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Keeping it all together is what fasteners are all about. At first, some may consider this a simple objective to achieve given what appears to be a relatively basic component. However, the ever increasing demands for higher durability, enhanced decorative appearance, extended warranty life, as well as meeting OEM design requirements and consumer preferences, have made 'keeping it all together', more than mechanical. Defined friction properties that are of paramount importance for reliable automatic assembly in manufacturing and safe re-assembly in maintenance procedures, OEMs and their tier suppliers have established comprehensive specifications to ensure exacting performance requirements are consistently achieved and maintained.

To address these challenges, a new generation of zinc-nickel corrosion protection coating systems have been introduced that reliably deliver durable, highly functional and appealing coatings for safely fixing components together. Currently being used by major plating facilities worldwide, the OEM approved coatings withstand exposure to a diverse range of global environmental conditions.

Over the last few years, new car warranties have evolved to go well beyond the standard five year anti-corrosion guarantee. Such extended warranty times call for improved corrosion protection on numerous automotive components. Within those components that contribute to the structural stability and functionality of a car, fasteners play a dominant role. Sufficient fastener quality throughout the service life is a crucial pre-requisite to be met in order to achieve the required high overall stringent OEM quality standards of today's automotive production.

This need for higher quality throughout the in-service life finds itself expressed in an ongoing change in the surface finishing industry from pure zinc layers towards zinc-alloy based sacrificial coatings. This transition is due to the ability of zinc-alloy coatings to generate higher corrosion protection. More specifically the zinc-nickel alloy provides the maximum protection to corrosion as the so called zinc-nickel gamma-phase (γ -phase) alloy can be achieved with a 12% – 16%-wt nickel alloy content from qualified plating solutions. The γ -phase describes a specific crystal structure of this intermetallic phase, which has proven to be highly beneficial for the highest performance cathodic corrosion protection coatings.

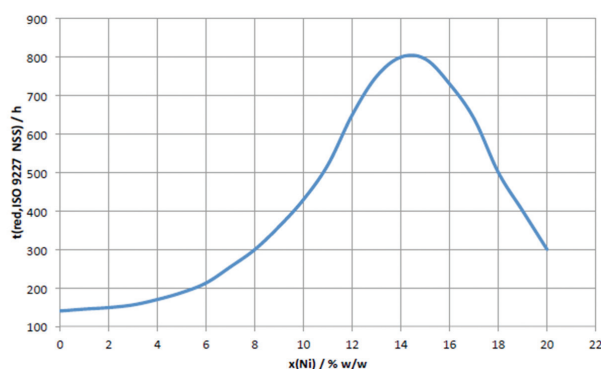
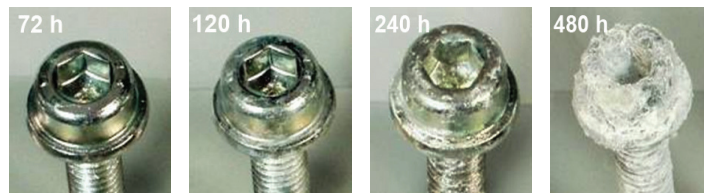
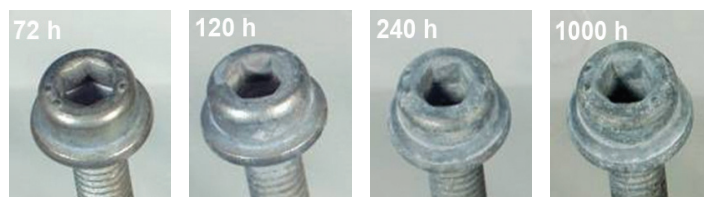


Figure 1: A diagram showing the basis material corrosion resistance to red rust in the neutral salt spray test versus the nickel incorporation rate in the plated zinc-nickel alloy layer (8 μ m) without any post-treatment (no passivation, no sealant) applied. The protection peaks with a maximum at 14% w/w Ni, best performance in the range of 12% – 16%-wt Ni.

