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Polyolefin pipes and fittings — Determination of carbon black content by calcination and pyrolysis — Test method

Tubes et raccords en polyoléfines — Détermination de la teneur en noir de carbone par calcination et pyrolyse — Méthode d'essai

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 138, *Plastics pipes, fittings and valves for the transport of fluids*, Subcommittee SC 5, *General properties of pipes, fittings and valves of plastic materials and their accessories — Test methods and basic specifications*.

This second edition cancels and replaces the first edition (ISO 6964:1986), which has been technically revised. The main changes compared with the last edition are the following:

— Conventional and microwave muffle furnace test methods, and a thermogravimetric analyzer (TGA) test method have been added.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Polyolefin pipes and fittings — Determination of carbon black content by calcination and pyrolysis — Test method

1 Scope

This document specifies test methods for the determination of the carbon black content of polyolefin compositions used in particular for the manufacture of pipes and fittings, and provides a basic specification for polyethylene pipes and fittings.

This document applies equally to the material for manufacture and to any material taken from a pipe or fitting.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11358-1, *Plastics — Thermogravimetry (TG) of polymers — Part 1: General principles*

3 Principle

It is possible to determine the carbon black content of polyolefin compositions by one of the following three methods:

a) Pyrolysis of the sample at (550 ± 50) °C in a stream of nitrogen for 45 min followed by calcination at (900 ± 25) °C, by using an electrical tube furnace (Method A).

b) Pyrolysis of the sample in a quartz crystal crucible with lid, by using a muffle furnace. According to the type of muffle furnace used there are two different procedures:

   1) Conventional muffle furnace (Method B1): pyrolysis from (325 ± 25) °C to (550 ± 25) °C at 15 °C/min and at (550 ± 25) °C for (10 ± 0,5) min followed by calcination at (900 ± 25) °C.

   2) Microwave muffle furnace (Method B2): pyrolysis at (520 ± 25) °C for (10 ± 0,5) min followed by calcination at (900 ± 25) °C.

c) Pyrolysis of the sample at a constant rate in a thermogravimetric analyzer (TGA) under inert atmosphere at 800 °C followed by calcination under oxidizing atmosphere at 900 °C (Method C).

NOTE 1 Carbon black is decomposed from 500 °C in air or oxygen. Therefore, the loss observed between 500 °C and 700 °C in air or oxygen corresponds to the overall decomposition of the carbon black.

NOTE 2 If the composition contains, in addition to the carbon black, additives likely to decompose at 900 °C, for example ingredients such as calcium carbonate, the calculation can lead to an over-estimation of the carbon black content. If the ash yield is more than 1 %, further investigation can be required.

Calculate the carbon black content from the difference in mass before and after calcination and pyrolysis.

4 Method A: Electrical tube furnace

4.1 Reagents

4.1.1 Dry nitrogen, having an oxygen content less than 20 ppm, under pressure in a steel cylinder provided with a pressure-reducing valve and flow meter.

NOTE If required, the nitrogen can be purified by bubbling the gas through a pyrogallol solution or by passing it over heated copper tinsel, foil, wire or turnings or by passing it through a gas purifier prior to passing into the furnace.

4.2 Apparatus

4.2.1 Silica combustion sample boat, with a sleeve of 50 mm to 60 mm long.

4.2.2 Electric tube furnace, fitted with a device to allow the sample boat to be inserted and withdrawn. The tube is fitted with nozzles to admit the nitrogen and to evacuate the fumes. A diaphragm closed by means of a glass-wool bung placed behind the entry nozzle ensures that the nitrogen stream is distributed uniformly.

The minimum length of the electric tube furnace should be ≥ 3 times the length of the sample boat, and the minimum length of the quartz tube should be ≥ 7 times the length of the sample boat.

4.2.3 Desiccator, capable of holding the silica sample boat (4.2.1).

4.2.4 Balance, with an accuracy of ± 0,1 mg.

4.2.5 Timer, with an accuracy of ± 1 s.

4.3 Procedure

4.3.1 Test conditions

Determination of mass shall be carried out in a room at standard temperature (23 ± 2) °C.

