Controlled Liquid Ionic Nitrocarburizing Processes (TENIFER® and ARCOR®) as Alternative to Galvanic Coatings

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It is well known that due to their process characteristics, like best reproducibility on high quality level, nitrocarburizing in ionic liquids provides excellent resistance to wear, pitting, galling, seizure and surface fatigue resistance to the treated parts. However, the corrosion protection is still moderate. This problem can be solved by post heat treatment in oxidizing salt melts, producing a very thin but compact oxide layer on the surface of the nitride layer. Combined with polishing and impregnation the oxidized parts can have smooth, attractive black surfaces allowing dramatic improvements in corrosion resistance up to 1000 hrs in salt spray tests without loosing the above mentioned benefits.

This article discusses the application of the Controlled Liquid Ionic Nitrocarburizing (CLIN) processes like TENIFER® and ARCOR® to replace galvanic coatings like chrome, nickel and zinc plating due to excellent corrosion resistance and wear properties and highlights economical and environmental advantages of their usage. Due to easy handling, complex plant equipment is not required. The process times are rather short and allow flexible work without building up bigger buffer capacities for the work load.

1. INDRODUCTION

CLIN is a family name of modern and environment friendly processes for nitrocarburizing and oxidation of steel and cast iron. Diffusing nitrogen and carbon results in a so called compound layer, which possesses a non-metallic character. The outstanding advantage of this edge zone in relation to other coatings is the firm compound diffused on the base material and not applied on the surface. Therefore they exhibit a very good adhesion and crack sensitivity is clearly reduced. Depending upon material used these layers possess hardnesses from 800 to 1500 Vickers. The compound layer is supported by the underlying diffusion layer. CLIN treated parts offer eminent protection against wear, seizure, galling, pitting and fatigue.

2. PROCESS CHARACTERISTICS

Basically all kinds of ferrous material can be nitrocaburized in salt melts without any special preliminary pre-treatment, such as tool steels, mild steels, valve steels, austenitic steels, cast iron or sintered materials. The process sequence is not complicated. After a short pre-cleaning and pre-heating in air to 350 - 400 °C, the parts are nitrocarburized in the salt melt, generally for 60 - 120 minutes. Treating temperature is usually 570 - 590 °C. In special cases lower (480 °C) or higher temperatures (630 °C) are possible. For quenching, water, air, nitrogen, vacuum or an oxidizing cooling bath are used. Thereafter the charge is cleaned with hot water in a cascade. For the nitrocarburizing melt only the following few parameters have to be controlled:

- Chemical composition of the melt
- Treatment temperature
- Treatment time

Salt melts possess an exceptional high offer of nitrogen in comparison to other treatment media. The nitrocarburizing process starts immediately after immersion into the liquid salt bath. Already after a few minutes there is a formation of a compact compound layer. The industrial used salts base upon non-toxic sodium and potassium cyanate as nitrogen source. Due to reaction on the part surface alkali cyanate transforms into carbonate whereas the composition of the salt melt only changes slowly. Continuously adding the non-toxic, polymeric organic regenerator the decomposition product carbonate is recycled into active cyanate directly within the melt. Because having practically no change in volume no bail out salt accrues from the desired adjustment of the composition (see fig. 1).

