warped laminate can be estimated from the relationship

$$\delta = \epsilon E + Ey/R - mE$$

In this equation y represents the distance in from the surface of the laminate to the point at which the stress is being calculated. The values of m and E are those for the layer in which the point lies. The strain E can be calculated from eq. (4) in the Appendix.

Figures 4 and 5 illustrate the stress distribution through the thickness of the warped laminate used in the previous example. The stress levels are substantial, rising to close to 2000 psi in compression for the overlay and up to 1400 psi in tension in the core layer.

Information on the stress levels in warped laminates is of interest for several reasons. In particular, laminates cyclically exposed to high humidity frequently develop a permanent warp when redried. This permanent warp can be increased by recycling the panel to the wet condition and then back to the dry. The effect can be so magnified that the ends of a full size (4 × 8 ft.) panel have been observed to touch. The proportional limit in tension of typical core material appears to be in the neighborhood of 5000 psi (at 50% R.H.) and probably considerably lower when the resin is undercured or the resin content is low. In addition, the elastic limit is sharply reduced under wet conditions.[3] Thus it is easy to visualize a situation in which the elastic limit of at least one component of the laminate (usually the core) can be exceeded, a condition that would lead to permanent warpage of the composite structure. It will be shown later that unstressed components can also develop deformations as a result of an environmental exposure which could also contribute to permanent warpage in the laminate. But this is a distinctly different problem from the one presently under consideration.

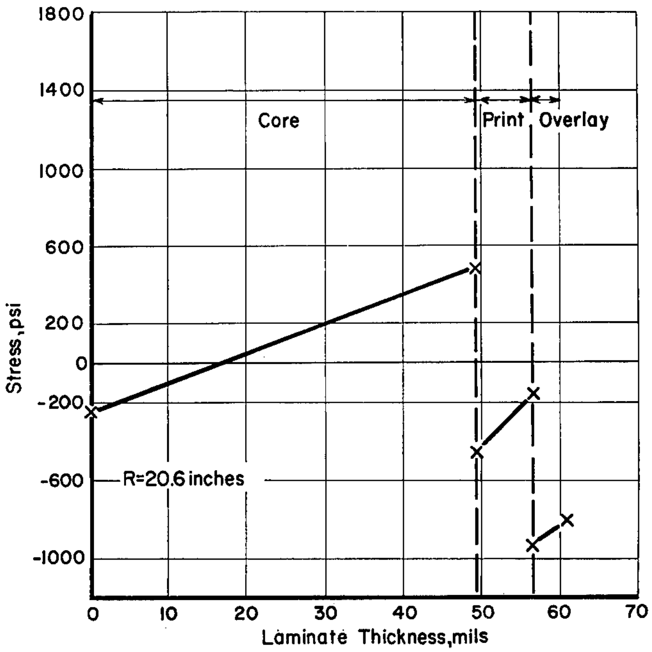


Fig. 4. Stress distribution through laminate thickness in the transverse direction.

At low humidities, installed laminates are also known to split (lengthwise) along the top, particularly at the corners of cutouts on wall panels or kitchen sink tops. These are, of course, normally points of high stress concentrations, but it is suggested that these failures are primarily due to the buildup of high internal stresses arising from the restrained laminate's inability to warp.

GEOMETRICAL EFFECTS OF TWO-DIMENSIONAL STRAINS

The properties of the individual components in a typical laminate are unbalanced in both the machine and transverse directions. This means that there should be warpage in two directions. However, in large panels (4 × 12 ft. and larger) typical of those sold commercially, this does not always appear to be the case. The large panels frequently appear to warp in only one direction, usually the transverse, and the only visible sign of warpage in the machine direction is a curling up of the corners. This phenomenon, for want of a better name, we have called the "sheeting effect," and can be illustrated by the following. Small samples from three commercial laminates were cut having the following dimensions:

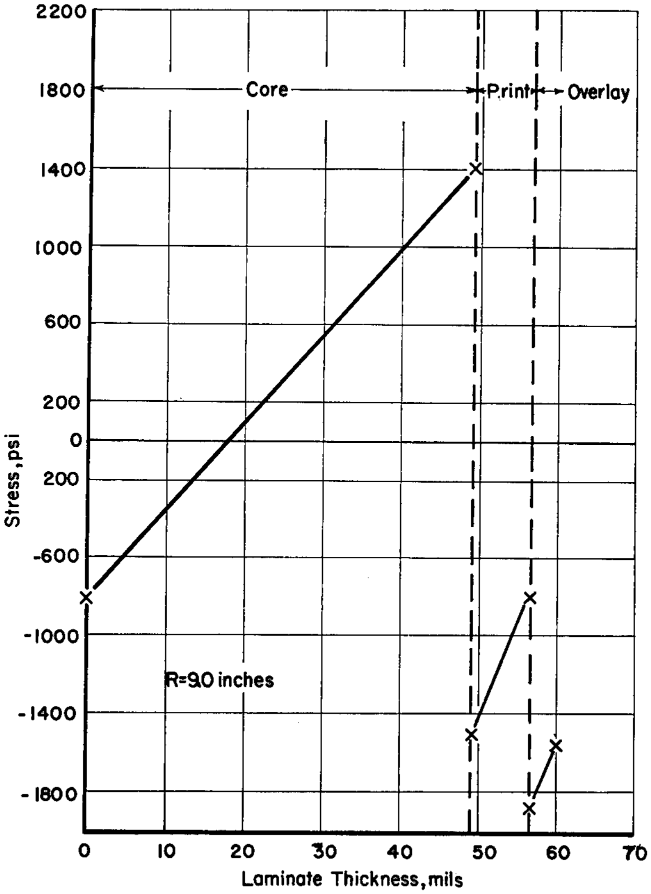


Fig. 5. Stress distribution through laminate thickness from curvature in the machine direction.

Length, in.	
M.D.	T.D.
6	1
6	3
6	4
6	6
4	6
3	6
1	6

The 6-in. long samples were exposed to 95°F. and 100% R.H. for 4 days. Each specimen was held with one end tangent to the flat surface and measurements of displacement from the surface were made at the opposite end. The results are shown in Figure 6. For a panel of fixed length, decreasing the width changed the lengthwise bending significantly. The bending changed monotonically with the width, usually increasing in magnitude, but in two instances there were even changes in the direction of bending. The square panels assumed a pagoda-like configuration. It was difficult to make accurate measurements of these because they showed real curvature in two directions whereas the narrower samples developed almost no

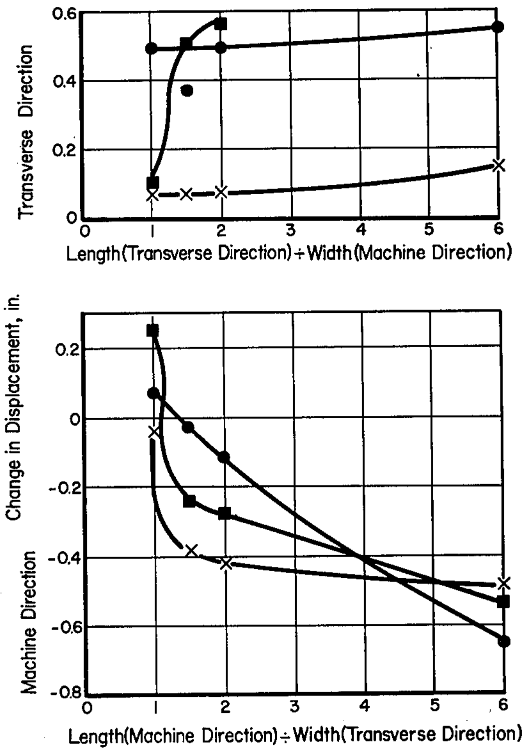


Fig. 6. Total change in warpage of commercial laminates held at 100% R.H. and 95°F. for 4 days as a function of the length-to-width ratio.

curl in their short dimension. The square panels were also quite stiff and difficult to flatten by hand pressure. The complex behavior of the square panels is not surprising since the 6 × 1 in. strips show positive transverse curvature (concave to melamine) and negative machine direction curvature.

Since all samples were cut from the same panel and were exposed to identical conditions, it is safe to assume that the properties of the individual components of all specimens were similar. Yet the observed curvature depended greatly on the sample shape. One may infer that the only simple unambiguous way to measure the true tendency of a laminate to curl is to use infinitely narrow samples.

As indicated previously, the mathematical analysis of this situation has not been fully developed. However, a physical interpretation of this peculiar behavior is possible. If the panel has a tendency to bend in both directions, then unhampered bending would produce a doubly curved surface such as a sphere or a toroid. Such bending, however, would require either that sections of the panel near its edges stretch more than those near the center, or that angles drawn on the surface of the panel should increase or decrease. To accomplish either of these kinds of deformation, large membrane forces would be required in the panel. Less force is required by the panel in simply restraining the bending so that the toroidal bending simply does not occur on any large scale. The complete interplay of the bending and membrane forces determines the shape that the panel actually takes. The exact effect depends on the magnitudes and directions of the one-dimensional curvature tendencies and the size and shape of the sheet. Generally speaking, curvature on lines running through or near the center of a sheet will be substantially lower than for a small, narrow strip if there is a significant curvature tendency in both directions. Curvatures near the edges will be closer to those for narrow strips. The effect of sheet size can be demonstrated readily by observing that most laminates as large sheets curl predominantly in the transverse or short direction, while small pieces of similar dimensional ratio cut from the same laminates will usually show more curvature in length.

Heebink and Haskell[3] have concluded that small-size samples can give accurate information about large sheets. We would concur with this with the qualification that the behavior of the large sheets is greatly modified by the sheeting effect and the nature of these effects needs to be better understood. Meanwhile, as will be seen, there is room for considerable investigation even of one-dimensional bending so it is not unreasonable to defer the study of the two-dimensional case.

Component Anisotropism

Every component of standard decorative laminates is anisotropic to some degree. This is because the resinous binder cannot completely overcome the fibrous nature of the paper base. Qualitatively, one might say that the environmental instability of decorative laminates is in part a measure of the relative degree of paper-like quality retained by the various components.

Percentagewise, a wet fiber will swell to the greatest extent in its thickness and least in its length. In a sheet of paper, the largest dimensional change is in the thickness, the next largest in the cross-fiber (transverse) direction, and the smallest in the machine direction. The curved, resin-impregnated components of a laminate follow this behavior pattern also. Since thickness changes do not cause curvature, the relationship between the longitudinal and lateral dimensional changes are of prime interest.

The ratio of these two-dimensional changes, referred to as the directional factor, is a function of total resin content and cure level, and to a lesser degree the nature of the paper base. Directionality decreases if either resin content and cure are increased. Since the components of decorative laminates differ widely in resin content and cure, they also differ in their directionality.

The phenolic core, which contains the least resin, is the most directional of the components. The melamine overlay, supersaturated with resin, is the least directional. In addition, the relative difference between components is a function of humidity. The directionality of melamine overlay is practically constant over the entire humidity range. In contrast, the phenolic core becomes more and more directional as the humidity, or moisture content, increases due to a tendency of the paper base of this component to shrink lengthwise. In Table II are tabulated the directionality factors (based on linear dimensional changes) for typical components as determined for three conditions:

TABLE II
Directionality Factors (m_{TD}/m_{MD}) of Typical Components

	Condition a	Condition b	Condition c
Core	4.28	$\sim$23.0	2.62
Print	1.82	2.20	1.37
Overlay	1.34	1.25	1.39

(*a*) From dry at 73°F. to saturated condition at 73°F. and 90% R.H.

(*b*) From equilibrium at 73°F. and 50% R.H. to saturation at 73°F. and 98% R.H.

(*c*) From equilibrium at 73°F. and 50% R.H. to dry at about 10% R.H. and 73°F.

UNRESTRAINED MOVEMENTS OF LAMINATE COMPONENTS

A study of the behavior of the laminate components prepared separately has potential value for several reasons. First, it will reveal accurately the gross differences in behavior of these components which are responsible for the primary curvature problem. Second, the reaction of these components to changing environments sheds considerable light on the secondary aspects of laminate behavior such as development of permanent warpage. Third, the accurate measurement of component properties such as strain coefficients is necessary in order to study the applicability of eq. (6). The remaining sections of this paper deal with all three aspects.

The first experiments were conducted on separately molded sheets. Phenolic resin–Kraft paper moldings, melamine resin–print paper moldings, etc., were prepared individually and cut into $2^1/_2$-in. squares with the edges machined flat until parallel. They were then conditioned to constant weight at 50% R.H. and 73°F. The sample thickness was made large enough to insure specimen rigidity.

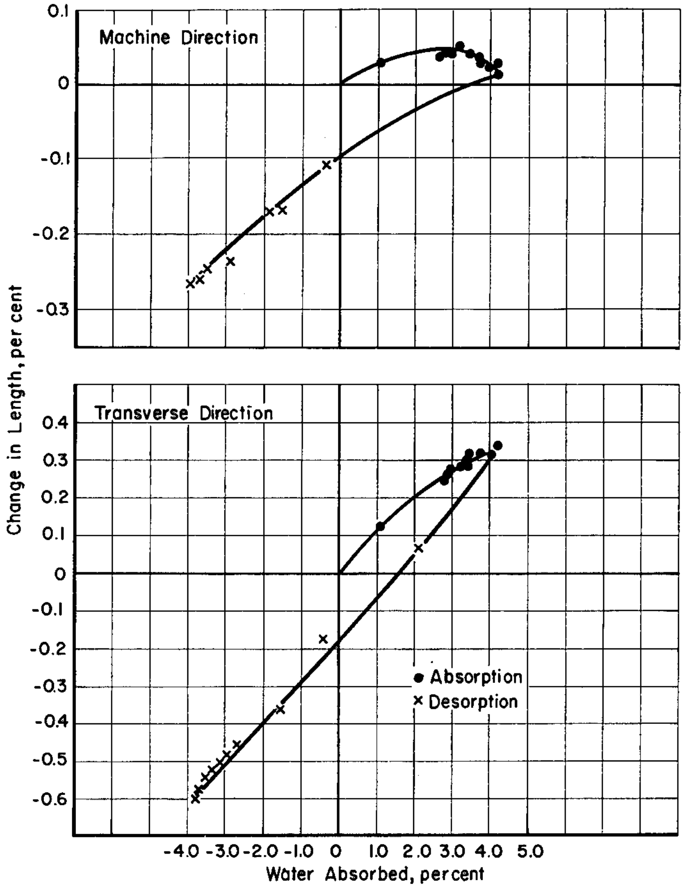


Fig. 7. Effect of wet–dry exposure on the lateral dimensions of a typical core.

Specimens prepared as above were exposed to various environmental changes between approximately 10 and 98% R.H. at 73°F. Changes in weight, thickness, length, and width were monitored as a function of time. Exposures were usually carried on until the specimens reached essentially constant weight. This usually corresponded to constant dimensions but in

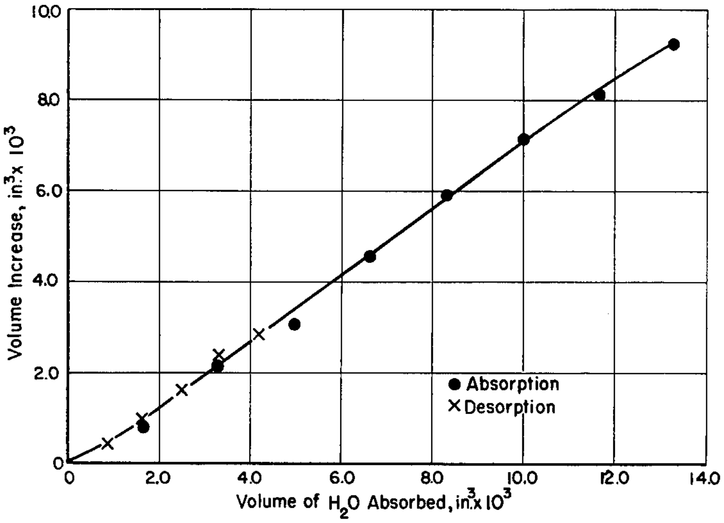


Fig. 8. Swelling of core as a function of absorption and desorption of moisture.

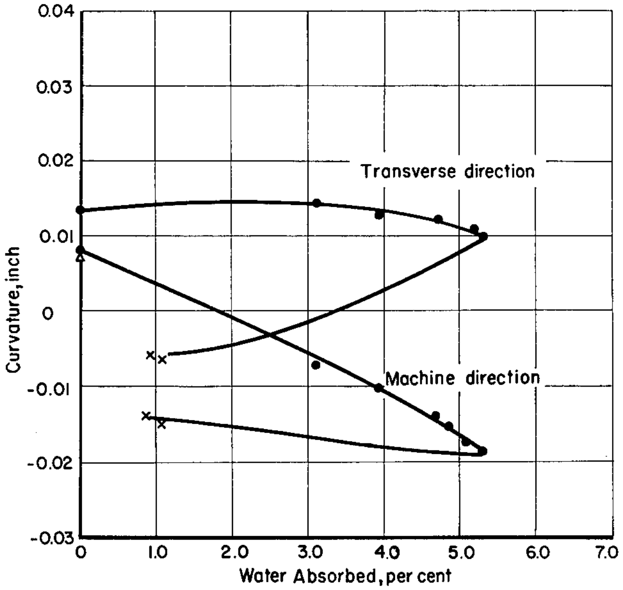


Fig. 9. Effect of water absorption and subsequent redrying on the curvature of a commercially prepared laminate.

a few cases slow dimensional changes were still occurring. Specimen dimensions were measured with a 3-in. micrometer caliper calibrated to 0.0001 in. The exposed specimens covered a wide spectrum of parameters, including resin contents, cure levels, paper density, and processing variables such as "as pressed" volatile content and flow. It is not the purpose of this paper to cover these relationships in detail. However, it is important to note

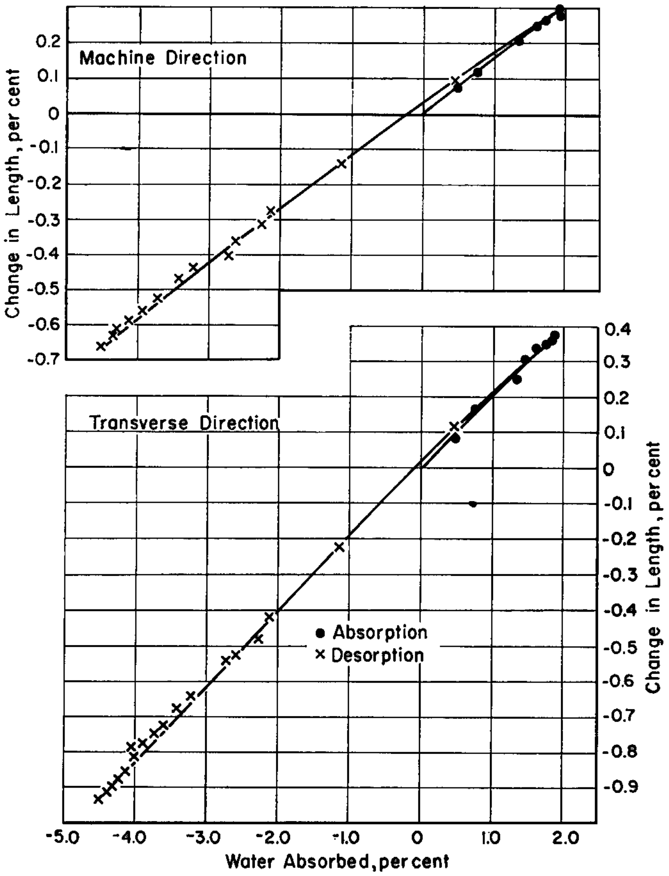


Fig. 10. Effect of absorption–desorption on the lateral dimensions of standard overlay.

that weight change, dimensional change, and rate of change were all affected to various degrees by those variables.

One of the most striking relationships observed was the paper-like behavior of phenolic resin–Kraft paper core material. Figure 7 illustrates the relationship between moisture content and dimensional change for a core structure comparable to that found in a typical commercial laminate. The data shown are for specimens taken from 50% R.H. to equilibrium at 98% R.H., and then to equilibrium at about 10% R.H. (all at 73°F.).

The initial machine direction expansion of this material is rapidly followed by shrinkage as saturation is approached. The particular material used in the illustration had a very small, overall increase in length in going to high humidity. Some duplicates actually finished with a net decrease in length.

More significant is the permanent distortion, or shrinkage, shown in both directions as the wet specimen was dried. These shrinkages in length and width are compensated for by an increase in thickness, so that the

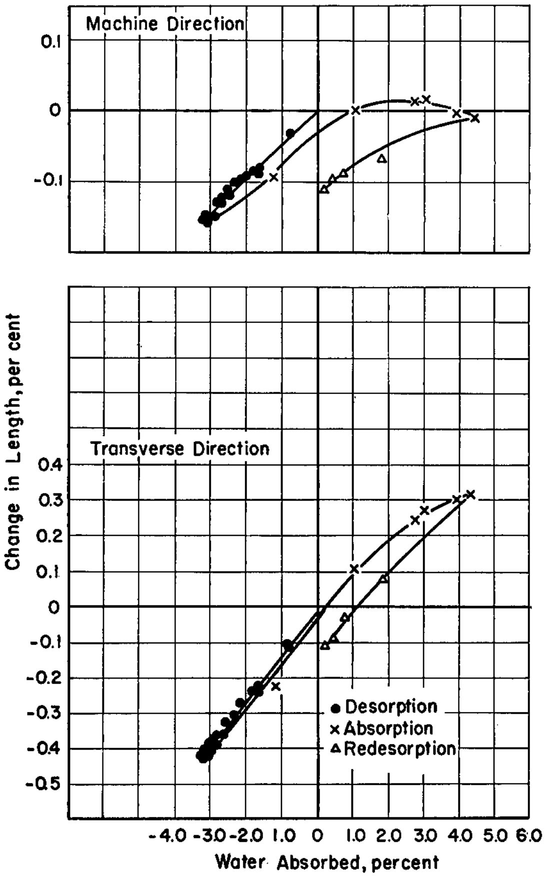


Fig. 11. Effect of dry–wet–dry exposure on the lateral dimensions of a typical core.

volume after return to the original condition is unchanged. This is illustrated in Figure 8, a plot of the volume increase of a core specimen against the volume of absorbed water during wetting and subsequent drying.

In a composite laminate, permanent shrinkage in the core material after a wet–dry cycle would be expected to produce a negative or permanent curl concave to the phenolic face. Cyclic exposure of this sort actually produces this effect, as shown in Figure 9. The data in this figure are based on the behavior of small strips cut from commercial laminates.

This paper-like behavior of the phenolic core is closely dependent on resin content and cure. Thus if both variables are decreased, the permanent shrinkage in both directions and the initial high-humidity machine direction shrinkage are both increased. Conversely, both characteristics can be reduced by increasing the core resin content or cure level.

