A comparative analysis of industrial coating processes and atmospheric plasma for metal passivation

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Frame of the study

Corrosion protection treatment in the metal finishing industry

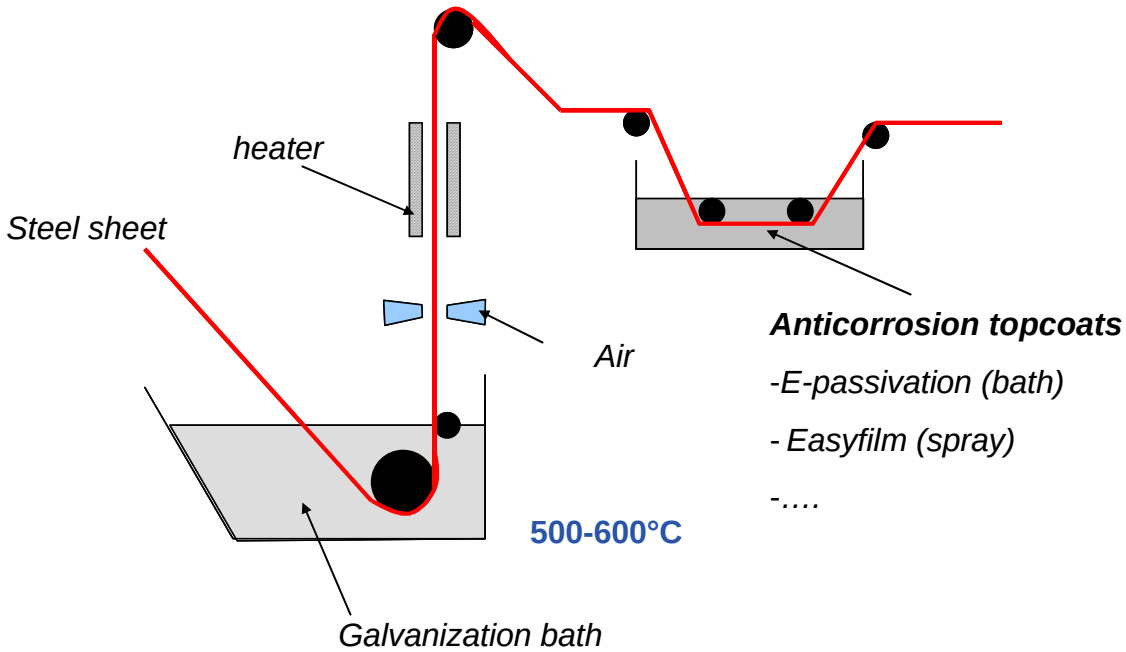
✓ Need for alternative processes to chromium treatment

✓ Atmospheric plasma is a promising process in the field of surface finishing industry (cleaning, activating, coating)

✓ Dry-coating technique (= perceived as environmentally friendly)

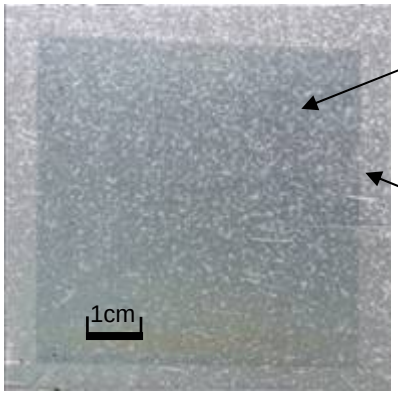
Atmospheric plasma : a sustainable alternative to wet coating processes for metal passivation?

