



**Technical Working Area 12  
Efficient Test Procedures  
for Polymer Properties**

**A Review of  
Accelerated Durability Tests**

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# A Review of Accelerated Durability Tests

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## ABSTRACT

This review formed part of the work programme of VAMAS Technical Working Area 12 (TWA12) and followed from a detailed survey that examined the availability, status and usage in the VAMAS countries of accelerated durability tests and is aimed at assisting the development of an ISO standard. It includes information on degradation agents and mechanisms, published standards, designing an accelerated durability testing programme, predictive models, variability and uncertainty, heat ageing, weathering, exposure to liquids and gases, ionizing radiation, pitfalls, and simulated design life exposure of products.

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## 1 INTRODUCTION

By definition durability of a material or product implies its performance over a long time scale. The expected life span of polymer products varies considerably but is generally measurable in years and can be 20 or even 50 years. With such time scales it becomes virtually impossible to prove a product under service conditions over its whole design life and it becomes necessary to rely on accelerated tests to predict long term performance.

There is hence an enormous need for reliable accelerated testing methods and prediction techniques which is only matched in magnitude by the inherent difficulties of designing tests which can be relied upon to give meaningful predictions. Whilst large amounts of durability data are produced by accelerated methods, relatively little has been validated as realistically representing service and there is great scepticism on the part of both polymer suppliers and end users as to the value of any accelerated data. Nevertheless there is much valuable information which has resulted from studies of polymer durability which can be applied to help maximise the value of any accelerated testing programme. It is the object of this Guide to make such information readily available.

## 2 SCOPE

Durability in its broadest sense covers any aspect of irreversible property change with time and use. For the purposes of this work, the scope is restricted to the effect of the environment ie dynamic mechanical degradation such as abrasion and fatigue is excluded. However, any test to measure the effect of the environment can use any mechanical, physical or chemical parameter, including abrasion or fatigue to monitor change. The environment includes heat, light, liquids, gases and ionising radiation.

## 3 THE OBJECTIVES OF ACCELERATED TESTS

Accelerated durability tests may be carried out for different purposes and with different objectives in mind. The reasons for accelerated testing may be summarised as:-

- Product performance prediction
- Comparison of materials
- Quality assurance
- Design data

It is important that the purpose and objective of testing is clearly established because they will influence to a considerable degree the design of the durability trial and the interpretation of the results.

Simplistically, when the purpose is simple comparison or a check against a given specification the critical dependence of the value of the results on the relation of the test conditions to real service is much reduced. This does not mean that test conditions are unimportant for comparison or quality checks but their relevance to service need not be so rigorously proven.

When the results are to be used for performance prediction or design it is essential that extrapolation rules from the test conditions to those of service are known and that they can be used with confidence.

The essential requirement for comparison is that the test conditions are not such that they give a distorted view of relative performance. For quality assurance it is also particularly important that test conditions are standardised and reproducible.

The purpose of the trial will also influence the time scales, the number of experimental points, the choice of degradation agents and the parameters to be measured. For example, comparison and quality check trials may achieve their purpose with comparatively short time scales and/or experimental points. Whereas multiple degradation agents may be more realistic as regards service, this will make extrapolation rules more complicated. The choice of parameter to be measured will in part depend on whether a general assessment is being made or the interest is in a particular parameter critical to performance. There are of course many other considerations which will affect the choice of test conditions.

Having defined the objectives of the trial and in the light of these decided on the details of test conditions and analysis of results, it will be possible to state the limitations of the results and hence estimate their significance.

#### **4 THE DEGRADATION AGENTS**

These can be summarised as:-

- Heat
- Light
- Liquids
- Gases
- Radiation
- Mechanical stress
- Electrical stress

In durability testing, heat as a single agent is generally taken to mean the action of both temperature and atmospheric oxygen. Hence a test for effect of temperature must consider the availability of oxygen and its diffusion in the test piece.

Heat is also very commonly used in combination with other agents, notably light, liquids and other gases.

Light may extend beyond the visible range, particularly to the UV region.

Liquids encompass a whole range of chemicals either pure or solutions which may be applied to the test pieces by immersion or by such particular means as salt spray or high humidity.

Gases may include the use of an inert gas atmosphere to exclude oxygen.

Radiation covers x and gamma radiation and the various nuclear particles.

Heat, light, liquids, gases and radiation are collectively known as aggressive environments.

For the purpose of this guide the effects of mechanical and electrical stress are not considered in isolation but are treated either as an additional test condition to enhance the effect of the aggressive environment or as a parameter to measure the effect of the environment.

Two degradation agents may have a synergistic effect in that their effect, in combination, is greater or lesser than the sum of their individual effects. This is clearly very important when considering the use of multiple agents and in predicting service performance.

The degradation agent may be applied continuously or intermittently to give cyclic exposure. The exposure cycles may include two or more agents applied alternatively. The effects of

cyclic exposure may not be the same as the equivalent dose of continuous exposure.

In many cases it will be possible to identify the critical degradation agent(s) for the particular application or the particular objective such that for the purposes of the trial other agents are ignored. Whilst this may limit the trial it will allow a manageable test programme to be designed.

## 5 DEGRADATION MECHANISMS IN POLYMERS

The mechanisms which produce degradation depend on the polymer, additives, the degradation agents present and their concentration level. In many cases there will be more than one mechanism involved and their relative importance will depend on the mix of degradation agents present and their levels. Consequently it is important that at least a general appreciation of the degradation reactions of the polymers being tested is obtained before planning a trial so that the test conditions can be sensibly chosen.

In practice the degradation of polymers is very involved and the following notes are only a brief basic and rough outline. The literature should be consulted for the detailed processes for a given polymer.

Polymer Degradation - the irreversible change of chemical or physical properties - can be caused by the chemical or/and physical action of agents. Degradation comprises the deterioration of macro-molecules caused by bond scissions in the polymer backbone and chemical reactions in the side-chains as well as intermolecular crosslinking with formation of new chemical bonds between different molecules.

Degradation processes can be graded in two different chemical reactions:-

- single step reactions, with the rate of reaction proportional to the rate of initiation and
- chain reactions, with a self-propagation of degradation processes, eg autoxidation.

In practice degradation mechanisms in polymers always are influenced by more than one of the degradation agents mentioned in Chapter 4. There is, for example:-

- no heat without gases or liquids, and
- no (UV-) light, radiation, mechanical or electrical stress without heat and gases/liquids.

In many cases the degradation process starts with an attack by the degradation agents on chemical irregularities of polymer molecules or on additives or impurities in the bulk of technical polymers. Therefore also the test piece history, see Chapter 12, may have a great influence on the durability of polymers.

### Thermal degradation

The term thermal degradation refers to the chemical and physical processes in polymers which start at elevated temperatures. Atoms in macromolecules are linked together by covalent bonds with relatively small strength. At temperatures between 100 °C and 300 °C thermal-chemical reactions with oxygen or impurities are the dominating processes. Pure thermal degradation without the involvement of other molecules eg bond scissions are the dominating reactions at higher temperatures.

### Photodegradation

Photodegradation of polymers refers to the chemical and physical changes caused by the absorption of actinic radiation. Photodegradation plays an important part during outdoor exposure of polymers.

Degradation by the action of weathering is mainly initiated by the effect of solar radiation, which results in the absorption of UV radiation by chromophores and in the activation of excited states in macromolecules. However, other climatic quantities such as heat, moisture, wetting and ingredients of the atmosphere influence the mechanisms of degradation and are answerable for the final ageing results of photodegradation. Photodegradation processes mostly are limited to the irradiated surface of a sample.

### Chemical degradation

Polymers which contain or always are surrounded by low molecular weight compounds can be degraded by a vast number of processes caused by the action of these compounds. Depending on the kind of action these compounds can be sub-divided in two groups:-

- chemical active compounds which react with the polymer, and
- physical active compounds which swell or solve the polymer.

These interactions between low molecular weight compounds eg molecular oxygen and polymers are strongly dependent on temperature.

In connection with high levels of mechanical stress inside a sample the action of low molecular weight compounds can cause stress corrosion or stress cracking.

### Degradation by high energy radiation

High energy radiation or ionizing radiation induces degradation of polymers by forming free radicals or ions in the bulk of polymers. These reactive intermediates are capable of initiating chemical reactions which occur by free radical or ionic mechanisms and which result in scission as well as in crosslinking reactions.

Free radicals with a long lifetime which are often present in the bulk of the polymers after an irradiation trial are answerable for changes in properties even a long time after the trials. High energy radiation often initiates autoxidation reactions which result in an oxidation of the irradiated surface and of the backside of the sample.

### Mechanical degradation

Mechanical degradation refers to fracture processes as well as to chemical reactions caused by mechanical stress. Mechanical stress by tensile or shear forces, eg during processing, can result in ruptures of chemical bonds, indicated by free radicals or induce chemical changes by the displacement of molecules and the disruption of molecular interactions. Bond scissions strongly depend on the physical state of the polymer.

Even polymers in dilute solutions degrade under the influence of mechanical stress e.g. induced by flowing through a capillary or by ultra-sound treatment.

## 6 FUNDAMENTAL PROBLEMS OF ACCELERATED TESTS

Accelerated tests have a number of intrinsic problems which have to be considered both when designing the trial and its analysis and when estimating the significance and limitations of the results.

There is need for a proven procedure to relate the degree of degradation with the level of the degrading agent and time. As mentioned earlier, this is more critical with tests for performance prediction or design data but in all cases some understanding of the degradation process in relation to degree of acceleration is necessary.

Any relation between degradation, acceleration and time may only be valid for a limited range of acceleration ie the degradation mechanisms may change with level of agent.

It is not generally easy to simulate the service environment accurately as there may be a number of agents acting simultaneously, the level of agent may vary with time and its exact nature may be difficult to match.

