



The Association of  
Plastic Recyclers

## PET Degradable Additives Test PET-S-06

### **Note to the Reader**

This guide has been prepared by the Association of Plastic Recyclers as a service to the plastic packaging industry to promote the most efficient use of the nation's plastics recycling infrastructure and to enhance the quality and quantity of recycled postconsumer plastics. The information contained herein reflects the input of APR members from a diverse cross-section of the plastics recycling industry, including professionals experienced in the recycling of all postconsumer plastic bottles discussed in this guideline. It offers a valuable overview of how package design impacts conventional plastics recycling systems and products made from postconsumer material. Because new technological developments are always being made, this guide cannot anticipate how these new developments might impact plastic bottle recycling. Thus, while the information in this guide is offered in good faith by APR as an accurate and reliable discussion of the current challenges faced by the plastics recycling industry, it is offered without warranty of any kind, either expressed or implied, including WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE, which are expressly disclaimed. Meeting the guidance here given does not obligate any APR member to accept bottles containing the innovation. APR and its members accept no responsibility for any harm or damages arising from the use of or reliance upon this information by any party. APR intends to update this document periodically to reflect new developments and practices.

### **About APR**

The Association of Plastic Recyclers is the North American trade association representing companies that acquire, reprocess and sell the output of more than 90% of the postconsumer plastic bottle processing capacity in North America. Its membership includes independent recycling companies of all sizes and the recycling interests of many other companies. APR strongly advocates the recycling of all postconsumer plastic packaging and recommends the use of postconsumer plastics in products, where possible.



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APR strives to eliminate obstacles to plastic recycling with technical programs and guidelines. These initiatives have been produced in response to a need to provide information to the plastic packaging industry on what elements of package design may or may not affect the recycling of that package in current systems.

### **Introduction**

APR's position is that suppliers of degradable additives have the burden of showing that their materials have 'drop in replacement' compatibility for the recycling process and for the next application with postconsumer PET not containing the degradable additives.

Degradable additives as this term is used in this guidance refers to those additives, catalytic and non-catalytic, that are intended to reduce the molecular weight of PET, fragment the polymer and/or convert the carbon of the polymer to carbon dioxide or methane. These additives may or may not be compatible with PET recycling and they may or may not affect the service life of postconsumer PET.

Other APR guidance test protocols for PET recycling do not include time as a test variable. As such, those protocols alone are insufficient to understand the impact of the degradable additives on the service life of postconsumer PET. For this reason, Critical Guidance testing alone is insufficient to demonstrate 'drop-in replacement' compatibility. Modified APR Applications Guidance testing is needed to demonstrate fitness-for-use in the primary end uses for postconsumer recycled PET.

Any testing can only examine one or a limited set of circumstances. Success at any given circumstance does not mean a system is always successful, only success at that circumstance. Therefore, a series of tests are provided in this guidance in order to specifically gain an understanding of the impact of degradable additives on current estimates for the service life of postconsumer PET in specified applications. Sample preparation aging conditions suggested by this guidance are intended to simulate reasonably severe but realistic conditions for the test materials. Testing is generally in comparison to controls and also some measurements for absolute properties.

Due to the emerging nature of the degradable additive technologies, these materials are not currently part of the APR recognition program.

APR offers this guidance to provide a framework for decision making. The evaluation guidances are based on the experience of sellers of recycled plastic. In most respects the testing called for is conventional and often includes ASTM Standard Test Methods. During the initial implementation of this guidance, however, some method development and validation should be anticipated by users of the guidance concerning the accelerated aging procedures described in the guidance, to represent the specific



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real time exposures. Efforts in this area will need to be determined on a case-by-case basis for each commercial degradable additive chemistry.

### **Specified Product Applications Covered by this Guidance**

PET recycle is in a number of applications. The applications to be addressed by this guidance include bale storage, fiber, bottles, and strapping as described below:

- 1. PCR Bales** Bales of PET bottles may be stored inside, outside on concrete slabs protected from sun exposure, or outside on soil and with full exposure to sun and rain for as long as two or three years after collection. This guidance is based on an APR-contracted survey of actual practices which showed outside storage for 12 or more months is done.
- 2. Fiber** Products may consist of up to 100% recycled PET. Service life for carpets may be 20 years for indoor uses at ambient temperature under normal sunlight exposure. Product quality specification considerations include wear and color shift during production and use. Reduction in service life or lower product quality may lead to extensive replacement cost and product reputation loss.
- 3. Bottles** Bottles may include 25%, but also up to 100%, recycled PET. A service life of up to 3 years may be expected. Product quality specification considerations include the ability to withstand a combination of temperature, sunlight exposure, moisture, and microbial contact conditions. Bottle failure or reduced service life may cause extensive replacement cost, possible injury, and product reputation loss.
- 4. Strapping** Products may consist of up to 100% recycled PET. Service life capability of 4 years may be expected for bricks with storage on soil with weather exposure. Product quality specifications include the ability to withstand a combination of temperature, sunlight exposure, moisture, and microbial contact conditions. Strapping failure may cause extensive replacement costs, possible injury, and product reputation loss.
- 5. Geotextiles** Products may consist of up to 100% recycled PET. Service life is expected to be 30 or more years of exposure to soil. Product quality specifications include non-rotting. Geotextile failure may cause



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structure failure, extensive replacement costs, possible injury, and product reputation loss.

## Modified Critical Guidance Testing

The following steps and considerations must be addressed in recycling effects testing.

Step 1. Any given additive formulation is not necessarily applicable to another formulation. Each additive formulation calls for separate examination at normal concentrations.

Step 2. Make test bottles/films containing the additive at manufacturer’s recommended maximum concentration.

a. Bottles or 12 mil film must be tested, not pellets, to allow for proper surface/volume exposure and material transport.

b. One of the APR PET control resins should be used.

<i>Low IV, Water Bottle Innovation Controls</i>	<i>CSD and Non-Water Bottle Innovation Controls</i>
<b>Auriga Polyclear® Splash 3301</b>	<b>Auriga Polyclear® Refresh 1101</b>
<b>M&amp;G Cleartuf® Turbo II</b>	<b>M&amp;G Cleartuf® MAX</b>
<b>DAK Laser+® W L40A</b>	<b>DAK Laser+® B90A</b>

c. Any standard PET bottle can be used.

d. 12 mil film can be substituted for bottles for initial aging.

e. For those degradable additives which include an antioxidant, no more antioxidant can be included than sold in regular formulations. **Any antioxidant must be present at no greater amount than is part of sales formulations.** Control shall not include any antioxidant. No addition of antioxidants should be included in aged bottles/film samples.

f. Make control bottles/films without the additive in the same form as the test bottles/films using the same control resin base material.

