BS ISO 11236:2017

BSI Standards Publication

# Rubber compounding ingredients — *p*-Phenylenediamine antidegradants (PPDs) — Test methods

Documents
Document Sharing Hub

Full document details: BS ISO 11236:2017

# National foreword

This British Standard is the UK implementation of ISO 11236:2017.

The UK participation in its preparation was entrusted to Technical Committee PRI/50, Raw materials (including latex) for use in the rubber industry.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

© The British Standards Institution 2017
Published by BSI Standards Limited 2017

ISBN 978 0 580 92857 4

ICS 83.040.20; 01.040.83

**Compliance with a British Standard cannot confer immunity from legal obligations.**

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 September 2017.

**Amendments/corrigenda issued since publication**

| Date | Text affected |
|---|---|

Documents
Document Sharing Hub

Full document details: BS ISO 11236:2017

INTERNATIONAL STANDARD

# ISO 11236

Second edition
2017-08

# Rubber compounding ingredients — *p*-Phenylenediamine antidegradants (PPDs) — Test methods

*Ingrédients de mélange du caoutchouc — Antidégradants du type* p-*phénylènediamine (PPDs) — Méthodes d'essai*

Reference number
ISO 11236:2017(E)

Documents
Document Sharing Hub

© ISO 2017

Full document details: BS ISO 11236:2017

**COPYRIGHT PROTECTED DOCUMENT**

© ISO 2017, Published in Switzerland

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org


© ISO 2017 – All rights reserved

Documents
Document Sharing Hub

Full document details: BS ISO 11236:2017

# Contents

Page

**Foreword** ... **iv**

**1 Scope** ... **1**

**2 Normative references** ... **1**

**3 Terms and definitions** ... **1**

**4 Abbreviated terms** ... **2**

**5 Use and classification** ... **2**

**6 Sampling and repeat determinations** ... **3**

**7 Determination of purity by gas chromatography (GC)** ... **3**
- 7.1 General ... 3
- 7.2 Interference ... 3
- 7.3 Apparatus ... 3
- 7.4 Calibration and standardization ... 5
- 7.5 Procedure ... 5
  - 7.5.1 Sample preparation ... 5
  - 7.5.2 Procedure A ... 5
- 7.6 Calculation ... 11
- 7.7 Precision and bias ... 11
- 7.8 Test report ... 11

**8 Determination of purity by high-performance liquid chromatography (HPLC)** ... **11**
- 8.1 General ... 11
- 8.2 Apparatus ... 11
- 8.3 Reagents ... 12
- 8.4 Procedure ... 12
- 8.5 Calculation ... 14
- 8.6 Precision and bias ... 14
- 8.7 Test report ... 15

**9 Determination of ash** ... **15**
- 9.1 General ... 15
- 9.2 Apparatus ... 15
- 9.3 Procedure ... 15
- 9.4 Calculation ... 16
- 9.5 Precision and bias ... 16
- 9.6 Test report ... 16

**10 Determination of volatile matter** ... **16**
- 10.1 General ... 16
- 10.2 Apparatus ... 17
- 10.3 Preparation of sample ... 17
- 10.4 Procedure ... 17
- 10.5 Calculation ... 17
- 10.6 Precision and bias ... 17
- 10.7 Test report ... 18

**Annex A** (informative) **Precision and bias** ... **19**

**Bibliography** ... **22**

© ISO 2017 – All rights reserved



Documents
Document Sharing Hub

Full document details: BS ISO 11236:2017

# 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 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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

This second edition cancels and replaces the first edition (ISO 11236:2000), which has been technically revised. It also incorporates the Technical Corrigendum ISO 11236:2000/Cor.1:2006.

The main changes compared to the previous version are as follows:

— removal of DTPD (*N*,*N*′-ditolyl-*p*-phenylenediamine), which is widely acknowledged to be hazardous to health and environment;

— transfer in an informative Annex A of the precision and bias for the determination of purity by gas chromatography by procedure A, for the determination of ash and for the determination of volatile matter;

— addition of a Bibliography.


© ISO 2017 – All rights reserved
Documents
Document Sharing Hub
Full document details: BS ISO 11236:2017

# Rubber compounding ingredients — *p*-Phenylenediamine antidegradants (PPDs) — Test methods

**WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.**

## 1 Scope

This document applies to a variety of substituted *p*-phenylenediamine antidegradants (PPDs) used in the rubber industry. The three general classes of PPDs are dialkyl, alkyl-aryl and diaryl, which are used to impart ozone resistance to rubber.

The following test methods are of greatest significance in assessing the purity of production PPDs, and hence their suitability for use in rubber. They are specified in this document as follows:

— determination of purity by gas chromatography (GC);

— determination of purity by high-performance liquid chromatography (HPLC);

— determination of ash;

— determination of volatile matter.