4.3.2 Sampling

Test specimen may be in the form of pellet or finished product. In the last case, the specimen shall be reduced to small fragments.

4.3.3 Conditioning

The test sample shall be conditioned for 24 h at (23 ± 2) °C before preparation.

4.3.4 Silica sample boat preparation for the test

Take the silica sample boat which shall be clean and weighed, and proceed as follows:

Place the silica sample boat in the electric tube furnace and adjust the temperature to (900 ± 25) °C. Once this temperature is reached, leave to calcination for approximately 1 h. Then, dry the silica sample boat in the desiccator at room temperature and weigh. Place again the silica sample boat into the desiccator for 30 min and weigh again. This operation shall be repeated until constant mass, i.e. until two consecutive weighing do not differ by more than 0,5 mg. This weighing is recorded as m.

4.3.5 Test portion

Three test portions shall be prepared as follows:

Tare the silica sample boat. Weigh, to the nearest 0,1 mg, approximately 1 g of material from the test sample (4.3.2). Record this mass as m_1.

4.3.6 Determination

The determination on each test sample shall be carried out as described below.

Place the silica sample boat with the test portion (4.3.4) in the inlet of the combustion tube of the electric tube furnace (4.2.2) which has been previously heated to (550 ± 50) °C. Fix the nozzle to the tube inlet and then connect it to the outlet of the nitrogen stream after, if necessary, the nitrogen has passed through the purification system; circulate the nitrogen in the apparatus at a rate of (200 ± 20) cm^3/min for approximately 5 min.

Move the combustion tube with the silica sample boat towards the centre of the electric tube furnace, adjust the nitrogen flow rate to (100 ± 10) cm^3/min and leave it to pyrolyse for approximately 45 min.

At the end of this period, return the combustion tube with the silica sample boat to the cold section of the electric tube furnace and leave it there for 10 min while maintaining the flow of nitrogen.

Remove the silica sample boat from the combustion tube of the electric tube furnace, allow it to cool in the desiccator (4.2.4) and weigh under the same conditions as prior to the pyrolysis (4.3.3). Record the mass to the nearest 0,1 mg as m_2.

Place the silica sample boat in the furnace at a temperature of (900 ± 25) °C and calcine until all traces of carbon black have disappeared. Allow it to cool in the desiccator (4.2.4) and weigh under the same conditions as prior to the pyrolysis (4.3.3). Record the mass to the nearest 0,1 mg as m_3.

4.4 Calculation and expression of results (Method A)

Calculate the carbon black content, expressed as a percentage by mass, from Formula (1).

$$\frac{m_2 - m_3}{m_1} \times 100\% \qquad (1)$$

where

m_1 is the mass, in grams, of the test portion;

m_2 is the mass, in grams, of the silica sample boat plus the test portion after pyrolysis at 550 °C;

m_3 is the mass, in grams, of the sample boat plus the test portion after calcination at 900 °C, with ash where appropriate.

Calculate the arithmetic mean of the carbon black content determined on the three test portions and report the result rounded mathematically to two significant figures.

NOTE Where appropriate (see NOTE 2 to Clause 3), calculate the ash content, expressed as a percentage of the original mass, from Formula (2):

$$\frac{m_3 - m}{m_1} \times 100\% \qquad (2)$$

where

m is the mass, in grams, of the silica sample boat;

m_1 is the mass, in grams, of the test portion;

m_3 is the mass, in grams, of the sample boat plus the test portion after calcination at 900 °C, with ash where appropriate.

Calculate the arithmetic mean of the ash content determined on the three test portions and report the result rounded mathematically to two significant figures.

5 Method B1 or B2: Muffle furnace (conventional B1) or (microwave B2)

5.1 Apparatus

5.1.1 Crucible, recipient of quartz crystal with a lid of the same material which closes the recipient just by superposition on the recipient, with approximately 10 ml capacity.

The crucible system generates an inert atmosphere by replacing the air in the crucible due to the gases released by the sample during the pyrolysis. It is important that there is no damage on the crucible edge or on the lid because it would allow air to enter and the consequent burning of the sample.