A major advantage of zinc-nickel alloys over pure zinc coatings or other alloy coatings like zinc-iron is the high corrosion resistance from the plated alloy material without taking an additional post-treatment into account. Figure 1 shows the dependency of the neutral spray corrosion protection (ISO 9227 NSS) from the nickel alloy concentration without any post-treatment. An alloy composition of approximately 14% by weight nickel yields 700 – 800 hours to red corrosion as demonstrated in the testing. Industrial experience proves that >720 hours to red corrosion is safely met by this type of coating. This high corrosion protection together with less voluminous white corrosion products is a unique feature of the 12% – 16% γ -phase zinc-nickel alloy (Figure 2).



Zn with passivate. No sealant



ZnNi with passivate. No sealant

Figure 2: The difference between pure zinc and γ -phase zinc-nickel alloy without a sealant (only passivation applied), hours given are time in ISO 9227 NSS test. The zinc plated fastener shows voluminous white corrosion at 480h, whereas only a thin layer of white haze forms on the zinc-nickel coated fasteners (all 8 μ m – 12 μ m Zn resp. ZnNi, thick film passivate)

Through the additional application of high performance sealants on top of the passivated surface, the corrosion resistance is significantly reinforced as well as other functional properties such as adjusted coefficient of friction, improved decorative appearance, etc. Reinforced by such sealants, zinc-iron (0.5% – 1% Fe) alloy or even pure zinc coatings show excellent corrosion protection results (Figure 3 – see next page).

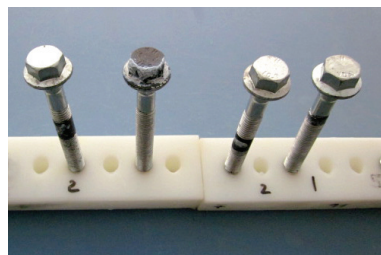


Figure 3: 720h ISO 9227 NSS exposure to zinc (top), zinc-iron (middle) and zinc-nickel (bottom) plated, passivated and sealed (ENSEAL 26) fasteners. Application of a sealant significantly increases the fasteners corrosion protection



The major advantage of the zinc-nickel coating is that it provides superior corrosion protection from the bare zinc-nickel layer, independent of the chosen post-treatment.

The protection of zinc or zinc-iron coatings strongly depends on the post-treatment, most importantly the sealant applied. Once this post-treatment layer is damaged, corrosion

will proceed at an accelerated pace and also create more voluminous white corrosion products. Harm to these layers can be due to any mechanical impact in assembly (tools) or service life (stone chipping, etc). In addition to the low corrosion rate of the zinc-nickel alloy in comparison to zinc and zinc-iron layers, the γ -phase zinc-nickel alloy features increased wear resistance, due to its high hardness of 500HV – 550HV (14% Ni) compared to lower hardness of zinc (approximately 100HV) and zinc-iron (0.5% – 1% Fe) layers (150HV – 250HV).

High strength fasteners of $>1,000\text{N/mm}^2$ tensile strength (property class 10.9 and higher) suffer a risk of hydrogen embrittlement. With increasing tensile strengths being used in fastener technology, this is a critical factor.

Very long experience in industrial zinc-nickel fastener finishing and scientific investigations have shown that the zinc-nickel alloy is unique in terms of its dramatically reduced risk for hydrogen embrittlement¹. Pure zinc coatings or other zinc alloy coatings bear a significantly higher risk to cause hydrogen embrittlement. This very advantageous property of the zinc-nickel alloy has made it a prime selection for cadmium substitution in the aviation industry, even on very high strength steel materials of $>1,400\text{N/mm}^2$ and therefore should always be taken into consideration for finishing of even very high strength fasteners.

Last but not least, zinc-nickel coatings are the preferred choice where thermal resistance of the layer is needed, due to the coating's ability to maintain the corrosion protection, even after being subjected to elevated temperature. This makes zinc-nickel coatings the preferred choice, for example for automotive applications – such as brake components or engine compartment parts.