Step 3. Test bottles/films from Step 2 are aged under identical conditions of temperature, light (UV), moisture and soil contact to simulate storage of postconsumer bales.

a. Aging time must equal one year of such exposure.



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- b. Conditions that simulate outdoor exposure conditions in south Florida are needed. These include the following parameters: Full exposure to sun and rain, contact with biologically active soil, such as top soil.
- c. Bales of bottles, or films, should be placed on the ground, on soil, with full sunlight and rain exposure. Bales should be turned every 3 months so all sides, not including ends, of the bale have equal soil and sun exposure.
- d. Bales should be nominal 125 pound bales.
- e. Any accelerated aging of bottles needs to be validated to equal one year storage yard exposure for south Florida conditions including soil contact. Any accelerated aging must be shown valid for the system of additive and resin in the physical thicknesses of the end use as the additives involve surface transport mechanism and activity. Aging thick moldings is not the same as aging thin films. Accelerated aging must consider the multiple chemical, biological, and physical mechanisms present and operating and represent the limiting mechanism at ambient conditions. Simple time/temperature superposition must be validated before included in the test design. Any accelerated aging for catalytic or non-catalytic strictly biological systems must be validated against real time testing.
- f. Aged blends containing the degradable additive will be tested for whether they meet or exceed the strictest Critical Guidance. Investigators should plan for more test material than needed for Critical Guidance testing when conducting the original aging because additional testing will be in order if the Critical Guidance results are first met.
- g. Save 25 pounds of the unaged material for fiber, testing.

Step 4. Aged control and test bottles/films are processed separately to washed flake per the APR Critical Guidance washing procedure, detailed in Appendix 1.

- a. Make blend of 50% test bottle flake and 50% control bottle flake.
- b. **The 50:50 blend should be tested vs. 100% control bottle flake per the APR Critical Guidance tests for recycled PET, included as Appendix 1. Testing includes changes in color, haze, IV,  $\Delta$  IV on melting, specks, filtration, melting point, and solid stating potential. Failure to meet the strictest**



**guidance recommended by the Critical Guidance indicates that the test material is not technically compatible with current PET recycling conditions. Passage of the recommended Critical Guidance levels is a pre-condition to performing additional testing.**

### **Modified Applications Guidance Testing**

1. FIBER – Testing PET containing maximum recommended concentration of degradable additive level vs. control.

While making, aging, and testing carpet would be ideal, the burden is severe on all parties, making actual carpet aging and testing impractical. Limited testing here given should confirm key production compatibility and service life. TiO<sub>2</sub> delusterant is included because of potential interactions with degradable additives.

- a. Prepare test fibers (nominal 6 denier per filament and tenacity over 3 grams/denier), from washed flake material in Step 4 made from aged material from Step 3 using original bottle/film materials from Step 2 above in Modified Critical Guidance. Also make fibers from flake from unaged materials from Step 2.
  - i. The spinning speed needs to represent high speed, consistent with continuous filament commercial operations.
  - ii. Filaments need to be stretched and heat set.
  - iii. Include a second set of fibers with commercial TiO<sub>2</sub> concentrate for 0.4% TiO<sub>2</sub> in the fiber, consistent with semi-bright carpet fiber.
  - iv. This results in 8 sets of filaments for materials from the Modified Critical Guidance above:
    1. Step 2f unaged raw material, neat, without additive; (control)
    2. Step 2 unaged raw material, neat, with additive
    3. Step 2f unaged raw material with TiO<sub>2</sub>, without additive; (control)
    4. Step 2 unaged raw material with TiO<sub>2</sub>, with additive
    5. Step 3 aged raw material from Step 2f, neat, without additive; (control)
    6. Step 3 aged raw material from Step 2, neat, with additive;
    7. Step 3 aged raw material from Step 2f, with TiO<sub>2</sub>, without additive; (control)
    8. Step 3 aged raw material from Step 2, with TiO<sub>2</sub>, with additive.
- b. On all fibers from 1.a iv above, examine disperse dyeing and show no difference greater than test variability in dye uptake between corresponding fibers with and without additive. [Test protocol in Appendix 3]



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- c. On all fibers from 1.a iv above, compare tenacity at break (grams/denier), % elongation at break, initial modulus, and thermal shrinkage at 177°C. Differences greater than test variability are unacceptable for corresponding fibers with and without additive.
- d. On all fibers from 1.a iv above, examine fibers for gels and slubs or other defects. No more defects are allowed in the 100% additive-containing PET fibers than in the corresponding 0% additive-containing PET fiber.
- e. On all fibers from 1.a iv above, expose fibers to continuous Xenon light for 40 hours per AATCC Test Method 16, option 3, colorfastness to light test. Differences greater than test variability are unacceptable for corresponding fibers with and without additive.
- f. On test and control fibers from 1.a iv above, age the equal of 20 years of nominal aging exposure (25°C, 50% RH, sunlight) (20 years of expected service life). Measure IV and color on corresponding sets of aged fibers.  $\Delta IV$  no greater than 0.025 dl/gm and color  $\Delta b^*$  no greater than test variability are allowed. Measure tenacity of both sets of aged fiber.  $\Delta$  tenacity no greater than test variability allowed. Statistical significance is defined at 0.05 for Student t evaluation of population means.
- g. Any accelerated testing must be validated to reflect nominal exposure.

### 1A. GEOTEXTILE FIBERS

While making, aging, and testing geotextile staple and non-woven structures would be ideal, the burden is severe on all parties, making actual geotextile aging and testing impractical. Limited testing here given should confirm key production compatibility and service life.