The other major components of decorative laminates which are based on melamine–formaldehyde resins and alpha cellulose paper usually contain

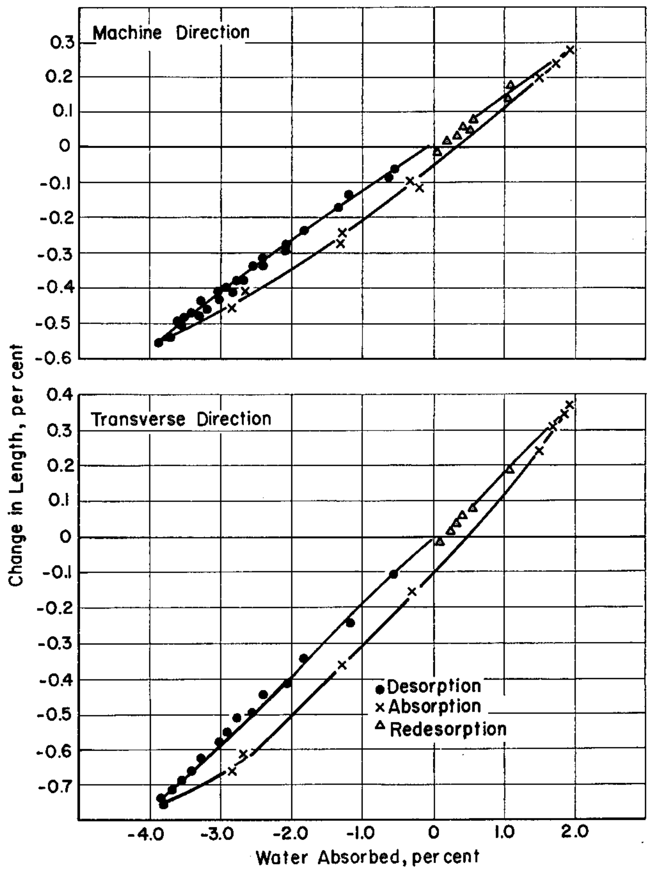


Fig. 12. Effect of desorption–absorption and redesorption on the lateral dimensions of a typical overlay.

a considerably higher proportion of resin than the phenolic core. Also, they are more tightly cured, particularly in the case of the overlay. As a result, the paper-like properties are much less noticeable and deformation after high humidity exposure is almost negligible. This is shown in Figure 10 for a typical melamine overlay. The sample was taken from 50% R.H. to 98% R.H., and then down to about 10% R.H.

Laminate components also experience deformation if the sequence of exposure is reversed, that is, when a drying step precedes the high humidity exposure. The effects of this exposure on the phenolic core and melamine overlay are shown in Figures 11 and 12. In the case of the phenolic core, the lateral dimensions change very little on drying from 50% R.H. but are substantially reduced on redrying to 50% R.H. after high-humidity exposure. These shrinkages are similar to those shown in Figure 7.

In contrast, the distortion developed in the melamine overlay is greater for a dry–wet exposure than for a wet–dry exposure. However, if the dry–

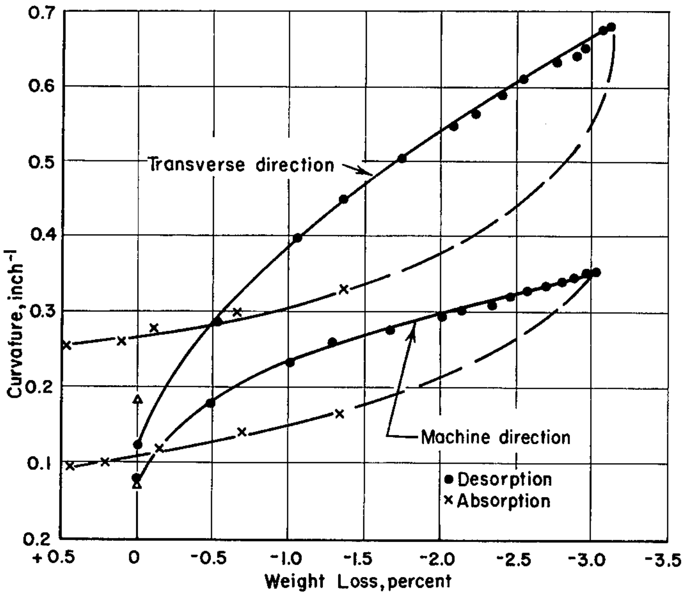


Fig. 13. The effect of low humidity on the warpage of a commercially produced laminate.

wet overlay is brought back to its original moisture content, it shows very little deformation for the complete cycle.

Multicomponent laminates, cycled to low humidity and back, develop a positive curvature concave to the melamine face. (The method of measuring curvature is explained in the Appendix.) As shown in Figure 13, the increase is larger in the transverse direction. This may be due to the overlay shrinkage shown in Figure 12 or to an increase in lateral dimensions of the core as a result of the increased stress on the core at the high curvatures developed at low humidity. It is probable that both factors contribute. The dried overlay, after returning to its original moisture content, shows a shrinkage of about 0.1% in the transverse direction and about 0.05% in the machine direction. The phenolic core shows a shrinkage of about 0.03% in both directions. The difference is greatest in the transverse direction, which agrees with the observed behavior of the composite laminate in Figure 13.

A comparison of the dimensional change curves of the melamine overlay and phenolic core reveals the large difference in movement existing between the two materials. This fact has been described by others, and will not be discussed further here. However, it should be pointed out that most of the environmental difficulties originate with this characteristic.

The curves of dimensional change versus moisture content are in effect hysteresis loops. Such loops were obtained for every component specimen measured. Some loops are open and wide, particularly in the case of the low resin content material such as core stock. Others are very narrow and essentially closed such as for the overlay in Figure 12. The tendency to develop such a loop seems to depend more on the absolute amount of resin employed (and its cure level) than on the chemical nature of the resin itself. Although it has not been attempted, it is suspected that an overlay with a resin content similar to that found in the core would be very comparable to that material.

CURVATURE CALCULATIONS FROM EXPERIMENTAL DATA

Using strain coefficient and modulus data obtained from separately molded laminate components, the low humidity multicomponent laminate curvatures were calculated for six different panels. These values are compared to the curvatures actually measured for those constructions in Table III. The agreement is obviously poor. In all but one case (*A* in the machine direction), the measured curvature is more concave to the melamine face than anticipated. This can indicate greater shrinkage in the melamine, less shrinkage in the phenolic, or a combination of the two. The actual reason for the discrepancy became clear when the multicomponent laminates were sectioned, and the properties of the now-isolated components determined.

The isolated components were obtained by slowly grinding away the unwanted layers. Thus, the melamine overlay and print were ground off to leave an "isolated" core, etc. The following isolated sections were prepared:

(*1*) Phenolic cores
(*2*) Melamine prints
(*3*) Core-print composite laminate
(*4*) Print-overlay composite laminate

Isolating the overlay was almost impossible, and in any event, the extreme thinness of this component precluded the possibility of any precise measurement. A similar problem, including considerable warpage, existed with the isolated print and print–overlay combination, and dimensional measurements made on those were subject to fairly large errors.

The isolated specimens were exposed to the same humidity conditions as had the comparable separately molded components. It was discovered that the weight losses and dimensional changes of the isolated components were significantly different (generally larger) from the separately molded counterparts. The difference was most striking for the print layer where shrinkage at low humidity was more than twice that obtained for the separately molded specimen.

This excessive print shrinkage appears to be a critical factor in explaining low-humidity warpage, qualitatively and quantitatively. It had been standard procedure to view low-humidity curvature primarily in terms of the shrinkage difference between the high resin content overlay and the core. The role of the print had not been considered to be critical. However, in the light of data on isolated components, it is more important than the overlay.

TABLE III

Comparison of Calculated with Actual Laminate Curvatures

	Change in curvature,[a] in. × 10^4									
	As measured		Calculation I[b]		Calculation II		Calculation III		Calculation IV	
Sample	MD	TD	MD	TD	MD	TD	MD	TD	MD	TD
A	+274	+543	+325	+163	+390	+792	+408	+531	+440	+633
B	+320	+516	+45	−272	+449	+625	+206	+193	+325	+542
C	+212	+339	−32	−401	+718	+397	+73	+19	+170	+195
D	+431	+713	+247	+28	+980	+791	+414	+32	+464	+348
E	+398	+532	+149	−92	+697	+972	+259	+379	+182	+345
F	+468	+721	+229	+44	+649	+1094	+489	+572	+550	+716

[a] Low humidity.

[b] From as-molded components.

The difference in strain coefficients between separately molded and isolated specimens appears to be at least partly caused by diffusion of moisture between components during molding. It is not clear, however, why this should cause the susceptibility of all layers to increase as they did in many cases. Again it is not obvious why the print layer should be much more markedly affected than either the core or the overlay. One might predict that the moisture would tend to migrate to the component having the highest paper content. This would be the core, of course. It is possible that migration in this direction is the pattern but that the thickness of the core prevents complete diffusion from taking place.

Curvatures were calculated for experimental laminates using four different sets of data:

(*1*) All strain data based on separately molded components (Calculation I, Table III).

(*2*) Strain data based on isolated core and print and separately molded overlay (Calculation II, Table III).

(*3*) Strain data based on isolated core, separately molded overlay, and calculated for print from the curvature of core–print composite (Calculation III, Table III).

(*4*) Strain data based on isolated core, isolated core-print composite (for print), and isolated print–overlay composite (for overlay) (Calculation IV, Table III).

The results of these calculations are summarized in Table III. None of them is in absolute agreement with the measured values, but use of isolated component data considerably improves the agreement. In fact, considering the difficulty in accurately measuring strains and curvatures on these very thin, flexible specimens, the agreement is gratifying.

SUMMARY

Warpage in a laminate has been examined both analytically and experimentally. The warpage developed by a laminate is shown to be determined, in theory, by the difference in expansion (or contraction) induced in the different layers of the structure as a result of moisture absorption or desorption. (Thermal effects have not been considered.) It is shown that moderate changes in the tendency of any segment of the structure to change dimension greatly influences the curvature developed by the total structure. The analysis of hypothetical laminate indicates that the high internal stresses are developed which, under certain conditions, are probably high enough to account in part for the permanent warpage frequently developed.

The moisture content–dimension relationship of two laminate components, phenolic core and melamine overlay, are compared. The much larger movement of the melamine layer is sufficient to account for the environmental instability, at least in a qualitative sense. However, the problem is made more complex by the varying degree of paper-like behavior inherent

in each component part of the whole structure. Because of their cellulosic base, laminate components are all anisotropic. That is, environmentally induced dimensional change differs in each of the three principal directions. If the anisotropism were the same in every component, the composite structure would be easier to deal with. However, the phenolic core is much more anisotropic than the melamine components. In addition, the core, due to its relatively low resin content, behaves more like paper in high humidity; instead of expanding in the fiber direction, it actually tends to shrink. The core also develops a permanent change in dimension during a cyclical humidity exposure due to this shrinkage, and this behavior is reflected in composite laminates, which when exposed to the same conditions, develop a permanent warpage compatible with the concept of phenolic shrinkage.

< Data obtained from separately molded components fail to explain quantitatively the curvature developed by the multicomponent laminate. Data derived from a study of components sectioned from a premolded laminate provide better agreement. >

APPENDIX

Mathematical Analysis of Warped Laminates

One-Dimensional Curvature. Assume that the length l of a slender strip of fiber of any material in a laminate can be determined from its moisture concentration C, its temperature T, and its stress G, and suppose this fiber would have length l_0 if $\sigma = 0$; while $C = C_r$ and $T = T_r$, these being reference values. That is, suppose

$$l = l(C,T,\sigma)$$

and

$$l_0 = l(C_r,T_r,0)$$

The total strain in the fiber at C,T,σ is:

$$\frac{l(C,T,\sigma) - l_0}{l_0}$$

Let m be the part of the strain due to changes in moisture concentration and temperature only, i.e.,

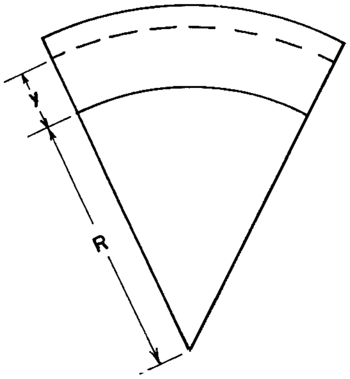
$$m = \frac{l(C,T,0) - l_0}{l_0}$$

Hereafter, this ratio m will be called the strain coefficient. Further, define $E(C,T)$ (Young's modulus), so that

$$E(C,T) = \frac{\sigma}{\left[\dfrac{l(C,T,\sigma) - l(C,T,0)}{l_0}\right]} \tag{1}$$

[Equation (1) is similar to the standard stress–strain relationship, where stress σ is proportional to strain ϵ, or $\sigma = E\epsilon$. Such an equation is valid within the elastic range of the material.] Then the total strain is:

$$\frac{l(C,T,\sigma) - l_0}{l_0} = \frac{l(C,T,\sigma = 0) - l_0}{l_0} + \frac{l(C,T,\sigma) - l(C,T,\sigma = 0)}{l_0} = m + \frac{\sigma}{E}$$



In a bent laminate, let ϵ denote the strain of a fiber on the inner surface. If its initial length was l_0, then its new length is $l_0(1 + \epsilon)$. For a fiber a distance y from the inner one (having the initial length l_0), the length then becomes

$$l_0(1 + \epsilon)(R + y)/R$$

where R = the radius of curvature of the inner surface. The strain in the general fiber is:

$$\frac{l_0(1 + \epsilon)[(R + y)/R] - l_0}{l_0} = (1 + \epsilon)\left(1 + \frac{y}{R}\right) - 1$$

$$= 1 + \epsilon + (1 + \epsilon)\frac{y}{R} - 1 = \epsilon + (1 + \epsilon)\frac{y}{R}$$

$$\approx \epsilon + \frac{y}{R}, \text{ as } 1 + \epsilon \cong 1$$

This is the geometrical expression for strain at any distance y from the inner surface. Equating the physical and geometrical expressions for strain:

$$m + \frac{\sigma}{E} = \epsilon + \frac{y}{R}$$

Solving for σ:

$$\sigma = \epsilon E + \frac{Ey}{R} - mE$$

This σ is a stress in a fiber at position y when the laminate is bent to radius R and the inner fiber has strain ϵ.

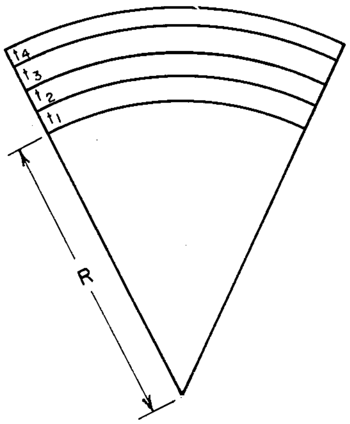
To find ϵ and R, we need to establish two conditions for the stresses. These conditions are:

(*1*) The total stress must be zero if taken over a radial cross-section, or

$$\int \sigma dy = 0 \tag{2}$$

(2) The total moment of stress must be zero if taken over a radial cross-section, or

$$\int y\sigma dy = 0 \tag{3}$$



Let t_i = thickness ith layer, $S_i = t_1 + t_2 + t_3 + \ldots t_i$, n = number of layers:

$$\begin{aligned}\int_0^{S_n} \sigma dy &= \int_0^{S_i} \sigma dy + \int_{S_i}^{S_2} \sigma dy + \int_{S_2}^{S_3} \sigma dy \ldots + \int_{S_{n-1}}^{S_n} \sigma dy \\ &= \sum_{i=1}^{n} \int_{S_{i-1}}^{S_i} \sigma dy = \sum_{i=1}^{n} \int_{S_{i-1}}^{S_i} \left[\epsilon E - mE + \frac{Ey}{R}\right] dy \\ &= \sum_{i=1}^{n} \left\{\epsilon E_i \int_{S_{i-1}}^{S_i} dy - m_i E_i \int_{S_{i-1}}^{S_i} dy + \frac{E_i}{R} \int_{S_{i-1}}^{S_i} y dy\right\} \\ &= \sum_{i=1}^{n} \left\{\epsilon E_i t_i - m_i E_i t_i + \frac{E_i}{2R} (S^2{}_i - S^2{}_{i-1}) = 0\right\}\end{aligned}$$

Therefore,

$$\epsilon \sum_{i=1}^{n} E_i t_i + \frac{1}{2R} \sum_{i=1}^{n} E_i (S^2{}_i - S^2{}_{i-1}) = \sum_{i=1}^{n} m_i E_i t_i \tag{4}$$

Similarly, from eq. (3)

$$\frac{\epsilon}{2}\sum_{i=1}^{n} E_i(S_i{}^2 - S^2{}_{i-1}) + \frac{1}{3R}\sum_{i=1}^{n} E_i(S^3{}_i - S^3{}_{i-1}) = \frac{1}{2}\sum_{i=1}^{n} m_iE_i(S^2{}_i - S^2{}_{i-1}) \tag{5}$$

Solving this pair of equations for $1/R$:

$$\frac{1}{R} = \frac{\frac{1}{2}\left[\sum_{i=1}^{n} m_iE_it_i\right]\left[\sum_{i=1}^{n} E_i(S^2{}_i - S^2{}_{i-1})\right] - \frac{1}{2}\left[\sum_{i=1}^{n} m_iE_i(S^2{}_i - S^2{}_{i-1})\right]\left[\sum_{i=1}^{n} E_it_i\right]}{\frac{1}{4}\left[\sum_{i=1}^{n} E_i(S^2{}_i - S^2{}_{i-1})\right]^2 - \frac{1}{3}\left[\sum_{i=1}^{n} E_it_i\right]\left[\sum_{1=1}^{n} E_i(S^3{}_i - S^3{}_{i-1})\right]} \tag{6}$$

Measurement of Curvature. To assign a finite value to the curvature of a warped panel, it is necessary to select first a suitable sample for study, and second, a technique capable of producing a measurable value translatable into curvature. All measured curvature values reported in this paper were determined on strips 6 in. long by 1 in. wide.

The technique consisted of holding one end of the strip tangent to a flat surface and measuring the height of the other end relative to the flat surface. This was accomplished with a height gage calibrated to the nearest thousandth of an inch. Corrections were made for the thickness of the sample. It was then assumed that the arc of the warped piece was circular. (This assumption is not completely correct, particularly at the ends of the strip.) Using the value determined for the height of one end of the sample relative to the other, geometrical considerations permitted the calculation of a radius of curvature for the arc of the strip. The reciprocal values of those radii are reported as the sample curvature.

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Résumé

La courbure d'un laminé décoratif tissé est mathématiquement une fonction des coefficients de tension, des modules de tension, de l'épaisseur des couches individuelles comprises dans la structure. La plus importante de ces fonctions sont les coefficients de tension. L'interaction des tensions en deux directions est discutée et on démontre que la grandeur et la forme du panneau influencent la courbure observée. Ainsi en réduisant la largeur de la feuille, on augmente la formation développée par le laminé dans la direction de la longueur. Une anisotropie existe à différents degrés dans tout composant d'un laminé typique par suite de leur base fibreuse. Certains composants sont de façon significative, plus anisotropiques que d'autres suivant la teneur totale en résine et l'état de traitement de cette résine. Le composant majeur du laminé, le papier résine phénolique à base de papier Kraft, était plus anisotrope particulièrement à humidité

élevée lorsque les fibres de cellulose étaient le plus sérieusement affectées par l'humidité. Ce composant est très instable. L'exposition cyclique à l'humidité élevée induit un rétrécissement permanent de la longueur et de la largeur qui à leur tout produisent une déformation permanente du laminé dans des conditions similaires. En outre, le noyau phénolique tend à se rétrécir dans le sens de la longueur (dans la direction de la fibre) à humidité très élevée alors que les composants de mélamine ne le font pas. Les propriétés des composants séparément moulus sont différentes de celles des matériaux comparables isolés au départ du laminé composite. La couche imprimée en particulier absorbe une quantité considérable d'humidité produite par les autres composants au cours du traitement de recuit du laminé. Ceci résulte d'un rétrécissement potentiel très élevé du composant. La cause principale de déformation à humidité faible est le rétrécissement élevé de l'impression par rapport à celle de la masse centrale phénolique.

Zusammenfassung

Die Krümmung eines verzogenen Dekorationslaminates ist, wie sich mathematisch zeigen lässt, eine Funktion der Spannungskoeffizienten, des Zugmoduls und der Dicke der individuellen, die Struktur aufbauenden Schichten. Die wichtigsten unter diesen Funktionen sind die Spannungskoeffizienten. Die Wechselwirkung zwischen Spannungen in zwei Richtungen wird diskutiert und es wird gezeigt, dass Grösse und Gestalt der Tafel die beobachtete Krümmung beeinflussen. So erhöht eine Verringerung der Tafelbreite die vom Laminat in der Längsrichtung entwickelte Verwerfund. Wegen ihrer Faserstruktur besteht in allen Komponenten eines typischen Laminates in verschiedenem Ausmass eine Anisotropie. Einige Komponenten sind wesentlich stärker anisotrops als andere, was wieder von ihrem Gesamtgehalt an Harz und vom Härtungszustand des Harzes abhängt. Die Hauptkomponente des Laminates, der Kern aus Phenolharz und Kraftpapier, ist am stärksten anisotrop, besonders bei hoher Feuchtigkeit, wo die Cellulosefasern am meisten durch die Feuchtigkeit gefährdet werden. Diese Komponente erweist sich als sehr instabil. Cyclische Einwirkung hoher Feuchtigkeit induziert eine permanente Längen- und Breitenschrumpfung, welche ihrerseits wieder in einem Laminat unter den gleichen Bedingungen zu einer permanenten Verwefung führen. Zusätlich zeigt der Phenolharzkern eine Tendenz zur Längsschrumpfung (in der Faserrichtung) bei sehr hoher Feuchtigkeit, während die Melaminkomponenten nicht dazu neigen. Die Eigenschaften von getrennt verarbeiteten Komponenten sind von denjenigen der entsprechenden, aus einem zusammengesetzten Laminat isolierten Stofle verschieden. Besonders die Bedruckungsschichte absorbiert eine beträchtliche, von den anderen Komponenten während der Härtung der Laminate freigesetzte Menge an Feuchtigkeit. Das führt zu einer sehr hohen potentiellen Schrumpfung dieser Komponente. Die Hauptursache der Verwerfung bei niedriger Feuchtigkeit liegt in der hohen Schrumpfung der Bedruckung im Vergleich zu derjenigen des Phenolharzkernes.

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Analysis of Plastic Weathering Results

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Synopsis

The development of new, outdoor weather-resistant materials possessing desirable physical, optical, and/or electrical properties is a long, complex procedure and a difficult objective to achieve. The time is extended because (*1*) the multitude of fabrication and compositional variables require study to determine their effect on performance, and (*2*) no accelerated test is readily available for predicting just how well a new material will maintain its integrity during outdoor exposure. Statistical methods are described and discussed which might be useful in attaining the above objective. Some of these methods may be valuable in the planning and conducting of outdoor weathering experiments, particularly in (*a*) reducing and measuring the uncontrollable, experimental variation, (*b*) selecting test methods, and (*c*) attaching limits of certainty to the results. Examples are given which illustrate applications of *analysis of variance* and the *correlation–regression strategy*. The former can be helpful in planning and analyzing the results of outdoor exposure programs, while the latter is of value in correlation of accelerated with outdoor performance and in predicting expected service life under normal use conditions.

INTRODUCTION

Outdoor weathering is one of the most insidious, variable and destructive forces of nature. For as long as man has been on this planet he has tried to protect himself from the weather. The earliest traces of prehistoric man indicate that, where it was possible, he lived in caves and/or covered himself with foliage or animal skins. It is believed he did this to reduce partially the destructive and inconveniencing characteristics of the weather during some portion, at least, of the 24-hr. period designated as a day. Because protection from the weather was not easily attained, a sizeable number of man-hours have also been spent over the past 40,000 yr. in trying to understand and control this natural phenomenon.

Man's successes to date have been relatively modest and very expensive, considering only all the fuel consumed to warm us in cool weather and to cool us in warm weather. The challenge to minimize the effects of weather remains. Nowhere does this challenge stand out more clearly than in the field of polymer chemistry in general and in the field of rigid plastics in particular. A part of the challenge is that no one wants to wait 20 yr. to learn whether a new material will still be acceptable at that time.

Weather consists of a combination of many things such as visible light, ultraviolet light, water (vapor, liquid, solid), heat, wind, (and barometric pressure), and may also be considered to include microorganisms, chemicals in the atmosphere, dust, smoke, and pollen. Weather is not just one combination of these many constituents but is in a sense kaleidoscopic, and its components are constantly changing in direction and intensity at unpredictable and varying rates.

A rapid test procedure is desired that not only duplicates the weather but effects the same changes in a few years which natural weathering will induce only in 20, 30, or more years. Because of the complexity of the problem and the long time required to obtain outdoor weathering results, it is important that the entire product development program for any new durable material be conducted with an absolute minimum of errors of both omission and commission. Proper advance planning, scheduling, and appraisal of the overall program before work is started are essential.