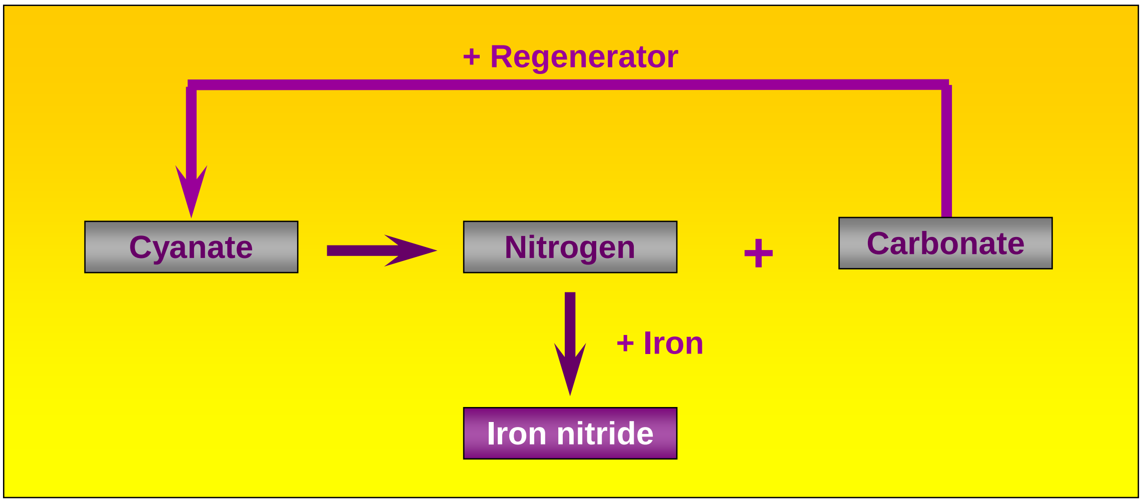
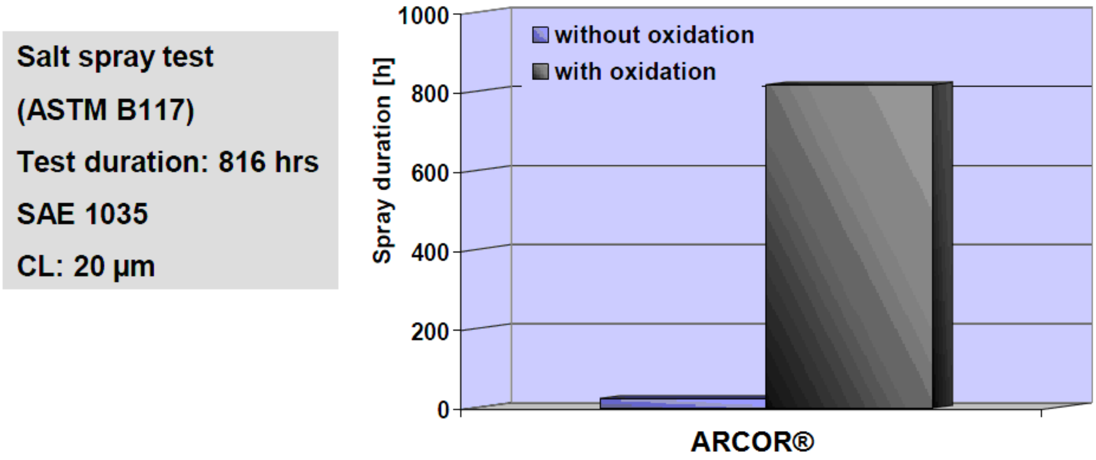


Fig. 1: Principle of Regeneration

The special characteristic of CLIN treated parts is the almost mono phase ε - Carbonitride compound layer with very high nitrogen content of 6 - 11 mass-% and carbon content of 0.5 - 2 mass-%. At the usual treatment times of 60 to 120 minutes the compound layer reaches 10 - 20 µm. With increasing alloying proportion the layer growth decreases.

3. INFLUENCE OF POST-OXIDATION TO CORROSION RESISTANCE

CLIN treated parts are well know for their excellent resistance to wear, pitting and fatigue. Furthermore the tendency to galling or sticking is remarkably reduced. Only corrosion protection is moderately increased. But, at direct quench of the parts into an oxidizing salt melt and if necessary, followed by an impregnation step, corrosion resistance can be dramatically improved. As it is demonstrated in fig. 2 the average corrosion resistance of a SAE 1035 steel nitrocarburized part shifted from 24 hrs to 810 hrs until first sign of corrosion was visible on specimens exposed to a salt spray test according ASTM B117. In all cases only single rust spots were visible when the parts failed, never bigger areas were affected.



Salt spray test
(ASTM B117)
Test duration: 816 hrs
SAE 1035
CL: 20 µm

Fig. 2: Improvement of corrosion resistance by oxidizing quenching

Fig. 3 shows the quality of the compound layer of parts who were passing the complete test distance of 1008 hrs. Besides a slightly darkening effect on the top of the layer and its pores the layer itself conserved an excellent condition. Reasons for this high level are the formation of a thin, but compact magnetite layer (Fe_3O_4) on the surface and beneath a compound layer which exists predominantly of ε - Carbonitride. Micro-sections confirm that the thickness of the magnetite layer is not more than 1 µm. By using liquid oxidizing salts as quenching media the top of the nitride layer is transformed into magnetite by an exothermic reaction. If the parts are oxidized after cooling down to room temperature, the rise in corrosion resistance will be lower.

