


enthone


Hex-Cr Free Zinc and Zinc Alloy Technology



enthone

Topics

- Current OEM Approvals
- Corrosion mechanism
- Advances in hex-chromium free passivates
- Nano-material to improve performance
- Threaded fastener study, Zn-Ni




enthone

OEM Approvals



enthone

OEM	STANDARD	Perma SHIELD PROCESS SYSTEM	APPLICATION - TYPE	STATUS	
GM	GMW 3044	ENTHOBRITE Zn, PERMA PASS IMMUNOX 3K, ENSEAL 26	Non-threaded fasteners	Barrel	Approved
	GMW 4700	ZINCROLYTE Zn/Cu/Fe, PERMA PASS 7012, ENSEAL 26	Non-threaded fasteners	Rack only	Approved
	GMW 4700	ZINCROLYTE Zn/Ni, PERMA PASS 3095, ENSEAL C22	Non-threaded fasteners	Barrel	Approved
Ford	WSS-M21P17-B1	ENTHOBRITE Zn, PERMA PASS ULTRA III, ENSEAL C23	Non-threaded fasteners	Barrel	Approved
	WSS-M21P17-83	ENTHOBRITE Zn, PERMA PASS IMMUNOX 3K, ENSEAL 29	Fasteners	Barrel	Require Tier 1 sponsor
Honda	MFZ32-C	ENTHOBRITE Zn, PERMA PASS 3095	Fasteners	Barrel	Approved
	MFZ41C-K	ZINCROLYTE Zn/Ni, PERMA PASS 3095, ENSEAL C23	Fasteners	Barrel	Approved
Toyota	TSH624G	ENTHOBRITE Zn, PERMA PASS 3095	Non-threaded fasteners	Barrel	Approved
Delphi	DX551200	ENTHOBRITE Zn, PERMA PASS ULTRA III, ENSEAL C23	Non-threaded fasteners	Barrel	Approved
	DX551300	ENTHOBRITE Zn, PERMA PASS ULTRA III, ENSEAL 26	Non-threaded fasteners	Barrel	Approved
		ENTHOBRITE Zn, PERMA PASS 3095, ENSEAL C23	Non-threaded fasteners	Barrel	Approved
DCX	PS-8814	ENSEAL 29	Fasteners (Mg contact)	Barrel	Approved
	PS-1207	PERMA PASS 5000	Non-threaded fasteners	Barrel	Approved, DCX evaluation
TRW	S-14171201	ENTHOBRITE Zn, PERMA PASS 3095 - Type 0	Non-threaded fasteners	Barrel	Approved
		ENTHOBRITE Zn, PERMA PASS 3095, ENSEAL 29 - Type 1	Non-threaded fasteners	Barrel	Approved



enthone

Corrosion Mechanism



enthone


Corrosion Protection Using Metallic Coatings

- Plating of one metal over another provides corrosion protection by two methods:#1

Barrier Protection:

A more noble metal is deposited on top of a more active metal forming a barrier to corrosion. Also known as **encapsulation**.

As long as the more noble coat is not damaged the base metal will be protected from corrosion.



enthone

Corrosion Protection Using Metallic Coatings

- Plating of one metal over another provides corrosion protection by two methods: #2

Cathodic Protection:
A more active metal is deposited on top of a more noble metal. The more active top metal will preferentially corrode protecting the base metal from corrosion.


Also known as a **sacrificial coating**.



enthone

Galvanic Series

- Ranks metals by their open circuit potential in a given electrolyte
- More noble metals are more electropositive
- More active metals are more electronegative
- The probability that one metal will corrode faster in a galvanic couple is estimated from relative difference in potentials
- Actual corrosion rates determined by many other factors



enthone


Galvanic Series

3% NaCl vs SCE

	(+) Noble
	↑
Barrier Coatings to Steel	-0.27V Low P Electroless Nickel -0.38V High P Electroless Nickel

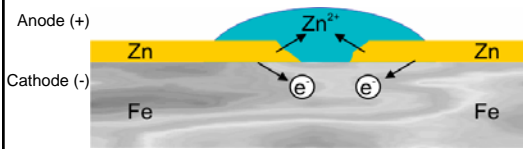
	-0.50V Iron
Sacrificial Coatings to Steel	-0.76 Cadmium -0.80V ZnNi, 12%

	-1.02V ZnCo, ZnFe, 0.5%
	-1.08V Zinc
	↓
	(-) Active




enthone

Cathodic Corrosion Protection Mechanism




Principle:

- Zinc dissolves as the anode. The electrons which are set free move to the base material. This will protect the iron as cathode.
- The zinc surface becomes coated with zinc oxidation product (white rust) which reduces the corrosion rate.
- The zinc corrosion rate can be further reduced by application of a "passivate".