- a. Prepare test fibers (nominal 10 denier per filament and tenacity over 3 grams/denier), from washed flake material in Step 4 made from aged material from Step 3 using original bottle/film materials from Step 2 above in Modified Critical Guidance. Also make fibers from flake from unaged materials from Step 2.
  - i. The spinning speed needs to represent high speed, consistent with continuous filament commercial operations.
  - ii. Filaments are not drawn and heat set, but are of lower crystallinity.iii. This results in 4 sets of filaments for materials from the Modified Critical Guidance above:
    1. Step 2f unaged raw material, neat, without additive; (control):
    2. Step 2 unaged raw material, neat, with additive:
    3. Step 3 aged raw material from Step 2f, neat, without additive; (control)
    4. Step 3 aged raw material from Step 2, neat, with additive;



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- b. On all fibers from 1.a iv above, compare tenacity at break (grams/denier), % elongation at break, initial modulus, and thermal shrinkage at 177°C. Differences greater than test variability are unacceptable for corresponding fibers with and without additive.
  - c. On all fibers from 1.a iv above, examine fibers for gels and slubs or other defects. No more defects are allowed in the 100% additive-containing PET fibers than in the corresponding 0% additive-containing PET fiber.
    - d. On test and control fibers from 1.1 iv above, age the equal of 30 years of soil exposure (20°C, moist) (30 years of expected service life).

Use the inoculum defined for ASTM D 5526 at a ratio of 1part inoculum to 6 parts dry top soil to 1 part PET fibers. Keep mix at the equal of south Florida ground temperature and moisture.
  - e. Measure IV on corresponding sets of aged fibers.  $\Delta$  IV no greater than 0.025 dl/gm is allowed. Measure tenacity and modulus of both sets of aged fiber.  $\Delta$  tenacity and modulus no greater than test variability allowed. Statistical significance is defined at 0.05 for Student t evaluation of population means.
  - f. Any accelerated testing must be validated to reflect nominal exposure.
2. BOTTLES – Testing PET with 25% degradable additive level vs. control.
- Bottles shall be made per the APR Bottle-to-Bottle Applications protocol, aged, and tested per the protocol, attached as Appendix 2.
- a. Raw material test bottles shall be made as in Step 2 above and be aged per Step 3 above for Modified Critical Guidance.
  - b. Per the APR Applications Guidance, the Bottle-to-Bottle test bottles are to be made from a 50:50 blend of the 0.80 dL/g pellets from the CGD (made from a pelletized and solid stated blend of 50% aged degradable additive flake and 50% aged control flake) and 50% virgin PET pellets. This results in the additive being tested at 25% its normal concentration vs. the control. The Bottle-to-Bottle control bottles are to be made from a 50:50 blend of the solid stated 0.80 dL/g aged control flake pellets from the CGD study and virgin pellets. Flakes from Step 3 aged bottles are to be washed, blended, pelletized, and solid state polymerized to 0.80 IV per the APR Applications Guidance and then blended with virgin PET pellets.
  - c. Test bottles and control bottles shall be made per the APR Bottle to Bottle Applications Guidance Document. Bottles, control and test, shall be tested after blowing and results examined per the guidance given in the APR Bottle-to-Bottle protocol in the Applications Guidance Document.
  - d. Test and control bottles shall be aged 3 years of nominal exposure (three years second bottle service life capability). Nominal conditions are 25°C, 50% RH, sunlight.





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- d. Any accelerated aging must be validated to reflect nominal exposure.
- e. Aged test and control bottles shall be examined by the procedures called for and guidance given in the APR Bottle-to-Bottle protocol in the Applications Guidance Document.

Note: Food and beverage companies will be concerned about extractables and taste changes.

### 3. STRAPPING – Testing PET with maximum recommended degradable additive level vs. control.

While making, aging, and testing strapping would be ideal, the burden is severe on all parties, making actual strapping aging and testing impractical. Limited testing here given should confirm key production compatibility and service life.

- a. Bottles or film containing the degradable additive at normal concentrations and control bottles or films with no additive (Step 2) shall be aged per Step 3 above and converted to flake and pelletized (per the APR PET Critical Guidance Document, Appendix 1 below) and pellets solid state polymerized to 0.95 IV within 39 hours of solid state processing, per the APR PET Applications Guidance Document, Appendix 3 below. Pellets are then processed into amorphous sheets 35 mils thick (0.035 inches). 35 mil sheets shall then have been made of maximum recommended level of additive-containing aged bottles/film raised to 0.95 IV and 35 mil sheets shall have been made of 0% additive-containing aged bottles/film raised to 0.95 IV.
- b. Sheets of maximum recommended level degradable-added resin and 0% degradable-added control resins shall be aged 4 years in outside conditions of south Florida including top soil contact (4 years of expected service life) or equivalent.
- c. Any accelerated aging must be validated.
- d. Aged sheets of maximum recommended degradable-added resin and control resins must show no greater  $\Delta$  IV than 0.025 dl/gram after aging.

For technical assistance please contact: [APR.Technical.Director@earthlink.net](mailto:APR.Technical.Director@earthlink.net)

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**SUMMARY OF TEST PREPARATION AND TESTS**

	<b>Critical Guidance Testing</b>	<b>Fiber Testing</b>	<b>Bottle Testing</b>	<b>Strapping Testing</b>
Starting material	Aged (1 year, Florida conditions) bottle or film to process into flake and test. Acceleration must be validated	Aged (1 year, Florida conditions) and unaged bottle or film, processed into washed flake.	Aged (1 year, Florida conditions) bottle or film, washed and processed into 0.80 IV solid stated pellets.	Aged (1 year, Florida conditions) bottle or film, washed and processed into 0.95 IV pellets within 39 hours of solid stating.
% degradable additive in test specimens	Testing blend of 50% flake with additive at 100% normal level, 50% control (APR Critical Guidance)	Testing fiber made from 100% flake with additive at maximum specified additive level, with and without TiO <sub>2</sub> , with and without starting material aging.	Testing bottles made from pellets made from 25% flake with normal additive level from aged bottles, 25% control flake from aged bottles, 50% virgin PET pellets (APR Bottle-to-Bottle level)	Testing sheet made of 0.95 IV pellets from 100% flake with additive with additive at maximum specified additive level
Test specimens and aging	Flake, pellets and plaques. No additional aging of Critical Guidance test specimens.	Fibers, as made and aged 20 years of indoor conditions, or validated acceleration.	Bottles, as made and aged 3 years in indoor conditions, or validated acceleration	35 mill thick sheet., aged 4 years, outside (Florida) conditions, with soil contact, or validated acceleration
Tests	APR Critical Guidance. Meet or exceed all	Dye take up, fiber defects, colorfastness, tensiles, and	APR Bottle-to-Bottle tests on bottles as made and after aging.	IV difference on aged sheet samples



