Making the chemical pretreatment process for Duplex (powder coating) on galvanized steel ready for the future in terms of quality, durability and sustainability

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2 Phases

Phase 1: Replacing Chromium(VI)

- The main objective
- Process conditions
- Chemical pretreatment
- Results

Phase 2: Making the process future ready

- EU climate directives and sustainability goals of WeCoat
- Process optimalization; saving on energy, gas, maintenance, and waste costs

Phase 1: Replacing Chrome(VI)

The main objective

- Powdercoating HDG since 1980
- Switch to chromium(III) in 2016
- Chemical pretreatment with conversion layer and 2 layer powdercoating (DUPLEX)
- High end corrosion protection (C3/C4/C5-I/C5-M)

Tabelle 3: Beispiele für Pulverbeschichtung auf Stückverzinkung (Duplexsysteme)

Oberflächen Vorbereitung	Grundbeschichtung(en)			Deckbeschichtung(en)			Beschichtungssystem		Erwartete Schutzdauer (siehe ISO 12944-1) Korrosivitätskategorie														
	Binde-mittel	Anzahl der Schichten	Soll-schicht-dicke µm	Binde-mittel	Anzahl der Schichten	Soll-schicht-dicke µm	Anzahl der Schichten	Gesamtsoll-schichtdicke µm	C 2			C 3			C 4			C 5-I			C 5-M		
									K	M	L	K	M	L	K	M	L	K	M	L	K	M	L
Sw	--	--	--	SP	1	80	1	80	X	X	X	X	X	X	X								
ZnP		--	--		1	80	1	80	X	X	X	X	X	X	X	X							
Cr		--	--		1	80	1	80	X	X	X	X	X	X	X	X	X						
Sw		--	--		2	60	2	120	X	X	X	X	X	X	X	X							
Sw		1	60		1	70	2	130	X	X	X	X	X	X	X	X		X					
ZnP	EP	1	60		1	70	2	130	X	X	X	X	X	X	X	X	X	X	X		X	X	
Cr		1	60		1	70	2	130	X	X	X	X	X	X	X	X	X	X	X		X	X	X
Cr	--	--	--	EP / SP	1	80	1	80	X	X	X	X	X	X	X	X	X	X			X		

Erläuterung:
Cr = Chromat, ZnP = Zinkphosphat, Sw = Sweepen

EP = Epoxidharz, SP = Polyesterharz, EP/SP = Epoxid-Polyesterharz
EP und EP/SP erfüllen nicht die Anforderungen an die UV Beständigkeit der Freibewitterung
K, M, L geben die zu erreichende Schutzdauer der Beschichtung in der jeweiligen Korrosivitätskategorie an:
K = kurze Schutzdauer (2-5 Jahre), M = mittlere Schutzdauer (5-15 Jahre), L = lange Schutzdauer (>15 Jahre)
Die Korrosivitätskategorien C 2 – C 5 beziehen sich auf die Korrosionsschutzwirkung der Beschichtung auf dem Zinküberzug:
C 2 = gering, C 3 = mäßig, C 4 = stark, C 5-I = sehr stark (Industrieatmosphäre), C 5-M = sehr stark (Meeresatmosphäre)

Types of Zinc coating layers

- Each galvanizing facility has its own HDG process
- Differences in Zinc coating based on elements PB,Bi,Ni,Al,Mn
  - Composition and thickness of base material
- >Si level, >thickness, welds → which results > Fe level
- **Main question: How to deal with the different compositions of the zinc layers ?**

Different compositions of Zinc coating layer

Tables; Different Zinc layers measured with XRF

High temperature galvanized (Delta Wecoat)			
Zn	89.50	0.192	
Fe	10.50	0.070	0.00 – 100.00

Dull Zinc (S355)			
Zn	95,89	0,190	
Fe	3.76	0.041	0.00 – 100.00

Shiny Zinc (S235)			
Zn	97.81	0.190	
Fe	2.06	0.030	0.00 – 100.00

Shiny & Smooth Zinc (MC steel)			
Zn	99,03	0.191	
Fe	0.79	0,019	0.00 – 100.00

Adjusting the process to different Zinc coating layers

- Extensive testing was needed to translate the effect of different Zinc coating layers into a stable process
- No direct influence between elements present in alloy and paint adhesion
- Surface structure is of importance (which can differ per alloy)
  - very smooth shiny homogeneous versus dark Zinc coated layer
- Key is the duration of the etching process in relation to the surface structure
  - A minimum of 2 gram/m² is applied for a shiny smooth Zinc layer. For everything else, an etching degree to a minimum of 2 grams/ m² can be achieved by reduction in etch duration
  - The difference in etching can be up to 4 or 5 times longer