enthone


Advances in Hex-Cr Free Passivates

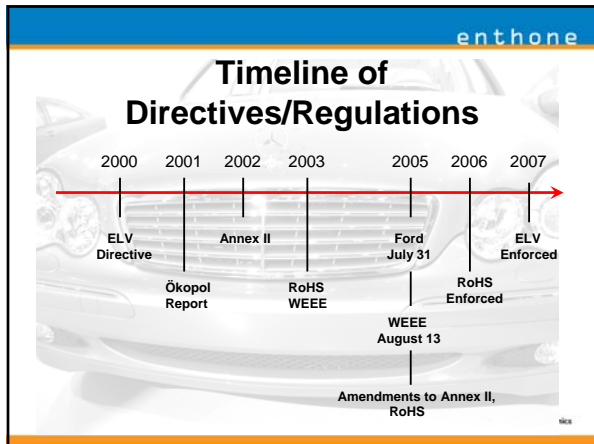


enthone

Recent History

- Early 1980's - Commercialization of hex-Cr free passivates
- Early 1990's - Addition of cobalt to improve performance
- Late 1990's - Thick film passivates
- Improvements with nano-material - 2005





enthone

Introduction of Hex-Cr Free Passivates

- Transparent or clear color
- Promoted for lower waste treatment cost
- Achieve 24 hours NSS

Cookson Electronics

enthone

“Improved” Clear Passivates

- Addition of cobalt to improve corrosion performance
- Heat treat at 80°C for best performance
- Transparent or clear color
- Achieve 96 hours to white corrosion

Cookson Electronics

enthone

Hex-Port Pressure Sensor

Zn, Clear Passivate

Cookson Electronics

enthone

Side Air Bag Supports

Zn, Clear Passivate

Cookson Electronics

enthone

Thick Film Passivates

- Solution heated to 60°C
- Film thickness equivalent to chromates
- Iridescent color
- Achieve 120 hours to white corrosion

Cookson Electronics

enthone

Thick Film Passivates

Alkaline Zinc



Acid Zinc






enthone


ZINCROLYTE® NCZ 315 Metal distribution and Ni incorporation

Plated on rack: coated with ZINCROLYTE® NCZ 315 at 2,5 A/dm²
trivalent passivated with PERMA PASS® 3095



Thickness and Ni-incorporation

	thickness	incorporation
outer layer		
1	9,7 µm	14,9 %
2	9,4 µm	14,7 %
3	8,9 µm	14,4 %
4	9,2 µm	14,6 %
inner layer		
1	5,5 µm	14,4 %
2	6,0 µm	13,9 %
3	5,8 µm	14,2 %
4	6,6 µm	14,5 %



enthone

ZnFe ZINCROLYTE® NCZ 191 Trivalent black passivated with PERMA PASS® 7012 Transparent sealed with ENSEAL® C 22



Example:
Series production of 3-valent coated rack parts.
Size roughly 30 x 30 cm


Fixing board for engine control unit
Approval by AUDI AG, May 2003




enthone

Zinc-Nickel Black coats applied by Cr-VI-free systems

- A trivalent black passivate is available: PERMA PASS® EXP black.
- In any case a sealant is required in order to obtain high corrosion resistance.
- The PERMA PASS® EXP black is suitable for rack and barrel application. Barrel application has preferably should to be done externally using a centrifuge.




Example:
ZnNi ZINCROLYTE® NCZ 315
+ PERMA PASS® EXP black trivalent black passivate
+ ENSEAL® 38 DC transparent sealant




enthone

PERMA PASS® EXP-black Black Passivate on alkaline ZnNi NCZ Ni 315




- 1.200 parts on one flight bar
- NSS test:
 - 300 hrs to WR
 - > 720 hrs to RR



enthone


Nano-Material for Hex-Cr Free Passivates



enthone

Nanotechnology

- Nano-particles ≤ 100 nanometer
- Single step passivate/sealant
- Achieve ≥ 200 hours to white corrosion




enthone

Nano-particle Passivates

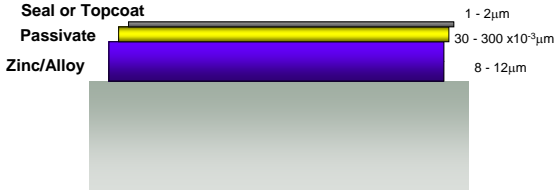
PERMA PASS® 5000

- New generation of hex-Cr free passivates
- Improved corrosion protection
- Provides self-healing capability
- Can eliminate sealant to reduce operating cost
- Meet specifications that do not allow sealants




