Designation: D 4499 – 95 (Reapproved 2000)

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

This standard is issued under the fixed designation D 4499; 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:*

D 907 Terminology of Adhesives[2]

D 1544 Test Method for Color of Transparent Liquids (Gardner Color Scale)[3,4]

D 3236 Test Method for Apparent Viscosity of Hot-Melt Adhesives and Coating Materials[5]

## 3. Terminology

3.1 *Definitions*—Several terms in this test method are defined in accordance with Terminology D 907.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *color*—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*—measure of the ratio of shear stress to shear rate when the hot-melt is in its molten state.

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

3.2.4 *skin formation*—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 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

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[1] This test method is under the jurisdiction of ASTM Committee D-14 on Adhesives and is the direct responsibility of Subcommittee D14.50 on Hot-Melt and Pressure-Sensitive Adhesives.

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[2] *Annual Book of ASTM Standards*, Vol 15.06.

[3] *Annual Book of ASTM Standards*, Vol 06.01.

[4] Visual color standards such as the Pantone Color System can be used in place of the Gardner Color System with pigmented adhesives.

[5] *Annual Book of ASTM Standards*, Vol 05.02.

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]

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.[7]

6.4 *Eighteen Gardner Standards*. [8]

6.5 *Glass tubes*, clear, 10.65-mm inside diameter, 114-mm length.[8]

## 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 D 3236. For some hot-melt adhesives, the change in viscosity with aging can be affected by changes in shear rate. If at all possible, 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 Gardner color 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 Gardner Color Comparator. Make the color determination, in accordance with Test Method D 1544, 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 (0.010 in.) thick on white paper. Select appropriate visual color standards such as the Pantone Color-Matching System.[9] 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 terms such as: dark color, thin, thick, brittle, or sticky. Check for the presence of a skin immediately after removal from the oven to avoid confusing a chilled adhesive surface for a skin.

[6] Mechanical convection ovens such as Blue M, model Power-O-matic 60 with ± 0.5°C control temperature available from Blue M Electric Co., Garland, TX 75040, have been found suitable.

[7] The viscometer and accessories available from Brookfield Engineering Laboratories Inc., Stoughton, MA 02072 (Brookfield Thermosel System), have been found suitable.

[8] Color comparator apparatus, standards, and glass tubes available from Fisher Scientific Co., Pittsburgh, PA 15219, have been found suitable.

[9] Available from Pantone Color-Matching System, Pantone, Inc., Moonache, NJ 07074.

**TABLE 1 Statistical Information**

| Property | Adhesive Type | Mean Initial Property | Mean Final Property | Mean Change in Property, % | Standard Deviation Of % Change | Reproducibility of Change in Property, % |
|---|---|---|---|---|---|---|
| Melt Viscosity, Pa·s | EVA[A] | 1.158 | 1.144 | −0.2 | 3.4 | 11.7 |
| | Polyolefin[A] | 2.158 | 2.092 | −3.8 | 7.6 | 21.9 |
| | Polyamide[B] | 8.585 | 8.470 | −1.4 | 4.1 | 11.4 |
| | Block Polymer[A] | 30.750 | 15.765 | −47.2 | 26.4 | 73 |
| Gardner Color | EVA[A] | 7.0 | 11.8 | 70 | 19.5 | 54 |
| | Polyolefin[A] | 2.9 | 10.8 | 284 | 89.9 | 249 |
| | Polyamide[B] | 4.1 | 11.2 | 173 | 49.8 | 140 |
| | Block Polymer[A] | 10.9 | 14.6 | 36 | 17.0 | 47 |
| Skin Formation | EVA[A] | ... | 1.1 | 1.1 | 3.3 | 8.9 |
| | Polyolefin[A] | ... | 5.0 | 5.0 | 9.3 | 25.1 |
| | Polyamide[B] | ... | 0 | 0.0 | 0 | 0 |
| | Block Polymer[A] | ... | 66 | 66 | 43.1 | ... |

[A] Adhesive aged under Cycle I at 177°C.
[B] Adhesive aged under Cycle II at 190°C.

8.5.2 *Phase Separation*— Examine the conditioned adhesive for phase separation (as evidenced by appearance of discrete layers, opacity, cloudiness, or formation of visible particles), using a fresh sample of molten adhesive for comparison purpose. Describe observed phase separation with particular attention directed at specifying the relative amounts and physical characteristics of the separated materials.

8.5.3 *Melt Viscosity*— Carefully remove any skin from the conditioned adhesive and measure the viscosity according to Test Method D 3236. If possible, use the same spindle size and speed of rotation as was used to measure the viscosity of the unaged sample. Discontinue the test if phase separation or gellation occurs.

8.5.4 *Color*:

8.5.4.1 *Nonpigmented Adhesives*—Fill a Gardner color tube with conditioned adhesive, taking care to exclude skin fragments. Determine Gardner color while molten as described in 8.3.