This is where *statistics* can be of assistance. *Statistics* is a branch of mathematics that deals with observational data. It is based on the assumption that experimental results are always going to vary around an average. It attempts to classify the sources of variation, and to determine the shape of the frequency distribution with which results occur. Then, on a probability basis inferences are drawn from the data.

The keystone of the statistical method is the isolation and measurement of the uncontrolled variation in the results. This is often designated as the *experimental error* or the *inherent error* in the experiment. All other results are then compared to this error and, depending on that comparison, conclusions are drawn on a probability basis for the cause and effect relationships of factors under study.

Generally, statistics are of use to researchers for three important reasons. These are: (*1*) they inject objectivity and eliminate subjectivity in analysis of results; (*2*) they bring efficiency into experimentation; and (*3*) a degree of certainty may be attached to the conclusions.

DISCUSSION AND RESULTS

Preliminary Stages

Because of the variability of the weather, both at any one location and from one geographical location to another, and the length of time required to determine weather resistance, statistics can be a useful set of tools to use on test results in obtaining answers to such questions as:

(*1*) How long will a ______ plastic retain ______% of its physical, optical, or electrical properties during continuous use outdoors?

(*2*) Is A more resistant to outdoor weathering than B, C, etc.?

(*3*) Does a certain accelerated (laboratory) test method provide results which correlate with outdoor weathering?

(*4*) What weather condition or combination of weather conditions cause(s) a plastic to lose ______% of its initial value?

Each of these questions leads to several more questions. For instance, what is meant by the simple expression "outdoor weathering?" Does it mean weather as it existed in the author's front yard at 12:31 P.M. August 5, 1965, 20 ft. north from the mail post and at an elevation of 168 ft. above sea level? Or does it mean continuous outdoor exposure to the elements, anywhere within the continental United States for a period of 27 yr.? Obviously the two kinds of "outdoor weather" are going to be quite different.

Furthermore, what is meant by a ——— plastic? Does this mean the actual full-scale component constructed entirely from one particular plant batch of ——— plastic? Or does it mean a simulated component, a scale model, or a test specimen? If a test specimen, what should be its size, shape, surface condition, residual stresses, anisotropy, and preconditioning?

Still other questions ought to be asked concerning the properties of interest. What properties are to be measured and how are these properties to be measured? Also, how should the ——— plastic, full-scale component or test specimen, be exposed as to type of mount and position on the mount?

After the problems are defined, the objectives agreed upon, and the properties-to-be-measured identified, the usual next step is to plan a laboratory study program aimed at answering the questions, solving the problems, and attaining the objective. In the planning of a laboratory study program, the variables believed likely to correct the difficulty, improve the results, and attain the objective are considered.

From a statistical viewpoint, there are five (and only five) types of variables that influence experimental results. They are listed in Table I. These five types of variables are important in the planning of all experiments, no matter what part of the study program is being considered. They are just as important in studying raw materials as in the finished product, as important in studying the chemistry of the process as in the mechanics, and as important in studying the design of a test specimen as in selecting and operating a test instrument. Type 5 is generally designated as the uncontrolled experimental variation or the experimental error.

TABLE I
Five Types of Variables

Type 1	Those that are well known as to effect from previous studies.
Type 2	Those that are known from previous studies to have no effect.
Type 3	Those that are controllable and considered worthy of study, such as compositional, fabrication, size, and location factors.
Type 4	Those that are uncontrollable but measurable, such as barometric pressure, wind velocity, temperature, and rainfall.
Type 5	All others (those that are uncontrollable and unmeasurable and those that are controllable but not considered worthy of study).

A statistician would treat these variables as follows:

Type 1. Hold at a fixed, economical, and well-performing level.
Type 2. Ignore.
Type 3. Use an efficient and effective experimental design encompassing as many variables and levels of each variable as possible.
Type 4. Record.
Type 5. Randomize to minimize their effects.

Some of the sources of variation in outdoor exposure programs that are often overlooked[1] (and consequently not recorded or randomized) are:

1. The preparation of the material.
2. The preparation of the test specimen.
3. The conditions before exposure.
4. The location of the exposure site.
5. The type of rack.
6. The position of the specimen on the rack.
7. The weather at the start of outdoor exposure.
8. The weather over the complete period of the test.
9. The human element in assessing a change in property.

Related to the variables discussed above are the test results. Results may be of three general types, i.e., quantitative, counts, judgments. Statistical methods are most efficient when quantitative data derived from measurement scales are obtained, but methods of analysis are also available for use with counted data (e.g., the *number* of items failing) and for ranked data.

Often more than one property and more than one method of measuring each property is available. The test instrument should be chosen according to the criteria shown in Table II.

TABLE II
Seven Measures of a Good Test Device

1. Accurate.
2. Reproducible.
3. Calibratable (a standard for comparison is available).
4. Useful over a wide range (of materials and under various testing temperature and humidity conditions). It has a large but accurate scale.
5. Simple to operate.
6. Related to actual service as to the test results it produces.
7. Inexpensive.

Statistical methods are available to assist in evaluating items 1, 2, 3, and 6 in Table II.

Let us now consider a few specific examples illustrating the usefulness of statistical methods in outdoor weathering studies.

Analysis of Variance

One of the most elegant, powerful, and useful statistical techniques is that one designated *analysis of variance*, sometimes shortened to ANOVA. I will not attempt to describe the details of ANOVA here, as this is adequately done in many readily available textbooks and technical articles.[2] Generally speaking, ANOVA allocates the total variation in an experiment to each of the several components associated with the possible sources of variation. Thus, ANOVA is a method of relating several input variables, each one of which may be at any of several levels, to an output result. The data in Table III were taken from a paper by Clark.[3] The author reported that "an analysis of variance study applied to the four Florida and the four Bound Brook seasons and to the 19 compounds showed:

1. A highly significant difference in stability among the 19 compounds tested.
2. A highly significant difference for fading on the sun hour basis among specimens exposed at different seasons of the year in both Bound Brook and Florida.

TABLE III

Sun Hours Exposed Before Fading

		Location and Season							
		Miami				Bound Brook			
Supplier	Color	Sp	S	F	W	Sp	S	F	W
A	Peach	280	160	240	240	160	80	80	320
	Green	320	160	240	320	120	80	80	240
	Blue	120	80	60	80	80	40	40	80
	Yellow	240	160	160	240	160	80	80	240
B	Peach	320	160	240	240	40	160	160	80
	Green	500	500	240	240	500	240	320	625
	Blue	500	320	>500	>500	320	240	240	500
	Yellow	320	160	320	320	160	160	160	320
D	Peach	160	80	80	80	160	60	60	410
	Green	160	80	80	120	160	80	80	410
	Blue	80	80	40	80	80	40	40	240
	Yellow	80	80	40	80	40	40	40	240

I have rearranged some of the data in the original paper to form a full factorial experiment (Table III). Admittedly this has violated some of the rules of statistics but should be acceptable for illustrative purposes. Factors other than those under study, such as thickness, pigment content, and composition, probably differed among suppliers. This is immediately revealed in the ANOVA in Table IV. At the 5% level, two of the interactions are inversely significant. Such an occurrence is usually an indication that some factor other than those under study is exerting a strong, nonrandom influence on the results.

TABLE IV
ANOVA of Data from Table III

	Sums of squares	Degrees of freedom	Mean square	F	Significance
Supplier, S	661000.60	2	330500.30	42.6	1%
Color, C	101742.35	3	33914.12	4.37	5%
Weather, W	236204.70	3	78734.90	10.15	1%
Location, L	30637.60	1	30637.60	3.95	Not sig.
$S \times C$	339347.60	6	56557.93	7.29	1%
$S \times W$	15410.20	6	2568.37	3.02 inverse	Not sig.
$S \times L$	86363.20	2	43181.60	5.57	5%
$C \times W$	19268.47	9	2140.94	3.62 inverse	5%
$C \times L$	10242.41	3	3414.14	2.27 inverse	Not sig.
$W \times L$	127038.40	3	42346.13	5.46	1%
$S \times C \times W$	55844.48	18	3102.47	2.50 inverse	5%
$S \times W \times L$	22213.90	6	3702.32	2.10 inverse	Not sig.
$S \times C \times L$	65084.84	6	10847.47	1.40	Not sig.
$C \times W \times L$	34435.82	9	3826.20	2.03 inverse	Not sig.
$S \times C \times W \times L$	139652.83	18	7758.49		
Total	1944487.40	95			

TABLE V

Components of Variance in Expected Mean Square

	Sums of squares	Degrees of freedom	Mean square	Fixed model EMS
Supplier	661000.60	2	330500.30	$\sigma_0^2 + 32\sigma_s^2$
Color	101742.35	3	33914.12	$\sigma_0^2 + 24\sigma_c^2$
Weather	236204.70	3	78734.90	$\sigma_0^2 + 24\sigma_w^2$
Location	30637.60	1	30637.60	$\sigma_0^2 + 48\sigma_l^2$
S × C	339347.60	6	56557.93	$\sigma_0^2 + 8\sigma_{(sc)}^2$
$S \times W$	15410.20	6	2568.37	$\sigma_0^2 + 8\sigma_{(sw)}^2$
$S \times L$	86363.20	2	43181.60	$\sigma_0^2 + 16\sigma_{(sl)}^2$
$C \times W$	19268.47	9	2140.94	$\sigma_0^2 + 6\sigma_{(cw)}^2$
$C \times L$	10242.41	3	3414.14	$\sigma_0^2 + 12\sigma_{(cl)}^2$
$W \times L$	127038.40	3	42346.13	$\sigma_0^2 + 12\sigma_{(wl)}^2$
$S \times C \times W$	55844.48	18	3102.47	$\sigma_0^2 + 2\sigma_{(scw)}^2$
$S \times W \times L$	22213.90	6	3702.32	$\sigma_0^2 + 4\sigma_{(swl)}^2$
$S \times C \times L$	65084.84	6	10847.47	$\sigma_0^2 + 4\sigma_{(scl)}^2$
$C \times W \times L$	34435.82	9	3826.20	$\sigma_0^2 + 3\sigma_{(cwl)}^2$
$S \times C \times W \times L$	139652.83	18	7758.49	σ_0^2
Total	19444847.0	95		

At the 1% level, however, the following are the conclusions:

With a risk of 1% for *each statement*, we can say that the supplier and color interaction and the weather and location interaction contribute more to the total variation in fading of colors that can be attributed to sampling error. In other words, these supplier differences are not independent of color, and the exposure location differences are not independent of the season. There are almost certainly nonchance effects contributed by supplier–color and season–location combinations.

Still at the 1% significance level and breaking out the interactions, we obtain the following:

For the Supplier and Color Interaction. Supplier A has the Peach with the best performance and the Blue with the poorest. Blue is Supplier B's best color and Peach his poorest. Blue is Supplier D's next to poorest color and Peach his next to best color.

For the Season and Location Interaction. Spring, summer, and fall in Miami are not as severe as in Bound Brook; winter in Miami is more severe. Furthermore, the components of variance can be estimated as indicated in Table V.

From Table V, we estimate $\sigma_s^2 = 10{,}104$, $\sigma_w^2 = 2982$, $\sigma_{sc}^2 = 6173$, and $\sigma_{(wl)}^2 = 2931$. These plus σ_0^2 give a total variance estimate of 29,362 of which 34.4% is contributed by suppliers, 10.2% is contributed by the seasons, 21.0% by supplier–color combinations, 10.0% by season–location combinations, and 24.4% by pure random error plus as yet undiscovered but possible main and interaction effects. Thus, the variance per color fading determination may be partitioned as follows:

Suppliers		
Independent variance	10,104	(34.4%)
Interaction with colors	6,173	(21.0%)
Weather (seasons)		
Independent variance	2,982	(10.2%)
Interaction with location	2,931	(10.0%)
Residual variance	7,172	(24.4%)
Total	29,362	(100.0%)

Clearly, suppliers contribute about 55.4% of the total variance in this study and represent the factor deserving major attention if an improvement in fading resistance is needed. The seasons contribute about 20.2% of the total variance in a determination and represent a much less important factor. Experimental error contributes the balance of the total variance.

The full factorial design is the perfect example for ANOVA. In this example four input variables were studied. What made this a full factorial was that each variable was studied at each level in all twelve possible combinations with the other variables and levels.

This one example illustrates four things ANOVA does well. These are:

1. The ability to pinpoint main effects.
2. The uncanny technique of indicating when some variable not included in the study is influencing the results.
3. Locating and identifying interactions.
4. Partitioning the total variation in a study.

DESIGN OF EXPERIMENTS

Because of the close interrelationship between analysis of results and the manner in which the experiments were conducted, statistical design of experiments often benefits outdoor exposure studies. The example described above illustrated an experimental design of the full factorial type. In outdoor exposure studies, interest frequently resides solely in identifying and evaluating the main effects. Interactions which may readily be identified using a full factorial experiment are often of no interest. For example, in evaluating a series of new coatings, the question of most interest might be: "Which of the series is the most weather-resistant anywhere in the United States whether applied to aluminum, bonderized steel, or galvanized steel?" rather than, "Which combination of coating and metal backing is best in Florida, which in New York, and which in Arizona?".

When one is searching solely for main effects, partial factorial experimental designs are often both useful and efficient. A partial factorial design of particular value is the 2 × 2 Latin square.

With the 2 × 2 Latin square, three variables at two levels each may be studied with only four arrangements. As an illustration, suppose one wished to choose between two types of plastic prepared by either of two manufacturing processes at either of two manufacturing locations. The four arrangements of the 2 × 2 Latin square are shown in Table VI. A full factorial studying the same variables and levels would call for eight arrangements.

TABLE VI
A 2 × 2 Latin Square

(Arrangement 1) A_1 B_1 C_1	(Arrangement 2) A_1 B_2 C_2
(Arrangement 3) A_2 B_1 C_2	(Arrangement 4) A_2 B_2 C_1

(A_1) Plastic 1; (A_2) plastic 2; (B_1) manufacturing process 1; (B_2) manufacturing process 2; (C_1) manufacturing location 1; (C_2) manufacturing location 2.

Extending this idea further brings us to the so-called 3 × 3 Latin square design wherein four variables (A, B, C, and D) at three levels (1, 2, and 3) are studied using nine arrangements (Table VII).

TABLE VII

A 3 × 3 Latin Square

(Arrangement 1) $A_1B_1C_1D_3$	(Arrangement 2) $A_1B_2C_2D_2$	(Arrangement 3) $A_1B_3C_3D_1$
(Arrangement 4) $A_2B_1C_3D_2$	(Arrangement 5) $A_2B_2C_1D_1$	(Arrangement 6) $A_2B_3C_2D_3$
(Arrangement 7) $A_3B_1C_2D_1$	(Arrangement 8) $A_3B_2C_3D_3$	(Arrangement 9) $A_3B_3C_1D_2$

If it is desirable to study one of the variables at four levels, three additional arrangements such as

(Arrangement 10)	(Arrangement 11)	(Arrangement 12)
$A_1B_1C_1D_4$	$A_2B_3C_2D_4$	$A_3B_2C_3D_4$

may be included. For the analysis, the results from these latter three arrangements would replace those from arrangements 1, 6, and 8, respectively. Additional (or fewer) levels of this or the other three variables may be similarly accommodated.

Occasionally it is desirable to investigate more than four variables in an outdoor weathering program. Sometimes, superimposing one Latin square inside another is an efficient way of conducting such a study. Table VIII illustrates a method of studying seven variables at a time, four of them at three levels each and three of them at two levels each. In this manner, 36 arrangements suffice. A full factorial containing four variables (A, B, C, and D) at three levels each and three variables (E, F, and G) at two levels each would call for 648 arrangements.

TABLE VIII

A 3 × 3 Latin Square Inside a 2 × 2 Latin Square

	$A_1B_1C_1D_3$	$A_1B_2C_2D_2$	$A_1B_3C_3D_1$	$A_1B_1C_1D_2$	$A_2B_3C_1D_2$	$A_3B_2C_1D_3$	
$E_1F_1G_1$	$A_2B_1C_3D_2$	$A_2B_2C_1D_1$	$A_2B_3C_2D_3$	$A_1B_3C_2D_3$	$A_2B_2C_2D_1$	$A_3B_1C_2D_2$	$E_1F_2G_2$
	$A_3B_1C_2D_1$	$A_3B_2C_3D_3$	$A_3B_3C_1D_2$	$A_1B_2C_3D_2$	$A_2B_1C_3D_3$	$A_3B_3C_3D_1$	
	$A_1B_1C_2D_2$	$A_3B_1C_3D_3$	$A_2B_1C_1D_1$	$A_3B_1C_1D_2$	$A_2B_2C_2D_2$	$A_1B_3C_3D_2$	
$E_2F_1G_2$	$A_2B_3C_3D_2$	$A_1B_3C_1D_3$	$A_3B_3C_2D_1$	$A_2B_3C_1D_1$	$A_1B_1C_2D_1$	$A_3B_2C_3D_1$	$E_2F_2G_1$
	$A_3B_2C_1D_2$	$A_2B_2C_2D_3$	$A_1B_2C_3D_1$	$A_1B_2C_1D_3$	$A_3B_3C_2D_3$	$A_2B_1C_3D_3$	

Another efficient experimental design of the partial factorial type is described by Li.[4] In Li's design, seven variables at two levels each are investigated for main effects with only eight arrangements. Then a second series of about five experiments is designed to arrive at an optimum combination of the seven variables.

Replicates

How many replicates should be used in exposure trials? Statistical methods are capable of answering this question, up to a point. There cannot be a universal answer covering all trials. It depends on the type of design of experiment. In order to decide in advance how many replicates should be employed, it was necessary to have an estimate of the uncontrolled experimental variation.

If you are beginning some investigations where nothing is known of this so-called "experimental error," you should provide at least two and preferably three replicates. A replicate, to be truly a replicate, should be derived far enough back in the manufacturing process to contain all of the uncontrolled sources of variation likely to influence the final results. In other words, it would be better to obtain three test samples of a cast phenol–formaldehyde plastic, each one made from a different lot of phenol and lot of formaldehyde, than it would be to cut the three test samples all from a single casting from a single lot of a phenol–formaldehyde syrup.

A reliable assessment of durability cannot be obtained from only one exposure site or 1 yr. exposure. There is enough variation in weather from one year to the next even at one exposure site to require an average of at least 3 yr. Usually, it is preferable to make fresh samples for duplicate sets when they are to be exposed at different times.

There is also argument for preparing and exposing replicate sets from time to time to give results of wider applicability, for weather prevalent immediately upon exposure often influences the entire life.

Correlation–Regression Strategy

Several of the questions posed at the start of this paper were correlation type questions, such as: "Do results from one test condition (or test specimen) agree with the results obtained from another test condition (or test specimen)?" When we characterized a good Test Device, characteristic 6 was a correlation type for it stated that the test results produced must be related to actual service. Statistical methods not only allow the determination of a correlation coefficient but often also the calculation of equations representing the relationship between the two or more variables found to be related. These equations are then used to estimate the results that would be obtained beyond the conditions (in time or stress) of the test.

Analysis of variance and regression analysis are interrelated in a statistical sense. An analysis of variance is conducted to determine the "fit" of experimental data to a certain type of regression (e.g., linear, quadratic, cubic, etc.). Also, regression analysis may be superimposed on the data used for analysis of variance. In this instance, an algebraic equation is developed describing the matrix of events and results as a multidimensional surface similar to a contour map. A great many problems in exposure studies call for the use of correlation and regression analysis. An outstanding example is in the correlation of natural and laboratory (accelerated) weathering.

In his paper, "Some Applications of Statistical Methods to Exposure Trials," Touchin[5] reviewed the results of an A.S.T.M. Committee study concerned with the chalking of paint films. In this study, eight different paints were exposed on six accelerated weathering machines and also exposed naturally in Florida. The Committee concluded that Machine P gave increased chalking over Florida, Machine BW gave less chalking than Florida, and Machine J gave the nearest results to Florida, a fact supported by six out of the eight painted panels. The committee voted to terminate its effort to develop an accelerated weathering machine because of the large variation in results. Unfortunately, statistical analysis was not used in arriving at the conclusions and recommendation. After applying appropriate statistical techniques, Touchin found that there was a significant correlation between the machines and Florida exposure and that the machines did not differ among themselves.

This brings us face-to-face with one of the most perplexing problems concerned with outdoor weathering, that weather does not duplicate itself. The weather is never the same on two different days, over two different weeks, months, years, decades, or centuries. How can one ever expect a laboratory method to duplicate the weather when the weather never duplicates itself? All one can really do is work with averages and on the average, from Touchin's analysis, the machines were able to duplicate Florida weather better than Florida weather could duplicate itself.

Another study, of a nature similar to the one above, appeared in a recent issue of the *Official Digest.*[6] Once again, statistical analysis was not used. Painted panels were exposed at Miami, Florida and Columbus, Ohio, and also in two twin carbon arc, a sunshine arc, and a xenon arc Weather-Ometer (Atlas Electric Devices Co.). Conclusions drawn in the original paper in regard to rate of chalking were:

1. Twin arcs caused chalking at a greater rate than xenon and sunshine units.
2. Inconsistencies between the performance of different paints in the four machines and outdoors indicates that considerable judgment is necessary in setting up accelerated weather studies.
3. Weather-Ometers are valuable research tools.

I have taken the 900-hr. data from the four Weather-Ometers and statistically analyzed them to learn if differences in effect exist between the machines. The method of analysis was to rank the results (from 1 = best to 4 = poorest) for each paint and to use a nonparametric statistical procedure.[7] Table IX presents the 900-hr. results. Based on this analysis, it is inferred that there is not sufficient evidence (at the 10% or lower probability level) to say that any of the four machines differ at either the 900-hr. or 1500-hr. exposure time. Such being the case, the results for all four exposure machines can be combined. Next, the chalking data for the two outdoor exposure locations were analyzed for both the 12-mo. and 26-mo. periods. The Wilcoxon Signed Rank Test[7] indicated that there was insufficient evidence to conclude that outdoor exposure at Miami and at Columbus differ as to chalking effects. We may, therefore, combine these results and attempt to determine if there is a time relationship between

TABLE IX
900-hr. Data for Analysis of Four-Weather-Ometers

	Twin carbon arcs			
	A	B	Xenon	Sunshine
		a. 900-hr. Raw Data		
Panel 1	3	2	3	4
Panel 2	9+	9	9	9
Panel 3	6	6	6	6
Panel 4	8	9	8+	9
Panel 5	1	1	1	1
Panel 6	9+	9+	9+	9+
Panel 7	10−	10−	15−	10−
Panel 8	7+	7	7	7
		b. Ranking 900-hr. of Results		
Panel 1	$2^1/_2$	1	$2^1/_2$	4
Panel 2	4	2	2	3
Panel 3	$2^1/_2$	$2^1/_2$	$2^1/_2$	$2^1/_2$
Panel 4	1	$3^1/_2$	2	$3^1/_2$
Panel 5	$2^1/_2$	$2^1/_2$	$2^1/_2$	$2^1/_2$
Panel 6	$2^1/_2$	$2^1/_2$	$2^1/_2$	$2^1/_2$
Panel 7	$2^1/_2$	$2^1/_2$	$2^1/_2$	$2^1/_2$
Panel 8	4	2	2	2
Total	$21^1/_2$	$18^1/_2$	$18^1/_2$	$22^1/_2$

the machines and outdoor exposure. The least squares best straight line fit of each of the four possible sets of relationships between accelerated and natural results was developed. These lines were next statistically analyzed for "goodness of fit" to the data. "Good fits" were obtained relating (*a*) 900 hr. on the machines to 1 yr. outdoor exposure, and also (*b*) 1500 hr. on the machines to 1 yr. outdoor exposure. The fits were not "good" between the machines at either 900 hr. or 1500 hr. and 26 mo. outdoor exposure. These findings indicate that in 900 hr. exposure on the machines a good estimate of the amount of chalking likely to result from 1 yr. outdoor exposure has been obtained. The equation is:

$$y = 0.9985X + 0.6976$$

where y = estimated 1 yr. outdoor results; X = results obtained in 900 hr. exposure on the machines. To illustrate the "goodness of fit," the calculated and observed data are shown in Table X. Coating 1 has the largest deviation of the eight coatings. The differences between the observed and calculated results for the remaining seven are quite close and probably within the normal variation of replicate panels.

