Stop-off Technologies for Heat Treatment

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There are a wide variety of stop-off technologies available to selectively prevent the diffusion of carbon and or nitrogen during atmosphere carburizing, carbonitriding, vacuum carburizing and various forms of nitriding. These technologies are used to prevent selective areas of a part from hardening during the heat treat process. This allows secondary operations such as machining, drilling, broaching, cold-forming, straightening and welding to be achieved in the soft areas after the heat treating operation. In addition to selective stop -off, technologies are also available for scale prevention in open fired furnaces.

Copper Plating

Copper plating has been proven to be very effective in preventing the absorption of carbon and or nitrogen during heat treatment. However, it is expensive, time consuming and by no means environmentally friendly. Initially, the entire part is electroplated with copper. Copper is then removed by machining areas which are to be case hardened by leaving only the areas requiring stop-off plated. After heat treatment, the copper is typically removed by stripping in cyanide or acid based solutions.

Case Removal Prior to Quenching

Another method is to add machine stock on the areas which are required to remain soft. The parts are then subjected to a carburize only cycle. After carburizing and slow cooling, the carburized layer is still relatively soft allowing the removal of the machine stock. The parts are then reheated and quenched. The areas of the part which were machined after the carburize cycle will only show the core hardness since the case layer had been removed prior to quench.

Mechanical Protection

In the case of internal threads, blind holes and other areas which are too small to adequately access, carbon and nitrogen diffusion can be minimized by inserting barriers in the form of bolts, copper plugs and clay in an attempt to seal these areas from atmosphere penetration. Closely fitted conical bolts can be inserted into blind holes. As an option, clay is inserted to fill the gap between the bolt and the wall of the part. Sometimes the hole is plugged with clay or a mixture of clay and iron oxide, commonly referred to as De-Ox sticks. Coating under the head of a bolt and/or the threads with stop-off paint is another option. Most of these options require some mechanical cleaning to remove the clay or paint after heat treatment. Plugs offer another possibility but some means of venting the trapped air during heat-up must be employed to relieve the pressure and ensure the plug is not forced out of the hole.

Another practice is to place closely fitted heat resistant alloy caps over external threads. This method can minimize carbon or nitrogen penetration but by no means is it 100% effective. The caps tend to distort over time, especially if they are oil quenched causing frequent replacement.

For plasmanitriding shielding is used to prevent nitrogen penetration effectively. However, shielding often is not possible due to part geometry.

Induction Tempering

After case hardening, selective areas of the work pieces can be “softened” by induction tempering. External threads of gears or shafts are typical applications. This method is not suitable for steels of high hardenability.

Stop-Off Paints

Stop-off paints today offer state of the art technology for selective protection of steel parts during carburizing and nitriding. Easily applied by painting, immersion, spraying or dispensing, they provide a gas tight layer on the surface of the work piece. Stop-off paints are easily adaptable to low volume applications as well as mass production as found in the automotive industry.

NOTE: The use of the term “paint” is misleading. These stop-off products are actually coatings and should be treated as such. These coated surfaces must have a uniform coating thickness, per the manufacturer’s specification, to insure consistent results. Coating thickness usually ranges between 0.2 - 1.0 mm. This is easily measured with a thin film gauge. Thin film gauges are inexpensive and easily obtained from industrial paint suppliers and industrial product distributors.

Stop-off paints have evolved from a just a few products a couple decades ago to a wide array of specifically formulated paints for each of the following processes: carburizing, deep case carburizing, carbonitriding, vacuum carburizing, nitriding, nitrocarburizing and plasmanitriding. In addition, stop-off paints are also available for annealing processes to prevent scaling and decarburization in open air furnaces. [Fig. 01]

Part Cleanliness

Before proceeding with the proper selection of stop-off paint, it is imperative to address the cleanliness of the part surface prior to stop-off application. Insuring the surface of the part is free from oil, grease, dust and oxides/scale will eliminate the majority of possible failures. Allowing sufficient drying time of the paint, per the manufacturer’s specification, is another requirement that cannot be overlooked.

