Designation: D4499 – 07 (Reapproved 2015)

Standard Test Method for Heat Stability of Hot-Melt Adhesives[1]

This standard is issued under the fixed designation D4499; 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 the evaluation of hot-melt adhesives with respect to the change in properties that occurs while the adhesive is aged in the molten state during hot-melt application. Melt properties monitored are viscosity, color, skin formation, and phase separation.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D907 Terminology of Adhesives

D1544 Test Method for Color of Transparent Liquids (Gardner Color Scale)

D3236 Test Method for Apparent Viscosity of Hot Melt Adhesives and Coating Materials

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—Many of the terms found in this test method are defined in Terminology D907.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *color, n*—the aspect of the appearance of an object dependent upon the spectral composition of the incident light, the spectral reflectance or transmittance of the object, and the spectral response of an observer.

3.2.2 *melt viscosity, n*—measure of the ratio of shear stress to shear rate when the hot-melt is in its molten state.

3.2.3 *phase separation, n*—formation of a second liquid portion from a previously homogenous liquid over time.

3.2.4 *skin formation, n*—appearance of a relatively loose layer at the surface of a polymeric material.

4. Summary of Test Method

4.1 Samples of hot-melt adhesives are conditioned at the adhesive manufacturer's recommended application temperature for a conditioning cycle that corresponds to the expected residence time during which the adhesive will be held molten in the storage and application equipment. If so specified by the adhesive manufacturer, the molten adhesive will be protected against exposure to air. The total residence time is divided into two or three intervals at which points the aged adhesive color and melt viscosity are measured and compared to the initial adhesive color and viscosity. Prior to measuring the melt viscosity and color, the adhesive is subjectively evaluated for evidence of phase separation and surface skinning. Separate adhesive samples are conditioned for each test period.

4.2 The test report includes percent change in melt viscosity, percent of adhesive surface skinned, percent change in Gardner color, and description of phase separation, if any.

5. Significance and Use

5.1 Hot-melt adhesives must generally be applied at relatively high temperatures in order that the adhesive viscosity is low enough that it can be readily handled in typical hot-melt equipment. Changes in the adhesive caused by exposure to the severe environment required during hot-melt processing will disrupt the adhesive application process and may affect the quality of the adhesive bond. Changes in adhesive viscosity may affect the quantity of adhesive dispensed by the applicator. Phase separation or changes in viscosity and color may be an indication of changes occurring in the adhesive which could affect the quality of the adhesive joint. A skin formed on the adhesive may eventually clog the applicator nozzle or die.

5.2 The data generated in this test procedure are comparative in nature. Results can be useful in observing batch-to-batch variation or relative thermal stability of alternate adhesive formulations. Results can also be useful in selecting

[1] This test method is under the jurisdiction of ASTM Committee D10 on Packaging and is the direct responsibility of Subcommittee D10.14 on Tape and Labels.

Current edition approved Oct. 15, 2015. Published October 2015. Originally approved in 1985. Last previous edition approved in 2007 as D4499 – 07. DOI: 10.1520/D4499-07R15.

[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.

application equipment and establishing operating conditions for satisfactory handling of a particular hot-melt adhesive.

5.3 Round-robin testing showed that the reproducibility of this test method can depend strongly on the characteristics of the adhesive being tested. Results showed that, for the particular adhesives tested in the round robin, the test method was well suited for testing the heat stability of the adhesives based on an EVA copolymer, a polyolefin, and a polyamide. However, because of poor reproducibility, the test method proved to be unsuitable for assessing the heat stability of the adhesive based on a block copolymer. Precision of this test method is discussed in Section 11.

6. Apparatus

6.1 *Glass Beakers,* 300-mL, each approximately 6.6-cm inside diameter by 11.7 cm high.

6.2 *Mechanical Convection Oven,* with specified temperature uniformity of ±1°C (1.8°F).

6.3 *Viscometer,* rotating-spindle type with leveling stand, stainless steel spindles, and sample chamber with precision temperature controller which provides accuracy of ±1.0°C or better through the range from 100 to 200°C.

