

MECHANICAL VACUUM PUMP SELECTION CONSIDERATIONS FOR LOW PRESSURE NITRIDING, PLASMA NITRIDING AND NITRO-CARBURISING

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ABSTRACT

Low pressure nitriding applications typically involve the use of ammonia gas as the source of nitrogen. Careful consideration of material selection is needed for the vacuum pump system. In addition the process can generate significant quantities of hydrogen gas. Careful consideration of the dilution and removal of this explosive gas is needed for the vacuum pump system. In the plasma process there is the additional consideration of using nitrogen, argon and in particular water, which presents significant challenges to the safe and reliable operation of the vacuum pump system. This paper presents various solutions to these application challenges and provides guidance on how to select the right solution in low pressure and plasma nitriding.

KEYWORDS

vacuum, pumps, low pressure nitriding, plasma nitriding, nitro-carburising, safety, selection

INTRODUCTION

There are very many industrial applications where case hardening of steel components is a vital requirement, and these range from basic tool manufacture through to many types of machine components. Most particularly, combustion engine components and other moving parts are extensively processed for improved wear resistance and better fatigue performance, and this applies especially in the automotive industry. The range of component hardening processes is wide and includes specific techniques for chemically modifying steel surfaces by the incorporation of carbon, boron or nitrogen atoms into the metal surface structure through carburising, boriding or nitriding respectively. Of these processes, nitriding is especially suitable for a wide range of steels and can be used to produce extremely hard surface layers without changing the phase structure or introducing distortion, providing greatly enhanced wear resistance. This is ideal for many types of components designed for metal-to-metal contact. The degree of nitriding obtained, and hence the resulting surface properties of the work-piece, is controlled by adjusting various process parameters which govern the rate and depth of nitrogen diffusion into the metal surface.

Nitriding was historically developed using very high temperature molten salt baths in which the components are immersed in order to diffuse nitrogen atoms into metal surfaces. These are still used in situations where a quick turn-around is needed and where some minor component distortion, due to the high bath temperature, can be tolerated. However there are obvious safety and environmental risks with such facilities, and nitriding with gases is now generally preferred in many cases, especially since these operate at lower temperatures and produce much less risk of distortion, although these processes usually take longer.

There are two main gaseous processes currently in use - low pressure nitriding (LPN), and plasma (or ionic) nitriding (PN) - and both are vacuum processes. In both cases various measures are used

to control the thickness and properties of both the nitride compound layer (“white layer”) at the surface and the important diffusion layer (or case zone) underlying it where nitrogen is in solid interstitial solution. Furthermore, both treatments can be enhanced by adding a post-process oxidation phase, which provides the already-nitrided surface with even more corrosion resistance in the form of an attractive and lubricant-retaining matt black oxide surface.

A wide range of vacuum pump types have been applied to vacuum nitriding processes and much practical experience has been gained. Avoiding potential problems, optimising reliability and performance, ensuring safety in operation, and minimising the costs of ownership of these systems, are all issues of major concern. Careful selection of the most appropriate vacuum pump technology, and sensible design of the vacuum system, will ensure that these issues are dealt with effectively.

1. LOW PRESSURE NITRIDING

Although nitriding using ammonia at higher pressures developed as an alternative to the salt bath processes, low pressure nitriding (LPN - i.e. under a partial vacuum) became preferred as a safer and more easily controlled mode of operation. In a typical system anhydrous ammonia gas is injected into the process chamber as the source of active nitrogen atoms, since thermal decomposition of ammonia to nitrogen and hydrogen occurs at the hot work-piece surface, and the nitrogen atoms can immediately diffuse directly into the metal surface. The use of ammonia rather than pure nitrogen allows operation at a comparatively lower temperature. Additional hydrogen may also be introduced to control the nitriding potential and white layer formation. More recent advances include enhanced real-time measurement and control of the composition of the chamber atmosphere, with full computer control of the process “recipe” to achieve precise surface properties and much greater product consistency.

LPN process cycle conditions vary according to furnace manufacturer and operator preferences, but generally comprise initial evacuation of atmospheric air, inert backfilling with nitrogen and heating the load to around 490–530°C, then re-evacuation followed by a processing phase in which the ammonia gas is injected into the chamber, either directly or through an intermediate pre-cracking furnace. The process phase can last for many hours depending on the chamber load and desired results. The process pressure is usually controlled at up to 200-300 mbar by throttling the vacuum pump system with a motorised control valve linked to the chamber pressure measurement. At the process pressures not all of the ammonia is completely dissociated into nitrogen and hydrogen, and so the resulting furnace atmosphere is a mixture which contains a significant amount of un-reacted ammonia. Furthermore, although the components being treated are (or should be) nominally clean and dry, a significant quantity of atmospheric water vapour can outgas from all of the exposed surfaces - from the chamber materials, from the fixtures, and not least from the load itself - while the chamber is under vacuum. Together these gases form a potentially corrosive, toxic mixture, containing flammable hydrogen, which is continually evacuated through the vacuum pump system.