Reducing the Duration of a Test

Three techniques are available for reducing the time required (in an outdoor exposure program) to determine the life span of a new item. No one

TABLE X
Comparison of Observed with Calculated Results from the 900-hr. Data
(Outdoor Exposure for 12 months)

Coating No.	Calculated, Y	Observed, X		
		Miami	Columbus	Average
1	4	0	0	0
2	10	10	10	10
3	7	7+	8	$7^1/_2{}^+$
4	9	10	10	10
5	2	4	3	$3^1/_2$
6	10	9^+	8	$8^1/_2{}^+$
7	10	10^-	10^-	10^-
8	8	10	110	10

of these three is simple or easy to use but, in spite of their complexity, they often provide a high return on investment, particularly where time is money. These three techniques are concerned with (*a*) tests of increased severity, (*b*) probability distribution, and (*c*) key property correlation. All three require correlation or regression analysis for transposing the accelerated results to normal exposure.

Tests of Increased Severity

Testing time can be reduced by (*a*) using higher stress levels during outdoor exposure than will normally be encountered, (*b*) subjecting the test specimens to a more severe (artificial) environment, or (*c*) using a more sensitive measure than ultimate collapse or failure. We have already touched briefly on the problems of developing a more severe environment and will return to them again when we discuss key property correlation. Those who are familiar with fatigue testing will recognize a certain similarity between weathering of paints or plastics and fatigue. In vibration fatigue or long-time creep–load studies we know that at very low loads or amplitudes of vibration, time-to-failure is often quite long. As the stress increases, the time to failure becomes shorter. Finally, if the stress or the amplitude is great enough, the part fails immediately upon application of the load. A typical fatigue curve is an S-shaped curve when plotted on ordinary rectangular coordinate paper. When plotted on log–log paper, the curve becomes two straight lines, one straight line having a negative slope while the other, which intersects it, is horizontal. The point of intersection is often designated as the endurance limit and indicates the load or amplitude that could be sustained indefinitely (or at least for 10,000,000 cycles) at the rate of stress reversal used in the test device. Frequently, the endurance limit is about 10% of the static load to failure.

Probability Distribution

The distributional nature of failures is a subject that has been more often omitted than included when discussing outdoor weathering. The usual concept of a uniform failure like "The Wonderful One Horse Shay" is not a true picture. The fact is that failure distributions, whether vibration fatigue, outdoor durability, or human mortality, are typified by very wide scatter whenever a large enough set of samples is tested similarly. If one can learn the shape of the failure distribution function, then, from the first failure of a set of samples, it is possible to estimate the average, the median, the maximum life, etc., of all samples in the set. Often the shape of the failure distribution function can be obtained from accelerated laboratory studies. Occasionally, the distributions are normal, log-normal, or exponential and when such is the case, graphical methods are available for handling the material. In 1951, a paper was presented at a meeting of the American Society of Mechanical Engineers[8] which showed that failures of the "weakest link in a chain" type fitted quite well a specific empirical distribution. Examples included yield strength of steel, size distribution of fly ash, fiber strength of cotton, stature of adult males born in the British Isles, length of Cyrtoideae, and breadth of beans of Phaseolus Vulgares.

Recently engineers at General Motors[9,10] have demonstrated the appropriateness of this procedure for planning and interpreting life tests and, with the aid of the Weibull Distribution, have developed two methods of slashing test times. Method A consists of testing simultaneously more specimens than eventually fail. It is based on the finding that it takes much less time to fail 10 items out of 20 than it does to fail 10 out of 10. In one example, the median time required to fail 10 out of 20 was only about 24% of the time required to fail 10 out of 10 specimens.

Method B has been designated "Sudden Death" testing. "Sudden Death" testing is a technique of reducing testing time in cases where the lower quartile of a life distribution is considerably inferior to the upper quartile. It consists of grouping test specimens into sets of two or more and then looking upon each set as an assembly of specimens in series. All the specimens in a set are run simultaneously until the first specimen in each set fails. The entire set is considered a failure at this point. The use of "sudden death" techniques has reportedly shortened test times to $^1/_4$ or $^1/_3$ of what would be required in tests where all specimens are run to failure.

Key Property Correlation

The method of key property correlation ideally requires the development of an accelerated test which, for the materials under study, is known to correlate well with natural aging. The accelerated test involves exposing the sample to a concentration of some of the elements of weather and requires a carefully selected measuring device. This device must measure a property that is of major interest and which is one of the first to deteriorate during outdoor exposure. A good example of an early application of key property correlation to the development of an improved plastic is described in ref. 11.

Keeping in mind much of what has been presented earlier, particularly in regard to selection of the test specimen, exposure location, method of exposure, and number of replicates, the ideal stages in the method of key property correlation are outlined. Rarely are these steps strictly followed. Often an accelerated test is used that has not been proved to produce chemically similar changes.

1. Start exposure of specimens (different but of same family) to the weather as early as possible, at two or more locations.
2. Determine the physical, optical, and/or electrical property changes that occur on outdoor exposure.
3. Select a test method that:
   - *a.* Is related to the properties changed most rapidly by outdoor exposure.
   - *b.* Is of major interest (related to actual service).
   - *c.* Is as sensitive or, preferably, more sensitive to change than the physical, optical, or electrical properties changed most rapidly by outdoor exposure.
4. Determine the chemical nature of the changes that occur in the new material on outdoor exposure.
5. Devise an accelerated test that:
   - *a.* Consists of one or more components of the weather (light, heat, moisture, etc.).
   - *b.* Causes the same or nearly the same chemical changes in the compound as does natural, outdoor weather, but at a faster rate.
   - *c.* Does not cause chemical changes that do not occur upon natural outdoor exposure.
   - *d.* Causes the same basic physical, optical, and/or electrical property changes as does natural outdoor weather, but at a faster rate.
6. *a.* Correlate the results from the accelerated test with those from the outdoor exposures.
   - *b.* If acceleration is too slow or too fast, adjust the ratio or amount of components to provide the desired acceleration, e.g., 200 hr. on the accelerated device equivalent to 2 yr. outdoors 400 hr. 4 yr. outdoors, etc.
7. Prepare modifications of the original materials to improve their resistance to the deterioration caused by exposure in the accelerated test.
8. Determine the effectiveness of the modifications and also monitor the chemical changes resulting from the accelerated exposure.
9. Continue modifying the original compositions until acceptable resistance to the accelerated test is practicably achieved or no further progress is obtained.

CONCLUSION

In conclusion, it is believed that statistical methods are a relatively untapped source of valuable assistance to any program concerned with the long-term weatherability of plastic materials. Knowledge and proper use of these methods should assist in reducing the time and increasing the reliability of decisions when developing more outdoor-durable plastic materials.

The author is grateful for the assistance of Robert P. Fellmann in the preparation of this manuscript and Lester R. DeFonso for many of the computations.

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Résumé

Le développement de matériaux nouveaux résistants aux conditions atmosphériques et possédant des propriétés physiques, optiques et électriques désirables ets un processus long et complexe et un objectif difficile à réaliser. La durée est longue parce que (*1*) la multitude de fabrications et de variables de compositions nécessite une étude pour déterminer leur effet du point de vue de leur performance et (*2*) il n'existe aucun test accéléré facilement valable pour prédire exactement comment un nouveau matériaux se comportera du point de vue de son intégrité a l'exposition aux agents atmosphériques. Des méthodes statistiques sont décrites et discutées qui peuvent être utiles pour obtenir l'objectif vise ei-dessus. Certaines de ces méthodes peuvent être valables pour planifier et conduite des expériences de vieillissement à l'extérieur particulièrement, (*a*) en réduisant et mesurant des variations incontrolables et expérimentales, (*b*) en choisisant des méthodes d'essai et (*c*) en attachant une certaine certitude aux résultats. Des exemples sont donnés qui illustrent l'application de *l'analyse de la variance* et *la strategie correlation–regression*. Le premier peut être utile pour la planification de l'analyse des résultats des programmes d'exposition à l'extérieur tandis que le second est de valeur pour relier les performances des essais accélérés aux essais à l'extérieur en prédisant la durée de service normalement attendu dans des conditions usuelles.

Zusammenfassung

Die Entwicklung neuer, im Freien wetterbeständiger Stoffe mit erwünschten physikalischen, optischen oder elektrischen Eigenschaften ist eine lange und komplexe Prozedur und ein schwer zu erreichendes Ziel. Die Entwicklungsdauer dehnt sich, weil (*1*) eine Vielfalt von Fabrikations- und Zusammensetzungsvariabeln untersucht werden muss, um ihren Einfluss auf die Gebrauchsfähigkeit zu bestimmen und (*2*) kein beschleunigter Test zur Voraussage, wie gut ein neuer Stoff während eines Gebrauchs in Frien seine Integrität bewahren wird, leicht zugänglich ist. Statistische Methoden, die zur Erreichung des angeführten Zieles brauchbar sein könnten, werden beschrieben. Einige dieser

Methoden könnten bei der Planung und Durchführung von Bewitterungsversuchen im Freien wertvoll sein, besonders (*a*) zur Herabsetzung und Messung der nicht kontrollierbaren Versuchsschwankungen, (*b*) zur Auswahl von Testmethoden und (*c*) zur Angabe der Sicherheitsgrenzen der Ergebnisse. Beispiele für die Anwendung der *Varianalyse* und der *Korrelations-Regressionsstrategie* werden angeführt. Erstere kann eine Hilfe bei der Planung und der Analyse der Ergenisse des Programmes der Exponierung im Frien bieten, während letztere für die Korrelation des Verhaltens bei beschleunigten Tests mit demjenigen im Freien, sowie zur Voraussage der unter normalen Gebrauchsbedingungen zu erwartenden Lebensdauer von Wert ist.

APPLIED POLYMER SYMPOSIA NO. 4, 263–287 (1967)

Information Retrieval (IR) for an Outdoor Exposure Evaluation Facility

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Synopsis

The outdoor exposure evaluation facilities of the Armstrong Cork Co., in Lancaster, Pa., consist of an outdoor exposure field, evaluation laboratory, on-the-site weather station, and the necessary instrumentation. Use is also made of commercial laboratory test sites in Arizona, Florida, and Minnesota. The need for accurate record keeping, evaluation of the data obtained, and rapid recall led to the development of a unique IR system for this facility. This system uses coordinate concept indexing based on optical coincidence techniques and includes specimen information such as composition, plastic type, specific resin, ingredient trade names, chemical nomenclature, use, visual and physical properties after various exposure times, geographical location, direction and angle of exposure, direct and under glass information, substrate material (when used), and specimen processing information. Rapid recall can be carried out by entering the system by any of the above addresses or combinations of them. For example, requests such as, "Do we have a paint system which has been exposed to direct sunlight in Lancaster, Pa., facing south at a 45° angle, with the following characteristics: primer MX-121 sprayed at a rate of 5 g./sq. ft. on experimental exterior siding SHB-197; top coat X sprayed at a rate of 12 g./sq. ft; a chalking value of 9 or better after 6 mo. and 8 or better after 12 and 18 mo.; a color change of 10 after 6 mo., 9 or better after 12 mo., and 8 or better after 18 mo.; are any of these still under test," can be answered in a few minutes and is demonstrated. The answer will contain data on the exact composition, notebook references, originator of the test, and all visual and physical properties obtained for each inspection period. Since data are reported cumulatively, old reports can be discarded to keep filing volume to a minimum.

Introduction

According to Klempner,[1] "Unorganized and irretrievable data do not contribute anything to the advancement of scientific and technological disciplines; on the contrary, they sap the already-limited physical and manpower resources of the documentation center or library. . . If the results of scientific research . . . are to be of any value, they must be utilized." It follows, then, that information retrieval (IR) is a vital complement of all outdoor exposure test facilities, if the results of the evaluations are to be of any value. IR systems are not shelf items to be purchased as desired; they must be designed to do a particular job. You will find that in most cases, the results of a search appear as documents containing the information or data requested.

The system I am going to discuss was designed to retrieve specimen numbers of materials subjected to outdoor exposure and having specific visual and physical property changes with time and location. It was also designed to retrieve specific documents and data by including in the original request information about both specimen composition and data. And finally, it was designed to do this job rapidly.

Facilities

Because of the Armstrong Cork Company's highly diversified interest in plastics, it is necessary for us to give considerable emphasis to the evaluation of their exposure to outdoor environmental conditions. We have established at our Research and Development Center in Lancaster, Pa., an outdoor exposure field, an evaluation laboratory, an on-the-site weather station, and the necessary instrumentation. Use is also made of commercial laboratory test sites in Phoenix, Arizona; Miami, Florida; and St. Paul, Minnesota.

Our outdoor exposure evaluation facility has grown since 1952 from a collection of panels and specimens placed on window sills and roofs by individuals to a carefully coordinated, controlled operation of our Physical Standards Department (PSD).

The outdoor exposure field (Fig. 1), which occupies about an acre, surfaced with rolled crushed stones, is located so that there are no obstructions to the south and no multistory buildings within 50 ft. in other directions. One section is reserved for large horizontal areas and simulated roof assemblies. Another section (Fig. 2) contains twenty-four 27-ft.-long racks (capacity about 4000 specimens) with 90° test fences for north and south

Fig. 1. General view of the Armstrong Cork Company exposure field in Lancaster, Pa.

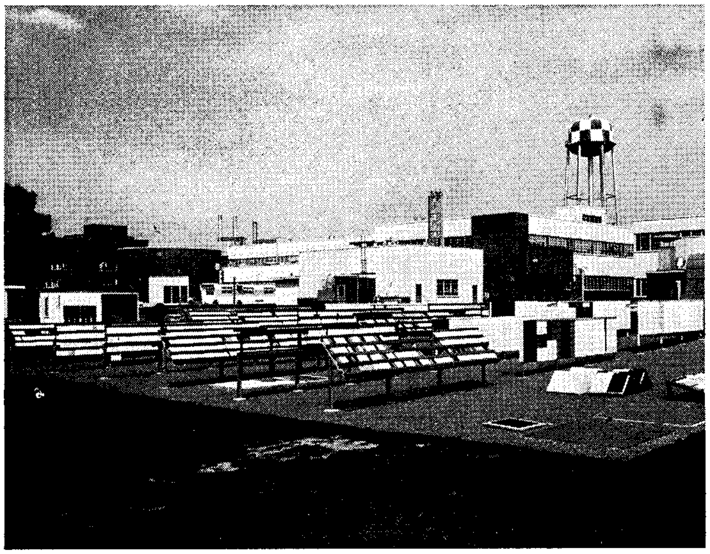


Fig. 2. Various exposure racks for rigid specimens.

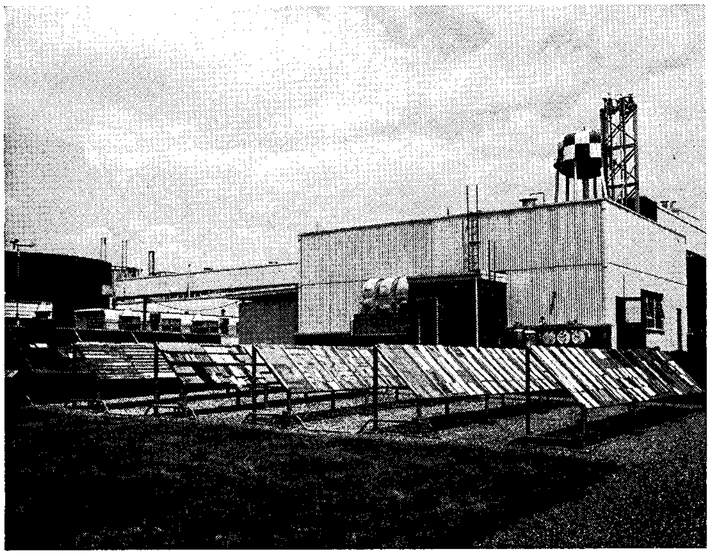


Fig. 3. Steel exposure racks for plastic sheets, both rigid and flexible.

exposure, 90° redwood open-back racks, and 45° and 90° redwood convertible open-back racks facing south for 6 × 12 in. rigid specimens. We mention the redwood construction since it has been claimed that after a year, a coating forms on the wood that prevents a run off stain. This has not been our experience; consequently, we found it necessary to paint them and recommend this practice. In addition, there are 45° steel racks (Fig. 3) facing south for 12 × 12 in. plastic sheets, both rigid and flexible.

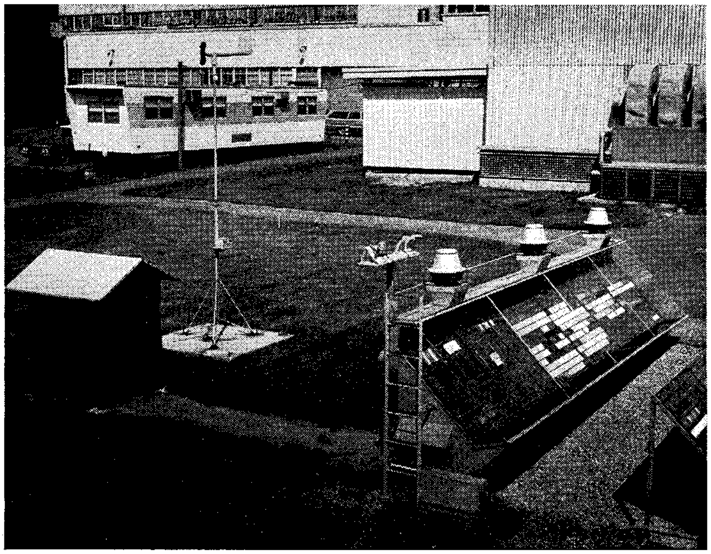


Fig. 4. Under glass exposure rack to simulate conditions found in showrooms, and weather station.

Two are plywood-backed and three have expanded aluminum backs to allow air circulation around the specimens. There is also (Fig. 4) a unique 45° glass-enclosed rack facing south to simulate conditions found in showrooms. This is supplied with filtered air to prevent overheating and contamination. Measurements indicate an air temperature rise of less than 10°F. above ambient and a black body temperature of less than 145°F.

At the weather station (Fig. 4), daily weather conditions are sensed at specimen level. For solar radiation measurements, two standard Eppley 180° ten-junction pyrheliometers, similar to those employed by the U. S. Weather Bureau, are used. The thermopiles are hermetically sealed in a soda-lime glass bulb. Radiation intensity is recorded and three integrators indicate the total radiation count in langleys (g.-cal./cm.^{2}) for both direct and underglass exposures. Temperatures and relative humidity are sensed by a protected thermocouple and Foxboro dew cell. Other thermocouples are located throughout the area for determining the temperatures of specimens under different exposure conditions. An Aminco dew duration recorder is used to obtain data on time of specimen surface wetness. Wind direction and velocity are measured by a Bendix aerovane transmitter, and a Bendix microbarograph records the barometric pressure. The data are recorded (Fig. 5) in the evaluation laboratory adjoining the test area.

For evaluation of visual properties, specimens are examined under a north sky daylight Macbeth light.[2] The ratings are made in accordance with procedures of the American Society for Testing and Materials[3] (ASTM) and the Federation of Societies for Paint and Technology.[4] For the evaluation of physical properties ASTM procedures[5] are used where applicable.

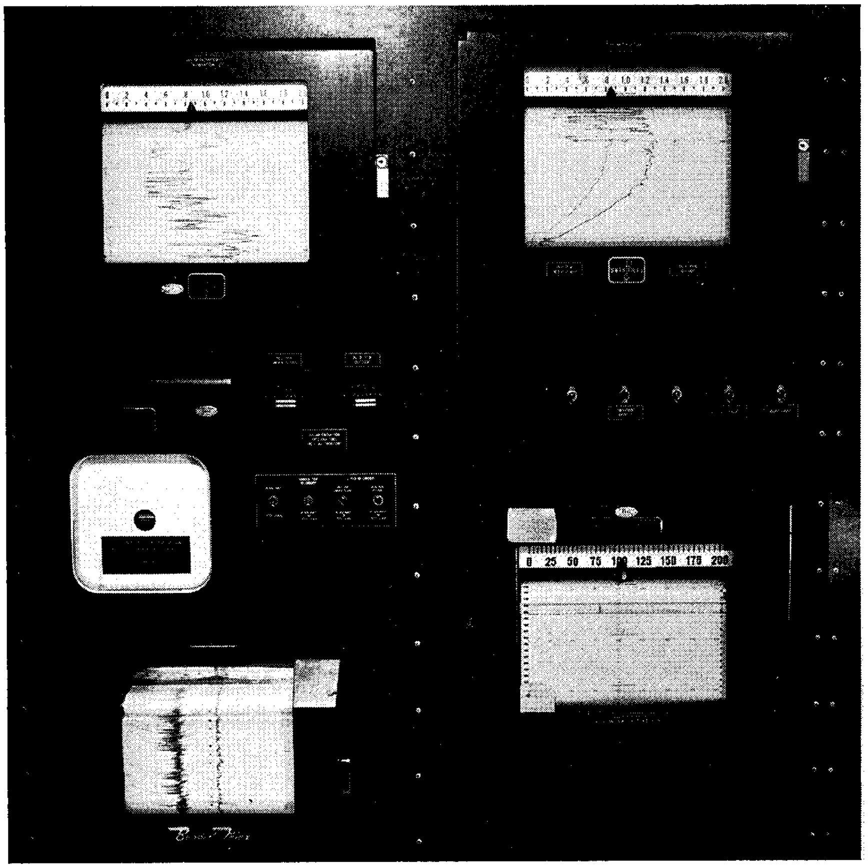


Fig. 5. Recorder panel for data obtained from the weather station and other areas of the exposure field.

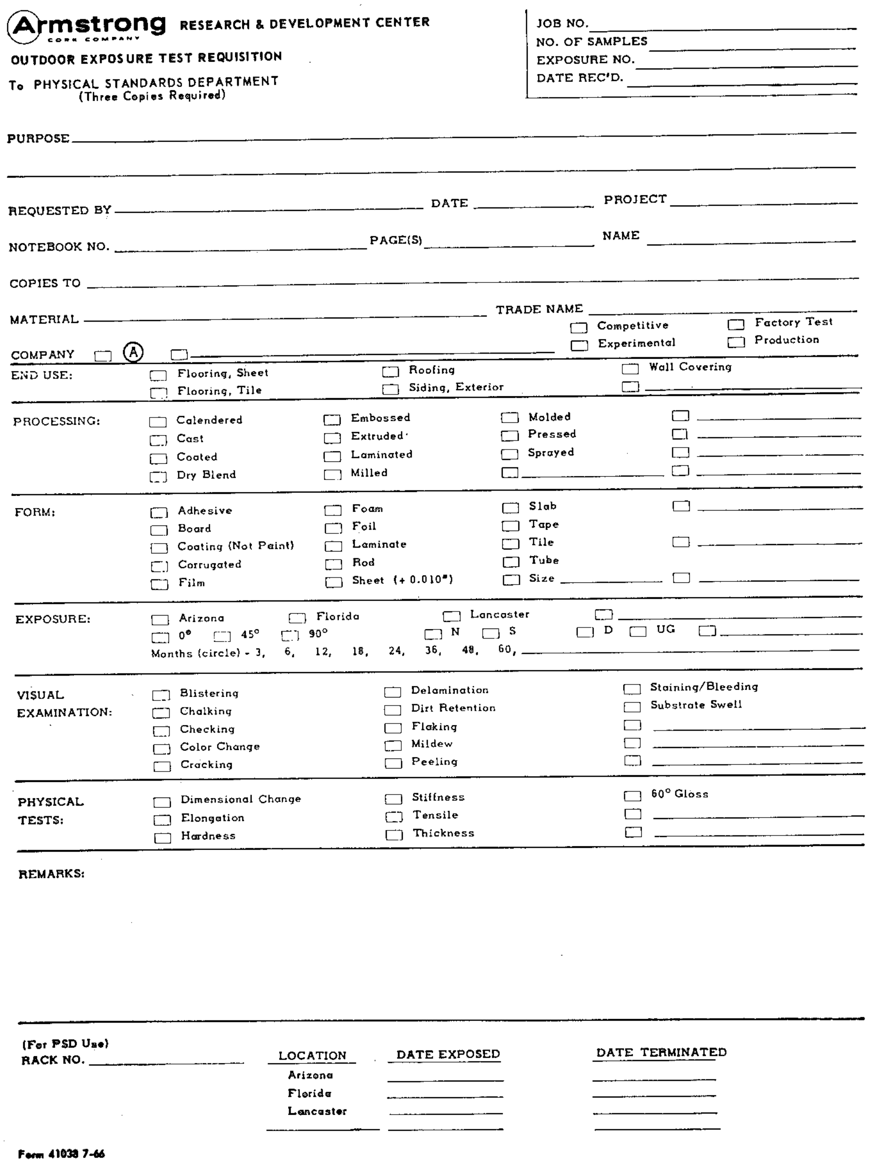
The System

Before designing an IR system, the types of questions the prospective clients will want answered must be known. In our case, it was necessary to design a system capable of retrieving data on any one or a combination of the following: end use; processing method; form of the material; specific resin (trade name); generic resin; and specimen composition. The system also had to retrieve data on changes in visual and physical properties with time after exposure at different geographical locations, different directions, various angles, and direct or under glass. In addition, for paint coatings, up to three-coat systems applied to various substrates should be capable of identification and retrieval.

