TECHNICAL REPORT

ISO TR 10837

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Determination of the thermal stability of polyethylene (PE) for use in gas pipes and fittings

Détermination de la stabilité thermique du polyéthylène (PE) destiné à être utilisé dans les tubes et raccords pour la distribution du gaz

Reference number
ISO/TR 10837:1991(E)

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.

The main task of technical committees is to prepare International Standards, but in exceptional circumstances a technical committee may propose the publication of a Technical Report of one of the following types:

— type 1, when the required support cannot be obtained for the publication of an International Standard, despite repeated efforts;

— type 2, when the subject is still under technical development or where for any other reason there is the future but not immediate possibility of an agreement on an International Standard;

— type 3, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example).

Technical Reports of types 1 and 2 are subject to review within three years of publication, to decide whether they can be transformed into International Standards. Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.

ISO/TR 10837, which is a Technical Report of type 2, was prepared by Technical Committee ISO/TC 138, *Plastics pipes, fittings and valves for the transport of fluids.*

At the 23rd meeting of what was then ISO/TC 138/WG 4, *Plastics pipes and fittings for the supply of gaseous fuels,* held in Oslo, Norway, on 21st May, 1979, it was agreed to establish a "Thermal Stability" task group with the following confirmed terms of references:

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a) To consider the available information on the determination of the anti-oxidant content of polyethylene by thermal-stability analysis with a view to incorporating a suitable test method in the polyethylene pipes and fittings specification for gas.

b) If unsuccessful in a), to prepare a report of its findings to enable WG 5 to proceed with its work as quickly as possible.

c) To report its findings to WG 4.

In the period 1979 to 1983, seven task group meetings were held, and only at the initial meeting were proposals put forward to WG 4. These were rejected. The task group was unable to agree further proposals, despite a very extensive round-robin test programme involving eleven laboratories.

It is apparent that agreement on a specification is not possible at this time, and therefore this Technical Report has been prepared in accordance with clause G.6 of the IEC/ISO Directives.

Introduction

0.1 General

Polyethylene pipes and fittings are designed to be joined together by means of fusion techniques which can involve temperatures in excess of 200 °C. To prevent the polymers from which the pipes and fittings are made from degrading during fusion, it is necessary to incorporate stabilizers which impart thermal stability to the polymers.

The measurement of the thermal stability of a polymer can be determined by either measurement of the oxidation induction temperature of the polymer, or measurement of the oxidation induction time at a set temperature. These determinations are generally carried out in oxygen or air.

The task group (see foreword) agreed that the measurement of the oxidation induction time should be the preferred method because it offered greater sensitivity. A standard method of test for the measurement of thermal stability by means of oxidation induction time has been prepared.

0.2 Basic technical problem

In studying the polyethylenes used in the production of gas pipes and fittings and already shown to meet the performance requirements of national gas pipe and fitting specifications, the following major problem was identified which accounted for the task group's failure to reach agreement on proposals to be forwarded to the sub-committee.

When measuring the thermal stability of a polymer by determining the oxidation induction time at either 200 °C or 210 °C, two distinctly different stability levels were identified due to the use of different stabilizer systems.

It was therefore not possible to agree a specification level which could be met by acceptable polymers, yet ensure in all cases sufficient thermal stability to permit the assembly of pipes and fittings by fusion.

The problem faced by the task group is illustrated by figure 0.1.

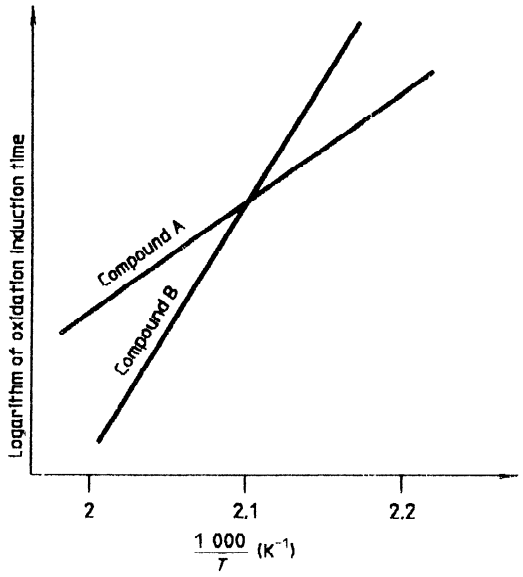

Figure 0.1 — Oxidation of two different stabilizer systems

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WARNING — The use of this Technical Report may involve hazardous materials, operations and equipment. This Technical Report does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this Technical Report to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This Technical Report specifies a method of measuring the oxidative thermal stability of polyethylene pipe and fitting material in oxygen at typical processing and welding temperatures. It may be used to measure the stability of either raw materials or finished products, and may be taken as an indication of polymer or anti-oxidant performance.

