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

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

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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.

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.

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

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 C₆ 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.

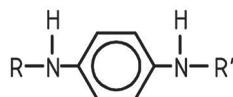


Figure 1 — Type I: *N,N'*-dialkyl *p*-phenylenediamines

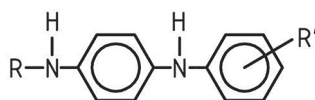


Figure 2 — Type II: *N*-alkyl-*N'*-aryl *p*-phenylenediamines

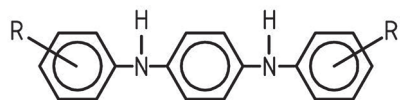


Figure 3 — Type III: *N,N'*-diaryl *p*-phenylenediamines

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.

7.3.1.2 Procedure B

Any high-quality temperature-programmed gas chromatograph with a flame-ionization detector and equipped for capillary columns is suitable. When utilizing standard capillary columns (0,25 mm), a split injection system is required. However, a “cold on-column” injector is preferred for the wide-bore (0,53 mm) capillaries. The FID shall have sufficient sensitivity to give a minimum peak-height response of 30 µV for 0,1 mass % of 6PPD when operated at the stated conditions. Background noise at these conditions shall not exceed 3 µV.

7.3.2 Gas-chromatographic columns.

7.3.2.1 Procedure A

Use a glass column with the following dimensions: 1,8 m × 6,4 mm outside diameter × 4 mm inside diameter. The glass column shall be packed with 10 % methyl silicone fluid (100 %) on a 0,15/0,08 mm (80/100 mesh) acid-washed and silanized diatomite support.

Condition the column with a helium flow of approximately 20 cm³/min by programming from ambient temperature to 350 °C at the rate of 2 °C/min to 3 °C/min and holding at 350 °C overnight with the detector disconnected.

When using a packed column, a minimum of 5 000 theoretical plates, as measured from the analyte peak, under the chromatographic conditions stated in [Table 1](#), is required for analysis. The number of theoretical plates, N , is determined by [Formula \(1\)](#).

$$N = 5,5 \left[\frac{X(R)}{Y(0,5)} \right]^2 \quad (1)$$

where

$X(R)$ is the retention time measured from the injection point to the apex of the 6PPD peak (adjusted the attenuation to keep peak on scale), in mm;

$Y(0,5)$ is the 6PPD peak width at half height, in mm.

7.3.2.2 Procedure B

Use one of the following:

- a 30 m × 0,25 mm fused-silica capillary internally coated to a film thickness of 0,25 µm (bonded) with methyl silicone (column 1), or
- a 15 m × 0,53 mm fused-silica (megabore) capillary coated with a 3,0 µm bonded film of 5 % phenyl silicone, HP-5 or equivalent (column 2).

7.3.3 Integrator/data system.

Use an integrator/data system capable of determining the relative amount of each component by integration of the detector output as a function of time. When using capillary columns (procedure B), the equipment shall be capable of integrating at a sufficiently fast rate so that narrow peaks (1 s peak width) are accurately measured.

7.3.4 Volumetric flask, capacity 10 cm³, meeting the requirements of ISO 1042.

7.3.5 Mortar and pestle.

7.3.6 Precision balance, accurate to ±1 mg or better.

7.3.7 Syringe, of suitable size (see relevant procedure).

7.4 Calibration and standardization

Chromatograms from typical PPDs run on the packed columns in accordance with the prescribed procedure are given in [Figures 4](#) and [5](#).

NOTE When using the conditions described for procedure A (packed column), the detector response for injections of 500 µg to 5 000 µg of 6PPD was found to be somewhat nonlinear. However, over the more limited range 750 µg to 2 500 µg, the response was nearly linear. It is important that the samples be prepared so that 1 250 µg to 1 500 µg injections are made.

7.5 Procedure

7.5.1 Sample preparation

To ensure homogeneity, grind lot samples of PPDs with a mortar and pestle prior to weighing out the test portion. In the case of liquid PPDs where partial crystallization might have occurred resulting in fractionation, melt the lot sample, with occasional stirring, prior to weighing out the test portion. Care should be taken that the sample does not decompose during the process. For example, in the case of 6PPD, it is recommended to melt the sample in an oven at 50 °C to 60 °C.

7.5.2 Procedure A

7.5.2.1 Use the following chromatographic conditions:

- helium flow rate 50 cm³/min;
- injection-port temperature 300 °C;
- initial column temperature 100 °C;
- heating rate 8 °C/min;
- final temperature 350 °C;
- detector temperature 350 °C;
- detector attenuation 8.