If the accelerated tests do not include all the degradation agents present in service, procedures are needed to model any synergistic or simply superimposed effects.

These problems form the basic limitation of accelerated tests simply because the requirements of relationships between degree of acceleration and time and between degree of acceleration and degradation mechanisms, the interaction of degradation agents and the validity of test conditions in relation to service are not generally known with sufficient accuracy or certainty. They are hence the reason why the vast majority of accelerated durability trials are really only comparative and cannot be used for prediction with confidence.

A further difficulty is that the degree of effect of a degradation agent will be different for different properties or parameters measured. Hence it is necessary to know the critical parameter for any given application in advance of designing the trial.

## 7 COMPARISON WITH NATURAL DEGRADATION

Accelerated tests are used because the time scales for proving products under natural or service conditions are too long. However, it is clear that to completely prove the validity of accelerated tests and predictions made from them it is necessary to obtain correlation with natural exposure or service performance. Whilst this perfect situation cannot always be achieved it is highly important that every effort is made to verify accelerated results by comparison with natural exposure or service.

Hence, whenever possible natural exposure or service trials as appropriate should be established in addition to any accelerated test programme. Not only will the results add to information verifying or otherwise the validity of accelerated tests but in the case of new products or applications may provide early warning of unforeseen failure.

## 8 PUBLISHED STANDARDS

It is always desirable, and for quality assurance purposes normally essential, to use recognised standard test methods and procedures. A survey of the status of test methods for accelerated durability testing indicated that current national and international standards were not totally adequate for all purposes, but, nevertheless, despite their limitations they should be used where possible.

A list of current relevant standards is given in Appendix A.

## **9 STEPS IN DESIGNING AN ACCELERATED TEST PROGRAMME**

Any accelerated test programme or trial should be systematically designed and a number of steps in this process can be identified:-

Define the purpose and objective of the trial (see Section 3).

Specify the lifetime prediction needed, the acceptable uncertainty and the acceleration levels which are viable.

(See Sections 10, 12 and 13, 14, 15, 16 or 17, as appropriate)

Decide the critical degradation agents.

(See Section 4)

Decide whether whole products or test pieces are to be exposed to the degradation agents.

(See Section 12)

Consider synergistic effects and combined agents to establish the limitations of the trial in relation to service conditions.

(See Sections 4 and 6)

Decide the critical monitoring parameters.

(See Section 18)

Select analysis model(s).

(See Sections 5 and 10)

Decide on test conditions.

(See Section 7, 10 and 20, 14, 15, 16 or 17, as appropriate)

Decide on experimental procedures.

(See Sections 7, 18 and 13, 14, 15, 16 or 17, as appropriate)

Specify test piece or product preparation.

(See Section 12)

## **10 PREDICTIVE TECHNIQUES AND MODELS**

### **10.1 INTRODUCTION**

The general purpose of accelerated tests is to predict service performance. Hence procedures are needed to extrapolate the accelerated test data to service conditions. To model the degradation process requires:

- a) A function for the change of the parameter with time.
- b) A function for the rate of change of the parameter with level of the degrading agent.

The change in parameter with time may take several forms and the form may vary with the

level of the degrading agent. Indeed using too great an acceleration resulting in changing the degrading mechanism and hence the rate of change is a common pitfall.

Some of the possible forms of the change of parameter with time are shown in Figure 1.

Figure 1      Examples of Degradation Curves

The easiest form to handle, a linear relationship, is unfortunately frequently not found because of the complicating effect of several factors. There may be an induction time due, for example, to protective additives or an initial non-linear portion while equilibrium conditions are reached. A chemical reaction may produce a linear change whilst a physical effect may be logarithmic and the two may occur together. An auto catalytic reaction will show an increasing rate after a period of time. The cyclic trace shown is a real example of a rubber at elevated temperature first curing more then softening and finally becoming brittle.

In some cases it may be possible to transform a curve to linear form by, for example, taking logarithms. With composite curves it can be sensible to deal with only one portion, for example that after equilibrium has been reached and which may then be linear. Very commonly when similar materials are being compared, the shape of the curve is ignored and the time taken to say 50% of the initial value. This could be very misleading if materials with different curves were compared.

When the form with time has been established and a suitable measure to represent that form selected, the relation with the level of the degradation agent is needed to extrapolate to the service level from measures made at several accelerated levels. It would be feasible to make an empirical fit to the graph of rate of change against level although it is inevitably dangerous to do this with no theoretical justification. In cases with multiple degrading agents and hence a complicated relation it could however be the only possible option. Normally an established form with theoretical justification is fitted if possible.

## 10.2 ARRHENIUS RELATIONSHIP AND EFFECT OF TEMPERATURE

The Arrhenius relationship is:-

$$K(T) = A \exp(-E/RT)$$

Thus:-  $\ln K(T) = -E/RT + C$

Where:-  
K(T) is the reaction rate for the process  
E is the reaction energy  
R is the gas constant  
T is absolute temperature  
C is a constant

A plot of  $\ln K(T)$  against  $1/T$  should yield a straight line with slope  $E/R$  which can with caution be extrapolated as shown in Fig 2.

Figure 2 Arrhenius Plot

An alternative way of using the Arrhenius equation is to consider  $E/RT + C$  as a shift factor when a master curve can be built up from the material's response at different temperatures. This technique has the advantage that no particular measure of the reaction rate has to be chosen nor any form assumed for the change of parameter with time. However, as always considerable care has to be taken with extrapolation.

The Arrhenius relation is generally the first choice to apply to the effects of temperature but no

general rule can be given for the measure of reaction rate (change of parameter with time) to be used with it. Very frequently the time taken to a given % of the initial value is chosen.

When a form of the change of parameter with time is proposed, a power law is usually tried first:-

$$f(X) = X^n$$

Combining these gives the Avrami equation:-

$$X = X_0 \exp[-At^n \exp(E_n/RT)]$$

Clearly other forms of reaction rate may be more appropriate as outlined in 10.1.

There are occasions when the Arrhenius equation does not give a straight line and hence there is clear indication that predictions from it will not be valid. An alternative expression which has improved the line in certain cases is:-

$$\ln K = \ln K_0 + B(T_0 - T)/10$$

Where:-  $K_0$  is the reaction rate at a reference temperature  $T_0$ .

### 10.3 ARTIFICIAL WEATHERING

Weathering is clearly a more complicated case than heat ageing alone because there are temperature effects added to the light and probably other agents such as moisture, ozone, etc as well. Not surprisingly there is no very widely accepted relationship equivalent to Arrhenius. The result is that many workers have developed empirical relations which are usually only shown to be applicable to a narrow range of materials and conditions.

An attempt can be made to combine the various effects. In a number of cases at least the rate of degradation can be considered as proportional to intensity of light and hence to radiation dose:

$$X = X_0 + bD$$

Where:-  $D$  = Radiation dose

This can be combined with Arrhenius for temperature effects to give a relation of the form:-

$$X = X_0 D \exp(-E/RT)$$

Rather than linear, other proposals for the relation between property and radiation dosage include a power law and an exponential relationship:-

$$X = X_0 + bD^n$$

or  $X = X_0 + a \exp(D)$

Note that dosage has been used, although this is substituted by time of exposure by many workers.

Another form used is:-

$$K = 10^{b(D-a)}$$

Where :- K is ratio of properties  $X / X_0$

The constant a represents an induction period before degradation starts which is commonly found.

A further approach is to start with a relation of the form:-

$$X = f(y_1 + y_2 + y_3 \dots + y_n)$$

Where  $y_1$  etc represent the various factors or agents which may cause degradation, e.g. dosage, intensity, temperature, humidity.

Regression analysis techniques are then used to find the significant agents and produce a model for the particular data in question. This is essentially an empirical approach and alternatively a mathematical form for the data could be found by curve fitting without consideration of the effect of individual agents. Extrapolation is then particularly dangerous.

In many weathering trials results are only available for one set of conditions and strictly no extrapolation can be made for temperature and the degradation is assumed to be independent of dosage rate.

#### 10.4 EFFECT OF LIQUIDS

The case of liquids is simpler than weathering in that it is essentially a two agent situation, liquid and temperature. However it is generally necessary to take account of the rate of diffusion of the liquid into the material which may be slow in relation to the time scale of an accelerated test. Also, it is necessary to consider that there may be physical change (swelling) of the polymer as well as chemical degradation.

When there is equilibrium absorption the situation is similar to heat ageing, the form of change with time has to be modelled to a degree of degradation specified and then it is sensible to use an Arrhenius relation to account for temperature change. Clearly it is advantageous to work with thin test pieces such that equilibrium is obtained, but this is not always possible and extrapolation to thicker products may be needed.

Diffusion in the unsteady state before equilibrium is described by Fick's 2nd law:

$$dC/dt = D d^2C/dx^2$$

Where: C = volume  
t = time  
D = diffusion coefficient  
x = thickness

As a general rule the time to equilibrium is proportional to the square of thickness. When the diffusion coefficient is known a suggested estimation of the time to reach equilibrium to a depth b is:

$$t = b^2 / 2D$$

Both the diffusion coefficient and the solubility coefficient vary with temperature in

accordance with an Arrhenius relationship. The diffusion coefficient increases with temperature but the solubility coefficient increases for gases and decreases for vapours. For a full treatment of absorption a text on mass transport should be consulted.

For the particular case of water at less than 100% humidity the amount of water absorbed at equilibrium is dependent on humidity. In some, but by no means all, cases it may be simply linear and the relation needs to be known if performance at different humidities is to be estimated. Again absorption will change with temperature.

It becomes apparent that to transpose data from different humidities, temperatures, thicknesses and varying levels of approach to equilibrium can be very involved. Further, whilst the transport relationships apply to the uptake of fluid, the effect on properties at times below equilibrium can never be simple because of the varying concentration with thickness.

