



Designation: D3156 – 96 (Reapproved 2021)

# Standard Practice for Rubber—Chromatographic Analysis of Antidegradants (Antioxidants, Antiozonants and Stabilizers)<sup>1</sup>

This standard is issued under the fixed designation D3156; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This practice covers the detection and identification by thin-layer chromatography of antidegradants (antioxidants, antiozonants, and stabilizers) that may be present in raw rubber or rubber products. Analysis for other types of antidegradants is possible as long as the requirements of the practice are met.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Document

2.1 *ASTM Standards:*<sup>2</sup>

**D297 Test Methods for Rubber Products—Chemical Analysis**

## 3. Summary of Practice

3.1 A simplified procedure (Method A, Section 13.1) based on a single-solvent system is presented, which provides for the identification of known materials. This may be used to check the presence or absence in a rubber vulcanizate or raw rubber, of an antidegradant which should be present. However, since

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee D11 on Rubber and Rubber-like Materials and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

Current edition approved Nov. 1, 2021. Published November 2021. Originally approved in 1973. Last previous edition approved in 2016 as D3156 – 96 (2016). DOI: 10.1520/D3156-96R21.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

the chromatograms obtained may not be absolutely specific for any given antidegradant, a more detailed scheme is given in 13.2.

3.2 Method B, Section 13.2, using additional solvents and sprays is included, which enables a greater degree of separation of the spots to be made and therefore may enable detection and identification of an unknown antidegradant.

3.3 Other techniques, for example: gas chromatographic (with or without treatment to obtain derivatives), spectroscopic (ultraviolet and infrared), more sophisticated thin-layer variations (two dimensional techniques), may be applied to identification of spots for improved detection and identification of an unknown antidegradant.

3.4 It is possible that the chromatographic pattern of one antidegradant may overlap that of another antidegradant; therefore each laboratory must prepare its own reference standards, based on the technique chosen from this practice.

## 4. Significance and Use

4.1 This practice is useful for the examination of rubber compounds or products for the presence of chemicals that prevent or greatly reduce degradation due to oxygen, ozone, or other agents.

4.2 This practice is suitable for quality assurance, factory control, and research and development applications.

## 5. Interferences

5.1 In the absence of extender oils, antidegradants are extracted from the rubber by a solvent and the evaporated extract is applied directly to a thin-layer chromatographic plate.

5.2 In the presence of extender oils, the oils are removed by either a pre-treatment of the plate, with light petroleum ether or by a column chromatographic technique.

5.3 Identification of the antidegradant is made by the standard technique of thin-layer chromatography, herein described.

## 6. Apparatus

6.1 *Spreading Device*, for making thin layer chromatographic plates with a coating 250 to 300  $\mu\text{m}$  thick.

6.2 *Glass Plates*, 200 by 200-mm, or suitable for the selected tank. As an alternative to preparing plates, the use of precoated plates with a coating of 250 to 300  $\mu\text{m}$  is permitted. Precoated film-backed plates are not recommended.

6.3 *Drying Oven*, 105°C minimum.

6.4 *Desiccator*, or drying box for storing plates at fixed humidity.

6.5 *Micro-pipets*, 5 and 10- $\text{mm}^3$  ( $\mu\text{L}$ ).

6.6 *Chromatographic Developing Tank*, of a size suitable to hold plates, approximately 250 by 250 by 70 mm to 330 by 240 by 110 mm. Small “sandwich-type” tanks are not recommended. Add about 200  $\text{cm}^3$  of developing solvent (7.4) to the tank, swirl, cover, and allow to stand 15 min before using. Tank may be reused by repeating the swirling and standing step, as long as the solvent ratio remains constant.

6.7 *Extraction Apparatus*, in accordance with Section 18 or 25 of Test Methods **D297**.

6.8 *Chromatographic Columns*, short, liquid-solid. Those found satisfactory are as follows:

6.8.1 *Hypodermic Syringe Barrel*, 5- $\text{cm}^3$ , fitted with a needle about 35 mm in length and 1.27 mm outside diameter (No. 18 BWG).

6.8.2 *Glass Tubes*, 120 mm in length and 10 to 12 mm in diameter, holding about 5  $\text{cm}^3$  of silica gel.

## 7. Reagents

7.1 *Plate Adsorbent*—Silica gel containing calcium sulfate.<sup>3</sup> Silica gel containing a fluorescent indicator may be useful in some cases to allow visualization of spots (before spraying) with ultraviolet light.

7.2 *Column Adsorbent*—Silica gel 200 to 600  $\mu\text{m}$  (30 to 70-mesh),<sup>3</sup> activated by drying at 110°C for at least 2 h, if dry in that period, or overnight ( $\pm 16$  h) for convenience.

7.3 *Solvents*—Use of fume hoods with volatile and toxic solvents is *mandatory*. Approved health and safety precautions should be observed for the use of any solvent or chemical mentioned in this procedure. ACS grade or equivalent should be used.

7.3.1 *Methanol*.

