

The present invention relates to a method for phosphating steel parts to improve their resistance to corrosion and wear and, more particularly, to a preliminary treatment of the surface of the parts.

The performance of parts that have undergone phosphating, whatever their application, is known to depend essentially on two characteristics: the crystallinity and the quality of adhesion of the phosphated layer to a substrate.

These two characteristics depend directly on the quality of the preparation of the metal surface prior to the actual phosphating process. The physico-chemical state of this surface in fact influences its reactivity with regard to the active agents in the phosphating bath, as well as the epitaxial growth of the layer of complex phosphates.

Generally, the aim is then to obtain a fine, regular crystallization, resulting in a layer which is as dense as possible.

Out of the whole layer building process, it is the germination stage which plays the predominant role in achieving this effect. This is why techniques have been sought which are capable of maximum activation of the metal surface and of creating thereon the largest possible number of germination sites. A certain number of solutions are known.

One of these solutions involves electrolytically polishing the steel substrate, followed by depassivation and sanding with a cutting abrasive.

Another solution consists of "seeding" the surface with crystallisation germs, for example, by pre-rinsing the basic steel with a suspension of titanium salts.

Another solution consists of adapting the composition of the phosphating bath, for example by using additives such as certain nickel or cadmium salts.

Finally so-called "spraying" techniques are also known, in which acicular crystallisation is induced through the action of jets.

It is known, furthermore, that not all steels can be phosphated, notably those containing over 5% of metallic addition elements, such as Cr, Mo and Ni, with which low-coherence layers would be obtained. This effect can be attenuated, to a certain extent, by specially adjusting the acidity of the phosphating bath, or by preliminary depassivation.

In conventional applications and when the parts are not required to have exceptional qualities, the aforementioned techniques give manufacturers satisfactory results, for example resistance to corrosion of 50 to 100 hours' exposure to a saline mist or, for example, an improvement in running-in conditions during the very first hours thereof.

On the other hand, once the requirements for resistance to corrosion and wear become more strict, these solutions prove inadequate. Other methods have thus been developed.

Such as, for example, in the document DE-A-28 53 542, which discloses that good protection against corrosion of steel parts can be obtained by initially nitriding the parts and then, secondly, phosphating them and, more particularly, phosphating them using manganese.

Variants of this technology are described in the documents JP-A-53-001647 and SU-A-926070.

Here again, however, in view of the constantly increasing

technical requirements with regard to resistance to wear and corrosion, the properties conferred on the parts by these

methods also often prove to be inadequate nowadays. They cannot, notably, guarantee the 400 hours' resistance to saline mist desired by the car industry. In the case of highly stressed carbonitrided steel gears, the surface phosphating is entirely removed in barely more than ten hours or so, that is to say in approximately the time required for running-in, resulting, when this period of time has elapsed, in the loss of the beneficial effect of the phosphated layer on the retention, and hence the stability, of lubricant films.

The present invention aims to overcome these shortcomings by making it possible:

- firstly, to achieve a much improved surface activation, with a proliferation of the germination sites, resulting in the perfectly reliable and reproducible obtaining of phosphated layers that are very dense, finely crystallized and very adherent;
- secondly, to avoid limiting the phosphating substrate to the nitrided layers, as was the case in the method described in the document DE-A-28 53 542;
- and, finally, to broaden the field of application of phosphating to steels other than those containing less than 5% of metallic addition elements.

For this purpose, the present invention proposes a method for phosphating steel parts to improve their resistance to corrosion and wear, in which, after preliminary surface treatment of the surface of the parts, the latter is brought into contact with a solution containing essentially protons, phosphate anions and cations selected from amongst Ca^{2+} , Zn^{2+} and Mn^{2+} , characterised in that the preliminary treatment is a salt bath treatment in the presence of sulphur-containing

species causing the formation of a layer of iron compounds with at least one element selected from carbon and nitrogen, and reciprocal thermal diffusion of the compounds of the layer and of the iron of the part so that the surface of the latter has, per 1000 atoms, at least 150 atoms of free iron and 5 to 150 atoms of sulphur, and has a porosity defined by a ratio of actual surface area to macroscopic surface area of at least 20.