Alloys tested
Zn-0.7%Pb-0.004%Al
Zn-0.25PB-0.1Bi-0.004%Al
Zn-0.25Pb-0.1Bi-0.04%Ni-0.004%Al
Zn-0.1%Bi-0.004%Al
Zn-0.1Bi-0.04%Ni-0.004%Al
Magnelis Zm 250
Zm310
Sendzimir
Delta galvanized in Zn-0.25PB-0.1Bi-0.004%Al

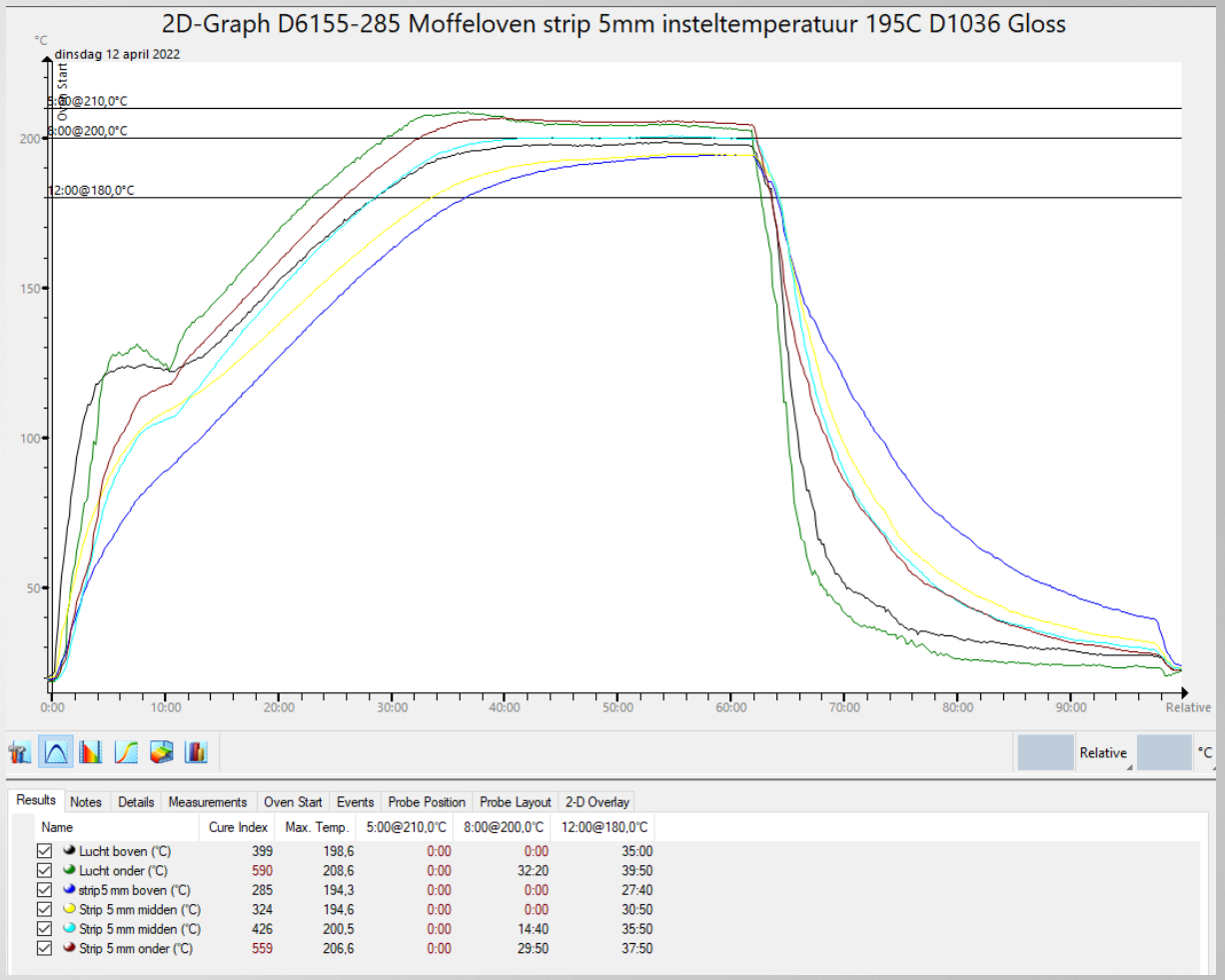
Determining duration of etching process

- Ideal times cannot be determined in general, they depend on temperature, concentrations, spraying or dipping application, etc.
- Difference: With dull material the reaction starts immediately and with shiny material the reaction starts very slowly
- The etch step before applying the conversion layer is essential in managing the full process
- All other chemical baths, including rinse baths must be clean (cleaner than with traditional chromium(VI))

