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# Plastics — Methodology for assessing polymer photoageing by FTIR and UV/visible spectroscopy

*Plastiques — Méthodologie d'évaluation du photovieillissement des polymères par spectroscopie IRTF et UV/visible*

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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# Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 10640 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 6, *Ageing, chemical and environmental resistance*.

# Introduction

One of the main interests in the use of artificial accelerated weathering tests is to provide an estimate of the lifetime of polymeric materials exposed in outdoor conditions. This is a very difficult task, and ISO 4892-1[1] describes some of the reasons why it is difficult and why the use of simple "acceleration factors" relating time in an accelerated test versus time in an outdoor exposure is not recommended without special care.

One way to evaluate whether an artificial accelerated test can predict the relative performance of materials used in outdoor applications is to compare the chemical changes caused by the artificial accelerated test with the chemical changes that occur in outdoor exposure.

Changes in visual appearance (gloss, discoloration, yellowing, bleaching, micro-cracks, etc.) and deterioration in physical (or functional) properties are consequences of chemical changes, even if there is not always a direct relationship between the chemical changes and the mechanical changes. The use of Fourier transform infrared (FTIR) spectroscopy to follow the chemical changes can facilitate the research of correlations between different ageing tests (natural or any kinds of accelerated devices).

This International Standard describes the methodology and a procedure for using FTIR spectroscopy and UV/visible spectroscopy.

# Plastics — Methodology for assessing polymer photoageing by FTIR and UV/visible spectroscopy

## 1 Scope

This International Standard provides a methodology to assess the ageing of polymeric systems during exposure to laboratory accelerated weathering as well as in outdoor exposures.

NOTE This methodology applies mainly to photoageing, but it can also be applied to thermal ageing.

This methodology identifies analyses that follow the chemical changes which control the deterioration of physical properties of materials during photoageing. The main procedure is based on infrared (IR) spectroscopy analysis and is described in this International Standard. In addition, UV spectroscopy is used for monitoring the behaviour of some additives and to identify the origin of discoloration in polymeric materials (degradation of pigments and colorants, or polymer yellowing).

Examples of applications of this methodology are given in Annex A as guidance for the interpretation of the results.

## 2 Terms and definitions and abbreviated terms

### 2.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

**2.1.1**
**photoageing**
entirety of the irreversible chemical and physical processes occurring in a material over the course of time that are initiated by radiation and that can be affected by heat, oxygen and moisture

**2.1.2**
**artificial accelerated weathering**
exposure of a material in a laboratory weathering device to conditions which can be cyclic and intensified over those encountered in outdoor or in-service exposure

NOTE 1 This involves a laboratory radiation source, heat and moisture (in the form of relative humidity and/or water spray, condensation or immersion) in an attempt to produce more rapidly the same changes that occur in long-term outdoor exposure.

NOTE 2 The device can include means for controlling and/or monitoring the light source and other weathering variables. It can also include exposure to special conditions, such as acid spray to simulate the effect of industrial gases.

**2.1.3**
**natural outdoor weathering**
exposure of a material to global solar radiation under outdoor climatic conditions

**2.1.4**
**absorption spectrum**
fraction of the incident electromagnetic radiation absorbed by a material or a molecular entity over a range of frequencies

**2.1.5**
**transmission spectrum**
fraction of the incident electromagnetic radiation that is not absorbed but passes through a material or a molecular entity over a range of frequencies

**2.1.6**
**reflection spectrum**
**reflectance spectrum**
fraction of the incident electromagnetic radiation reflected or scattered by a material or a molecular entity over a range of frequencies

NOTE The re-emitted radiation can be composed of two kinds of radiation referred to as specular reflection (when the angle of reflection is equal to the angle of incidence) and diffuse reflection (at all other angles).

## 2.2 Abbreviated terms

| | |
|---|---|
| ABS | acrylonitrile-butadiene-styrene |
| ATR | attenuated total (internal) reflection |
| EVAC | ethylene-(vinyl acetate) plastic |
| FTIR | Fourier transform infrared |
| PA | polyamide |
| PAS | photoacoustic spectroscopy |
| PBT | poly(butylene terephthalate) |
| PC | polycarbonate |
| PE | polyethylene |
| PEBA | polyether block amide |
| PEEK | polyetheretherketone |
| PE-LD | polyethylene, low density |
| PET | poly(ethylene terephthalate) |
| PMMA | poly(methyl methacrylate) |
| POM | poly(oxymethylene); polyacetal; polyformaldehyde |
| PP | polypropylene |
| PPE | poly(phenylene ether) |
| PS | polystyrene |
| PUR | polyurethane |
| PVC-P | plasticized poly(vinyl chloride) |
| PVC-U | unplasticized poly(vinyl chloride) |

| | |
|---|---|
| SAN | styrene-acrylonitrile plastic |
| TPU | thermoplastic polyurethane |
| UP | unsaturated polyester resin |
| UV/VIS | ultraviolet/visible |

## 3 Principle

When a polymeric material is exposed to UV radiation and other moderate environmental stresses, the change in most physical properties is attributable to chemical ageing, and the extent of the chemical changes can be related to the duration of the exposure under natural outdoor weathering or artificial weathering exposure.

Chemical changes control the degradation of mechanical properties and contribute to changes in the visual appearance of polymer materials during photoageing. These chemical changes are analysed primarily by IR spectroscopy, with additional analyses using UV/visible spectroscopy during the photoageing of polymers. The analysis at this earliest stage of degradation allows the identification of the critical oxidation products, allows the stoichiometry of reactions to be checked and, in some cases, indicates weak points in the polymer material (e.g. a weakness in the specific structure of the polymer, such as a double bond, an ether group or a urethane group, unstable colorant, lack of UV stabilizers, or migration of low-molecular-mass components of formulations to the surface and their accumulation there).

The relevance of artificial ageing can be determined by comparing the chemical changes that occur in the accelerated test to those that occur in natural weathering. It should be pointed out that, in some cases, oxidation products can be partially eliminated by hydrolysis, or erosion caused by water under humid climates (e.g. southern Florida) or by wind under very dry climates (e.g. Arizona). Kinetic analysis is recommended to determine the rate of degradation under different conditions of ageing in order to rank different formulations or to determine the range of acceleration possible for an artificial ageing test compared to a given natural outdoor weathering exposure (without distortion of the photodegradation mechanism of the polymer). In addition, these analyses can be used as a tool for developing improvements in polymers and polymeric products.

## 4 Methodology

### 4.1 General

Since the mechanism of degradation of polymers is a function of the polymer composition, it might be necessary to identify the chemical composition of the exposed plastics to allow comparison of results from laboratory experiments with those from actual use conditions. This will help in the design of better accelerated tests in those cases when existing accelerated tests have not given useful results for comparison with actual use conditions.

The specific chemical changes which control a given physical deterioration should be identified. For example, mechanical failures are generally controlled by the extent of oxidation, which makes their prediction possible.

In many cases, the extent of oxidation and the extent of changes in mechanical properties are often closely linked via main-chain scissions. A specific correlation study could be carried out for a given material in order to predict mechanical-property changes from the measurement of the concentration of oxidation products.

Except in the case of yellowing due to direct phototransformation, e.g. in the case of aromatic polymers, the change in visual appearance is generally controlled by several chemical processes (loss of gloss, discoloration, bleaching, micro-cracks, etc.). Therefore, an accelerated photoageing test is only predictive if one single process prevails over the others.

## 4.2 Guidance on the assessment of chemical changes

### 4.2.1 General

Different chemical changes take place that depend on the mechanisms of the degradation. These changes vary in importance and include matrix oxidation, chain scission and/or crosslinking, yellowing, bleaching, formation of fluorescent products, modification of stabilizer molecules, hydrolysis and photolysis.

Analysis of the chemical changes in polymeric materials submitted to exposure is performed by applying the following two rules:

a) only changes in the solid state are relevant, so the analysis shall be carried out on solid-state materials, of particular importance when examining the stability of intermediate products.

b) chemical changes shall only be considered at very low levels of change since the physical (mechanical or appearance) deterioration occurs at a very early stage in the chemical process, except when the “ultimate” fate of polymeric materials is being examined for environmental-protection purposes (e.g. the oxodegradation or oxobiodegradation of polyolefin films).

Although the main chemical changes take place in the polymer matrix, the fate of additives and colorants shall also be considered.

NOTE These rules are general ones and apply to any polymeric material exposed to light, heat, $O_2$, $H_2O$ and other potentially degrading exposure stresses.

### 4.2.2 Identification of the main degradation route

An important route of degradation for many polymers is a photooxidation mechanism, the products of which are formed at concentrations high enough (depending on the extinction coefficient) to be observed by vibrational spectroscopy. Changes in visual appearance caused by photoageing are the result of chemical changes that occur by several different routes. Acceleration of these chemical changes cannot occur without distortion of the results, except in special cases.

The extent of the chemical changes is better determined from the degree of accumulation in the matrix of “critical” photoproducts that, when properly chosen, will measure the main degradation pathway of the matrix. Although a chemical change such as oxidation might involve many elementary photochemical and thermal processes, it is possible to describe such chemical changes in a simplified manner through the accumulation of the critical photoproducts, chosen based on the best understanding of the ageing mechanism.[2]

A critical photoproduct is defined as follows:

- It shall allow the main degradation pathway of the matrix to be determined.
- Ideally, it shall be a stable final product which accumulates in the matrix (but not a low-molecular-mass product or a yellowing product). It shall be chemically and photochemically inert in the matrix, shall not diffuse out, and shall accumulate linearly with time until the relevant functional property of the polymer has been completely lost.

The degradation of the polymeric matrix may also be followed by monitoring the decrease in the relevant functional groups.

FTIR spectroscopy is used to identify critical photoproducts[3] with complementary information obtained using UV/visible spectroscopy, such as:

- the monitoring of the screening effect of organic UV-absorbers and pigments;
- the determination of changes in UV-stabilizers and absorbers and colorants;
- the determination of the origin of the sample's discoloration (degradation of colorants or degradation of the polymer material).

A list of critical photoproducts associated with the degradation of polymeric materials, and their identification, is given in Table 1.

Since the spectroscopic techniques used are mostly non-destructive (or need only small quantities of aged test specimens), it is recommended that an analysis of the kinetics of the oxidation be carried out in order to determine the rate of photooxidation and whether there is a pseudo-induction period. A procedure to measure the development of relevant functional groups that is based on FTIR spectroscopy is described in Clause 6.