The application of zinc-nickel alloys is widely conducted using alkaline electrolytes for the finishing of fasteners and many other steel based automotive components. Alkaline ZnNi plating solutions offer an excellent thickness distribution even

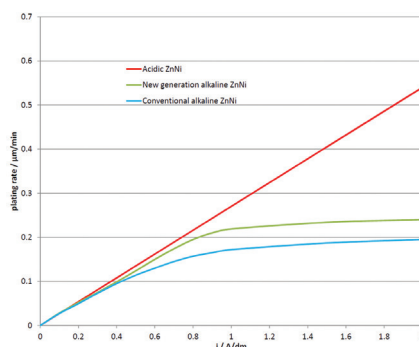


Figure 4: Plating rates obtained from an acidic zinc-nickel electrolyte (red) and from an standard alkaline zinc-nickel electrolyte (blue) as well as from a new generation alkaline ZnNi electrolyte (green) plotted vs current density

on complex formed parts and are a well suited process for example on rack plating of complex formed stamped steel parts.

Alkaline plating solutions are also widely employed for barrel application of bulk parts. Here, the advantage of an excellent thickness distribution over the part is less relevant than in rack plating operations. Due to the nature of the barrel plating application, the different thickness distribution of the electrolytic process has only a minor impact on fastener plating.

Technically, a good thickness distribution translates into a lower cathodic current efficiency at higher current densities (Figure 4). Therefore to enjoy a good thickness distribution one trades off some plating efficiency on certain areas of a workpiece for a more even plated layer thickness.

An attractive alternative to the well known alkaline zinc-nickel electrolytes is the acidic zinc-nickel electrolytes of the latest generation. An outstanding feature of the latest generation of acidic zinc-nickel electrolytes such as the newly developed ZINCROLYTE® KCl-Ni IV is the very high efficiency of $>90\%$ which is consistently maintained over the entire bath life.

With approximately 30% higher current efficiency than conventional alkaline zinc-nickel electrolytes have, the latest generation of alkaline ZnNi plating solutions provides an additional alternative where the highest performance from alkaline plating solution is needed.

The nickel incorporation is of paramount importance to achieve the desired high corrosion protection. Strict control of 12% – 16% of Ni in the alloy is crucial to obtain the optimum corrosion protection of zinc-nickel alloy coatings.

With the latest generation of acidic zinc-nickel electrolytes a constant and narrow ranged nickel incorporation rate is achieved in rack and barrel application on the same level as obtained from alkaline electrolytes. This makes acidic zinc-nickel an application alternative for the same purpose: Yielding exactly the same kind of layer is of paramount importance to ensure the same performance of the finished component.

The crystal structure and orientation of the zinc-nickel layer are both highly important to achieve the desired physical and chemical properties of the coating and can be taken as a critical indicator to characterise the layers.

The structure and the orientation of the electroplated layer from either electrolyte can best be assessed by X-ray diffractometry (XRD). The diagrams obtained for layers from conventional alkaline zinc-nickel ZINCROLYTE NCZ 315 Plus, from the acidic ZnNi ZINCROLYTE KCl-Ni and from the new alkaline ZnNi electrolyte ZINCROLYTE Sprint™ do not show significant differences (Figure 5 – see next page). Thus the resulting zinc-nickel layer is the same zinc-nickel material showing the same crystallographic structure and texture, independent from choosing an acidic or alkaline electrolyte.

¹ W. Paatsch, R. Landgrebe, M. M. Lohrengel, *Mat. Sci & Eng. Tech.*, 2008, Vol 39, Issue 1, 75-78