After pretreatment

Optimizing the curing process of powdercoatings

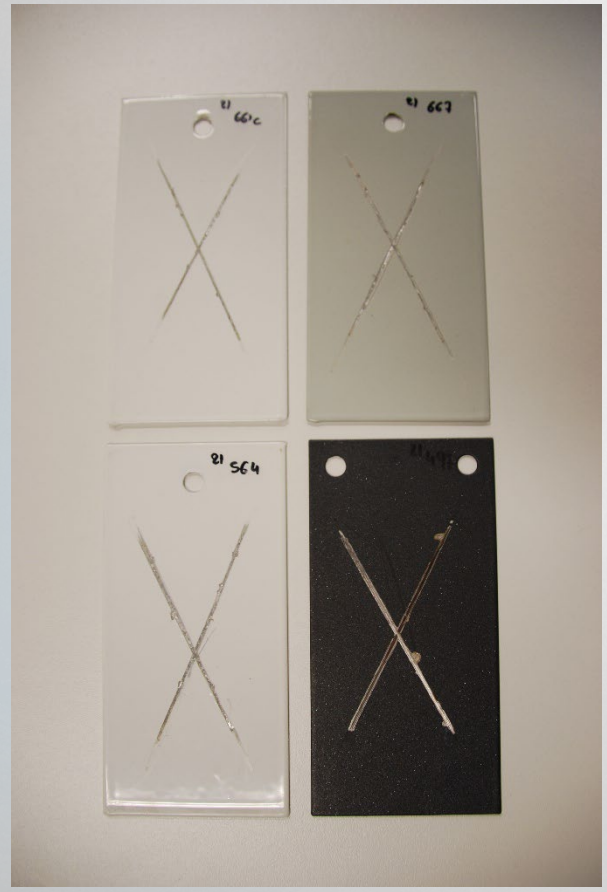
- Main use is GSB accredited powders (normal and low bake) from renown suppliers
  - Right properties, constant quality → important for a stable process
- Curing oven process adjusted based on thickness of material
  - Lower temperature between batches



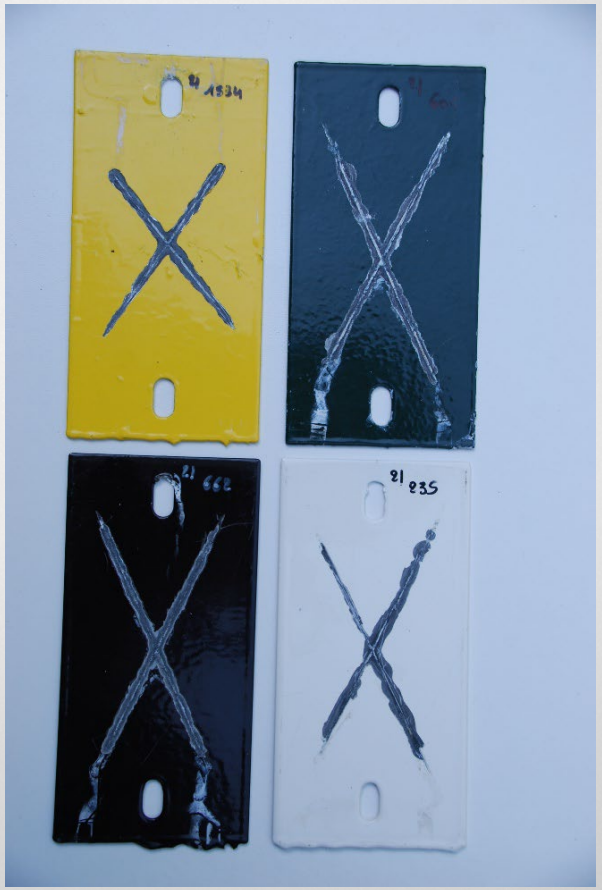
Name	Cure Index	Max. Temp.	5:00@210,0°C	8:00@200,0°C	12:00@180,0°C
Lucht boven (°C)	399	198,6	0:00	0:00	35:00
Lucht onder (°C)	590	208,6	0:00	32:20	39:50
strip5 mm boven (°C)	285	194,3	0:00	0:00	27:40
Strip 5 mm midden (°C)	324	194,6	0:00	0:00	30:50
Strip 5 mm midden (°C)	426	200,5	0:00	14:40	35:50
Strip 5 mm onder (°C)	559	206,6	0:00	29:50	37:50