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	guidance for 50% additive blend.	shrinkage for test vs. control on initial fibers. IV, tenacity, color difference, test vs. control on aged fibers		
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	<b>Geo-textile</b>
Starting material	Aged (1 year, Florida conditions) and unaged bottle or film, processed into washed flake.
% degradable additive in test specimens	Testing fiber made from 100% flake with additive at maximum specified additive level
Test specimens and aging	Fibers, as made and aged 30 years in top soil (biologically active) South Florida conditions, or validated acceleration.
Tests	IV, tenacity, and modulus, test vs. control on aged fibers

## Appendix 1.

**Critical Guidance Testing**, per APR’s Critical Guidance Document

### Evaluation Protocol Steps

#### 1.2.1 Control and Innovation/Variant Bottle Manufacture

- Control bottles should be made from one of the acceptable resins listed here. The Innovation bottles should be made with this same resin incorporating the additive at the maximum recommended use level.

<i>Low IV, Water Bottle Innovation Controls</i>	<i>CSD and Non-Water Bottle Innovation Controls</i>
<b>Auriga Polyclear® Splash 3301</b>	<b>Auriga Polyclear® Refresh 1101</b>
<b>M&amp;G Cleartuf® Turbo II</b>	<b>M&amp;G Cleartuf® MAX</b>
<b>DAK Laser+® WL40A</b>	<b>DAK Laser+® B90A</b>



### 1.2.2 Flake Preparation

1. The Control bottles and Innovation bottles should be separately dry-ground to nominal ¼” to ½” size flake.
2. Air elutriation to remove light fractions with one pass and with set up to accomplish less than 2% PET flake loss from the feed for Control Flake.

### 1.2.3 Flake Wash

1. Prepare a wash solution of 0.3% by weight Triton X-100 (6.0 grams or 5.7 ml per 2,000 ml water) and 1.0% by weight caustic (20 grams NaOH per 2,000 ml water). Note: Triton X-100 must be dissolved in warm (nominal 100°F) water prior to the addition of caustic!
2. Mix bottle flake or pellets at a ratio of 500 grams solids per 2,000 ml wash solution. Wash in highly agitated (1,000 rpm with impeller 0.6 cm from bottom of wash container) water at 88+/-2°C for 15 minutes. Record composition of the wash solution.
3. After 15 minutes of washing, stop agitation and remove agitator. Remove heating. Let mixture of solids and solution stand for several minutes to allow floatable materials to float. Skim off floatables. Separate sinking solids from wash solution by pouring mixture through a strainer. Add sinking solids to room temperature rinse water at an approximate ratio of 500 grams sinking solids to 2 liters of water. Let stand for five minutes to allow remaining lights to float to the surface. Repeat sink/float step once again.
4. Transfer PET flakes to strainer, rinse flakes in cold running tap water while vigorously stirring the flakes for 10 minutes using the manual stirring bar. Drain the material. Air dry flake.
5. A second air elutriation to remove light fractions with one pass and with less than 2% loss set for the Control Flake may be carried out on the dried washed flake.

### 1.2.4 Sample Blending

Washed flake will be used to make the required Samples.

1. Create the following two test blends from the washed flake for study:

Sample A1:	100% Control Material	0% Innovation Material
Sample C1:	50% Control Material	50% Innovation Material

### 1.2.5 Extrusion/Pelletization



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1. Dry Samples A1 and C1 at 320°F ± 20°F (160°C ± 12°C) or higher for at least 4 hours to <50 ppm moisture.
2. Extrude under conditions determined by the control sample using a 40/250/40 mesh screen pack.
3. Pelletize each of the sample blends giving each their second melt heat history.

### **1.2.5.1 Guidelines comparing Sample C2 to Control A2**

- a. No more than 10% higher pressure required on extrusion of the Innovation/Variant compared to the Control.**
- b. The extrusion rate should be at least 375 gm/cm<sup>2</sup> per hour for 30 minutes.**
- c. No additional fuming, smoking or odors should be noticed when extruding the Innovation/Variant compared to the Control.**
- d. No additional fluorescence in the pellets as measured by the APR test protocol.**
- e. Resin pellets or flakes should not stick together during drying.**
- f. IV change on extrusion of Samples A1 to A2, and C1 to C2**
  - i. An IV drop ≤0.025 dL/g should not be a problem**
  - ii. An IV drop of >0.025-0.040 dL/g needs study**
  - iii. An IV drop >0.040 dL/g probably is a problem**

**Note: The starting IV of the blend samples should be estimated as a blended weight average of the individual pellet IV's (the Control pellet or flake and the Innovation pellet or flake).**

### 1.2.6 Solid State Processing

1. Solid state each Sample (A2 and C2) at a minimum of 205°C for 15 hours. The initial starting IV of each of the samples should be obtained after pelletization. The SSP conditions of temperature and vacuum should be identical for Sample C2 compared to Sample A2. Solid stating times should be measured from T<sub>0</sub>, which is defined as the time when the heat transfer fluid reaches 190°C.
2. At T<sub>8</sub> hours, remove a sample and measure the IV
3. Stop the SSP at T<sub>15</sub> hours and measure the IV.

### **1.2.6.1 Guidelines comparing Sample C3 to Control A3**

- a. Sample C3 should be within 0.04 dL/g of Sample A3 after 8 hr.**
- b. Sample C3 should be within 0.075 dL/g of Sample A3 after 15 hr.**

4. Solid state another set of Samples (A2 and C2) under conditions suitable to raise the IV of the extruded pellets to 0.80±0.02dL/g. NOTE: If large enough batch sizes of Samples A2 and C2 are available, it is permissible to remove enough



sample from the SSP device from the above experiments (Step 1) when each sample has reached the  $0.80 \pm 0.02$  dL/g target. Enough sample must be removed to allow for molding of 3mm plaques and, if necessary, for blending with virgin resin to make preforms and bottles for additional testing. It is also necessary to maintain a sufficient quantity of material in the SSP unit for continuing the solid stating experiment to 8 and 15 hours. Note: This sampling must be done quickly in order to not affect the IV build rate for the long SSP trial and under conditions to protect the 0.80 dL/g sample being removed.