## 10.5 DYNAMIC CONDITIONS

All the treatments discussed above have been concerned with static conditions, ie where in the accelerated tests the level of the degrading agents has been held constant throughout one exposure, and any extrapolation to service implicitly assumes that conditions there will also be constant. In real life however it is much more likely that service conditions will be cyclic. Generally therefore, further approximations have to be made.

Most commonly the worst situation is assumed, for example with temperature the reaction rate will be something like doubled for a 10 °C rise and lower temperatures will be relatively insignificant. With natural weathering the conditions change daily and geographically and this is the basic reason why light dosages should be used rather than time. Even with temperature it is theoretically possible to estimate an equivalent "dose", ie the temperature which represents the mean of temperatures encountered, duly weighted for their degradation effects. With fluids contact can be intermittent with drying out possible. The total chemical effect is likely to be less for less contact but there may be effects of expansion and contraction. Such conditions would best be modelled in the accelerated experiment.

In some simple cases an additive approach can be successful. The service life is divided into stages, for example moderate exposure for one year, severe exposure for one month and low exposure for five years. The predicted effects for the three periods can be summed and the condition of the product at the end, and hence residual, lifetime estimated.

## 10.6 LIMITATIONS

From the foregoing it is clear that prediction from accelerated tests is at best a hazardous procedure. To minimise the limitations in any particular case it is essential to design the accelerated trials to simplify and ease as far as possible the prediction process. Of the limitations the most important can be summarised as :

Statistical uncertainty due to quality and number of test results.

Quality of accelerated data in terms of test conditions being sufficiently valid to relate to service conditions.

Validity of extrapolation procedure

The first is a matter of minimising variability, maximising the quantity of data and minimising the degree of extrapolation needed. The quality of accelerated data in relation to service is dependent on a considerable number of factors all of which have been identified in this guide and must be systematically addressed when designing the trials. The validity of extrapolation

is likely to be better the more proven the procedures used and the smaller the degree of extrapolation.

## 11 VARIABILITY AND UNCERTAINTY

### 11.1 REPEATABILITY AND REPRODUCIBILITY

Variability in accelerated durability tests has a profound effect on interpretation of results obtained from each of the primary uses for ADT. Repeatability and reproducibility are two terms used to characterise variability. Repeatability is defined as the ability of a single test to produce the same result in replicate specimens of a material exposed simultaneously in a single device. Reproducibility is defined as the ability of an ADT to produce the same result in replicate specimens exposed in identical devices, each running the same ADT. Typically, the devices are operated in separate laboratories.

Artificial weathering is used as an example here as it generally exhibits the worst variability. Repeatability of an ADT is illustrated in Figures 3 and 4. Figure 3 is a graph of 60° gloss for eight replicate specimens (all cut from a single 25 cm x 40 cm piece) of a material exposed in a single open-flame carbon arc device. Each of the eight replicate specimens was kept in the same position throughout the exposure.

Figure 3      Repeatability in ADT. Eight replicate specimens exposed without repositioning in a single device.

Figure 4 is a graph of 60° gloss for eight replicate specimens of the same material exposed in the same open flame carbon arc device. Each of the eight replicate specimens was repositioned within the specimen drum once per week during the exposure using the procedure recommended by ASTM G23. When the replicate specimens are repositioned during the exposure, the repeatability of ADT's is significantly improved.

Figure 4 Repeatability in ADT. Results for eight replicate specimens exposed in a single open flame carbon arc device, specimens repositioned weekly during the exposure.

The importance of the improvement in repeatability between these examples is seen in the "difference 2-sigma limits" shown in Table 1. The difference 2-sigma limit is the difference that must be observed between two specimens in order to be 95% confident that the difference between the specimens is statistically significant. When the specimens are repositioned during the exposure, a much smaller measured difference is needed to detect differences between materials.

Table 1  
Effect of Repeatability and Reproducibility on Difference  
Two Sigma Limits for ADT

Repeatability Within a Single Test Device				
Specimen Repositioning	Hours Exposed	Mean 60° Gloss	Standard Deviation	Difference 2-sigma limit
none	1025	57.0	10.4	29.4
weekly	1025	67.1	2.5	7.0
Reproducibility Between Eight Identical Test Devices				
Specimen Repositioning	Hours Exposed	Mean 60° Gloss	Standard Deviation	Difference 2-sigma limit
weekly	1400	59.9	20.6	58.3

weekly	1600	46.1	22.1	62.9
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As seen in the top half of Table 1, accelerated durability tests must have good repeatability in order to detect reasonable differences between materials with any confidence. However, good repeatability for an ADT does **not** ensure good reproducibility. Reproducibility is a function of the variability within an individual test device or chamber (repeatability) **and** between identical test devices running the same exposure cycle. In order for results from accelerated durability tests to be of value, good reproducibility is essential. Unfortunately, it is very difficult to achieve, and is very poor in most accelerated durability tests.

Figure 5 shows results for eight specimens of the same material used in Figures 3 and 4. In this case, the eight specimens (again, all were cut from a single 24 cm x 40 cm piece) were exposed in eight filtered open flame carbon arc devices, all running the same test cycle. However, the differences in degradation rates between the ADT devices for these eight identical samples is very large. In other words, the reproducibility is very poor. The impact of this poor reproducibility is dramatic. The data in the bottom half of Table 1 shows that this poor reproducibility causes the difference 2-sigma limits to be very high. For example, a single specimen from each of two lots of this material tested in two separate devices must show a 60° gloss difference of 58.3 units in order to be confident that the lots are different.

Figure 5      Reproducibility for eight filtered open flame carbon arc devices running the same test cycle, identical specimens exposed in each device.

Research now being conducted in the ASTM G3 Committee on Durability of Non-metallic Materials shows that this poor reproducibility between devices is not isolated to carbon arc devices. The most modern devices with more sophisticated control should be better. The causes of poor reproducibility are many but are largely consequent on the level of control and distribution of exposure parameters such as temperature and irradiance. An effective way to compensate for this variability is to use a reference lot of material exposed at the same time and in the same device as test material and normalise all results to those for the reference or "control" lot. In order to be useful, the reference material used must show changes that relate to the properties of interest for the test specimens.

## 11.2 UNCERTAINTY OF RESULTS CAUSED BY POOR REPRODUCIBILITY

In many industries, product or material specifications require a defined level of performance after exposure in an accelerated durability test. These specifications are designed to assure product quality and consistency in purchased materials, and the test cycle and exposure time are carefully defined. Such specifications are intended to evaluate variability in purchased products or materials but often ignore the variability in the ADT itself. Poor reproducibility in an ADT used for a specification test can lead to dramatic differences in perceived "quality" for a single lot of material. Consider the data in Figure 5 as an example. If this material had to pass a specification which required a minimum 60° gloss value of 50 units after 1500 hours, the results from three of the devices could be used to reject the lot, data from three devices would show that it marginally passed, and data from two of the devices would show that it had excellent performance. Poor reproducibility means that specifications which require an arbitrary level of performance after a specified exposure time in an ADT can be very misleading. Without use of a control or reference lot, specification test results will be highly variable, and much time will be wasted on re-testing and re-evaluations of rejected material. If the variability of the ADT is taken into consideration without use of a reference or control lot, the specified level of performance after exposure would have to be set so low that the test would be meaningless.

Accelerated durability tests are often used to get an early indication of the durability of materials before results from long term exterior or field exposures are available. These usually involve comparisons between polymers, stabilisers, or "old" and "new" formulations. Hopefully, the ADT tests that are used realistically approximate and accelerate actual use or service conditions. However, the poor reproducibility typical for ADT's means that material comparisons based on exposures in identical devices run at different times or in different locations are rarely meaningful. As illustrated by the data in Table 1, reasonable comparisons are best made between materials exposed (with periodic repositioning) at the same time in the same device. Even when this is done, the variability within the materials and within the test chamber itself must also be considered. Unfortunately, the variability cannot be reduced to zero, so exposures of replicate specimens of each material is essential. The materials can then be compared using some elementary statistical approaches to determine whether differences in the measured properties after exposure are significant. This can be done using:-

$$\bar{X}_1 - \bar{X}_2 = t_{(v_1+v_2)} S_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}} \quad (1)$$

where:

$X_1$  = mean property, property change, or property retention for material 1

$X_2$  = mean property, property change, or property retention for material 2

$t_{(v_1+v_2)}$  = students t for two tailed 95% confidence for stated degrees of freedom

$S_p$  = pooled standard deviation:  $((v_1 S_{12} + v_2 S_{22}) / (v_1 + v_2))^{0.5}$

$n_1$  = number of replicates for material number 1

$n_2$  = number of replicates for material number 2

Percent retention of a measured physical property is often used as the basis for material comparison. Table 2 shows how much the mean property retention of two materials must

differ in order to be 95% confident that the materials are really different. Note how increased variability or decreased reproducibility (as defined by the pooled standard deviation) significantly increases the required difference necessary to achieve the 95% confidence for real material differences. When more replicates of each material are tested, the difference between the means can be much smaller and still be significant. Note that one cannot test a single specimen of each material and be confident that any observed differences are real.

Table 2

Required Difference Between Mean Percent Property Retention for Two Materials Needed to be 95% Confident that the Materials are Actually Different

Number of replicates for each material	Degrees of freedom ( $v_1 + v_2$ )	Student's t needed for 95% confidence	Pooled standard deviation for two materials exposed in one device (in percent property retention)			
			2%	4%	6%	8%
2	2	4.3027	8.6	17.2	25.8	34.4
3	4	2.7764	4.5	9.1	13.6	18.1
4	6	2.4469	3.5	6.9	10.4	13.8

In order to compensate for poor repeatability and reproducibility in ADT, comparisons should not be made at arbitrary, preset exposure times. Test specimens should be analysed at relatively frequent exposure intervals so comparisons can be made when the differences between the materials are at their maximum. When more than two materials are being evaluated, data should be analysed using procedures such as Analysis of Variance in order to make meaningful comparisons.