This presents a variety of challenges to the vacuum pump system:-

- the ammonia content of the pumped gases is both flammable and toxic
- the hydrogen content of the pumped gases is flammable
- the moisture content of the pumped gases may be considerable
- moisture and ammonia will absorb into the lubricating oil in an oil-sealed vacuum pump
- ammonia reacts with moisture on any cool surfaces, and especially in the oil, to form ammonium hydroxide (NH₄OH) - a corrosive alkali (or base)

- ammonia attacks any exposed Viton fluoroelastomer seals, used inside many vacuum pumps, and also any exposed brass or copper components
- resulting oil contamination leads to oil degradation, poor lubrication, formation of gums, blockages, increased pump wear, and general internal corrosion of the pump

Although the processing pressure required is in the rough vacuum region, well within the capability of a suitably-sized primary vacuum pump (i.e. a pump exhausting to atmosphere), a typical vacuum pumping system for a LPN furnace will comprise a primary vacuum pump with a mechanical vacuum booster (“Roots” booster) in series. Such booster combinations achieve faster pump down times for the evacuation stages of the process, and are much more cost-effective than simply increasing the primary pumping capacity.

The mechanical booster is an efficient dry pumping mechanism and is generally resistant to the challenges posed by these processes. Since the booster operates at low inlet pressures and generates reasonable heat of compression in the pumped gases, there is little risk of any condensation and corrosion. The low pressure of operation also means that any fluoroelastomer seals are not likely to be attacked and also that flammability risks are decreased, however steps must be taken to avoid any air leaking into the pump system to mix with the flammable process gas.

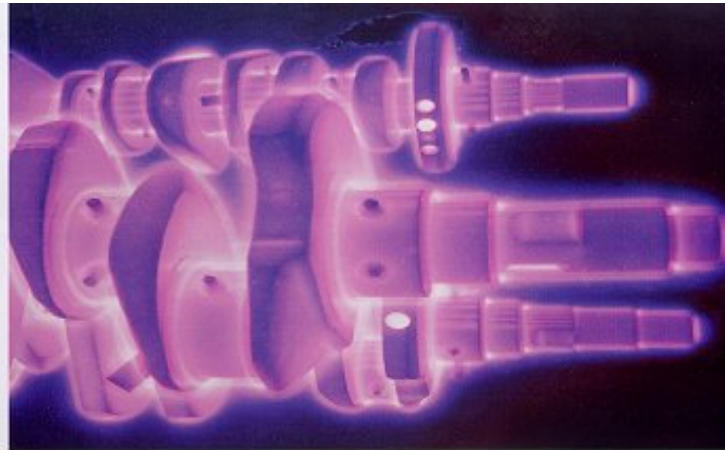
The main problems arise with the operation of the primary pumps in LPN. If a traditional oil-sealed “wet” vacuum pump is in use all of the challenges listed above are likely to be encountered, and experience shows this leads to significant routine maintenance demands and ongoing cost of ownership. Conversely, if dry-running primary pumps are used the only significant issues remaining are those of flammability and toxicity of the exhaust gases. All of these concerns are addressed later.

2. PLASMA NITRIDING

Plasma nitriding (PN, or ionic nitriding), has become the main nitriding process, offering a faster, much less hazardous, and more environmentally friendly option for achieving excellent results in hardening steel surfaces. In addition, even greater control of the nitriding potential during the process is available by direct programming of all of the process parameters including temperature, time, pressure, pulse voltage, pulse current and gas mixture. PN operates by exposing the work-pieces to a nitrogen plasma under a medium vacuum, through which the steel surface is directly bombarded with nitrogen ions which then undergo thermal diffusion into the metal. Much of the required heat for the process comes from this ionic bombardment.

A typical PN process starts with a rapid evacuation to 1 – 2 mbar followed by backfilling the nitrogen gas to around 950 mbar. The chamber and load is then heated by radiation and convection to the starting temperature (typically 520°C), which may take 2 or 3 hours. The chamber is then re-evacuated down to 5 mbar for the plasma process. A gas mixture of nitrogen and hydrogen is introduced into the chamber and a glowing plasma of gas ions is created by applying a DC voltage of 400–1500V, pulsed at 10kHz or more, between the chamber and the load. The plasma appears close to the work-piece surfaces, where emitted electron density is highest, see Fig. 1. As the load is the cathode in this circuit, the positive nitrogen ions from the plasma are accelerated directly into it.