Thus, in the preliminary treatment, a thermochemical treatment involving diffusion between the iron of the substrate and one or more filler metalloids of the nitrogen and/or carbon type is carried out simultaneously with an addition of sulphur-containing species.

According to one variant, in the preliminary treatment, sulphur-containing species are added independently in a second step. As in the above-mentioned method, thermochemical diffusion is initially effected between the iron of the substrate and one or more filler metalloids of the nitrogen and/or carbon type, followed by a conventional sulphuration operation.

According to another variant, the sulphur-containing species are also added in a second step through a sulphuration process and the diffusion step is carried out by depositing a metal capable of forming intermetallic compounds with iron, with reciprocal thermal diffusion of the intermetallic compounds and of the iron of the part, this metal being, for example, chromium or tin.

Thermochemical diffusion processes in molten salt baths, with or without sulphur-containing species, are carried out, for example, according to the disclosures of the patents FR-A-2 171 993 and FR-A-2 271 307, wherein steel parts are immersed in a bath containing cyanates, carbonates and/or S^{2-} ions.

The sulphuration process is carried out, for example, according to the disclosures of the patent FR-A-2 050 754, in molten salt baths.

It can also be carried out by sulphur ion implantation.

Thermal diffusion by depositing a metal is carried out in accordance with conventional, so-called case hardening techniques.

By means of the methods of the invention, after the preliminary treatment a surface layer is obtained which has the following three characteristics:

- it contains active free iron, in a proportion of at least 150 atoms per 1000 atoms;
- it also contains free or combined sulphur in a proportion of 5 to 150 atoms per 1000 atoms;
- and its actual area is at least 20 times greater than its apparent area, without for all that being powdery or having the consistency of a foam.

The invention results from the unexpected synergetic effect due to the combination of these three characteristics.

The present invention will be more clearly understood from the following description illustrated by examples of experiments.

Example 1: Corrosion resistance tests

A series of experiments were carried out on ground rings made of non-alloy steel containing 0.38% carbon, with a diameter of 35 mm and a height of 15 mm.

In each experiment, a different preliminary treatment was

carried out, resulting in the formation of a surface layer having different characteristics.

The parts were then subjected to phosphating under the same operating conditions, by immersing them for 15 minutes in a bath of the zinc/iron type, at a temperature of 90°C, the composition of which was as follows:

- 12 g/l of P_2O_5
- 5 g/l of NO_3^-
- 6 g/l of Zn^{2+}
- 2.5 g/l of Fe^{2+}

The resistance to corrosion of the parts treated was then measured in a standardised saline mist.

Experiment 1:

The steel rings were immersed in a nitriding bath in accordance with the disclosures of patents FR-A-2 171 993 and FR-A-2 271 307, containing by weight 37% alkaline carbonate ions, cyanate ions and 10 ppm S^{2-} ions, the temperature of the molten salts being 570°C and the time of immersion of the parts being 90 minutes. When the parts were removed from the bath, they were washed in water so as to rid them of the surrounding gangue of salts, and then dried.

This treatment led to the formation, on the surface of the parts, of a nitrided layer in accordance with the present invention having the following characteristics:

- the outer part was porous, the actual surface area of the rings being approximately 25 times greater than their apparent surface area;
- it included sulphur-containing species in a proportion of 20 sulphur atoms per 1000;

- it also contained free iron, in a proportion of 300 atoms per 1000.

The parts were then phosphated and then subjected to corrosion tests in a standardised saline mist. It was found that they withstood these conditions for at least 700 hours and, in certain cases, more than 1200 hours, the average for a series of 50 being 900 hours.

Experiment 2:

The operating conditions were those of the preliminary treatment of Experiment 1, everything being the same except that there was no sulphur in the nitriding bath.