Salt Spray test results NSS 740 hours

Aluminium



HDG



Delta galvanized

The chemical pretreatment process for HDG

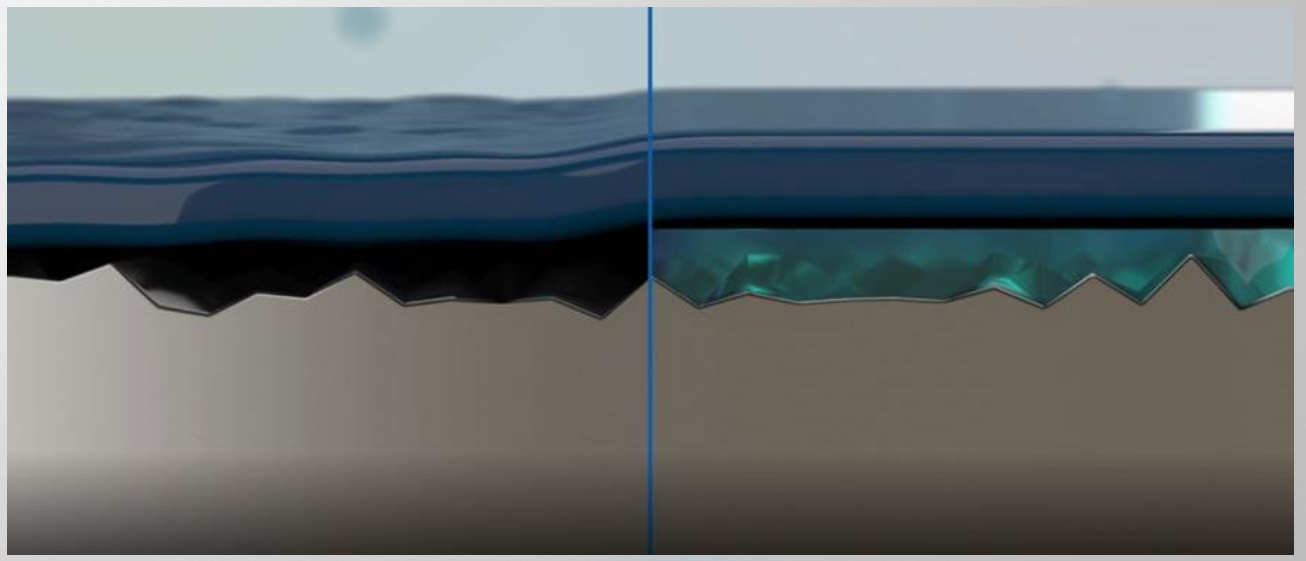
Degreasing	Rinse	Acid Etching	Rinse	D.I. Rinse	Conversion Coating	Rinse	Dry	Powdercoat
Alkaline		Acid based etch to remove pollutions/contaminants and creating surface magnification			Chrome(VI) or alternative system			

Conversion coating

- Sets in the crystalline structure of the Zinc layer
- Creates paint adhesion, corrosion protection and bare metal protection properties (passivation)

No conversion coating

Conversion coating



Developing a high end Chromium(VI) alternative

- Journey of more than 7 years

Property	Chrome(VI)	Chrome(III)	Titanium, Zirkonium	Silane	Iron phosphating	Zinc phosphating
Stable process	√	√	√	√	√	√
Conversion coating	√	√	√	√	√	√
Paint adhesion	√	√	√(sensitive)	√ (sensitive)	Poor	Poor
Corrosion protection	√	√/Poor	Poor	Poor	Low quality	Poor
Passivation (bare corrosion protection)	√	√/X	X	X	X	X
Meets GSB standard	√	√	X	X	X	X
Meets QualiSteelCoat standard	√	√	X	X	X	X
Multi-metal	√	√	√	√ (sensitive)	Low quality	Low quality

