Delta ENGINEERING GROUP

Barrier Coatings 101

A Future-Proof, Sustainable Solution

Business Development Division

ABOUT DELTA ENGINEERING - HISTORY

- **Founded in 1992**

- **Today:**
  - ✓ A team of > 200 people, incl. > 40 engineers, spread across 3 sites:
    - ➢ Main R&D site in Belgium
    - ➢ Production site in Romania
    - ➢ Sales & support site in the USA
  - ✓ Several sales representatives worldwide
  - ✓ Part of the Delta Engineering Group (together with Isytech & Delta Application Technics)




ABOUT DELTA ENGINEERING - EXPERIENCE

Lots of different (automation) solutions for the blow molding industry:

- ✓ Quality control
- ✓ Packaging
- ✓ Barrier treatment
- ✓ (De)palletizing
- ✓ Conveying
- ✓ … and many more!

Factory designing:

Let us help you design your blow molding & filling facilities using our extensive experience!

- ➢ **Save labor with:**
  - ✓ Automation
  - ✓ The right layout, achieved by optimizing your internal flows

ABOUT DELTA APPLICATION TECHNICS - EXPERIENCE

Specialist in application & mixing of difficult products:

- ✓ Extrusion
- ✓ Dosing
- ✓ Mixing
- ✓ Winding
- ✓ Conveying
- ✓ … and many more!

ABOUT ISYTECH - EXPERIENCE

Specialist in plasma:

- ✓ Drying
- ✓ Coating
- ✓ Surface modification
- ✓ Etching
- ✓ … and many more!

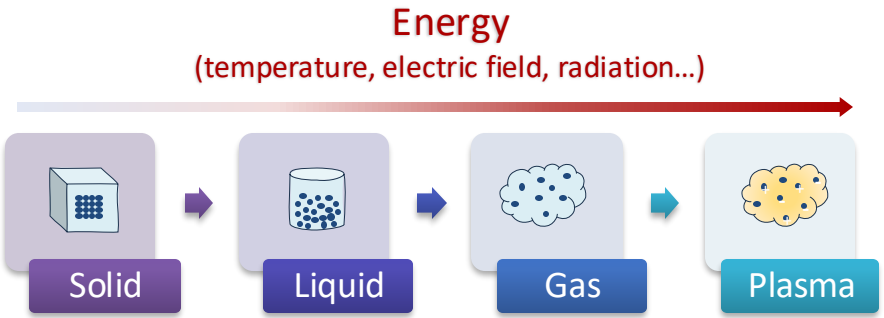
ISYTECH'S EXPERIENCE WITH BARRIER PLASMA TREATMENTS

History:

- **1998**: Actis process development for Sidel company.
  - Amorphous carbon (a:C-H) treatment on **internal surface of PET bottles** to obtain **oxygen barrier**.
- **2005**: SiOx **Anti-staining process** and machine development for Tupperware company.
  - Patented.
- **2005**: Amorphous fluorinated carbon (a:C-F) **barrier coating** for **HDPE agrochemical packaging.**
  - Patented.
- **2007**: First plasma machine in **EBM** factory in France.

WHAT IS PLASMA COATING?

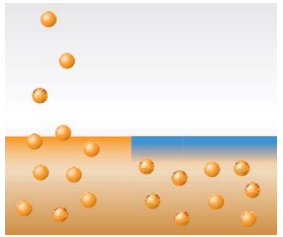
- Plasma = the 4th state of matter
- Plasma = a highly reactive gas composed of molecules, ions, electrons, radicals…
- Plasma coating = a well-known, stable and reliable technology, industrialized for the blow molding industry
- *EVOLVE **PET***, *EVOLVE **PE***, *EVOLVE **FF***



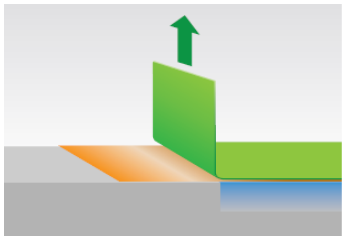
WHAT IS PLASMA COATING?

- Obtaining dedicated material properties:
  - **Barrier improvement:**
    - ✓ Migration
    - ✓ Permeation
  - **Surface tension modification:**
    - ✓ Slideability
    - ✓ Adhesion
    - ✓ Wettability