The nitriding led to the formation, on the surface, of a layer that:

- contained approximately 350 atoms per 1000 of free iron;
- had an actual surface area 20 times greater than the apparent surface area.

In comparison with the nitrided layer obtained under the conditions of Experiment 1, the layer did not include any sulphur-containing species, but the other characteristics, free iron content and actual surface area in relation to apparent area, were of the same order of magnitude.

It was found that the phosphated parts had a resistance to corrosion in a saline mist not exceeding 350 hours.

This experiment clearly demonstrates the importance of the presence of sulphur in the outer layer since, in the absence of sulphur-containing species, resistance drops from 900 to 350 hours.

Experiment 3:

The rings underwent chemical pickling followed by blasting, so that their actual surface area was 2 to 3 times greater than their apparent surface area.

After phosphating, the tests in a saline mist showed a resistance to corrosion of an average of 70 hours, which was in accordance with the results currently obtained using conventional techniques.

This experiment shows the considerable improvement in resistance to corrosion afforded by the invention in comparison with the conventional techniques since, in Experiment 1, resistance to corrosion of up to 1200 hours in a saline mist was obtained.

Experiment 4:

The parts from Experiment 3 were taken, having been chemically pickled and then blasted, and sulphuration was then carried out (in accordance with the disclosures of patents FR-A-2 171 993 and FR-A-2 271 307), by immersing them in a molten salt bath containing potassium thiocyanate, sodium thiocyanate and potassium and/or sodium cyanide, the duration of this immersion being reduced to a few seconds only, instead of the conventional 2 to 3 minutes, so as not to carry out total sulphuration but to obtain a surface sulphur content limited to approximately 100 atoms per 1000.

The saline mist tests demonstrated a resistance to corrosion of not more than 250 hours.

Comments:

These experiments clearly confirm the synergetic effect afforded by the three characteristics sought for the surface

prior to phosphating, relating to the free iron content, the sulphur content and the actual to apparent surface area ratio.

By adopting the conditions according to the invention, corrosion resistance values are obtained which are very much higher, the increase being from approximately 300 hours' to 900 hours' resistance on average and even as much as 1200 hours.

It will be noted however that, in the case of Experiment 4, non-observance of the specification concerning the ratio of the actual to apparent surface areas results in a performance that is far below the 900 hour average of the first experiment.

Example 2: Resistance to wear tests

Hardened tempered 35 NC 6 steel gears with a pitch circle diameter of 240 mm and a modulus of 8 were tested, the gears being operated on a suitable machine rotating at 1660 rev/min, transmitting a torque of 450 mN.

A first experiment in the absence of any surface treatment of the gears indicated that running-in was not satisfactory. After 15 hours' operation, numerous scores were noted on the tooth flanks.

In a second experiment, the gears were subjected to a conventional preliminary treatment before phosphating. After the same 15-hour period of operation, the phosphated parts were found to have smooth tooth flanks. This time, running-in took place satisfactorily. On the other hand, the entire phosphated layer was observed to have disappeared, leaving the steel bare. It was also noted that, as long as there was adequate lubrication, the gears could continue to function normally. However, if a lack of lubrication was instigated, for example as a result of it being momentarily interrupted, a

very swift deterioration in friction was observed: vibrations occurred and the flanks of the teeth were, on dismantling, deeply scored.

Finally, in a last experiment, phosphating was carried out according to the invention, that is to say with a preliminary surface treatment by nitriding with the addition of sulphur, under the same conditions as in Experiment 1, Example 1. The life of the phosphated layer was then found to be very substantially improved. After the gears had been operating for 150 hours, the phosphated layer of the gears had still not worn off. It could therefore still fulfil its function. Thus, if a momentary lack of lubrication was instigated, the surface condition of the teeth remained intact and, once the normal lubrication process was restored, friction was able to resume satisfactorily.

Example 3:

The same rings were used as in Example 1 and, prior to phosphating, a preliminary treatment using another thermal diffusion technique was carried out, the aim being identical characteristics for the surface layer to be obtained.

