INTERNATIONAL

Designation: ~~D6953 – 11~~ D6953 – 18

Standard Test Method for Determination of Antioxidants and Erucamide Slip Additives in Polyethylene Using Liquid Chromatography (LC)[1]

This standard is issued under the fixed designation D6953; 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 test method covers a liquid-chromatographic procedure for the separation of primary and secondary antioxidant and slip additives currently used in polyethylene plastics. These additives are extracted with either isopropanol (resin densities < 0.94 g/cm^3) or cyclohexane (resin densities > 0.94 g/cm^3) prior to liquid-chromatographic separation. The ultraviolet absorbance of the eluting compound(s) is measured and quantitation is performed using external calibration.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 9.

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

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 Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics
D1600 Terminology for Abbreviated Terms Relating to Plastics
D4697 Guide for Maintaining Test Methods in the User's Laboratory (Withdrawn 2009)[3]
E131 Terminology Relating to Molecular Spectroscopy
E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E1657 Practice for Testing Variable-Wavelength Photometric Detectors Used in Liquid Chromatography
IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI): The Modern Metric System

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of plastic terms and detector terminology used in this test method, see Terminologies D883, D1600, and E1657.

3.1.2 For units and symbols used in this test method, refer to Terminology E131 or IEEE/ASTM SI 10.

4. Summary of Test Method

4.1 The polyethylene sample is ground to a 1-mm (~20 mesh) or 0.5-mm (~40 mesh) particle size and extracted by refluxing with either isopropanol or cyclohexane.

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[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

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

TABLE 1 Common Polyolefin Additives

Chemical Name	Chemical Formula	Classification	CAS Number
BHEB, 2,6-di-t-butyl-4-ethylphenol or butylated hydroxyethyl benzene	$C_{16}H_{26}O$	1º Antioxidant	4130-42-1
BHT, 2,6-di-t-butylcresol or butylated hydroxy toluene	$C_{15}H_{24}O$	1º Antioxidant	128-37-0
Tris (2,4-di-t-butylphenyl)-phosphite	$C_{42}H_{63}O_3P$	2º Antioxidant	31570-04-4
Tris(2,4-di-t-butylphenyl)-phosphate	$C_{30}H_{39}O_4P$	Degradation product	78-33-1
Tetrakis[methylene(3,5-di-t-butyl-4- hydroxyhydrocinnamate)] methane	$C_{73}H_{108}O_{12}$	1º Antioxidant	6683-19-8
Octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)- propionate	$C_{35}H_{62}O_3$	1º Antioxidant	2082-79-3
2,2'-ethylidene bis(4,6-di-t-butylphenol)	$C_{30}H_{46}O_2$	1º Antioxidant	35958-30-6
Erucamide—Cis-13-docosenamide	$C_{28}H_{43}NO$	Fatty acid amide, slip agent	112-84-5
TNPP,Tris(nonylphenyl)phosphite	$C_{45}H_{69}O_3P$	2º Antioxidant	26523-78-4
Nonylphenol	$C_{15}H_{24}O$	2º Antioxidant	104-40-5
Tris(nonylphenyl)phosphate	$C_{45}H_{69}O_4P$	Degradation product	26569-53-9

4.2 The solvent extract is analyzed by liquid chromatography.

4.3 Additive concentrations are determined from external calibration curves using reverse phase chromatography (C-8 or C-18 column) with ultraviolet (UV) detection at wavelengths corresponding to the wavelengths of an absorption apex of each additive (except erucamide which does not have an absorption maximum in the accessible UV region).

5. Significance and Use

5.1 Separation and identification of stabilizers used in the manufacture of polyethylene resins are necessary in order to correlate performance properties with polymer composition. This test method provides a means to determine the polymer additives listed in Table 1 in polyethylene samples. This test method is capable of the determination of other antioxidants, but the stability of these during extraction has not been investigated.

5.2 The additive extraction procedure is made effective by the relatively low solubility of the polymer sample in solvents generally used for liquid chromatographic analysis. In this method, isopropanol and cyclohexane were chosen because of their excellent extraction efficiencies as well as for safety reasons. Other solvents including ethylacetate, isobutanol, chloroform and methylene chloride can also be used.

5.3 Methods other than refluxing that have been used to remove additives from the polymer matrix including pressurized liquid, microwave, ultrasonic, and supercritical fluid extractions. For the separation of the extracted additives, SFC and GC have been used successfully for several of the additives.

5.4 Under optimum conditions, the lowest level of detection for an antioxidant is approximately 2 ppm.

6. Interferences

6.1 Any material eluting at or near the same retention time as the additive can cause erroneous results. This includes degradation products of the additives.

6.2 A major source of interferences can be from solvent impurities. For this reason, the solvents shall be examined by HPLC using the same analysis conditions as for the samples (see Section 12).