6.4 *Glass Standards,* 18, as described in Test Method D1544.

6.5 *Glass Tubes,* clear, 10.65-mm in inside diameter, and about 114-mm in outside length, as described in Test Method D1544.

6.6 Suitable apparatus for comparing sample and standard, as described in Test Method D1544.

7. Sample Preparation

7.1 Large differences exist among hot-melt adhesives in their hot-melt processing requirements. Many types of adhesives, such as those based on an unsaturated or a reactive polymer, can be held molten for only a short period of time. In some cases, these adhesives must be protected against exposure of the hot adhesive to the atmosphere. Other types of adhesives, such as those based on a saturated polymer, can be held molten and unprotected from the atmosphere for extended periods of time. The adhesive manufacturer's recommendations on exposure time and temperature and the need to protect the molten adhesive against exposure to air must be followed.

7.2 Repeated melting or extended storage of a hot-melt adhesive will adversely affect the product's performance in a heat-stability test. Choose a representative sample material from batches recently received from the manufacturer.

7.3 Avoid contamination of adhesive with water to prevent foaming problems during melting and possible reactivity with adhesive components.

8. Procedure

8.1 *Test Temperature*—Set oven and viscometer temperature controller at adhesive manufacturer's recommended application temperature.

8.2 *Test Cycle*—Choose a test cycle which is representative of the time period during which the adhesive will be held molten in the application equipment to be used. Verify that the cycle chosen is consistent with the adhesive manufacturer's recommendations. Two typical test cycles of heat-aging times at which samples are taken for testing are as follows:

Cycle I	Cycle II
Initial (no preconditioning)	Initial
24 h	8 h
48 h	18 h
96 h	24 h
	48 h

8.3 *Initial Data:*

8.3.1 *Melt Viscosity*—Select a representative sample of adhesive, as received from the manufacturer, and measure the melt viscosity at the chosen conditioning temperature in accordance with Test Method D3236. For some hot-melt adhesives, the change in viscosity with aging can be affected by changes in shear rate. Use the same spindle size and speed of rotation to measure the viscosity of the unaged and all of the heat-aged samples.

8.3.2 *Color:*

8.3.2.1 *Nonpigmented Adhesives*—Fill a clear glass tube with slivers of the hot-melt adhesive in "as-received" condition. Place the tube in an oven set at the minimum temperature necessary to produce a transparent melt. Remove the tube of molten adhesive from the oven and immediately place into the color comparator apparatus. Make the color determination, in accordance with Test Method D1544, before the adhesive cools below the cloud point. Record the adhesive color to the nearest color unit.

8.3.2.2 *Pigmented Adhesives*—Place about 150 g of adhesive in "as-received" condition into a 300-mL beaker. Heat in an oven to the manufacturer's recommended application temperature, and stir the adhesive thoroughly to ensure uniform pigment dispersion. Avoid aeration of the adhesive. Prepare an adhesive film 0.25 mm thick on white paper. Select appropriate visual color standards such as those used in the Pantone Matching System color chip sets and books. Identify the color chip that most closely matches the initial adhesive color.

NOTE 1—The adhesive supplier and adhesive user can jointly prepare custom-made color standard for individual adhesives to be tested.

8.4 *Sample Preparation*—Weigh 150 g of adhesive into a 300-mL beaker and place in the oven. Glass beakers are used instead of metal containers to allow the observation of phase separation. Prepare three samples for Test Cycle I or four samples for Test Cycle II. Cover the samples with aluminum foil prior to placement in the oven. If the use of an inert gas atmosphere during molten processing is recommended by the adhesive manufacturer, provide a continuous inert gas purge for the adhesive samples during the elevated temperature conditioning.

8.5 *Test Data—First Test Period:*

8.5.1 *Skinning*—Remove one beaker from the oven at the conclusion of the first conditioning period. Examine the molten adhesive for the presence of a skin (a thermoset membrane) by carefully probing the adhesive surface with a metal spatula. If skinning is observed, estimate the percentage of adhesive surface covered. Describe the characteristics of the skin using