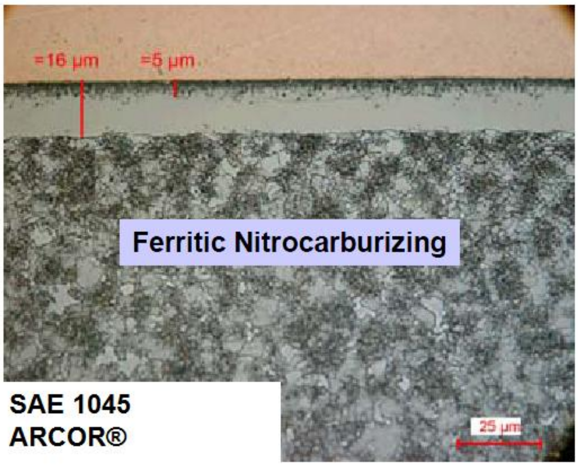


Fig. 3: Quality of compound layer after 1008 hrs in salt spray test

Fig. 4 shows the corrosion resistance in salt spray test of various galvanic processes in comparison with TENIFER® (with post-oxidation). Even after a test period of 500 hours no corrosion attack was visible on the surface of TENIFER® treated piston rods. Depending on the component geometry and roughness resistance in the salt spray test reach up to 500 hours or more. In principle, the corrosion resistance increases with decreasing surface roughness.

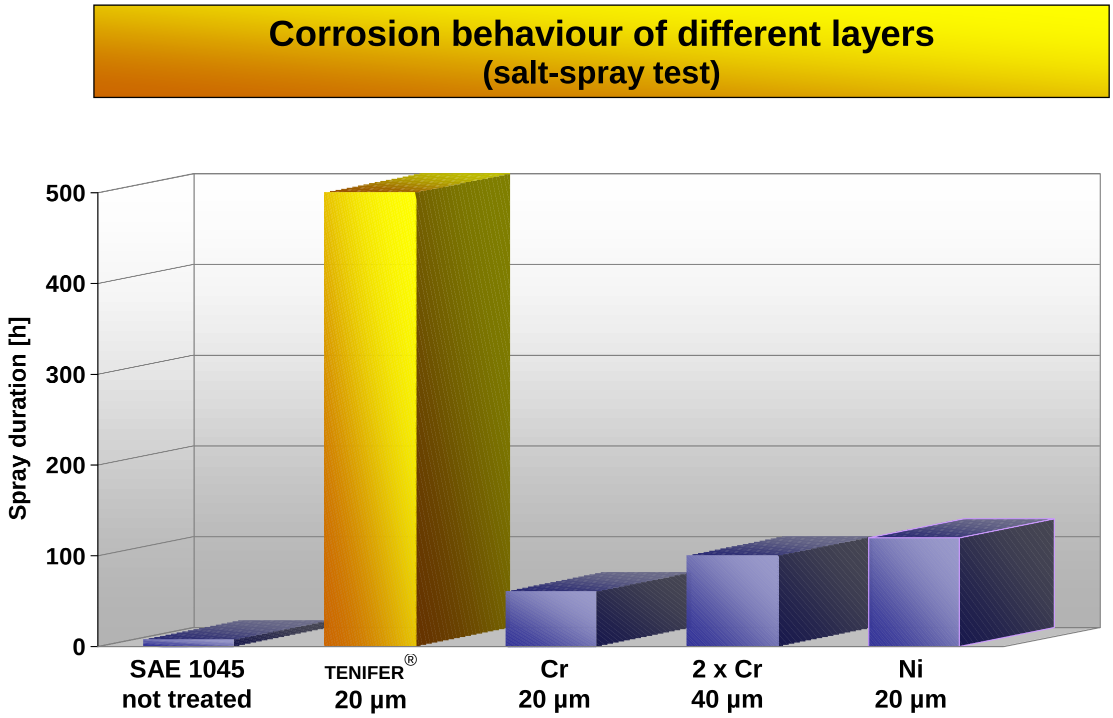
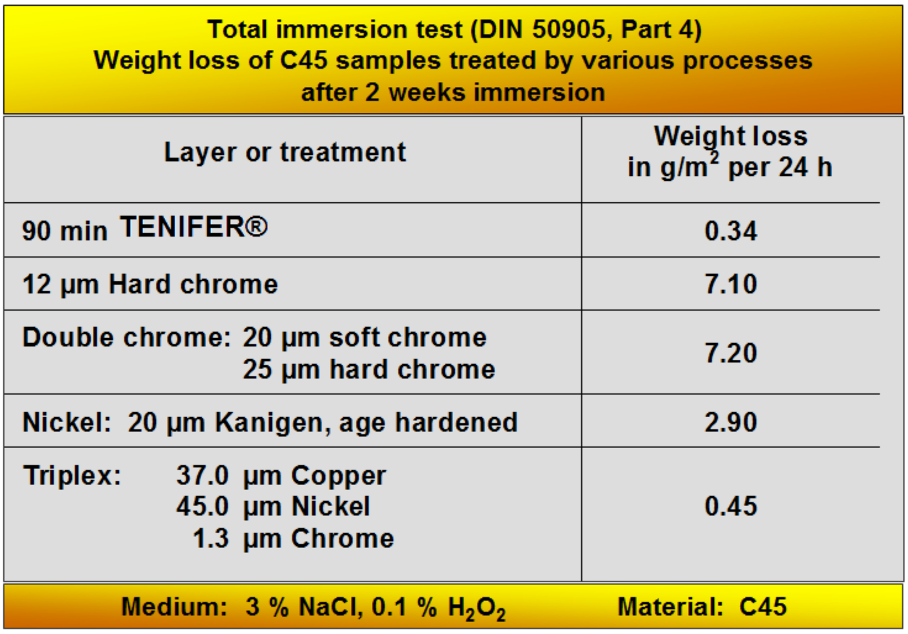