Some typical questions might be:

(*1*) Do we have any experimental vinyl sheet flooring under test?

(*2*) Do we have any experimental vinyl sheet flooring exposed in Florida, at an angle of 45° to the south under glass?



Armstrong CORK COMPANY **RESEARCH & DEVELOPMENT CENTER**

OUTDOOR EXPOSURE TEST REQUISITION

To PHYSICAL STANDARDS DEPARTMENT
(Three Copies Required)

JOB NO. ____
NO. OF SAMPLES ____
EXPOSURE NO. ____
DATE REC'D. ____

PURPOSE ____

REQUESTED BY ____ DATE ____ PROJECT ____

NOTEBOOK NO. ____ PAGE(S) ____ NAME ____

COPIES TO ____

MATERIAL ____ TRADE NAME ____

☐ Competitive ☐ Experimental ☐ Factory Test ☐ Production

COMPANY ☐ Ⓐ ☐ ____

END USE:
☐ Flooring, Sheet
☐ Flooring, Tile
☐ Roofing
☐ Siding, Exterior
☐ Wall Covering
☐ ____

PROCESSING:
☐ Calendered
☐ Cast
☐ Coated
☐ Dry Blend
☐ Embossed
☐ Extruded
☐ Laminated
☐ Milled
☐ Molded
☐ Pressed
☐ Sprayed
☐ ____
☐ ____
☐ ____
☐ ____
☐ ____

FORM:
☐ Adhesive
☐ Board
☐ Coating (Not Paint)
☐ Corrugated
☐ Film
☐ Foam
☐ Foil
☐ Laminate
☐ Rod
☐ Sheet (+ 0.010")
☐ Slab
☐ Tape
☐ Tile
☐ Tube
☐ Size ____
☐ ____
☐ ____
☐ ____

EXPOSURE:
☐ Arizona ☐ Florida ☐ Lancaster ☐ ____
☐ 0° ☐ 45° ☐ 90° ☐ N ☐ S ☐ D ☐ UG ☐ ____
Months (circle) - 3, 6, 12, 18, 24, 36, 48, 60, ____

VISUAL EXAMINATION:
☐ Blistering
☐ Chalking
☐ Checking
☐ Color Change
☐ Cracking
☐ Delamination
☐ Dirt Retention
☐ Flaking
☐ Mildew
☐ Peeling
☐ Staining/Bleeding
☐ Substrate Swell
☐ ____
☐ ____
☐ ____

PHYSICAL TESTS:
☐ Dimensional Change
☐ Elongation
☐ Hardness
☐ Stiffness
☐ Tensile
☐ Thickness
☐ 60° Gloss
☐ ____
☐ ____

REMARKS:

(For PSD Use)
RACK NO. ____

LOCATION	DATE EXPOSED	DATE TERMINATED
Arizona		
Florida		
Lancaster		

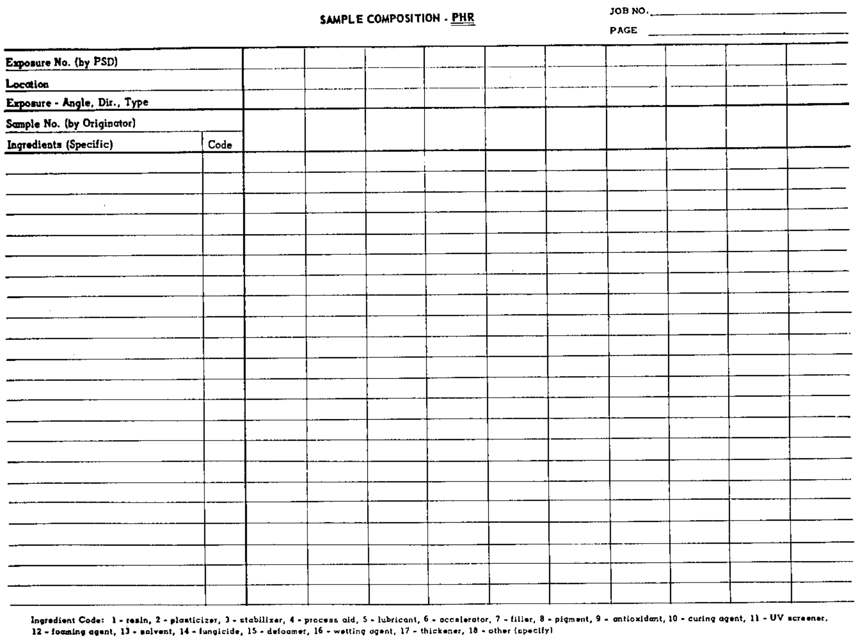
Form 41038 7-66

Fig. 6. Page 1 of the Test Requisition for Outdoor Exposure Evaluations.

(*3*) Do we have any experimental vinyl sheet flooring exposed in Florida, at an angle of 45° to the south under glass, with dioctyl phthalate (DOP) plasticizer?

(*4*) Do we have any experimental vinyl sheet flooring exposed in Florida, at an angle of 45° to the south under glass, with 10 parts per hundred of resin (phr) DOP plasticizer?

You will note that with each question we are becoming more and more specific. The specificity of the questions can become such that possibly



SAMPLE COMPOSITION - PHR

JOB NO.

PAGE

Exposure No. (by PSD)

Location

Exposure - Angle, Dir., Type

Sample No. (by Originator)

Ingredients (Specific) | Code

Ingredient Code: 1 - resin, 2 - plasticizer, 3 - stabilizer, 4 - process aid, 5 - lubricant, 6 - accelerator, 7 - filler, 8 - pigment, 9 - antioxidant, 10 - curing agent, 11 - UV screener, 12 - foaming agent, 13 - solvent, 14 - fungicide, 15 - defoamer, 16 - wetting agent, 17 - thickener, 18 - other (specify)

Fig. 7. Page 2 of the Test Requisition for Outdoor Exposure Evaluations.

only a few specimens may have the desired characteristics. For example, we might have the request: Do we have any experimental calendered sheet vinyl flooring containing Escambia 2160, 10 phr of DOP, 5 phr of Paraplex G-62, and 0.4 phr of Tinuvin P; exposed in Lancaster, under glass, at a 45° angle facing south?

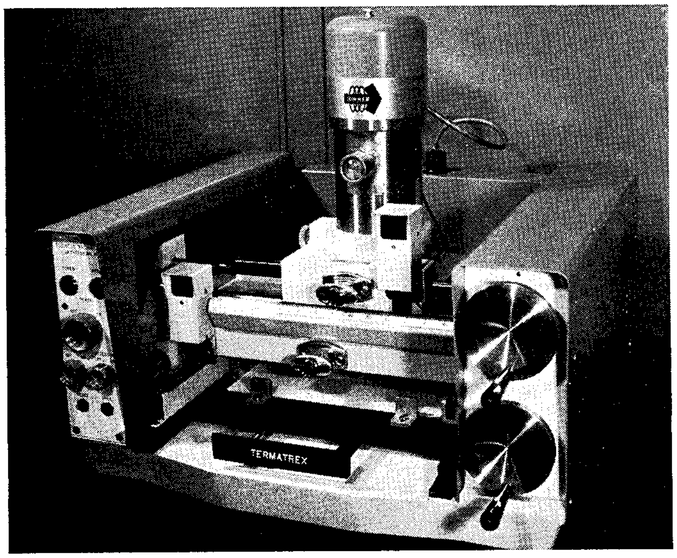


Fig. 8. Termatrex input data machine.

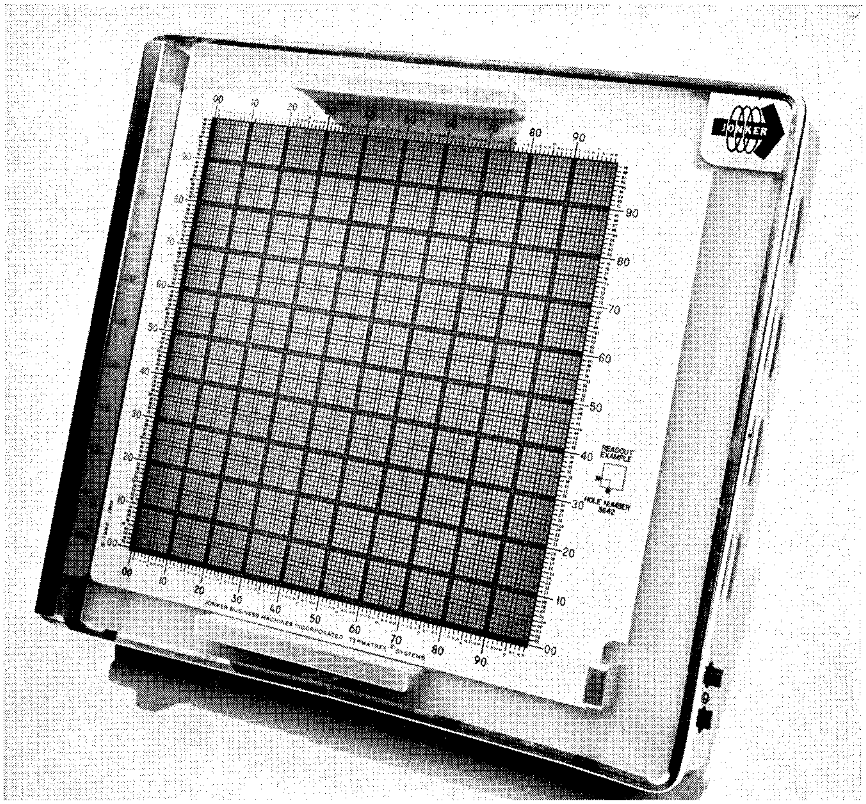


Fig. 9. Termatrex reader with the transparent coordinate matrix in place.

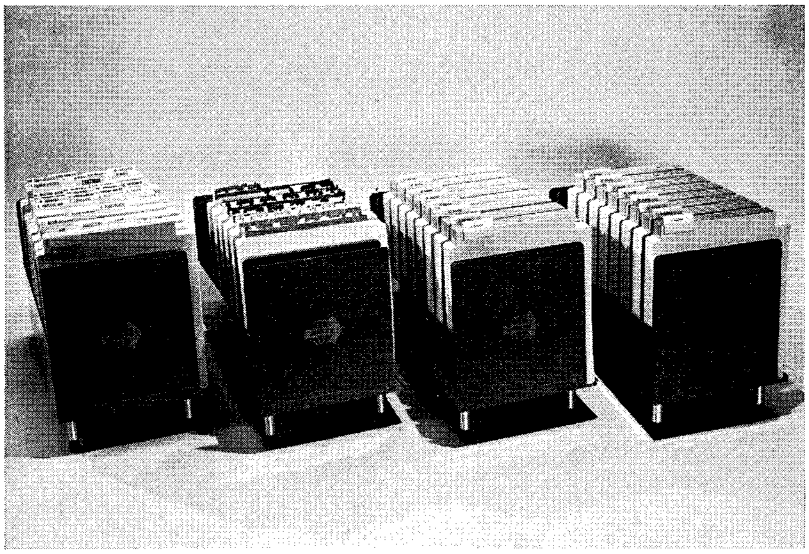


Fig. 10. The four decks of term cards containing the data.

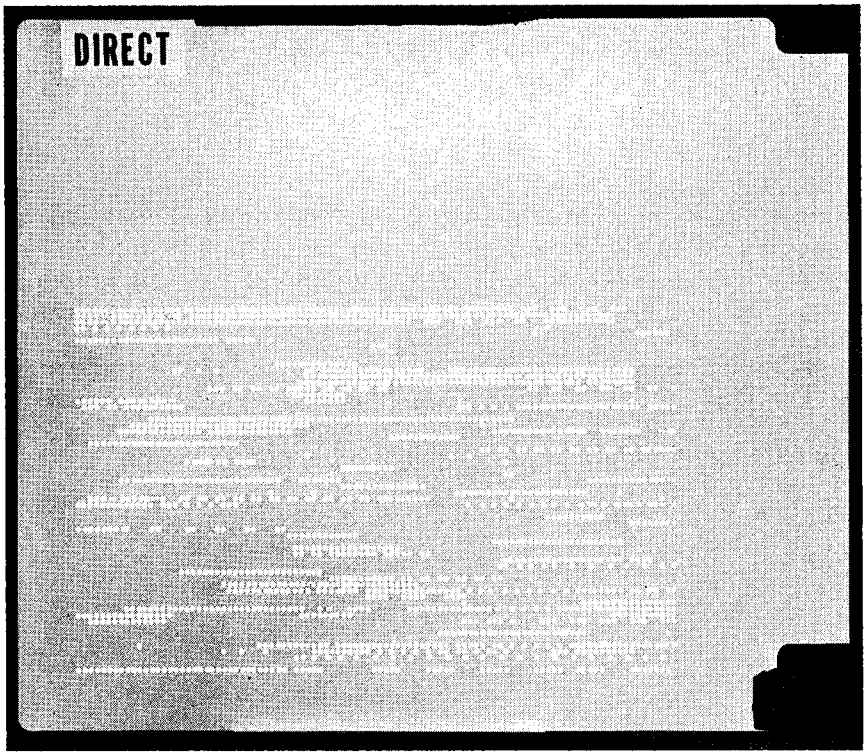


Fig. 11. Termatrex reader with the term card "Direct" in place. Indicates approximately 1700 specimens.

In order to be able to answer questions like these, very specific data must be obtained and recorded. A test requisition was designed to obtain all of the pertinent input information concerning the specimens. The first page (Fig. 6) lists information about use, processing, specimen description (physical), exposure desired, visual examinations and physical tests desired, date exposed, and date terminated.

The other side (Fig. 7) is designed so that the originator can list the ingredients in each composition by parts per hundred of resin. A code was devised so that the data input operator would know the function of each of the ingredients. The ingredient code consisting of 18 classifications is printed at the bottom of the page. Note that the exposure number is posted across the top of the page. This number is the accession number or specimen number used for retrieval purposes.

Initially, electronic data processing equipment (EDP) was considered for this job; however, preliminary investigations indicated that a very large memory storage would be required. Such equipment was not available at our Research Center so it was necessary to look elsewhere. Since we had several Termatrex[6] systems in operation, it was decided to see whether a system based on this technique could be developed. This system utilizes coordinate concept indexing and plastic optical coincidence term cards. Coordinate concept indexing is a system whereby the interrelations of terms are shown by coupling individual words or concepts. It has the advantages of speed and browsability, both of which are important for this type of retrieval. We also found that input time was less than that of EDP equipment for this particular job.

Each term card represents a single characteristic of interest and will accommodate 10,000 specimen numbers according to a 100 × 100 coordinate matrix. Small holes drilled into a given card represent the numbers of the specimens in the system having the characteristic represented by that card. Data input is accomplished by selecting all of the term cards having the characteristics of a specimen and drilling a hole through all of the term cards simultaneously at the location reserved for that particular specimen number. Output is carried out by selecting the term cards having the desired characteristics and superimposing them over a light source. The points at which light shines through represent those specimen numbers having all of the desired characteristics. By superimposing a transparent coordinate matrix over the cards, the specimen numbers can be read.

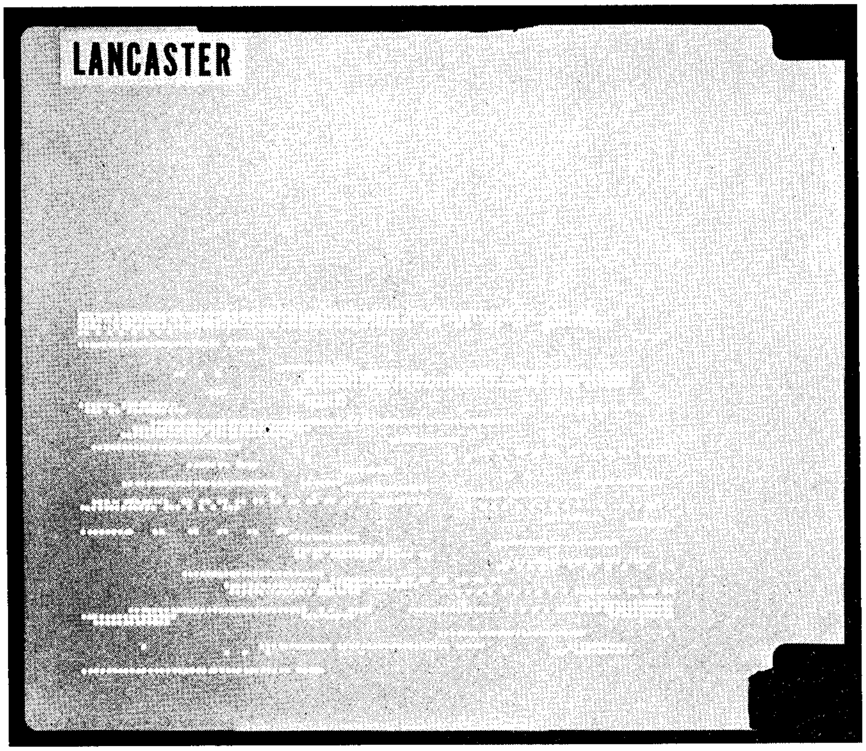


Fig. 12. Termatrex reader with the term card "Lancaster" superimposed.

Fig. 13. Termatrex reader with the term card "South" superimposed.

Equipment

The equipment used for this system consists of a data input machine (Fig. 8) which is a precision drill with a movable carriage, a light box or reader with a transparent coordinate matrix (Fig. 9); and the four decks of term cards (Fig. 10).

To demonstrate the output of this system, let us take an example. Do we have a paint system which has been exposed to direct sunlight in Lancaster, facing south at a 45° angle, with the following characteristics:

(*1*) Primer MX-121, sprayed at a rate of 5 g./sq. ft. on experimental exterior siding SHB-197.

(*2*) Top coat X sprayed at a rate of 12 g./sq. ft.

(*3*) A chalking value of 9 or better after 6 mo. *and* 8 or better after 12 *and* 18 mo.

(*4*) A color change of 10 after 6 mo., 9 or better after 12 mo., *and* 8 or better after 18 mo.

(*5*) Are any of these still under test?

For retrieval, we superimpose the following term cards on the reader one at a time:

Direct (Fig. 11) (This indicates there are slightly less than 1700 specimens exposed to direct sunlight.)

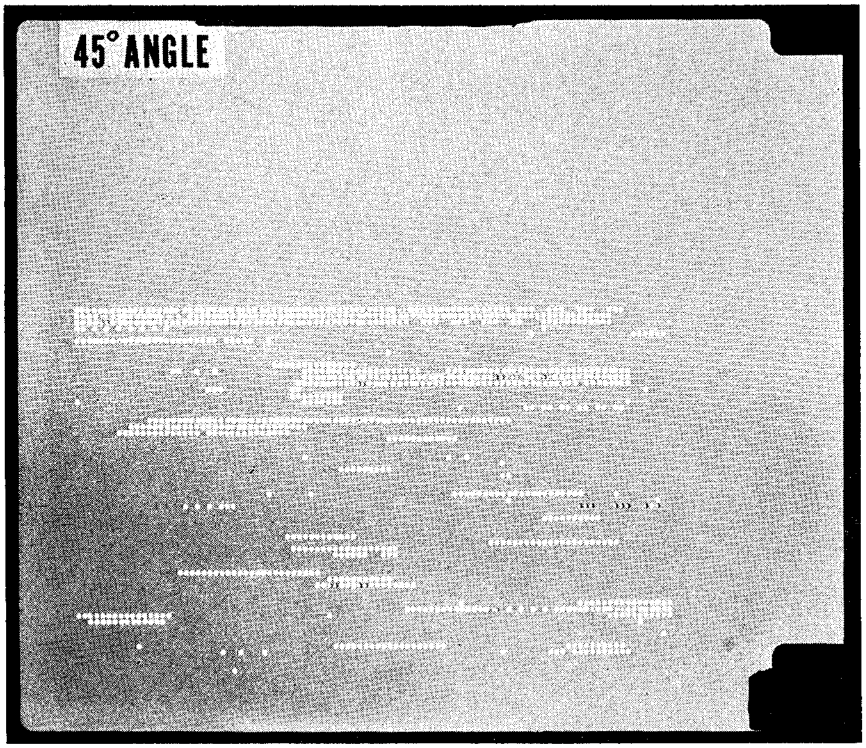


Fig. 14. Termatrex reader with the term card "45° angle" superimposed.

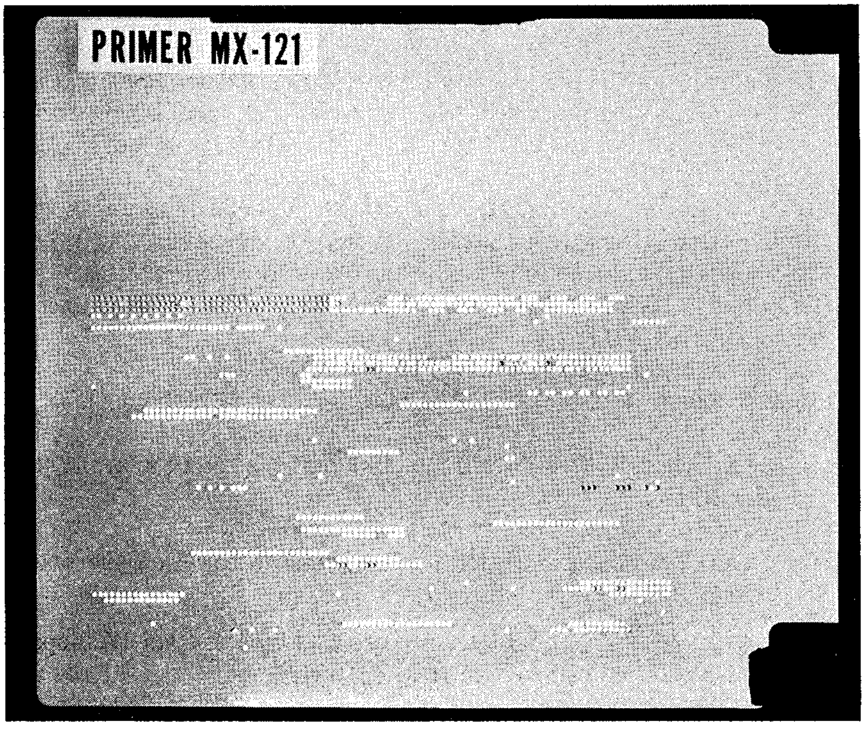


Fig. 15. Termatrex reader with the term card "Primer MX-121" superimposed.

