Designation: D7210 − 13

Standard Practice for
Extraction of Additives in Polyolefin Plastics[1]

This standard is issued under the fixed designation D7210; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This practice covers a variety of extraction techniques for antioxidant and slip additives used in polyolefins. Typically, the extracted additives are separated and quantified using a chromatographic technique such as the procedure explained in Test Method D6953. Chromatographic analysis of the extracts is not included in this practice.

1.2 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—There is no known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

D1600 Terminology for Abbreviated Terms Relating to Plastics

D6953 Test Method for Determination of Antioxidants and Erucamide Slip Additives in Polyethylene Using Liquid Chromatography (LC)

E131 Terminology Relating to Molecular Spectroscopy

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of plastic terms used in this practice, see Terminologies D883 and D1600.

3.2 For units, symbols, and abbreviations used in this practice refer to Terminology E131.

3.3 *Abbreviations:*

3.3.1 *LDPE*—Low-Density Polyethylene

3.3.2 *LLDPE*—Linear Low-Density Polyethylene

3.3.3 *HDPE*—High-Density Polyethylene

3.3.4 *PP*—Polypropylene

3.4 *Definitions: Additives:*

3.4.1 *BHEB*—2,6-di-t-butyl-4-ethyl-phenol or butylated hydroxyethyl benzene, CAS No. 4130-42-1

3.4.2 *BHT*—2,6-di-t-butyl-cresol or butylated hydroxytoluene, CAS No. 128-37-0

3.4.3 *2-benzotriazol-2-yl-4-methylphenol,* CAS No. 2440-22-4

3.4.4 *bis(3,3,5,5-tetramethyl-4-piperidyl)decanedioate,* CAS No. 91450-21-4

3.4.5 *Cis-13-docosenamide or erucamide slip,* CAS No. 112-84-5

3.4.6 *N,N'-diphenylbenzene-1,4-diamine,* CAS No. 74-31-7

3.4.7 *2,2'-ethylidene bis (4,6-di-t-butyl phenol),* CAS No. 112-84-5

3.4.8 *Tetrakis[methylene (3,5-di-t-butyl-4-hydroxy hydrocinnamate)] methane,* CAS No. 98584-37-3

3.4.9 *1,3,5-trimethyl-2,4,6-tris (3,5-di-t-butyl-4-hydroxybenzyl) benzene,* CAS No. 99346-90-4

3.4.10 *Octadecyl-3,5-di-t-butyl-4-hydroxy hydrocinnamate,* CAS No. 2082-79-3

3.4.11 *Sodium Alkyl Sulfonate,* CAS No. 68411-30-3

3.4.12 *Tris(2,4-di-t-butylphenyl) phosphite,* CAS No. 31570-04-4

3.4.13 *Tris(2,4-di-t-butylphenyl) phosphate (oxidized Tris(2,4-di-t-butylphenyl) phosphite)*

3.4.14 *TNPP*—Tris(nonylphenyl) phosphite, CAS No. 26523-78-4

3.4.15 *Hydrolyzed TNPP*—Nonylphenol, CAS No. 104-40-5

3.4.16 *Oxidized TNPP*—Tris(nonylphenol)phosphate CAS No. 26569-53-9

4. Summary of Practice

4.1 The polymer sample is ground to approximately a 0.5-mm (≈40-mesh) or 1-mm (≈20-mesh) particle size and extracted by one of the techniques listed in this practice.

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[1] This practice is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods and Section D20.70.01 on Physical Methods.

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

***A Summary of Changes section appears at the end of this standard**

5. Significance and Use

5.1 Separation and identification of additives used in the manufacture of polyolefin plastics is necessary in order to correlate performance properties with polymer composition. This practice provides guidelines for extracting phenolic antioxidants, phosphite antioxidants, UV stabilizers, antistatic agents, and slip additives, from milled polyolefin plastics .

5.2 Water bath shakers and steam-reflux Soxhlet extraction techniques have also been used to successfully remove additives from polyolefin plastics.

6. Interferences

6.1 A major source of interferences can be from solvent impurities. For this reason, quality, high-grade solvents shall be used with this practice. It is recommended that solvents be examined prior to use.

6.1.1 Solvent evaporation after an extraction technique can increase the concentration of impurities.

6.2 The milling or grinding process has the potential to cause a low bias. For example, some erucamide slip is known to be lost during milling. Excessive grinding will cause degradation of some antioxidant additives.

6.3 Excessive fillers (for example, pigments, talc, etc.) in the polymer formulation can mask the sensitivity of polymer additive detection.

7. Apparatus

7.1 *Wiley Mill,* or equivalent, equipped with a 20-mesh screen and water-cooled jacket to prevent the thermodegradation of antioxidants such as BHT.

NOTE 2—A SPEX Certiprep, 6750 Freezer Mill using liquid nitrogen as a coolant has also been used to successfully prepare milled polyolefin samples.