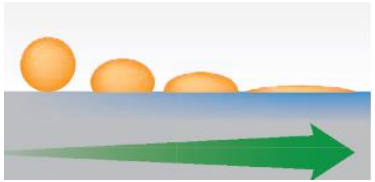
Barrier improvement



Less permeation & migration



Improved adhesion



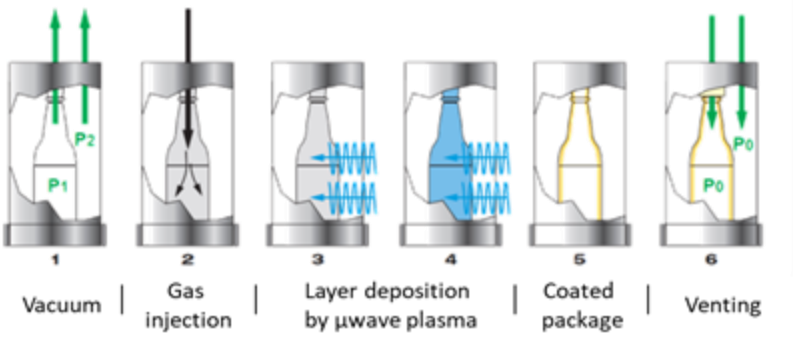
Improved surface wettability

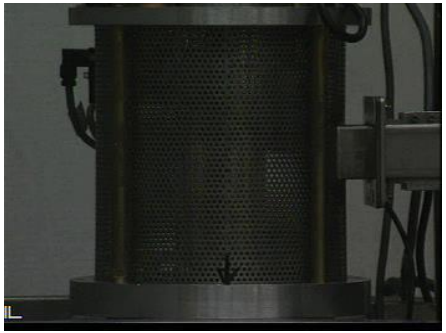
HOW DOES PLASMA COATING WORK?

Coating of plastic products:

- By decomposition of a gas
- Using microwave power in a low-pressure (0,1 mbar) environment: in a reactor
- Using electromagnetic energy (2,45 GHz)

➔ Creating a thin coating layer on the inside wall of the product





GENERAL LEGISLATION & ACTUAL RELEVANCE

General legislation:

- ADR/RID 6.1.5.7 - Procedure for Testing Chemical Compatibility and Rate of Permeation in Plastic Packaging and Receptacles

- 49 CFR Appendix B_to_part_173 - Procedure for Testing Chemical Compatibility and Rate of Permeation in Plastic Packaging and Receptacles

PET:

- Amorphous **Carbon** deposition on **PET**:
  - About 100 nm thickness of a C-H layer is deposited on the inside wall of the bottle during plasma step
  - Deposit from **acetylene** gas

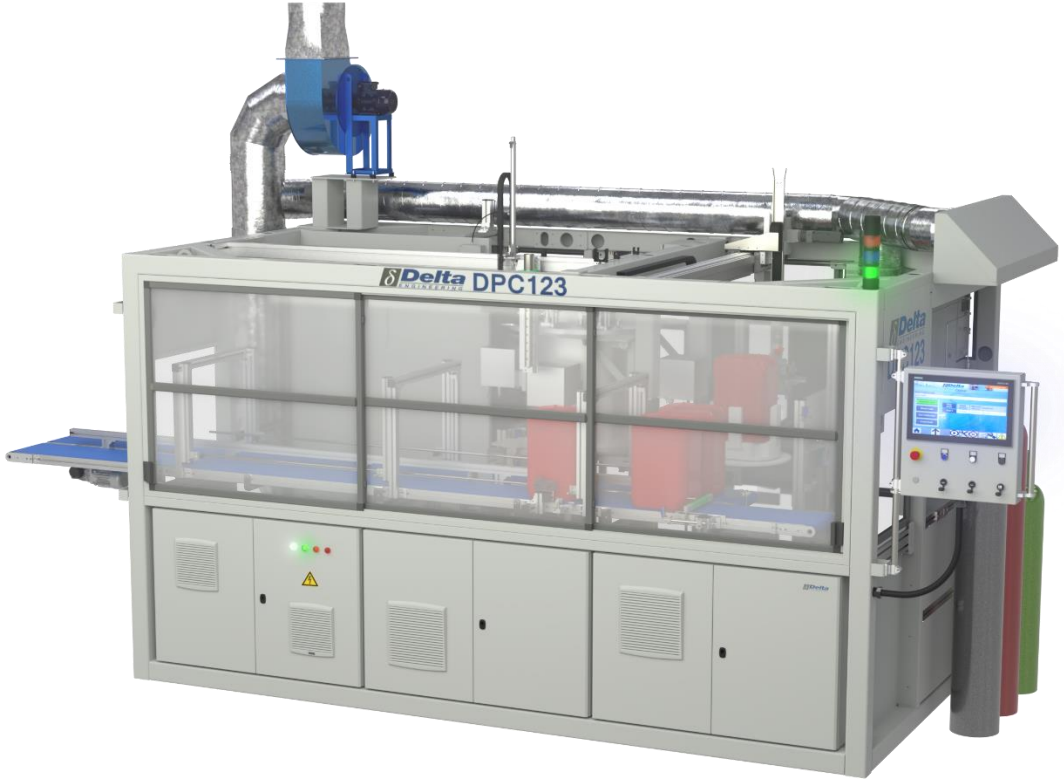
- Applications:
  - Juices, vitamine & energy drinks (oxydation-sensitive), carbonated drinks, beer, cosmetics, industrial applications

HDPE:

- Amorphous **Carbon Fluor** deposition on **HDPE**:
  - About 100 nm thickness of a C-F layer is deposited inside wall of the bottle during plasma step
  - Deposit from **argon - acetylene – HFC** or **HFO** gasses (e.g. R1234yf)