Cleaning in Industrial Washers

The majority of industrial washers in commercial heat treating facilities and captive heat treating departments utilize single stage washers. The washer media is typically a hot water or an alkaline solution heated to 140-180F. In some instances hot water only with a rust inhibitor additive. These washers are either spray type or spray / dunk combination. A single stage washer rinses the part after the wash cycle with the same emulsion used in the wash operation. This type of washer removes the majority of surface contaminates but leaves a residual of oil which can provide short term rust prevention. The bottom line is that parts cleaned in a single stage washer are <u>not</u> oil free. Applying a stop-off coating onto a part which has a film of oil on the surface will result in spotty hardness. As the part is heated, the oil will vaporize and lift areas of the paint off the part surface. Upon inspection, hardness checks of the failed areas will show full hardness which is evidence that paint protection was lost during the heat-up portion of the cycle.

A hot alkaline wash, as described above, should be sufficient if a clean water rinse is utilized to insure all contaminants are rinsed off. A common practice with industrial washers, with a clean water wash capability, is to add a rust inhibitor to prevent oxidation of the part surface after the cleaning operation. A water rinse with a rust inhibitor, of any percentage, will result in spotty hardness, under areas which have been coated with the stop-off paint.

To insure parts are free of oil after cleaning in a single stage washer, it is an accepted practice to thermally remove these contaminants by heating the parts above 400°C to vaporize any residual surface oils left after the wash operation. These parts are then to be cooled to room temperature prior to paint application.

Shot/ Sand Blasting

A common practice to prepare part surfaces for the application of a stop-off coating is to blast the part with steel shot, alumina oxide, garnet or glass beads. Parts which have been blasted should be washed after the blast operation for two reasons. The majority of blast equipment incorporates a media reclamation system. The blast media is reclaimed and reused. This reclaimed media is often contaminated from previous operations with oil and dirt which is re-deposited onto the part surface. Ideally, virgin blast media should only be used in these applications. Even virgin media is problematic. After blasting, the part surface is contaminated with residuals from the blast operation in the form of dust. This surface contamination inhibits adherence of the stop-off coating resulting in non-uniform protection. A note of caution: There are blast media on the market which consists of reclaimed abrasive from grinding wheels and other previous operations. These medias have been processed and cleaned but can be contaminated from glues and binders which can be left on the part surface. You must verify the media you are using is virgin material.

Hand Cleaning

In the case where the parts to be coated are too large to wash, the areas to be coated must be cleaned by hand. There are various cleaning agents available and special care should be taken to insure these cleaning agents are 100% effective. Since it is difficult to verify the area cleaned by hand is free of oil, a thermal clean cycle following hand cleaning would offer further insurance the area to be coated is free of contaminants. This cycle would consist of heating the part above 400°C.

Paint Curing / Drying

Insufficient drying time is another leading cause of stop-off paint failures. All stop-off paints utilize either a solvent or aqueous thinning agent. These thinning agents must be fully evaporated prior to introduction into the furnace. Insufficient drying will cause the thinning agent to outgas lifting areas of the paint off the part surface during heat-up. It is most important that the first coat be thoroughly dried before application of a second coat. Applying a coat onto a coat which has not been thoroughly cured will result in hard spots. The second coat will seal the first and prevent the thinning agent from dissipating. When heated, the thinning agent will then outgas popping areas of the first coat off the part surface during the heat up cycle.

Stop-off Paints for Carburizing and Carbonitriding

The most commonly used stop-off paints for carburizing and carbonitriding are solvent or water-based coatings with boron as the main ingredient. The biggest advantage of boron based paints is that the residues, after heat treatment, are water soluble in a hot water or alkaline wash. These paints are the best choice for applications where mechanical cleaning is not an option. The protection of threads is a typical application. These paints are widely used in the automotive industry in mass production of small and medium sized car components. They provide local protection during carburizing and carbonitriding with the residues removed during the wash operation eliminating an additional cleaning operation. Fig. 2 shows an added benefit of boron paint; hardness response in the protected area with such a product is even lower than the core hardness because the quenching speed is lowered due to the insulating characteristic of the paint.