enthone

Hex-Cr Free Coating System




Basis Metal




enthone

New Hex-Cr Free Coating System



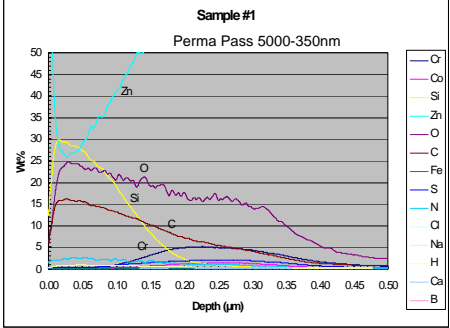
Basis Metal




enthone

Sample #1

Perma Pass 5000-350nm






enthone

Laboratory Evaluation

M10 x 1.5 Bolts



enthone

Laboratory Evaluation of M10 Hex Test Bolts

- Plated 50 M10 test bolts in lab scale barrel using ENTHOBRITE CLZ 933
- Passivate parameters tested
 - PERMA PASS 3082 - pH 2, 60s, 25 °C
 - PERMA PASS 3082 - pH 2.7, 75s, 25 °C
 - PERMA PASS 5000 - pH 2, 60s, 25 °C
 - PERMA PASS 5000 - pH 2.7, 75s, 25 °C

PERMA PASS 3082	15% by volume
PERMA PASS 5000 A	15% by volume
PERMA PASS 5000 B	4% by volume

pH 2.0 produces clear/ iridescent finish
pH 2.7 produces a blue color cosmetic finish

Objective: Exceed 200 hours to WR

Cookson Electronics

enthone

PERMA PASS 3082 *pH 2.7*



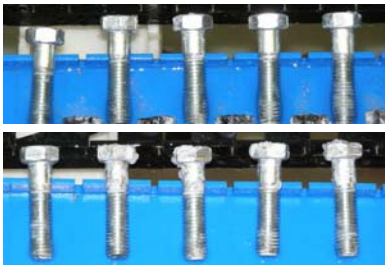
163 hrs.

234 hrs.
White Rust

Cookson Electronics

enthone

PERMA PASS 5000 *pH 2.7*



234 hrs

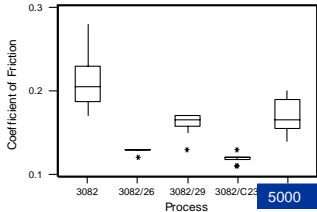
282 hrs.
White Rust

Cookson Electronics

enthone

Coefficient of Friction

Per DIN 946, M10 test bolts, acid zinc



Cookson Electronics

enthone

Production Evaluation *Fasteners*

Cookson Electronics

enthone

Motorcycle Bolt Evaluation

- Tests conducted at Tier 1 supplier
- Acid zinc plated bolts, 2 part numbers
- Specification is 200 hours to white rust

Cookson Electronics

enthone

Socket Head Cap Screws



0 hours

48 hours

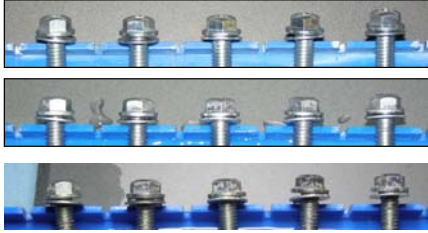
358 hours

10% PERMA PASS 3082, 4% OCS2, pH 2.07



enthone

Hex Head Bolts




0 hours

48 hours


358 hours

20% PERMA PASS 3082, 4% OCS2, pH 2.07



enthone


Pilot Plant Evaluation *Cast Iron Parts*



enthone

Pilot Plant Evaluation

- Cast iron brake calipers and brackets with acid zinc
- Passivate with PERMA PASS 5000
- Parts heat treated at 150°C, 2 hours
- Objective: 400 hours without corrosion products
- Results: Passed 400 hours without corrosion, 5% white rust >800 hours



enthone

Appearance after passivation at 26°C




enthone

840 hrs. with <5% white corrosion




enthone

PERMA PASS 3098 with Nano-material

120 h NSS-Test
240 h NSS-Test

enthone

PERMA PASS 3098 with Nano-material

360 h NSS-Test
480 h NSS-Test

enthone

PERMA PASS 3098 with Nano-material and ENSEAL 120

120 h NSS-Test
240 h NSS-Test

enthone

PERMA PASS 3098 with Nano-material and ENSEAL 120

360 h NSS-Test
480 h NSS-Test

enthone

Production Evaluation *Cast Iron Parts*

enthone

Customer Production Line *PERMA PASS 5000*

384 hours, <5% WR
Appearance of WR, 160 hours
552 hours, WR

720 hours, RR
720 hours, RR

enthone

Customer Production Line

PERMA PASS 5000

384 hours, <5% WR
Appearance of WR, 192 hours

552 hours, WR

720 hours, RR

720 hours, RR

enthone

Production Evaluation

Shock Absorber Unit Post Formed Parts

enthone

PERMA PASS® on Alkaline Zinc

Thick Film Passivate vs Nanopassivate, both with ENSEAL 110

Hot working Thick Film Passivate
Severe RR in crimping area
10 - 20 % WR on the surface.