The recommended test temperatures of 200 °C and 210 °C are suitable for adequately stabilized pipe and fitting materials.

The thermal stability measured by this method is dependent on test specimen mass and size.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this Technical Report. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this Technical Report are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 293:1986, *Plastics — Compression moulding test specimens of thermoplastic materials.*

3 Principle

The test measures the time during which the anti-oxidant present in a test specimen inhibits oxidation whilst the specimen is held at 200 °C (or 210 °C) in a stream of oxygen.

The progress of the oxidation is monitored by measuring the difference in temperature between the specimen compartment and reference compartment of a thermal analyser and recording this against time. The thermal stability is then derived from this record.

4 Apparatus and materials

4.1 Differential thermal analyser or **differential scanning calorimeter**, capable of

a) recording the difference in temperature or in energy flow between specimen and reference compartments against time;

b) maintaining the test temperature within $\pm 0{,}5$ °C for the duration of the test;

c) exposing the specimen to a flow of oxygen equal to 50 cm^3/min $\pm$ 10 %;

d) programming the specimen temperatures over the range 150 °C to 250 °C, at a rate of 1 °C/min or less;

e) programming the specimen temperature to rise from ambient temperature to the test temperature at a rate of 20 °C ± 1 °C;

f) continuously recording the specimen temperature with a resolution of 0,1 °C (if this facility is not available, then 4.2 applies).

4.2 Temperature-measuring apparatus, capable of continously monitoring the specimen temperature with a resolution of 0,1 °C.

A high-impedance digital voltmeter with a resolution of 1 µV has been found suitable when connected to the specimen thermocouple and the associated cold junction, or cold-junction compensator, of the thermal analyser.

4.3 Analytical balance, capable of weighing the 15 mg ± 0,5 mg test specimen to an accuracy of 0,1 mg.

4.4 Oxygen and high-purity nitrogen supplies, able to be switched to give alternate flow. The changeover shall be made sufficiently close to the differential thermal analyser or differential scanning calorimeter cell so that the atmosphere is completely changed within 1 min of switchover.

No purification train is deemed necessary in either compressed-gas supply.

4.5 Gas-flow-measuring devices.

Rotameters are suitable, but their calibration shall be checked against a positive-displacement device.

4.6 High-purity metal standards.

Indium: Melting point 156,6 °C ± 0,5 °C;

Tin: Melting point 231,9 °C ± 0,5 °C.

5 Preparation of test specimens

5.1 Test specimens from pipe and fittings

The position from which the test specimen is taken shall be as defined in the relevant product standard.

a) Saw a 2 cm to 3 cm ring from the sample pipe or fitting.

b) Cut a 2 cm segment from the ring.

c) Holding the segment in a vice, cut a through-wall cylinder sample with a diameter just less than the inner diameter of the sample pans of the thermal analyser.

d) Using a scalpel, cut a test specimen from the through-wall cylinder of appropriate thickness to give a specimen weight of 15 mg ± 0,5 mg.

The test specimen is designed to allow measurement of the thermal stability at points throughout the wall thickness.

e) Handle the specimen with care and do not expose it to direct sunlight.

NOTE 1 A hole-borer, driven by an electric drill, is a suitable device for taking a through-wall core directly from a pipe or fitting. Care should be taken not to overheat the sample.

5.2 Test specimens from raw materials in the form of moulded sheet

a) Prepare a compression-moulded plaque in accordance with ISO 293. Limit heating to 2 min at 150 °C ± 3 °C.

b) Cut a cylindrical sample with a diameter just less than the inner diameter of the specimen.

c) Using a scalpel, cut a specimen from the cylinder to give a specimen weight of 15 mg ± 0,5 mg.