Fig.1: nitrogen plasma around typical work-pieces



Usually a short period of cleaning is allowed first in which the chamber gas mixture is briefly dosed with argon, which causes heavy argon ions to bombard the work-piece surfaces – this cleans and opens up the surfaces via a sputtering effect.

The main part of the PN process then follows and this can last for several hours, depending on the load quantity and the gas load “recipe” selected to give the desired surface properties. The temperature is maintained around 520°C by the bombardment effect without additional heating, and the pressure is controlled at around 5 mbar against the injected gas load by throttling the vacuum pump system with a motorised control valve linked to the chamber pressure measurement. The process ends with nitrogen flooding to 950 mbar and circulation for 2 hours or so, to reduce the load temperature before the chamber is finally vented and opened for unloading.

The optional post-process oxidation phase can be included just before the nitrogen flood. This uses the direct injection of enough pure water into the chamber to bring the process pressure up from 5 to typically 12 mbar for some minutes, allowing water molecules to dissociate and provide oxygen ions to the hot metal surface to create the desired superficial metal oxide layer.

The PN process is clearly less challenging to the vacuum pump system but still has issues to address:

- the hydrogen content of the pumped gases is flammable
- the moisture content of the pumped gases may be considerable, especially with post-process oxidation
- resulting oil contamination by moisture leads to oil degradation, poor lubrication, increased pump wear, and some internal corrosion of the pump

The processing pressure required is in the medium vacuum region and this always requires a primary vacuum pump with a mechanical vacuum booster (“Roots” booster) in series. Any problems will generally arise with the operation of the primary pump and, as before, using oil-sealed “wet” vacuum pumps will usually lead to more routine maintenance demands and cost of ownership. With dry-running primary pumps the only significant issues remaining are those of flammability of the exhaust gases.

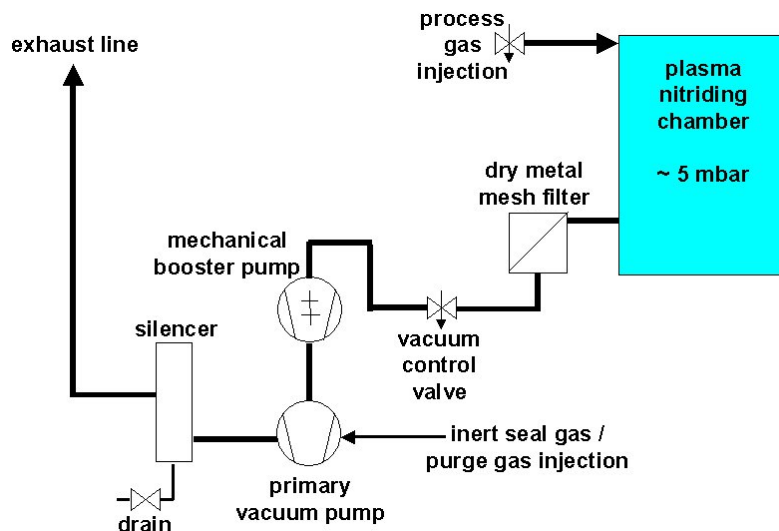
3. NITRO-CARBURISING

When associated with the PN process, nitro-carburising is a further optional post-process treatment which can be added after, or in conjunction with, the post-process oxidation stage. This involves the inclusion of a hydrocarbon gas such as methane into the low pressure gas mixture, which allows carbon atoms to be incorporated into the steel surfaces in addition. It should be noted that while the pure carburising process itself can involve the generation of substantial amounts of hydrocarbon breakdown products, which can lead to potential problems with tars and resins being formed in the vacuum system, nitro-carburising utilises lower quantities of hydrocarbon gases and under the plasma conditions does not normally present such problems.

4. VACUUM PUMP SYSTEMS, TECHNOLOGY AND OPTIONS

An ideal vacuum pump system used for the PN process is detailed in Fig. 2, and a typical example of a smaller system is illustrated in Fig. 3.