Metal finishing: galvanized steel topcoat

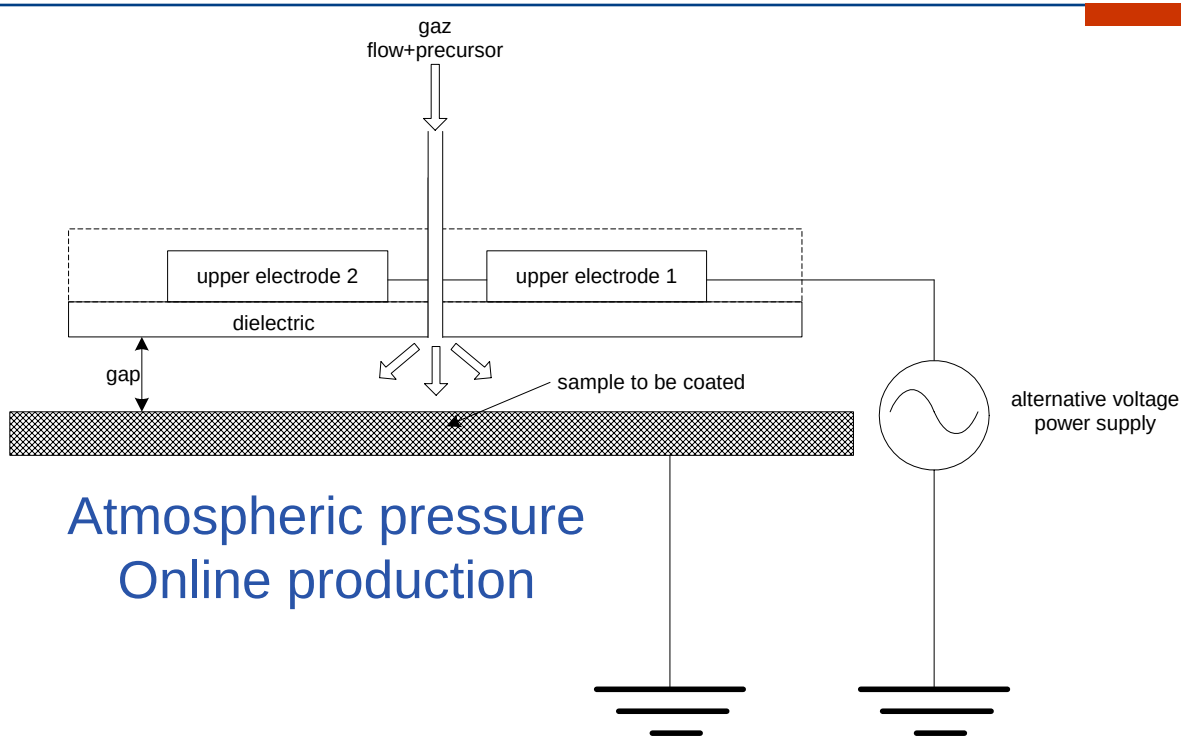


Industrial galvanisation line and anticorrosion topcoat

Atmospheric plasma based coating



Galvanized steel



Atmospheric pressure
Online production

1: **coating** (organosilicon polymer) controlled by electrical discharge, carrier gases and chemical precursors
2: **curing** (plasma post-treatment)

Comparison of 3 technologies

Technology 1 : **E-passivation** (wet mineral coating)

✓ Water-based solution spread onto the surface of metal by roll coaters.

✓ Solution: **Zinc dihydrogenophosphate** (10÷25%), **manganese dihydrogenophosphate** (2.5÷10%), **hexafluorotitanic acid** (2.5÷10 %).

✓ **Proven** industrial technology

Technology 2 : **Easyfilm** (wet organic coating)

✓ Water-based solution spread onto the surface of metal by roll coaters.

✓ Solution : **acrylic polymers in aqueous solution**.

✓ **Proven** industrial technology

Technology 3 : **ppHMDSO** (dry organic coating)

✓ Plasma polymerized **hexamethyldisiloxane** (ppHMDSO).

✓ Pure organic siloxane **atomized into a plasma zone**, broken down, rearranged and deposited as a polymer at the surface of metal.