- Applications:
  - Agrochemicals, car care, cleaning, degreasers, d-limonene, essential oils, flavours, concentrates, fuels, insecticides, lubricants, paint thinners, polishes, solvents, toluene, waxes…

EQUIPMENT



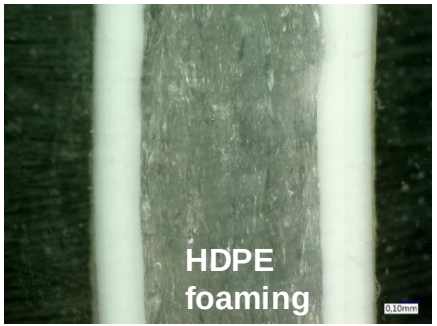
MACHINE RANGE

DPC	VOLUME	PRODUCTS	SPEED (BPH)		LEAD TIME
			HDPE	*PET*	
123	1.3 – 7.9 gal (5 – 30 L)	CONTAINER	90 - 130	135 - 260	AVAILABLE
133	13.2 – 66 gal (50 – 250 L)	L-RING DRUM	35 - 55	50 - 110	AVAILABLE
223	1.3 – 7.9 gal (5 – 30 L)	CONTAINER	180 - 260	270 - 520	AVAILABLE
403	3.4 – 67.6 fl oz (0.1 - 2 L)	BOTTLE	500 - 700	750 - 1400	AVAILABLE
413	0.8 – 4 gal (3 – 15 L)	CONTAINER	400 - 550	600 - 1100	AVAILABLE
613	0.8 – 4 gal (3 – 15 L)	CONTAINER	700 - 800	1050 - 1600	AVAILABLE
803	3.4 – 67.6 fl oz (0.1 - 2 L)	BOTTLE	1000 - 1400	1500 - 2800	Q4 2025
1603	3.4 – 67.6 fl oz (0.1 - 2 L)	BOTTLE	2000 - 2800	3000 - 5600	Q1 2026
16M03	0.17 – 5.07 fl oz (5 – 150 ml)	BOTTLE	3000 - 4000	6000 - 8000	Q4 2026

ADVANTAGES

Coating process advantages:

- Easy to use
- Plasma coating on fresh and warm HDPE results in better properties.
- Pores are ‘filled’ better while shrinking is still active on warm products.
- Lower risk of contamination
- The plasma coating process adds relatively little heat to the container.
- The barrier can be tuned using different gasses.
- Can be used in combination with HDPE foaming.
- Customer-specific developments possible.



ADVANTAGES

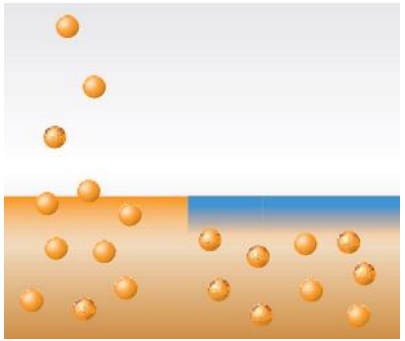
Coated product advantages (part 1):

- **Improved barrier** (PET):
  - ✓ O_2 ➔ 20-40 times
  - ✓ CO_2 ➔ 7 times
  - ✓ H_2O ➔ 2-3 times

  - ➢ Preventing compound migration (aldehyde, pigments…)

- **Improved solvent barrier** (HDPE):

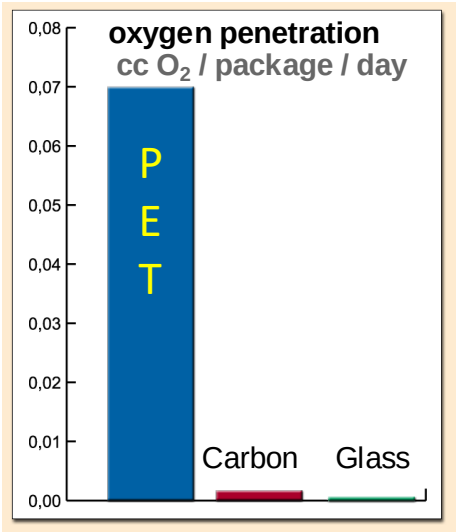
  - ➢ Preventing compound migration (pigments…)
  - ➢ Preventing permeation of limonene