The critical photoproducts of degradation must be known in order to determine the photodegradation mechanism. Many different photoproducts can be identified by coupling infrared analysis and specific chemical derivatization (e.g. conversion of carboxylic acid groups to acid fluoride groups using SF$_4$ gas). Additional correlation between oxidation and in-use properties can also be carried out. Table 1 shows the critical photoproducts, how they are identified, and the properties that are affected by photoxidation for a number of different polymers.[4][5]

**Table 1 — Critical photoproducts and modified properties**

| Polymer | Critical photoproducts | Identification of critical photoproducts | Effect/properties modified | References |
|---|---|---|---|---|
| PVC-P, PVC-U | $\beta$-chlorocarboxylic acid group | IR at 1 718 cm$^{-1}$ | Chalking<br>Discoloration<br>Mechanical resistance | [6], [7] |
| | Acid chloride | IR at 1 785 cm$^{-1}$ | | |
| Extruded PE film | Carboxylic acid | IR at 1 714 cm$^{-1}$ | Tensile strength<br>Elongation | [8], [9], [10] |
| | Vinyl unsaturation | IR at 909 cm$^{-1}$ | Tensile strength<br>Elongation | |
| EVAC film | Carboxylic acid | IR at 1 705 cm$^{-1}$ | Tensile strength<br>Elongation | [11], [12] |
| Moulded PP | Carboxylic acid | IR at 1 714 cm$^{-1}$ | Micro-cracks<br>Bleaching<br>Chalking | [13], [14] |
| Moulded, filled PA, PA6 and PA66 | Carboxylic acid | IR at 1 715 cm$^{-1}$ | Appearance<br>Mechanical resistance | [15] |
| | Imide group | IR at 1 735 cm$^{-1}$ and 1 690 cm$^{-1}$ | | |
| PET, PBT, moulded, filled PET and PBT | Carboxylic acid | IR at 1 717 cm$^{-1}$ and 1 776 cm$^{-1}$ | Mechanical resistance | [16], [17], [18] |
| | Benzoic acid | IR at 1 696 cm$^{-1}$ and 1 733 cm$^{-1}$ | | |
| | Acid hydroxyl groups | IR at 3 260 cm$^{-1}$ | | |
| PMMA and acrylics | Carboxylic acid | IR at 1 705 cm$^{-1}$ | Increased haze | [19] |
| | Hydroxyl groups | IR at 3 250 cm$^{-1}$ | | |

**Table 1** (*continued*)

| Polymer | Critical photoproducts | Identification of critical photoproduct | Effect/properties modified | References |
|---|---|---|---|---|
| PC | Carboxylic acid | IR at 1 713 $\text{cm}^{-1}$ | Mechanical properties | [20], [21] |
| | Photo-Fries rearrangement products: | | Yellowing | |
| | — phenylsalicylate | IR at 1 689 $\text{cm}^{-1}$; UV at 320 nm | | |
| | — dihydroxybenzophenone | IR at 1 629 $\text{cm}^{-1}$; UV at 355 nm | | |
| | — biphenyl species | IR at 3 607 $\text{cm}^{-1}$, 3 547 $\text{cm}^{-1}$ and 3 470 $\text{cm}^{-1}$; Vis at 450 nm | | |
| PUR, TPU | Carboxylic acid | IR at 1 705 $\text{cm}^{-1}$ | Whitening<br>Yellowing<br>Cracks (aggravated by hydrolysis) | [22], [23] |
| | Urethane group degradation products | IR at ~1 530 $\text{cm}^{-1}$ (band decreasing in size) | | |
| Moulded ABS, PS, SAN | Butadiene degradation products (in ABS) | IR at 912 $\text{cm}^{-1}$ (band decreasing in size) | Mechanical resistance<br>Appearance | [19], [24] |
| | Carboxylic acid | IR at 1 717 $\text{cm}^{-1}$ | | |
| UP | Aromatic carboxylic acid | IR at 1 700 $\text{cm}^{-1}$ | Yellowing<br>Mechanical properties | [25], [26] |
| | Carbonyl group | IR at 1 780 $\text{cm}^{-1}$ | | |
| | Hydroxyl groups, mainly from carboxylic acid | IR at 3 300 $\text{cm}^{-1}$ | | |
| | Conjugated aromatic species | UV at 350 nm; Vis at $>$400 nm | | |
| POM | Formate/ester | IR at 1 714 $\text{cm}^{-1}$ | Brittleness<br>Mechanical properties | [27] |
| | Alcohol from chain scission | IR at 3 475 $\text{cm}^{-1}$ | | |
| PPE | Saturated carboxylic acid | IR at 1 714 $\text{cm}^{-1}$ | Bleaching<br>Mechanical properties | [28], [29] |
| | Quinone methide | IR at 1 657 $\text{cm}^{-1}$ | | |
| | Ether group degradation products | IR at 2 736 $\text{cm}^{-1}$ (band decreasing in size) | | |
| | | IR at 1 021 $\text{cm}^{-1}$ (band decreasing in size) | | |
| | Quinone methide | UV at 330 nm | Yellowing | |
| PEEK | Aromatic carboxylic acid | IR at 1 725 $\text{cm}^{-1}$ | Yellowing | [30] |
| | Hydroxyl groups | IR at 3 370 $\text{cm}^{-1}$ | | |
| | | Vis at 400 nm to 600 nm | | |
| PEBA | Ether group degradation products | IR at 2 791 $\text{cm}^{-1}$ | Cracks<br>Mechanical properties | [2], [31] |
| | | IR at 1 111 $\text{cm}^{-1}$ (band decreasing in size) | | |
| | Carboxylic ester | IR at 1 725 $\text{cm}^{-1}$ | | |
| | | IR at 1 180 $\text{cm}^{-1}$ | | |

### 4.2.3 Ageing parameters to be taken into account

#### 4.2.3.1 Influence of water

It should be pointed out that, in some cases, water can have chemical effects on the photochemical behaviour of polymer materials, such as the following:

- it can enhance the photocatalytic effect of untreated photoconductor pigments, such as titanium dioxide and zinc oxide, significantly increasing the photooxidation of some polymers;
- the photoinstability of some colorants is enhanced in the ionic forms;
- hydrolysis of some photoproducts can take place.

NOTE 1 Hydrolysis of unexposed polymers and additives can also occur.

It should be also pointed out that water can have physical effects on the behaviour of polymer materials, e.g. plasticizing, extraction and washing out of low-molecular-mass additives. An important physical effect of water on the degradation of materials is the continuous cycle of expansion and contraction as the polymer swells as water is absorbed and shrinks as it dries out. This will lead to micro-cracks and gloss loss at lower levels of photooxidation in a wet climate.

Extraction and hydrolysis of stabilizers by water can lead to loss of stabilizer at a much faster than expected rate, which will result in faster degradation of the polymer. Conversely, some initiators of degradation, such as fire-retardant additives, can be eliminated and their negative influence thus attenuated.

NOTE 2 The use of liquid-water spray or the creation of water-vapour condensation during artificial photoageing is not essential when the chemistry of the degradation is the main basis for the evaluation, but it is necessary when the purpose of the laboratory test is to reproduce the change in the visual appearance that can occur in outdoor use. Water reveals and enhances the degradation in appearance (bleaching, micro-cracks, erosion, etc.) resulting from oxidation of the polymer material. Exposed samples can be also immersed periodically in demineralized water maintained at a given temperature between 40 °C and 60 °C. For reliable artificial accelerated weathering testing, the time and frequency of wetting with condensation or water spray is very important.

The consequence of water immersion on an oxidized polymer sample should be checked by carrying out IR analysis before and after the water treatment. This check is necessary to avoid misleading results due to the choice of a critical product that could be extracted by water from the polymer matrix.

#### 4.2.3.2 Migration of additives

Low-molecular-mass organic components (e.g. antistatic additives, lubricants, UV-stabilizers, etc.) can migrate from the core toward the surface of polymers during the exposure. The accumulation of these components at the surface of exposed plates can hamper the detection of the polymer oxidation products by specific FTIR analysis techniques at the surface. The exposed surface should be gently washed with demineralized water or ethanol and dried before carrying out the analysis to avoid interfering with the detection of the polymer degradation. The same precaution should be taken for samples polluted after outdoor exposure.

## 5 Determination of chemical variations in polymer materials by FTIR spectrometry

### 5.1 General

Infrared spectroscopy is a vibrational technique in which absorption bands at specific wavelengths allow the identification of specific functional groups in the polymer structure. IR spectroscopy can be used in a quantitative manner as an FTIR spectroscopy technique.

Different infrared technologies [transmission, reflection, photoacoustic, attenuated total reflection (ATR), microspectroscopy] can be used depending on the geometry, transparency and scattering behaviour of the sample being analysed.

The polymer degradation can be characterized by:

- the emergence of new absorption bands specific to the critical photooxidative products produced by the polymer matrix, e.g. bands corresponding to chemical components containing carbonyl or hydroxyl groups;
- the decrease in a specific absorption band which is characteristic of a weak site in the polymer structure, e.g. bands corresponding to urethane, ether or unsaturated functional groups.

Measuring the change in absorbance in relation to the initial state for specific bands allows the way in which oxidation is progressing to be determined or the oxidation rate to be determined for kinetic analysis.

## 5.2 Apparatus

**5.2.1 Calibrated infrared spectrometer**, capable of recording a spectrum (in the transmission, reflection or photoacoustic-emission mode) over the range from about 4 000 $\text{cm}^{-1}$ to about 700 $\text{cm}^{-1}$ with a resolution of 4 $\text{cm}^{-1}$. Measurement shall be performed under a dry atmosphere (dry air or nitrogen).

When an FTIR spectrometer is used, a minimum of 16 scans shall be made per spectrum.

**5.2.2 Specimen holder**, capable of accurately positioning the test specimen under the aperture. The design of the holder will depend on the infrared technique used.

**5.2.3 Microtome** (if necessary), capable of producing thin slices (films of a few microns up to several hundred microns thick) from a sample.

## 5.3 Test method

### 5.3.1 Preparation of test specimens

Test specimens for infrared measurement are prepared in the form of:

- plates or sheets for reflection (e.g. ATR) or photoacoustic (PAS) measurements;
- films for transmission measurements.

Films are preferably obtained by cutting into the bulk of a thick sample using a microtome. When this is not possible (e.g. for granules), the films can be obtained by compression moulding. For measurement of oxidation profiles using microspectroscopy, cross-sectional films can be cut perpendicular to the exposed surface using a microtome. A succession of thin films cut parallel to the exposed surface of thick samples can be analysed by FTIR and UV/visible spectroscopy. These slices are typically taken near the centre of the exposed sample.

NOTE The oxidation profile is useful to understand better the photochemical behaviour of the sample and to evaluate how various additives can improve the durability.

The thickness of the film is precisely measured with a micrometer. The thickness is usually less than 200 µm for spectroscopy measurement, but it should be chosen with respect to the oxygen permeability when the film is intended to be exposed to UV light. Also, the thickness of the film has to take into account the actual absorbance, which should not exceed a level at which it is no longer linear with respect to concentration in order that it can be used quantitatively.

All contamination from fingerprints, adhesives or marking ink shall be prevented. It is recommended that the test specimens be stored under dry conditions before analysis in order to remove water, which can interfere with the spectrum.

The thickness of the specimen can also be checked by measuring the absorbance of a stable IR absorption band of the polymer, notably when using ATR and PAS techniques.

### 5.3.2 Kinetic control during ageing

First, the homogeneity of the polymer material shall be checked. IR analysis shall then normally be performed on at least five different specimens of the same material (see, however, next paragraph).

A periodic analysis of the chemical changes in polymer materials is recommended throughout artificial ageing or natural weathering. Indeed, this kind of analysis provides a fairly good indication of the photochemical fate of the polymer material. Provided the homogeneity of the polymer material has been demonstrated for its initial and aged state, IR analysis of the exposure could be carried out on only one single specimen (film for IR transmission analysis, small specimen for FTIR-PAS analysis, etc.). If such homogeneity cannot be demonstrated, specimens for analysis shall be taken from three exposed samples. When a large sample is exposed, IR or micro-IR analysis shall be carried out at least on three different locations on the sample. Apart from the initial and final ageing state, at least two intermediate exposure states should be investigated by IR analysis.

### 5.3.3 Aged samples

IR or micro-IR analysis shall be carried out on at least three exposed samples or at three different locations on a large sample. If the results are not homogeneous, the number of analyses shall be increased.