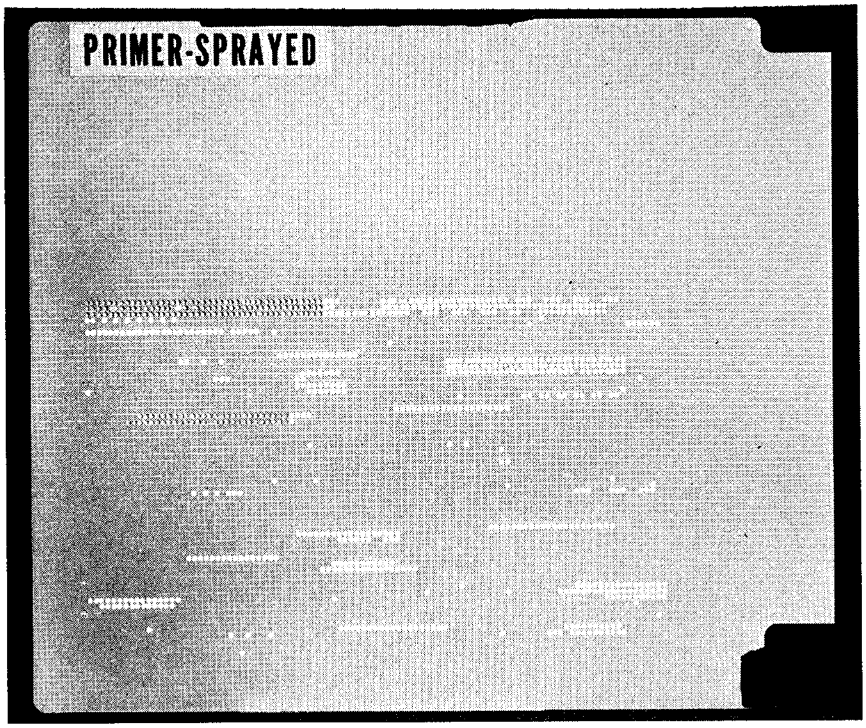


Fig. 16. Termatrex reader with the term card "Primer-Sprayed" superimposed.

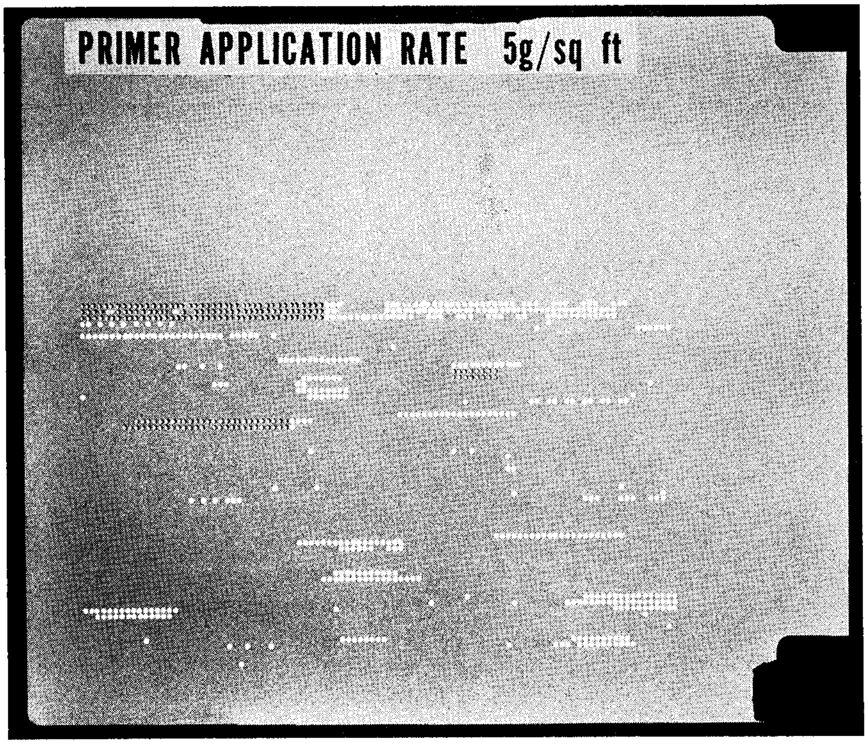


Fig. 17. Termatrex reader with the term card "Primer Application Rate—5 g./sq. ft." superimposed.

Fig. 18. Termatrex reader with the term card "Top Coat X" superimposed.

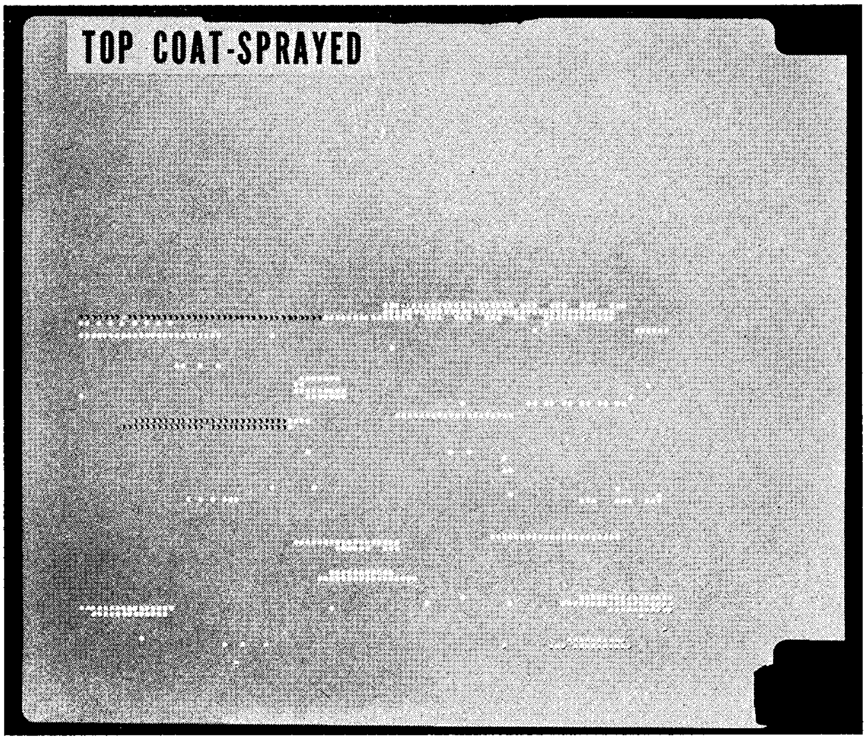


Fig. 19. Termatrex reader with the term card "Top Coat—Sprayed" superimposed.

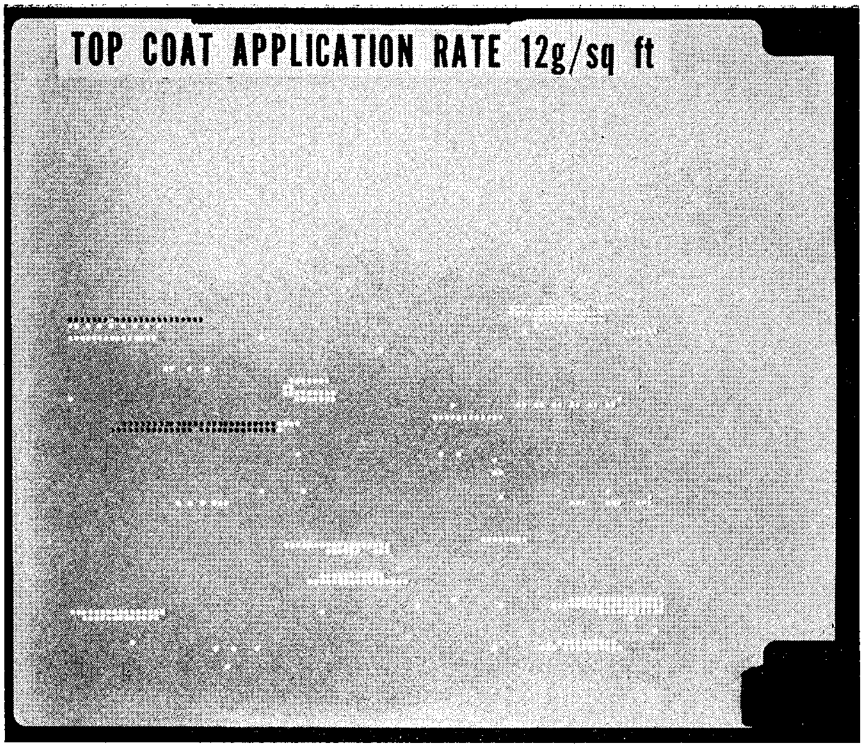


Fig. 20. Termatrex reader with the term card "Top Coat Application Rate—12 g./sq. ft." superimposed.

Fig. 21. Termatrex reader with the term card "Substrate—Experimental Exterior Siding SHB-197" superimposed. Indicates there are 269 specimens having all of the characteristics noted by the term cards in Figures 11–21 inclusive.

Fig. 22. Termatrex reader with the term card "Chalking—6 months—9 or better" superimposed.

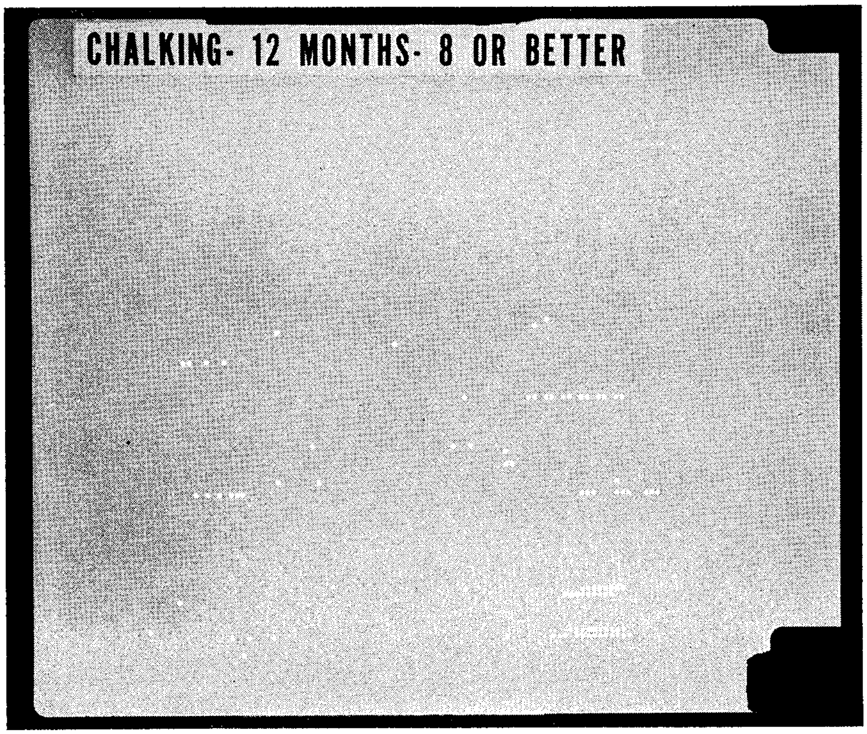


Fig. 23. Termatrex reader with the term card "Chalking—12 months—8 or better" superimposed.

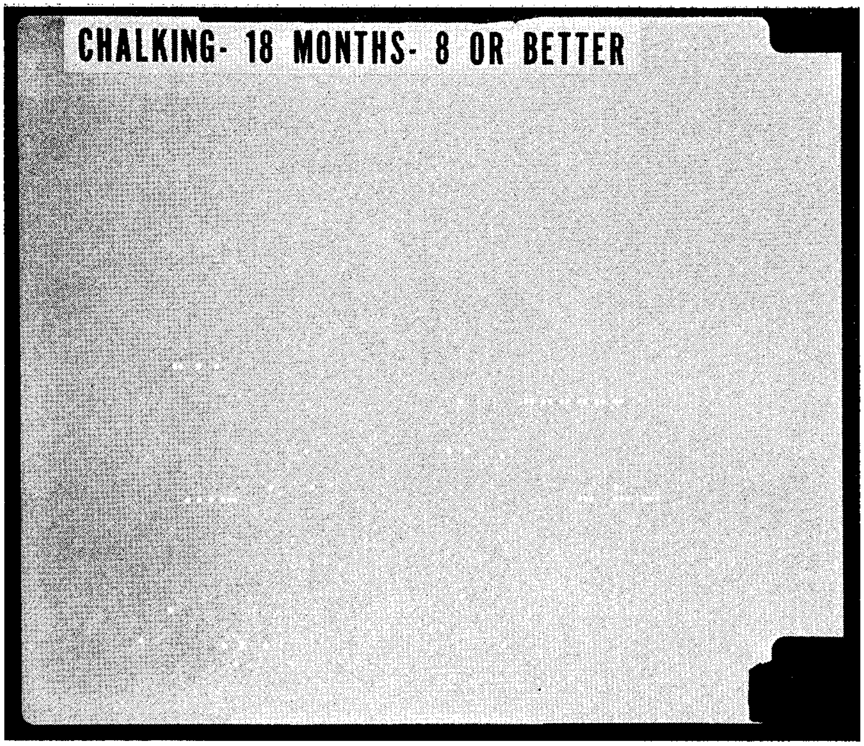


Fig. 24. Termatrex reader with the term card "Chalking—18 months—8 or better" superimposed. Indicates there are now only 51 specimens having all of the characteristics noted by the term cards in Figures 11–24 inclusive.

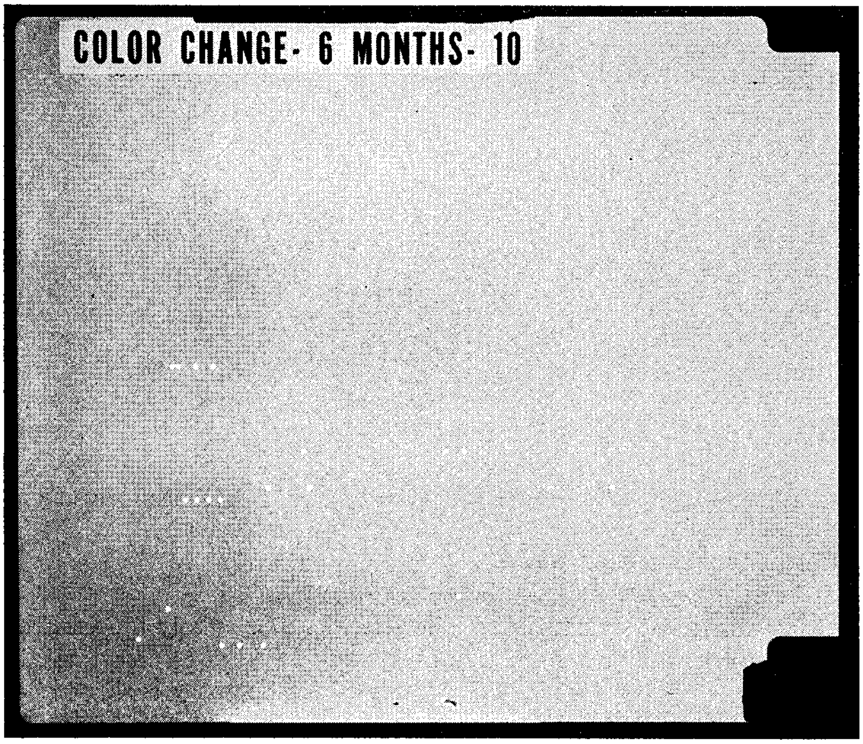


Fig. 25. Termatrex reader with the term card "Color Change—6 months—10" superimposed.

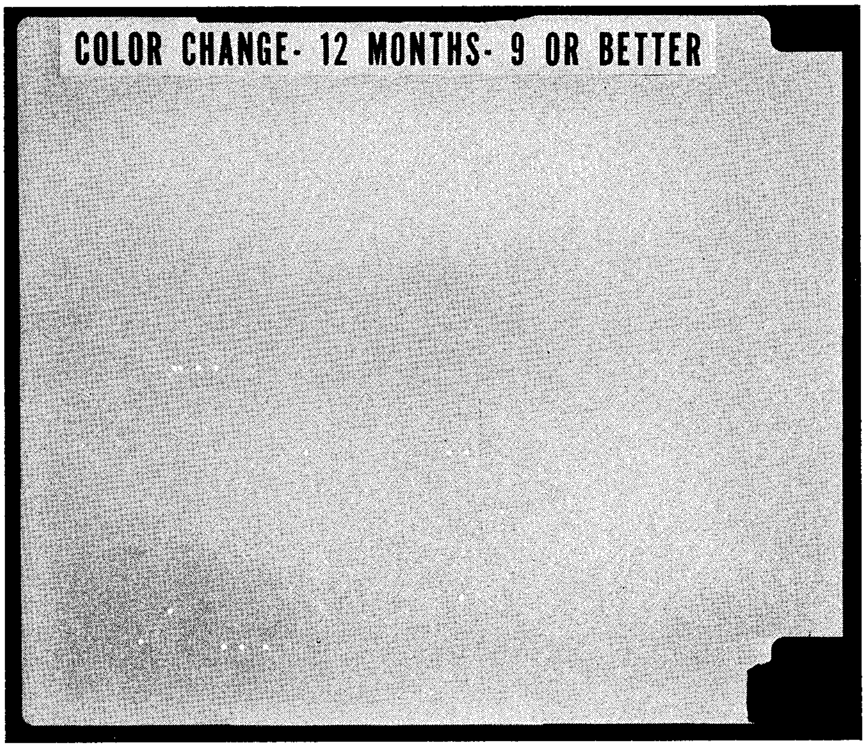


Fig. 26. Termatrex reader with the term card "Color Change—12 months—9 or better" superimposed.

Lancaster (Fig. 12).
South (Fig. 13).
45° Angle (Fig. 14).
Primer MX-121 (Fig. 15).
Primer-Sprayed (Fig. 16).
Primer Application Rate, 5 g./sq. ft. (Fig. 17).
Top Coat X (Fig. 18).
Top Coat—Sprayed (Fig. 19).
Top Coat Application Rate—12 g./sq. ft. (Fig. 20).
Substrate—Experimental Exterior Siding SHB-197 (Fig. 21), (269 specimens have all of the above characteristics.)
Chalking—6 months—9 or better (Fig. 22).
Chalking—12 months—8 or better (Fig. 23).
Chalking—18 months—8 or better (Fig. 24). (51 specimens have all of the above characteristics.)
Color Change—6 months—10 (Fig. 25).
Color Change—12 months—9 or better (Fig. 26).
Color Change—18 months—8 or better (Fig. 27). (Only 8 specimens have all of the above characteristics.)
Samples Terminated (Fig. 28). (A colored transparency is slipped beneath the top card.)

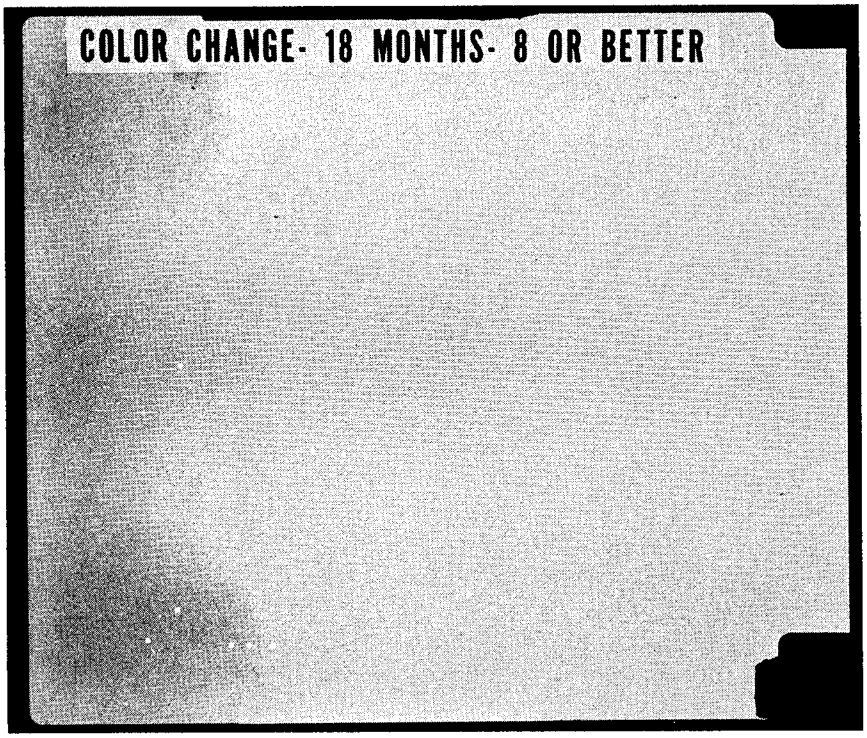


Fig. 27. Termatrex reader with the term card "Color Change—18 months—8 or better" superimposed. Indicates that there are only eight specimens having all of the characteristics noted by the term cards in Figures 11–27 inclusive.

We finally end up with some white and some colored dots showing. The four white dots indicate those samples which have been removed from the test racks and the four colored dots represent those that are still under test. The latter group can be viewed by the requester if he so desires.

TABLE I
Ingredients and General Information Deck

Samples exposed
Samples terminated
Use
Processing
Form
Exposure
1a. Resin-specific
1b. Resin-generic
2. Plasticizer
3. Stabilizer
4. Process aid
5. Lubricant
6. Accelerator
7. Filler
8. Pigment
9. Antioxidant
10. Curing agent
11. UV screener
12. Foaming agent
13. Solvent
14. Fungicide
15. Defoamer
16. Wetting agent
17. Thickener
18. Other
Coatings
Primer, specific
Primer, generic
Intermediate, specific
Intermediate, generic
Top Coat, specific
Top Coat, generic

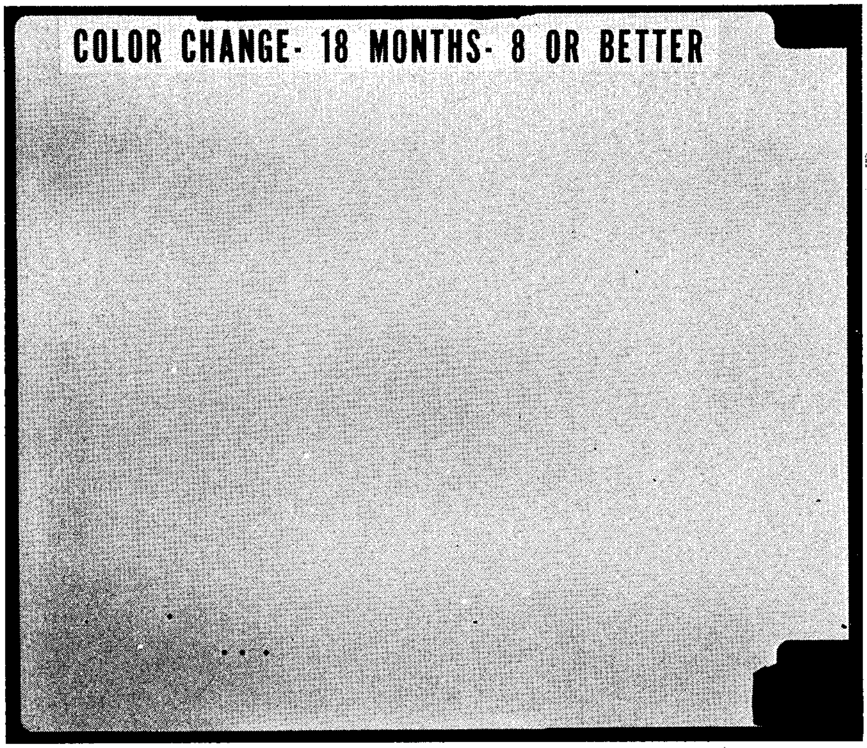


Fig. 28. Termatrex reader with the colored transparency term card "Samples Terminated" inserted beneath the top term card shown in Figure 27. The white dots are the specimens terminated and the black dots represent specimens still under test.