Improved barrier

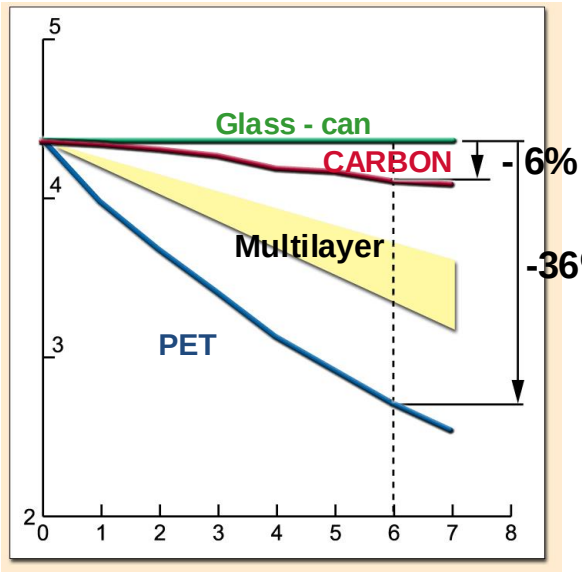
ADVANTAGES

Positive effect on permeation and migration: Amorphous carbon on PET

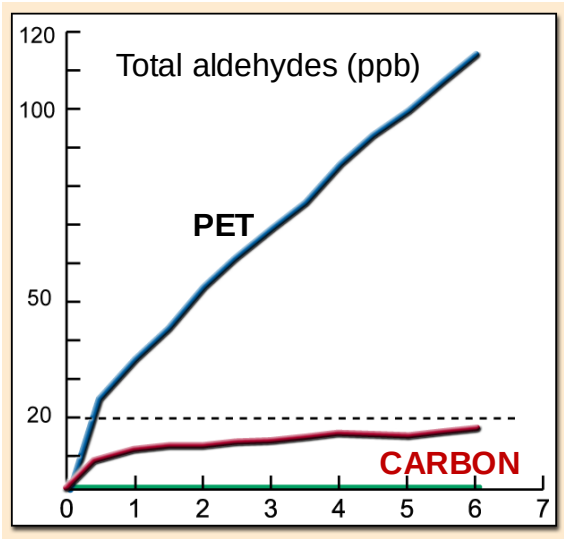


oxygen barrier

Pressure Evolution (and CO_2 content) (bar)



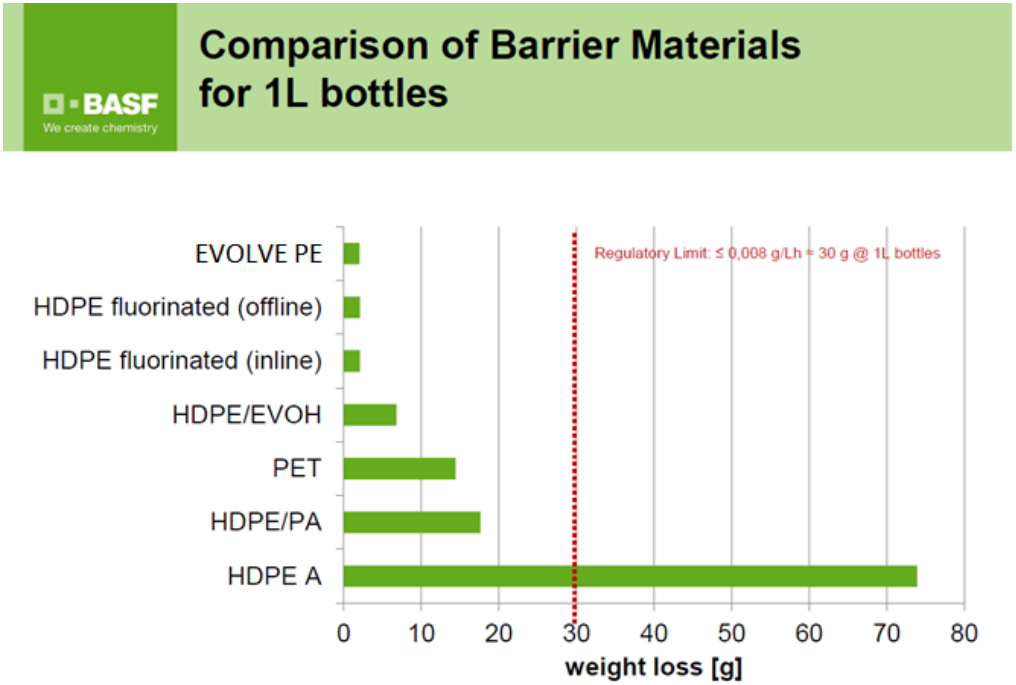
CO_2 barrier



Total aldehyde penetration

ADVANTAGES

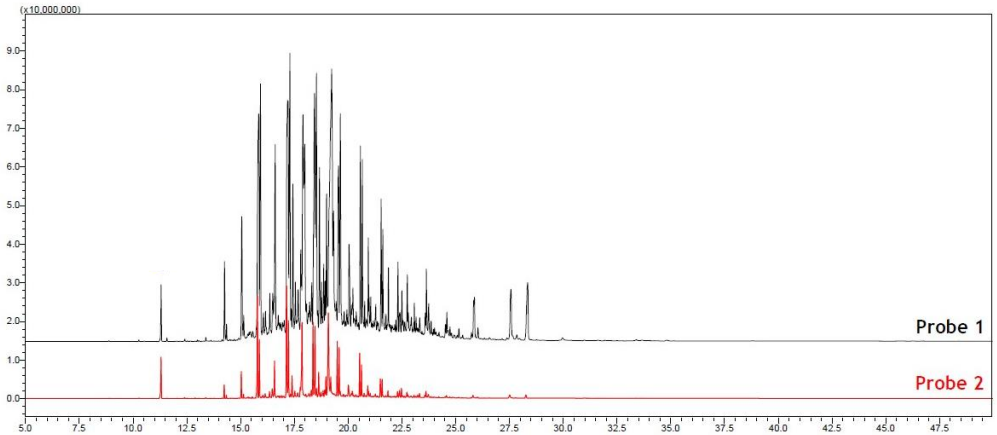
Positive effect on permeation and migration: Fluorinated carbon on HDPE