### 5.3.4 Positioning of test specimen in the IR spectrometer

When repeat measurements are made on a given sample to monitor changes in the IR spectrum as a function of exposure, it is essential that the measurements be made at the same position on the sample every time an IR spectrum is produced.

When an oxidation profile is determined by microspectroscopic analysis of a cross-sectional film, the infrared beam is first focused on the edge of the exposed side and then displaced, step by step, towards the centre of the film (the core layers of the sample).

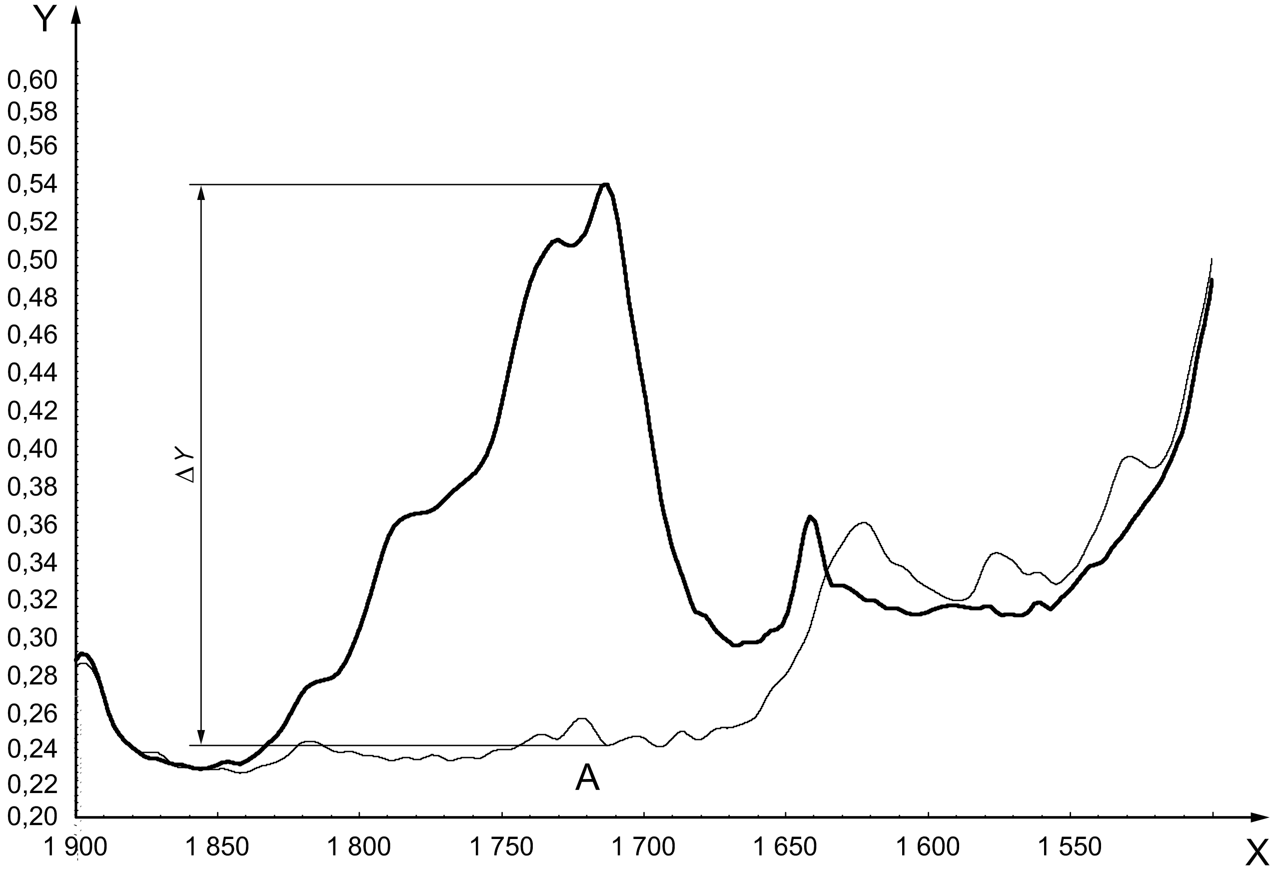
### 5.3.5 Measurement

When a single-beam FTIR spectrometer is used, the background is acquired with the same parameters as those used for the test specimen (size of the IR beam delimited by the specimen holder, number of scans).

The spectrum produced is recorded before any spectral treatments, such as intensity, baseline or smoothing corrections, are carried out.

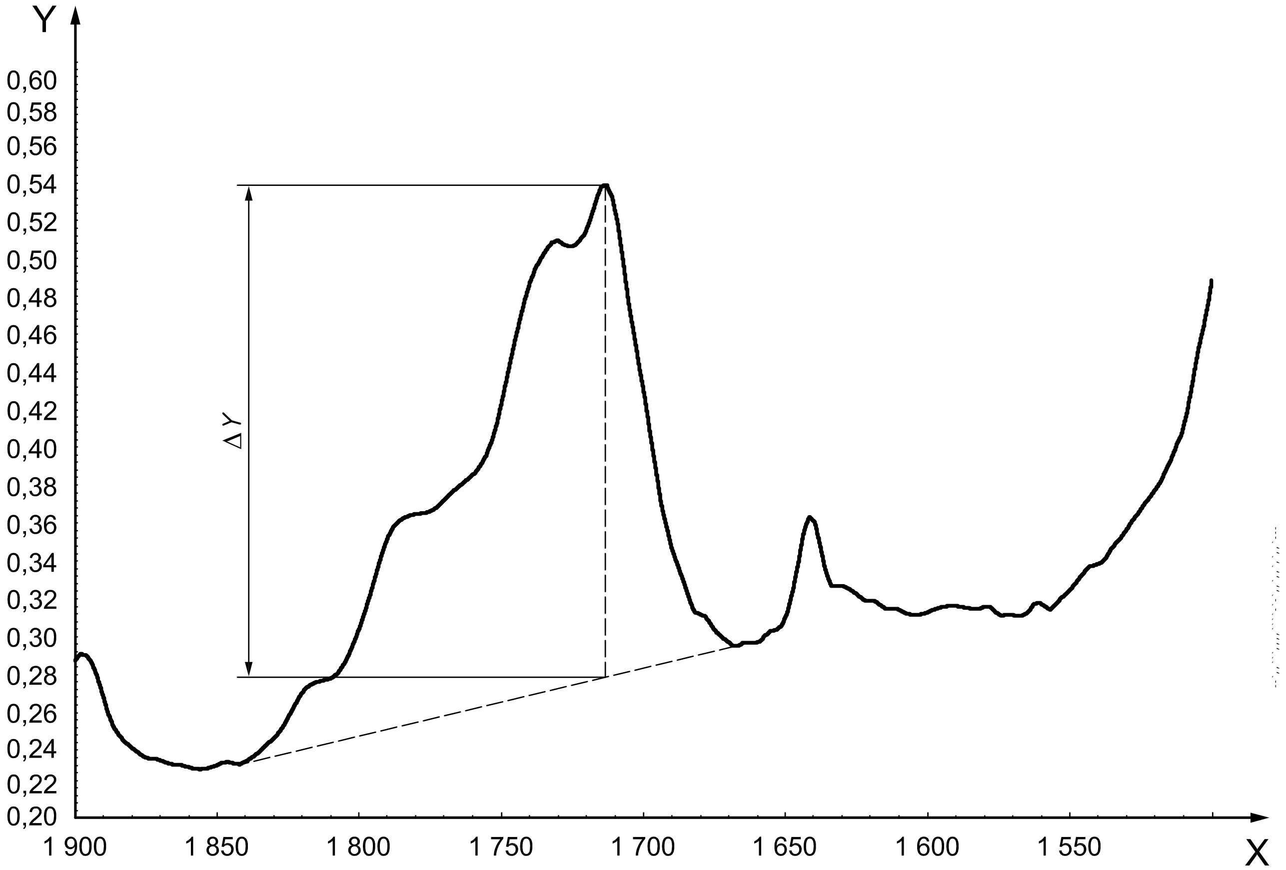
## 5.4 Determination of the absorbance and its change with exposure time

Absorbance at a specific wavelength is measured by comparison with the spectrum of the initial state [see Figure 1 a)] or on the basis of the peak height of the absorption band [see Figure 1 b)]. The thickness of the film has to be taken into account as a check on the amount of material analysed.



**a) Spectrum in the initial state**

**Figure 1** (*continued on next page*)



**b) Limits of the absorption band**

**Key**

X wave number, $cm^{-1}$

Y absorbance

$\Delta Y$ change in absorbance

A initial state

**Figure 1 — Typical IR spectrum**

Absorbance at a specific wavelength is measured by comparison with the spectrum of the initial state or on the basis of the peak height of the absorption band. Absorbance of an invariant reference band of the polymer is used to account for variations in thickness and surface irregularities.

NOTE 1 Absorbance is more useful than transmittance as the scale for the IR spectrum when IR spectroscopy is used as a quantitative measurement. Absorbance is proportional to the concentration of the absorbing organic functional group.

The rate of progression of the oxidation is measured by the variation in absorbance with time, i.e. an increase in absorbance for oxidation products (generally containing a carbonyl group) or a decrease in absorbance for a reactive unit of the polymer.

NOTE 2 Components of some UV-stabilizers (e.g. ester or s-triazine groups of hindered-amine light stabilizers) may be detected by virtue of specific weak IR-absorption bands, and their fates can be determined from the decrease in the IR bands attributed to them. This analysis might be helpful in improving the formulation of some UV-stabilizers.

The oxidation profile is characterized by the variation of absorbance with depth.

# 6 Complementary analysis by UV/visible spectroscopy

## 6.1 General

UV/visible spectroscopy is an electronic-transition spectroscopy and is a helpful complement to IR analysis. Some functional groups (or chromophores) in a molecule absorb UV/visible electromagnetic radiation that promotes bonding and non-bonding electrons to higher-energy orbits. UV/visible spectra are relatively broad-band and, if the polymer material is a mixture, they often overlap.

Transmission spectra of films and reflection spectra at the surface of thick specimens should be carried out with an integrating-sphere attachment to the spectrometer.

UV/visible spectrometry is used to determine the screening effect of UV-absorbing additives or to monitor spectral changes that occur when a polymer discolours during exposure. For example, yellowing of a polymer by photooxidation or photolysis is detected by the development of a very broad absorbance band in the UV region with an extension into the visible region at wavelengths greater than 400 nm. Degradation of organic additives or colorants is detected by monitoring the decrease in absorbance at wavelengths characteristic of the additive or colorant in question.

When bleaching of the oxidized polymer occurs, the increase in light scattering leads to progressive shifting of the whole spectrum towards higher absorbances. Bleaching of chromophores that occurs as part of the weathering process generally results in weaker absorption at longer UV wavelengths.

## 6.2 Apparatus

**6.2.1 Calibrated two-channel UV/visible spectrometer**, fitted with an integrating-sphere attachment capable of recording a spectrum (in the transmission or reflection mode) over the range from about 200 nm to about 800 nm with a resolution of around 1 nm or better.

**6.2.2 Specimen holder** (see 5.2.2).

**6.2.3 Microtome** (see 5.2.3).

## 6.3 Test method

### 6.3.1 Preparation of test specimens

See 5.3.1.

### 6.3.2 Positioning of test specimen in the spectrometer

See 5.3.4.

