Liquid Nitrocarburizing with low environmental impact for tribological applications: heat transfer and energy management

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Liquid nitrocarburizing is a well-known surface treatment when it comes to tribological parts and systems. The surface layers formed through liquid nitrocarburizing processing (compound layer and diffusion zone) make it possible to combine the corrosion, wear, and fatigue resistance properties of the treated materials (mainly ferrous alloys, from low-carbon to high-alloy steels and even cast iron) while enhancing their tribological behavior. Based on its worldwide presence, its continuous improvement and high industrial maturity, HEF Groupe's Liquid Nitrocarburizing is the technology ready for future with its CLIN 4.0 program and it ambitious ECOCLIN program which allow the recycling of effluents from nitriding installations and their transformation into directly reusable consumables. That is why HEF's SBN is proven to be not only an alternative to other surface treatments (such as Chromium plating) on both technical aspects and price competitiveness but also a real solution answering the current environmental challenges: optimized energy consumption and low natural resources impacts.

Keywords: tribology, energy sobriety, X-ray, liquid nitrocarburizing, recycling, low environmental process.

1. Tribology and surface treatment

In the field of tribology, surfaces in relative motion interact, and hence surface treatments and coatings play a crucial role in improving component performance and durability.

Traditionally surface treatments were used to compensate for poor design choices, such as materials or dimensions, they are now included in the project or design stage when developing a new product or improving an existing system.

Today, surface treatments and coatings have become a value driver, offering manufacturers significant benefits by allowing them to create high-performance products; simplify production processes by streamlining procedures; or reusing strategically or economically advantageous metals.

Of all the surface treatments and coatings available, thermochemical treatments – particularly nitrocarburizing treatments – have established themselves as the best solutions to tackle current tribological challenges. Since a single treatment can respond to the critical needs of the interfaces of moving parts (friction capacity/wear resistance/corrosion resistance), they are seen to be the perfect solution for numerous applications.

| Carburize | | Carbonitride | | Ferritic nitrocarburize | | Boronize | | Nitride | |
|--|----------|---|----------|--|----------|---|-----|--|---------|
| ack Gas | Salt Ion | Gas | Salt Ion | Gas | Salt Ion | Pack | Gas | Pack Gas | Salt Io |
| Diffuses carbon into the steel surface. Process temperatures: 1600–1950°F (870–1056°C). Case depth: medium | | Diffuses carbon and nitrogen into the steel surface. Process temperatures: 1550–1650°F (845–900°C). Case depth: shallow | | Diffuses carbon, nitrogen, sulfur, oxygen (individually or combined) into the steel surface. Process temperatures: 1050–1300°F (565–705°C). Case depth: shallow | | Diffuses boron into the steel surface. Process temperatures: 1400–2000'F (760–1095°C). Case depth: shallow | | Diffuses nitrogen intr the steel surface. Process temperatures: 600–1020'F (315–550'C). Case depth: shallow | |

FIGURE 8.1 Comparison of various diffusion surface hardening techniques. (From Pye, D., Practical Nitriding and Ferritic Nitrocarburizing, ASM International, Cleveland, OH, 2004.)

2. Focus on liquid ionic nitrocarburizing

Among all the treatment variant, Liquid ionic nitrocarburizing has proven to be the process variant with the most significant advantages in tribological systems. In this method, the material is immersed in a bath of molten salts providing a nitrogen and carbon source. The high heat transfer and specific composition of the salts allow the nitrogen and carbon to diffuse into the material very quickly for enhanced corrosion resistance while limiting part deformation thanks to the lower temperature than other thermochemical treatments and the possibility of using staged cooling.

On the metal component surface, the diffused nitrogen firstly reacts with iron to form a compound layer that contains a single-phase or two-phase structure of nitrides ε and γ' . Their proportions differ depending on the substrate and the operating conditions. This layer (with an intrinsic hardness between 700 and 1200 HV) helps increase the surface hardness of the treated material but also plays a vital role in the friction and anti-corrosion properties of the nitrated components.

The large quantity of atomic nitrogen in the top part of the compound layer, facilitated by the abundant active species in the salt bath, also enables molecular nitrogen microcavities to form, creating surface porosity with beneficial properties.

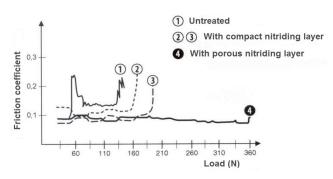
Finally, this surface transformation usually ends with an oxidation phase, using a passivation reaction to convert the nitrided surface into iron oxide. This magnetite-type oxide is aesthetic and offers improved anti-corrosion properties.