Chrome(VI) versus PreCoat Z31

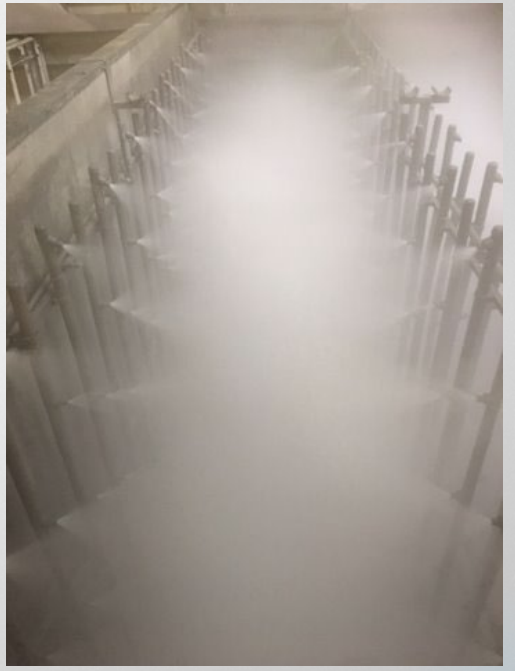
- Passivation properties equivalent to Chromium(VI)
- The quality of Chromium(VI) without the toxic properties

Property	Chrome(VI)	Chrome(III) PreCoat Z31
Economic viability	- -	++
SHEQ	- - 	++ 
Corrosion protection and paint adhesion	+ +	++
Multi-metal application	+/-	++
Stable process	++	++
Meets quality standards	GSB, Qualisteelcoat	GSB, Qualisteelcoat
Corrosion classes	High C3/C4/C5	High C3/C4/C5

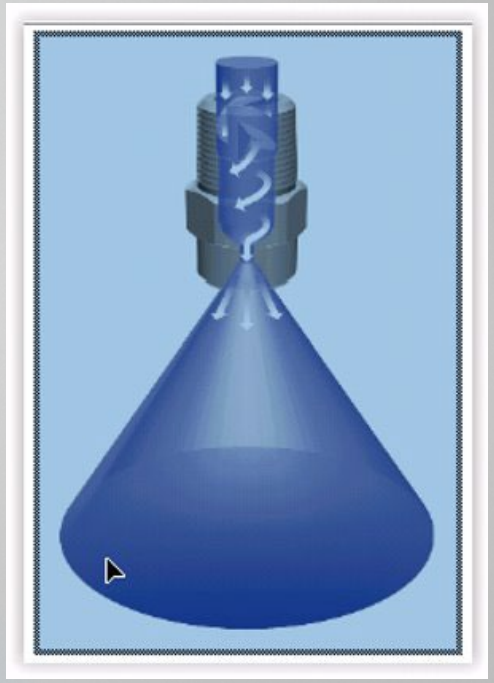
Testing on the lab and production environment

- Optimizing process parameters
- From 95% tot 99,9% quality
- Immersion versus spray
  - Conical spraying nozzles
- Speed of pretreatment line
- How to handle different Zinc coating layers

Cloud of +/675 liter per m²



Spray Nozzle



Chemical pretreatment for HDG (1/2)

- Degreasing
  - Alkaline based, control based on pH (buffer technique).
  - The used detergent is selected based on surfactants which absorb grease but also enable a good rinsing in subsequent steps.
  - The degreaser may also not have a negative effect on the passivity of the substrate which would result in problems during etching
- Etching
  - Strong acidic environment where a mixture of acids has been chosen which ensures a good absorption of alloying elements while also penetrating the passivity of the zinc layer (etching).
  - Each different Zinc alloy needs a different treatment time
  - The etching bath is replenished when a certain Zinc level has been reached.

Chemical pretreatment for HDG (2/2)

- Conversion coating
  - The unique chrome(III) based formulation of the PreCoat Z31 has an enormous tolerance built in, which ensures a solid process operation
  - Independent on the zinc alloy composition.
  - Monitoring build-up of alloy elements in conversion coating bath is important to prevent saturation of the bath
- Powder coating process
  - Optimization of curing process
  - Speed and temperature