5. Using DSC with a heating rate of  $10^{\circ}\text{C}/\text{minute}$ , measure the melting point of Blend Samples A4 and C4 on the second melt after rapid quenching of the first melt.

#### **1.2.6.2 Guidelines comparing Sample C4 to Control A4**

- a. ***The melting point for Blend Samples A4 and C4 should be  $235^{\circ}$  to  $255^{\circ}\text{C}$  on the second melt after rapid quenching of the first melt.***

#### **1.2.7 Plaque Molding**

1. Dry the 0.80 dL/g Samples A4 and C4 with desiccated air at  $320^{\circ}\text{F} \pm 20^{\circ}\text{F}$  ( $160^{\circ}\text{C} \pm 12^{\circ}\text{C}$ ) for 4 to 6 hours to achieve less than 50 ppm moisture content.
2. Injection mold 3mm plaques from the control Sample A4 first. Then mold 3mm plaques from Sample C4 under identical conditions if possible. If the processing conditions need to be changed, then these changes must be documented and reported.

#### **1.2.7.1 Guidelines comparing Sample C5 to Control A5**

- a. ***IV Change on injection molding of plaques***
  - i. ***Plaque IV drop for Sample Blend C5 compared to Sample Blend A5 should be  $\leq 0.025$  dL/g.***
  - ii. ***IV drop from  $>0.025$  to  $\leq 0.040$  dL/g needs further study***
  - iii. ***and an IV drop  $>0.040$  dL/g probably is a problem.***
- b. ***3mm Plaque Color for Sample Blends A5 and C5***
  - i. ***For clear PET,  $L^*$  should be  $>82$  for Samples A5 and C5***
  - ii.  ***$b^*$  of Sample Blends C5 compared to A5***
    1.  ***$\leq 1.5$  should not be a problem***
    2.  ***$>1.5$  to  $5.5$  needs further study***
    3.  ***$>5.5$  is unsuitable for many applications***
- c. ***Haze for Sample Blends A5 and C5***
  - i.  ***$\leq 9.5\%$  should not be a problem***
  - ii.  ***$9.5\%$  to  $14\%$  needs further study***
  - iii.  ***$>14\%$  is likely noticeable***



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- d. ***Black Specs (plaques viewed without magnification)***
  - i. ***Visual inspection on at least 50 plaques from 12 inches away, counting any plaque as failed if one or more specs seen greater than 0.015 inches. If failed A5 plaques total 0, 2 or fewer failed C5 plaques are acceptable. If failed A5 plaques total 1, 4 or fewer failed B5 plaques are acceptable. If failed A5 plaques total 2, 6 or fewer failed B5 plaques are acceptable. If failed A5 plaques total 3, clean the extruder and repeat plaque preparation.***

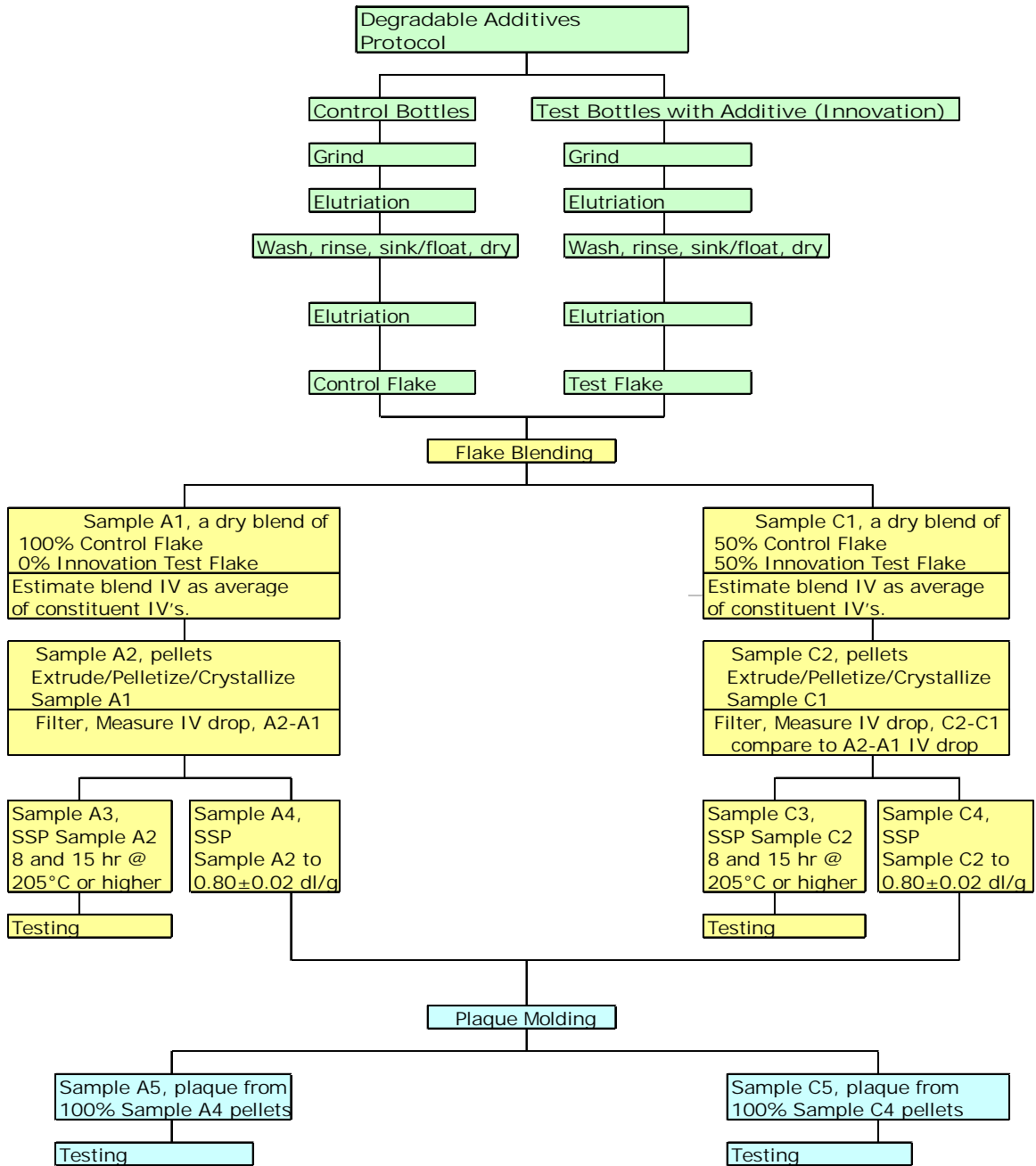
### 1.2.8 General Issues:

***No additional fuming, smoking, or odors during extrusion.***

***No sticking between flakes during drying.***

***No fouling of process equipment.***

***No creation of unsafe conditions, such as increased fire potential.***







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## Appendix 2

APR PET Applications Guidance

### 2.0 APPLICATIONS GUIDANCE DOCUMENT

#### Control Resins

The control resins to be used are listed above.