In a first step, chromium was thermochemically diffused in the steel, according to the so-called chromizing method, also known as chromium case hardening, at a temperature of 1000°C.

A layer of mixed carbides was thus obtained containing free iron, the finely porous outer part of which had a large specific surface area.

In a second step, this layer was enriched with sulphur using the so-called ion implantation technique with a high-energy ion beam, following, or accompanying, this implantation with a heat treatment at a temperature of 250°C for 30 minutes.

The parts thus prepared were then phosphated under the same conditions as in Example 1.

The phosphated parts then underwent the corrosion tests in a standardised saline mist. No corrosion pitting was observed after 1000 hours.

By comparison, the parts that had been chromized in the same way, but had not undergone sulphur implantation, did not withstand corrosion for more than 300 to 400 hours.

Example 4:

Tests were conducted on steel cylindrically-shaped fixing pins for steam turbine blades which connect the hub to the vanes.

In service, these parts are subjected to severe contact corrosion stress ("fretting corrosion") as well as corrosion from steam. They also have to resist seizure and scoring when they are being fitted and removed, whether when first installed or at the time of periodic inspections.

A phosphating treatment carried out on these pins under conventional conditions enabled them to resist corrosion at best for a few dozen hours and ensured protection against friction damage only when they were mounted for the first time.

The pins were subjected to phosphating preceded by the following treatment. Tin was electrolytically deposited, this being followed by a heat treatment in a neutral nitrogen atmosphere, so as to produce on the surface of the parts a finely porous metallic diffusion layer containing free iron, which was slightly enriched with sulphur by one or the means described in the previous examples (ion implantation or thermal diffusion).

A service life of several hundred or even several thousand

hours was then found, with periodic mounting and removal operations.

In view of the results of the experiments described in these examples, an attempt has been made to refer the phenomena observed back to the probable theoretical mechanisms.

The reaction mechanism of phosphating is relatively complex; briefly it involves first of all phosphoric acid attacking the metal forming the part to be treated (generally the iron of the steel), followed by the precipitation of insoluble phosphates, generally of the $(PO_4)_2 Me_3$ type (Me being Zn, Ca or Mn), but also $(HPO_4)_2 Me_2$, $(HPO_4)_2 Fe_2$, $(HPO_4)_2 MeFe$.

It is a question therefore of heterogeneous liquid/solid phase reactions which are easier the more the solid phase is divided. Hence the advantage of the surface of the part to be treated having numerous fine pores, that is to say a large specific surface area.

In practice, however, there is a porosity threshold beyond which the cohesion of the surface layers is no longer sufficient to enable the part to perform its mechanical and tribological functions.

The presence of active iron is also essential for the attacking reaction to take place between the iron and the phosphoric acid contained in the bath.

Among the techniques at the disposal of the practitioner for obtaining the two aforementioned effects simultaneously, those based on thermochemical mechanisms of metal and/or metalloid diffusion are of considerable industrial interest as they combine ease of implementation with a low operating cost.

In these techniques, the presence of active iron in the vicinity of the surface is linked with the migration of this

element through the diffusion layer from the steel substrate. As for the fine surface pores, these are generated by the KIRKENDALL effect, that is to say the effect associated with the difference in mobility of the atoms of the elements forming part of the diffusion layer.

With regard to the function of the sulphur, the basic concept behind its interpretation is connected with the mechanism of the phosphating of the iron, which brings into play the oxidation (in the sense of the degree of oxidation) of this iron and the combining of the oxidated iron with the phosphate ions.

It can thus be assumed that the phosphating process is facilitated by carrying it out on a previously oxidated surface, wherein the iron would be stabilised by a species leading to a reversible reaction, so that the subsequent iron/phosphorus combination is obtained by means of an exchange reaction: in this way, a large proportion of the energy used to phosphate the iron would be saved.

It will be noted that the above stabilising species could not be the oxygen itself as it would result in compounds that were too thermodynamically stable.