Fig. 4: Salt spray corrosion resistance of galvanic processes in comparison with TENIFER®

Fig. 5 shows the corrosion resistance of C45 (SAE 1045) steel samples submitted to a total immersion test during a period of 2 weeks (according to DIN 50905, part 4) of various galvanic processes in comparison with TENIFER® (with post-oxidation). With an average weight loss of 0.34 g/m² per 24 hours, the TENIFER® samples resisted much better than the electrical or chemical plated samples. For the sample coated with 12 µm hard chrome and even for the 45 µm double chrome layer, the weight loss was more than 20 times higher in comparison with the TENIFER® treated samples. Only for the triplex layer (37 µm copper, 45 µm nickel, 1,3 µm chrome) the corrosion resistance is comparable with the TENIFER® treated samples.



Total immersion test (DIN 50905, Part 4)
Weight loss of C45 samples treated by various processes
after 2 weeks immersion

Layer or treatment	Weight loss in g/m^2 per 24 h
90 min TENIFER®	0.34
12 µm Hard chrome	7.10
Double chrome: 20 µm soft chrome 25 µm hard chrome	7.20
Nickel: 20 µm Kanigen, age hardened	2.90
Triplex: 37.0 µm Copper 45.0 µm Nickel 1.3 µm Chrome	0.45

Medium: 3 % NaCl, 0.1 % H_2O_2 **Material: C45**

Fig. 5: Total immersion corrosion resistance of galvanic processes in comparison with TENIFER®

It is also well known that Controlled Liquid Ionic Nitrocarburizing (CLIN) processes like TENIFER® and ARCOR® when combined with post-oxidation in salt melts produce far superior corrosion resistance in comparison with other nitrocarburizing processes like gas or plasma.