7.2 *Extraction Apparatus*

7.2.1 *Reflux-Extraction Apparatus,* consisting of a condenser (24/40 ground-glass joint), a flat bottom 125-mL flask having a 24/40 ground glass joint, and a hot plate with magnetic stirrer.

7.2.2 *Soxhlet Apparatus,* consisting of a Soxhlet extraction tube (24/40 ground-glass joint at bottom and a 34/45 ground-glass joint at top), an Allihn condenser (34/45 ground-glass joint), a flat bottom 125-mL flask having a 24/40 ground-glass joint, and a hot plate with magnetic stirrer. Soxtec Solvent extraction systems or equivalent devices are also acceptable for use.

7.2.3 *Accelerated Solvent Extractor (ASE) Apparatus*[3,4,5], equipped with 11-mL extraction cells and a solvent controller (optional) or equivalent.

7.2.4 *Microwave Extraction Apparatus (MAE)*[5,6], equipped with 100-mL extraction vessels or equivalent.

7.2.5 *Sonication Extraction Apparatus,* consisting of a suitable ultrasonic cleaner such as an Aquasonic Model 75D Ultrasonic Cleaner or equivalent.

7.3 *Filter System,* for nonaqueous solutions (pore size of 0.22 µm to 0.5µm).

7.4 *Analytical Balance,* capable of weighing to ±0.0001 g.

8. Reagents and Materials

8.1 *Cellulose Extraction Thimble*—16 mm by 60 mm, single thickness for use with Soxhlet apparatus.

8.2 *Cellulose Extraction Thimble*—17 by 19 by 37 mm, for use in the ASE system.

8.3 *Microwave Extraction Vessels*—100-mL extraction vessel.

NOTE 3—11-mL extraction cells were used to evaluate the ASE portion of this practice and 100-mL extraction vessels were used to evaluate the MAE portion of this practice.

8.4 *Cyclohexane,* optima grade, spectroquality, or chromatography quality reagent.

8.5 *Isobutanol,* optima grade, spectroquality, or chromatography quality reagent.

8.6 *2-Propanol or Isopropanol,* optima grade, spectroquality, or chromatography quality reagent.

8.7 *Methylene Chloride,* optima grade, spectroquality or chromatography quality reagent.

9. Safety Precautions

9.1 Isopropanol, isobutanol, and cyclohexane are flammable. The extraction cells used in the instruments shall be free of leaks.

9.2 Accelerated solvent and microwave extraction systems operate at elevated temperatures and pressures. Follow all safety precautions supplied by the instrument manufacturer.

10. Sample Preparation

10.1 Mill the sample to a particle size of 1-mm or smaller using a cooled Wiley Mill or another suitable grinding apparatus.

10.2 Weigh 0.5 ± 0.01 to 10.0 ± 0.01 g of sample into the appropriate vessel (that is, flat-bottom flask for reflux extraction procedures, cellulose extraction thimble for Soxhlet or ASE extraction, or microwave vessel for MAE extraction, 8 oz glass jar for ultrasonic bath extraction). The required sample size will vary from laboratory to laboratory and will depend on the sensitivity of the analytical determinative method employed.

10.3 Depending on the extraction procedure chosen and the type of polyolefin, or additive, or both, to be extracted, prepare the extraction solvent as follows:

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[3] The Accelerated Solvent Extractor (ASE) Apparatus is a registered trademark of Dionex Corporation.

[4] The sole source of supply of the apparatus (ASE 200) known to the committee at this time is Thermo Fisher/Dionex Corporation, 1228 Titan Way, P.O. Box 3603, Sunnyvale, CA 94088-3603, USA; www.Dionex.com.

[5] 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,[1] which you may attend.

[6] The sole source of supply of the microwave extraction apparatus (MARS-X) known to the committee at this time is CEM Corporation, PO Box 200, Matthews, NC 28106-0200, USA; www.cem.com.

10.3.1 *Reflux or Soxhlet Extraction*

10.3.1.1 LDPE add 5.0 ± 0.01 g of sample into the flask, add a stirring bar, accurately add 50.0 mL of a suitable solvent such as 2-propanol and boil for 1 h (with stirring).

10.3.1.2 LLDPE add 5.0 ± 0.01 g of sample into the flask, add a stirring bar, accurately add 50.0 mL of a suitable solvent such as either isobutanol or 2-propanol and boil for 90 min (with stirring).

10.3.1.3 HDPE add 5.0 ± 0.01 g of sample into the flask, add a stirring bar, accurately add 50.0 mL of a suitable solvent such as cyclohexane and boil for 1 h (with stirring).

10.3.1.4 PP add 5.0 ± 0.01 g of sample into the flask, add a stirring bar, accurately add 50.0 mL of a suitable solvent such as methylene chloride: cyclohexane (75+25) and boil for 90 min (with stirring).