7.5.2.2 Weigh a 2,5 g to 3,0 g test portion (to the nearest milligram) into a 10 cm³ volumetric flask, dilute to volume with methylene chloride and shake well to dissolve.

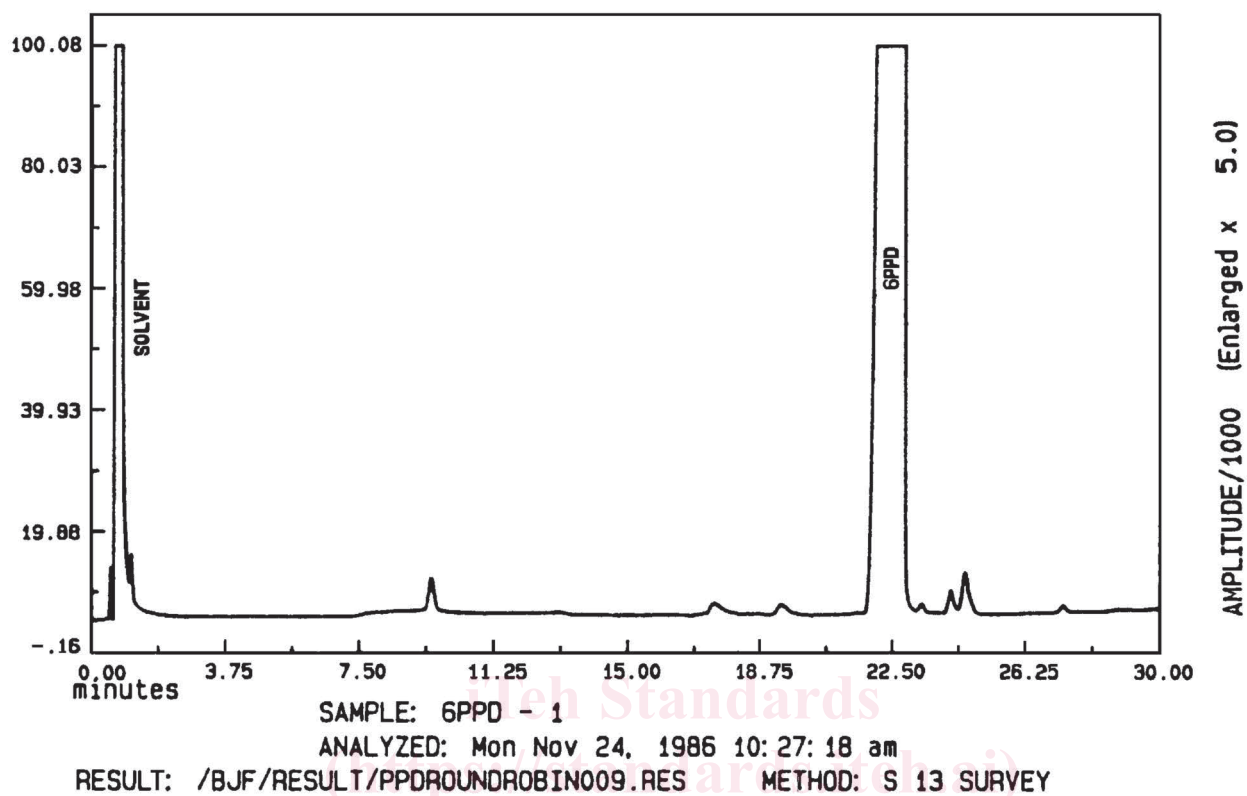
7.5.2.3 When the instrument has equilibrated at the initial conditions described above, inject 5,0 mm³ (µl) of sample solution (see [7.5.2.2](#)) and initiate the temperature programme and data collection.

Sample size and carrier-gas flow rates shall be adjusted according to the cross-sectional area of the column utilized. For example, if a nominally 3,2 mm outside diameter column (1,87 mm inside diameter) is used rather than a 6,4 mm outside diameter column (3,54 mm inside diameter), the adjustment would be as follows: the ratio of the cross-sectional areas is $(3,54/1,87)^2$, which equals 3,6. Thus, the sample size and helium-carrier flow rate shall be decreased by this factor, i.e. the sample size to 5/3,6 or 1,4 mm³ (µl) and the flow rate to 50/3,6 or 14 cm³/min.

7.5.2.4 When the run is complete, inspect the chromatogram and output data for proper appearance and peak identification (see [Figure 4](#)).

7.5.2.5 Repeat the run described in [7.5.2.3](#) on the same sample.

7.5.2.6 Typical chromatograms obtained by procedure A for 6PPD, IPPD and 77PD are shown in Figures 4 a) to 4 c), respectively.



a) 6PPD

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