#### ***2.10 Bottle-to-Bottle Protocol, (BtB)***

The Bottle-to-Bottle evaluation program is designed to show processing and bottle performance differences between a control material and that control material containing recycle-content Innovation material. It is a **comparative** study that does not rely on the final blown bottles meeting absolute performance criteria.

Since the BtB program is designed to make 2L Carbonated Soft Drink (CSD) bottles, the optimal study will be one where the initial control resin selected for use in the CGD screening will be selected from the list of APR approved CSD and non-Water Bottle Innovation Control PET resins listed above. The Control CSD virgin resin called for in Step 1 below ideally would be identical to the CGD control resin.

***It is recognized that if the Innovation being studied in the CGD was a non-CSD resin or an additive that was incorporated into a non-CSD resin, then the  $0.80 \pm 0.2$  dL/g material that is produced in the CGD study (Solid State Processing, Step 4), may not be ideal for CSD bottle performance.*** However this non-CSD base material can still be blended with a CSD control (selected from the table on page 2) to begin the BtB evaluation. When this is the case, it is important to recognize that the resulting control bottles and Innovation recycle-content bottles may not perform ideally in all of the CSD tests. Since the bottle test performance of the Innovation recycle-content bottles will be compared to the control bottles, it will still be possible to judge the Innovation's acceptability for the recycle stream if the bottle test criteria are met. Because the non-CSD control materials are currently found in the recycle stream, then any new materials similar to these that do not result in significant differences in recycle-content bottle performance are, therefore, also expected to be acceptable.



2.1.1 Injection Molding of Preforms and Plaques (needed if submitting data to PETCORE)

1. Create the following test blends of Samples A4 and C4 by blending each at 50% with the Control CSD virgin resin.  
Sample D: 50% Virgin PET 50% Sample A4 (0% Innovation Bottle)      Sample F: 50% Virgin PET 50% Sample C4 (25% Innovation Bottle)
2. Dry the 0.80 dL/g Samples D, E and F with desiccated air at 320°F ± 20°F (160°C ± 12°C) for 4 to 6 hours to achieve less than 50 ppm moisture content.
3. Remove a portion of each sample, maintain dryness and use to mold plaques in Step 4.
4. Injection mold preforms from the control Sample D first. Then mold preforms from Samples F under identical conditions used for Sample D if possible. If the processing conditions need to be changed, then these changes must be documented and reported.

**2.1.1.1 Guidelines compare Sample F to Control D**

- a. *There should be no significant processing changes needed for Samples F compared to D. Small differences in process settings are acceptable.*
  - b. *IV Change on injection molding of preforms*
    - i. *IV drop for Sample F preforms compared to Sample D preforms should be ≤ 0.025 dL/g.*
    - ii. *IV drop from >0.025 to ≤0.040 dL/g needs further study*
    - iii. *An IV drop >0.040 dL/g probably is a problem.*
  - c. *Acetaldehyde concentration*
    - i. *The preforms from Samples F should not exhibit an acetaldehyde increase of more than 35% compared to Sample D.*
  - d. *Black Specs, particulates or gels (preforms viewed without magnification)*
    - i. *Visual inspection of preforms should not show more than a 10% increase in the number of black specks in Sample Blend C5 plaques compare to A5.*
5. Injection mold 3mm plaques from each of the 50:50 blend samples. (Note: this step is required only to meet PETCORE requirements.)

2.1.2 Blow Molding of Bottles

1. The preforms molded from Samples D and F should be blow molded into 2L straight-wall petaloid base CSD bottles. Sample D preforms should be blown first and followed by Samples E and F each blown under the identical conditions used



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for A if possible. If the processing conditions need to be changed, then these changes must be documented and reported.

### **2.1.2.1 Guidelines comparing Sample F to Control D**

- a. There should be no significant differences required when processing Samples F compared to D. Small differences in blow mold settings are acceptable.**
- b. A reduction in performance of bottles made from Sample F should not exceed the specified test limits when compared to Sample Bottles D for the following performance tests:**
  - i. Visual inspection for black specs, particulates or gels**
  - ii. Section weights**
  - iii. Brimful and fillpoint volumes**
  - iv. Burst strength**
  - v. Drop impact**
  - vi. Top Load**
  - vii. Stress Crack resistance**
  - viii. Thermal stability**
  - ix. CO<sub>2</sub> loss by FTIR or by Septum Test**

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**Bottle Test Guideline Criteria**

<b>Test</b>	<b>Measurement</b>	<b>Guidance</b>
Appearance	Black specks	No more than 10% increase over Control D
	Particulates	No more than 10% increase over Control D
	Gels	No more than 10% increase over Control D
Color & Haze	L*	Report measurement, no guidance
	a*	Report measurement, no guidance
	b*	Report measurement, no guidance
	Haze	Report measurement, no guidance
Bottle Dimensions	Height	± 5% of Control D
	Upper Label Panel Diameter	± 5% of Control D
	Lower Label Panel Diameter	± 5% of Control D
Section Weights	Base	± 5% of Control D
	Panel	± 5% of Control D
	Shoulder	± 5% of Control D
Material Distribution	Base	Report measurement, no guidance
	Foot	Report measurement, no guidance
	Label	Report measurement, no guidance
	Shoulder	Report measurement, no guidance
Total Bottle Weight	Weight	± 5% of Control D
Capacity	Brimful	± 5% of Control D
	Fillpoint	± 5% of Control D
Burst Strength	Burst Pressure	Less than 10% decrease from Control D
Top Load	Max. Load Empty	Less than a 10% decrease from Control D
Drop Impact	40°F, Bottle axis vertical	No more than 1 additional failure than the Control D
	40°F Bottle axis horizontal	No more than 1 additional failure than the Control D
	Average Time	<25% reduction compared to Control D: No problem 25%-50% reduction: Needs further study >50% reduction: May be problematic
Stress Crack Resistance		
Shelf-Life	CO2 Loss by FTIR	No more than a 5% decrease compared to the Control D
	Septum Test	No more than a 5% decrease compared to the Control D
Thermal Stability	Height	No more than 5% increase over Control D
	Change in Fill Line	No more than 5% increase over Control D