### 6.3.3 Measurement

The wavelength-scanning rate is set to a convenient value to avoid underestimation of the actual absorbance and displacement of the absorption-band maxima.

The raw spectral data should be recorded before any spectral treatments, such as intensity, baseline or smoothing corrections, are carried out. When corrections cannot be avoided, the parameters shall be given and documented in the test report.

## 6.4 Determination of the absorbance and its change with exposure time

The rate of progression of photochemical processes is measured by the variation in absorbance with time, i.e. an increase in absorbance (in the range 400 nm to 500 nm) for yellowing or a decrease in absorbance for UV-absorbers or colorants.

For quantitative analysis in accordance with the Beer-Lambert law, the absorbance at the chosen wavelength should be less than 2.

## 7 Test report

The test report shall contain the following information:

a) a reference to this International Standard;

b) the relevant parameters identifying and characterizing the aged samples;

c) a complete description of the test procedure used for determining the chemical changes in the material analysed, including:

   1) the procedure used for cleaning the exposed samples before analysis and details of any other special treatment carried out in order to improve the analysis of the oxidation products (e.g. elimination of low-molecular-mass additives on the sample surface),

   2) details of the preparation of films or other types of specimen,

   3) the number of specimens analysed,

   4) details of the IR spectroscopy technique used:

      — transmission: ATR geometry, type of crystal,

      — micro-FTIR: size of the area analysed, number of scans, resolution,

      — photoacoustic: modulation frequency or mirror speed used, whether continuous or step scan mode used,

   5) details of complementary analysis by UV/visible spectrometry, if relevant,

   6) details of any spectral treatment carried out, e.g. smoothing, thickness correction, baseline correction, ATR correction,

   7) the type of critical oxidation product (or the functional group of the aged polymer material) chosen, including information on the means used to determine the amount of polymer material analysed (film thickness, absorbance of a stable IR absorption band of the polymer, etc.),

   8) the parameters of the weathering exposure (artificial or natural) that could have affected the amounts of oxidation products which accumulated in the aged materials;

d) details of the rate of progression of the chemical changes in the material and, if relevant, the oxidation induction time:

   1) the oxidation limit used to determine the lifetime of the material tested and any correlation with a physical property of the material in use,

   2) any differences in results between exposures of thin films and the surface layer of thick samples that might indicate additive migration,

   3) details of any comparison made between artificial ageing and natural ageing.

# Annex A
(informative)

# Comparison of test results for artificial accelerated photoageing, artificial accelerated weathering and natural outdoor weathering

## A.1 PE-LD film for agriculture or horticulture

### A.1.1 General

The main feature for the degradation of the macromolecular polyethylene chain is the accumulation of critical carboxylic end-groups (increase in the IR band at 1 713 $\text{cm}^{-1}$) and vinyl unsaturated groups (increase in the IR bands at 1 640 $\text{cm}^{-1}$ and 909 $\text{cm}^{-1}$).[32]

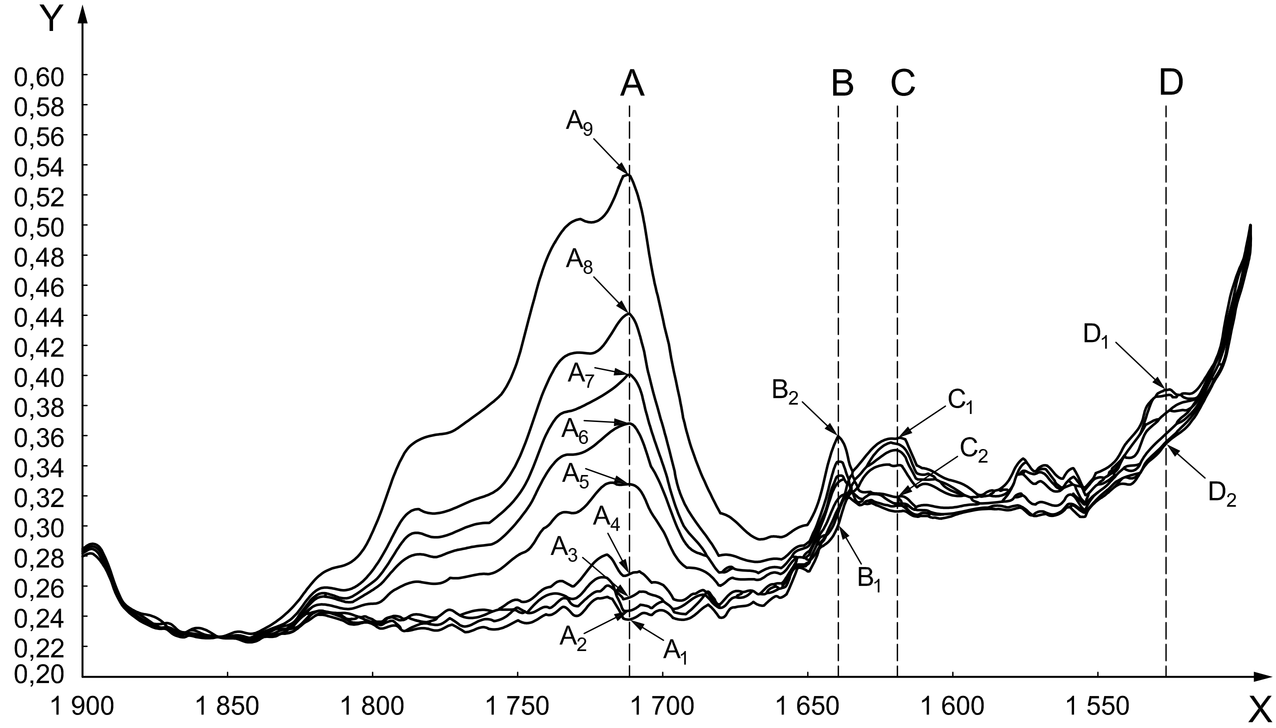
### A.1.2 Comparison

Twenty-one samples of PE-LD film (thickness 200 µm) for greenhouse use, containing different formulations of stabilizers (antioxidants, UV-absorbers, hindered-amine light stabilizers), were exposed in an artificial accelerated weathering device and in natural conditions.

The accelerated weathering device was equipped with four mercury-vapour arc lamps (400 W). The borosilicate envelope of the lamps cut off all wavelengths lower than 290 nm. The UV irradiance at the surface of the samples was measured as 90 $\text{W}\cdot\text{m}^{-2}$ in the range 300 nm to 400 nm. The temperature of the samples was regulated at 60 °C.

Natural ageing was carried out in Clermont-Ferrand (France), where the climate can be considered to be temperate, for seven years at an angle of 45° to the horizontal. The average total annual solar irradiation for a 45° surface in Clermont-Ferrand is 4,87 $\text{GJ/m}^2$.

The chemical changes in the films were followed by means of FTIR spectroscopy in the transmission mode. For these samples, the equivalence in the chemical behaviour of the PE-LD films aged in artificial and in natural conditions is illustrated by the IR spectra given in Figures A.1 and A.2.