The original stop-off paint, developed over 60 years ago, consisted of boron oxide and a solvent based coating. These solvent based paints are still used today and still offer the best protection in this class of coatings. Water based products have been developed and offer a more environmentally friendly alternative when the use of a solvent based paint is not acceptable. However, the use of boron in an aqueous base has limitations which can be detrimental to the interior of the furnace chamber. Both solvent and water based boron stop-off paints break down during the heat treat cycle. It is a time / temperature relationship. These paints offer protection up to 2mm case depths. Beyond these depths the paints are no longer effective. The combination of water and boron forms boric acid. The outgassing of the boric acid based coating during the atmosphere cycle can react with the silicon in the refractory causing a eutectic lowering the melting point of the silicon. This can result in a glazing of the furnace chamber. The degree of glazing is dependent on the amount of paint used and number of cycles with painted parts the furnace chamber has been subjected too. The glazing will vary within the chamber due to variation of silicon in the various refractory components within the chamber. This glazing effect has also been observed on substrates used in oxygen probes. The glaze can coat the electrical contact area between the outer electrode and the inner substrate increasing the probe resistance and offsetting readings. To correct this situation, the probe must be replaced and sent back to the manufacturer to be cleaned. The interface area between the electrode and substrate must be mechanically cleaned and tested. It is for these reasons a solvent based boron stop-off should be your first choice since it is not subject to this phenomena.

Boron based paints differ from all other alternatives. When heated, these paints go into a semi-liquid state at temperature. If the coating is too thick, the mass of the paint could cause the paint to run into uncoated areas and stop off in addition to the intended areas. It is for this reason the paint thickness of 0.2 - 1.0 mm should be maintained. Only one coat is required as long as this coating is uniform. Thicker is not better .Two coats are only recommended for certain applications such as threads. A second coat is recommended to insure the tips of the threads are adequately protected.

Deep Case Carburizing

There are a number of stop-off paints which have been developed as an alternative to boron based paints for case depth requirements exceeding 2 mm. These silicate based paints can provide safe protection for case depths up to 10mm ; for example large gear parts for the wind energy industry [Fig. 3] and other energy transmissions. Apart from the aqueous silicate liquid carrier, the main ingredients are metals / metal oxides. Paints containing copper are not particularly suited for carbonitriding because of the possible chemical reaction between the metal and ammonia of the processing atmosphere. Silicate based stop-off paints are normally applied in 2 or 3 layers depending on the case depth in question. After heat treatment, the glasslike residue of the paint is not water soluble nor can it be removed using solvents. The residue is removed by shot blasting. An advantage of these paints, unlike the boron based products, is they will not run even if the coating thickness is excessive. They also are not subject to the possibility of glazing the furnace interior as the water based boron paints.

Vacuum Carburizing

Stop-off paints used for vacuum carburizing are similar to those used in atmosphere carburizing. Boron paints are used for applications requiring the paint to be washed off after heat treatment.
The only boron paint which should be used in a vacuum carburizing furnace is one which has been specifically formulated for this process. Conventional boron paints can be a particular concern especially in high pressure vacuum quench furnaces. The extreme turbulence of the nitrogen or argon quench can blow some of the residues off the part surface and contaminate the interior of the furnace chamber. The real concern is the possibility that these residues make their way into the vacuum pump. If mechanical removal (shot blasting) of the stop-off paint is acceptable, a silicate based copper oxide paint should be your first choice. This type of paint is extremely effective and negates the possibility of contaminating the furnace chamber during the turbulence of the quench cycle.

Nitriding and Nitrocarburizing

Stop-off for nitriding and nitrocarburizing in gas are mainly based on a fine tin powder dispersed in a lacquer consisting of a solvent + synthetic binder or water + synthetic emulsion. The stop-off effect is based on a layer of molten tin dispersed on the steel surface. It acts as a gas tight barrier preventing the diffusion of nitrogen. It must be noted that preheating the coated parts in air must be limited to 380°C max. Exceeding this temperature limitation will prove detrimental to the uniformity of the tin plating as required for safe protection. Residues of these paints are of a powdery appearance after the nitriding process which can be easily removed by wiping or brushing. It must be noted that there is a microscopic layer of tin left on the part surface after the powdery residues are removed. Often times this does not present a problem as to the functionality of the part. In the event this does present a problem, it can be removed by blasting or machining.

NOTES:

- Occasionally the tin layer left behind on the steel surface of the coated area is misinterpreted by metallography as nitride layer. If there are respective doubts, micro-hardness measurement helps clarify as to whether it is soft tin or a hard nitrided area.