Ranking of materials after exposure is one way to compensate for poor reproducibility in ADT, especially when comparing results between accelerated durability tests and exterior exposures or between separate accelerated durability tests. Studies in the ASTM G3 Committee on Durability of Non-metallic Materials have shown that materials exposed in ADT's with poor reproducibility can be compared using Spearman Rank Correlation. In several cases where the rates of degradation for a series of identical materials exposed in different devices running the same cycle showed poor reproducibility, the devices all ranked the materials in essentially the same way, with typical Spearman Rank Correlation Coefficients of 0.95 or higher.

Use of accelerated durability tests to estimate service life is becoming more and more attractive as the inherent durability of polymers and products improves. In many cases, the Arrhenius model is the method of choice for service life estimates. In order to estimate service life using the Arrhenius model, a series of experiments at several temperatures are conducted and the rate of degradation or property change is determined for each temperature. The logarithms of the degradation rates are then plotted against the reciprocal of the absolute temperature to determine the equation describing the rate/temperature relationship. This equation is then used to estimate the time to produce a defined property change associated with failure. Alternatively, the time to produce a property change associated with failure is plotted against the reciprocal temperature. Graphical interpolation or linear regression analysis is then used to estimate the time necessary to produce failure at the anticipated service temperature. Unfortunately, most estimates of service life reported using this procedure ignore the variability inherent in the testing. It has been shown that very small errors (4.2 kJ/mole) in

determination of the activation energy can cause errors of 100% in extrapolated estimates of service life.

The regression equation describing the relationship between log time to failure and reciprocal temperature usually shows a high degree of correlation (typical  $r^2$  for regression is 0.92 or higher). However, because the Arrhenius relationship between service life and temperature is logarithmic, the uncertainty in calculated service life can be very large.

Service life estimates based on the Arrhenius model should be considered as "maximum possible" rather than "expected" because of the errors associated with the estimates, even with data that seems to fit the Arrhenius model very well. Where there is any significant risk associated with failure, the lower 95% confidence interval for the estimate of service life is much more important than the mean.

Some researchers persist in using "acceleration factors" between ADT's and exterior exposures. They use an acceleration factor relation "x hours" in the ADT to "y months" in a particular exterior exposure to make claims about expected service life. Figure 6 shows the results from Florida exposures of the same material tested in the carbon arc exposures shown in Figures 3 - 5. The data shown in Figure 6 is for 48 replicate samples of this material simultaneously exposed on a single exposure rack.

Figure 6      Gloss data for 48 identical samples exposed simultaneously on a single exposure rack (same material used in Figures 3 - 5).

The exterior exposure data in Figure 6 is the "best case" for use in calculating an "acceleration factor" because the poor reproducibility inherent in exterior exposures is not considered. After 24 months, the 95% confidence interval for 60° gloss is 43.7 to 70.5. Using this data and the plots of gloss as a function of exposure time for the ADT devices shown in Figure 5, the exposure time necessary to produce the results which could be expected after 24 months ranges from 1040 to approximately 2300 hours. This clearly demonstrates the futility in calculating and using "acceleration factors". The poor reproducibility shown for ADT's combined with the poor repeatability and reproducibility inherent in exterior exposures makes use of these "acceleration factors" meaningless.

A more recent approach to prediction of service life from ADT is based on the use of probability or reliability theory. In this approach, time to failure (or service life) is considered as a distribution rather than a mean. This method offers an advantage because variability in time to failure (poor reproducibility between ADT devices) is considered automatically. However, variability in time to failure is typically considered to be strictly a function of the material with little or no variability from the ADT devices. In some cases, service life predictions based on this approach simply assume an acceleration factor between an ADT and field exposure. However, because variability is expected, this approach may be very promising. Before it can be fully implemented, however, accelerated durability tests which accurately simulate service conditions must be developed. This approach also requires use of large numbers of test specimens and a number of test devices dedicated to the ADT cycles needed.

### 11.3 CONCLUSIONS

Poor reproducibility in ADT means that specification tests requiring an arbitrary level of performance after a specified exposure time can be very misleading. Normalising results for test materials to those from reference or control lots in this use of ADT will help minimise the effects of variability.

To compensate for poor reproducibility and repeatability in ADT's, materials must be exposed in the same device at the same time. This is essential to obtain meaningful comparisons between materials. Ranking of materials or normalising results to those for reference or control lots can reduce the impact of poor reproducibility between devices running the same test. Use of multiple replicates and analysis of data using procedures such as analysis of variance is necessary to minimise the effect of variability.

Use of acceleration factors equating "x hours" in an ADT to a specific field or exterior exposure is meaningless because of the poor reproducibility in accelerated durability tests and in exterior exposures.

Service life predictions based on ADT are very sensitive to the effects of variability. Such estimates should be considered "maximum possible" rather than "expected" service life. When estimates of service life are made, the lower 95% confidence interval of the calculated service life should always be reported. This is especially important when there is any risk associated with failure.

## 12 TEST PIECE HISTORY

As degradation processes often start with attack of the degradation agents on chemical irregularities of polymer molecules or on additives or impurities in the bulk of the polymer, all treatments of the polymer or of the specimen which influence these parameters also influence the degradation behaviour. Therefore production methods and processing variables, machining and conditioning etc, influence the degradation of a test piece or a product of polymeric material.

Annealing of a polymer to increase the degree of crystallinity may, for instance, result in a better stability against chemical degradation and photo-oxidation, because the chemical agent or oxygen cannot penetrate in crystalline regions.

If the speed of cooling of an injection moulded sample can influence the degree of crystallinity at the surface it also influences the degradation behaviour. Poor moulding conditions of a polymer sample which result in high levels of internal stress can reduce the weathering stability.

Preliminary treatment of a PVC-surface, with a solvent for instance, may produce some additional chromophores which increase the attack by photons during weathering, but on the other hand, a smooth surface of PVC or residues of the solvent may improve the stability against discoloration.

The testing of a material does not necessarily suffice to make a prediction in respect of the ageing behaviour of a component part manufactured from it. The ageing behaviour of the component part also depends on the processing conditions and installation conditions when it is finally used. Therefore, an additional test of complete component parts is at times desirable but will be limited to size restraint of exposure cabinets.

Test piece history is often the cause for lack of correlation between the results of the ageing behaviour in practice and in accelerated durability tests. Consequently, it is important to standardise the production of test pieces and their conditioning. Preferably, the production of the components should be simulated as closely as possible.

## 13 HEAT AGEING

### 13.1 EQUIPMENT

Ovens for ageing may be either the single chamber or multi-cell type. If the former is used only very similar materials should be exposed together to prevent cross migration of ingredients such as plasticisers or antioxidants.

No copper or copper alloys which may accelerate ageing of, for example, rubbers should be used in the oven.

Because the rate of air exchange is likely to affect the degree of ageing this should be standardised. Effects have not been fully investigated and the best advice at present is to conform to the requirements of ISO 188 which calls for between 3 and 10 complete changes of air per hour. The velocity of air over the test pieces may very significantly effect the rate of degradation and should therefore also be standardised. Investigation of this effect is currently being carried out for rubbers.

Arrangements are necessary for hanging test pieces such that they are fully exposed to the air flow and can only be hung in the volume of oven which has been proven to be within temperature tolerance.

Many standards call for temperature control to  $\pm 2$  °C but  $\pm 1$  is recommended and  $\pm 0.5$  is desirable. The temperature measuring devices should be formally calibrated and it is desirable that the temperature is continually recorded during test.

Tests are normally made using air at ambient pressure but if other atmospheres are required then special arrangements have to be made. If an inert atmosphere such as nitrogen is used it is necessary to flush the chamber initially as small amounts of oxygen may affect the result.

Tests have been standardised for both air and oxygen at elevated pressures but are less often used because of the complication of the extra accelerating agent.

Whereas the vast majority of heat ageing tests are carried out with test pieces in the unstrained state, compression or tension set and continuous stress relaxation tests on rubbers, either in tension or compression, require straining jigs and possibly measuring apparatus to be exposed either in or mounted on the oven. The requirements of ISO 6914, ISO 3384 or ISO 6056 should

be followed for stress relaxation, and ISO 815 or ISO 2285 for set depending on the mode of straining. Similarly, for creep apparatus is given in ISO 899 and ISO 6602.

### 13.2 TEST PIECES

The number and form of test pieces has, de facto, to be suited to the tests used to monitor degradation and the number of measuring points as a function of time and temperature.

For general purposes it is recommended that internationally standardised test methods are used to monitor degradation so that the results will be comparable with others. One factor which should be considered, however, is the test piece thickness or bulk which will limit the rate of oxygen diffusion. Increasingly at higher ageing temperatures the oxidation processes may proceed faster than oxygen can diffuse through the bulk of the sample and hence ageing effects will be curtailed. Hence results may only be valid for products of similar size when bulk properties are measured. For rubbers at least it has been suggested that the effect of oxygen diffusion is minimised if test pieces below 1 mm in thickness are used.

### 13.3 TEST CONDITIONS

For simple comparative trials a single temperature is chosen, either a commonly specified standard temperature or one relevant to service. Similarly, either one or relatively few exposure times are used.

For trials where the trends with time and temperature are to be followed, measurements will be made over a range of both these factors. It is recommended that a minimum of 5 temperatures are used. If the purpose of the trial is to establishing a form of service temperature limit the procedure of IEC 216 or ISO 2578 is a satisfactory way of choosing the temperature range. If the purpose is to make extrapolation to a lower temperature then the lowest temperature of test compatible with a satisfactory degree of degradation within the allowed time scale of the experiment is included. Also, in this case, the highest temperature used cannot be such that reactions taking place are not relevant to lower temperatures.