ADVANTAGES

Coated product advantages:

Comparative study - migration



Migration report on recycled material HDPE with C-Fl coating

Black line = uncoated bottle,
red line = plasma coated bottle

➔ Plasma coating = a migration stopper

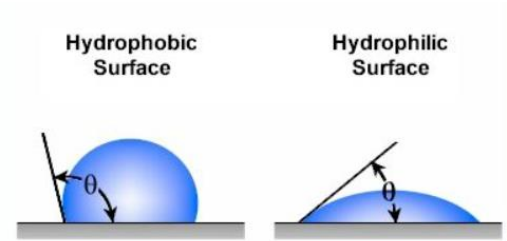
ADVANTAGES

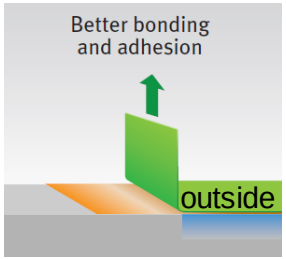
Coated product advantages (part 2):

- **Modify the surface tension:**
  - On the INSIDE of the bottle
    - ✓ Eliminates adhesion = improved **slideability**

Improved slideability

  - On the OUTSIDE of the bottle (optionally, when coating the outside):
    - ✓ Increases adhesion = improved **wettability**





Labels sticking better to the bottle

ADVANTAGES

Coated product advantages (part 3):

- **Lightweighting**:

  Reduce wall thickness of the bottle (replacing multilayer bottles), compensating by adding a Carbon or Carbon Fluor layer
  ➔ reducing the bottle weight!

- **Improved shelf life**. Long-lasting, stable coating and performance
- **No delamination**
- **Product dimensions are not affected**

ADVANTAGES

Cost advantages:

- **Low operational costs**
- Case study dd 2019:
  - ✓ Cost 20 L container: +/- USD 2.1
  - ✓ Cost traditional fluorination: +/- USD 2.3
  - ✓ Cost plasma coating: +/- USD 0.1
    - ➢ Difference: **+/- USD 2 lower cost per 20 L container**

- **Payback period** of investment in plasma coating:
  typically, **6 months** with a DPC123 compared to Fluorination

ADVANTAGES

Environmental advantages:

- 100 % recyclable
- Replaces non-recyclable multilayer products and metal packaging
- Replaces scavengers
- Replaces fluorination
- Use of environmentally friendly HFO gasses with a low GWP (Global Warming Potential)
- Very low-level exhaust of acetylene gas
- Can be used on biodegradable material

ADVANTAGES

Food safety advantages:

- No impact on the approval of materials suitable for food (EU regulation 10/2011)
- FDA approved (PET)
- Food taste is not affected (Robinson/EN1230-2)

Other advantages:

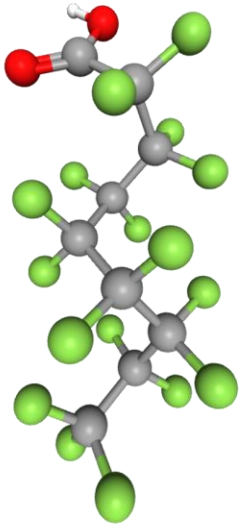
- No drop test implications

PFAS

What is PFAS?

- PFAS are **P**er-and Poly**f**luoro**a**lkyl **S**ubstances
- Long chain molecules which contain C-F (Carbon-Fluor) bonds
- Restricted molecules have formula: CnF(2n +1)COOH with n > 7

All of them contain COOH = carboxylic acid group
(O = oxygen, H = hydrogen)



PFAS REGULATIONS

Current European PFAS restrictions

"From 25 February 2023, it shall not be used in, or placed on the market in:

(a) another substance, as a constituent;

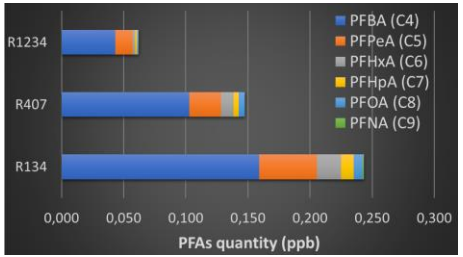
(b) a mixture;

(c) an article,

except if the concentration in the substance, the mixture, or the article is below ***25 ppb*** for the sum of C9-C14 PFCAs and their salts or 260 ppb for the sum of C9-C14 PFCA-related substances."

PFAS CONCENTRATION IN PLASMA-TREATED BOTTLES?

