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PET Barrier Materials Test

Introduction – Scope, significance and use

This test protocol is a screening test procedure for identifying and quantifying residual amounts of three barrier materials, EVOH, MXD6 nylon, and epoxy diamine, in clean recycled PET flake. Test methods are provided for both clear and colored PET flake evaluation.

This test would be employed by PET recyclers to determine the presence of certain barrier materials in the flake, and to illustrate the effects of such residue on PET flake quality.

The test requires subjecting PET flakes to various reagent solutions shown to reveal the effects of residual barrier materials through staining. Flake is soaked in the reagent, dried, and examined for staining or discoloration.

This test protocol was prepared with assistance from Professor R. Mohseni, East Tennessee State University, Johnson City, TN

Method Summary

Hazards/Safety Statement: *APR Test and Practice documents do NOT CLAIM TO ADDRESS ALL OF THE SAFETY ISSUES, IF ANY, ASSOCIATED WITH THEIR USE. These Tests and Practices may require the use of electrically powered equipment, heated equipment and molten polymers, rotating motors and drive assemblies, hydraulic powered equipment, high pressure air, and laboratory chemicals. IT IS THE RESPONSIBILITY OF THE USER TO ESTABLISH AND FOLLOW APPROPRIATE SAFETY AND HEALTH PROCEDURES WHEN UNDERTAKING THESE TESTS AND PRACTICES THAT COMPLY WITH APPLICABLE FEDERAL, STATE AND LOCAL REGULATORY REQUIREMENTS. APR and its members accept no responsibility for any harm or damages arising from the use of or reliance of these Tests and Practice documents by any party.*

Equipment/Supplies List

- Clean, PET flakes about 3/8" nominal (1,000 grams/test)
- Two bucket containers of sufficient capacity to hold 1,000 grams of flake with at least 2 inches (5 cm) between top of flake pile and rim of container. One container will be used for the stain, the other for rinsing.
- A plastic mesh basket to hold 1,000 grams of the flake and allow it all to be submerged in the container. Plastic mesh is better than metal wire mesh
- A second mesh basket to hold up to 100 grams of flake for handling few flakes
- A smaller container capable of holding the second wire basket
- Scale or balance capable of measuring 1,200 (+\- 0.1*)* grams
- White, waterproof surface at least 24 inches square (60 cm square)
- Manual stirring rod
- Funnel for pouring reagent solutions back into plastic bottles.
- Thermometer
- 250 ml beakers
- A short wave/long wave UV "black light", emitting at 254 and 365 nm, for colored PET only
- Two gallon plastic bottles with screw caps to hold reagent solutions.
- Distilled or deionized water
- Graduated cylinder
- Reagent grade potassium iodate, KIO_3
- Reagent grade potassium iodide, KI
- RIT "Whitener & Brightener for colored PET only
- Wisk detergent, regular, for colored PET only
- Clorox liquid bleach, regular strength, or 6% sodium hypochlorite in water

- White vinegar, or 5% solution of glacial acetic acid in water
- White paper towels

Clear RPET Evaluation for Epoxy, EVOH, and MXD6 Nylon

See Appendix A for Flow Diagram

- Prepare a reagent solution of acidified water, iodide, and iodate.
- Dissolve 6.42 grams of potassium iodate, KIO_3, crystals in 3,000 ml of water.
- Add 60.0 grams of potassium iodide, KI, and stir until all is dissolved.
- Mix 300 milliliters of white vinegar, or 5% acetic acid in water, to 300 ml water and mix until solution is uniform.
- Add vinegar/water solution to iodate/iodide solution and mix until a deep red color is generated. The total volume will be slightly less than one gallon.

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Solution should be an intensely dark red color with no solids present.
If solution is not intensely dark red, remix using distilled water.
Label final solution "IODIDE/IODATE SOLUTION".

Keep bottle out of sunlight and away from high heat. Avoid skin or eye contact. Do not ingest. The iodide/iodate solution will oxidize with exposure to air and lose the deep red color. As long as the solution color is dark red, the solution is useful.

Keep the solution closed to the air except when testing. Solutions will last only days if continuously exposed to air, but at least a week if kept from exposure to air. Solution can be returned to its container for reuse after testing.

If any of the iodide/iodate solution is spilled, it can be safely released to the municipal sewer systems when diluted with approximately 100 times as much water.

1. Weigh 1,000 grams (+/- 0.5 grams) of dry, washed, clear PET flake. Spread the flake on the white surface and remove any orange/brown particles and reweigh and record as "initial weight". Then place the flake into the large basket. Place the basket into the bucket container with at least 2 inches of space between the top of the flake and the edge of the bucket.

