

The present invention concerns a treatment process for improving simultaneously the corrosion resistance and friction properties of ferrous metal components.

In order to confer both friction and corrosion resistance properties on ferrous metal components, the general procedure involves two distinct successive treatments, a first treatment to give the components the friction properties and a second, surface treatment in order to provide protection against corrosion, the latter for example by carrying out a deposition of zinc followed by chromating.

The friction and corrosion resistance properties achieved by these treatments are often sufficient for conventional components.

However, for certain applications where ever higher technical performance is now demanded for components, notably for components subjected to severe stresses causing several different phenomena to occur simultaneously (friction, wear, particularly abrasive wear, shock, corrosion), the properties conferred by conventional methods are not sufficient.

This is the case, for example, with components intended for lock mechanisms, for certain types of bolt and precision screw, control screws, hinge pins, rods of jacks and shock absorbers, and sporting bowls. The industries concerned are notably those of motor vehicles, civil engineering, handling, plant, household appliances and hydraulic equipment.

It is known that it is possible to confer good friction properties and good corrosion resistance on ferrous metal components through nitriding followed by oxidation.

To this end, nitriding processes for ferrous metal components are known, notably nitriding using baths of molten cyanates and carbonates as described in FR-A-2 171 993 and FR-A-2 271 307, or nitriding in an ionized nitrogen atmosphere, which enable the friction properties of these components to be improved, while reducing the coefficient of friction and increasing resistance to wear and seizing.

It is also known that, if a previously nitrated component is subjected to oxidation, changes are produced in the nitrided surface and the corrosion resistance of these components is thus improved, while preserving the friction properties acquired by nitriding. To this end, document FR-A-2 525 637 describes a particularly effective oxidation treatment in a bath of molten oxidizing salts. Comparable results for corrosion resistance are obtained through a process of oxidation in an ionized atmosphere of a gas containing oxygen.

However, this type of process confers, on the nitrided and then oxidised components, friction properties and corrosion resistance that are insufficient for the aforementioned applications.

It has been discovered that it was possible to overcome these drawbacks by supplementing the nitriding and oxidation treatment with the application of a final coating.

The present invention is also based on the observation that numerous components are habitually cleaned, notably before their assembly, whereas it is well known that they do not justify such a cleaning and for which it is not therefore necessary to carry out a surface treatment resistant to conventional cleaning products.

The present invention proposes a treatment process for ferrous metal components to improve simultaneously their corrosion resistance and their friction properties, a process in which

the components are nitrided and oxidized and receive a final coating, characterised in that the nitriding followed by oxidation leads to the formation of a layer consisting of a deep, compact sub-layer and a porous surface sub-layer, the said surface sub-layer having a thickness of between 5 and 25  $\mu\text{m}$  and having open pores whose diameter is between 0.2 and 3  $\mu\text{m}$ , and in that the nitrided and oxidised components are impregnated with a hydrophobic wax, the said wax being a carbon-containing organic compound of high molecular weight of between 500 and 10,000 and with a surface tension in the liquid state of between 10 and 73 mN/m, the angle of contact between the solid phase of the surface layer and the wax in the liquid state being between 0 and 75 degrees.

According to other characteristics, the surface sub-layer contains over 60% solid phase  $\text{Fe}_{2,3}\text{N}$ , has a hardness of between 550 and 650 HV 0.1 and a roughness of between 0.3 and 1.5  $\mu\text{CLA}$ .

The impregnation wax is chosen from the list: natural waxes, or synthetic polyethylene, polypropylene, polyester or fluorinated waxes, or modified petroleum residues.

The process according to the invention offers the advantages of being inexpensive and easy to implement, even for industrial mass-production of components, and of conferring high technical performance on the components treated even when the latter are of complex shape.

Furthermore, the protective effects of a surface treated in accordance with this process vis-a-vis ageing through friction, through abrasive wear, through impacts and through wet corrosion are multiplied to astonishing degrees compared with the solutions presently employed and enable these types of deterioration to be resisted over a long period. These results will be developed further on in examples.

The composition of the nitrided layer, its thickness and its hardness are adjusted so that it is resistant to wear, without, however, being fragile, since it would then flake off under the effect of impacts. The compact hexagonal structure of the  $\text{Fe}_{2,3}\text{N}$  phase of the iron/nitrogen equilibrium diagram offers a good deformation capability, owing to a high atomic density on the sliding plane, and thus favours friction applications in particular.