4. APPLICATIONS

Valves in combustion engines are parts with high demands in respect of thermal stress, wear and corrosion resistance (see fig. 6). Compared to the former usual chrome plating the manufacturing costs can be reduced by nitrocarburizing, because the induction hardening and the final grinding can be omitted. Furthermore, the stem of the exhaust valve must not be made from induction hardening steel. The valve can be completely manufactured of heat resistant austenitic steel. Meantime, more than 250 million valves per year are treated in salt melts. The treatment times for CLIN processes ranges between 15 and 90 minutes according to specification. Depending upon plant size the batch sizes varies from 2500 to 4000 parts. A productivity of less than 1s per valve is thus accomplished. As well, due to short treatment times, no big buffer capacities even for changing geometries, materials or requirements are necessary.

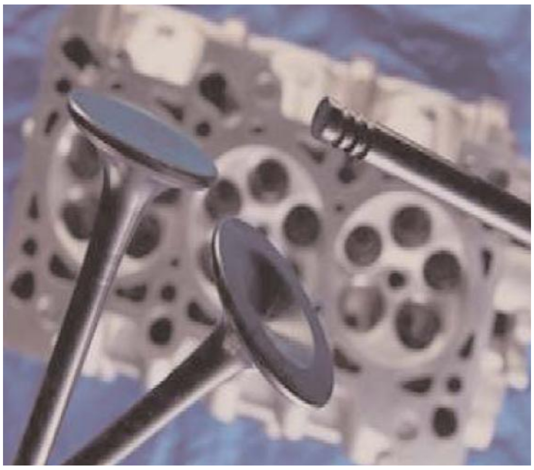


Fig. 6: CLIN treated valves

The salt bath nitrocarburizing in combination with oxidizing post treatment is more and more applied for piston rods, hydraulic cylinders or bushings. Materials, such as construction steel, unalloyed or low alloyed steel are used. The demanded holding time of the salt spray test is mostly 144 hrs without corrosion spot. In some cases the requirement is 400 hrs, which is also obtained. Figure 7 shows representative a gas spring piston rod, which is employed in the automobile and aircraft industry, in mechanical engineering or in office chairs. By substitution of the chrome layer remarkable cost savings have been achieved. The nitrocarburizing treatment is performed in a fully automated plant. The combination of up to 4 nitrocarburizing furnaces within one plant enables cycle times of 0.5 - 0.6 s per piston rod.

Fig. 7: CLIN treated gas spring rods

The driving axle of the wind screen wiper was mostly used to be zinc plated or galvanized with nickel, but during operation corrosion problems often occurred. Furthermore, on galvanic coated parts the helical gearing is relatively soft, so that within service life it tends to slip through. Meantime, more than 50 million/year of these axles are CLIN treated (see fig. 8) and are used by almost all leading automotive manufacturer. The thread has a better torsion resistance and so it allows at installation to fix the counter nut with a higher torque. Depending on the construction and end customer the corrosion resistance is up to 400 hrs in the salt spray test. The nonmetallic character of the nitrocarburizing layer also leads to a lower friction coefficient at the run of the axle within the aluminum housing. As a result of the high nitrogen offer in the salt melt as well as the robustness of the processes better and more consistent results are achieved under production conditions as with other nitrocarburizing processes.