8.5.4.2 *Pigmented Adhesives*—Stir the conditioned molten adhesive carefully to disperse any settled pigment. Avoid aeration of the sample. Prepare an adhesive film, 0.25 mm thick on white paper. Compare the adhesive color with the visual standards used to identify the initial adhesive color. Since color matches are likely to be approximate, make the color comparisons with color chips in same color series as the initial color chip. For example:

Initial Adhesive Color—Pantone 127 Creme (Yellow)

96−h Adhesive Color—Compare with Pantone 128–133

Since the presence of a skin tends to preserve light color, note the occurrence of a skin with color data.

8.6 *Test Data—Remaining Test Periods*—Repeat 8.5 until the chosen test sequence is complete or prematurely terminated due to adhesive gellation or phase separation.

## 9. Calculation

9.1 *Melt Viscosity*:

9.1.1 Tabulate viscosity data, and calculate percent change in viscosity ($\Delta V$) for each test period using the following formula:

$$\Delta V = \frac{(V_8\ \text{h} - V_I) \times 100}{V_I} \quad (1)$$

$V_I$ = initial viscosity, and
$V_8$ h = viscosity after 8 h of oven conditioning.

9.1.2 See 10.1.4 for report instructions.

9.2 *Color*:

9.2.1 Tabulate color data along with the percentage of adhesive surface which had a skin. Calculate percent change in Gardner color ($\delta C$) for each test period using the following formula:

$$\Delta C = \frac{(C_8\ \text{h} - C_I)}{C_I} \times 100 \quad (2)$$

$C_I$ = initial Gardner color, and
$C_8$ = Gardner color after 8 h of oven conditioning.

9.2.2 See 10.1.5 for report instructions.

## 10. Report

10.1 Report the following information:

10.1.1 *Test Conditions*:

10.1.1.1 Aging temperature.

10.1.1.2 Adhesive exposed to or protected from atmosphere.

10.1.2 *Skin Formation*:

10.1.2.1 Heat aging time at which skin was observed.

10.1.2.2 Description of skin.

10.1.2.3 Percentage of surface covered.

10.1.3 *Phase Separation*:

10.1.3.1 Heat aging time at which phase separation was observed.

10.1.3.2 Description of phases.

10.1.3.3 Percentage of adhesive in each phase.

10.1.4 *Melt Viscosity* (see 9.1):

10.1.4.1 Use designations $V_{18}$ h; $V_{24}$ h; $V_{48}$ h; $V_{96}$ h for appropriate test periods. Record the direction of change (− or + ) with calculated data.

10.1.4.2 Report temperature, spindle size, and revolutions per minute (rpm) used for each viscosity determination.

10.1.5 *Color* (see 9.2):

10.1.5.1 Use designations $C_{18}$ h, $C_{24}$ h, $C_{48}$ h, $C_{96}$ h, for appropriate test periods.

## 11. Precision and Bias

11.1 Nine laboratories participated in testing this test method using four hot-melt adhesives representing four different chemical types.[10] Results of interlaboratory reproducibility are summarized in Table 1. No data were gathered to allow assessment of intralaboratory reproducibility.

11.1.1 *Reproducibility*:

11.1.1.1 It is impossible to state the reproducibility of this test method. The user of this test must establish an estimate of the reproducibility of this test method for the particular adhesive on which the test will be run.

11.1.1.2 Results in Table 1 exemplify the interlaboratory reproducibility found in round-robin testing of four types of adhesives. The interpretation of results in Table 1 is as follows. If two laboratories measure percentage change in melt viscosity, color, or skin formation on the same adhesive following this procedure and using the same aging condition and cycle, then the significance of the difference between results from the two laboratories can be assessed as follows. The results from the two laboratories shall be considered to be significantly different from each other at the 95 % confidence level whenever the two values differ by more than the reproducibility value (units are percent) given in Table 1 for that particular adhesive. For example, consider the case of two laboratories measuring the melt viscosity change of the adhesive based on the EVA copolymer. If the result from one laboratory is a 1.2 % reduction in viscosity, then the result from the other laboratory will be between a 10.5 % increase in viscosity and a 12.9 % reduction in viscosity, 95 % of the time.

11.1.1.3 Results in Table 1 show that, for the particular adhesives tested, this test method was fairly well suited for testing the heat stability of the adhesives based on the EVA copolymer, the polyolefin, and the polyamide. However, because of poor reproducibility, this test method proved to be unsuitable for assessing the heat stability of the adhesive based on a block copolymer.

## 12. Keywords

12.1 color; heat stability; hot-melt adhesive; melt viscosity; phase separation; skin formation

[10] Supporting data are available from ASTM Headquarters, 1916 Race St., Philadelphia, PA 19103. Request RR: D14-1003.