5.1.2 Desiccator, capable of holding the crucibles (5.1.1).

5.1.3 Balance, with an accuracy of ±0,1 mg.

5.1.4 Conventional muffle furnace, for method B1 (5.2.6.1).

NOTE For a muffle furnace that does not have a programming system, a scan of (15 ± 1) °C/min is equivalent to heating from 300 °C to 500 °C in approximately 15 min and similarly for the cooling scan.

5.1.5 Microwave muffle furnace, for method B2 (5.2.6.2).

5.1.6 Timer, with an accuracy of (±1) s.

5.2 Procedure

5.2.1 Test conditions

Determination of mass shall be carried out in a room at standard temperature (23 ± 2) °C.

5.2.2 Conditioning

The test sample shall be conditioned for 24 h at (23 ± 2) °C before preparation.

5.2.3 Sampling

The test specimen may be in the form of a pellet or finished product. In the last case, the specimen shall be reduced to small fragments.

5.2.4 Crucible preparation for the test

Take the crucible which shall be clean and weighed, and proceed as follows:

Place the crucible in the conventional muffle furnace and adjust the temperature to (900 ± 25) °C. Once this temperature is reached, leave to calcinate for approximately 1 h. Then, dry the crucible in the desiccator at room temperature and weigh. Place again the crucible into the desiccator for 30 min and weigh again. This operation shall be repeated until constant mass, i.e. until two consecutive weighing do not differ by more than 0,5 mg. This weighing is recorded as m.

This procedure could be carried out also in a microwave muffle furnace at the same temperature but for 15 min.

5.2.5 Test portion

Three test portions shall be prepared as follows with the mass selected in the range dependent on the equipment used:

Tare the crucible. Weigh, to the nearest 0,1 mg, approximately 1 g to 10 g of the material according to the type of crucible used.

Record this mass as m_1.

5.2.6 Determination

5.2.6.1 Method B1: Conventional muffle furnace

Place the crucible with lid and with the test portion (5.2.4) in the conventional muffle furnace (5.1.4). The temperature shall be at (325 ± 25) °C. Program the heating scan to (10 to 15 ± 1) °C/min until reaching (550 ± 25) °C. Let it pyrolize at this temperature for (10 ± 5) minutes. Program cooling scan to (15 ± 1) °C/min until reaching (325 ± 25) °C, initial temperature of the pyrolysis cycle.

Remove the crucible with lid from the muffle furnace and allow it to cool in the desiccator until room temperature is reached. Dry the crucible with lid in the desiccator at room temperature and remove the lid to weigh the crucible. Place the crucible in the desiccator for 30 min and weigh again. This operation shall be repeated until constant mass, i.e. until two consecutive weighing do not differ by more than 0,5 mg. This weighing is recorded as m_2.

Place the crucible without lid in the muffle furnace and adjust the temperature to (900 ± 25) °C. When this temperature is reached, calcine for (30 ± 5) min.

Turn off the muffle furnace, wait until the temperature has dropped below 500 °C and remove the crucible. Dry the crucible without the lid in the desiccator at room temperature and weigh. Place the crucible in the desiccator for 30 min and weigh again. This operation shall be repeated until constant mass, i.e. until two consecutive weighing do not differ by more than 0,5 mg. This weighing is recorded as m_3.

5.2.6.2 Method B2: Microwave muffle furnace

Place the crucible with lid and with the test portion (4.2.4) in the microwave muffle furnace (5.1.5), which temperature shall be at (520 ± 25) °C. Leave it to pyrolyse for (10 ± 0,5) min.

Remove the crucible with lid from the microwave muffle furnace and allow it to cool in the desiccator until room temperature is reached. Dry the crucible with lid in the desiccator at room temperature and weigh the crucible without the lid. Place the crucible in the desiccator for 30 min and weigh again. This operation shall be repeated until constant mass, i.e. until two consecutive weighing don't differ by more than 0,5 mg. This weighing is recorded as m_2.

Place the crucible without lid in the microwave muffle furnace and adjust the temperature at (900 ± 25) °C. When this temperature is reached, calcine for (10 ± 1) min.