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Upper Panel Increase	No more than 5% increase over Control D
Lower Panel Increase	No more than 5% increase over Control D
Number of Rockers	0

Bottle test methods are available with membership from the International Society of Beverage Technologists, a global, non-commercial, non-profit technical society of beverage professionals, <http://www.bevtech.org/>.



### **2.30 Bottle-to-Strapping Protocol (BtSt)**

Strapping is a high performance product made from high molecular weight PET. High tensile strength needed to hold items in place is achieved by the orientation of high molecular weight resin. Strapping manufacturers consider that if PET is suitable for making biaxially oriented bottles and can be solid state polymerized to a target intrinsic viscosity, a measure of molecular weight, that it will be suitable for making strapping. The target intrinsic viscosity, ItV, is 0.95 dl/gram when measured by solution viscosity.

The Critical Guidance Document considers solid stating performance as part of the protocol and has incorporated within its guidelines provisions for performance at 15 hours of solid stating as a relative comparison between innovation samples and control samples. The Critical Guidance Document does not define an absolute ItV value to be achieved.

The strapping industry recognizes that variation occurs in recycled PET including the solid stating rates of various resins, the influences of additives, the activity of solid stating catalysts after the life cycle of the bottle, and the ItV of the cleaned flake product. As recognized in the Control Resins definition, there are two populations of intrinsic viscosity for PET bottles.

This Bottle-to-Strapping Protocol calls for the innovation bottle sample to demonstrate the ability of achieve a minimum intrinsic viscosity after a defined number of hours of solid state polymerization. Further testing to web extrusion and orientation are not needed. It is suggested for purposes of economy that the Bottle-to-Strapping solid stating examination be conducted as an extension of the Critical Guidance solid stating examination.

#### **2.3.1 Sample**

##### **Sample Blending and Preparation**

If the New Resin protocol is being followed, pellets will be blended at this step.

Otherwise flake will be used to make the required Samples.

1. Create the following three test blends from the washed flake for study:

Sample A1:	100% Control Material	0% Innovation Material
Sample D1:	0% Control Material	100% Innovation Material

2. Dry Samples A1 and D1 at 320°F ± 20°F (160°C ± 12°C) for at least 4 hours to <50 ppm moisture.
  1. Extrude under conditions determined by the control sample using a 40/250/40 mesh screen pack.



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2. Pelletize each of the sample blends. These are the samples prepared for the Critical Guidance examination
  - Sample A2, pellets made of Sample A1, control
  - Sample D2, pellets made of Sample D1, 100% additive-containing material

The Critical Guidance Document (CGD) calls for the ItV of the Innovation Blends to be within 0.04 dl/g of the control after 8 hours and 0.075 dl/g of the control after 15 hours of solid stating at a temperature of at least 205°C and full vacuum.

In considering the practicality of laboratory testing and minimizing test expense, we suggest the investigator collect Critical Guidance data and samples as dictated by that protocol. Extend the solid state polymerization for all three samples for 39 hours to demonstrate attainment of 0.95 dl/gm ItV. 39 hours reflects the experience of the industry and should be readily met by favorable innovations and control resins.

### 2.3.1.1 Test Protocol Schedule Suggestion

- Load rotary vacuum dryer at noon, Day 1. Set temperature and pull vacuum.
- At 3:00pm, heating fluid temperature reaches minimum 190°C. Start time 0, Day 1
- 8 hr sampling is taken at 11:00pm, Day 1 (may require two people for safety, Estimate time to achieve 0.80 dl/gm for test material preparation for Critical Guidance evaluation and Bottle-to-Bottle Protocol evaluation or conduct second solid state polymerization to make sample. Collect sample for Critical Guidance solid stating evaluation
- 15 hr sampling taken at 6:00 am, Day 2  
Collect sample for Critical Guidance solid stating evaluation  
Measure ItV and estimate solid stating rate and time to 0.95 dl/gm for each sample.
- 22 hr sampling taken at 1:00pm, Day 2  
Measure ItV and estimate solid stating rate and time to 0.95 dl/gm for each sample.
- 26 hr sampling taken at 5:00pm, Day 2  
Collect sample and measure ItV based on earlier estimates of needed time.
- 32 hr sampling taken at 11:00pm, Day 2  
Collect sample and measure ItV based on earlier estimates of needed time.
- 39 hr sampling taken at 6:00am, Day 3



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Collect final sample and measure ItV if 0.95 dl/gm not already achieved.  
Samples now defined as **Samples A2<sub>39</sub> and D2<sub>39</sub>**

### **2.3.2 Guidelines comparing Samples D2<sub>39</sub> to Control A2<sub>39</sub>**

- a. There should be no significant differences in operating parameters (vacuum or dry inert gas, heat transfer fluid temperature and flow rate) between tests for the various samples. Note differences.***
- b. All samples after as many as 39 hours of solid stating treatment should exhibit intrinsic viscosities at or above 0.95 dl/gm.***
- c. Failure of the Sample A2<sub>39</sub> to exceed 0.95 dl/gm indicates the process conditions were not adequate.***

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## **Appendix 3**

### **Dye Take Up Testing for Fibers**

#### I. Summary

In this test the fibers are dyed with a dye standard and compared using the Hunter Miniscan XE or equivalent.