## 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 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 1772, *Laboratory crucibles in porcelain and silica*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

## 3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at http://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

**3.1**
**area normalization**
method of calculating the percent composition by measuring the area of each component peak observed in a chromatogram and dividing the area of the peak by the total peak area for all the components observed

**3.2**
**lot sample**
production sample representative of a standard production unit

© ISO 2017 – All rights reserved

Documents
Document Sharing Hub
Full document details: BS ISO 11236:2017

**3.3**
**test portion**
actual material used in the analysis

Note 1 to entry: The test portion shall be representative of the lot sample.

## 4 Abbreviated terms

PPDs substituted *p*-phenylenediamine antidegradants

The following abbreviations, taken from ISO 6472, are used in the text.

77PD *N,N′*-bis(1,4-dimethylpentyl)-*p*-phenylenediamine

IPPD *N*-isopropyl-*N′*-phenyl-*p*-phenylenediamine

6PPD *N*-1,3-dimethylbutyl-*N′*-phenyl-*p*-phenylenediamine

## 5 Use and classification

PPDs represent the primary additive used in tyres and other mechanical rubber goods to impart ozone protection and to improve resistance to fatigue cracking. PPDs are also used as antioxidants in a number of applications.

Although all PPDs exhibit similar performance characteristics, particular types are frequently preferred for certain end-use conditions, for example, the type and degree of flexing experienced by the rubber article.

PPDs are classified into the following types.

a) Type I: *N,N′*-dialkyl PPDs (see Figure 1)

R and R′ are secondary alkyl groups, usually $C_6$ or larger. These materials are generally liquids at ambient conditions and consist for the most part (>90 %) of a single chemical component.

b) Type II: *N*-alkyl-*N′*-aryl PPDs (see Figure 2)

R is a secondary alkyl group and R′ is an aryl substituent (usually phenyl). These materials generally consist of a single component or a mixture containing two or more major components (mainly isomers).

c) Type III: *N*, *N′*-diaryl PPDs (see Figure 3)

R and R′ can be the same aryl group or different (usually phenyl or *p*-tolyl) and can be single components or mixtures of three or more isomers. This type of PPDs is generally solid at ambient conditions.

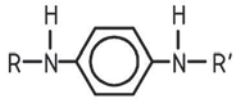


**Figure 1 — Type I: *N,N′*-dialkyl *p*-phenylenediamines**

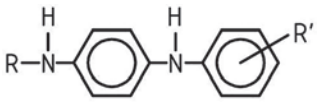


**Figure 2 — Type II: *N*-alkyl-*N′*-aryl *p*-phenylenediamines**


© ISO 2017 – All rights reserved
Documents
Document Sharing Hub
Full document details: BS ISO 11236:2017

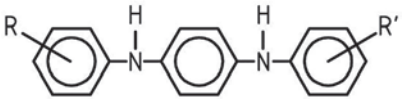


**Figure 3 — Type III: *N*,*N*′-diaryl *p*-phenylenediamines**

## 6 Sampling and repeat determinations

Carry out sampling in accordance with ISO 15528. To ensure homogeneity, blend at least 250 g of the lot sample thoroughly prior to removing any test portions.

If the difference between the results of duplicate determinations exceeds the repeatability given for the method concerned, repeat the test. If no repeatability figure is given for a particular method, report the results of both determinations.

## 7 Determination of purity by gas chromatography (GC)

### 7.1 General

This method is designed to assess the relative purity of production PPDs by determining the purity of type I, II and III PPDs using temperature-programmed gas chromatography with either a packed column (procedure A) or a capillary column (procedure B). Quantification is achieved by area normalization using a peak integrator or chromatography data system.

Since the results are based on area normalization, the method assumes that all components are eluted from the column and each component has the same detector response. Although this is not strictly true, the errors introduced are relatively small and much the same for all samples. Thus, they can be ignored, since the intent of the method is to establish relative purity.

Although trace amounts of “low boilers” are present in production samples, they are disguised by the solvent peak when using packed columns (procedure A).

### 7.2 Interference

Utilizing the chromatographic conditions prescribed, there are no significant co-eluting peaks. However, degradation of column performance could result in interference problems. Thus, when using the packed column, it is essential that the total system be capable of 5 000 theoretical plates. Evaluation of system efficiency is described in 7.3.2.

### 7.3 Apparatus

#### 7.3.1 Gas chromatograph.

##### 7.3.1.1 Procedure A

Any high-quality temperature-programmed gas chromatograph equipped with a thermal-conductivity detector and a peak integrator or chromatography data system is sufficient for this analysis.

Although a thermal-conductivity detector is recommended, a flame-ionization detector (FID) can be used if appropriate adjustment is made for flow rate and sample size. This will probably involve using a smaller-diameter column, in which case, the adjustment in flow rate and injection volume shall be proportional to the cross-sectional area of the column.

© ISO 2017 – All rights reserved

Documents
Document Sharing Hub
Full document details: BS ISO 11236:2017