- It is possible that some of the powdery residuals after nitriding may come off at the end of the cycle due to gas turbulence in the retort or during the unloading stage of the cycle .These residuals will settle on the bottom of the retort. It is recommended that the inside of the retort be vacuumed out after each cycle to insure that residues of this powder do not redeposit on non-coated areas of parts in the next load. Failure to follow this procedure could result in soft spots in uncoated areas of these parts.

Typical parts for nitriding processes are crankshafts, camshafts, cam followers, valve parts, extrusion screws, die-casting tools, forging dies, extrusion dies, injectors and plastic-mold tools [Fig. 4].

Plasmanitriding

For plasmanitriding the most commonly used stop-off technology is shielding. If the geometry of the part does not lend itself to shielding, stop-off paints are available either based on copper (electrically conductive) or ceramic ingredients (non-conductive). The residues of these paints are powdery and can be removed easily by wiping or brushing.

Scale Prevention

Stop-off paints are available to prevent scale and oxidation in open fired furnaces. These paints are used for annealing, stress relieving, normalizing and hardening. They are used in applications where a protective atmosphere is not available or cost prohibitive. In these applications the entire part surface is coated. There are boron paints available which will prevent scale in applications up to a maximum temperature of 850°C. After heat treatment, the residues of these paints are water soluble and easily removed in a hot water wash. These paints are not recommended in applications over 850°C as the paint is no longer water soluble and even mechanical removal extremely difficult.

There are lacquers and ceramic based coatings available for applications up to 1200°C. These coatings form a glass-like barrier to prevent the scale from forming. Upon cooling, the coating will begin to spall off due to differential expansion of the coating and the steel part. While much of the coating will break off, typically mechanical removal of areas of the part will be required.

Instructions for the Use of Stop-off Paints

General Considerations

- Masking of steel parts during heat treatment can be successfully and economically applied using stop-off paints practically for the whole range of diffusion based gas carburizing and nitriding processes including the latest vacuum technologies. New products and modes of application provide a versatile and reliable technology, offering major benefits regarding cost reduction, health and safety protection of the workers, and protection of the environment compared to formerly used techniques such as copper plating.

- Stop-off paints are used on expensive parts which are nearly ready for use. There has been a lot of value added to each part before it is sent for heat treatment. Failure to properly clean the part surface and adhere to the manufacturers' application instructions will result in costly scrap. Also, it must be considered that the stop-off paints are not standardized but manufactured according to the proprietary formula of their manufacturer. So it is mandatory to strictly follow the advice given in their technical documentations.

- There is a general rule of thumb that no more than 30% of the total area of the parts within a furnace load be coated with stop-off paint. Exceeding this amount could delay the furnace cycle due to a temporary imbalance in the furnace atmosphere. As the parts are heated, water vapor or gases generated by thermally cracked binders in the paint are released to the atmosphere. An excessive amount will cause an imbalance of the furnace atmosphere stopping the process. In time, the furnace atmosphere will recover but the cycle would have been interrupted resulting in a shallower case than had been intended.

- Stop-off paints typically have a minimum shelf life of 1 to several years. These paints should be stored at room temperature and distribution use should always be first in - first out. Water base paints must not be allowed to freeze. In the event freezing has occurred, the paint must be allowed to thaw to room temperature and then mixed thoroughly before application. As discussed earlier, the parts must be thoroughly cleaned and dried prior to application of the stop-off paint. They must be free of contaminants such as oil, grease, dust and oxides/scale. Ideally, parts and paint should both be at room temperature (about 25°C / 77°F) when the paint is applied. After thoroughly stirring up the paint, the coating should be applied as uniformly as possible in a way that the steel surface is covered completely and the steel does not shine through the painted surface. Excessive coating thickness must be avoided. It does not enhance the protective performance of the paint. However, it could cause some of the paints to run into unwanted areas and it will definitely extend drying time. Required drying time is dependent on various factors such as paint composition, viscosity, coating thickness, ambient and part temperature as well as atmospheric humidity. Drying time can range from approx. 3 to 16 hours depending on atmospheric conditions, coating thickness and number of coats applied. Solvent based paints will dry relatively fast due to the accelerated evaporation of the solvent as compared to an aqueous based paint. Drying time on all these paints can be shortened by preheating the parts at a maximum temperature of 180C in air. Exceeding this maximum temperature could cause the paint to run into non-coated areas as well as compromise the effectiveness of the paint.