Turn off the microwave muffle furnace, wait until the temperature has dropped below 500 °C and remove the crucible. Cover the crucible with the lid and introduce it in the desiccator at room temperature and weigh the crucible without the lid. Place the crucible in the desiccator for 30 min and weigh again. This operation shall be repeated until constant mass, i.e. until two consecutive weighing do not differ by more than 0,5 mg. This weighing is recorded as m_3.

5.3 Calculation and expression of results (Method B1 and B2)

Calculate the carbon black content, expressed as a percentage by mass, from Formula (3):

$$\frac{m_2 - m_3}{m_1} \times 100\% \qquad (3)$$

where

m_1 is the mass, in grams, of the original test portion;

m_2 is the mass, in grams, of the crucible plus the test portion after pyrolysis;

m_3 is the mass, in grams, of the crucible plus the test portion after calcination, with ash where appropriate.

Calculate the arithmetic mean of the carbon black content determined on the three test portions and report the result rounded mathematically to two significant figures.

NOTE Where appropriate (see NOTE 2, Clause 3), calculate the ash content, expressed as a percentage of the original mass, from Formula (4):

$$\frac{m_3 - m}{m_1} \times 100\% \qquad (4)$$

where m is the mass, in grams, of the crucible.

Calculate the arithmetic mean of the ash content determined on the three test portions and report the result rounded mathematically to two significant figures.

6 Method C: Thermogravimetric analyzer (TGA)

6.1 Apparatus

For the purposes of this document, the instruments suitable for this test method given in ISO 11358-1 shall apply.

6.2 Procedure

6.2.1 Conditioning

The test sample shall be conditioned for 24 h at (23 ± 2) °C before preparation.

6.2.2 Sampling

The test specimen may be in the form of a pellet or finished product. In the last case, the specimen shall be reduced to small fragments.

NOTE This method is suitable for pellet and products containing more than 2 % carbon black.

6.2.3 Test portion

Three test portions shall be prepared from the sample in an appropriate size for the specimen holder. Microtome or razor blades are suitable for this purpose. For each sample portion proceed as follows:

- Cut 15 mg to 40 mg of test sample.
- Tare the sample holder.

— Place the test portion in the sample holder; check whether the mass is between 15 mg and 40 mg.

In case of dispute a sample between 20 mg and 30 mg should be used.

6.2.4 Temperature scanning program

The temperature scan method shall follow the next steps:

a) Scan at 10 °C/min or at 20 °C/min from 23 °C to 800 °C (under purge of an appropriate inert gas).

b) Isotherm at 800 °C for 15 min (under purge of an appropriate inert gas).

c) Without cooling, scan at 10 °C/min or 20 °C/min from 800 °C to 900 °C (under purge of air/oxygen).

6.2.5 Gas-flow rate

Choose the gas-flow rate in accordance with ISO 11358-1 taking into account the equipment used.

6.2.6 Determination

Start the test and determine the percentage of carbon black measuring the mass loss produced from the air or oxygen entering.

In order to determine the percentage of carbon black, the mass loss that the test portion suffers during the heating scan [see 6.2.4 c)] shall be measured, expressed as a percentage. As the scope of this document only refers to the carbon black content, it is not necessary to obtain all indicated possible data of the curve (see Figure 1). The values of initial mass at 23 °C (m_i) and after the scan to 900 °C (m_f) the mass loss shall be recorded, as well as the mass of the test portion before the start of the test method (m_s).

6.3 Calculation and expression of results (Method C)

Calculate the carbon black content, expressed as a percentage by mass, from Formula (5):

$$\frac{m_i - m_f}{m_s} \times 100\,\% \qquad (5)$$

where

m_s is the mass, in milligrams, of the test portion before the start of the test method;

m_i is the mass, in milligrams, before mass loss;

m_f is the mass, in milligrams, after mass loss.

Calculate the arithmetic mean of the carbon black content (in percentage) determined on the three test portions and report the result rounded mathematically to two significant figures.

NOTE 1 Where appropriate (see NOTE 2, Clause 3), calculate the ash content, expressed as a percentage of the original mass, from Formula (6):

$$\frac{m_f}{m_s} \times 100\,\% \qquad (6)$$

Calculate the arithmetic mean of the ash content determined on the three test portions and report the result rounded mathematically to two significant figures.