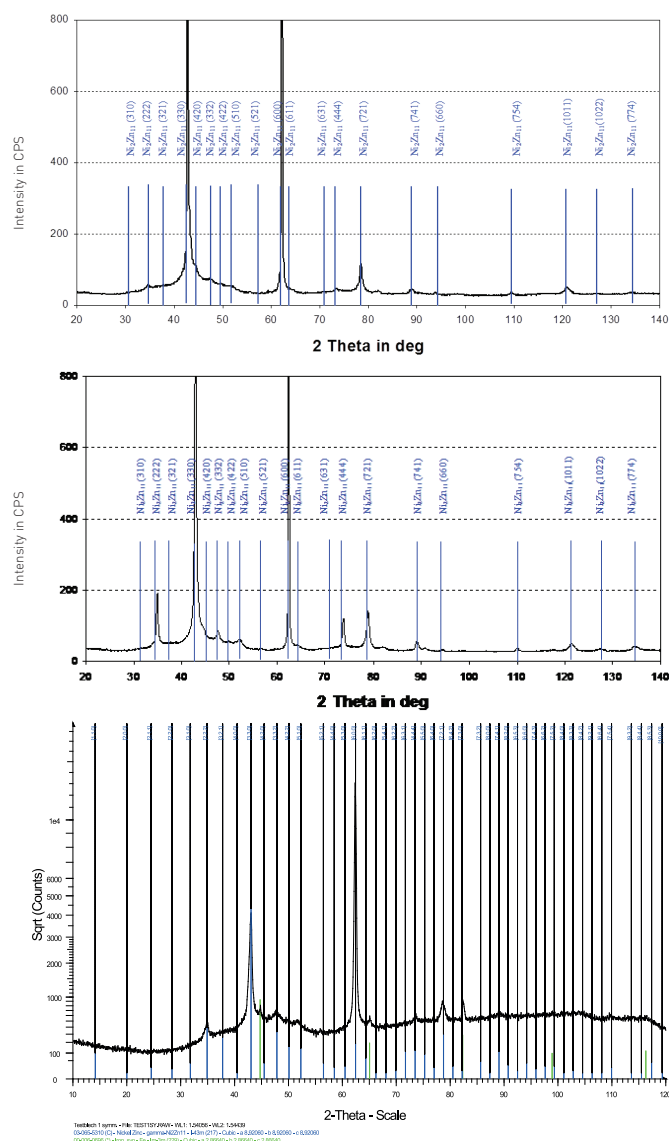


Figure 5: XRD diagrams (Cu K_{α} -radiation) of ZnNi on mild steel from conventional alkaline ZINCROLYTE NCZ 315 Plus (top), acidic ZINCROLYTE KCI-Ni electrolyte (middle) and new generation alkaline ZINCROLYTE Sprint (bottom) all plated at 15% Ni. All layers bear the same texture, preferred (330), (600) orientation indicating same columnar γ - Ni_2Zn_{11} phases

Therefore, the choice for the best suited electrolyte for the application in question can technically be met based on performance preference. Significantly reduced plating time does not only contribute to cost savings, but also reduces the mechanical stress to the fastener during the plating sequence and supports perfect thread appearance with low mechanical damage.

Comparing M8 x 40 fastener plating in barrel application using an acidic versus the alkaline electrolyte set up to yield the same thickness in the head area results in the situation as shown in Figure 6. With virtually the same thickness being achieved on the fasteners head, the difference in thickness in the middle of the fastener is minor.

The differences in plating times are major as shown in the example given. Application of a conventional alkaline zinc-nickel electrolyte requires plating for 75 minutes until the desired thickness is achieved. Using the latest generation of alkaline ZnNi electrolytes (ZINCROLYTE Sprint), the same result is achieved in approximately 50 minutes. The highest plating rate is provided by the acidic ZnNi electrolyte, which needs only 42 minutes to achieve the demanded thickness.

Another important advantage in the new alkaline process is that the high plating performance is achieved consistently without the use of any auxiliary equipment.



Figure 6: M8 x 40 bolt plated to the same thickness on the head (11.6μm – 11.9μm) in the three different zinc-nickel electrolytes: A conventional alkaline plating solution (left, ZINCROLYTE NCZ 315 Plus, 75 min plating time), newest development alkaline plating electrolyte ZINCROLYTE Sprint™ (middle, 50 min plating time) and the new generation acidic electrolyte ZINCROLYTE KCI-Ni IV (right, plating time 42 min). Minor differences in thickness distribution

The clear advantage from choosing an acidic electrolyte for barrel application is the higher plating speed resulting in shorter plating times and higher throughput making the process economically well suited for a bulk application. Additionally, the excellent initiation behaviour of the electrolyte allows for very fast coverage even on materials with a low hydrogen over potential such as particular case-hardened, carburised fasteners.