7.3.2 *Acetone*.

7.3.3 *Isopropanol*.

7.3.4 *Light Petroleum Ether*.

7.3.5 *Chloroform*.

7.3.6 *Toluene*.

7.3.7 *Ethyl Acetate*.

7.3.8 *n-Hexane*.

7.3.9 *n-Heptane*.

7.3.10 *Cyclohexane*.

7.3.11 *Diethylamine*.

7.3.12 *Ammonium Hydroxide* ( $\text{NH}_4\text{OH}$ , 28–30 % ammonia  $\text{NH}_3$ ).

7.3.13 *Water*—References to water shall be understood to mean distilled water or water of equal purity.

7.4 *Developing Solvents*:

7.4.1 *Test Method A*—90 parts *n*-heptane and 10 parts ethyl acetate by volume.

7.4.2 *Test Method B*, used in the following order:

7.4.2.1 Toluene.

7.4.2.2 95 parts toluene and 5 parts ethyl acetate by volume.

7.4.2.3 75 parts cyclohexane and 25 parts diethylamine by volume.

7.4.2.4 50 parts toluene and 50 parts *n*-heptane by volume.

7.4.3 Additional developing solvents which may prove useful for special problems:

7.4.3.1 100 parts toluene, 5 parts acetone and 0.1 part ammonium hydroxide ( $\text{NH}_4\text{OH}$ ).

7.4.3.2 100 parts toluene, 5 to 10 parts acetone and 0.1 to 0.2 parts  $\text{NH}_4\text{OH}$ .

7.5 *Spray Reagents for Color Development*:

7.5.1 *Amines*:

7.5.1.1 *Diazotized Sulfanilic Acid*—0.5 g of sulfanilic acid and 0.5 g of potassium nitrite ( $\text{KNO}_2$ ) dissolved in 100  $\text{cm}^3$  of 1 *M* hydrochloric acid ( $\text{HCl}$ ). Make fresh daily.

7.5.1.2 *Benzoyl Peroxide* (4 % solution in toluene).

7.5.1.3 *Tollen's Reagent* (0.5  $\text{cm}^3$  of 5 % silver nitrate ( $\text{AgNO}_3$ ) solution + 2 drops of 2 *M* sodium hydroxide ( $\text{NaOH}$ ). Dissolve the precipitate in as little 2 % ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) as possible, and add an equal volume of 96 % alcohol.

7.5.1.4 *Bismuth Nitrate* ( $\text{Bi}(\text{NO}_3)_3$ ) (7.5 g) dissolved in a mixture of 1  $\text{cm}^3$  of concentrated nitric acid ( $\text{HNO}_3$ , density 1.42  $\text{Mg}/\text{m}^3$ ) in 150  $\text{cm}^3$  of distilled water.

7.5.1.5 *Tetracyanoethylene (ethenetetracarbonitrile)*—Saturated solution in methylene chloride.

7.5.2 *Phenols*:

7.5.2.1 *Overspray*, for use with solution 7.5.1.1 1-*M* sodium hydroxide ( $\text{NaOH}$ ) solution.

7.5.2.2 *p-Nitrophenyldiazonium Fluoroborate* (1 % solution in methanol containing 0.5 % hydrochloric acid ( $\text{HCl}$ , density 1.16  $\text{Mg}/\text{m}^3$ )).

7.5.2.3 *2,6-Dichloroquinonechlorimide* (0.1 % solution in methanol or toluene)—Used with 7.5.2.4.

7.5.2.4 *Buffer Spray*, for use with 7.5.2.3—Dissolve 23.4 g of sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) and 3.3 g of sodium hydroxide ( $\text{NaOH}$ ) in 1  $\text{dm}^3$  of water.

7.6 Reagents for preliminary “screening” tests are as follows:

7.6.1 *Ferric Chloride Solution*—Mix 0.5 g of anhydrous ferric chloride ( $\text{FeCl}_3$ ) with 100  $\text{cm}^3$  of ethanol or 3A alcohol.

7.6.2 *Ferric Sulfate Solution*—Mix 1 g of ferric sulfate ( $\text{FeSO}_4$ )<sub>3</sub> with 100  $\text{cm}^3$  of water.

7.6.3 *Hydroxylamine Hydrochloride Solution*—Mix 1.0 g of hydroxylamine hydrochloride with 100  $\text{cm}^3$  of water.

7.6.4 *p-Nitroaniline Solution*—Mix 2.8 g of *p*-nitroaniline with 32  $\text{cm}^3$  of hydrochloric acid (density 1.16  $\text{Mg}/\text{m}^3$ ). Dilute to 250  $\text{cm}^3$  with water.

7.6.5 *Sodium Nitrite Solution*—Mix 1.44 g of sodium nitrite ( $\text{NaNO}_2$ ) with 250  $\text{cm}^3$  of water.

<sup>3</sup> The sole source of supply of silica gel known to the committee at this time is E. Merck A.G., Frankfurter Str. 250, Darmstadt, Germany. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.