Economic comparison

	E-passivation	Easyfilm	ppHMDSO
Qualitative evaluation of coating process costs	☺☺	☺	☹

Detailed coating process costs of ppHMDSO technology

	HMDSO raw material	Gas flows (N_2 and O_2)	Electrical energy	Total cost
Cost	0.096 €/m^2	**0.777 €/m^2**	0.006 €/m^2	**0.879 €/m^2**

Technical comparison

Resistance to corrosion

	E-passivation	Easyfilm	ppHMDSO
Salt spray Criteria: time needed to have 5% of corrosion pits [days] (experimental)	2 to 3*	20 to 21*	10 to 14**
Electrochemistry Criteria: corrosion intensity [A/cm^2] (experimental)	8.02 E-6*** (☺)	3.34E-7*** (☺☺)	1.51 E-7** (☺☺☺)

* Experimental figures from industry

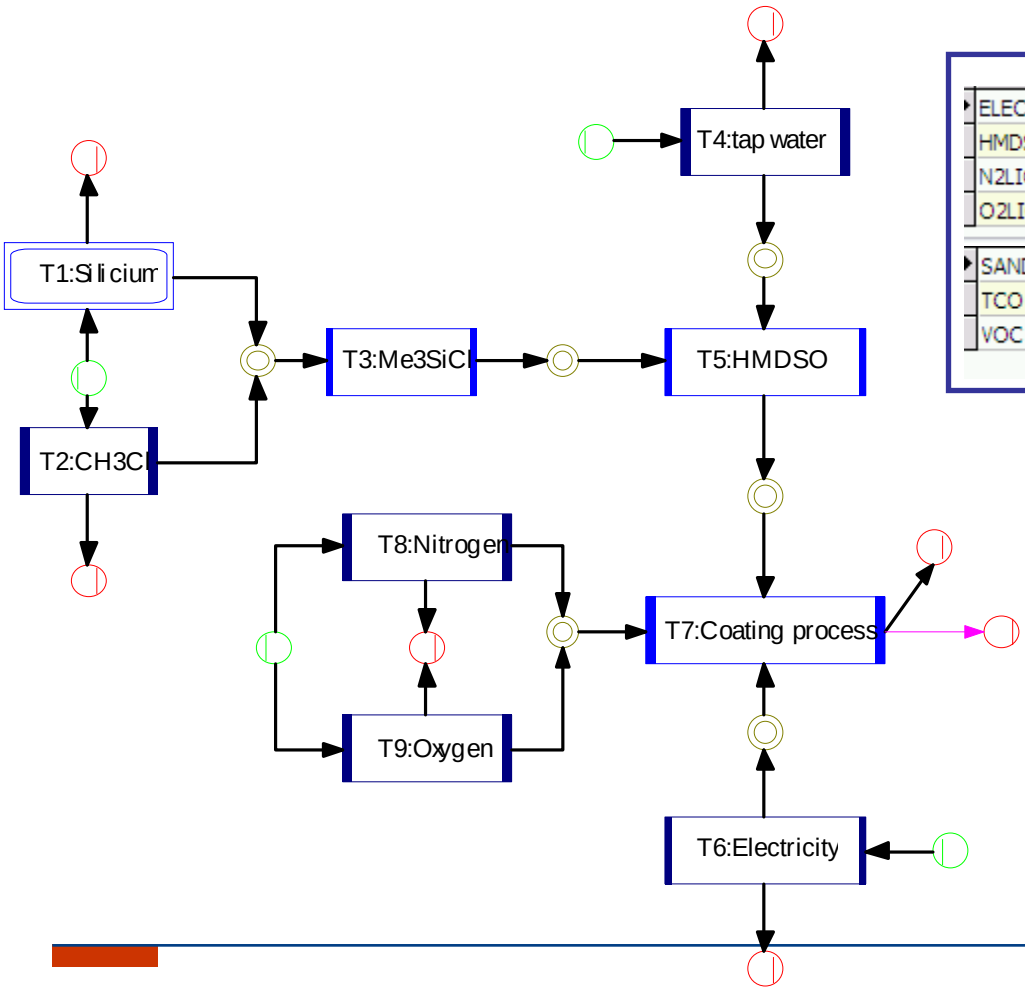
** Provisional experimental figure from CRP H. Tudor

*** Experimental figure from CRP H. Tudor

Environmental comparison

Based on simplified Life Cycle Assessment (LCA, ISO14040-44)

- raw materials and energy consumption lifecycles
- ecoinvent database (www.ecoinvent.ch) and Umberto® software tool