Fig. 2: PN vacuum system schematic



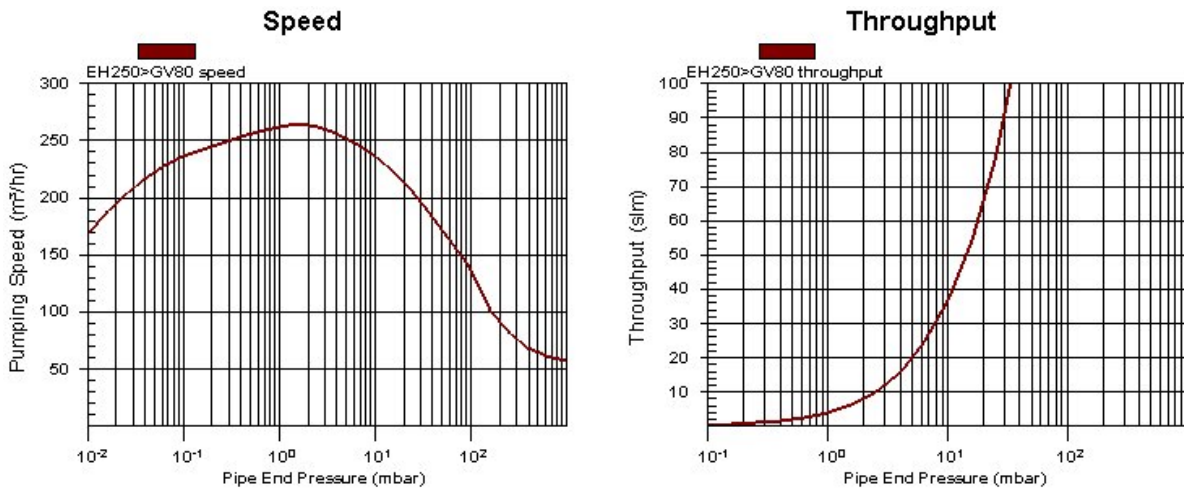
The primary vacuum pump exhausts to atmosphere through a silencer and a fixed wide bore exhaust line leading to a safe vent point on the roof of the installation. The silencer is fitted with a drain valve since it is the first cold point reached by the exhausted process gases. If a dry claw or dry screw mechanism primary pump is used this operates at elevated temperature, which ensures there is no possibility of internal condensation, and the pumped water vapour will all condense in the silencer. There is therefore an operating requirement to drain the silencer of collected moisture after each process run. The pump set is connected to the PN chamber through a standard metal mesh filter unit as a precautionary measure in this case. For metallurgical processes which generate more dust and particles the mesh filter is an essential component. The usual dry pump shaft seal purge must be supplied with inert nitrogen in this application, and it is not permitted to connect any compressed air supply to this, because of the hydrogen content of the pumped gases. The amount of seal purge and gas ballast purge nitrogen supplied to the pump is calculated and controlled to ensure that adequate dilution of the hydrogen content to a safe margin below the lower explosive limit (LEL) for hydrogen is always achieved inside the primary pump (where the pumped gas mixture is

compressed to atmospheric pressure), even when the process is using the maximum available hydrogen gas flow.

Fig. 3: typical small PN vacuum installation



The size and performance required for the pump set is largely determined by the chamber volume and initial pump down time requirement in this application, since the maximum process gas flows are usually well within the pump set capabilities at the low pressures involved. The example illustrated shows a typical 80 m³/h dry claw primary vacuum pump with a typical 250m³/h mechanical booster pump. The vacuum pumping speed curve and throughput (gas load) curve for this typical small system are shown below.



For low pressure nitriding (LPN) systems the vacuum system design would be very similar, with the higher chamber pressure being controlled through a similar control valve between the filter and the mechanical booster, however the major additional problem of the ammonia content of the pumped gases has to be considered. From an operational perspective this means that the potential for corrosion due to NH_4OH formation with moisture, and the risk of attack by ammonia on any susceptible pump components, must be understood and dealt with. The consequences of this will depend largely on the selected technology for the primary vacuum pump.

With a dry pump technology, such as the multi-stage dry claw pump or dry screw pump, internal gas temperatures are high and the pump thermostat can also be set to hold a high body temperature, which means that there is no risk of internal moisture condensation. Ammonia and other gases will also pass straight through the pump, particularly since there is no contact between the pumped gases and any lubricating oil. There are also no exposed components susceptible to attack by the ammonia. The important precautions will be to ensure that the correct seal purge and gas ballast purge are applied using inert nitrogen, the exhaust silencer is regularly drained of condensate, and that the pump is allowed to run on atmospheric air for 15 minutes after the process is complete to cool it in a completely dry state before stopping.