For the combination of surface roughness, molecular weight and surface tension of the wax, and angle of contact between solid phase and liquid phase, the ranges indicated are those which lead to maximum efficacy of the impregnation of the wax, the latter under these circumstances being able to be eliminated only under extreme, and therefore unusual, conditions, exceptional, in any case, for the applications being aimed at.

Experiments have also shown that the improvement in corrosion resistance is not due solely to the wax, since the latter, applied to another surface, even one reputed to favour the adhesion of organic products, leads to only a very much lower corrosion resistance.

Conversely, the absence of wax lowers the efficacy of nitriding, from the point of view of both friction properties and resistance to impacts, the wax contributing to minimizing the bounce effects.

In a particularly advantageous arrangement of the invention, the nitriding is carried out in a molten salt bath in accordance with FR-A-2 171 993, consisting essentially of carbonates and cyanates of alkali metals K, Na and Li, the anion  $\text{CO}_3^{2-}$  being present at 1 to 35% by weight and the anion  $\text{CNO}^-$  at 35 to 65% by weight, whereas, in the total weight of the alkali cations, the proportions by weight are 25-42.6% for  $\text{Na}^+$ , 42.6-62.5% for  $\text{K}^+$  and 11.3-17.1% for  $\text{Li}^+$ .

Also preferably, the nitriding salt bath further comprises a sulphur-containing species in a quantity such that the sulphur element content by weight is between 0.001 and 1%, in accordance with FR-A-2 271 307.

It is thus possible to control with high precision the formation of the saturated surface sub-layer following the diffusion of the heteroelement and assist the appearance in significant proportions, higher than 60%, of the  $\text{Fe}_{23}\text{N}$  phase of the iron/nitrogen equilibrium diagram.

Besides in itself improving the corrosion resistance, the oxidation treatment, when it is correctly carried out, also enables the surface properties of the solid phase to be optimized, in such a way as to lead to maximum efficacy in the wax impregnation.

The inventors have good reasons for believing that the presence in the combination layer of a strong electron donor or electron acceptor element capable of locally creating electrical dipoles is highly desirable; in this case, chemical bonding forces are created which locally reinforce the capillary forces. To this end, great importance will be placed on the presence of sulphur as well as of oxygen in the surface sub-layer.

According to preferred arrangements, the oxidation will be conducted in a molten salt bath according to FR-A-2 525 637, generally at temperatures of between 350° and 450° C.

The characteristics and other advantages of the invention will become more clear from the following description illustrated with experimental examples.

#### EXAMPLE 1

Test specimens were used, consisting of pairs comprising a

ring with a diameter of 35 mm and a plate whose dimensions were 30 x 18 x 8 mm, made of XC 38 steel.

These samples were nitrided in a molten salt bath, made from sodium carbonates and cyanates, potassium and lithium according to FR-A-2 171 993 and FR-A-2 271 307, with 37% by weight of cyanate ions  $\text{CNO}^-$  and 10 ppm of  $\text{S}^{2-}$  approximately, the temperature of the bath being  $570 \pm 15^\circ\text{C}$  and the period of immersion of the components being 90 mins.

The sulphonitrided layer comprises, in composition by weight, approximately 87% iron nitride  $\epsilon$  ( $\text{Fe}_{23}\text{N}$ ), approximately 10% nitride  $\gamma^1$  ( $\text{Fe}_4\text{N}$ ), the rest being iron oxides, sulphides and oxysulphides. It has a hardness of 600 HV 0.1.

Structurally, the sulphonitrided layer has a thickness of 15  $\mu\text{m}$  with a compact deep sub-layer with a thickness of 8  $\mu\text{m}$  and a 7  $\mu\text{m}$  porous surface sub-layer, the diameter of the pores being between 1 and 2.5  $\mu\text{m}$ , with a maximum pore density in the 1.5 - 2  $\mu\text{m}$  range.

On removal from the nitriding bath, the components are immersed for 20 mins in a salt bath according to FR-A-2 525 637, at a temperature of  $420 \pm 15^\circ\text{C}$ .

After this treatment, the nitrided layer of the components includes nitride  $\epsilon$  with 6% nitride  $\gamma^1$ , while all the oxysulphur compounds have been transformed into magnetite iron oxide ( $\text{Fe}_3\text{O}_4$ ), with inclusion oxygen in the first 2 to 3 surface micrometres.

The surface roughness is now 0.6  $\mu$  CLA.