2. Add enough IODIDE/IODATE SOLUTION to submerge all flakes. The iodide/iodate solution should be at room temperature. Let flake soak for 30+/- 2 minutes. Stir gently to be sure all

flakes are wetted and no bubbles adhere to the flake. After soaking for 30 minutes, raise the basket and let the solution drain back into the bucket. Carefully transfer the basket with flake into a second bucket. Add enough cool tap water to submerge the flake. Stir gently for five, (5), minutes, then lift basket and allow water to drain back into the bucket. Dispose of rinse water into the sewer system with a full flow of diluting water. Repeat the rinse cycle a second time.

Pour the IODIDE/IODATE solution back into its bottle to prevent contamination and air exposure and close the bottle. Wash down any spills with plenty of water.

3. Spread the flakes on the white surface. With good illumination, pick out the orange/brown discolored flakes. Do not try to distinguish degrees of color at this time. Place all orange/brown flakes in a 250 ml beaker. Use the small mesh strainer as needed.

NOTE: Be aware PVC flakes may stain with the iodide/iodate solution, although testing to date has not shown PVC to interfere with the iodide/iodate staining. Remove flakes that are obviously as thick as a bottle sidewall and stained on both sides. Do not remove flakes for which the barrier layer on one side of the flake has stained.

NOTE: "Sandwiches" of PET/barrier material/PET will stain around the edges of the barrier material if no delamination has occurred. With delamination, the barrier material will stain significantly. For flakes with apparent orange/brown stain around the cut edges, peel away the PET layers and retain the edge-stained barrier layer

4. Using adequate eye protection, add enough full strength regular Clorox bleach (not lemon scented) [6% hypochlorous acid or sodium hypochlorite in water] to the beaker to completely cover the orange/brown stained flakes. Let soak at room temperature for 30+/- 5 minutes, stirring gently to be sure no bubbles adhere to the flake.

5. After the flakes have soaked in the bleach solution, carefully decant the liquid bleach back into the liquid bleach bottle being careful not to allow any flakes to leave the beaker and rinse the flakes with lukewarm water three times, allowing the rinse water to go to the sewer. Carefully dry the flakes by blotting with clean paper towels, being careful not to lose any material.

NOTE: Inadequate drying can lead to grossly high estimates of barrier material.

- An over estimation error of 5+% can happen if drying is not done carefully.
- Air drying alone is likely to be inadequate unless left for many hours.
- Careful blotting with paper towels is the preferred drying technique.

6. Spread the contents of beaker on white paper towels for observation.
    - Epoxy will now be colorless and will be thin layers. Thick layers of colorless material will be PET that was attached to barrier material which stained and should not be included with the epoxy.
    - EVOH will be a light, transparent orange
    - MXD6 will be a very dark orange/red, almost opaque

7. Separate the materials into separate piles and dry again by blotting if necessary. Be careful not to lose any material.

8. Weigh each separated pile of EVOH, MXD6, and epoxy.
    - To correct for water sorption during testing, multiply the weight of EVOH by 0.965 and record the value. Divide the corrected weight of coating by the "initial weight" of the original PET flake sample and multiply by 1,000,000 to determine the parts per million EVOH. Record the value.
    - The MXD6 will not absorb water in this test. Divide the weight of the coating by the weight of the original PET sample and multiply by 1,000,000 to determine the parts per million MXD6. Record the value.
    - The epoxy will not absorb water. Divide the weight of epoxy by the weight of the original PET sample and multiply by 1,000,000 to determine the parts per million epoxy. Record the value.

Note: If the epoxy coating is still attached to the PET substrate, the coating will be up to approximately 0.9% of a PET/epoxy "sandwich" and pieces of PET/epoxy sandwich may not be fully covered with epoxy on one side. If pieces of PET with an epoxy coating still attached are seen (the stained epoxy is readily visible through the PET before treatment with Clorox) complete the following:

- Looking at the PET/epoxy pieces, estimate the fraction of total surface of one side of the PET pieces with epoxy on it (it can happened that only a portion of the PET flake surface will still have epoxy present). Call this value "X", a value between 0 and 1.0.
- Weigh the PET/epoxy pieces. Call this value "Y".
- The ppm epoxy is 1,000,000 x [weight of free epoxy film + (X)(Y)(0.009)] / [initial sample weight]

Testing has shown this procedure to have a standard deviation of 9% for 100 ppm to 1,000 ppm of any of the three barrier materials.