The exposure times chosen need to be such that an adequate measure of the reaction rate can be made and equilibrium has been reached in the sense that any transient short term degradation mechanisms have passed. For many materials the change in the parameter chosen to monitor degradation will not be a simple function of time such as linear or logarithmic and hence the reaction rate cannot readily be taken as the slope of the property/time graph. In each case the form of the degradation time graph has to be considered in the light of degradation mechanisms likely to be taking place before choosing both the exposure period and the measure of reaction rate.

Very commonly the reaction rate is taken as the time for the chosen parameter to fall to a given level, for example 50%, of its initial value. This is most likely to be satisfactory when the degradation/time plot is fairly uniform.

Conditioning and other general experimental procedures are best carried out in accordance with the relevant international standard to provide comparability. When all exposures cannot be carried out simultaneously in identical ovens there is no intrinsically best order to be adopted. However, if the tests are made in descending order of temperature some data is collected relatively quickly and the last samples are relatively young when exposure is started.

When single ageing periods are used it is good practice to make measurements of the parameter used to monitor degradation on both aged and unaged test pieces on the same occasion to minimise testing variability. When exposures are made over very long time scales it may be advantageous to have more than one set of unaged test pieces.

Heat ageing tests are usually carried out using constant temperatures but for special purposes a cyclic pattern might be used, for example to simulate service or to consider thermal shock.

## 14 WEATHERING

### 14.1 EQUIPMENT

The essential influencing variables of the weather are simulated in accelerated weathering devices. These are:

#### 14.1.1 Radiation

The global radiation on the earth's surface serves as reference, ie the sum total of direct solar radiation and diffuse sky radiation. The spectral distribution of global radiation is stated in Table 4 of the CIE Technical Report No. 85 (1989). To test the ageing behaviour of polymer materials, a good simulation of the spectral distribution of solar radiation in the UV and also in the visible spectral range is essential. The IR range does not contribute directly to the photochemically initiated ageing processes. However, it is important as far as heating of the object exposed to radiation is concerned and, thus, has an indirect influence on ageing.

The irradiance on the samples in accelerated weathering devices is, as a rule,  $550 \text{ W/m}^2$  in the spectral range  $290 \leq \lambda \leq 800 \text{ nm}$ . This corresponds to the irradiance at the equator with a cloudless sky, at midday, with a vertical solar altitude, ie at the time of equinox. However, the geometrical exposure conditions are not precisely defined because too little is known of their influence on the ageing result for a given total irradiance. The samples are exposed to a mixture of direct and scattered radiation. The ratio of both types of radiation depends on the design of the accelerated weathering device.

In the interest of a greater acceleration of ageing, higher irradiances are also used at times. In these cases, it is recommended to first examine the connection between irradiance and ageing in respect of the individual test problem. It is often not linear.

The following are used as radiation sources in accelerated weathering devices:

**Carbon Arc:** Until well into the Fifties, the carbon arc was the only radiation source which supplied a sufficiently high irradiance for artificial weathering purposes. In the early stages, the spectral energy distribution of the radiation was very poorly matched with that of the global radiation. Matching was improved by mixing additives with the carbon, but it is still unsatisfactory. For historical reasons and for special applications, the carbon arc is still being used by some workers.

**Xenon Lamps:** These emit a radiation, the spectral energy distribution of which is very similar to solar radiation across broad ranges. The spectrum is, to a far reaching degree, independent of the type and operating conditions of the lamp. Radiation with  $\lambda < 300 \text{ nm}$  is eliminated by means of a filter. Depending on the filter chosen, the radiation can be adjusted to different test conditions in the short-wave range. The maxima in the near infrared range are also reduced by means of a filter. The xenon lamp is considered to be the best source of radiation for simulating solar radiation in the UV and visible spectral ranges.

**Metal Halide Lamps:** These supply a radiation with a multi-line spectrum which, in the context being discussed here, is considered to be, as it were, continuous. The spectrum largely depends on the type and composition of the metal halide used, as well as on the type and operating conditions of the lamp. As against this disadvantage compared to xenon lamps, there is the advantage of 2.5 - 3 times higher radiant efficiency. The lower heat generation

linked with this, with the same effective radiant power, makes them particularly suitable for large radiation units or for equipping climatic chambers with artificial solar radiation. Experiments are at present being performed to determine to what extent the weathering results correspond between xenon or metal halide lamps when the other exposure conditions are identical.

**Fluorescent Lamps:** Due to their low radiance, fluorescent lamps are not suitable for simulating global radiation over the entire spectral range with the required high irradiance. However, with special fluorescent lamps, it is possible to simulate the spectral distribution of global radiation in the spectral range  $300 \leq \lambda \leq 360$  nm adequately well. When the distance between the fluorescent lamps and the sample is only a few centimetres, irradiances such as occur outdoors can be achieved on the sample.

This spectral range is decisive as far as the primary photochemical processes in the polymers is concerned. However, it depends on the respective test objective as to whether simulation of only this partial range of global radiation is permissible and expedient. Devices with fluorescent lamps are, eg well suited for the study of decomposition processes in the polymer matrix and the effect of different stabilisation systems. They are, to a certain degree, suitable for testing colour change in coloured pigments or dyed systems, but they are unsuitable for the study of ageing processes in which heating of the surface as a result of absorption of the visible IR radiation plays an essential role. They have the advantage of relatively low cost.

#### 14.1.2 Temperature

Many decomposition process in organic materials are temperature-dependent. The rate of a decomposition reaction is usually greater with increasing temperature. An approximation rule from reaction kinetics states that when the temperature increases by  $10^\circ\text{C}$ , the reaction rate approximately doubles. In many cases, it is found that photochemical decomposition is not simply dependent on the temperature, but that the change in a property has initially low temperature-dependence but increases very rapidly from a certain temperature onwards - which is material-specific.

In the case of amorphous or semi-crystalline polymers, the glass transition temperature  $T_G$  plays a role, since the mobility of the chains and the radicals above  $T_G$  increases and, simultaneously, oxygen diffusion is more rapid. The way in which this influences the decomposition rate depends on the material and the specific decomposition process.

The sample temperature is, on the one hand, determined by the environmental conditions, such as radiation and temperature and velocity of the ambient air, but on the other hand, it depends on the material-specific variables, such as the spectral absorptivity and degree of remission and thermal conductivity. It is difficult to measure the temperature of the sample exposed to radiation. Therefore, by way of substitution, the temperature of a black plate (black standard temperature) is measured in weathering devices. Lately, the black standard thermometer has been introduced in which the back of the black plate is thermally insulated with plastic. It gives a good approximation of the temperature of a black-coloured plastic plate during weathering in the device. With highly structured surfaces, eg with textiles, the sample temperature, particularly in the deeper areas of the structured surface, can even be above the black standard temperature. In the case of high black standard temperatures, such as are usual, for instance, for testing materials for interior fittings for motor vehicles, it has been found that the sampling room temperature also has an influence on the ageing behaviour. Therefore, it is necessary to measure both the black standard and the sampling room temperature, and to constantly adjust these independently of each other within the narrowest possible limits.

### 14.1.3 Water/Humidity

Differentiation is made between two mechanisms of action of water in the ageing of organic materials: on the one hand, the purely mechanical stress to which the material is subjected through swelling and shrinking as a result of changing humidity and water present in the environment and, on the other hand, the chemical reaction of the polymer material with the water, eg during hydrolysis or, indirectly, via the formation of OH and HO<sub>2</sub> radicals during exposure, which react with the organic material. In both cases, the penetration of the water into the material is decisive. Due to the low rate at which the water penetrates into the polymer, short humid or rain periods do not have the same influence on ageing as daytime and seasonal fluctuations in the use of the polymers outdoors. Therefore, to an increasing degree, preference is given to longer rain cycles, eg 102 minutes dry, 18 minutes rain. In special cases, rain and dry periods in the order of magnitude of several hours are employed.

The relative humidity of the air is measured at a defined point in the sampling room. It is an adjustment parameter for the weathering device. However, this data gives no indication of the relative humidity on the surface of the sample exposed to radiation since, as a result of the impinging radiation, the sample is warmer than the sampling room air.

## 14.2. REPRODUCIBILITY OF ACCELERATED WEATHERING RESULTS

The reproducibility of results in one and the same weathering device and in diverse weathering devices of the same or another type is an essential pre-requisite for communication between the different testing laboratories and for the applicability of accelerated weathering results to ageing behaviour in practice. It is, therefore, essential to continuously measure all exposure parameters in the weathering device - if possible, at the site of the sample - to keep them constantly within given tolerances over the weathering period, and to continuously record them. Moreover, it is expedient to additionally control the exposure conditions by simultaneously exposing a reference material, the ageing behaviour of which is well known. This can be a standardised reference material or, e.g. an in-house reference material. If the ageing behaviour is outside given tolerances, the weathering device must be technically checked.

## 14.3 ACCELERATION

In accelerated weathering devices, the sun shines 24 hours a day on the samples with an irradiance such as prevails at the equator at midday, with a cloudless sky, at the time of equinox. This is the essential reason for the acceleration of ageing processes in accelerated weathering devices. The radiant exposure  $H = \int E dt$ , to which an object is subjected in the course of a year in Florida, is achieved in the devices in approximately one fifth of the time. This results, purely mathematically, in an acceleration factor of 5 compared to the exposure conditions in Florida. This calculated factor does not take into account the other influencing variables which also contribute to accelerated ageing in weathering devices, eg the temperature. Also this factor will of course be different if related to other parts of the world or if the samples are intermittently exposed to the radiation source. There is no uniform acceleration factor for all test objectives. There cannot be one, because decomposition processes proceed differently, depending on the material and, consequently, react differently to the intensification of individual parameters of the weather. Even with one and the same material, different acceleration factors are observed, depending on which property change is considered. For instance, a colour change is based on quite different decomposition processes than a change in the mechanical properties.