With a wet pump technology, such as the oil-sealed rotary piston or rotary vane pump, the pumped gas is in intimate contact with the pump lubricating oil, which will absorb significant amounts of moisture and ammonia. To minimise retention of these contaminants the pump should be run for an hour before use to fully warm up. The thermostat should be set as high as practical to keep the oil hot. The internal shaft seals should be specified as Nitrile to avoid attack by the ammonia, and any copper or brass components exposed to the process gases must be replaced with alternative materials. Adequate gas ballast purge must be applied using inert nitrogen, especially since this will help flush some of the contaminants out of the oil. The exhaust silencer should be regularly drained of condensate, and the pump must be run on full nitrogen gas ballast for 30 minutes after to process is complete to help purge contaminants out of the oil before stopping. Routine oil changes must be strictly observed to minimise the rate of internal corrosion.

The essential points are summarised in Table 1. Where there are no special requirements the table is left blank (-).

Table 1: comparison of primary pump technology

	oil-sealed primary pump	dry multistage primary pump
ammonia in pumped gases (LPC)	use adequate N_2 for gas ballast, replace Viton, copper and brass components, use warm-up and shut-down procedures	-
hydrogen in pumped gases	use adequate N_2 for gas ballast and oil box purge	use adequate N_2 for seal purge, gas ballast and exhaust purge
moisture in pumped gases	use adequate N_2 for gas ballast, use warm-up and shut-down procedures. Drain silencer after each process cycle	drain silencer after each process cycle
warm-up procedure	1 hour run, full N_2 gas ballast	-
shut-down procedure	30 min run, full N_2 gas ballast	15 min run, on air
typical maintenance needs	quarterly or even monthly (LPC) oil changes (large quantity)	annual oil change (small quantity)

5. SAFETY AND ENVIRONMENTAL GUIDELINES

It is always the process operator's responsibility to conduct a proper risk assessment of any potentially hazardous process, and to operate the process safely. Therefore the following comments are made for general guidance only.

With LPC especially, health and safety concerns dictate that exhaust lines must be well maintained and exhaust vent points must be carefully located to ensure that process gases containing ammonia cannot escape into the working environment and are properly vented where they will not cause any health hazard.

Since the gases in both nitriding processes contain hydrogen, the pump system must incorporate measures to ensure that pumped gas concentrations remains at a safe margin below the LEL (lower explosive limit) concentration for hydrogen (4 vol.%) wherever the gas pressure is above 60 mbar, based on the maximum possible hydrogen process flow and the required gas ballast (and shaft seal purge flow where fitted) to dilute it. These dilution measures should be interlocked to stop the process if they fail, for example using a flow sensor to alarm and switch off the process gases if the nitrogen purge flow drops below acceptable levels. A recommended safe margin for below-LEL operation is $\leq 25\%$ LEL.

In process cases where the hydrogen concentration is very high, it is permissible to operate above the UEL (upper explosive limit) but professional safety advice should be taken. Essentially, the pump system must incorporate measures to ensure that pumped gas concentrations remains at a safe margin above the UEL concentration for hydrogen (75.6 vol.%) wherever the gas pressure is above 60 mbar, based on the minimum hydrogen process flow and allowing for any required gas ballast or shaft seal N₂ flow. This will involve measures and safeguards to ensure no air can leak into the system or into the vacuum pumps during operation, such as routine leak checks or pressure rise testing, routine replacement of shaft seals on oil-sealed pumps, and using mechanical vacuum boosters with hermetic shaft seals. This approach will also require inert purging of the exhaust line to avoid air mixing with the above-UEL gases before the final vent. A recommended safe margin for above-UEL operation is $\leq 60\%$ of the residual oxygen concentration which would be present at UEL.

From an environmental perspective the summary of key issues to be considered and dealt with is:

- emissions of ammonia gas (LPC only, but may be a significant concern)
- consumption and disposal of lubricating oil (mostly from oil-sealed pumps)
- occupational noise and vibration (especially from oil-sealed rotary piston pumps)
- condensate and cooling water drainage (usually only in small quantities)

6. CONCLUSION

Nitriding processes, and especially plasma nitriding, are widely used and very effective means of providing precise control of component surface properties for use in demanding applications throughout industry, and not least in automotive components. To ensure high levels of product consistency and process reliability, the essential vacuum system for these plants should be sensibly designed and properly installed, taking account of the important safety and environmental concerns. The issue of the hydrogen content in the pumped gases requires a suitable risk assessment to be undertaken and appropriate measures to be incorporated into the vacuum system.

The use of dry mechanism primary pumps represents a major factor in improved reliability, reduced maintenance and lower environmental impact in nitriding installations, due to their elevated operating temperatures and absence of oil in contact with pumped gases. Very significant numbers of dry claw primary vacuum pumps, in particular, are now operating in nitriding processes with excellent results. This positive experience with dry pumps also extends to many other heat treating and metallurgical applications such as investment casting, induction melting, vacuum brazing and similar high-volume and high-value processes.

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