- If parts previously coated with stop-off paints are preheated to temperatures exceeding 180°C, this may affect the protective performance depending on the paints' formula, the furnace atmosphere and the preheating temperature. So it is important to consider the respective advice provided by the manufacturer.

- Many of these paints are hygroscopic and will absorb moisture if exposed to high humidity for extended period of time. It is recommended that painted parts be heat treated within 24 hours of the last coat. In areas of high humidity, it is recommended to store painted parts in an oven at 80°C max. until they are ready to be placed into the furnace.

- The painted areas of the part must be arranged or fixtured to insure these areas do not come into contact with non-coated areas of other parts in the furnace load. Should contact occur during the furnace cycle, the protective layer might be damaged or unwanted insulation from the gas process of neighboring parts might occur.

- Care must be taken to insure that the stop-off paint not drip or be misapplied to unwanted surfaces. Manual cleaning of these areas is typically not sufficient. Even though the contaminated surface looks clean, case penetration in these areas may not be uniform. It is recommended that all the paint be removed mechanically by blasting, part washed and paint reapplied.

- After heat treatment, it is recommended that the residue of the paint does not remain on the parts for an extended period of time. The residue of some stop-off paints can react with humidity and can cause a corrosive attack of the part surface.

- Most stop-off paints are only effective for one atmosphere cycle. This is definitely the case with hardening cycles in which the parts are quenched. The parts must be cleaned and recoated if subsequent heat treatment is required. There is one exception to this rule. There are a couple of stop-off paints available which will prevent carbon penetration during a carburize cycle followed by atmosphere slow cooling. The parts can be cooled further in air to room temperature. These same parts can be reheated in atmosphere and oil quenched for the hardening cycle. These silicate based paints will offer stop-off protection during both cycles eliminating the need to re-coat.

- Do not combine, in the same furnace load, parts painted with two (2) different stop-off paints. This situation could compromise the effectiveness of one or both of the paints. This is definitely the case if a solvent based boron paint and a water or silicate based paint are in the same load. Water and silicate based paints give off water vapor during the heat-up cycle which can attack the solvent based paint causing it to run into uncoated areas.

- Edge effect: A common complaint is hardness is found under the edges of the painted surface. This is not a failure of the paint but caused by penetration of carbon or nitrogen through the uncoated area adjacent to the paint edge. The case diffuses into the part surface and wraps under the edge of the paint. If this is unacceptable, it can be alleviated by extending the edges of the painted surface to compensate for this condition.

Application Technologies

Small numbers of parts to be selectively protected are normally coated manually simply by painting using a flat soft brush. At the same time, stop-off paints can be tailored to the customers' needs which allow a variety of modern semi or fully automatic application technologies:

Prior to application of any of these technologies, proper mixing of the paint is of utmost importance. The majority of stop-off paints on the market today are non-Newtonian fluids meaning the viscosity of the paints are always changing based on time, temperature and other factors that can disrupt the fluid. These paints are thixotropic. Upon opening a container of paint, the contents look thick (viscous) almost gel- like. However, as the paint is sheared by the mixer, the paint becomes more fluid as the viscosity decreases due to the shear stress caused by the mixing. Typically these products cannot be shaken or agitated but must be mechanically mixed either by hand or mechanical mixer. Most stop-off paints can be used directly from the can when first opened. Thinning of the paint with either solvents or water is only required to replenish that which has been lost to evaporation. It is important that the paint be thoroughly mixed before considering the addition of thinner. Over-thinning of the paint can be detrimental to the effectiveness of the stop-off protection.

Brushing

As mentioned before, brushing is suited for single or small series of components such as large gears, shafts, tools etc. Using a flat clean brush with soft bristles, the stop-off paint should be applied in an even thin layer of uniform thickness. When applying the paint to the part, do not put any pressure on the brush but let the paint flow off the brush in a uniform manner. If you notice that the paint rolls off the painted surface back to the brush stop immediately. There is oil or some contaminates on the surface which must be removed. When storing the brush between coats, you must use the same solvent as the paint uses to insure there is no adverse chemical reaction or paint contamination.