#### II. Apparatus

- A. Atlas LD-16 Laundrometer or equivalent
- B. 100% Cotton Sample Bags
- C. 700 ml and 2000 ml Volumetric Flask
- D. Balance scale (weighs to 0.001g)
- E. Nalgene Container (12 gal)
- F. Nalgene Container (25 gal)
- G. Beakers (250 ml)
- H. Graduated Cylinder (2000 ml)
- I. Mechanical Stirrers
- J. Rubber Bands
- K. Vials with caps for weighing and storage of carrier
- L. Dye cans for the Laundrometer

#### III. Reagents





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- A. Cindye DAC-999 MSDS #274 (Dye Carrier)
- B. Tebstat 20/15 MSDS #276 (Anti-Static)
- C. Terasil Blue GLF MSDS #275 (Base Dye)

### IV. Safety Issues

- A. Safety glasses are required.
- B. Care should be exercised when opening hot Launderometer cans. Hot solutions under pressure can cause burns. Handle these cans with tongs and/or insulated gloves. Cool under cold water to reduce pressure and temperature.
- C. Wear chemical resistant gloves when handling dye carrier. Avoid breathing vapor and use with adequate ventilation.
- D. Never place hands below the water level in the Launderometer.
- E. Chemical resistant gloves and coat and face shield must be worn when mixing the dye base because of boiling water.

### V. Procedure

#### A. Dye Base Solution

1. Set ~1000 ml of distilled water on hot plate and bring to a slow boil in a 2000 ml flask.
2. Weigh out 9.15 gm + or - .005 gm Terasil Blue GLF.
3. Paste dye in the 250 ml beaker with 50 ml hot distilled water until no lumps are present. Use glass stirring rod.
4. Rinse pasted dye into 2,000 ml volumetric flask with the hot distilled water. Bring to volume with distilled water.

NOTE: Add water slowly to avoid foaming.

5. Add dye base to large 12 gallon glass container which is stirring continuously.



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6. Several batches of dye base are made and combined as necessary. Additional batches may be added to the dye base 12 gallon tank as needed.

NOTE: Dye base is constantly blended by a mechanical stirrer.

### B. Diluted Dye Base Solution for Dyeing

1. Measure 41,000 ml of distilled water into a large plastic container (25 gallon) by using a 2,000 ml graduated cylinder.

2. Transfer 2,000 ml of dye base to the large plastic container.

NOTE: Diluted dye base must be continuously stirred.

3. When dilution dye base is close to empty, empty the dilution tank. Refill as per above procedure.

### C. Dye Carrier

1. Weigh out 1.5 + .01 gm of Cindye DAC-999 per Can  
may be weighed out ahead of time in 1.5 gram portions  
stored in plastic vials to save time.

NOTE: Carrier  
and

### D. Dyeing Setup

1. Weigh exactly 2 +/- 0.01 grams for each fiber sample.

2. Place fiber samples in separate predyed cotton sample bags which have been labeled with embroidery. Do NOT use "Magic Marker" to label bags.

NOTE: New cotton sample bags should be pre-stained with dye by placing in launderometer can with dye liquor for one hour at 98+/- 2 degrees C

3. Pour 700 ml of dilute dye base into each launderometer can used. Dye fibers for each of eight samples per launderometer can. Secure fiber samples together with rubber band.

4. Add 1.5 +/-0.01gm Cindye DAC-999 per can, place top on can, shake to mix and check for leaks.

5. Pre-rinse samples and standard in tap water. Squeeze out excess water.



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6. Place a rubber band around each individual bag. Place the 8 bags in the proper can.

### E. Dyeing Conditions:

Atlas LD-16 Programming or similar device

#### Step Functions of Computerized Program

---

1. Ascent to 98 +/- 2 degrees C at 5.5 degrees C/minute
2. Indefinite pause to load samples
3. Ascent to 98 +/- 2 degrees C at 5.5 degrees C/minute
4. Hold to dye samples for 60 minutes at 98 +/- 2 degrees C
5. Indefinite pause to unload samples
6. Fall to 50 degrees C at 2.75 degrees C/minute
7. Program ends (buzzer alarms)

Atlas LD-16 Operating Instructions - This must be completed before entering cans into laundrometer.

1. Press ON button.
2. Press the MODE key until Reset---Run is seen. Press the ENT key to start the program running.
3. After ascent to 98 +/- 5 degrees C, Atlas LD-16 pauses and buzzer alarms to load samples.
  - a) Press OFF, to stop buzzer.
  - b) Press HOLD to stop the sequence.
  - c) Load samples. Only 6 or 8 cans are loaded at a time.
  - d) Press ON, to start-up (buzzer alarms)
  - e) Press RUN to start sequence.
4. After the 60 minute dyeing, Atlas LD-16 pauses and buzzer alarms to unload samples.
  - a) Press OFF, to stop buzzer.
  - b) Press hold to stop sequence.
  - c) Unload samples.
  - d) Press ON, to start-up (buzzer alarms).
  - e) Press RUN to start temperature fall cycle.



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5. Buzzer alarms and program ends after fall cycle.

### F. Post Dyeing

1. After removing from launderometer, cool cans under cold running tap water. Carefully open cans.

NOTE: Use insulated gloves.

2. Rinse bags in tap water (squeezing while immersed) until rinse water is clear.

3. Squeeze out excess water from bags.

4. Remove fiber samples from bags and air dry. Be careful to maintain identification..

5. Dyed fiber samples should be straightened prior to color measurement.

Samples and standards may be coated with an Anti-Static chemical (Tebestat 20/15) to aid in the removal of static electricity that may be present. The Tebstat is added on 2% of Sample weight.

6. Measure color with Hunter LabScan® XE spectrophotometer, or equivalent, in reflectance using d65 light and 10° observation angle, a white background with specular component included and diffuse/8 sphere geometry. The reported number should be the average of at least five color measurements of CIELAB.

### **G. Guidance:**

***Samples of similar control and test fibers shall not differ by more than two standard deviation units of the test for L\*, a\* and b\*.***

1. Sample 1.iv.1 and sample 1.iv.2 (unaged bale raw materials, neat, without and with degradable additive) are compared.

2. Sample 1.iv.3 and sample 1.iv.4 (unaged bale raw materials, with TiO<sub>2</sub>, without and with degradable additive) are compared.

3. Sample 1.iv.5 and sample 1.iv.6 (aged bale raw materials, neat, without and with degradable additive) are compared.

4. Sample 1.iv.7 and sample 1.iv.8 (aged bale raw materials, with TiO<sub>2</sub>, without and with degradable additive) are compared.