**Key**

X wave number, cm$^{-1}$

Y absorbance

A: 1 713 cm$^{-1}$, carboxylic acid

$A_1$: initial state

$A_2$: after 152 h

$A_3$: after 502 h

$A_4$: after 595 h

$A_5$: after 1 201 h

$A_6$: after 1 600 h

$A_7$: after 1 800 h

$A_8$: after 2 002 h

$A_9$: after 2 192 h

B: 1 640 cm$^{-1}$, vinyl

$B_1$: initial state

$B_2$: after 2 192 h

C: 1 622 cm$^{-1}$, UV-stabilizer No. 1

$C_1$: initial state

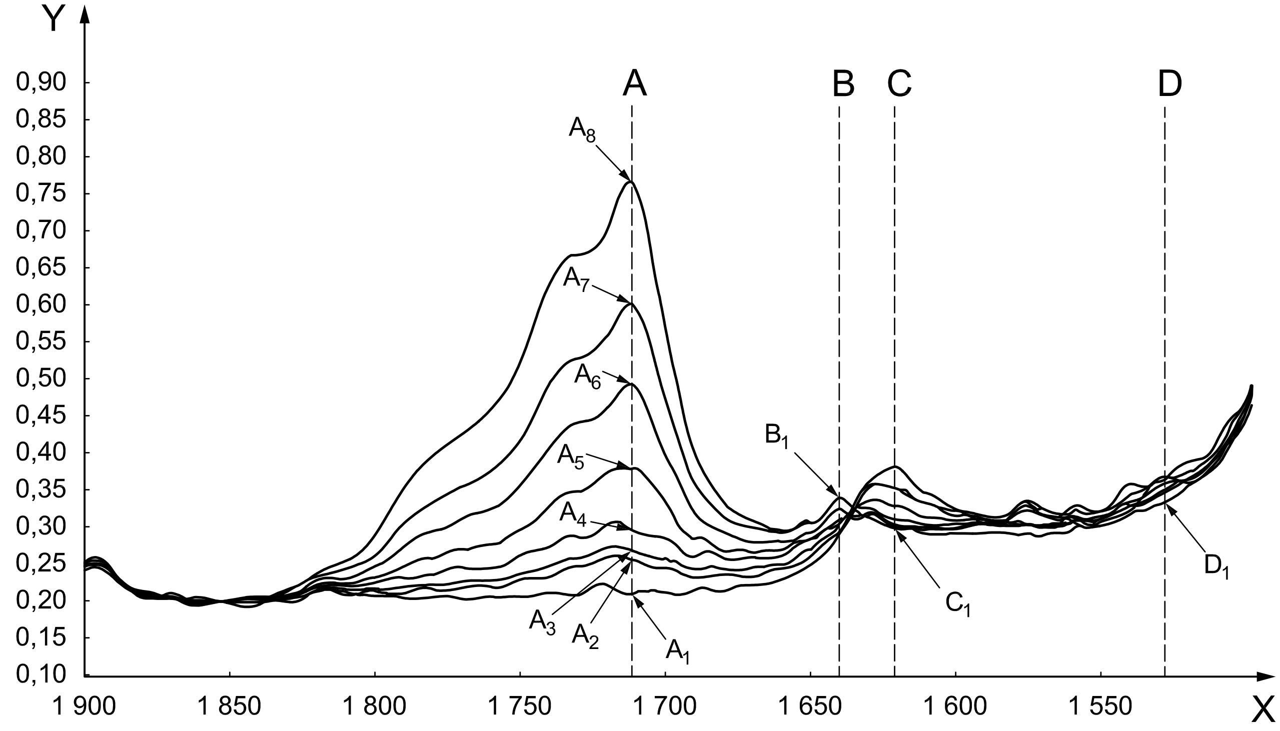
$C_2$: after 2 192 h

D: 1 530 cm$^{-1}$, UV-stabilizer No. 2

$D_1$: initial state

$D_2$: after 2 192 h

Figure A.1 — Changes in IR spectrum during artificial accelerated ageing



**Key**

X wave number, $\text{cm}^{-1}$

Y absorbance

A: 1 713 $\text{cm}^{-1}$, carboxylic acid

$A_1$: initial state

$A_2$: after 264 days

$A_3$: after 355 days

$A_4$: after 605 days

$A_5$: after 1 018 days

$A_6$: after 1 322 days

$A_7$: after 1 624 days

$A_8$: after 2 008 days

B: 1 640 $\text{cm}^{-1}$, vinyl

$B_1$: after 2 008 days

C: 1 622 $\text{cm}^{-1}$, UV-stabilizer No. 1

$C_1$: after 2 008 days

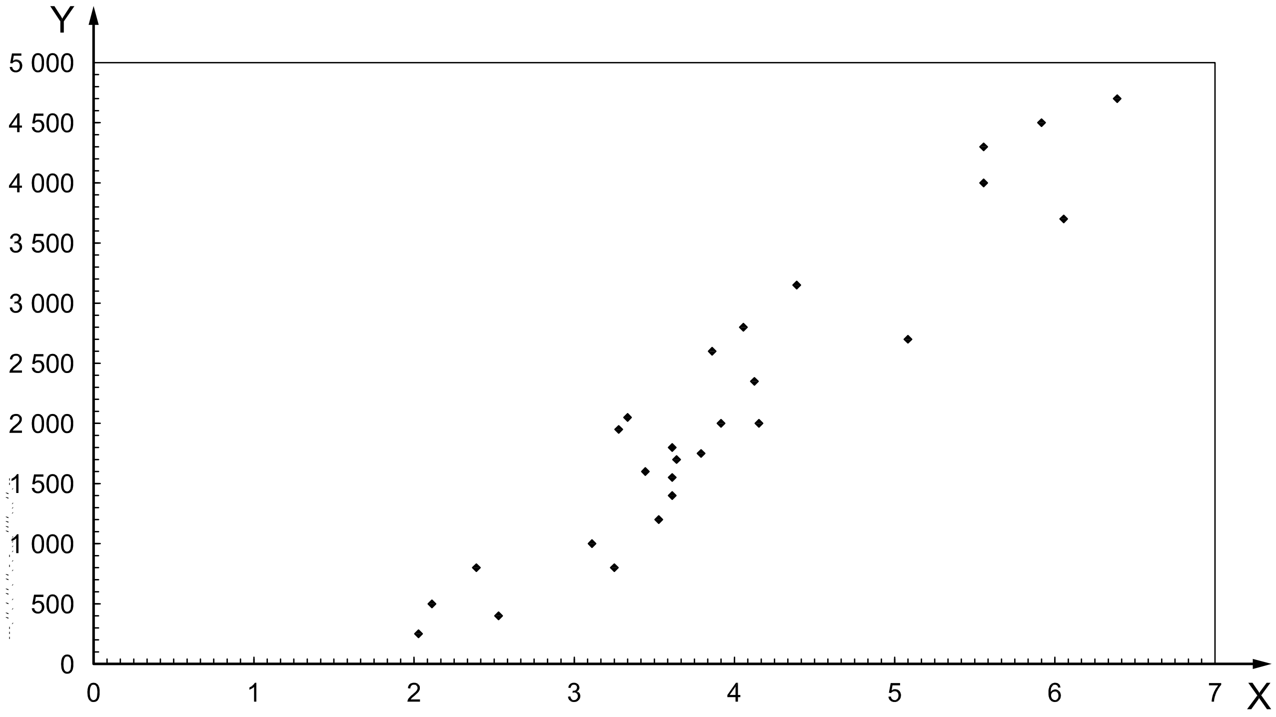
D: 1 530 $\text{cm}^{-1}$, UV-stabilizer No. 2

$D_1$: after 2 008 days

**Figure A.2 — Changes in IR spectrum during natural outdoor ageing**

NOTE FTIR analysis can also enable the efficiency of UV-stabilizers to be checked (decrease in specific IR bands at 1 622 $\text{cm}^{-1}$ and 1 530 $\text{cm}^{-1}$).

For these samples, it was established[33] that a decrease of 50 % in the elongation at break occurred when the absorbance at 1 713 $\text{cm}^{-1}$ rose to a value of 0,2 for a 200 µm film thickness. The time necessary for the exposed films to reach this extent of oxidation was determined for both artificial and natural ageing and is given in Figure A.3.



**Key**

X duration of exposure to natural outdoor weathering, years

Y duration of exposure to artificial accelerated weathering, h

**Figure A.3 — Service life as given by artificial accelerated weathering and by natural weathering in Clermont-Ferrand**

These data represent an example of the correlation that can be achieved from the chemical analysis of numerous PE-LD films exposed in an accelerated exposure device and outdoors. The data were obtained with a specific device and for the specific solar irradiation conditions in Clermont-Ferrand, but indicate the tendency to be expected in equivalent climates. The data for any accelerated test time translates into a relatively broad range of outdoor exposures (approximately one year in Figure A.3). One can choose the worst-case scenario to try to minimize the error in the estimate of the service life.

## A.2 ABS products

### A.2.1 General

ABS materials are very sensitive to photodegradation as styrene is a weak segment to yellowing and butadiene is a weak segment to oxidation.

Direct photoscission of chromophoric styrene groups at “short” UV wavelengths ($\lambda \leq 320$ nm) leads to yellowing due to modification of the aromatic structure.

Photoinduced oxidation by radical attack occurs under polychromatic exposure at $\lambda \geq 300$ nm. Free radicals are generated by any chromophoric defects, by any unstable chromophoric additives and by direct photoscission of styrene groups. Photooxidation of ABS takes place mainly in butadiene segments by radical attack at the $\alpha$-position of the unsaturated system.[34]

### A.2.2 Comparison

An evaluation of the photochemical degradation of black ABS blends was carried out for comparison between the following different conditions of exposure[35]:

- Artificial accelerated conditions, using a device equipped with four 400 W medium-pressure mercury-vapour lamps, each giving an average UV irradiance of 90 $W \cdot m^{-2}$ over the range 300 nm to 410 nm. The temperature of the samples was controlled at 60 °C. Samples were fixed on a rotating carousel in order to guarantee the uniformity of the exposure. Two kinds of run were carried out:
    - in dry conditions, without any contact with water,
    - with periodic immersion, every 50 h of exposure, for 1 h in demineralized water in an external bath controlled at 60 °C.
- Artificial accelerated conditions, using a device equipped with a xenon-arc lamp in accordance with ISO 4892-2[36] [0,55 $W/(m^2 \cdot nm)$ at 340 nm, black-panel temperature 70 °C, temperature of chamber air 50 °C, RH 50 %, exposure cycle 18 min water spray, 102 min dry].
- Outdoor natural ageing in Clermont-Ferrand (where the climate can be considered as temperate), facing south, –45° angle, unbacked samples.

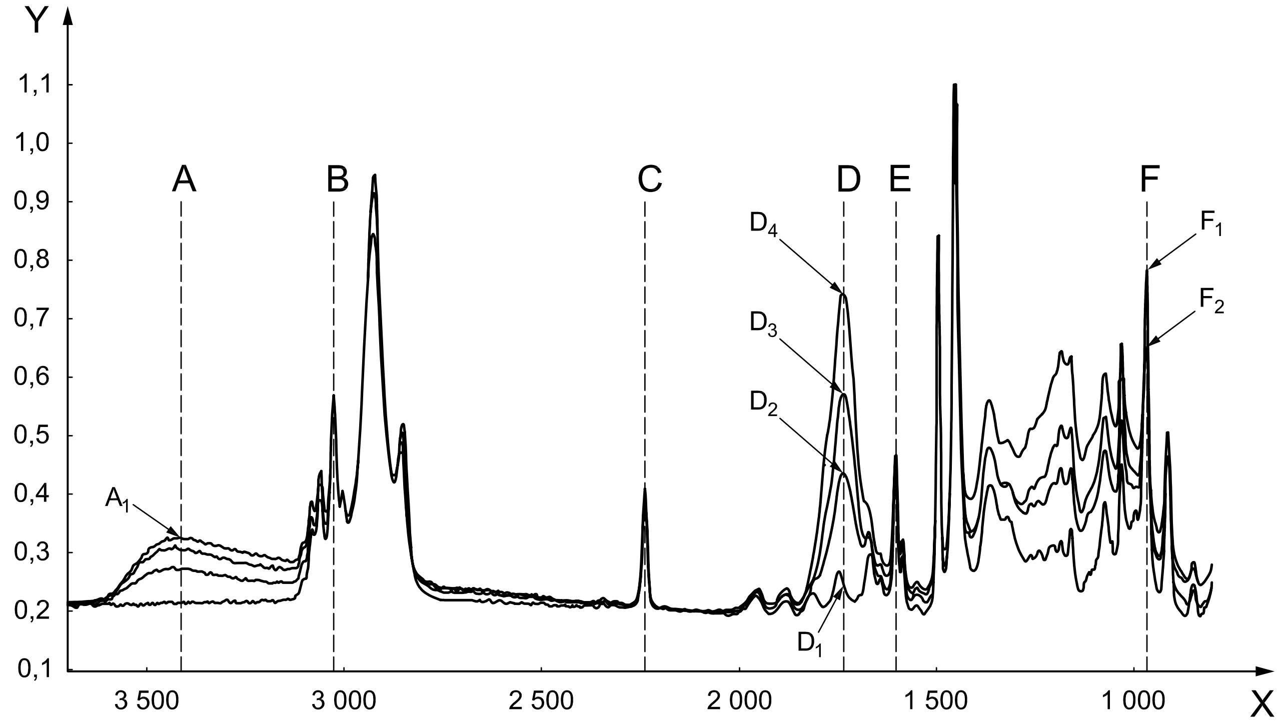
The degree of chemical degradation was determined by FTIR, using photoacoustic detection that allows the changes in the surface layers (< 10 µm) of the exposed plates to be analysed.

The changes in the IR spectra of the ABS blends were similar for outdoor exposure and for the various conditions of artificial exposure described above. Examples are given in Figures A.4, A.5 and A.6.

The degradation of ABS was mainly observed as follows:

- A decrease in the butadiene IR band at 967 $cm^{-1}$ (1,4-trans). The rate of oxidation was determined by plotting the relative absorbance at 967 $cm^{-1}$, expressed as a percentage, versus time.
- An accumulation of carbonylated oxidation products whose rate of formation was determined by plotting the increase in absorbance at 1 732 $cm^{-1}$ versus time.

The lifetime of black-pigmented ABS material can be determined by defining the extent of chemical oxidation which will cause micro-cracks and mechanical deterioration. For example, the rate of degradation of the butadiene groups allows the ranking of different formulations.