Testing shows PVC does not interfere with the results.
Testing also shows that PETG does not interfere with the results.
Testing also shows AMOSORB does not interfere with the results.
Testing also shows PET, PET with UV inhibitors, and HDPE do not interfere with the results.

Colored RPET Evaluation for Epoxy, EVOH, and MXD6 Nylon

See Appendix B for Flow Diagram

1. Mix up a solution of RIT "Whitener & Brightener", adding 1 part Wisk detergent to 5 parts RIT "Whitener & Brightener" to 100 parts deionized or distilled water in a 2 gallon bottle. Mark " OPTICAL BRIGHTENER". Keep bottle closed. Solution should last at least 2 weeks.

2. Weigh 1,000 grams (+/- 0.5 grams) of dry, washed, colored PET flake. Place the flake into the large basket. Place the basket into the bucket container with at least 2 inches of space between the top of the flake and the edge of the bucket.

3. Add enough OPTICAL BRIGHTENER to submerge all flakes. The solution should be at room temperature. Let flake soak for 60 +/- 5 minutes. Stir gently every 10 minutes to be sure all flakes are wetted and no bubbles adhere to the flake. After soaking for 60 minutes, raise the basket and let the solution drain back into the bucket. Carefully transfer the basket with flake into a second bucket. Add enough tap water to submerge the flake. Stir gently for one minute, then lift basket and allow water to drain back into the bucket. Dispose of rinse water into the sewer system with a full flow of diluting water. Repeat the rinse cycle a second time.

4. Cover the reagent bucket to prevent contamination or exposure or pour the optical brightener solution back into its bottle and close the bottle. Wash down any spills with plenty of water.

5. Using paper towels, dry the surface water off of the soaked flake until the flakes can be moved easily and do not stick to each other. Be careful to prevent losing any material.

6. Spread the flakes on the white surface. Using a portable black light held close to the flakes, examine the flakes. At 254 nm wavelength the MXD6 from will glow weakly. At 365 nm wavelength, the MXD6 will appear transparent. At 254 nm wavelength the EVOH will glow brightly. Separate the flakes that glow under black light illumination.

NOTE: This test will not detect epoxy material

NOTE: PVC may glow. Remove flakes that are obviously as thick as a bottle sidewall and glow on both sides. Do not remove flakes for which the barrier layer on one side of the flake glows. A reference sample should be produced and used for comparison so as not to misidentify PVC as either MXD6 or EVOH.

NOTE: If high levels of fluorescence are seen in many flakes that appear to have the average thickness of the PET flake, the observer may be seeing PET which contains special additives which are included to screen out ultraviolet light. If this happens, this test will not be useful. Neat PET and HDPE will not fluoresce or glow under black light.

7. Place separate glowing flakes into a small beaker. Submerge flakes with the IODIDE/IODATE solution at room temperature for 30+/-2 minutes. Remove all the darkly orange/red stained pieces

8. Place the stained flakes from Step 7 in a beaker, using the small strainer as needed, and add full strength Chlorox bleach. Let soak for 30+/- 5 minutes. Any PVC flakes will appear clear or unaffected by the bleach. Remove any PVC and discard.

NOTE: Epoxy – not detected in this procedure because epoxy does not absorb the optical brightener
NOTE: EVOH – flakes will appear transparent orange
NOTE: MXD6 – flakes will appear almost opaque, beige to red in color

9. Carefully rinse flakes with clean water and blot dry with paper towels.

NOTE: Inadequate drying can lead to grossly high estimates of barrier material.
An over estimation error of 5+% can happen if drying is not done carefully.
Air drying alone is likely to be inadequate unless left for many hours. Careful blotting with paper towels is the preferred drying method.

10. To correct for water sorption during testing, multiply the weight of EVOH by 0.965 and record the value. Divide the corrected EVOH weight by the weight of the original PET sample, approximately 1,000 grams, and multiply by 1,000,000 to determine the parts per million EVOH. Record the value.

The MXD6 will not absorb water in this test. Divide the MXD6 weight by the weight of the original PET sample, approximately 1,000 grams, and multiply by 1,000,000 to determine the parts per million MXD6. Record the value.

The standard deviation is 9% from100 to 1,000 ppm for MXD6 and EVOH barrier materials.

Testing also shows that the presence of PETG does not interfere with the results.