NOTE 4—If internal standard calibration is used with reflux or Soxhlet extraction, add the internal standard to the extraction solvent at the start of the extraction procedure. If internal standard calibration is used with accelerated solvent or microwave assisted extraction, add the internal standard to the extraction vessel prior to initiating the extraction.

NOTE 5—If Soxhlet extraction is used, add the sample to the cellulose extraction thimble and place the thimble in the Soxhlet extraction tube before initiating the extraction.

NOTE 6—A suitable solvent is one that results in a quantitative extraction of the additive(s) of interest.

10.3.1.5 Cool the solution to room temperature by raising the flask off the hot plate while it is still attached to the condenser.

10.3.1.6 Analyze the extract using an appropriate chromatographic technique.

10.3.2 Accelerated Solvent Extraction (refer to Dionex Application Note 331; www.Dionex.com/)

10.3.2.1 Insert a 17 by 19 by 37-mm cellulose extraction thimble into an 11-mL extraction cell.

10.3.2.2 Weigh 0.5 ± 0.001 g of the sample in a suitable weighing dish or in the extraction thimble. Add sample to an extraction cell that contains a cellulose extraction thimble or place the cellulose extraction thimble containing the sample to be extracted into the extraction cell.

10.3.2.3 Place the cell in the upper carousel of the accelerated solvent extractor and place the appropriate number of collection vials in the lower carousel.

10.3.2.4 Enter the following extraction conditions into the accelerated solvent system and initiate the run.

(1) Oven Temperature—120°C.

(2) Pressure—1500 psi (10.34 MPa).

(3) Solvent—5 % cyclohexane in 2-propanol or a suitable solvent (mixtures of acetonitrile and cyclohexane (95+5) and other solvent mixtures have also been found to be effective extraction solvents for this application).

(4) Static Time—3 min.

(5) Flush Volume—100 % (of cell volume).

(6) Static Cycles—3.

(7) Purge Time—60 s.

10.3.2.5 At the completion of the extraction, remove the collection vial containing the solvent extract from the lower carousel.

10.3.2.6 Analyze the extract using an appropriate chromatographic technique.

10.3.3 Microwave Accelerated Extraction (refer to CEM application notes E012 for HDPE, E017 for LDPE, and E020 for LLDPE; www.cem.com/)

10.3.3.1 Weigh approximately 1.5 g of sample to the nearest 0.001 g into a 100-mL extraction vessel and add 20 mL of a suitable solvent. Slide the vessel into the supplied protective sleeve and then into the support module. Using a torque wrench, tighten the cover screw to approximately 50 lb and place the support module into the microwave carousel.

10.3.3.2 Load the necessary extraction conditions into the MAE instrument and initiate the extraction. Typically, extractions are performed at 30-50°C above the boiling point of the solvent for 15-30 min. Cool to well below the boiling point of the solvent before removing the vessels from the microwave.

10.3.3.3 Analyze the extract using an appropriate chromatographic technique.

10.3.4 *Ultrasonic Extraction*

10.3.4.1 Weigh approximately 10.0 g of sample to the nearest 0.001 g and quantitatively transfer the sample into an 8 oz tightly-sealed glass jar. Add 100 mL of suitable solvent such as 75 % methylene chloride and 25 % cyclohexane to the jar containing the sample (toluene has also been successfully used as an extraction solvent using this technique). Tightly seal the jar containing the sample and solvent mixture.

10.3.4.2 Suspend the jar containing the sample and solvent in an ultrasonic water bath. Turn on the ultrasonic bath for 2 hours. The water temperature in the ultrasonic bath usually reaches about 50°C during this extraction procedure.

NOTE 7—Solvents expand when heated. Use caution during this procedure. Make certain the glass jar is free from chips, cracks, and other structural deformities. The ultrasonic extraction conditions above are not applicable for the extraction of Tetrakis [methylene (3,5-di-t-butyl-4-hydroxy hydrocinnamate)] methane.

NOTE 8—Allow the glass jar used in the ultrasonic extraction to cool prior to transferring the extract into vials for analysis. Allowing the jar to cool for 20 to 30 minutes will minimize the possibility of a potential chemical flash or "burp" when the jar is opened.

10.3.4.3 Analyze the extract using an appropriate chromatographic technique.

11. Precision and Bias

11.1 These procedures are for sample preparation and as such they depend on a determinative method to produce a result.

12. Keywords

12.1 accelerated solvent extraction; antistatic agents; BHEB; BHT; high-density polyethylene (HDPE); linear low-density polyethylene (LLDPE); low-density polyethylene (LDPE); microwave assisted extraction; phenolic antioxidants; phosphite antioxidants; polymer additive; polypropylene (PP); reflux extraction; slip additives; Soxhlet extraction; ultrasonic or sonication extraction; UV stabilizers

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D7210 – 06) that may impact the use of this standard. (April 1, 2013)

(1) Removed permissive language from 6.1 and 9.1.

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