A: 3 415 cm$^{-1}$, hydroxylation products

A$_1$: after 160 h

B: 3 027 cm$^{-1}$, styrene

C: 2 237 cm$^{-1}$, nitrile

D: 1 732 cm$^{-1}$, carbonylated products

D$_1$: initial

D$_2$: after 60 h

D$_3$: after 110 h

D$_4$: after 160 h

E: 1 601 cm$^{-1}$, styrene

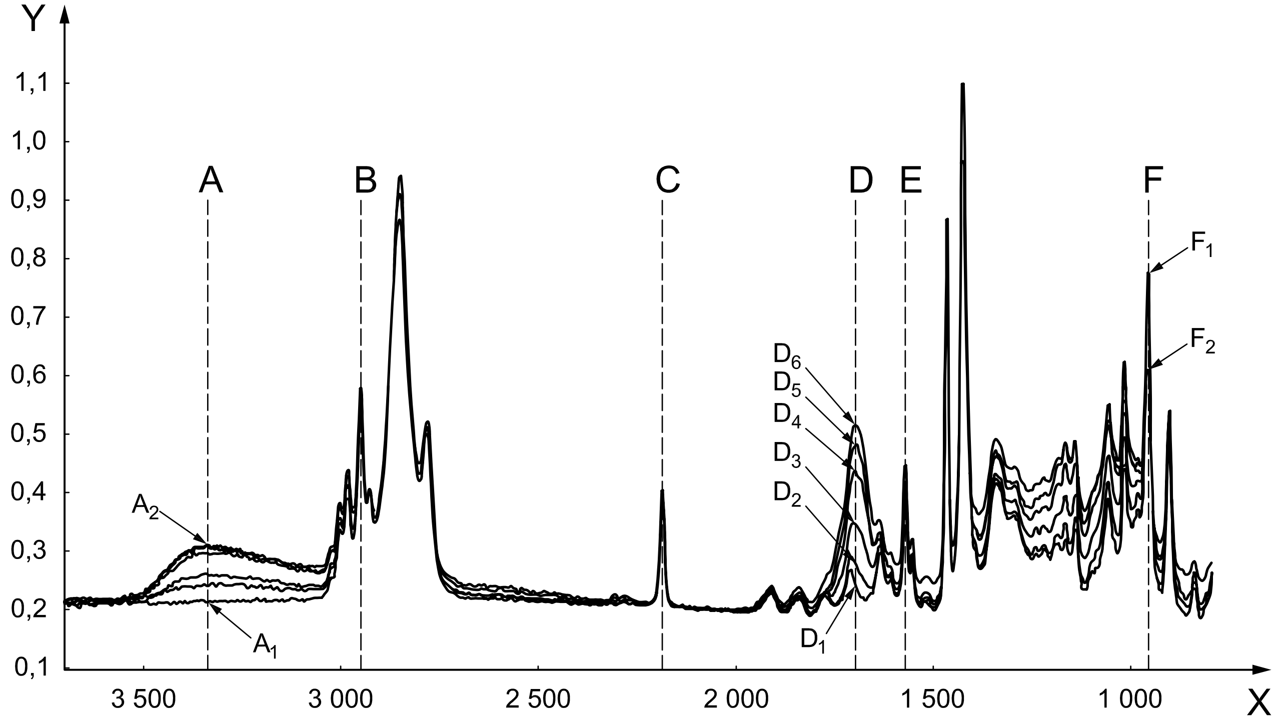
F: 967 cm$^{-1}$, 1,4-trans-butadiene

F$_1$: initial

F$_2$: after 160 h

**a) Artificial accelerated ageing with mercury-vapour lamps**

**Figure A.4** (*continued on next page*)



A: 3 415 cm$^{-1}$, hydroxylation products

$A_1$: initial

$A_2$: after 90 days

E: 1 601 cm$^{-1}$, styrene

B: 3 027 cm$^{-1}$, styrene

F: 967 cm$^{-1}$, 1,4-trans-butadiene

$F_1$: initial

$F_2$: after 90 days

C: 2 237 cm$^{-1}$, nitrile

D: 1 732 cm$^{-1}$, carbonylated products

$D_1$: initial

$D_2$: after 20 days

$D_3$: after 40 days

$D_4$: after 60 days

$D_5$: after 84 days

$D_6$: after 90 days

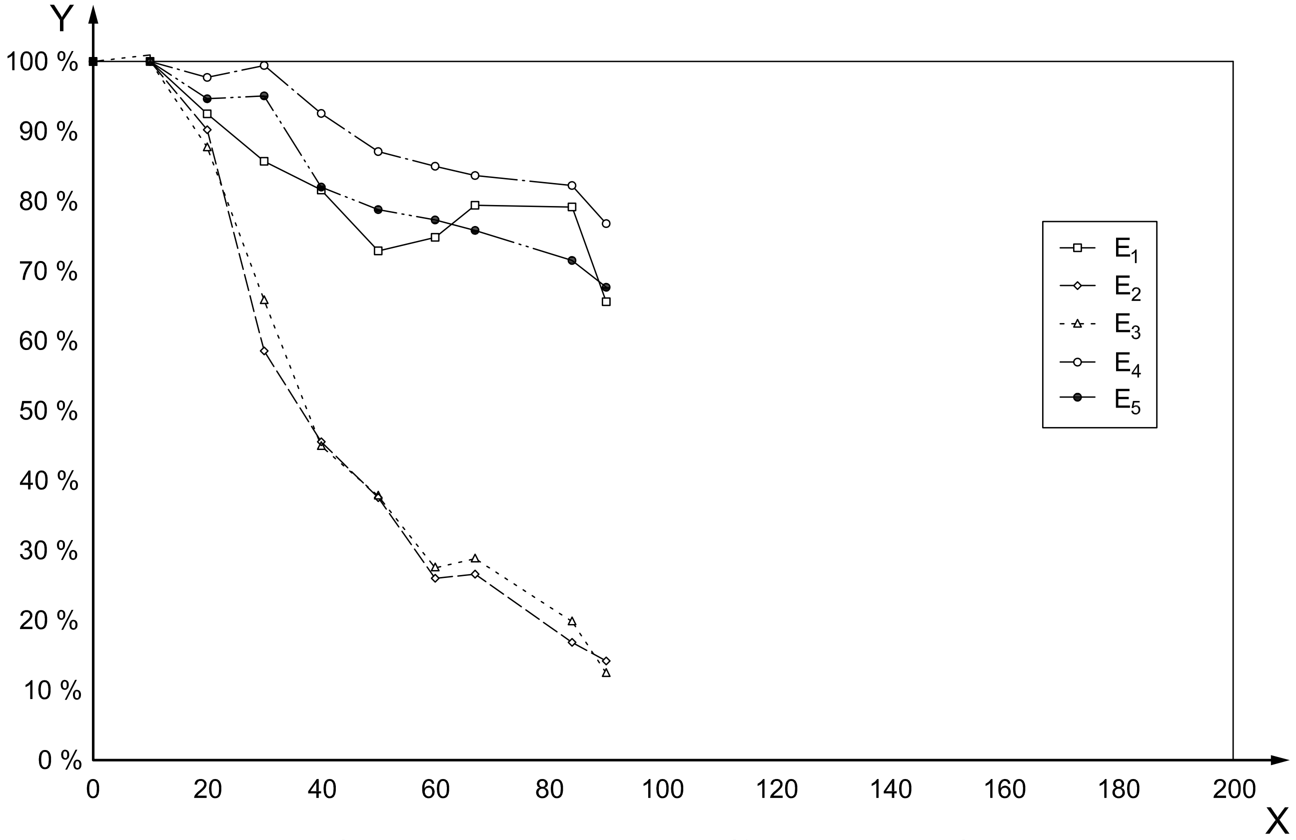
**b) Natural outdoor weathering**

**Key**

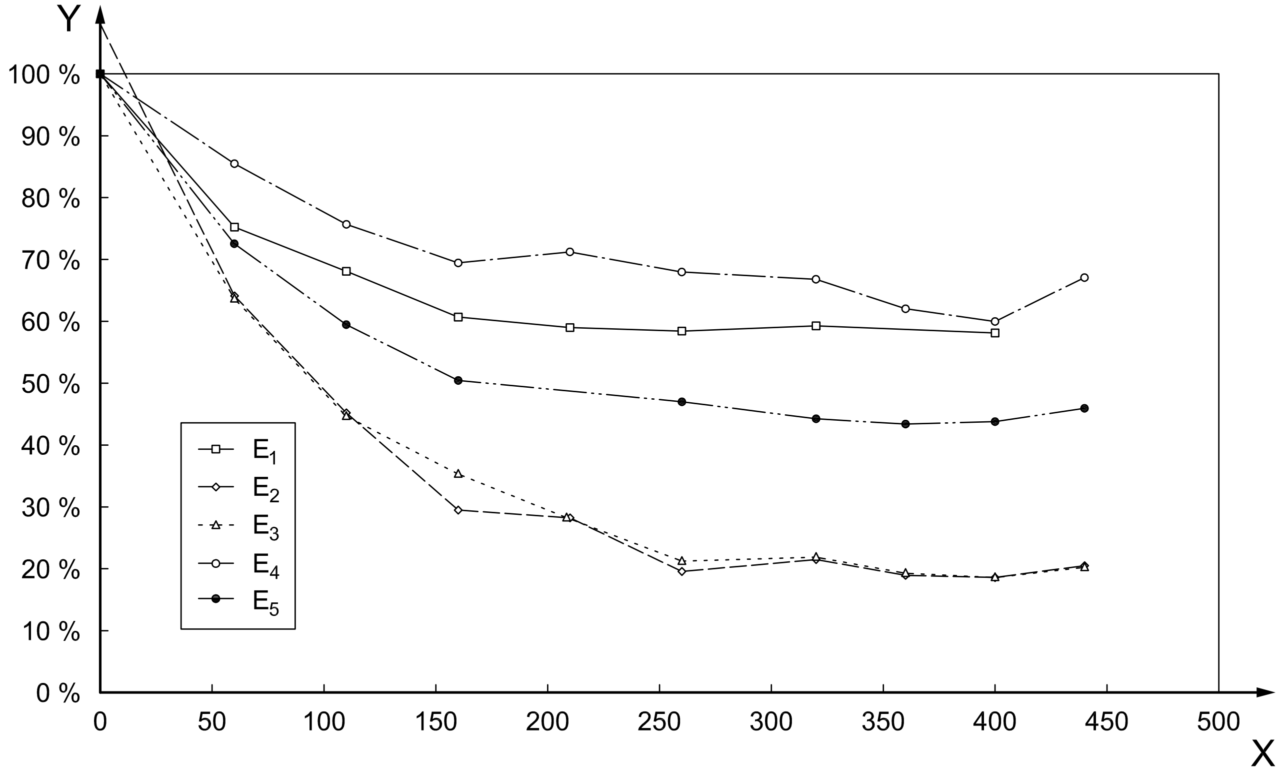
X wave number, cm$^{-1}$

Y absorbance

**Figure A.4 — FTIR photoacoustic analysis of the chemical changes in ABS during artificial accelerated ageing with mercury-vapour lamps and natural outdoor weathering**