The corrosion resistance in standard salt spray is 50 - 60 hours for the nitrided components and 200 - 250 hours for nitrided and then oxidized components, whereas before treatment components exhibit all-over corrosion after just a

few hours.

In a friction test, where a rotating ring bears on a parallelepipedal plate with a load increasing linearly from the initial value of 10 daN and with a sliding speed of 0.55 m/s, the duration of the test reaches 30 mins for the nitrided components, with a total wear in the two components of 50  $\mu\text{m}$  and a coefficient of friction of 0.40. With the nitrided then oxidized components, these figures change respectively to 45 minutes test duration, 40  $\mu\text{m}$  cumulative wear and 0.30 coefficient of friction.

On the components thus nitrided and then oxidized, an impregnation is carried out by immersing them for 2 mins in molten polyethylene wax at a temperature of 150°C. On leaving the bath of molten wax, the components are wiped with a clean, dry rag.

The surface tension of the viscous phase is 32 mN/m and the angle of contact between the solid phase, here the sulphonitrided and then oxidized layer, and the viscous phase, is 41 degrees.

The corrosion resistance then exceeds 2000 hours, whereas the friction test is able to take place over 50 mins, for a cumulative wear of only 25  $\mu\text{m}$  and a coefficient of friction of 0.18.

Experiments of the same type have been carried out on components having been nitrided either by gaseous method in an ammonia atmosphere, or by ionic method in a nitrogen atmosphere: comparable results are obtained.

The same is true for carrying out a thermochemical nitrocarburizing treatment in a nitride/carbon medium, for example in a salt bath or by gaseous method, provided however that the embrittling effect of the carbon is limited, which,

in practice, limits to 3% its proportion in the surface diffusion layer.

It has also been possible to verify that oxidation subsequent to the thermochemical treatment may be carried out, other than in a salt bath, by a simple or ionized gaseous method.

Lastly, the final coating may be produced by immersing the components, not in a bath of molten wax, but in a solvent containing the said wax in the dissolved state.

A series of examples of applications of the invention to prototypes of components representing industrial reality will be found hereinafter.

#### EXAMPLE 2

Lock components for motor vehicles, of complex shape, made from stamped, punched and folded sheet metal, were nitrided according to the conditions disclosed by FR-A-2 171 993, FR A-2 171 993 and FR-A-2 271 307. On leaving the nitriding treatment, the components underwent an oxidation treatment as disclosed by FR-A-2 525 637. Finally, an impregnation treatment was carried out using a wax of the sulphonate modified petroleum derivative type, by immersing the components in the said wax dissolved at 70g/litre in white spirit.

Thus conditioned, the components satisfy all the specifications demanded by motor vehicle manufacturers, and notably a corrosion resistance under salt spray of at least 200 hours without "white rust" and at least 400 hours without "red rust", the components having undergone, before being exposed to the salt spray, an oven drying for a period of 1 hour at a temperature of 120°C.

It will be noted that the solution commonly used up to now for

applications of this type, which is a deposition of zinc or of a zinc-nickel alloy followed by chromating, does not satisfy the above specifications.

At the same time as the corrosion resistance of the components is improved, a very smooth functioning of the locks and an absence of wear are noted, even after several tens of operations of unlocking/locking of the doors have been performed, some of them with sufficient abruptness for stress and shock effects to be produced.

### EXAMPLE 3

Under the same conditions as in Example 2, windscreen wiper spindles and supports for wiper blades, made of carbon steel, were treated.

The same corrosion resistance specifications as in Example 1 are also met here, and rubbing against sintered rings impregnated with oil takes place without obvious problems.

The reference solution used until now, which was an electrolytic nickel deposit, had two drawbacks: insufficient corrosion resistance and the existence of excessively thick deposits on the sharp edges, detrimental to the assembly of the components.

### EXAMPLE 4

Still under the same conditions as in the previous examples, self-tapping screws made of 20 CDV 5 steel, designed to pierce 30 mm of wood followed by 6 mm of steel with self-tapping in the steel, were treated.

Compared with the traditional solution of carburizing + quenching + zinc electroplating, a significant reduction in the coefficient of friction, a noticeable improvement in

resistance to wear and a clear increase in corrosion resistance are observed, not only in parts of the screw that are visible after assembly, that is in the head and in the protruding end, but also in threaded parts in contact with the wood or with the steel.

