1. Scope

1.1 This test method covers a liquid-chromatographic procedure for the separation of some additives currently used in polypropylene. These additives are extracted with a cyclohexane:methylene chloride mixture using either reflux or ultrasonic bath prior to liquid-chromatographic separation. The ultraviolet absorbance (200 nm) of the compound(s) is measured, and quantitation is performed using the internal standard method.

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. Specific precautionary statements are given in Section 9.

NOTE 1—There is no similar or equivalent ISO standard.

2. Referenced Documents

2.1 ASTM Standards:
D 883 Terminology Relating to Plastics
D 1600 Terminology for Abbreviated Terms Relating to Plastics
E 131 Terminology Relating to Molecular Spectroscopy
E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 For definitions of plastic terms used in this test method, see Terminologies D 883 and D 1600.

3.2 For the units, symbols, and abbreviations used in this test method, refer to Terminology E 131 or Practice E 380.

3.3 Abbreviations:

3.3.1 LC—liquid chromatography.
3.3.2 PP—polypropylene.
3.4 Trade Names:
3.5 Vitamin E—α-Tocopherol, or 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)-2H-1-benzopyran-6-ol.
3.6 Irgafos 168—Tris(2,4 di-tert-butylphenyl) phosphate.
3.7 Irganox 3114—Tris(3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate.
3.8 Kemamide-E—cis-13-docosenamide or erucamide.
3.9 Irganox 1010—tetrakis[methylene(3,5-di-t-butyl-4-hydroxy hydrocinnamate)]methane.
3.10 Irganox 1076—octadecyl-3,5-di-t-butyl-4-hydroxy hydrocinnamate.
3.11 Tinuvin P—2(2′-hydroxy-5′-methyl phenyl)benzotriazole.

4. Summary of Test Method

4.1 The PP sample is ground to a 20-mesh particle size (850 microns) and extracted by refluxing with a mixture of 75:25 methylene chloride:cyclohexane or placing in an ultrasonic bath with the same mixture.

4.2 The solvent extract is examined by liquid chromatography.

4.3 Additive concentrations are determined relative to an internal standard (contained in the solvent) using reverse-phase chromatography (C-18 column) with ultraviolet (UV) detection at 200 nm.

5. Significance and Use

5.1 Separation and identification of stabilizers used in the manufacture of polypropylene is necessary in order to correlate performance properties with polymer composition. This test method provides a means to determine erucamide slip, Vitamin E, Irgafos 168, Irganox 3114, Irganox 1010, and Irganox 1076 levels in polypropylene samples. This test method should be applicable for the determination of other antioxidants, such as Ultranox 626, Ethanox 330, Santanox R, and BHT, but the applicability of this test method has not been investigated for these antioxidants.
5.2 The additive-extraction procedure is made effective by the insolubility of the polymer sample in solvents generally used for liquid chromatographic analysis.

5.3 Under optimum conditions, the lowest level of detection for a phenolic antioxidant is approximately 2 ppm.

**Note 2**—Other methods that have been used successfully to remove additives from the plastics matrix include thin film, microwave, ultrasonic, and supercritical fluid extractions. Other methods have been used successfully to separate additives including SFC and capillary GC.

5.4 Irgafos 168 is a phosphite antioxidant. Phosphites are known to undergo both oxidation and hydrolysis reactions. Less Irgafos 168 may be seen in the polymer than originally added to the polymer due to oxidation during processing. The HPLC separation is capable of separating the phosphite, phosphate (oxidation product), and hydrolysis product. If standards are obtained, then the reaction products also can be quantified. No significant breakdown of the phosphite antioxidant has been seen due to either extraction technique or the separation presented in this standard.

6. **Interferences**

6.1 Any material eluting at or near the same retention time as the additive can cause erroneous results. A polymer-solvent-extract solution containing no internal standard should be examined to minimize the possibility of interferences.

6.2 A major source of interferences can be from solvent impurities. For this reason, the solvents should be examined prior to use by injecting a sample of solvent on the HPLC system and analyzing as in Section 10.

6.3 The oxidation product of Irgafos 168 can overlap with other additives with retention times of components that elute between Irganox 1010 and Irgafos 168. Standards should be run to ensure that components of interest do not coelute with the oxidation product of Irgafos 168.

7. **Apparatus**

7.1 **Liquid Chromatograph**, equipped with a variable-wavelength ultraviolet detector, heated column, and gradient-elution capabilities. The liquid chromatograph should be equipped with a means for a 10-µL-sample-solution injection, such as a sample loop.

7.2 **Chromatographic Column**, RP-18, 5-µm particle size, 15 cm by 4.6 mm.

**Note 3**—A Zorbax RX C-18 Column, MAC MOD Analytical, Inc., was used for this test method. The gradient described in 10.1 provides complete separation of antioxidants using this C-18 column.

7.3 **Computer System or Integrator**, coupled with the chromatograph is recommended to measure peak area.

7.4 **Wiley Mill**, equipped with a 20-mesh screen and water-cooled jacket to prevent thermodegradation of antioxidants.

7.5 **Recorder**, mV scale dependent upon the output of the detector.