Dipping / Immersion

Dipping/ Immersion is the simplest and most economical way to coat high volumes of light weight parts. If the area to be coated is at the end of the part, semi-automatic or continuous coating can be achieved with minimal investment in equipment to perform this task. [Fig. 5].

- [Fig. 5] Figure 1: Parts are loaded into a rack. The loaded rack is placed in a stationary position above a container of stop-off paint. The container is elevated to the part as required. The container is withdrawn. Excess paint drips back into container. Rack is removed and replaced with another rack.

- [Fig. 5] Figure 2: Parts are placed into a carrier. The carrier is indexed over a stationary container of stop-off paint. There is a shallow container which is submerged in the paint. The shallow container is elevated to the parts as required. The shallow container is withdrawn back into the stationary container to refill. Excess paint drips back into the container. Carrier indexes from the stationary container followed by another carrier to be processed.

Dispensing

Automatic dispensing of stop-off paint utilizes equipment similar to that used to apply adhesives. The process and equipment is similar to normal paint spraying technologies but the paint is not sprayed; it continuously flows from the nozzle like tooth paste. There are many installations using this technology which requires only moderate adjustment in respect of the paints' characteristics and the work piece area to be coated. Depending on the number of parts and how sophisticated the requirements are, either simple low cost devices [Fig. 6] can be implemented or high-end computer operated systems including automatic handling systems, drying zone etc. [Fig. 7]. Robotics and automated handling systems provide reproducible high production application. These systems are found in the automotive industry and by the manufacturers of high production gears as used in transmissions.

Spraying

Like dispensing, spraying also lends itself to high production coating. It is especially suited for applications requiring large areas to be coated. That said, spraying has been substituted more and more by dispensing which offers major benefits such as reduced consumption (no "overspray") and minimized mist exposure of the workers. In addition, spraying usually requires some form of masking to keep the overspray from contaminating unwanted areas.

Stamping

On large numbers of parts with intricately shaped areas to be coated, the paint can be applied by stamping. For this a counter-piece with the mirror-shape of the area to be coated is wetted with the paint and then pressed onto the work piece. Such a process can be set in practice semi or fully automatically at reasonable costs.

Process	base chemistry	liquid carrier	removal of residues	speacial features
Carburizing / Carbonitriding	Boron oxide	solvent	hot water	water washable
Carburizing / Carbonitriding	Boric acid	aqueous emulsion	hot water	water base water washable
Deep Carburizing	Silicates + metals Metal oxides	aqueous	shotblasting steel brush	solvent-free
Pack Carburizing	Silicates + metals Metal oxides	aqueous	shotblasting steel brush	solvent-free
Nitriding/ Nitrocarburizing	Tin	solvent	shotpeening steel brush/	-
Nitriding/ Nitrocarburizing	Tin	aqueous emulsion	shotpeening steel brush	-
Plasmanitriding	Copper	solvent	wiping	electrically conductive
Plasmanitriding	Ceramics	solvent	wiping	not conductive
Annealing	Silicon, silicates	solvent	wiping	-

Fig. 1: Protective paints, overview

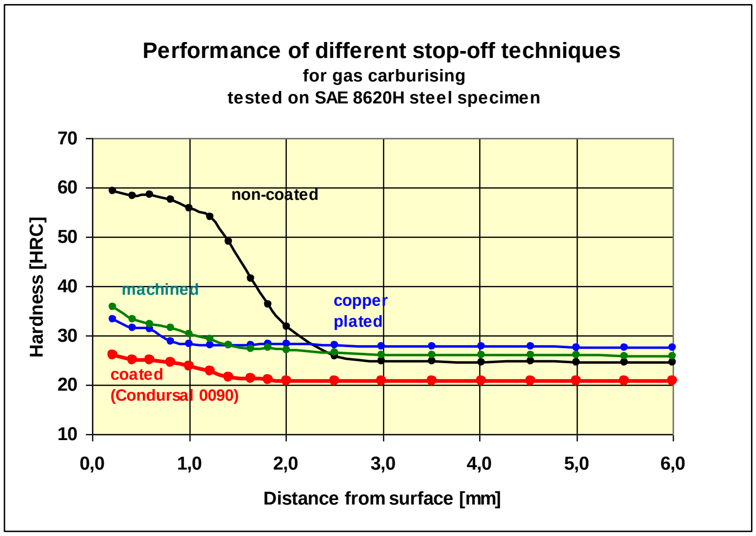

Fig. 2: Local protection of 27mm$^{\varnothing}$ specimen, of SAE 8620H steel, against carbon pickup during carburizing provided by CONDURSAL 0090 compared to copper plating [1]