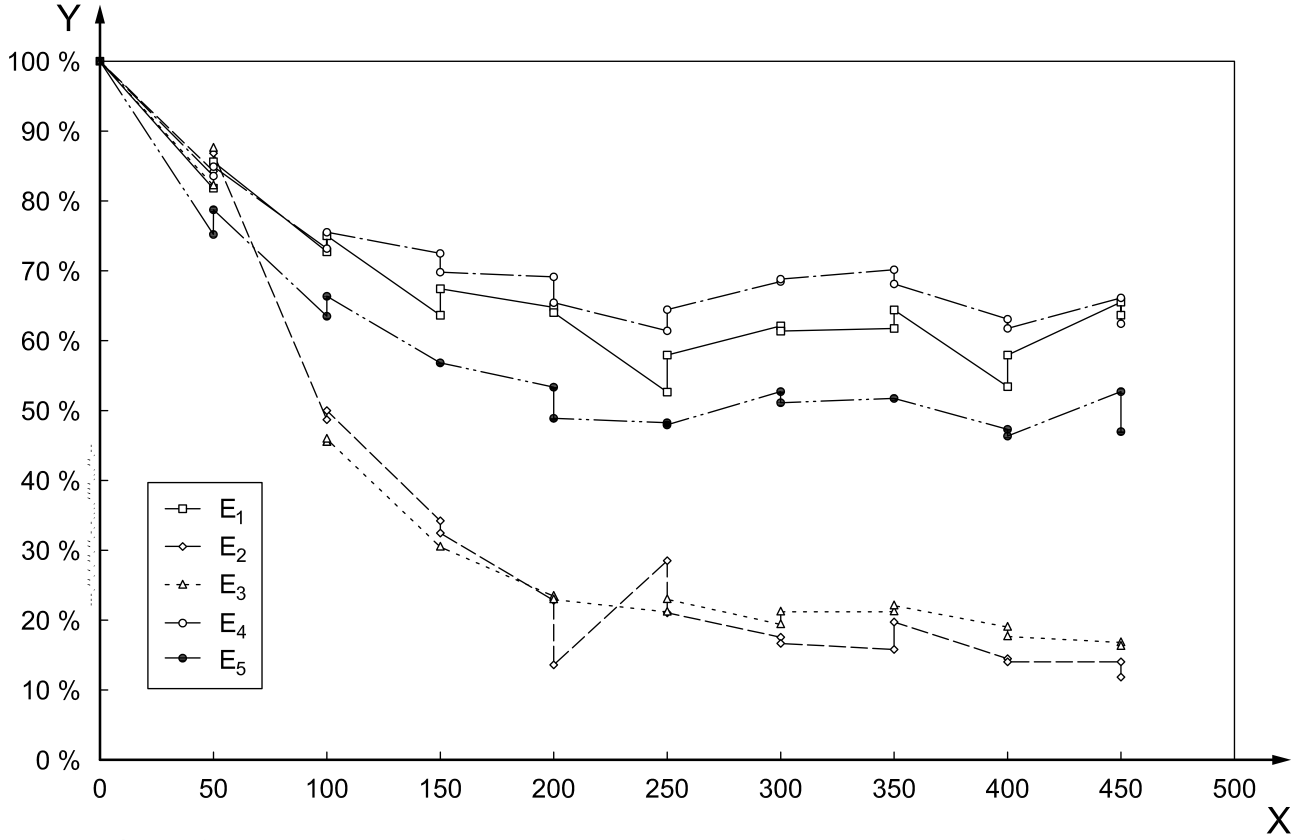


a) Natural outdoor weathering (Clermont-Ferrand)



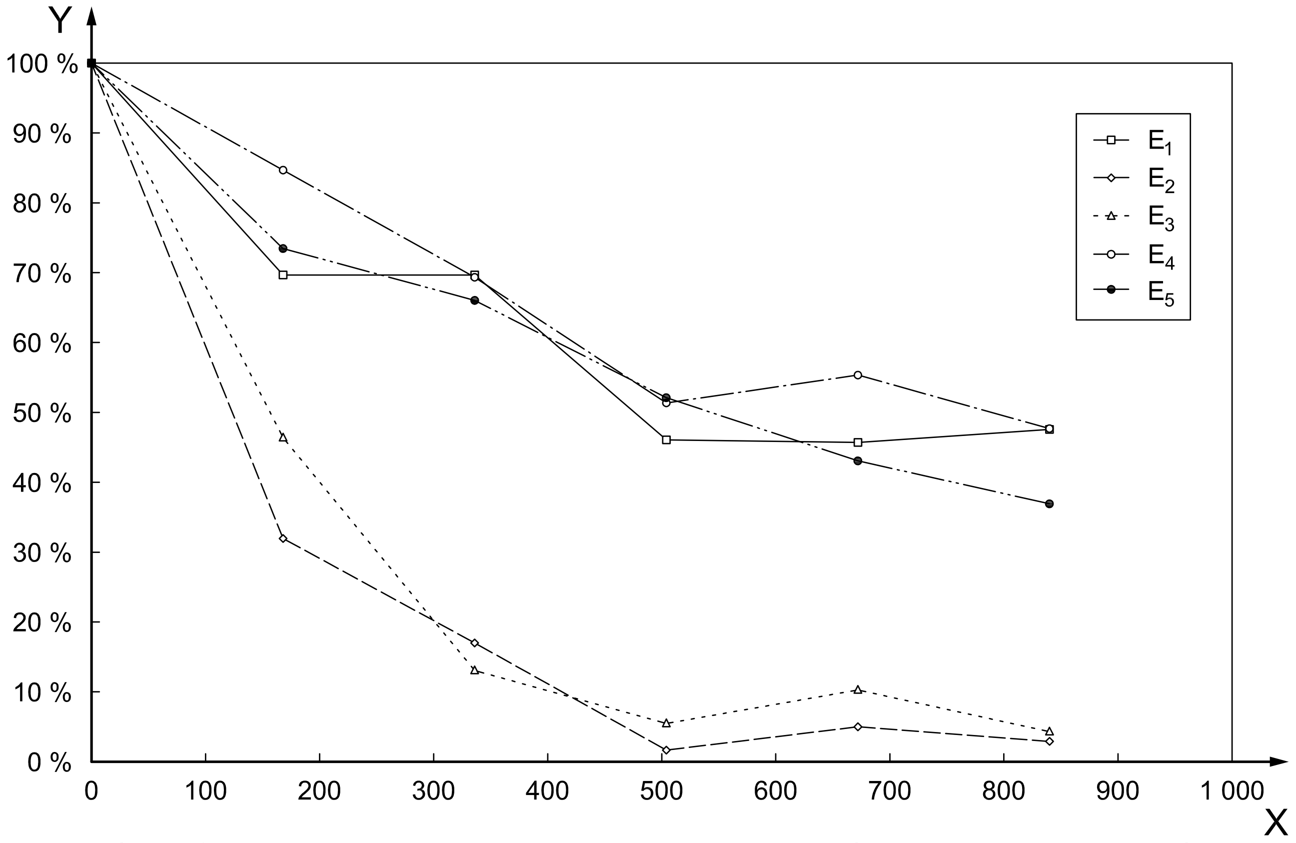
b) Artificial accelerated ageing using mercury-vapour lamps in dry conditions

**Figure A.5** (*continued on next page*)



**c) Artificial accelerated ageing using mercury-vapour lamps with periodic immersion**

**Figure A.5** (*continued on next page*)



d) Artificial accelerated weathering using xenon-arc lamp (18 min spray, 102 min dry)

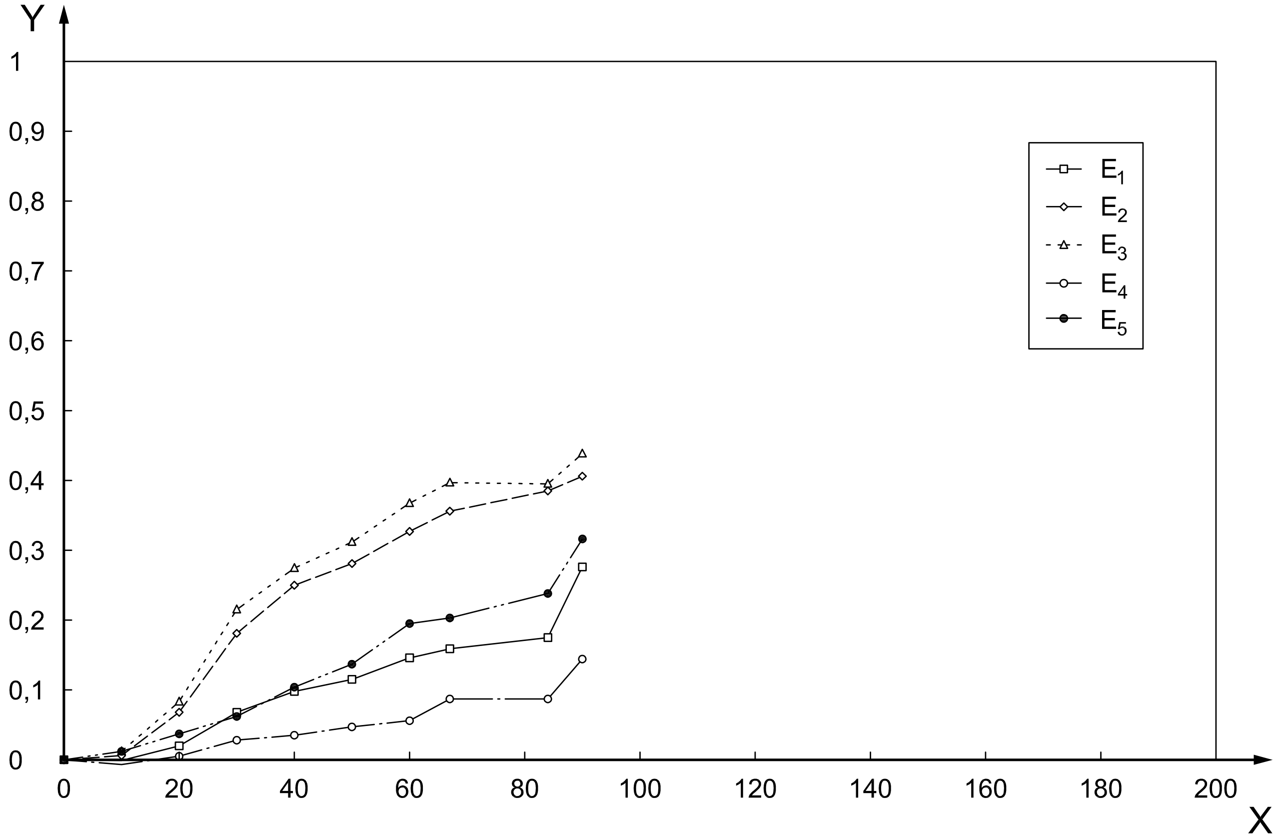
**Key**

X time, h

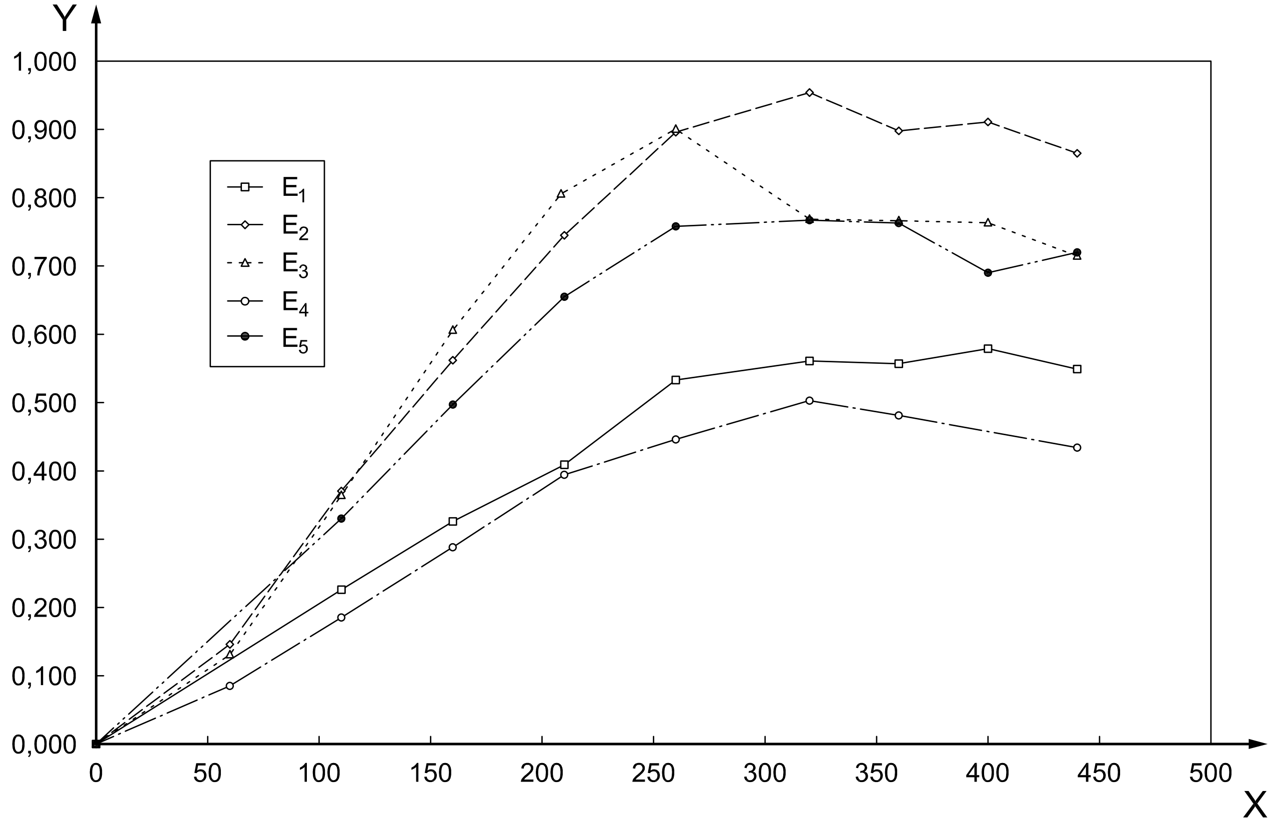
Y remaining butadiene concentration, expressed as a percentage