7.6 **Reflex 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 (see Fig. 1).

7.7 **Ultrasonic Bath Apparatus**, consisting of the ultrasonic bath, a flat bottom 125-mL flask having a 24/40 ground-glass joint, and a 24/40 ground-glass stopper.

7.8 **Filter System** (Teflon) for nonaqueous solutions (pore size of 0.22 µm) equipped with a glass 5-cm³ syringe.

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

8. **Reagents and Materials**

8.1 **Tinuvin-P**, 2(2’hydroxy-5′-methyl phenyl) benzotriazole.

8.2 **Methylene Chloride**, HPLC grade, spectral quality or chromatography quality reagent.

8.3 **Cyclohexane**, HPLC grade, spectral quality or chromatography quality reagent.

8.4 75:25 **Methylene Chloride:Cyclohexane T-P**, mixture with 51.8 mg/L Tinuvin-P added as an internal standard.

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8.5 Water, HPLC or UV quality reagent, degassed by sparging with high purity helium or by filtration under vacuum.

8.6 Acetonitrile, HPLC, spectral quality or chromatography quality reagent (a reagent whose UV cut-off is about 190 nm).

8.7 Isopropanol, HPLC, spectral quality or chromatography quality reagent.

9. Safety and Precautions

9.1 Methylene chloride and cyclohexane are flammable. Perform this extraction procedure in a fume hood.

10. Preparation of Liquid Chromatograph

10.1 Set the chromatograph to operate at the following conditions (see Fig. 2 for an example chromatogram):

10.1.1 Initial Mobile Phase Condition—75% acetonitrile: 25% water or whatever is appropriate for column used in order to retain Tinuvin P longer than solvent breakthrough.

10.1.2 Final Mobile Phase Condition—100% acetonitrile: 0% water.

10.1.3 Gradient Length—5 min or whatever is appropriate to cause a complete separation of additives and have a total chromatogram analysis time of 20 min or less.

10.1.4 Gradient Curve—Linear.

10.1.5 Flow Rate—1.5 mL/min.

10.1.6 Hold at 100% acetonitrile: 0% water for 10 min or whatever is required to allow all additives to elute.

10.1.7 At 15.1 min return to 75% acetonitrile: 25% water at a flow of 1.5 mL/min for 5 min.

10.1.8 Detector—Ultraviolet detector set at 200 nm, range set at about 0.1 Aufs.

10.1.9 Column—Reverse-phase C-18, 5 µm, 15 cm by 4.6 mm.

10.1.10 Temperature—Column set at 50°C.

10.1.11 Sample Size—10 µL.

10.1.12 Hold at 100% acetonitrile: 0% water for 10 min or whatever is required to allow all additives to elute.

11. Sample Preparation

11.1 Grind the sample to a particle size of 20-mesh using a water-cooled Wiley mill.

Note 4—Grind 7 to 8 g of the sample to run the analysis. It is important to minimize the time of grinding to prevent any thermodegradation of the additives in the polymer.

11.2 For reflux extraction, weigh 5 ± 0.01 g of the sample into a 125 mL flat bottom flask, add a stirring bar, add by pipet 50.0 mL of methylene chloride:cyclohexane T-P solvent containing the internal standard, and boil for 90 min (with stirring) using the reflux apparatus.

Note 5—The internal standard is present in the extraction solvent (51.8 µg/mL).

11.3 For ultrasonic bath extraction, weigh 5 ± 0.01 g of the sample into a 125-mL flat bottom flask, add by pipet 50.0 mL of methylene chloride:cyclohexane T-P solvent containing the internal standard, stopper flask, and place in an ultrasonic bath. Turn on the ultrasonic bath and extract for 1 h.

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

11.5 Attach a filter disc assembly to a 5-µL Luer-Lok tip hypodermic syringe (see Fig. 3).

11.6 Decant or pipet 4 mL of the solvent extract into the above syringe.

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

12. Calibration by Internal Standard

12.1 Weigh accurately into a 125-mL flat bottom flask 50 ± 1 mg of the desired additive. Weigh 51.8 mg of Tinuvin-P into the flask. Dissolve the components in 5–10 mL of warm isopropanol. Transfer the solution mixture to a 1000 mL
participating laboratories. \[ S_r = \left( S_1^2 + S_2^2 + \ldots + S_n^2 \right)^{1/2}. \]

15. Report

15.1 Report the additive (ppm) calculated in 14.1.

16. Precision and Bias

16.1 Table 1 is based on an interlaboratory study\(^6\) conducted in 1995 in accordance with Practice E691 involving two materials tested using two different techniques at eleven different laboratories. The additives in these materials were prepared at two different companies. The materials were sent out to participants for grinding, solvent extraction, and further analysis. Each test result is an individual determination. Each laboratory obtained three test results for each material using either the ultrasonic or reflux extraction method (or both). Each test was performed on a different day.

\(^6\) Supporting data are available from ASTM Headquarters. Request RR:D 20-1193.
17. Keywords

17.1 additive; antioxidants; erucamide slip; extraction; Irgafos 168; Irganox 1010; Irganox 1076; Irganox 3114; liquid chromatography (LC); polypropylene (PP); vitamin E