Nanopassivate
Slightly WR and few RR in crimping area,
5 - 10 % WR on the surface.

480 hours NSS

enthone

Alkaline Zn + Nanopassivate vs ZnNi, transparent after 168 hrs NSS

Zn + Nanopassivate
Slightly WR in crimping area, **no RR**.
No WR on the surface.

ZnNi + transparent passivate
Very few WR in crimping area, **some RR**.
Only white haze on the surface, no WR.

168 h NSS

enthone

Alkaline Zn + Nanopassivate vs ZnNi, transparent after 360 hrs NSS

System 3
Zn + Nanopassivate

System 6
ZnNi

360 h NSS

enthone


Production Evaluation

Sensor Cover Zinc-Iron

enthone

PERMA PASS 5000 *Zinc Iron Alloy*

- Barrel plated zinc-iron alloy, off-line passivation
- Good blue color obtained at alloy concentration of 1% Fe
- Enables blue and black passivation from same electrolyte




enthone

PERMA PASS 5000 *Zinc Iron Alloy*

Hours NSS	Passivate Only	Passivate + Sealant
120	10 = no WR 4 < 1% WR	10 = no WR
240	6 = no WR 4 < 1% WR	8 = no WR 2 < 1% WR
400	4 = no WR 2 < 1% WR 1 = 1% WR 3 = 5% WR	7 = no WR 2 < 1% WR 1 = 1% WR
480	1 = no WR 4 < 1% WR 1 = 1% WR 4 = 5% WR	6 = no WR 1 < 1% WR 3 = 1% WR


Standard: 120 hrs. no WR; 480 hrs. no RR



enthone


Threaded Fastener Study

Acid Zn-Ni (KCL Ni) and Alkaline Zn-Ni (NCZ-315)



enthone


Threaded Fasteners



1: acid ZnNi
ZINCROLYTE KCL Ni-III,
not passivated

2: acid ZnNi
ZINCROLYTE KCL Ni-III
trivalent passivated in
PERMA PASS Ultra III

3: alkaline ZnNi
ZINCROLYTE NCZ 315
trivalent passivated in
PERMA PASS 3095

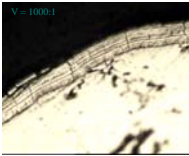


enthone

Threaded Fasteners

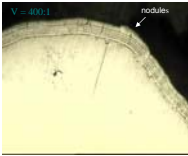
Results

Screw 1, acid ZnNi:
lamella structure with cracks




V = 1000.1

Screw 3, alkaline ZnNi:
lamella structure with nodules



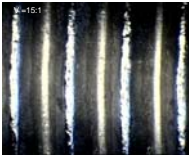

V = 400.1

The cross-section pictures were made by a light optical microscope (OLYMPUS PMG3).




enthone

Acid Zn-Ni without Passivate

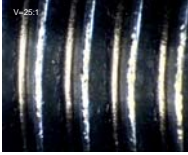




Photos of the thread-surface - light optical microscope (WILD M32) and scanning electron microscope




enthone

Acid Zn-Ni with Passivate

Photos of the thread-surface - light optical microscope (WILD M3Z) and scanning electron microscope



enthone

Alkaline Zn-Ni with Passivate

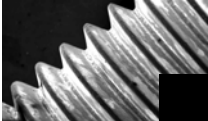



Photos of the thread-surface - light optical microscope (WILD M3Z) and scanning electron microscope

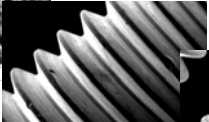


enthone

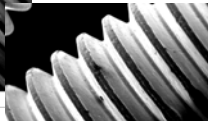
Threaded Fasteners



- Some mechanical damage on threads from tumbling in plating barrel
- Nodules pulled out during fastening




Acid Zn-Ni, no passivate



Alkaline Zn-Ni, passivate

Magnification 50X

Photos of the thread-surface - light optical microscope (WILD M3Z) and scanning electron microscope




enthone

Threaded Fasteners

Deposit thicknesses measurements

	Top	Flank	Core
Screw 1			
Acid ZnNi	5,5 µm ZnNi	5,5 µm ZnNi	5 µm
Screw 2			
Acid ZnNi	7 µm ZnNi	7 µm ZnNi	5,5 µm
Screw 3			
Alkaline ZnNi	12 µm ZnNi	11 µm ZnNi	7,5 µm



enthone

Thank you for your interest !