Experience has shown that, in the case of the exposure conditions described, results are obtained which can, in general, be applied in practice. In principle, further accelerations are possible. However, experiments must first be performed to test whether these are permissible

in respect of the specific test objective. These are, eg higher irradiance: Careful! There is often a non-linear connection between radiant exposure  $H = \int E dt$  and the property change; shorter wavelength radiation than corresponds to the case of application: Careful! Other photo-chemical processes are initiated which lead to a different ageing behaviour than in the case of application;

higher temperature: Careful! Other thermally related decomposition processes can be initiated which have nothing to do with the ageing behaviour of the material at the place of application.

#### 14.4 TESTING COMPLETE COMPONENT PARTS

The testing of a material does not suffice to make a prediction in respect of the ageing behaviour of a component part manufactured from it. The ageing behaviour of the component part also depends on the processing conditions and installation conditions when it is finally used. Therefore, an additional test of complete component parts is at times desirable but will be limited by size restraint of exposure cabinets.

### 15 EXPOSURE TO LIQUIDS

#### 15.1 EQUIPMENT

Tests are usually made with test pieces simply immersed in liquid held in a glass container. The volume of liquid should be 15 times that of the test pieces and care taken that the test pieces are exposed on all sides. The containers are then held at the required test temperature using a single chamber oven (Section 13.1). If the liquid is volatile, the container, for example a flask, is fitted with a reflux condenser and an oil bath used for heating.

To simulate service conditions tests may be needed with exposure being on one side of the material only which is normally achieved by using a jig in which the test piece effectively forms one end of a container. Occasionally, with total immersion or one sided exposure, tests are needed under pressure when a special test rig would have to be developed.

Partial immersion tests are also sometimes used when the possibly more serious effects of oxygen at the interface are to be investigated.

Whilst most tests are carried out with the test pieces in the unstrained state, creep, stress relaxation and set tests require apparatus as mentioned in Section 13.1. Some materials are severely affected by particular liquids when strained and hence exposure under strain is necessary to fully assess durability. Such tests are often called environmental stress cracking and a variety of exposure methods have been standardised (ISO 4599, ISO 4600, ISO 6252). Apparatus conforming to any of these standards could be used but for design data purposes the constant stress method of ISO 62522 is often preferred.

For the particular case of exposure to water, tests may be made at particular, high levels of relative humidity when a controlled humidity cabinet with calibrated humidity meter is needed. A further specialised condition is exposure to salt spray with apparatus as given in ISO 4611.

#### 15.2 TEST PIECES

The form and number of test pieces are generally as noted in Section 12.2. However, a particular factor to be considered with liquid exposure tests is the rate of diffusion of liquid into the sample. Equilibrium absorption may take months or even years and this has to be

considered both when deciding on the test piece dimensions and exposure periods and when extrapolating results.

### 15.3 TEST CONDITIONS

As for heat ageing, for simple comparative trials a single temperature and one or relatively few exposure times are used. In such cases the effects of diffusion rate may seriously affect comparisons.

For trials where the trends with time and temperature are to be followed, measurements will be made over a range of both these factors. For temperature the comments made in Section 12.3 generally apply.

The choice of exposure times and the measure of reaction rate is made more difficult by the need to consider the time for equilibrium absorption to be reached. In deciding on test schedules it is necessary to consider the mechanisms of degradation and their time relation as simple swelling hydrolysis or oxidation will have different patterns. Ideally all tests would be taken until equilibrium was reached and it is generally necessary for the form of the degradation time graph to be considered before deciding on the measure of reaction rate.

Because of differing rates of absorption the use of time for a chosen parameter to reach a given level can be very misleading, whereas for simple swelling the property level at equilibrium may be a satisfactory measure. However, in addition to swelling there may be extraction of material which proceeds at a different rate.

For environmental stress cracking, measurements will be made as a function of either stress or strain. For analysis the concept may be introduced of a critical level below which no cracking occurs.

Although logically the liquids which are critical to the end use would be used it is often convenient and common practice to use standard reference liquids such as those in ISO 1817 which simulate typical fuels, oils etc. However, care must then be taken to consider the possible important effect of an apparently minor constituent or additive. Alcohols in fuels are an example. The concentration of the liquid, when it is a solution, will generally be an important factor to be evaluated and it cannot be assumed that the degree of degradation/concentration relation will be simple.

When a material has absorbed a liquid it can also be "dried out" after removal. A decision has to be made whether properties are measured immediately on removal or after "drying" dependent on the application and the information needed. Using both procedures yields most information and may allow extraction to be measured and to distinguish between permanent and reversible effects.

Cyclic exposure is not commonly used but may have application to model a service condition particularly where heat and hence oxidation will occur between immersion periods.

## 16 EXPOSURE TO GASES

### 16.1 EQUIPMENT

Other than air in normal ageing ovens, only apparatus for air or oxygen at elevated pressure and exposure to ozone have been standardised at the national or international level.

Oxygen or air bombs are essentially pressure vessels to contain test pieces under pressure and several bombs are normally connected to a cylinder of gas and contained in an oven. Needless to say, strict safety precautions have to be taken and other than for air the bombs purged before final filling.

Specialised apparatus for ozone exposure is described in, for example, ISO 1431. It may be noted that the air velocity over the samples may effect degradation and should be standardised. There is also considerable controversy over the trueness of the different methods of measuring ozone concentration and the draft ISO 1431:Part 3 should be noted.

For all other cases test rigs would have to be specially developed. For total exposure the standard bombs may be adaptable to other gases or to simulate service, for example seals, the jig may give exposure only to selective areas of test sample. Such jigs may strain the test piece or product during exposure and include provision for the monitoring of creep, set or relaxation.

In the case of ozone exposure samples are always exposed in the strained state as there is generally a threshold strain below which no damage occurs. Tests are usually made with static strain but provision is made in ISO 1431 for dynamic exposure.

## 16.2 TEST PIECES

The form and number of test pieces are generally as noted in Sections 13.2 and 15.2.

## 16.3 TEST CONDITIONS

The general principles in terms of times and temperatures of exposure are as for heat or liquid exposure.

In many cases the exposure will be to the pure gas but in other cases, notably ozone testing, the test gas is used diluted with air. Then the effect of varying concentration may be studied but no simple relationship with degradation can be assumed. The reaction rate for ozone attack can be the time to cracking or the threshold strain for cracking deduced.

Depending on the gas and the resulting mechanism of degradation the questions of equilibrium absorption, swelling and extraction can arise as noted for liquid exposure. In this respect it is relatively easy to make tests under elevated gas pressure which will effect the absorption. An extreme case is at very high pressures when on release of pressure the absorbed gas causes damage to the test material by "exposure decompression".

Cyclic exposure is not commonly used except where the gas pressure is used to cause mechanical strain.

# 17 IONISING RADIATION

## 17.1 SOURCE

### 17.1.1 Types of Radiation

In-service exposure may be to a range of ionising radiations such a x-rays, gamma rays, electron beams, beta radiation or alpha particles. Exposure to neutron radiation is also a feature of some equipment. All of these ionising radiations have characteristics which need to be considered when accelerated radiation testing is done: the most important characteristics are penetrating power, energy and linear energy transfer, which are all inter-related.

Each of the types of radiation listed above have a characteristic way of interacting with matter. This interaction deposits the radiation's energy, which is measured in electron volts, in the material and its energy may be fully or partially absorbed, depending on the nature of the

interaction. If it is a strong one the penetrating power will be small and the linear energy transfer, the rate of energy deposition per unit track length, will be high.

Alpha radiation has the least penetrating power and its effects are limited to the surface layers of a material: this radiation only needs to be considered when a surface is contaminated by an alpha emitter.

Next comes beta radiation, which has a range of a few millimetres to a centimetre or so; its effects may, therefore, extend to the full thickness of a component but there is the possibility that they may be much reduced or even eliminated if the component under consideration is shielded by a relatively small thickness of metal. Alpha and beta radiation are characterised by a maximum range for a given energy, beyond which no significant radiation penetrates.

X-ray and gamma radiation are very penetrating, and, in contrast with the charged particle types of radiation above, do not have a maximum range but are progressively attenuated by materials; for this reason equipment housings, for example, may not offer a very significant screen.

Neutrons, a neutral particle radiation, also have great penetrating power.

Accelerated tests require a convenient and controllable source of radiation. Two types are commonly used: gamma radiation from an isotope source and electron beams from industrial equipment. Radiation from nuclear reactors can also be used but as this is a mixed radiation it may not be suitable for the simulation.

#### 17.1.2 Units

The present unit of absorbed radiation dose and dose rate is the Gray which is 100 times larger than the earlier unit, the Rad. As both of these units are used extensively in the literature and it is important that they are not confused. Because of the widely differing energy spectra and penetrating powers of the various types of radiation their effects are measured in terms of the energy deposition in the target material, the Gray being equal to 1 Joule per kilogramme. As energy deposition also depends to some extent on the composition of the target material its measurement or assessment can be complicated. Guidance is given in IEC 544, which explains how to make the measurements and to apply the necessary correction factors to estimate actual dose to the material.

### 17.2 INTENSITY

The one salient feature of an accelerated test is the very great difference between the test and in-service dose rates. Tests have been done at rates of up to  $10\text{Gy s}^{-1}$  whereas in-service exposure rates are often less than  $1\text{ mGy s}^{-1}$ , and can also be intermittent. Thus, the degree of acceleration can be very high and its effects sometimes become noticeable.