6 Procedure

6.1 Calibration

Establish an oxygen flow of 50 cm³/min ± 10 % over the specimen and reference compartments of the apparatus at a temperature 10 °C below the melting point of indium or tin.

Heat a 2 mg specimen of indium or tin in a sealed aluminium pan, using an empty aluminium pan as reference, at a rate not exceeding 1 °C/min until the melting endotherm has been recorded. If the apparatus does not automatically do so, mark the indicated temperature on the chart at intervals in the region of the endotherm so that the melting point can be determined to a precision of ± 0,1 °C. Determine the melting points of both indium and tin in this way.

The melting point of the metal is taken as the temperature given by the intercept of the extended baseline and the tangent to the first slope of the endotherm (see figure 1).

Adjust the apparatus so that the indicated melting points of indium and tin lie within the ranges 156,6 °C ± 0,5 °C and 231,9 °C ± 0,5 °C, respectively.

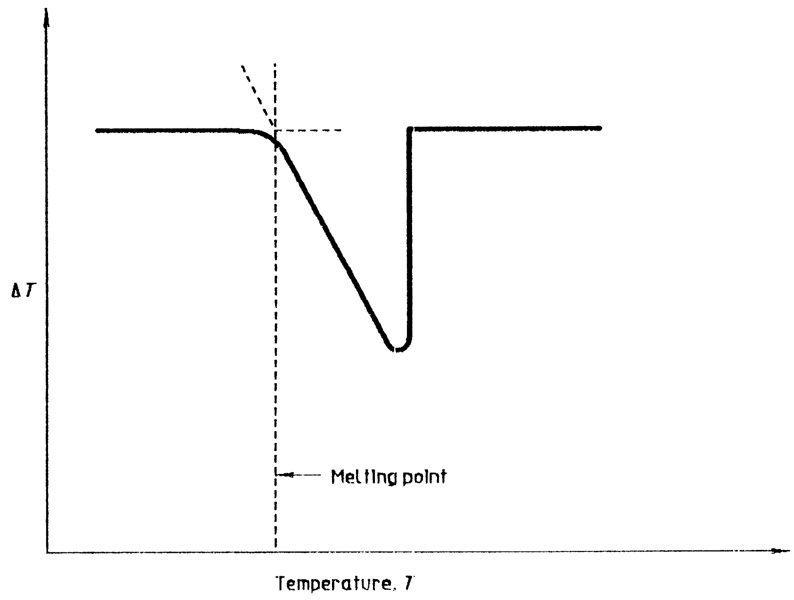

Figure 1 — Typical calibration curve

6.2 Time calibration

Using a stopwatch, check that the pen moves along the abscissa at the selected rate.

6.3 Measurement of oxidation induction time

Establish a nitrogen flow of 50 cm³/min ± 10 % through the differential thermal analysis or differential scanning calorimeter cell. Check that when a switchover to oxygen is made the gas flow will continue at the rate of 50 cm³/min ± 10 % and then revert to a nitrogen flow of 50 cm³/min ± 10 %.

Place a 15 mg ± 0,5 mg cylindrical polyethylene specimen in an open aluminium pan and an empty aluminium reference pan into the cell. Set the instrument to run isothermally at 200 °C ± 0,1 °C (or 210 °C ± 0,1 °C), raising the temperature at a rate of 20 °C/min and allowing the temperature to stabilize. Make any corrections to the heater voltage to bring the specimen temperature to 200 °C ± 0,1 °C (210 °C ± 0,1 °C). Start to record the thermogram (the plot of the temperature difference against time).

When stable conditions exist under the nitrogen flow, which should be the case after 5 min, switch over to oxygen and mark this point on the thermogram. The cell should be purged within 1 min of atmosphere changeover. Continue to run the thermogram until the oxidation exotherm has occurred, and has reached its maximum.

7 Interpretation of results

The thermal stability of the specimen is the time taken, in minutes, from the introduction of oxygen to the intercept of the extended baseline and the tangent drawn to the exotherm at the point of maximum slope (see figure 2).

The thermal stability of the sample is the arithmetic mean of at least five oxidation induction time measurements at 200 °C or 210 °C.