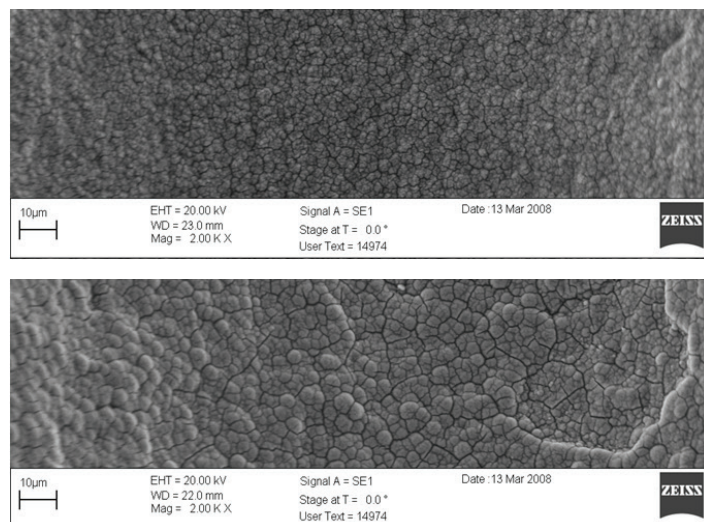


Figure 7: Bottom section of screw threads showing a fine grained deposit on the top image from the acidic ZnNi electrolyte and a more coarse grained morphology with more nodules on the bottom image (conventional alkaline electrolyte)

Acidic ZnNi, as well as the new alkaline ZINCROLYTE Sprint electrolyte, already provide smoother surfaces (Figure 7): An excellent pre-condition for good control of friction properties. Combined with well matched post-treatment processes such as PERMA PASS® trivalent chromium passivations and ENSEAL® lubricated sealants, such smoother surfaces are the perfect pre-requisite for consistently meeting narrow ranged coefficients of friction, resulting in constant clamping forces achieved in torque controlled automatic assembly applications (Table 1 – see next page).

	μ_{tot} vs steel	μ_{tot} vs aluminium
Conventional alkaline ZnNi	0.12	0.21
New ZnNi electrolyte (acidic)	0.12	0.18

Table 1: Coefficient of friction measured according to ISO 16047 of M10 fasteners plated in alkaline zinc-nickel from conventional alkaline ZnNi and acidic zinc-nickel. Post-treatment in both cases trivalent passivate (PERMA PASS® Ultra III) and a sealant with integrated lubricants (ENSEAL 21)

Choosing the right lubricated sealant process, depending on OEM demands, allows for excellent control of the coefficient of friction of the fastener in different ranges as required by the OEMs (Table 2).

	μ_{tot}
ENSEAL® 21	0.09 – 0.14
ENSEAL® 1303	0.10 – 0.16
ENSEAL® 26	0.12 – 0.18

Table 2: Coefficient of friction ranges matching different automotive OEM requirements. Measurement according to ISO 16047

Conclusion

Applications of zinc-nickel for cathodically protecting sacrificial coatings are increasing over the recent years, particularly in the automotive industry, and this process

is gaining more and more pace. This is clearly as a result of the many benefits of this coating:

- Highest corrosion protection already from the plated zinc-nickel layer.
- Increased wear resistance.
- Dramatically lower risk for hydrogen embrittlement compared to pure zinc or zinc-iron.
- Excellent thermal stability of the coating.
- Improved friction properties with appropriate post-treatment processes.

Resulting from this list of important benefits, the increased efficiency and productivity of the zinc-nickel plating process for high-throughput applications is a strong argument to best utilise existing production lines. The latest generations of acidic plating solutions (ZINCROLYTE KCl-Ni IV) and the alkaline process (ZINCROLYTE Sprint) open up the possibility to choose the best suited ZnNi plating electrolyte technically based just on the type of application and delivery specification demands. Excellent control of the nickel incorporation in the zinc-nickel gamma-phase region is crucial and is achieved with all discussed electrolytes.

Improved morphological features of the new generation electrolytes ZINCROLYTE Sprint and ZINCROLYTE KCl Ni IV provide excellent pre-conditions for fastener finishing with highest performance, in terms of surface properties as well as optimised productivity. ■

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