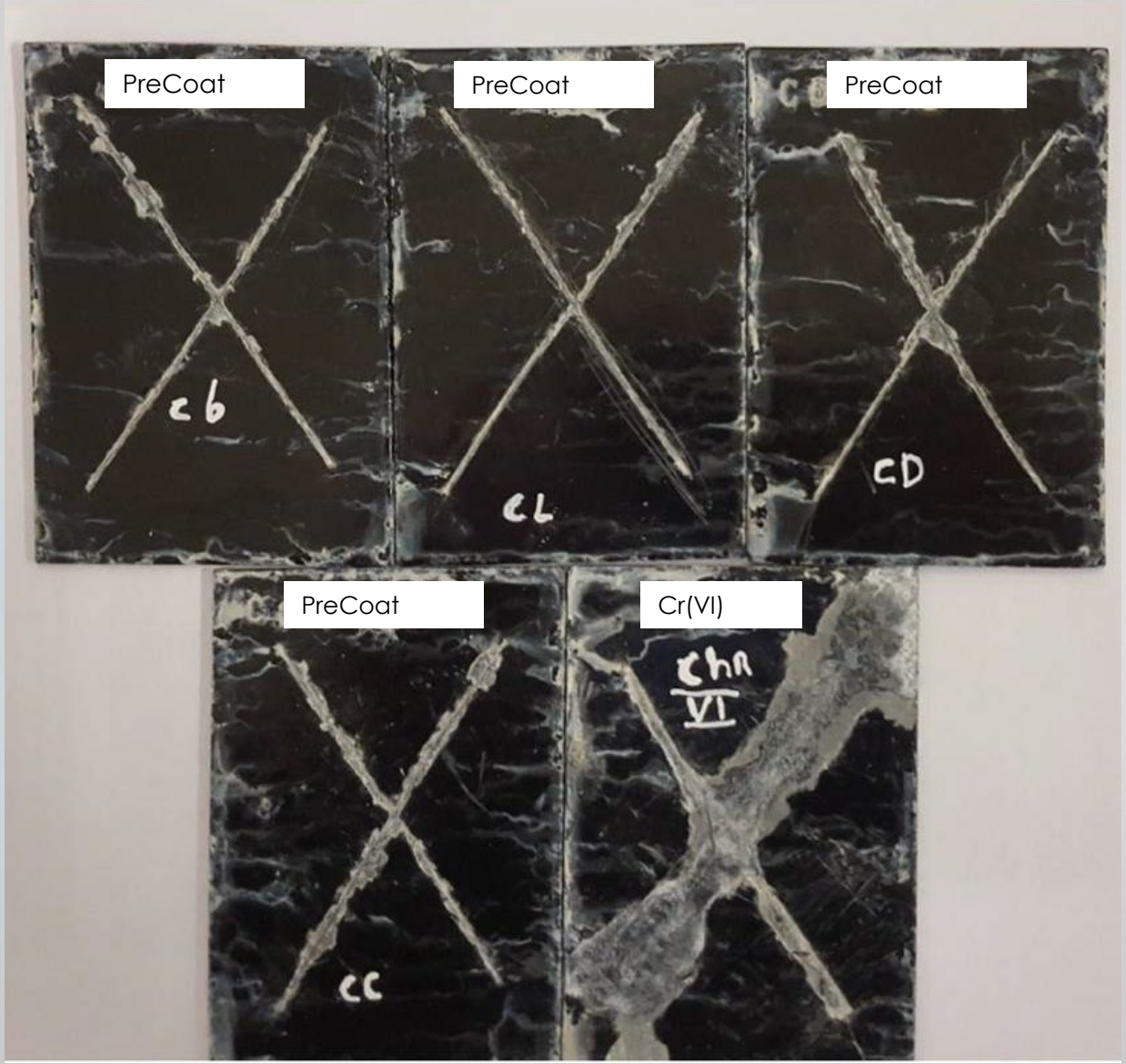
Quality labels

- C5 corrosion class, meets GSB and QualiSteelCoat standards

GSB INTERNATIONAL
Approved Coated Zinc & Steel

quali steel coat
International Quality Label for Coated Steel

Test results after 3000 hours NSS



Phase 2:Making the process future ready

Vision of WeCoat on the future

- EU directive, climate goals 2030
- Sustainable business
- Save on
  - Energy
  - Chemistry
  - Water
  - Maintenance

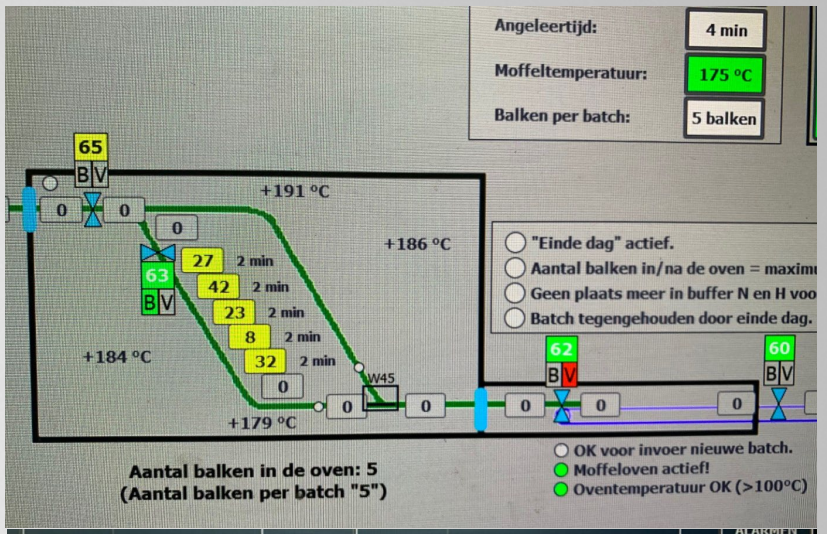
Lowering the temperature of the degreasing zone