#### EXAMPLE 5

This relates to hinge pins such as those which are to be found on rising tailgates such as goods lifts on lorries, or fork-lift trucks, made from 35 CD 4 steel.

Compared with the traditional solution which makes use of a heat treatment of quench-hardening/tempering followed by bichromate electrogalvanising, a noticeable improvement in the coefficient of friction and very good corrosion resistance in dynamic operation of the hinge are observed, without any risk of embrittling the components by hydrogen.

#### EXAMPLE 6

The process according to the invention was applied to sporting bowls, notably for petanque and boules. These bowls were formed from two hemispherical domes made from type 25 CD 4 alloy steel, welded along a diametral plane. After grinding to size, they are heat treated in order to exhibit a specified hardness through their mass, greater than or equal to 110 daN/mm<sup>2</sup>. They finally undergo the same surface conditioning as in the previous four examples.

Thus produced, the bowls have a set of characteristics, coefficients of friction and regularity of surface which, in the opinion of specialists, are particularly well appreciated by high-level players, participating in tournaments and official competitions, notably: very good corrosion resistance, very low levels of wear guaranteeing compliance with the rules that state that the loss in weight due to play

must not exceed 15 g below the marked weight, ability to take impacts without damage, and a pleasant appearance with a shiny black colour.

It will be appreciated that in this type of application, the final waxing may be undertaken by the player himself.

## CLAIMS

1. Treatment process for ferrous metal components to improve simultaneously their corrosion resistance and friction properties, a process in which the components are nitrided and oxidized and receive a final coating, characterised in that the nitriding followed by oxidation leads to the formation of a layer consisting of a deep, compact sub-layer and a porous surface sub-layer, the said surface sub-layer having a thickness of between 5 and 25  $\mu\text{m}$  and having open pores whose diameter is between 0.2 and 3  $\mu\text{m}$ , and in that the nitrided and oxidised components are impregnated with a hydrophobic wax, the said wax being a carbon-containing organic compound of high molecular weight of between 500 and 10,000 and with a surface tension in the liquid state of between 10 and 73 mN/m, the angle of contact between the solid phase of the surface layer and the wax in the liquid state being between 0 and 75 degrees.
2. Process according to Claim 1, characterised in that the surface sub-layer contains over 60% solid phase  $\text{Fe}_2\text{N}$ , has a hardness of between 550 and 650 HV 0.1 and a roughness of between 0.3 and 1.5  $\mu$  CLA.
3. Process according to Claim 1 or 2, characterised in that the nitriding is implemented according to a process chosen between a nitriding in a bath of molten salts based on cyanate ions  $\text{CNO}^-$  and a nitriding in an ionized nitrogen atmosphere.
4. Process according to Claim 3, characterised in that the nitriding is carried out in a molten salt bath consisting essentially of carbonates and cyanates of alkali metals K, Na and Li, the anion  $\text{CO}_3^{2-}$  being present at 1 to 35% by weight and the anion  $\text{CNO}^-$  at 35 to 65% by weight, whereas, in the total weight of the alkali cations, the proportions by weight are 25-42.6% for  $\text{Na}^+$ , 42.6-62.5% for  $\text{K}^+$  and 11.3-17.1% for  $\text{Li}^+$ .



5. Process according to Claim 4 or 3, characterised in that the nitriding is carried out in the presence of a quantity of carbon compounds determined so as to obtain a proportion of carbon in the surface sub-layer that is less than 3%.
6. Process according to any one of the preceding claims, characterised in that a sulphurizing chemical reaction is carried out simultaneously with the nitriding, through the addition of a sulphur-containing species to the nitriding medium.
7. Process according to any one of the preceding claims, characterised in that the oxidation is implemented according to a process chosen from amongst a process using baths of molten oxidizing alkali salts, by simple gaseous method and by ionized gaseous method.
8. Process according to Claim 7, characterised in that the oxidation is carried out in a bath of molten oxidizing alkali salts at temperatures of between 350°C and 450°C.
9. Process according to Claim 1, characterised in that the wax impregnation is carried out by immersion of the components, according to a process chosen between immersion in molten wax and immersion in a solution of wax dissolved in a solvent.
10. Process according to Claim 1, characterised in that the wax is chosen from amongst natural waxes, synthetic waxes and modified petroleum residues.
11. Process according to Claim 7, characterised in that the synthetic waxes are chosen from amongst fluorinated, polyethylene, polypropylene and polyester waxes.