- 33.8 fl oz (1L) bottles (measurements done at PACE Lab USA)



(ppb)	PFBA (C4)	PFPeA (C5)	PFHxA (C6)	PFHpA (C7)	PFOA (C8)	Others
R1234	0,04	<0,01	< 0,01	<0,01	<0,01	<0,01
R407	0,1	0,03	0,01	<0,01	<0,01	<0,01
R134	0,17	0,05	0,02	0,01	<0,01	<0,01

R407 = 50% R134 + 50% R125

- 5.3 gal (20L) jerrycans

(ppb)	PFBA (C4)	PFPeA (C5)	PFHxA (C6)	PFHpA (C7)	PFOA (C8)	Others
R134	0,6	1	0,79	0,2	0,35	0,05

PFAS CONCENTRATION IN PLASMA-TREATED BOTTLES?

- Main molecule PFBA (C4)
- Concentration of restricted molecules is negligible (<< 25 ppb)
- Concentrations are lower using R1234 refrigerant gas plasma
- On 5.3 gal (20L), concentration of all PFAs ≈ 3 ppb

Conclusion:

All plasma-treated bottles comply with the current ECHA (EU) regulation.

The use of R1234 gives better results.

NEW ECHA PROPOSAL TO BAN PFAS (2025**)

- **New definition of PFAS:** *"For the purpose of this restriction proposal PFASs are defined as substances that contain at least one fully fluorinated methyl (CF3-) or methylene (-CF2-) carbon atom, without any H/Cl/Br/I attached to it."* (Page 4 Column 1 of the proposal)

- **New restrictions:** maximum concentration allowed:
  I. *"**25 ppb for any PFAS as measured** with targeted PFAS analysis (polymeric PFASs excluded from quantification)"*

  II. *"**250 ppb for the sum of PFASs measured** as sum of targeted PFAS analysis, optionally with prior degradation of precursors (polymeric PFASs excluded from quantification)"*

  III. *"**50 ppm for PFASs (polymeric PFASs included). If total fluorine exceeds 50 mg F/kg** the manufacturer, importer or downstream user shall upon request provide to the enforcement authorities a **proof for the fluorine measured as content of either PFASs or non-PFASs**."*

    - ***"Total fluorine"*** measurement method: **"Combustion"**

** 2025 + transition period of 18 months (at the earliest)

NEW ECHA PROPOSAL TO BAN PFAS (2025**)

- **Isytech measurements:** *Article = 1.3 gal (5L) bottle. Total weight 7 oz (200 g) (bottle + cap). Gas R1234 plasma
- Criteria I. and II. : Total PFAS concentration: 1.5 ppb ✓
- Criteria III. : Total amount of fluorine (combustion measurement): 48 ppm ✓

  - This concentration will be lower for greater weight.
  - Process can be adjusted to reduce fluorine concentration.

- **Conclusion:** **Plasma-treated bottles will comply with the future regulation.**

** 2025 + transition period of 18 months (at the earliest)

TIMELINE NEW ECHA PROPOSAL

Q1 2023

I Phase

Preparation and submission of a restriction proposal

- Starting the restriction process
- Notification of intention to submit a restriction proposal
- Registry of Intentions
- Preparing the restriction dossier
- Submission and conformity check

Q1-Q3 2023

II-A Phase

Consultations

- Consultation on the restriction report
- Consultation on SEAC's draft opinion

2024

II-B Phase

Opinion development

- Advice from the Forum
- RAC's opinion
- SEAC's opinion

2025-2027…

III Phase

Decision and follow-up

- Commission decision on restriction
- Complying with restriction
- Enforcing the restriction

CAN WE GET RID OF PFAS IN PACKAGING?

How is PFAS created?

In most cases, PFAS is created when you have oxygen together with fluorine.

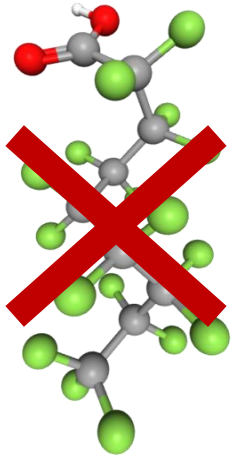
PFAS creation is prevented:

- In standard fluorination by flushing heavily with N_2.
- In our EVOLVE process – filtering out the oxygen.

BUT:

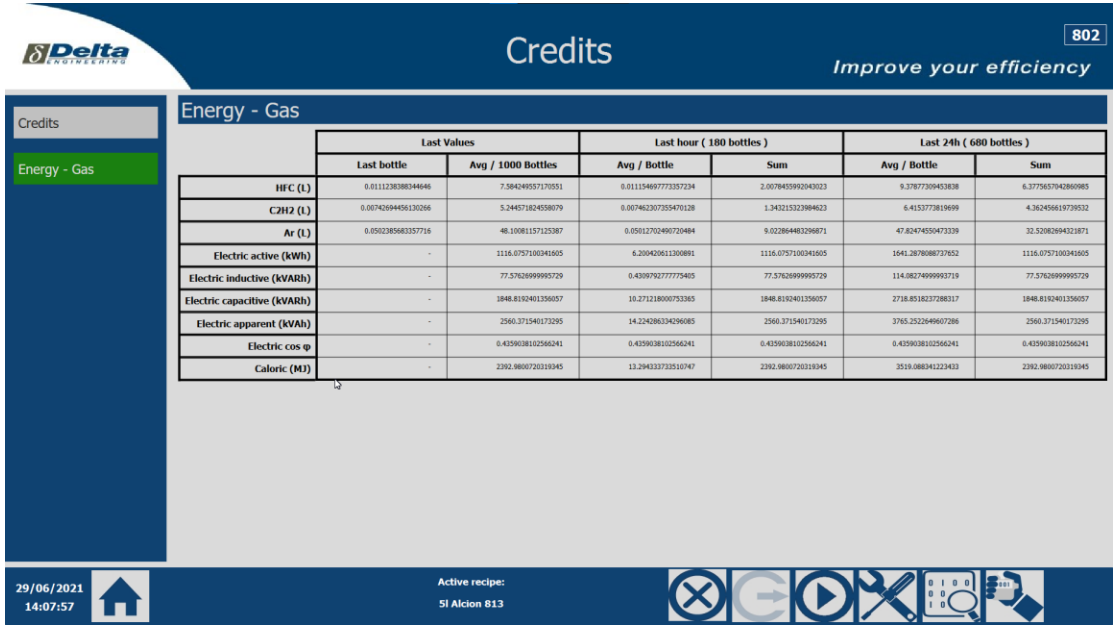
NEW 100% FLUORINE-FREE PROCESS: EVOLVE FF

- Even though our current process already complies with current & future PFAS regulations, we developed a **new hydrocarbon layer** obtained with a plasma in a **mixture of hydrocarbon gasses (without any fluorine!)**, which gives a similar level of barrier.
  - A **future-proof** technology
  - Process available on 33.8 fl oz (1L) & 1.3 gal (5L) bottles: Weight loss using xylene, 140 °F (60 °C), 14 days < 0,5%
- Process in development for +1.3 gal (5L) volumes
- Needed time for development: 1-2 years
- **Our new 100% fluorine-free process is compatible with current DPC plasma coating machines.**



COSTING TOOLS

Total Plasma Cost Calculation Tool: www.delta-engineering.be/total-plasma-cost-calculation



	Last Values		Last hour (180 bottles)		Last 24h (680 bottles)	
	Last bottle	Avg / 1000 Bottles	Avg / Bottle	Sum	Avg / Bottle	Sum
HFC (L)	0.011123838834646	7.584249557170551	0.011154697773357234	2.007845399204302 3	9.378773094538 38	6.377565704286098 5
C2H2 (L)	0.007426944561302 66	5.244571824558079	0.007462307355470128	1.343215232984623	6.41537738196 99	4.362456619739532
Ar (L)	0.050238568335771 6	48.10081157125387	0.050127024907204 84	9.022864483296871	47.824745504733 39	32.52082694321871
Electric active (kWh)	-	1116.07571003416 05	6.200420611300891	1116.07571003416 05	1641.28780887376 52	1116.07571003416 05
Electric inductive (kVARh)	-	77.57626999995729	0.430979277777540 5	77.57626999995729	114.08274999993719	77.57626999995729
Electric capacitive (kVARh)	-	1848.8192401356057	10.271218000753365	1848.8192401356057	2718.8518237288317	1848.8192401356057
Electric apparent (kVAh)	-	2560.371540173295	14.224286334296085	2560.371540173295	3765.2522649607286	2560.371540173295
Electric cos φ	-	0.4359038102566241	0.4359038102566241	0.4359038102566241	0.4359038102566241	0.4359038102566241
Caloric (MJ)	-	2392.9800720319345	13.294333733510747	2392.9800720319345	3519.088341223433	2392.9800720319345