Fig. 8: CLIN treated wiper shafts

5. PLANT TECHNOLOGY

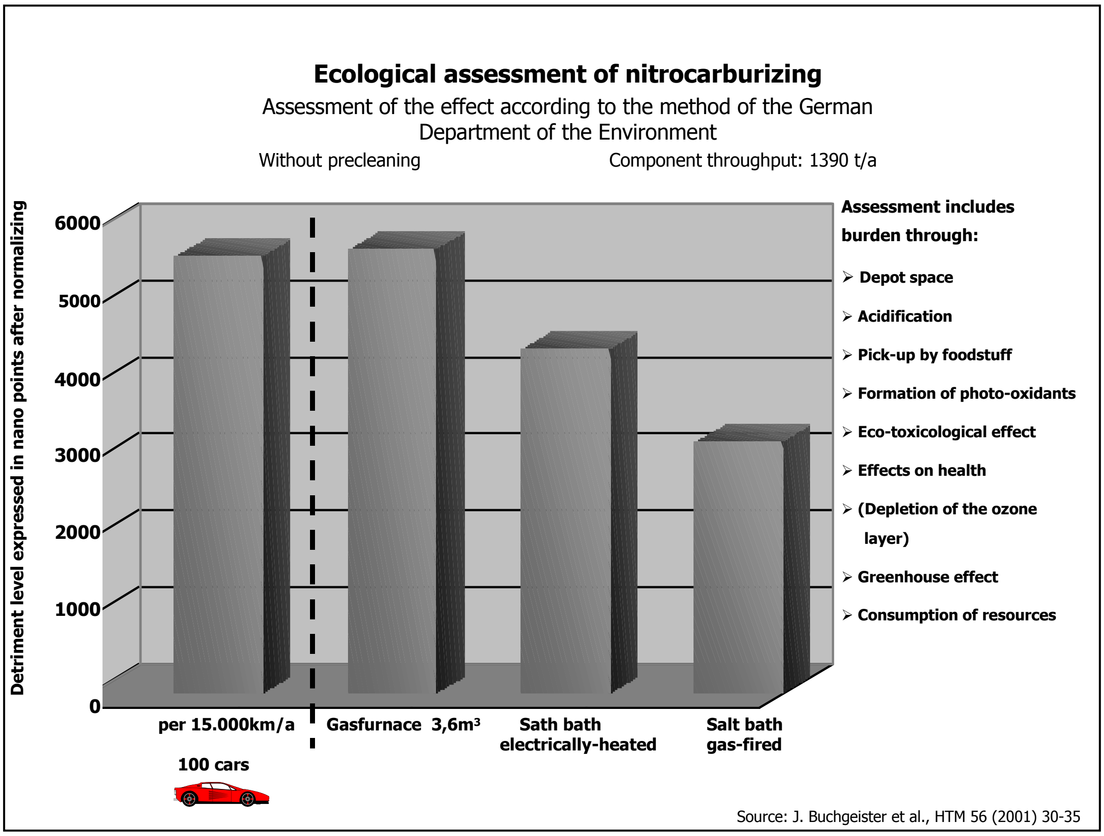
Meanwhile, it is understood that the heat treatment in liquid salts can be performed in automated computer controlled plants. For this purpose, there are open and capsule plants available. The automatic plant shown in figure 9 is placed in a production hall and treats serial parts for in-house production. A striking feature of this plant is the spotless working environment.

Fig. 9: Computer controlled CLIN plant

Due to short treatment times, there is no need to create big buffer capacities. The loading of the jigs is performed directly at the machining center. The computerized control system allows the on-line control of the parameter as well as complete batch documentation. Labor costs are reduced to a minimum. Among loading and unloading and input of the batch data the user has only to empty the filtration device once or twice a week and to fill up the operating supplies. The plant component is provided with a computerized filling level control and notifies the user to top up when necessary. The refilling of the salt, respectively the regenerator is performed outside of the capsule in a special apparatus so that the operator has neither to interfere into the heat treating process, nor to work directly at the furnace.

It has further to be mentioned that the plant is run waste water free and is featured with an efficient exhaust air purifying equipment. The prescribed limit values of harmful substances are below of dimensions. Therefore, it is absolutely no problem of getting authorization for starting new plants.

In addition an ecological assessment of nitrocarburizing, published by the University of Bremen in 2001, resulted that from an ecological point of view, salt bath nitrocarburizing (CLIN) is more favourable than gas nitrocarburizing (Fig. 10). If the study is considered objectively, the opinion often expressed that salt bath technology harms the environment, and therefore does not conform to present-day environment philosophy, cannot be confirmed.



Source: J. Buchgeister et al., HTM 56 (2001) 30-35

Fig. 10: Ecological assessment of nitrocarburizing

6. CONCLUSION

CLIN is in most cases the ideal alternative for galvanized layers, for distortion afflicted hardening processes and as well for gas or plasma nitrocarburizing processes. It also finds increasingly application as alternative to expensive corrosion resistant steels.

On the basis of the following specific process characteristics CLIN processes offer an excellent reproducibility on high quality level.

- No complex pre-cleaning necessary
- Homogeneous and very large offer of nitrogen in the entire melt
- Quick and constant heat transfer
- Only few process parameters are to be considered
- Structure and density of load has only minor effects
- Simple, automatable process engineering

The results achieved under test conditions can usually be easily transferred into series production.

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