Report Forms and Assessments

Clear PET Flake Evaluation	**PET Flake Sample Wt:**	
Residual	**Weight**	**PPM Calculated**
MXD6		
EVOH		
Epoxy		

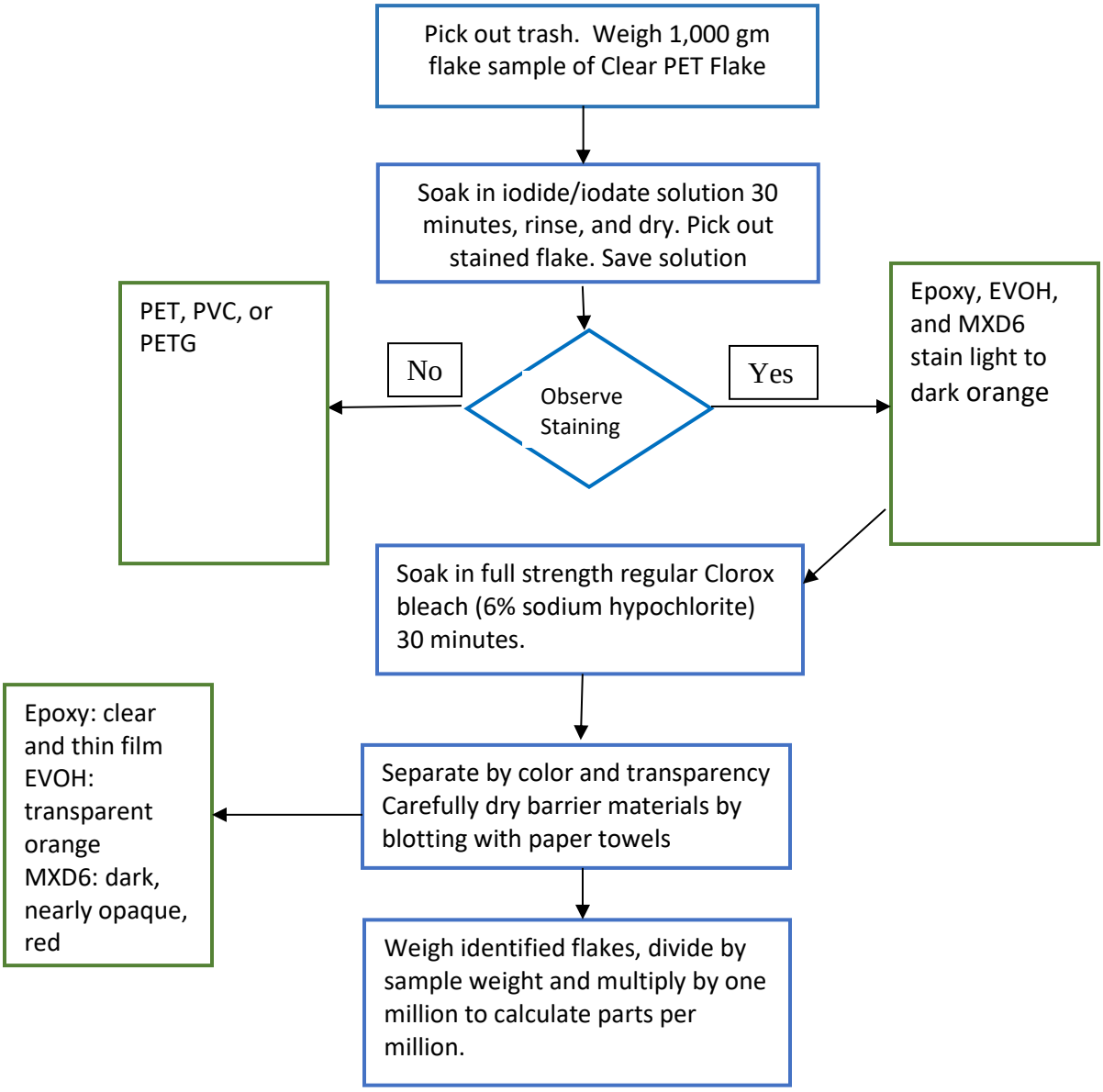
Colored PET Flake Evaluation	**PET Flake Sample Wt:**	
Residual	**Weight**	**PPM Calculated**
MXD6		
EVOH		

DOCUMENT VERSION HISTORY

Version	Publication Date	Change Summary
1	June, 2003	
2	August, 2018	Re-formatted; data tables added
3	November, 2018	Re-numbered for website per new PET test organization

The Association of Plastic Recyclers

Appendix A
FLOW DIAGRAM: CLEAR PET FLAKE EVALUATION



Appendix B
FLOW DIAGRAM: COLORED PET FLAKE EVALUATION