We then put the transparent coordinate matrix (Fig. 29) into place so that the specimen numbers can be read off. By reference to a log book, job file numbers are obtained and the documents can be withdrawn from the file. Complete information, including the original test requisitions and all data reports, is contained in each file under the original Job Number or requisition number. Retrieving all of this information actually takes less time than it took to demonstrate the search technique.

Indexes

Several times I have mentioned the decks of term cards. The development of these decks was done after careful consideration of all of the data available and the types of questions our clients might ask. Four separate decks of term cards are used (Fig. 10). These are:

(*1*) Ingredients and General Information
(*2*) Phr and Substrates
(*3*) Visual Examination Data
(*4*) Physical Properties Data

Table I lists the categories included in the Ingredients and General Information deck.

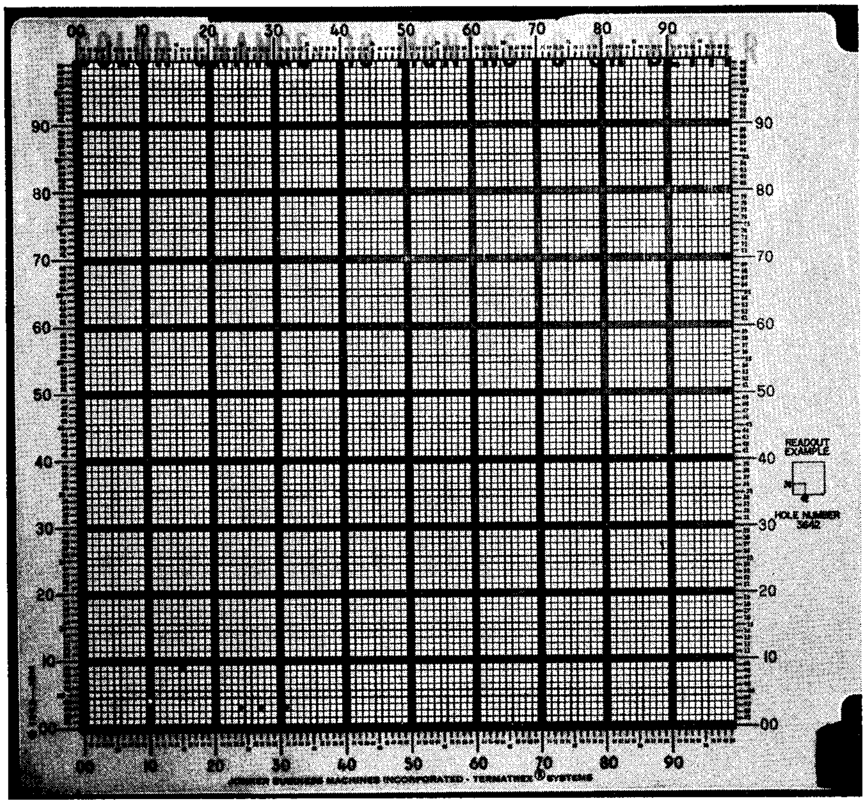


Fig. 29. Termatrex reader with the transparent coordinate matrix superimposed. The first two digits of the specimen numbers are read from the ordinate and the last two from the abscissa of the matrix.

The Phr and Substrate deck (Fig. 30) contains the term cards for the phr of the individual ingredients in the compositions; the substrates; and for paint specimens, per cent solids, pigment volume concentration, and application rate. Random Numerical (RN) cards are used to encode the information posted. RN cards are identified by colored, numbered tabs ranging from 0 to 99. Five colors were selected for this index. Coded RN cards permit a reduction in the number of term cards; for example, by use

TABLE II
Visual Examinations Subheadings

Bleaching/fading
Blistering
Chalking
Checking
Cracking
Delamination
Dirt Retention
Flaking
Mildew
Peeling
Staining/bleeding
Substrate swell
Yellowing/darkening

TABLE III
Physical Properties Subheadings

Dimensional change
Elongation
Shore hardness
Stiffness
Tensile strength
Thickness
60° gloss

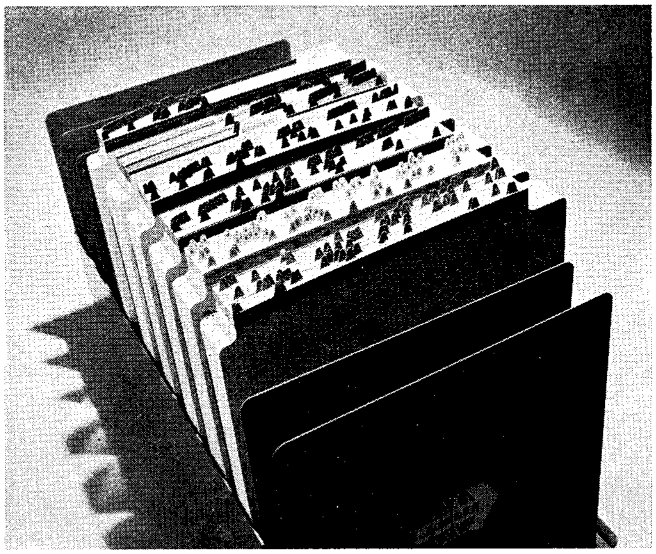


Fig. 30. The Phr and Substrate deck showing the use of random numerical term cards.

of a four-digit code system only 40 RN cards are required for the posting of up to 10,000 different substrates.

The Visual Examination deck contains the visual ratings found for each of eight inspection periods. Table II lists the subheadings in each inspection period group.

Under each subheading are term cards for the visual ratings *10, 9 or better, 8 or better, 7 or better, 6 or better,* and *failed.* We have arbitrarily decided that any rating less than 6 is failure.

The fourth deck, Physical Properties Data, is similar to the Visual Examination Data deck in that there is a multiplicity of similar groups of term cards: one group for each inspection period. The subheadings in each group are shown in Table III.

The ranges for each physical property are different. These were determined by reviewing data obtained in the past and selecting ranges believed to be significant. In most cases, per cent change is reported. However, for certain physical properties, such as Shore hardness, the actual change in value is recorded for either Shore A or Shore D hardness.

Data Reports

With IR systems of this type, we cannot overlook the importance of the method of reporting data. When we consider that there is the possibility of obtaining data for each specimen after at least eight different inspection periods, the mere filing of these data can become a space problem. Our Physical Standards Department solved this potential problem by developing a cumulative report sheet using an Ozalid master copy (any other reproducing system would be just as good) which would accommodate data for an entire group of specimens to be evaluated alike at the same time.

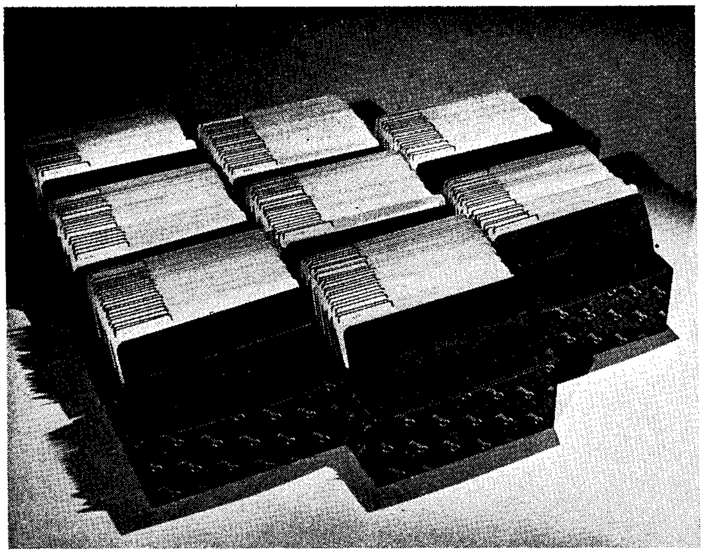


Fig. 31. Data files in vertical expandable file pockets. The equivalent of four standard file drawers.

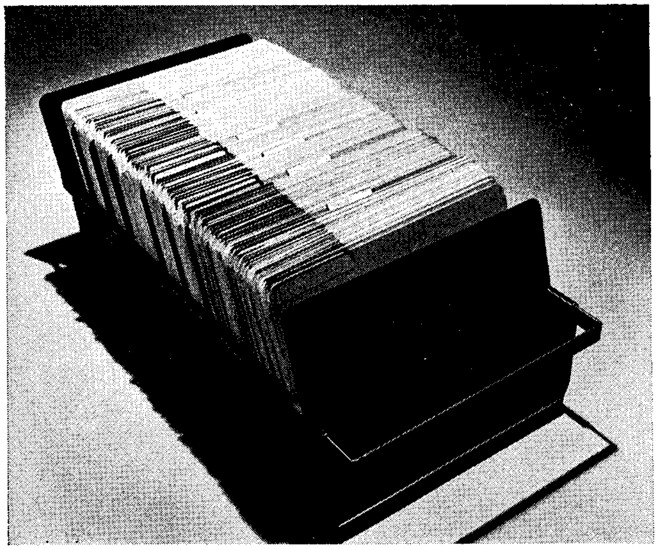


Fig. 32. The same data as shown in Figure 32 filed in a VISIrecord VEE file which fits into one standard file drawer.

The master copy is maintained by PSD, and after the data has been recorded for a specific test period, copies are distributed. Upon receipt, the old data sheet can be discarded since the information in it is included in the most recent report. This system serves the dual function of reducing the size of the file and bringing to the attention of the originator all previous data for those particular specimens.

Each group of specimens recorded on a test requisition is given a job number upon receipt. All reports on these are marked with the job number and are filed according to the job number. The individual specimens are numbered consecutively, as mentioned earlier, and these numbers are the accession numbers posted on the term cards. A log is kept to translate accession numbers into their respective job numbers.

When we first started our IR system, we used individual vertical expandable file pockets, one for each job number. Figure 31 shows the file for 200 job numbers. As you can see, this occupied about 8 lineal feet or 4 standard file drawers. By changing to a VISIrecord VEE file[7] (Fig. 32), we were able to reduce the storage space to 15 in. This file fits into a standard steel file cabinet drawer. We estimate it will hold about another year's supply of data. The cost was actually less than the cost of the expandable file pockets and reduced the file volume from four file drawers to one.

Conclusion

The IR system just described is not a static system. We are considering expanding it to include data on physical properties of the specimens as received. Before the proper term cards can be added, it will be necessary to collect these data and study them carefully to determine the significant value ranges. In addition, reference to specimens which have also been exposed to artificial environmental conditions could be included. The addition of such data would add to the value of the system.

With this system in operation the data from our outdoor exposure evaluations are now no longer unorganized and irretrievable or confined to use by the individual experimenter. They are being utilized and are proving to be of inestimable value.

References

1. Irving M. Klempner, *Am. Doc.*, **15**, 210 (1964).
2. Macbeth Corporation, Newburgh, N.Y. 12553.
3. Conducting Exterior Exposure Test of Finishes for Thermal Insulation (C488) and Recommended Practice for Conducting Natural Light "Sunlight and Daylight" Exposures Under Glass (E187), American Society for Testing and Materials.
4. *Exposure Standards Manual*, Society for Paint Technology.
5. *1966 Index to Standards*, American Society for Testing and Materials.
6. The Jonkers Corporation, Gaithersburg, Maryland.
7. VISIrecord, Inc., Copiague, Long Island, New York.

Résumé

Des facilités d'évaluation de l'exposition à l'extérieur de la Armstrong Cork Co, à Lancaster, Pa., consistent dans un champ d'exposition à l'extérieur un laboratoire d'évaluation, des stations de vieillissement et une instrumentation nécessaire. On fait également usage d'un site d'essai, d'un laboratoire commercial en Arizona, en Florida et en Minnesota. Les nécessités pour un enregistrement précis, l'évaluation des résultats obtenus et un rappel rapide permettaient le développement d'un système unique IR pour cette facilité. Ce système utilise l'indexation à coordonnées, basée sur les tech-

niques de coincidences optiques et inclut des informations d'échantillons telles que la composition, le type de plastique, la résine spécifique, les noms commerciaux des ingrédients, la nomenclature chimique, l'usage, les propriétés visuelles et physiques après des temps d'exposition variables, la localisation géographique, la direction et l'angle d'exposition, l'information directe et sous verre, le matériau de substrat (lorsqu'il est utilisé) et l'information pour le processus du spécimen. Un rappel rapide peut être effectué en entrant les systèmes dans n'importe quelles adresses, ou combinaisons de ces adresses ci-dessus. Par exemple, des exigences telles que "avons-nous un système de peinture qui permet une exposition à la lumière solaire directe dans le Lancaster, Pa., exposée au sud à 45° comme angle avec les caractéristiques suivants: primer MX-121 étendu à une vitesse de 5 g/sq ft sur une paroi extérieure expérimentale SHB-197 recouverte par le spray X à une vitesse de 12 g/sq ft, une valeur de 9 ou plus après 6 mois, ou 8 ou mieux après 12 et 18 mois, une variation de couleur de 10 après 6 mois, 9 ou mieux après 12 mois et 8 ou mieux après 18 mois, sont quelques uns de ces essais auxquels il peut être répondu endéans 10 minutes" et cela a été démontré. La réponse contiendra les résultats de la composition exacte des références des cahiers de notes, le promoteur du test et toutes les propriétés visuelles et physiques obtenues pour chaque période d'inspection. Puisque les résultats sont portés cumulativement, les anciens résultats peuvent être rejetés pour maintenir le volume de charge à un minimum.

Zusammenfassung

Die Einrichtungen der Armstrong Cork Co. in Lancaster, Pa., zur Auswertung von Exponierungsversuchen im Freien bestehen aus einem Exponierungsareal im Freien, einem Auswertungslaboratorium, einer damit verbundenen Wetterstation und der notwendigen instrumentellen Ausrüstung. Ausserem werden kommerzielle Testplätze in Arizona, Florida und Minnesota benützt. Der Bedarf an genauer Journalführung, Auswertung der erhaltenen Daten und rascher Auffindung führte zur Entwicklung eines besonderen IR-Systems für diese Anlage. Das System verwendet eine Indizierung nach einem koordinierten Konzept, das auf einem optischen Koinzidenzverfahren beruht und Informationen über die Proben, wie Zusammensetzung, Plastomertyp, Harzspezifität, Handelsnamen, chemische Nomenklatur, Verwendung, visuelle und physikalische Eigenschaften nach verschiedenen Exponierungsdauern, geographische Lage, Exponierungsrichtung und -winkel, direkt und unter Glas, Substratmaterial (wenn verwendet) und Probenverarbeitung einschliesst. Rasche Auffindung ist durch Eingang über irgend eine der angeführten Angaben oder Kombinationen davon möglich. Zum Beispiel kann eine Anfrage wie: "Besitzen wir ein Anstrichtsystem, welches dem direktion Sonnenlicht in Lancaster Pa. mit Richtung nach Süden unter einem Winkel von 45° exponiert wurde und folgende Charakteristik besitzt: Grundierung MX-121, auf experimentelle Aussenseite SHB-197 mit einer Geschwindigkeit von 5 g/sq ft aufgesprüht; ein "chalking"-Wert von 9 oder besser nach 6 Monaten und 8 oder besser nach 12 oder 18 Monaten; eine Farbänderung von 10 nach 6 Monaten, 9 oder besser nach 12 Monaten und 8 oder besser nach 18 Monaten; werden solche Systeme noch getestet," in einigen Minuten beantwortet werden. Die Antwort enthält Angaben über die genaue Zusammensetzung, Aufzeichungs-referenzen, Prüfer sowie alle visuellen und physikalischen Eigenschaften für jede Inspektionsperiode. Da die Daten kumulativ angegeben werden, können alte Berichte verworfen und so das Ordnervolumen auf einem Minimum gehalten werden.

18

APPLIED POLYMER SYMPOSIA NO. 4, 289–302 (1967)

The Quantitative Interpretation of Color Changes and the Calculation of Internal Light in Pigment-Coated Systems

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Synopsis

In order to study the mechanism of the chalk fading of pigmented materials and the degradation of substrate materials in coated systems, it is necessary (*1*) to quantitatively relate visual color changes to a physical cause and (*2*) to calculate light flux in the interior of the coated systems. The first aspect has been accomplished by assuming that chalk fading is caused by a white surface layer that reflects a fraction of the incident light. This reflectance, which is a quantitative measure of chalk fading, has been related to visual change by calculating the resultant displacement in color space. For a given reflectance, this visual change was found to be greater for darker and more saturated colors. In the second aspect, the internal light flux in a coated system has been related to the reflectances of surface film and substrate and to the transmittance of the surface film. A simple technique has been developed for measuring the necessary transmittance values.

INTRODUCTION

The weathering of materials which are protected by pigmented coatings may produce two types of sunlight-initiated degradation. The first occurs in the protective coating itself and results in the obvious surface changes—loss of gloss, chalking, and fading; the second occurs at a much lower rate in the interior of the system and may, for example, result in the degradation of a light-sensitive substrate such as wood. In order to study these phenomena quantitatively, one must be able to relate color changes to some physical effect which has occurred at the coating surface and be able to determine the light flux at the substrate surface.

To this end, we have related color changes to the reflectance of a hypothetical white layer over the original color and compared the results with measurements from weathered samples. We have also presented a simple relation for calculating internal light flux and an abridged method for measuring the spectral transmittance of high-opacity pigmented coatings, the only quantity necessary to this calculation which is difficult to obtain.

A RELATION BETWEEN COLOR LIGHTNESS CHANGES AND A SIMPLE MODEL FOR CHALK FADING

The observed increase in the lightness of weathered pigmented materials is due to one or both of two causes: (*1*) chalking due to vehicle erosion, or (*2*) pigment fading. When pigment fading does not change the hue, both of these causes will produce similar optical effects. For this case, the chalk-fading phenomenon will be called "whitening" since white is the end result of this degradation process.

Loose chalking is usually measured by rubbing a black cloth on the sample and observing the whiteness of the cloth[1] or by washing off and weighing the chalk.[2] A natural model for this effect suggests itself: a layer of white pigment over the original color. Fading and the component of chalk which cannot be removed probably create a whitening effect which gradually lessens with distance from the outer surface. This cannot be precisely described by the simple model above, but it seems intuitive that even this more complex case should be optically equivalent to this same model. Based on this assumption, it should be possible to describe the optical effects of whitening in terms of a layer of white over the original color.

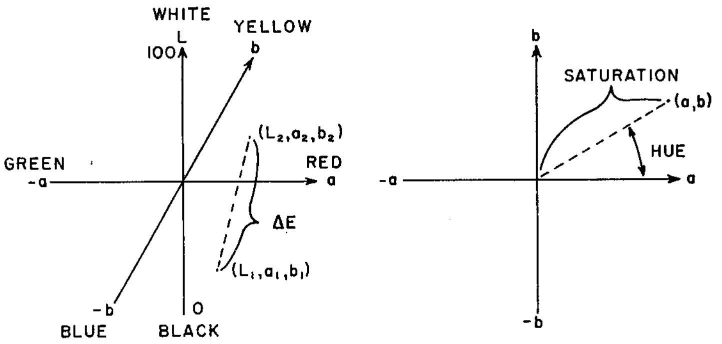

Fig. 1. Color coordinate relationships.

To describe color, we have used the Modified Adams Coordinate System[3,4] involving L (light–dark), a (red–green), and b (yellow–blue). These coordinates are so related that the resulting color space is essentially uniform, i.e., a just detectable color difference is approximately represented by the same distance everywhere in the coordinate system. The visual difference in color, ΔE, is represented in this color space by the distance

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \tag{1}$$

(Fig. 1*a*). A just detectable difference in color is approximately a ΔE of 0.3 unit.[5] The relation between this rectangular color space and the cylindrical color coordinates, lightness, saturation S, and hue is shown in Figures 1*a* and 1*b*.[4,5]

Theoretical

Our model for relating whitening to a physical effect assumes that whitening is caused by a layer of pure white pigment over the original color (Fig. 2). This layer diffusely reflects a certain fraction of the incident beam R_w called the "whiteness index." Because the white layer and original color both reflect, light bounces back and forth between them such that the net reflectance is

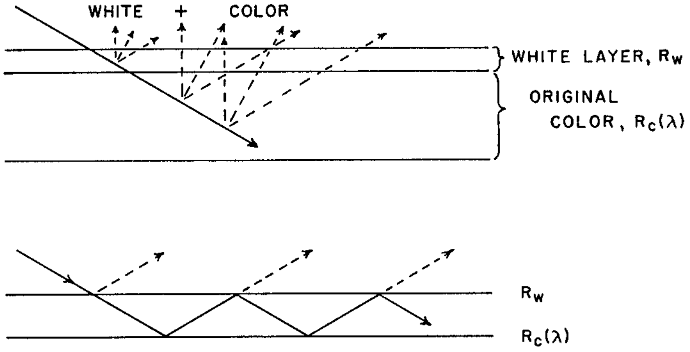

Fig. 2. Whitening model.

$$R(\lambda) = R_w + T_w^2 R_c(\lambda) + T_w^2 R_c(\lambda)[R_w R_c(\lambda)] + T_w^2 R_c(\lambda)[R_w R_c(\lambda)]^2 + \dots \quad (2)$$

$R_c(\lambda)$ is the reflectance of the original color and T_w is the transmittance of the white layer. Since $R_w + T_w = 1$,

$$R(\lambda) = R_w + \frac{(1 - R_w)^2 R_c(\lambda)}{1 - R_w R_c(\lambda)} \quad (3)$$

which is equivalent to eq. (12) in reference 6.

Colormaster tristimulus readings are integral reflectances such that[3,4]

$$X_i = \int R(\lambda) X_i(\lambda) d\lambda \quad (4)$$

X_i denotes B, G, or R, the tristimulus readings for illumination by source C^3, and the function $X_i(\lambda)$ is normalized so that the B, G, or R readings are 100 for a MgO standard whose reflectance is 0.975,[5] that is:

$$\int X_i(\lambda) d\lambda = 102.56$$

Substituting eq. (3) into eq. (4) gives

$$X_i = \int \left[R_w + \frac{(1 - R_w)^2 R_c(\lambda)}{1 - R_w R_c(\lambda)} \right] X(\lambda) d\lambda \quad (5)$$

Equation (5) cannot be integrated exactly unless $R_c(\lambda)$ is known at all visible wavelengths. In order to find a simple relationship between tristimulus values and the whiteness index, it is necessary to approximate the spectral reflectance $R_c(\lambda)$ by a step function R_j:

$$R_j = \int_{\lambda_j}^{\lambda_{j+1}} \frac{R_c(\lambda)d\lambda}{\lambda_{j+1} - \lambda_j} \tag{6}$$

such that R_j is the average $R_c(\lambda)$ over three distinct spectral regions ($\lambda_1 =$ 4000 A., $\lambda_2 =$ 5200 A., $\lambda_3 =$ 5950 A., $\lambda_4 =$ 7000 A.). The tristimulus regions overlap and are related to R_j by eq. (7)

$$\frac{X_i^0}{102.56} = \sum_{j=1}^{3} \alpha_{ij} R_j \tag{7}$$

X_i^0 denotes tristimulus values of the original color. α_{ij} values (Table I) were determined so that eq. (7) is exact for a pure gray [$R_c(\lambda) =$ constant $= R_c$]; i.e.,

TABLE I
The Coefficients α_{ij}

Tristimulus value	i	j 1	2	3
B	1	1	0	0
G	2	$^1/_6$	$^2/_3$	$^1/_6$
R	3	0	$^1/_2$	$^1/_2$

$$\alpha_{ij} = \int_{\lambda_j}^{\lambda_{j+1}} \frac{X_i(\lambda)d\lambda}{102.56} \tag{8}$$

Combining eqs. (5), (6), and (8) gives eq. (9):

$$\frac{X_i}{102.56} = R_w + (1 - R_w)^2 \sum_{j=1}^{3} \frac{\alpha_{ij} R_j}{1 - R_w R_j} \tag{9}$$

R_j values are determined from the three simultaneous equations represented by eq. (7).