One of the assumptions in radiation testing has been that the dose rate does not have any affect on the outcome, ie the effect for any particular dose does not depend on the rate at which that dose was delivered. In fact, it has been known for a considerable time that in some materials the effect of a given dose increases as the dose rate is reduced. A few polymers have shown this effect very strongly and it is now a recommendation that irradiation tests are done at two rates to identify any susceptibility to this effect.

### 17.3 TEMPERATURE

Temperature can have a significant effect on the end result of an irradiation as it controls both the rate of oxygen (or other reactant) diffusion into the material and the rates of reaction of the

products of the irradiation. Oxidation is the principal reason for the dose rate effect mentioned above, because conventional testing at a high dose rate causes oxidation reactions to increase to such an extent that they cease in the bulk of the material as its outer layers scavenge the inwardly diffusing oxygen. For this reason thick sections and materials of low permeability can be susceptible to this effect, as can be materials known to be sensitive to oxidative degradation.

## 17.4 EXPOSURE STRATEGY

### 17.4.1 Simulation by beta versus gamma radiation

As mentioned in section 16.1 exposure to the various types of radiation is simulated by exposure to gamma radiation or an electron beam. It should be noted that in the case of an electron beam its penetration is inherently limited which means that only thin samples can be treated. Gamma irradiation is, therefore, the more versatile technique and can be used to expose assemblies as well as material samples. There are, however, obvious difficulties in simulating the purely surface effects caused by alpha radiation.

### 17.4.2 Estimation of test dose

Section 16.1 made reference to the differing characteristics of the various types of radiation and these must be taken fully into account when the experimental radiation exposure is calculated. Within limits it is possible to simulate the in-service exposure by either beta or gamma radiation. If the differences in penetration power are put to one side it is a commonly recognised approximation that the effects of beta and gamma radiation are equivalent and gamma radiation can be substituted for beta. The greater depth of penetration of gamma radiation makes this approximation a conservative one when thick samples or assemblies are to be tested. The approximation also ignores the differences in linear energy transfer resulting from differences in the energy of the incident radiation. There are conversion factors to equate the various radiations and energies to an equivalent gamma dose but in many cases the factors are reasonably close to one and can be neglected if the radiation dose is increased by an amount sufficient to envelope them.

There is an approximate conversion factor for neutron radiation of  $10^{11}$  nvt per Gy, but this is only a first order estimate and if it is required to simulate a significant neutron radiation does then a more precise material and energy dependent conversion factor should be used.

### 17.4.3 Dose rate

Where dose rate effects are negligible or have been accounted for a dose rate of up to  $1 \text{ Gy s}^{-1}$  is commonly used.

If preliminary work has shown the presence of a small dose rate effect, or one is suspected, it may be possible to perform the irradiation at a high rate and to allow for the reduced effect by increasing the dose. As this additional dose will not fully simulate the oxidation effects it must be appreciated that this is an approximation.

In cases where there is a significant dose rate effect the test dose rate will have to be reduced. It is not possible to give firm guidance on a suitable dose rate as it is both material and structure dependent; however, strongly affected materials or very thick sections in assemblies may require rates of around  $10^2 \text{ Gy s}^{-1}$ . As such rates have a serious impact on the length of the test practical issues may dictate a higher rate, together with some increase in dose.

#### 17.4.4 Exposure temperature

Where materials are known to be exposed to radiation whilst at an elevated temperature it is desirable that the experimental exposure should also be at this temperature as there is no simple means of converting data at one temperature to another without considerable background information. However, this can increase the experimental complexity as the oven will need to be fully resistant to the effects of radiation. Thus, all electrical wiring will need inorganic insulation and the air circulation fan, if fitted, will have to use an air operated motor.

A strategy to avoid this complication is to expose the materials to heat and radiation sequentially. However, a decision has to be made on the order of these two exposures. As a general guideline it should be the order that causes the most significant damage: in most cases this will be when the thermal exposure follows the radiation dose but it should be remembered that radiation can cause cross linking in polymers which can significantly increase their resistance to thermal effects.

#### 17.4.5 Environment

It is expected that the normal environment will be air and the air local to the samples should be replaced regularly in order to prevent a build-up of reaction products or reactive species from the air itself, such as ozone or nitrogen oxides.

There have been suggestions that dose rate effects may be countered to some extent by performing the test under an elevated pressure of oxygen but this can lead to experimental difficulty, and there is the further difficulty of quantifying the effect of the increased pressure. In any case, the sample volume should be ventilated as discussed above.

Where materials are exposed to other environments such as inert gases, water or oils then it is important that they should be duplicated during the irradiation. Samples should also be fully conditioned to the environment before the radiation starts. Consideration should be given to the circulation or replacement of gases or liquids in order to prevent the build-up of undesirable reaction products.

Stress has been placed on the need to ventilate the samples but if the environment is a closed one, such as an hydraulic system, then this type of feature should be modelled in order to simulate the effects of the degraded fluid on the material under test.

#### 17.4.6 Physical considerations

The inverse square law absorption have a significant effect on the uniformity of the irradiation field. For example, a physically small gamma ray source used to irradiate an assembly of any significant dimension there will result in a sharply reducing field through the assembly. Similarly, assemblies having significant depth and mass can cause a marked fall-off in intensity through their thickness. A number of steps can be taken to smooth out the uneven dose distribution. One technique is to increase the distance between the source and the sample; as this will also reduce the dose rate according roughly to the inverse square law it may result in the test becoming too long to be practical. It is possible, in some irradiation cells, to arrange a number of sources around the samples and thus even out the field; many cells have fixed geometry, however. A frequently used technique is to interrupt the irradiation at regular intervals and to rotate the sample assembly relative to the source by a small angle (such as 45 or 90 degrees). In the case of tall assemblies some vertical movement will also have to be considered. The aim is to obtain at least one full revolution before the full dose has been accumulated.

Finally, it may be found necessary to interpose a barrier between the source and the samples in

order to even out the energy deposition. The reason for this is that the linear energy transfer function goes through a maximum in the first centimetre or so of interaction; thereafter it falls off in a regular manner and the inclusion of a barrier ensures that all the test samples are in this smooth part of the field.

Because of the difficulties in assessing absorbed dose it is strongly recommended that dose monitoring is included in the samples. Where the samples are physically large more than one monitoring point will be required and their results either averaged or, preferably, the irradiation continued until all monitors have exceeded the required dose.

## 17.5 EVALUATION

The irradiated materials may be examined by any of the techniques commonly used for thermally aged materials, the only precaution to take is that they should be allowed to condition for two to three days before testing. The purpose of this is to allow any residual free radicals to react and the material to approach an equilibrium state before testing.

Where mixed radiation from a nuclear reactor has been used and the radiation contained a significant neutron flux there may be a need to allow any induced radioactivity to decay before any testing is done. This precaution is not necessary in the case of beta and gamma radiation.

## 18 PARAMETERS TO MONITOR DEGRADATION

Properties used to monitor the effect of degrading agents will yield different magnitudes of change. However, as it is effectively impossible to measure all properties, a limited number, perhaps only one, has to be chosen to represent the changes taking place.

The factors which effect the choice of parameters are:-

- Relevance to service
- Sensitivity to the degradation agent
- Relation to fundamental molecular properties
- General applicability
- Reproducibility
- Experimental cost and convenience.

When the trial is directed at some particular service application, parameters critical to that application will usually have priority. Indeed, if judgments are to be made as to the fitness for service it is essential that the most critical parameters are identified and the effect on them measured.

Where the trial is directed more generally at assessing the resistance of materials to a degradation agent then the sensitivity to the agent and the relation to fundamental molecular changes will have greater importance. High sensitivity will minimise exposure time and demonstrate the worst situation, whilst the ability to relate to molecular change offers the possibility of better understanding of the degradation taking place.

In general evaluation trials there is apparent advantage in selecting parameters which may be relevant to a wide range of applications and hence the most commonly measured properties are chosen. This advantage is lost if the parameters in question are inferior when the other factors affecting choice are considered.

A parameter with distinct advantages may have to be rejected if its reproducibility is poor. With time scales extending over possibly months and the results being subject to extrapolation,

poor reproducibility will result in uncertainty levels which render the conclusions meaningless.

Whatever the other considerations may indicate, in the vast majority of trials the selection will be affected by the cost and convenience of the experimental requirements. There are decades of difference in the cost of test piece preparation, testing time, number and size of test pieces etc between different parameters. Particularly in artificial weathering trials, the limitation of exposure space will almost always be the limiting factor.

Reference to the literature shows that in practice a very limited range of properties is commonly used. For rubbers, almost inevitably hardness and tensile stress strain properties are the first choice. For exposure to liquids these are in addition to volume change which is the basic guide to a rubber's fluid resistance. For weathering, a visual inspection is most useful, especially when strained test pieces are exposed to detect environmental stress effects, for example ozone cracking. These methods all have the advantage of relative simplicity and use a thin test piece so that equilibrium absorption and oxygen diffusion problems are minimised.

For rubber seals the importance in service of their set and stress relaxation performance often makes these properties a high priority, despite the disadvantage of thick test pieces and the resultant restriction on permeation. Although compression set has traditionally been most popular, it is stress relaxation which matters in many applications and is then the better choice, even although the test is more difficult. One additional advantage of stress relaxation is that the same test piece is remeasured at intervals and hence reproducibility improved.

This advantage also applies to stress relaxation in tension which is a particularly efficient and elegant method for general purpose use and which may be related to reactions within the rubber network. Its only disadvantages are relative experimental difficulty and not providing a measure of ultimate strength properties.

International standards for plastics favour tensile stress-strain properties, particularly using small dumb-bells for space efficiency. It is often found that strain and yield or break are the most sensitive indicators. Because of the concentration of stress at the surface there is logic in using a flexural stress test but this does not appear to be common in practice.