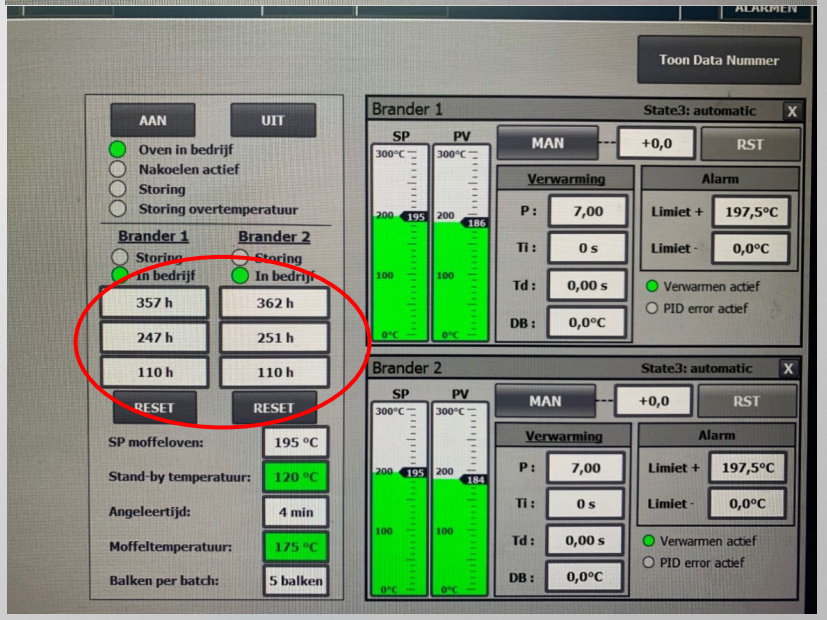
- Degreasing bath 60 °C
- Objective together with AD: Decrease temperature degreasing solution, especially in the spray installation where the liquid cools off quickly during spraying and there is a lot of evaporation of water.
- Result: Temperature of a degreasing bath reduced to 35 °C for two months, which **saves 30%** on energy consumption for the **evaporation energy alone.**
- In total about 60% savings on energy and 30% on water consumption have been realized

Optimzing the powder curing process

- from continuous standard 190 degrees °C to batch
  - intelligent (integrated in the track control)
- when entering and exiting beams, we send the temperature to 120 °C and the fans go to approx. 10%

- Result: temperature remains in oven and new material can directly enter the curing oven without going in the pre-heating (for bonding) oven first while the previous batch is curing
  - Energy saving in pre-heating (for bonding) oven: 100% (turned off)
  - Energy saving regular curing oven (gas): 30%