6.3 The grinding process may cause a low bias. For example, some erucamide slip is known to be lost to the grinder surface and excessive grinding may cause degradation of the antioxidants.

7. Apparatus

7.1 *Liquid Chromatograph,* equipped with a multiple wavelength (see Practices E169 and E275) or photodiode array ultraviolet detector, heated column compartment, and gradient elution capabilities. The liquid chromatograph shall be equipped with a means for a 10-µL injection such as a sample loop.

7.2 *Chromatographic Column,* C-8 or C-18 reverse phase, 5-µm particle size, 15 cm by 4.6 mm or equivalent, capable of separating the additives and their degradation products.

7.3 *Data Acquisition/Handling System,* providing the means for determining chromatographic peak areas and for handling and reporting data. This is best accomplished using a computer with appropriate software.

7.4 *Mill—Cutting Mill ~~(Wiley)~~ or Centrifugal Grinding ~~Mill (Brinkmann),~~ Mill,* equipped with 1-mm (~20 mesh) and 0.5-mm (~40 mesh) screens.

7.5 *Reflux Extraction Apparatus,* consisting of a condenser, (24/40 ground-glass joint), a round-bottom 125-mL flask having a 24/40 ground-glass joint, and a heating mantle.

7.6 *Boiling Chips.*

7.7 *Filter System,* (PTFE), for non-aqueous solutions (pore size of 0.22 µm).

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

7.9 *Top Loading Balance,* capable of weighing to ±0.01 g.

8. Reagents and Materials

8.1 *Solvents:*

8.1.1 *Isopropanol*—HPLC grade, spectro-quality or chromatography quality reagent.

8.1.2 *Cyclohexane*—HPLC grade, spectro-quality or chromatography quality reagent.

8.1.3 *Water*—HPLC, or UV quality reagent, degassed by sparging with high-purity helium or by filtration under vacuum.

8.1.4 *Acetonitrile*—HPLC, spectro-quality or chromatography quality reagent (a reagent whose UV cutoff is about 190 nm).

8.2 *Additives:*

8.2.1 High purity additives and degradation products (see Table 1).

9. Precautions

9.1 Isopropanol and cyclohexane are flammable. This extraction procedure should be carried out in a fume hood.

10. Preparation of Solutions

10.1 *Polymer Samples:*

10.1.1 Grind the sample to a particle size of 1 mm, that is, ~20 mesh (density < 0.94 g/cm^3) or 0.5 mm, that is, ~40 mesh (density > 0.94 g/cm^3).

NOTE 2—Unless sample amount is limited, grind a minimum of 10 g. It is important to minimize the time of grinding to prevent any thermal degradation of the additives in the polymer. Some erucamide is known to be lost during grinding.

NOTE 3—A cutting-type mill is needed for film samples. Because of its higher efficiency, a centrifugal-type mill is recommended for pellet samples.

10.1.2 Weigh, to the nearest 0.01 g, approximately 5 g of the sample, that is, W_{sample}, into a pre-weighed (to the nearest 0.01 g) 125-mL flat-bottom flask containing boiling chips, that is, W_{flask}. Add approximately 50.0 mL of isopropanol or cyclohexane and boil for a minimum of 2 h.

NOTE 4—Isopropanol is used as the extraction solvent for densities of less than 0.94 g/cm^3 and cyclohexane for densities higher than 0.94 g/cm^3.

10.1.3 Cool the solution to room temperature by raising the flask from the heating mantle while still attached to the condenser.

10.1.4 Weigh the cooled flask to the nearest 0.01 g, that is, $W_{(flask\ +\ sol)}$.

10.1.5 Attach a filter disk assembly to a 5-mL Luer-Lok tip hypodermic syringe.

10.1.6 Decant approximately 4 mL of the solvent extract into the above syringe.

10.1.7 Insert the plunger and carefully apply pressure to force the solvent extract through the filter into a sample vial.

10.1.8 Calculate the amount (mg) of sample per kg of solution, $[Sample]_{sol}$:

$$[Sample]_{sol} = \frac{10^6 W_{sample}}{\left(W_{(flask+sol)} - W_{flask}\right)} \quad (1)$$

10.2 *Concentrated Additive Standards:*

10.2.1 Prepare two to three mixtures in 125-mL septum bottles by weighing the bottles, including septum and cap, to the nearest 0.1 mg.

10.2.2 Weigh into a bottle, to the nearest 0.1 mg, approximately 0.2 g of each additive.

10.2.3 Fill the bottle with either isopropanol or cyclohexane, cap and weigh the bottle on a top loading balance to the nearest 10 mg.