Results and Discussion

By means of a straightforward computer program, B, G, and R values at several whiteness index levels were calculated from eq. (9) for various initial colors (Table II) and converted to L, a, b, S, and ΔE^4. Comparison with the original color coordinates L_0, a_0, etc., yields the color changes $\Delta L = L - L_0$, etc.

In an attempt to reduce the data for all colors to one graph, ΔL values for pure gray were calculated for a wide range of initial lightness L_0 from calculated values of $\Delta X_i = X_i - X_i^0$ (the tristimulus value for whitened

TABLE II
Color and Color Change Properties of Standard Tedlar[a] Poly(vinyl Fluoride) Films

Color									
Name	Code	L_0	a_0	b_0	$100 - L_0$	S_0	$\Delta E_{\max}$	$\Delta S^*/\Delta L^{*b}$	$C(S_0, L_0)^c$
Sunlight yellow	YE	87.25	−1.795	32.10	12.75	32.15	34.58	2.58	6.59
Beige	BG	69.55	7.581	17.06	30.45	18.66	35.72	2.20	1.67
Georgian gold	GO	67.25	1.764	27.98	32.75	28.04	43.11	2.59	2.43
Granite gray	GY	66.00	−0.182	−0.339	34.00	0.385	34.00	1.93	1.00
Spruce green	LG	65.53	−12.73	6.676	34.47	14.37	37.35	2.09	1.33
Aquamarine	AQ	64.07	−10.55	−10.45	35.93	14.85	38.88	2.02	1.30
Sandtone	SN	59.50	1.930	13.69	40.50	13.83	42.79	2.34	1.28
Turquoise	TQ	53.93	−16.85	−4.823	46.07	17.53	49.29	2.38	1.35
Sea blue	BE	44.81	−8.616	−15.16	55.19	17.44	57.88	2.25	1.23

[a] Du Pont registered trademark.

[b] Valid for $\Delta E \leq 5$.

[c] $C(S_0, L_0) = \Delta E/\Delta L$ for $\Delta E \leq 5$.

film minus the original tristimulus value). In this case, R_1, R_2, R_3, and $X_i^0/102.56$ are equal, and eq. (9) reduces to the simpler form

$$\Delta X_i = \frac{R_w(102.56 - X_i^0)^2}{(102.56 - R_w X_i)} \tag{10}$$

The relation between ΔL and L_0 at various R_w levels is shown in Figure 3. Comparison with calculations based on eq. (9) showed that Figure 3 adequately describes the relationship between ΔL, L_0, and R_w for all colors but yellow whose ΔL values correspond to those for $L_0 = 86$ and not 87.25, the actual L_0.

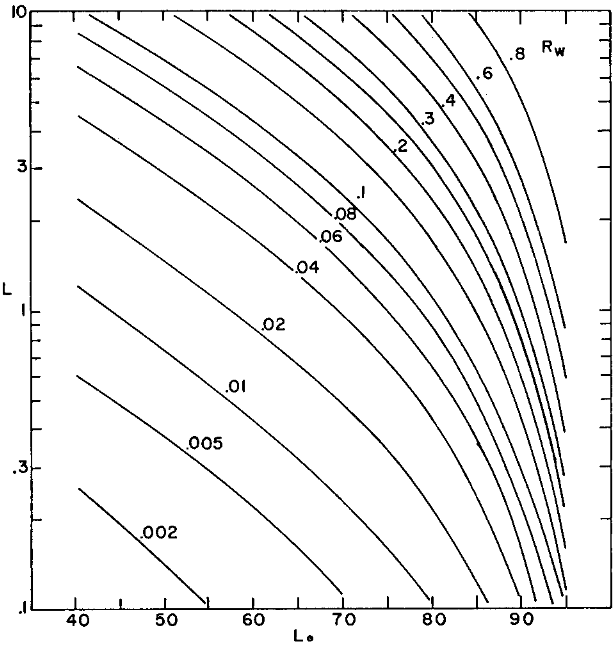

Fig. 3. ΔL versus L_0 at various levels of the whitness index, R_w.

In spite of the nonlinear relation between reflectance and visual response,[5] the relation between ΔL and R_w is remarkably linear for $\Delta L < 5$ and $R_w < 0.4$ (Fig. 4). In this useful range, ΔL can be approximately expressed by eq. (11):

$$\Delta L = A(L_0)R_w \tag{11}$$

The coefficient $A(L_0)$ is plotted in Figure 5. Thus, in the region of most interest, the physical effect R_w can be simply determined by dividing by $A(L_0)$.

The usefulness of eq. (11) depends on the assumption that weathering usually produces whitening and not a change in hue. We have verified this assumption by examining actual weathering data. In Figure 6, the component of color change in the a,b plane for typical data closely follows the constant hue line which represents Δa and Δb values calculated from eq. (9). When hue does change significantly, it usually means that one

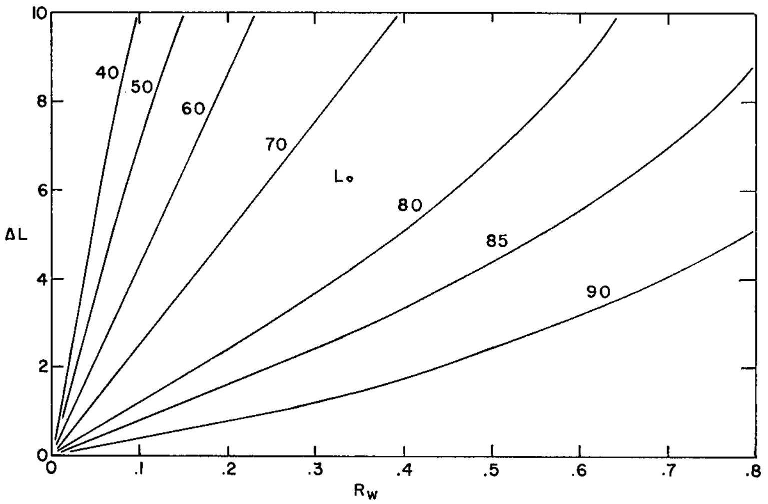

Fig. 4. ΔL versus R_w at various levels of the initial lightness, L_0.

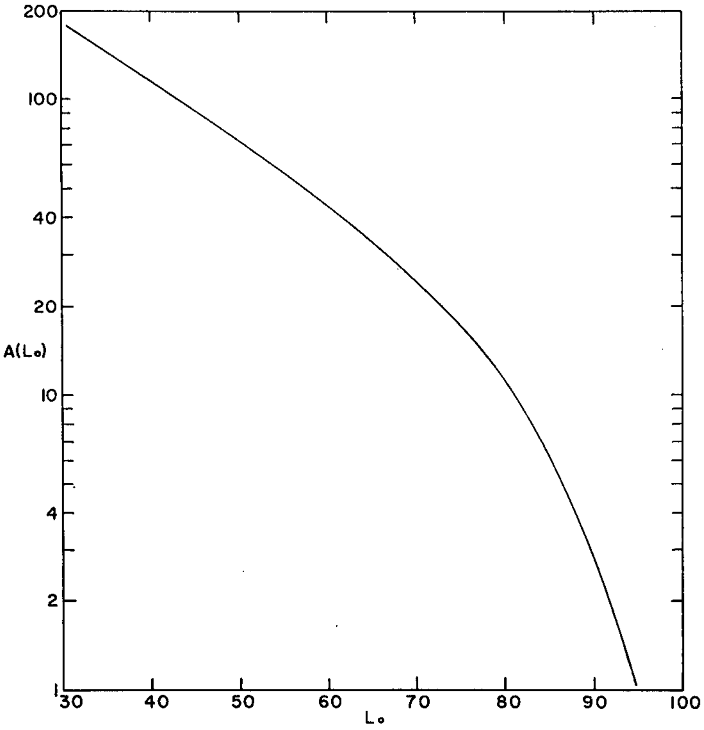

Fig. 5. The coefficient $A(L_0)$ versus the initial lightness, L_0.

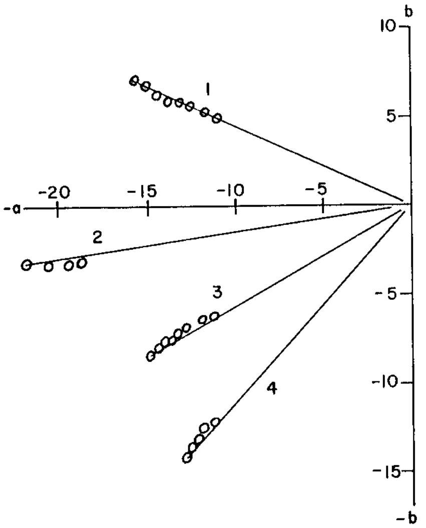

Fig. 6. The effect of whitening on color hue: (—) constant hue lines, (O) weathering data; (*1*) spruce green, (*2*) turquoise, (*3*) aquamarine, and (*4*) sea blue.

colored pigment of a multicomponent system is fading. In this case, the observable change in color space is the resultant of two nonparallel vectors, chalking and fading, and cannot be interpreted by means of this model.

The Effect of Whitening on ΔS and ΔE

Since hue remains constant during whitening (a/b is constant)

$$\Delta S = (\Delta a^2 + \Delta b^2)^{1/2} \tag{12}$$

and

$$\Delta E = (\Delta L^2 + \Delta S^2)^{1/2} \tag{13}$$

and color changes will occur in the constant hue plane defined by the L axis and the initial color (L_0,a_0,b_0). Typical calculated values of ΔL vs. ΔS (coordinates for the constant hue planes) are plotted in Figure 7 over the maximum range, zero to $\Delta L = 100 - L_0$ and $\Delta S = S_0$. The similarity of the curves suggests that a plot of the reduced variables ΔL^* versus ΔS^*

$$\Delta L^* = \Delta L/(100 - L_0) \tag{14}$$

$$\Delta S^* = \Delta S/S_0 \tag{15}$$

might transform the curves into one master curve. This is approximately true (Fig. 8). Furthermore, for $\Delta E < 5$, the relationship between ΔS^* and ΔL^* is linear and $\Delta S^*/\Delta L^*$ is nearly constant (Table II). From eqs. (13)–(15), it follows that

$$\frac{\Delta E}{\Delta L} = \left[1 + \left(\frac{\Delta S^*}{\Delta L^*}\right)^2 \left(\frac{S_0}{100 - L_0}\right)^2\right]^{1/2} = C(S_0,L_0) \tag{16}$$

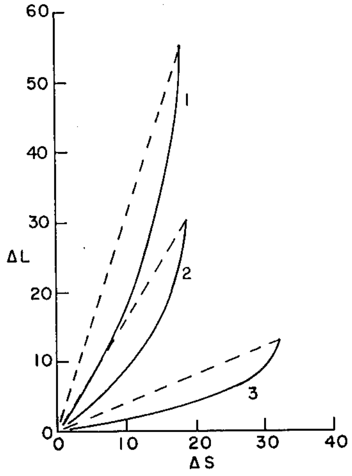

Fig. 7. ΔL versus ΔS: (*1*) sea blue, (*2*) beige, (*3*) sunlight yellow.

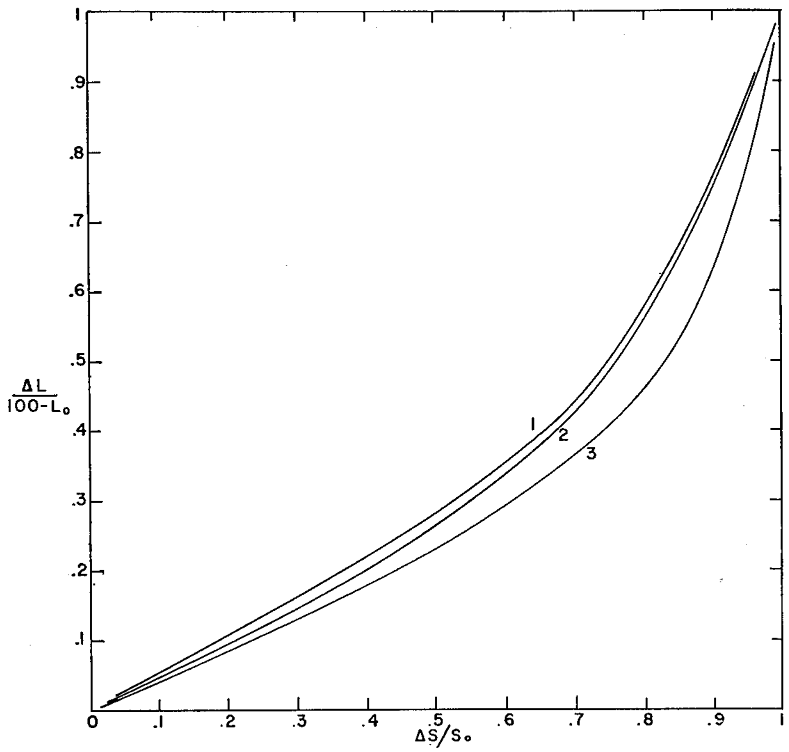

Fig. 8. $\Delta L^* = \Delta L/(100-L_0)$ versus $\Delta S^* = \Delta S/S_0$: (*1*) aquamarine, (*2*) sea blue, (*3*) sunlight yellow.

which is approximately a function of only the initial color coordinates S_0 and L_0. $C(S_0,L_0)$ values are also listed in Table II. Since ΔL is linear with R_w, ΔE is also linear with R_w:

$$\Delta E = A(L_0)\ C(S_0,L_0)R_w \tag{17}$$

Equation (17) is valid for $\Delta E < 5$, a region of practical interest since a ΔE of 5 represents an unsightly color difference.

Direct comparison between calculations and accelerated weathering data shows that calculated $\Delta E/\Delta L$ is within 15% of the observed value at $\Delta E = 5$; however, calculated $\Delta S^*/\Delta L^*$ deviates widely from observation (see Table III). Detailed examination of the weathering data revealed that, during the early stages of color change, saturation usually decreases about 0.5 unit while lightness remains constant or even decreases. Hopefully, additional experience with weathering data will provide an explanation of this and suggest a modification of the model which will make it possible to also calculate ΔS reasonably well.

TABLE III
Calculated and Observed Relation Between ΔS, ΔE, and ΔL

	$\Delta S^*/\Delta L^{*a}$		$\Delta E/\Delta L^a$	
Color	Obs.	Calc.	Obs.	Calc.
LG	2.13	2.09	1.46	1.33
AQ	2.24	2.02	1.47	1.30
TQ	1.48	2.38	1.23	1.35
BE	1.78	2.25	1.18	1.23

[a] For $\Delta E = 5$.

Conclusions

Because chalk fading usually does not affect hue, the above model is sufficiently accurate to describe the relation between ΔL and the whiteness index R_w. Below $\Delta L = 5$ and $R_w = 0.4$, this relation is linear to within 5%; the coefficient is a function only of the initial lightness. The model also predicts the relation between ΔE and ΔL to within 15%.

LIGHT FLUX IN THE INTERIOR OF COATED SYSTEMS

In the second aspect of this study, we are concerned with determining the light flux in the interior of a coated system such as a laminate or painted wood. This light flux is of interest because it may eventually cause the photodegradation of a light-sensitive substrate such as wood.

This flux is not just the flux transmitted by the pigmented layer but may be considerably greater because of multiple internal reflections between substrate and the pigmented layer (Fig. 9). The mathematical analysis of this situation closely follows that used by Kubelka in his deriva-

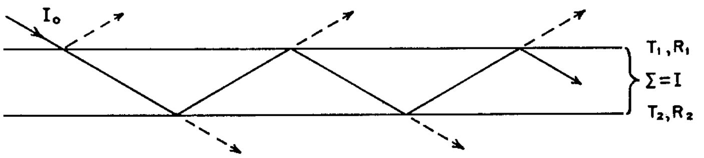

Fig. 9. Model for calculation of internal light flux.

tion of multilayer transmission [eq. (8) of reference 6]. The ratio of the internal flux I to the incident light flux I_0 is:

$$I/I_0 = T_1 + T_1R_2 + T_1(R_2R_1) + T_1R_2(R_1R_2) + \dots$$
$$= \frac{T_1(1 + R_2)}{1 - R_1R_2} \tag{18}$$

T, R denote transmittance and reflectance; 1, 2 denote film, substrate. Thus the relative internal light flux, I/I_0, is greater than the film transmittance by the factor $(1 + R_2)/(1 - R_1R_2)$.

Using a Spectronic 20 spectrophotometer with integrating head, reflectances were determined for several typical substrates and a white film (Table IV). The correction factor is as high as 2.82 for white film over aluminum. Obviously, this effect cannot be neglected.

TABLE IV
Substrate Reflectance and Its Effect on Internal Light Flux

	Reflectance, R_2		$\frac{1 + R_2}{1 - R_1R_2}$[a]	
Substrate	4000 A.	5000 A.	4000 A.	5000 A.
Fir plywood	0.162	0.316	1.27	1.78
Aluminum	0.537	0.553	2.11	2.82
Galvanized steel				
Spangle	0.316	0.316	1.57	1.78
Electroplated	0.105	0.117	1.17	1.24

[a] R_1 = Reflectance of L89 white Tedlar poly(vinyl fluoride) film.
= 0.510 and 0.812 at 4000 and 5000 A.

In order to attain 10% accuracy for light flux calculated by means of eq. (18), we must be able to measure film absorbance to within 0.04 unit and reflectance to within 0.03. The latter is easily accomplished by the above-mentioned simple method. Sufficiently accurate transmittance measurements are more difficult to obtain.

Measurement of Pigmented Film Light Transmittance

A simple direct measure of film absorbance that has a precision of ±0.04 up to an absorbance of five is commercially available (Fig. 10). The basic unit is a Photovolt Transmission Densitometer (Photovolt Corporation).

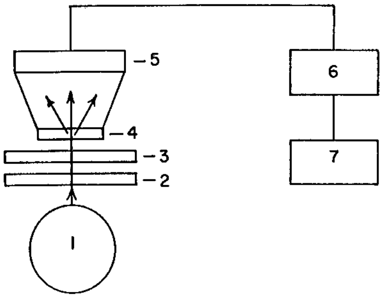

Fig. 10. Schematic of densitometer for measuring pigmented film absorbance: (*1*) light source, (*2*) filter, (*3*) film sample, (*4*) diffuser, (*5*) detector, (*6*) amplifier, and (*7*) meter.

Tungsten and mercury vapor lamps were used as light sources in appropriate wavelength regions. Nearly monochromatic light was obtained by means of narrow-band Corning filters or interference filters. A diffuser in front of the detector is necessary so that the instrument can be properly zeroed with diffuse light. Absorbance is read directly from the meter and easily converted to transmittance T'. However, T' is not the true transmittance T_1 needed in eq. (18) because diffuse reflection from film and diffuser increases the light flux passing through the diffuser to the detector so that

$$T_{1,d} = \frac{T_1 T_d}{1 - R_1 R_d} \tag{19}$$

where 1 denotes film and d denotes diffuser. [See eq. (8) of reference 6.] Since the densitometer is zeroed with the diffuser in the optical path, the observed transmittance T' is $T_{1,d}/T_d$ and

$$T_1 = T'(1 - R_1 R_d) \tag{20}$$

In our apparatus, R_d, the reflectance of the diffuser, is 0.69. True absorbance A_1 should be the meter reading plus a correction as indicated in eq. (21).

$$\begin{aligned} A_1 &= -\log T' - \log (1 - R_1 R_d) \\ &= \text{meter reading} + \text{correction} \end{aligned} \tag{21}$$

The reflectance of various colors was measured as before and used to calculate the correction term $-\log (1 - R_1 R_d)$.

Corrections for each color were determined experimentally by comparing photovolt readings with continuous transmission spectra measured on a Cary 14 Spectrophotometer by placing the films as close to the detector as possible.

The agreement between calculated and measured correction factors is generally good (Table V). Notable exceptions are for yellow film at 435 mμ and all colors at 405 mμ. In both regions, the additional correction is probably due to the very rapid change of absorbance with wavelength

TABLE V
Experimental and Calculated Absorbance Corrections

Film[a] color code		True absorbance − photovolt reading			
		545 mμ	485 mμ	435 mμ	405 mμ
WH	Calc.	0.36	0.36	0.36	0.19
	Obs.	0.37	0.36	0.40	0.35
YE	Calc.	0.31	0.24	0.14	0.10
	Obs.	0.40	0.26	0.74	1.78
BG	Calc.	0.16	0.15	0.11	0.09
	Obs.	0.31	0.25	0.30	0.80
GO	Calc.	0.15	0.12	0.07	0.05
	Obs.	0.11	0.08	0.11	0.43
GY	Calc.	0.16	0.18	0.17	0.15
	Obs.	0.30	0.29	0.31	0.35
LG	Calc.	0.17	0.17	0.12	0.09
	Obs.	0.18	0.17	0.16	0.35
AQ	Calc.	0.17	0.21	0.17	0.12
	Obs.	0.21	0.15	0.16	0.40
SN	Calc.	0.12	0.11	0.09	0.07
	Obs.	0.15	0.14	0.16	0.20
TQ	Calc.	0.12	0.13	0.10	0.09
	Obs.	0.05	0.00	0.09	0.50
BE	Calc.	0.07	0.11	0.09	0.08
	Obs.	0.17	0.07	0.07	0.00
Avg. difference (Obs. − Calc.)		+0.04	+0.03	+0.06	+0.42

[a] See Table II.

combined with the finite spectral width of the radiation passing through the filters.

In general, except in spectral regions where absorption is changing rapidly the densitometer technique plus an easily determined correction provides an absolute measure of the absorbance of pigmented films.

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Résumé

En vue d'étudier le mécanisme d'affadissement de matériels pigmentés et de la dégradation de matériaux dans des systèmes recouverts, il est nécessaire: (*1*) de relier quantitativement les modifications de couleurs visuelles à une cause physique et (*2*) de calculer le flux lumineux à l'intérieur des systèmes recouverts. Le premier aspect a été accompli en admettant que l'affadissement a été causé par la couche superficielle blanche qui réfléchit une fraction de lumière incidente. Cette réflexion qui est une mesure quantitative de l'affadissement est reliée à la variation visuelle en calculant le déplacement résultant de la couleur. Pour une réflexion déterminée cette variation visuelle est plus grande pour les couleurs plus foncées et plus prononcées. En ce qui concerne le second aspect le flux lumineux interne d'un système recouvert est relié à la réflexion du film en surface et du substract et à la transmission du film en surface. Une technique simple a été développée pour mesurer les valeurs de transmission nécessaires.

Zusammenfassung

Um den Mechanismus des kreidigen Ausbleichens von pigmentierten Materialien und den Abbau des Substratmaterials in Überzugssystemen zu untersuchen, ist es notwendig (*1*) eine quantitative Beziehung zwischen visuellen Farbänderungen und einer physikalischen Ursache herzustellen und (*2*) den Lichtfluss im Inneren des Überzugssystems zu berechnen. Das erste Ziel wurde durch die Annahme erreicht, dass die kreidige Ausbleichung durch eine weisse Oberflächenschichte verursacht wird, die einen Bruchteil des einfallenden Lichtes reflektiert. Dieses Reflexionsvermögen, welches ein quantitatives Mass für die kreidige Ausbleichung ist, wurde durch Berechnung der resultierenden Verschiebung im Farbraum zur visuellen Änderung in Beziehung gebracht. Bei gegebenem Reflexionsvermögen erwies sich die visuelle Änderung bei dunkleren und satteren Farben als grösser. Der zweite Aspekt, der innere Lichtfluss in einem Überzugssystem, wurde zum Reflexionsvermögen des Oberflächenfilms in Beziehung gebracht. Ein einfaches Verfahren zur Messung der notwendigen Durchlässigkeitswerte wurde entwickelt.

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SUBJECT INDEX