This oxidized porous surface gives improved surface wettability typical of liquid nitriding and is used for two specific properties:

- Improved corrosion resistance (up to 1000 hours in a salt spray for parts with simple geometry and

often up to 500 hours in a salt spray for parts with complex geometry) by adding a light, specifically developed impregnation to this porous layer during post-treatment and absorption.

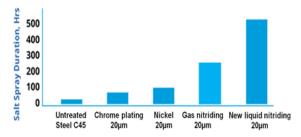
- Prolonged hydrodynamic lubrication, delaying the risk of critical wear in parts subject to friction forces under high loads in the event of the lubricating film rupturing (see below Figure, which shows the benefit of the porous nitride surface layer compared to the compact nitride layers that are achieved by traditional nitriding in a gaseous medium).



Graph showing improved friction by adding lubricant.

Below this compound layer, the lower quantity of diffused nitrogen penetrates the substrate's crystal structure (between the iron atoms). This penetration into the iron crystal lattice considerably increases the material's hardness and fatigue strength, increasing compressive stresses. This zone is called the diffusion zone. Its depth, hardness, and stress gradients help improve fatigue strength and surface resistance by providing a solid base for the compound layer.

As shown below, corrosion resistance performance is one of the liquid nitriding's significant advantages compared to other competing solutions. The graph in Figure 4 shows the salt spray corrosion resistance (measured according to international standard ISO9227) on samples (material C45) treated according to various technologies.



Corrosion resistance time measured according to ISO 9927 on a C45-type sample treated using various methods (exposure time before the first spots of red rust appear).

3. Controlled Ionic Liquid Nitrocarburizing with low environmental impact

Thanks to these versatile properties and rich of more than 60 years development in industrial conditions, Salt bath nitrocarburizing (SBN) has been able to adapt itself to match standards in many different fields (Aeronautics, Energy, Automotive, Construction Equipment, Military...). Thus, SBN is nowadays an essential surface treatment solution, globally established and recognized with more than 500.000 tons of parts yearly treated with SBN process. The safe liquid medium, in situ regenerated, used as nitrogen and carbon source permits homogeneous treatment of complex part's shapes. It also represents the highest robustness, stability and productivity compared to others thermochemical treatments (gas and plasma).

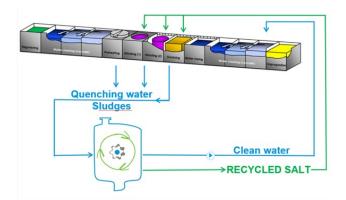
Based on its worldwide presence, its continuous improvement and high industrial maturity, HEF Groupe's Liquid Nitrocarburizing is the technology ready for future with its CLIN 4.0 program and it ambitious ECOCLIN program which allow the recycling of effluents from nitriding installations and their transformation into directly reusable consumables. That's why HEF's SBN is proven to be not only an alternative to other surface treatments (such as Chromium plating) on both technical aspects and price competitiveness but also a real solution answering the current environmental challenges: optimised energy consumption & low natural resources impacts.



CLIN[™] technologies (Controlled Liquid Ionic Nitriding, including

TENIFERTM/ARCORTM/QPQTM/MELONITETM/NUTRID ETM, TUFFTRIDETM etc.) developed by the HEF® Group are a significant improvement on the modern liquid nitrocarburizing technologies, further reducing their impact on natural resources.

As historical pioneers in regenerating salts, HEF® Group has applied its vertical integration strategy to these technologies to develop, patent, and roll out the ECO-CLINTM method. This innovative process enables the HEF® Group's nitriding installation by-products to be recycled into new consumables directly reused on the same lines.



Reusing the salts obtained by recycling by-products on treatment lines results in the following:

- Reduced impact on natural resources.
- Increased competitiveness of the treatment in the long term. This allows HEF® Group and its clients to reduce their dependency in terms of risk due to the cost of consumables and raw materials.
- Local manufacture of consumables, as close as possible to production lines worldwide, thus limiting the carbon footprint of consumables by reducing transport needs.
- The reuse and recycling of 99% of by-products: by reinjecting the recycled salt directly into production and by recycling the other products created during operation into materials that can be used by industry (cement plants in particular).

Using the ECO-CLINTM method, CLINTM technologies will eventually generate zero final waste and therefore become the nitrocarburizing technology with the lowest environmental impact.

4. Controlled Ionic Liquid Nitrocarburizing: heat transfer and energy management.

Regarding energy inflation, HEF Group has been able to limit its equipment consumption by first avoiding Electrical peak consumption (so that use of solar energy is now possible and feasible) and second by improving heat transfer to metallic components by use of liquid media, during the process. In that second point, advantage of liquid media is giving to molten salt bath technology a real and concrete advantage in energy management, versus gas processes.