Inputs and outputs of Coating process

ELEC	P10	electricity, medium voltage, at grid [LU]	kWh
HMDSO	P11	HMDSO	kg
N2LIQ	P14	nitrogen, liquid, at plant [RER]	kg
O2LIQ	P14	oxygen, liquid, at plant [RER]	kg
SAND	P12	Sand, unspecified, in ground [resource/in ground]	kg
TCO	P16	topcoat	m2
VOC	P12	NMVOC, non-methane volatile organic compounds, unspeci	kg

Inventory

```
HMDSO=QHMDS*TCO
ELEC=QELEC * TCO
N2LIQ=  QN2LI * TCO
O2LIQ=  QO2LI * TCO
VOC= eVOC * TCO
SAND = 0.1 * (2 * QHMDS / 162.4 * (28.1+32))*TCO
```

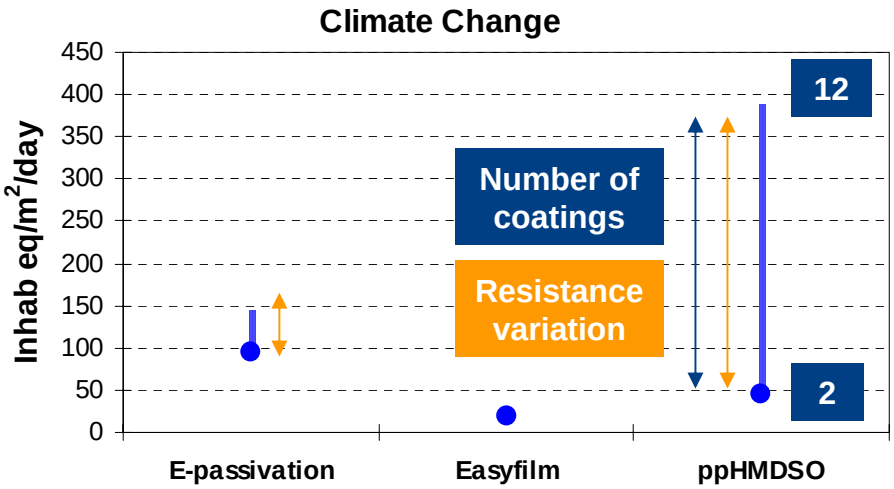
EVOC	qtt de Carbone emis	0.0013845	kg/m2
QCARB	qtt de Carbone/ kg de Me3SiCl	0.220994	kg/kg MeSC
QELEC	qtt d'electricité	0.0873	kWh/m2
QHMDS	qtt d'HMDSO	0.0038964	kg/m2
QMECL	qtt de MeCl /kg de Me3SiCl	1.395028	kg/kg MeSC
QMSIC	qtt de Me3SiCl / 1kg HMDSO	1.337438	kg/kg HMDS
QN2LI	qtt N2 liq	0.253877	kg/m2
QO2LI	qtt d'O2 liq	0.008574	kg/m2
QSIO2	qtt de SiO2 / kg Me3SiCl	0.553407	kg/kg MeSC
QTAWA	qtt de tap water / 1kg HMDSO	0.110837	kg/kg HMDS

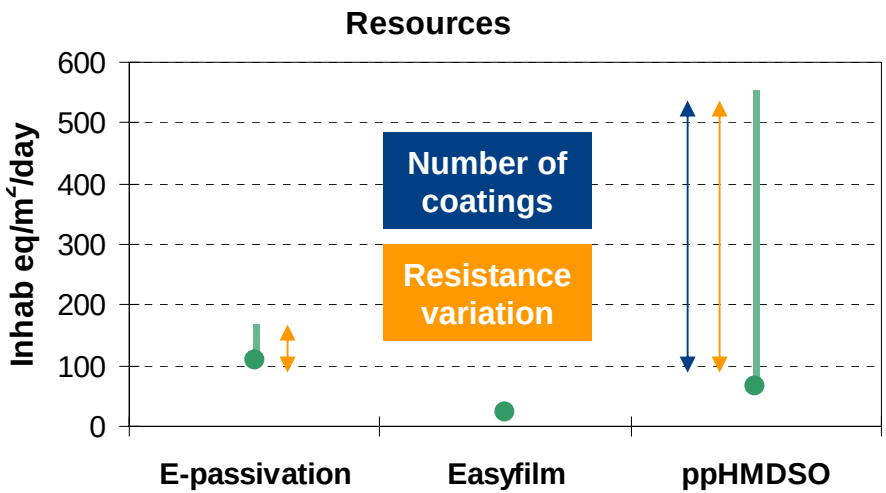
Environmental comparison

Functional unit : *one-day resistance to corrosion of the annual production of metal sheets of the industrial partner*