$E_1$, $E_2$, $E_3$, $E_4$, $E_5$ samples

**Figure A.5 — Remaining butadiene concentration (absorbance at 967 cm$^{-1}$) versus time**

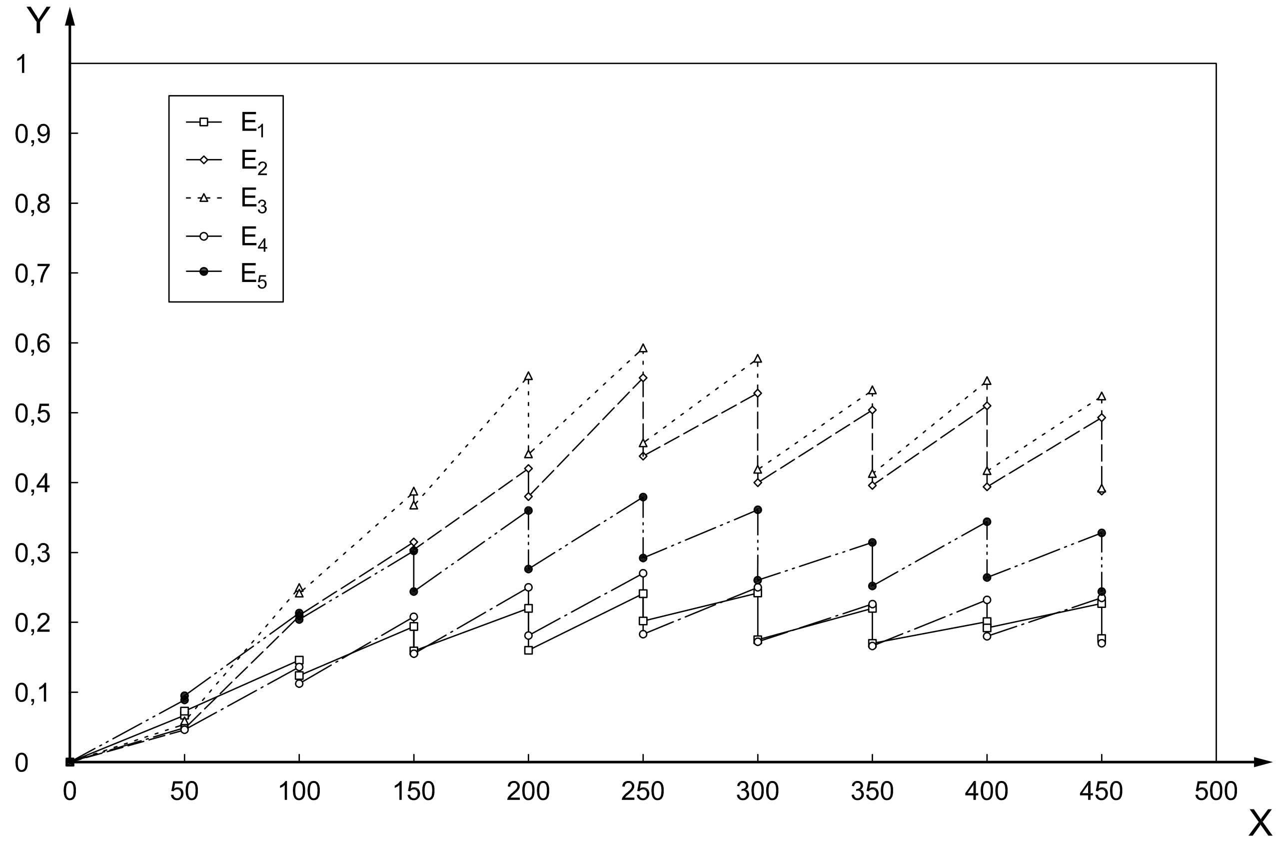


a) Natural outdoor weathering (Clermont-Ferrand)



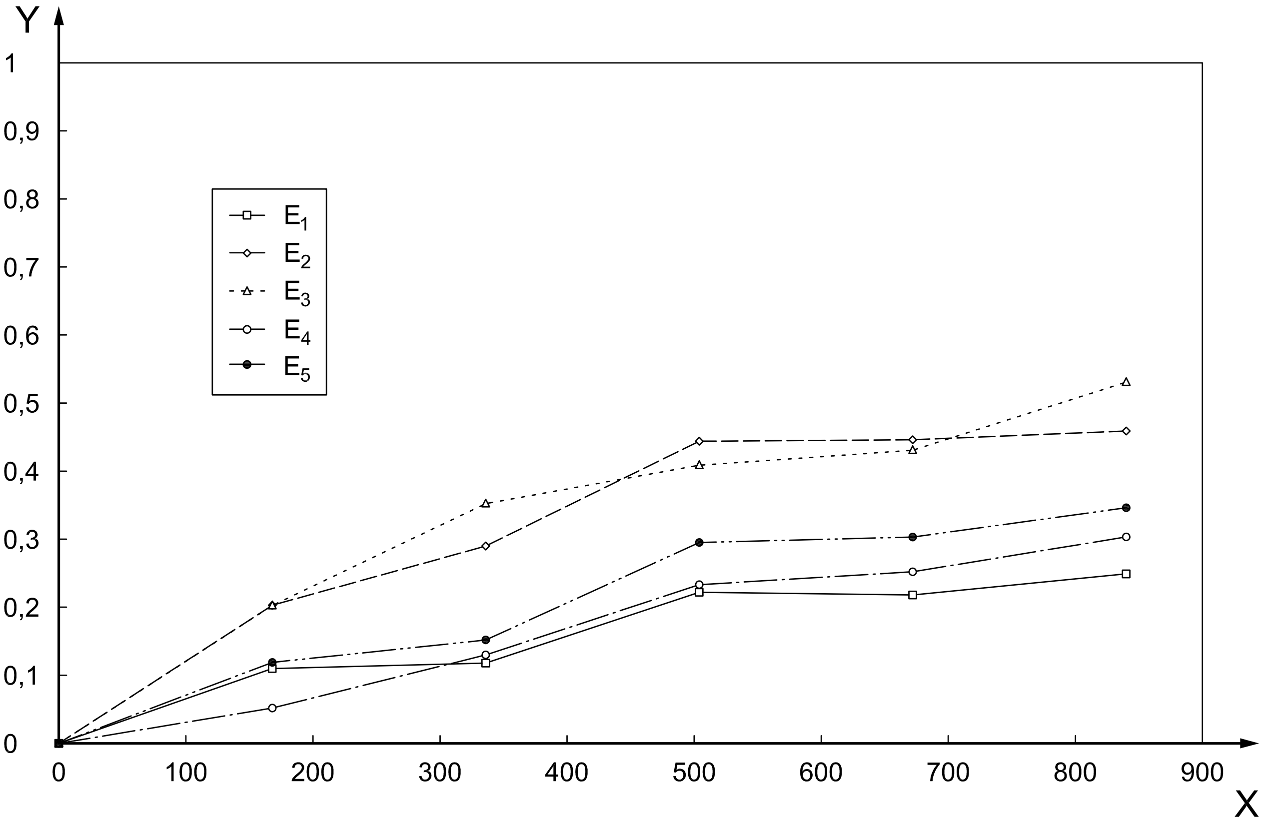
b) Artificial accelerated ageing using mercury-vapour lamps in dry conditions

**Figure A.6** (*continued on next page*)



**c) Artificial accelerated ageing using mercury-vapour lamps with periodic immersion**

**Figure A.6** (*continued on next page*)



**d) Artificial accelerated weathering using xenon-arc lamp (18 min spray, 102 min dry)**

**Key**

X time, h

Y accumulation of carbonylated products

$E_1$, $E_2$, $E_3$, $E_4$, $E_5$ samples

**Figure A.6 — Accumulation of carbonylated products (absorbance at 1 732 cm$^{-1}$) versus time**

When the required oxidation level was reached, water can lead to bleaching of the surface due to the leaching out of the ultimate carbonylated oxidation products. This discoloration can be determined by colorimetric measurements. Bleaching is a consequence of oxidation, so water was not necessary for ranking the ABS samples in terms of their photostability when oxidation, particularly oxidation of butadiene segments, was followed analytically using a suitable technique such as FTIR spectrometry. Moreover, the bleaching can be an ambiguous criterion for photodegradation because, in outdoor exposures, it can be variable and heterogeneous and depend on the rain or other accidental application of aqueous liquids.

Table A.1 shows the time taken to reach the beginning of significant bleaching (defined arbitrarily as 70 % degradation of the butadiene) for mercury-vapour lamps in dry and wet conditions, for xenon-arc artificial weathering and for natural outdoor weathering in Clermont-Ferrand.

**Table A.1 — Time to reach the beginning of significant bleaching**

| **Type of photoageing** (see Figures A.5 and A.6) | **Samples $E_2$ and $E_3$** | **Samples $E_1$, $E_4$ and $E_5$** |
|---|---|---|
| | **Time to reach 70 % degradation of butadiene** | **Time to reach 30 % degradation of butadiene** |
| Artificial accelerated photoageing using mercury-vapour lamps | 160 h | 100 h to 140 h |
| Artificial accelerated weathering using an xenon-arc lamp | 210 h | 300 h to 350 h |
| Natural outdoor weathering (in Clermont-Ferrand during the summer) | 60 days | 90 days |

Ranking of samples was similar between the artificial accelerated photoageing test, the artificial accelerated weathering test and the natural outdoor weathering (see Figure A.5 and Table A.1).

Samples $E_2$ and $E_3$ showed the same behaviour and were degraded approximately three times faster than samples $E_1$, $E_4$ and $E_5$.

NOTE The data shown in Table A.1 cannot be used as general acceleration factors relating time in these artificial accelerated weathering and photoageing tests to time outdoors for other ABS formulations, or for other materials, or for any other location except for Clermont-Ferrand. In addition, the lengths of time needed to produce the degree of degradation of ABS given in Table A.1 were based on a single series of exposures in each set of artificial ageing conditions and in Clermont-Ferrand. Multiple exposures at each location would be needed in order to establish the range of possible acceleration factors between the accelerated tests and this outdoor location for the materials studied.

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