10.2.4 Agitate the bottle to speed up dissolution.

10.2.5 Calculate the concentration, $[Additive]_{conc}$, of each additive in the concentrated standard in mg/kg (that is, ppm) as follows:

$$[Additive]_{conc} = \frac{10^6 W_{add}}{\left(W_{Tadd} + W_{sol}\right)} \quad (2)$$

where:

W_{add} = weight (g) of individual additive,
W_{Tadd} = total weight (g) of all additives, and
W_{sol} = weight (g) of solvent.

10.3 *Dilute Additive Standards:*

10.3.1 Prepare four dilute standards of each concentrated standard by weighing 30-mL septum bottles, including septum and cap, to the nearest 0.1 mg.

10.3.2 Add with a 5-mL syringe, 0.5 mL, 1.0 mL, 2.0 mL, and 5.0 mL of a concentrated solution to each of four of the 30-mL bottles and weigh to the nearest 0.1 mg.

10.3.3 Fill the bottles with isopropanol or cyclohexane, cap, mix and weigh to the nearest 1 mg.

10.3.4 Calculate the concentration, $[Additive]_{dil}$, of each additive in the dilute standards in mg/kg (that is, ppm) as follows:

$$[Additive]_{dil} = \frac{W_{conc}[Additive]_{conc}}{(W_{conc}+W_{sol})} \quad (3)$$

where:

W_{conc} = weight (g) of concentrated standard solution,
$[Additive]_{conc}$ = concentration (mg/kg) of additive in concentrated standard (see 10.2.5), and
W_{sol} = weight (g) of solvent used for dilution.

11. Performance Requirements

11.1 *Resolution*—The resolution (R) provides an indication of the component separation and band broadening of a column. For Gaussian-shaped peaks, the resolution is defined as:

$$R = \frac{2(t_{R,2} - t_{R,1})}{(W_1+W_2)} \quad (4)$$

where:

$t_{R,1}$, $t_{R,2}$ = peak elution time in minutes of Additives 1 and 2, and
W_1, W_2 = peak width in minutes of Additives 1 and 2 determined by measuring the distance between the baseline intercepts of lines drawn tangent to the peak inflection points.

11.1.1 For an extracted additives mixtures containing any combination (including degradation products) of those listed in Table 1, the resolution of any two peaks measured at a single wavelength must be greater than one, that is, $R > 1$. For peaks with $R \leq 1$, two wavelengths are needed to measure the two components (see 15.2).

NOTE 5—A resolution of $R = 1$ represents a peak overlap of approximately 3 %.

11.2 *Plate Count Number*—A 10-cm column packed with 5-µm particles is expected to have a plate count in excess of 60 000 plates calculated in accordance with the following expression:

$$N = 16\left(\frac{t_R}{W}\right)^2 \quad (5)$$

where:

t_R = peak elution time in minutes, and
W = peak width in minutes as determined as outlined in Section 11.

11.2.1 No minimum number is required as long as the resolution requirement of 11.1 is met.

12. Preparation of Liquid Chromatograph

12.1 *Flow Rate*—2.0 mL/min.

12.2 *Mobile Phase Gradient:*

12.2.1 *Initial Mobile Phase*—60 % acetonitrile and 40 % water.

12.2.2 *Final Mobile Phase Condition*—100 % acetonitrile and 0 % water.

12.2.3 *Gradient Length*—6 min.

12.2.4 *Gradient Curve*—Linear.

12.2.5 Hold at 100 % acetonitrile and 0 % water for 3 min.

12.2.6 Return to 60 % acetonitrile and 40 % water at 9 min at a flow rate of 2 mL/min for 4 min.

NOTE 6—The flow rate and gradient conditions listed in 12.1 and 12.2 have been used successfully with a 15-cm by 4.6-mm column packed with 5-µm C-8 reverse phase particles (see Fig. 1). The optimum flow rate (that is, 1.0 to 2.0 mL/min) and the exact gradient will depend on the column used and the additive formulations typically analyzed (see Section 11 for performance requirements).

12.3 *Detector*—Ultraviolet detector with a range setting of about 0.1 AUFS at the following wavelengths:

200 nm for erucamide slip
210 nm for CAS 78-33-1
217 nm for TNPP and its degradation products
270 nm for CAS 31570-04-4
280 nm for BHEB, BHT, CAS 6683-19-8. CAS 2082-79-3, and CAS 35958-30-6

NOTE 7—Erucamide does not have an absorption peak in the accessible UV region. The absorption at 200 nm represents the tailing end of an absorption peak at a wavelength of less than 190 nm. Because of the steep slope of the shoulder, a wavelength precision of better than 1 nm is needed to avoid unacceptable fluctuations in detector response (that is, extinction coefficient). Frequent injections of an erucamide standard are recommended.

12.4 *Column*—C-8 or C-18 reverse phase, 5-µm particle size, 15 cm by 4.6 mm or equivalent.

12.5 *Temperature*—A column temperature of between 50°C and 60°C is suggested.