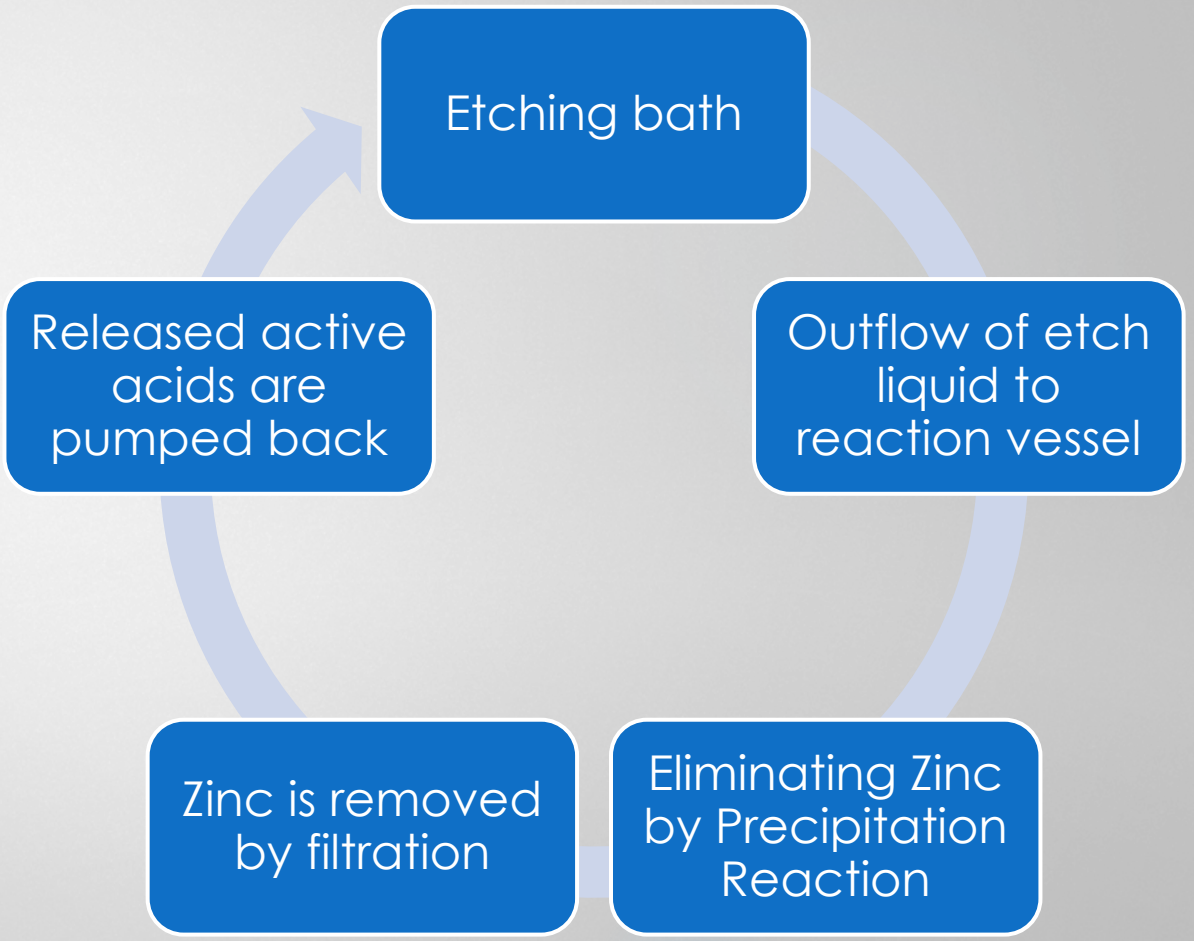


Optimizing the etching bath

- Because the Zinc is etched, Zinc quickly enters the etching bath.
- Etching bath should be with a maximum of 5 grams per liter of Zinc
- Contaminated etch solution (acid) needed to go through the wastewater treatment and etching solution needed to be replenished at a high rate
- Together with AD a system for regeneration of etching solution has been developed, saving water and chemicals
  - An installation separates the Zinc from the acid in a closed loop system with etching bath
- Result: saving on water, less limescale and additional savings on caustic soda needed for wastewater treatment process

Recycling of etching bath

- Investment needed in equipment to adjust process
- Chemical consumption similar to regular process
- 80% less waste water treatment costs
- 20-100K savings for average Duplex coat process
- Next step: Are there companies interested in the filtrered zinc residual (circular economy)



Degreasing at lower temperature

- AD has developed a completely new degreasing solution that can be applied at 30-35 °C.
- Traditional degreasing agents have their degreasing effect at temperatures > 50 °C.
- This new setting provides energy savings up to 60%.
- Improved working conditions: exposure due to evaporative loss is drastically reduced, which saves on water use, but also in the preservation of the building and surrounding equipment.
- pH level of the degreasing also changed. The newly developed cleaner has a neutral design, which saves on the costs for neutralization in the wastewater process
- Another benefit is that it reduces the degree of contamination in the bath.

Conclusion

- Together, WeCoat and AD have succeeded in realizing a range of improvements through innovation and joint expertise, which has led to the following summary of savings:
- Replacement of Chromium(VI)
- Savings in
  - Wastewater treatment
  - Process water
  - Chemical consumption
  - Energy
  - Maintenance equipment and premises

Let us keep improving every step in the process to create a sustainable future for the galvanizing world now and tomorrow!

References

- GSB, https://gsb-international.de/en/quality-regulations/galvanizers
- Qualisteelcoat, https://qualisteelcoat.net
- DIN 55633 zum Pulverbeschichten auf feuerverzinktem Stahl