Resistace to corrosion	E-passivation	Easyfilm	ppHMDSO
Criteria: time to 5% corrosion [days] (experimental)	2 to 3	20 to 21	10 to 14

3 damage categories : Human health, Ecosystem Quality, Resources
1 impact category: Climate Change





Environmental comparison

Contribution analysis

Process phase	N_2 feed (from liquid N_2)	Electricity	CH_3Cl Production	Others
Contribution to damages on targets	**73 to 82 %**	7 to 14 %	5 to 16 %	2 to 3 %

- ✓ Depends on the damage category considered
- ✓ Carrier gas contributes the most to environmental impacts (and economic costs!)
- ✓ Consider the replacement of liquid N_2 supply with filtered compressed air

Conclusions

1- E-passivation

✓ cost-effective,

✓ low resistance to corrosion but sufficient for many customers.

✓ lowest absolute contribution to environmental damages

✓ high contribution per unit of corrosion resistance.

Suggested technology for low resistance to corrosion needs

2- Easyfilm

✓ more expensive but high resistance to corrosion.

✓ low absolute contribution to environmental damages

✓ lowest contribution per unit of corrosion resistance.

Whenever corrosion appears to be a critical factor, the Easyfilm topcoat is suggested.

Conclusions

3- ppHMDSO

✓ most expensive and not competitive yet compared to other technologies

✓ anti-corrosion is by now of high quality and is continually improving.

✓ Wide range of variation of the environmental damages depending on the operating conditions and the resistance to corrosion level.

✓ The N_2 feed gas contributes at least by 73% to the damages and represents nearly 90% of the ppHMDSO process cost.

⇒ **costs** and **environmental damages** are strongly connected

⇒ **Optimization of material** and energy **flows** required to improve the competitiveness of atmospheric plasma for large-scale coating

Recommendations and outlook

1- **Optimised** use of carrier gas and inerting gas flows.

Promising solution (being tested) might be a combination of :

- ✓ use of air as gas feed instead of oxygen and (part of) N_2
- ✓ a decrease of the gas (and HMDSO) flow

2- **Required anti-corrosion efficiency**:

- ✓ Set anti-corrosion resistance according to customers' needs
- ✓ while lowering the electrical energy demand by decreasing the required number of coating and curing time, and/or by increasing the coating speed

It is important to recognize that plasma technology development for coating will be a marathon, not a sprint

Thank you for your attention !