Fig. 3: Gear parts for windcraft industry, coated with CONDURSAL 0118 prior to case hardening

Fig. 4: Tool parts, coated with CONDURSAL N633 prior to nitriding

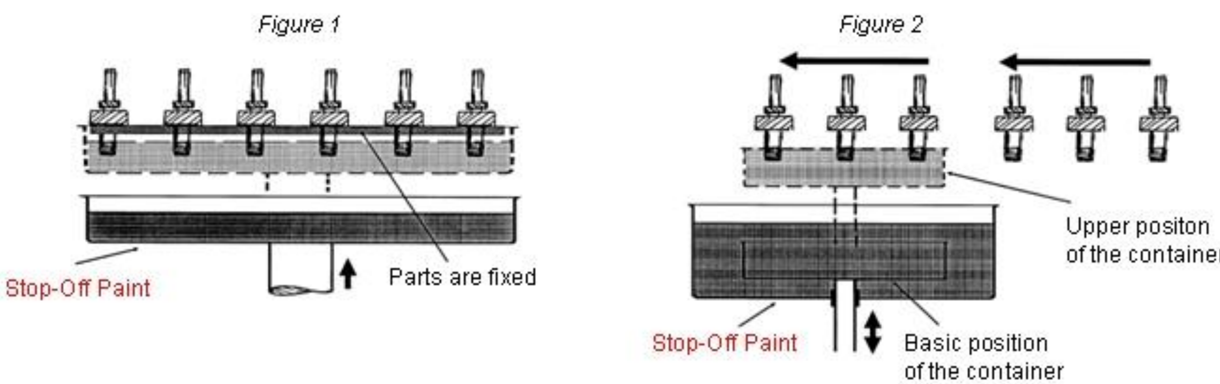

Fig. 5: Dipping installation (schematic view)

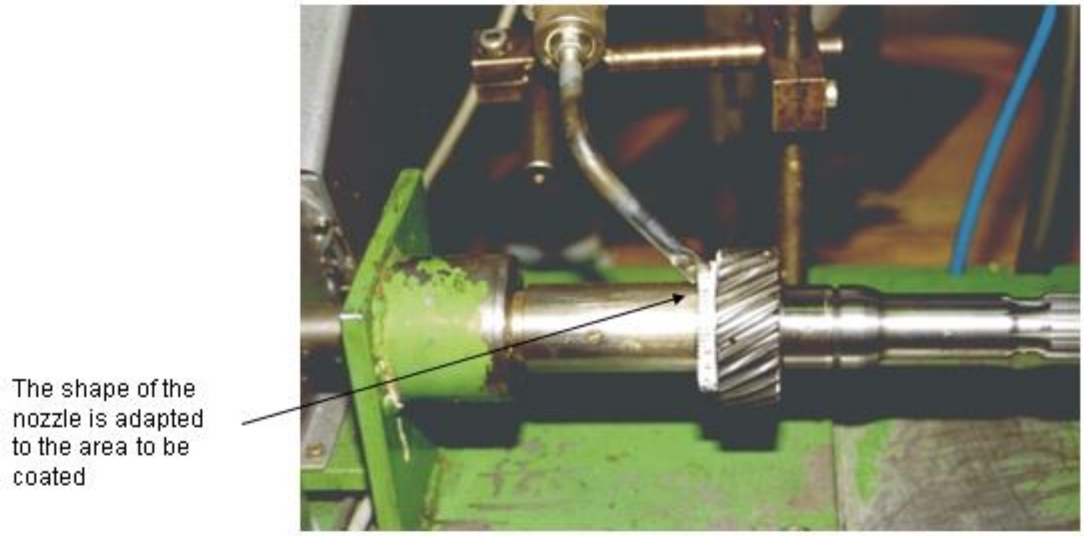

Fig. 6: Low cost feeding installation

Fig. 7: High-end computer-operated feeding installation