On the other hand, sulphur is an advantageous intermediate, the main reasons being as follows:

- the iron/sulphur compounds, of the $\text{Fe}_{(1-x)}\text{S}$ type with $x \leq 1$, which exist in a large range of the Fe/S ratio, correspond to an oxidised form of the metal;
- they also correspond to a reversible equilibrium in which the sulphur can easily be exchanged with another element or ion which is a stronger electron donor;
- they can easily be reduced by acids or reducing metals such

as zinc, so that it can be considered that their passage through the phosphating bath frees them from the substrate and that they play only an intermediate role, similar to that played by catalysts in chemistry.

CLAIMS

1. Method for phosphating steel parts to improve their resistance to corrosion and wear, in which, after a preliminary treatment of the surface of the parts, the latter is brought into contact with a solution containing essentially protons, phosphate anions and cations selected from amongst Ca^{2+} , Zn^{2+} and Mn^{2+} , characterised in that the preliminary treatment is a salt bath treatment in the presence of sulphur-containing species causing the formation of a layer of iron compounds with at least one element selected from carbon and nitrogen, and reciprocal thermal diffusion of the compounds of the layer and of the iron of the part so that the surface of the latter comprises, per 1000 atoms, at least 150 atoms of free iron and 5 to 150 atoms of sulphur, and has a porosity defined by a ratio of actual surface area to macroscopic surface area of at least 20.

2. Method according to Claim 1, characterised in that the salt bath includes alkaline carbonates and cyanates, with 10 ppm of sulphur S^{2-} .

3. Method for phosphating steel parts to improve their resistance to corrosion and wear, in which, after a preliminary treatment of the surface of the parts, the latter is brought into contact with a solution containing essentially protons, phosphate anions and cations selected from amongst Ca^{2+} , Zn^{2+} and Mn^{2+} , characterised in that the preliminary treatment includes a salt bath phase causing the formation of a layer of iron compounds with at least one element selected from carbon and nitrogen and reciprocal thermal diffusion of compounds of the layer and of the iron in the part, and then a sulphuration phase, so that the surface of the part has, per 1000 atoms, at least 150 atoms of free iron and 5 to 150 atoms of sulphur, and has a porosity defined by a ratio of actual surface area to macroscopic surface area of at least 20.



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4. Method according to Claim 3, characterised in that the salt bath includes alkaline carbonates and cyanates.

5. Method according to one of Claims 2 and 4, characterised in that, the salt bath being at $570^{\circ}\text{C} \pm 15^{\circ}\text{C}$, the parts are immersed therein for 90 minutes ± 15 minutes.

6. Method for phosphating steel parts to improve their resistance to corrosion and wear, in which, after a preliminary treatment of the surface of the parts, the latter is brought into contact with a solution containing essentially protons, phosphate anions and cations selected from amongst Ca^{2+} , Zn^{2+} and Mn^{2+} , characterised in that the preliminary treatment includes a phase consisting of depositing a metal capable of forming intermetallic compounds with the iron, with reciprocal thermal diffusion of the intermetallic compounds and the iron in the part, and then a sulphuration phase, so that the surface of the part has, per 1000 atoms, at least 150 atoms of free iron and 5 to 150 atoms of sulphur, and has a porosity defined by a ratio of actual surface area to macroscopic surface area of at least 20.

7. Method according to Claim 6, characterised in that the metal is chromium, diffusion being carried out in the region of 1000°C .

8. Method according to Claim 6, characterised in that the metal is electrolytically deposited tin, diffusion being carried out at between 300°C and 600°C in a nitrogen atmosphere.

9. Method according to one of Claims 3 and 6, characterised in that the sulphuration phase includes electrolysis in a bath of molten alkaline thiocyanates.

10. Method according to one of Claims 3 and 6, characterised in that the sulphuration phase is carried out through sulphur



ion implantation.

- Q. Method according to one of Claims 9 and 10, characterised in that the sulphuration phase includes diffusion at at least 180°C.