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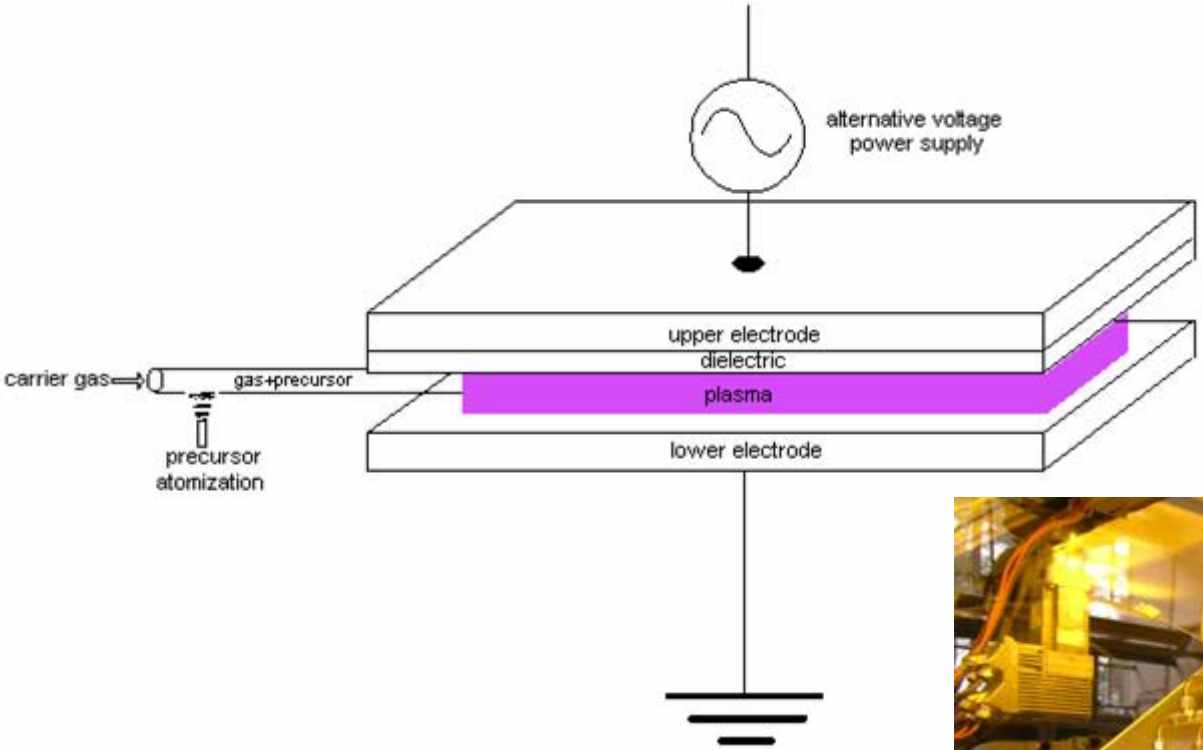
Current status and perceived advantages/drawbacks of technologies

Technology	E-passivation	Easyfilm	ppHMDSO
Status	Existing industrial process	Existing industrial process	Process in R&D
Perceived Advantages from survey	-Cost-effective -Process easy to implement/operate	-Very competitive coating quality -Easy process	Innovative and environmentally friendly alternative to wet chemical processes
Perceived drawbacks from survey	-Not sustainable -Limited performance	Costly	Not implemented yet at industrial scale Costly?

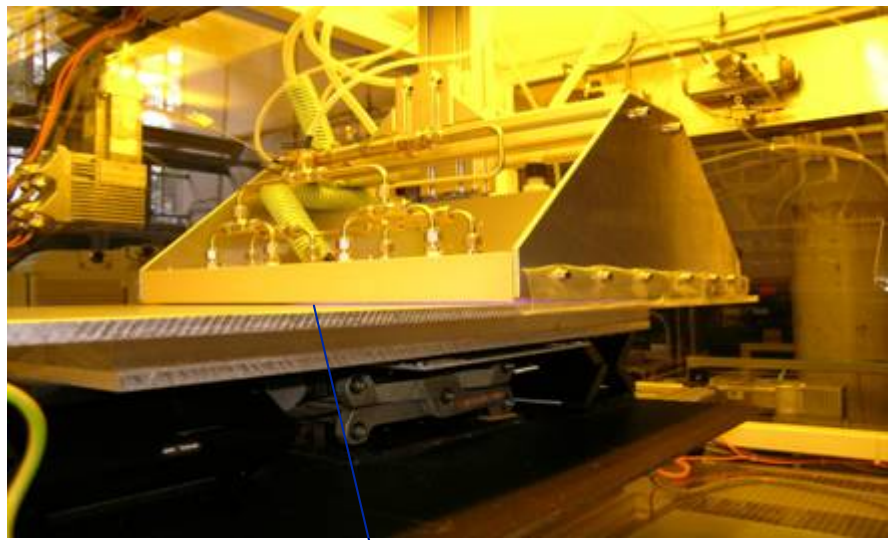
Principle of atmospheric plasma

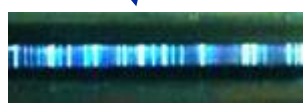


Atmospheric pressure

Online production

Deposition of coating controlled by electrical discharge, carrier gases and chemical precursors





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