APPLICATIONS

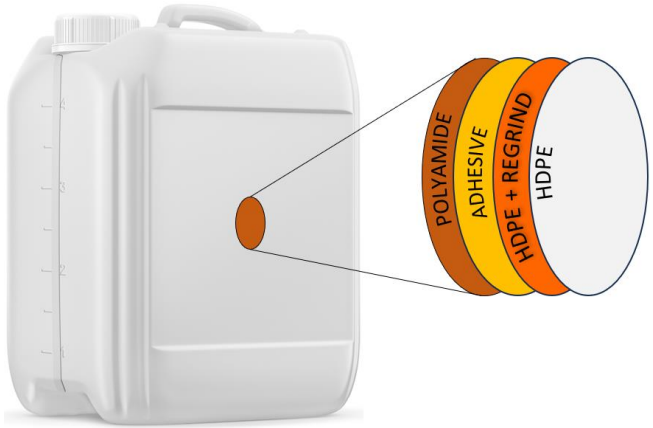
Replacement of metal packaging

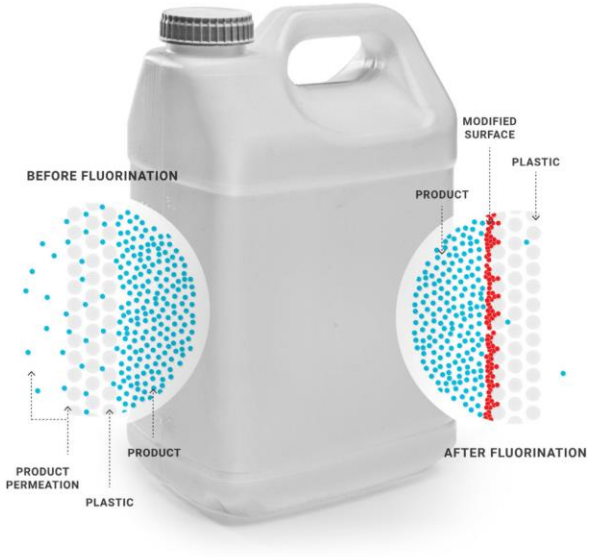
APPLICATIONS

Eliminating the need for scavenger materials

APPLICATIONS

Replacement of multilayer & fluorinated packaging





FAQ

Effect of plasma coating on fresh and warm HDPE?

- Results in better properties
- Pores are ‘filled’ better
- Shrinking still active
- Lower risk of contamination

Is plasma coating sensitive to stretching?

- Hot filling of bottles requires a “special process” or the O_2 barrier could be affected.

Does plasma coating affect my product dimensions?

- The dimensions are not affected since the plasma coating process adds relatively little heat to the container.
- The underpressure in the product might cause mechanical deformation and in certain conditions prevents lightweighting because of the underpressure in the product.
  This is mainly the case with big containers.

FAQ

If I send my bottle through the machine twice, do I get a better barrier?

- No. If the layer gets thicker, it doesn't "add" any additional barrier.

Do cracks or inside scratches have an impact on the barrier?

- This depends on the product's surface and the condition in which it is.

Is the product material chemically improved?

- No. If a material is affected by chemicals, the plasma coating will only delay the effect, not improve the chemical resistance.

How are we sure that the product is treated everywhere?

- By statistical process control. In combination with process control, the specially designed and coated blow pin ensures a good plasma distribution.

FAQ

Is the inside of a non-pinched handle coated as well?

- Yes, although it might have a slightly less good performance than the rest of the container's surfaces. However, this has no major impact on the container performance, as long as the handle bar is situated above the liquid phase.

How does the HPDE aging process (micro-cracking) influence the coating quality after keeping the uncoated bottle in stock for a long period of time? Will the coating fill in or cover the cracks?

- Tests on stored uncoated bottles with small cracks have not shown an impact on the quality of the coating. However, the surface preparation with argon might have to be about +- 1 s longer.

- Large cracks, however, will impact the coating quality and performance.

What happens when the coated bottle is stored for a long time?

- There is a risk of oxidation if the treated bottles are stored in an unprotected place with direct sunlight hitting the bottles. If protected from sunlight, the bottles last for many years.

FAQ

Why does the bottle collapse when testing with limonene as a product?

- The plasma barrier gives an excellent coating to prevent permeation of limonene. However, limonene will oxidize with the remaining air in the bottle when filled and, therefore, the bottle will collapse. The solution is to fill the remaining volume in the bottle with nitrogen or use a pressure release cap to stabilize the pressure.

Do we need to redo our UN approvals after plasma coating?

- Not in case of plasma coating of a monolayer product, since we only add 100 nm to the inside.
  In case of replacing a multilayer by a plasma coated monolayer, UN approval tests need to be done again.

Does plasma coating affect the product taste?

- No.

FAQ

Is plasma coating suitable for all kinds of food?

- Yes, EVOLVE PET

Does plasma coating have a negative impact on recyclability?

- No, Recyclass tested this and confirmed it does not.

Is plasma coating affected by exhaust gas regulations?

- Needs to be checked locally.

CONCLUSIONS

- Plasma coating is a well-known, **environmentally friendly** and **efficient** technology for the blow moulding industry with **low operational costs**.
- It is a stable and **reliable** technology, allowing you to replace non-recyclable multilayers by **easily recyclable** monolayers.
- Plasma coating generates **dedicated material properties** such as barrier improvement, migration, permeation and sliding properties, among others.
- This technology has **many advantages**: for the product, process, environment, food safety and cost level, among others.

CONCLUSIONS

- Plasma coating technology significantly **reduces the cost of ownership** as well as of the **raw materials** to be used in the production of plastic packaging.
- At Delta Engineering, we offer you an **extensive range of plasma coating equipment** for a wide range of plastic products – from 0.17 fl oz (5 ml) bottles to 264 gal (1000 L) IBCs – using plasma coaters with 1 up to 16 reactors.
- Our **current process** already **complies with the current** (February 2023; 25 ppb) **and future** (2025; 50 ppm) **ECHA regulations**.
- **Future-proofness** of our machines: our **new 100% fluorine-free process** is **compatible with our current DPC plasma coating machines**.

Open House 3 – 4 - 5 december 2024

- Focus on different technologies :
- **Plasma** : DPM123, DPC123, DPC223, DPC133 in demonstration
- New **Digital printing** technology
- **Bottle 2 Tube technology**
- **Plasma surface activation : Dropless drying & Anti Staining**.

Thank you for your attention