Both the fact that many ageing processes principally affect the surface of the material and that toughness is frequently an important reason for choosing a material explains why impact tests are also often used. Pendulum methods (Izod and Charpy) use similar quantities of material as tensile tests but generally falling weight tests require too many specimens.

As degradation affects toughness, and brittleness is dependent on temperature, impact tests making judicious choice of speed and/or test temperature offer an effective way of early detection of change. As instrumented impact apparatus becomes more commonplace it would seem reasonable that this could provide a useful monitoring tool.

Although long established for rubbers, microhardness tests have only relatively recently found significant use for plastics. Because of their extremely economic use of material, almost non-destructive nature, cheapness and simplicity, they are potentially most attractive for monitoring degradation. The small penetration also means that surface effects are emphasised and it would be possible to examine degradation on layers through a sample.

Visual assessments are usually included for weathered plastics but instrumental measurements of colour and gloss have clear advantages. Such properties, apart from being an indication of change having occurred, are often significant to the product end use. Colour change often reflects the performance of added pigments and hence may be quite misleading as to change in mechanical properties.

For exposure to liquids, linear dimensional and weight changes are used for plastics rather than volume change. Dimensional change may be very important in service but again does not necessarily correspond to mechanical property change. If environmental stress cracking is possible then exposure of stressed test pieces is essential and standard stress cracking tests used to monitor behaviour.

Other physical properties are relatively little used for rubbers or plastics, largely reflecting their less general interest and/or experimental convenience. Nevertheless, other properties are critical in particular applications and in consequence should be monitored where relevant.

Monitoring chemical changes allows more direct measurement of the fundamental mechanisms causing degradation and are essential for studies aimed at understanding the degradation processes. Chemical analysis methods also generally require quite small samples and in many cases are relatively quick to perform. However, the instrumentation required can be very sophisticated and available in relatively few laboratories. The measures of chemical change do not give a direct indication of effect on performance which is what is generally wanted by design engineers and to comply with performance specifications. For this latter reason in particular, chemical analysis methods are far less frequently used than physical methods. Nevertheless, because of their potential advantages, for example for quality control, it is desirable that more studies are made to establish correlations between the chemical changes and physical properties.

In cases involving complex degrading environments, critical applications and generally where direct evidence of performance is wanted, it is desirable that the total product is exposed to accelerated testing and functional tests used to assess the effects. Unfortunately this is rarely possible due to limitations of exposure space and costs. However, where it is possible to expose components consideration should always be given to the design of function based tests rather than the standard material methods.

## **19 PITFALLS IN ACCELERATED TESTING**

1. Migration of plasticisers etc between samples exposed together.
2. Test conditions cause distorted view of relative performance.
3. Degradation mechanism in test is different to that in service (e.g. through use of too high temperature, or wrong wavelengths).
4. Effect of oxygen diffusion not accounted for.
5. Equilibrium liquid absorption not reached invalidating comparison.
6. Incorrect relation between degradation and liquid concentration assumed.
7. Liquid/gas not truly representative of service.
8. Effect of drying out/cyclic exposure in service not accounted for.
9. Small quantities of oxygen mask true effect of a gas.
10. Parameter used to monitor degradation not the one critical to service performance.
11. Synergistic effects, not investigated, important in service.

12. Insufficient test pieces, times, exposure levels used to give reasonable uncertainty levels.
13. The extrapolation procedure is not valid.
14. Overestimating significance of results, e.g. using comparative results to make unjustified predictions.
15. Test piece history different to that of product.

## **20 SIMULATED DESIGN LIFE EXPOSURE OF PRODUCTS**

The usual approach to accelerated durability trials is either to make a simple comparison of materials or by extrapolation to predict performance at longer times under less severe conditions.

An alternative to predicting performance is to simulate a given design life by accelerated exposure and then to assess performance under service conditions. This approach can particularly be used with whole products where the end performance assessment can be made by operating the product. It is further particularly suited to where it is possible for a safety critical product to be subjected to abnormal harsh conditions and these are used for the end assessment.

The approach makes the assumptions that a valid extrapolation procedure is known and that the necessary input data has been determined. Whilst this may seem to be a typical chicken and egg situation, it is possible for the data needed to be known to a sufficient approximation (perhaps with a safety factor) for the important material but there need be no data on how the actual product manufactured from it may perform after ageing.

The process can be illustrated by an extremely simplistic example. It can be claimed that via the Arrhenius relation reaction rates for mechanical properties of a rubber are known at least approximately. Hence, for example, a tyre (which is a complicated structure) could be given a simulated life time of, say, 10 years by heat ageing and then actually run under heavy loading conditions.

It might be found that although the mechanical properties after 10 years were reasonable they deteriorated very rapidly in heavy service because the protection additives against high running temperatures had been depleted. Hence one would be advised not to use tyres stored for long periods even if they seemed intact.

In practical applications of the approach mechanical fatigue may be carried out simultaneously with the ageing and the end assessment involve multiple agents. A problem can be that with several material making up the product the simulated design life ageing in being correct for one material over-ages another which then is the element to fail.

## **21 ACKNOWLEDGEMENT**

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## APPENDIX A

## Relevant International Standards

**Note:** This list will not be complete as new standards continue to be published. Furthermore, standards are continually being reviewed and revised and it is necessary to check that the latest edition is being used.

There are also many national standards which address the same subjects; some of these are not direct equivalents and contain additional or different information.

**RUBBERS***Heat ageing, etc*

ISO 188 Accelerated Ageing or Heat Resistance Tests

ISO 6914 Determination of Ageing Characteristics by Measurement of Stress at a Given Elongation

*Stress relaxation in compression*

ISO 3384 Determination of Stress Relaxation in Compression at Normal and High Temperatures

ISO 6056 Determination of Compression Stress Relaxation (Rings)

*Effect of liquids*

ISO 1817 Determination of the Effect of Liquids

*Effect of ozone*

ISO 1431 Part 1 Resistance of Ozone Cracking - Static Strain Test

Part Resistance to Ozone Cracking - Dynamic Strain Test

Part 3 (Draft) Determination of Ozone Concentration

*Weathering*

ISO 4665 Part 1 Assessment of Change in Properties after Exposure to Natural Weathering or Artificial Light

ISO 4665 Part 2 Methods of Exposure to Natural Weathering

ISO 4665 Part 3 Methods of Exposure to Artificial Weathering

*Bacterial and fungal attack*

ISO 846 Determination of Behaviour under the Action of Fungi and Bacteria - Evaluation by Visual Examination or Measurement of Change in Mass or Physical Properties

## PLASTICS

### *Heat ageing, thermal stability etc*

ISO 176 (1976)	Determination of Loss of Plasticisers - Activated Carbon Method
ISO 177	Plastics - Determination of Migration of Plasticiser
ISO R182	Determination of the Thermal Stability of Polyvinyl Chloride and Related Co-polymers and their Compounds by Splitting off of Hydrogen Chloride
ISO 305	Determination of Thermal Stability of Polyvinyl Chloride Related Chlorine Containing Polymers, and their Compounds - Discoloration Method
ISO 1137	Plastics: Determination of Behaviour in a Ventilated Tubular Oven
ISO 1599	Cellulose Acetate- Determination of Viscosity
ISO 2578	Plastics: Determination of Time/Temperature Limits after Exposure to Prolonged Action of Heat
ISO 3671	Determination of Volatile Matter of Amino-plastics Moulding Materials
IEC Pub 216	Guide for the Preparation of Test Procedures for Evaluating the Thermal Endurance of Electrical Insulating Materials

### *Physical tests at non-ambient temperatures*

ISO 3205	Preferred Test Temperatures
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### *Effect of moist heat and steam*

ISO 4611	Plastics - Determination of the Effect of Exposure to Damp Heat, Water Spray and Salt
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### *Effect of liquids and chemicals*

ISO 62	Plastics - Determination of Water Absorption
ISO 175	Plastics - Determining the Effect of Liquid Chemical Including Water

### *Environmental stress cracking*

ISO 4599	Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Bent Strip Method
ISO 4600	Determination of Environmental Stress Cracking - Ball and Pin
ISO 6252	Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Constant Tensile Stress Method

### *Weathering and effect of light*

ISO 105/A	Textiles - Tests for Colour
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	Fastness - General Principles
ISO 877	Plastics - Determination of Resistance to Change upon Exposure under Glass to Daylight
ISO 2579	Plastics - Instrumental Evaluation of Colour Differences
ISO 3557	Plastics - Recommended Practice for Spectrophotometry and Calculation of Colour in CIE Systems
ISO 3558	Plastics - Assessment of the Colour of Near-White or Near-Colourless Materials
ISO 4582	Plastics - Determination of Changes in Colour and Variations in Properties and Exposure to Daylight under Glass, Natural Weathering of
ISO 4607	Plastics - Methods of Exposure to Natural Weathering
ISO 4892	Plastics - Methods of Exposure to Laboratory Light Sources
ISO 9370 (Draft)	Guide for the instrumental determination of radiant exposure in weathering tests
ISO TR 9673	Solar radiation and its measurements for determining outdoor weather exposure levels
ISO 11403 Part 3 (Draft)	Environmental influences on properties
<i>Bacterial and fungal attack</i>	
ISO 846	Determination of Behaviour under the Action of Fungi and Bacteria - Evaluation by Visual Examination or Measurement of Change in Mass or Physical Properties
Effect of radiation	The only method traced for effect of radiation is ASTM E1027, Practice for exposure of polymeric materials to ionising radiation.

## APPENDIX B

### Bibliography

There are literally thousands of references in the literature which are concerned with the degradation performance of polymers and clearly it would not be practical to cite them all in this Guide. The standards given in appendix A provide details of test procedures and to supplement this a short list is given below of texts which provide a comprehensive background and also provide many references for further reading.

Brown, R P, *Physical Testing of Rubber*, Elsevier Applied Science, 1986.

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