

The invention relates to a process for imparting excellent corrosion resistance to articles made from ferrous metal, with good friction properties, a low coefficient of friction and resistance to wear and seizing, a process in which the articles are nitrided and then oxidised either in a bath of molten oxidising alkaline salts or by means of an oxidising ionised atmosphere, so that the articles have a nitrided outer layer with a compact deep sublayer and a porous surface sublayer.

It is known, notably from FR-A-2 171 993 and FR-A-2 271 307, that nitriding of articles made from ferrous metal in molten cyanate and carbonate baths improves the friction properties of these articles, lowering the coefficient of friction and increasing the resistance to wear and seizing. Other nitriding processes, such as ionic nitriding, performed in an ionised atmosphere containing elemental or combined nitrogen, results in comparable properties.

It is known, furthermore, that oxidation in a bath of molten oxidising salts causes modifications to the nitrided surface, which thereby acquires a marked improvement in corrosion resistance without losing its good friction properties arising from the nitriding. Thus the document FR-A-2 525 637 describes a particularly effective oxidation treatment performed in a bath of molten salts comprising, by weight, from 99.5 to 85% by weight of a mixture consisting of 25 to 35% by weight of alkali nitrates, 8 to 15% of alkali carbonates and the remainder to 100% of alkali hydroxides, and from 0.5 to 15% of oxygen-containing salts of alkali metals whose normal oxidation-reduction potential relative to the reference hydrogen electrode is lower than -1.0 volt, into which bath a gas containing oxygen is injected at a flow rate sufficient for the bath to be saturated with dissolved oxygen, and the content of insoluble particles therein is maintained at less than 3% by weight.

It is also known how to oxidise the nitrided articles in an ionised atmosphere of a gas containing oxygen, with similar improvements to the corrosion resistance.

However, corrosion resistance requirements, either in corrosive atmospheres or in the absence of lubrication, or in the case of articles subjected to fatigue stresses, are increasing continually, and the corrosion resistances obtained by the processes referred to above are becoming inadequate. This appears to be particularly true in the case of articles whose shape is unfavourable for the homogeneity of the operations or for which, owing to relatively short production runs, it is difficult to optimise the sequence of operations while controlling, for example, the curves for the rate of temperature variations.

The aim of the invention is therefore to improve the corrosion resistance of previously nitrided and then oxidised articles made from ferrous metals, in a reliable manner, without reducing the friction properties imparted by the nitriding, but possibly improving them.

To achieve this aim, the invention proposes a process for imparting excellent corrosion resistance to articles made from ferrous metal, with good friction properties, a low coefficient of friction and resistance to wear and seizing, a process in which the articles are nitrided and then oxidised either in a bath of molten oxidising alkaline salts or by means of an oxidising ionised atmosphere, so that the articles have a nitrided outer layer with a compact deep sublayer and a porous surface sublayer, characterised in that the nitriding and oxidation are effected so that the deep sublayer has a thickness of at least 4  $\mu\text{m}$  and the surface sublayer has a thickness of between 2 and 20  $\mu\text{m}$ , the diameter of the pores being at least 100 nm, and in that, after the oxidation stage, the nitrided/oxidised layer is coated, to a thickness of between 3 and 20 micrometres, with a polymer selected from

amongst fluorocarbon polymers and copolymers, polyurethane polymers and copolymers which are either silicone-treated or fluorinated and which are used alone or mixed with each other or with hydrocarbon polyurethanes, urethane and acrylic copolymers, and polyamides-imides.

As will be shown by the examples below, the articles thus treated can withstand periods of exposure to saline most of 500 to 1500 hours without the appearance of any signs of corrosion. According to the state of the art, periods of exposure of only 250 hours were regarded as satisfactory in their time.

A process for improving the wear and corrosion resistance of metal surfaces is known from the document WO-A-8 705 335 (P FOX). The process consists essentially of a surface case hardening in a fluidised bed in a gaseous atmosphere. In a first stage an article is exposed to an atmosphere containing nitrogen, ammonia and natural gas at a temperature of between 400°C and 650°C for 1 to 5 hours. Then, in a second stage, the article is exposed to a gaseous atmosphere of humidified nitrogen and optionally containing oxygen, at a temperature of between 400°C and 650°C. Lastly, in a final stage, the treatment is completed by coating with a composition of water-based polymers, polysiloxanes and phosphating oils, a composition which is known for its intrinsic anticorrosion properties.

An article treated in this way has successive sublayers of different kinds. The first case-hardening stage has the effect of creating a deep underlying region of diffused nitrides with a thickness of approximately 150 to 200  $\mu\text{m}$ , having on top of it a "blank" sublayer of pure nitrides with a thickness of approximately 25  $\mu\text{m}$ . The second case-hardening stage has the effect of creating a sublayer of oxides with a thickness of approximately 13  $\mu\text{m}$  above the pure nitride sublayer.

The final treatment makes it possible to maintain all the acquired corrosion and wear resistance properties by means of the surface case-hardening of the article in a gaseous environment.

The articles treated by means of this process do not exhibit any traces of corrosion after exposure to saline mist for 450 hours.

However, this document does not record any particular improvement in the frictional characteristics.

On the other hand, the tests reported below will also demonstrate that, in friction tests and in comparison with nitrided and oxidised articles according to the state of the art, the articles treated according to the invention exhibit improved coefficients of friction, reduced wear, and load-bearing capacities which are at least as good.

The improvement in friction performance demonstrates that the coating produces an effect which is specific in aspects which are unexpected, especially in the case of the rate of wear and the load-bearing capacity. Furthermore, the improvement in corrosion resistance is not merely the fact of the presence of the coating since, as will be shown by the examples, the same coating does not bring about a comparable improvement in corrosion resistance when applied to surfaces of substrates which are well known for promoting the bonding of coatings and, in some cases, for themselves improving the corrosion resistance.

The preferred coating thicknesses are between 3 and 15  $\mu\text{m}$ ; thicknesses greater than 15  $\mu\text{m}$  do not contribute anything to the corrosion resistance and cause changes in the dimensions of articles which are sometimes awkward, together with a tendency to crumbling and sticking.

The nitriding is preferably 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  $\text{CO}_3^{--}$  anion being present at 1 to 35% by weight and the  $\text{CNO}^-$  anion at 35 to 65% by weight, while in the total weight of the alkali cations the proportions by weight are 25-42.6% in the case of  $\text{Na}^+$ , 46.6-62.5% in the case of  $\text{K}^+$  and 11.3-17.1 in the case of  $\text{Li}^+$ .

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

In a preferred arrangement the oxidation will be conducted in a molten salt bath according to FR-A-2 525 637, referred to above, and generally at temperatures of between  $350^\circ$  and  $450^\circ\text{C}$ .

The characteristics and advantages of the invention will emerge more clearly from the description which is to follow, illustrated by experimental examples.

#### Example 1 - Corrosion resistance

Sample plates of XC38 steel, 100 mm x 100 mm in size, were nitrided in a bath of molten salts, sodium, potassium and lithium carbonates and cyanates according to FR-A-2 171 993 and FR-A-2 271 307, with 37% by weight of  $\text{CNO}^-$  cyanate ions and approximately 10 ppm of  $\text{S}^{--}$  ions, the temperature of the bath being  $570 \pm 15^\circ\text{C}$  and the period of immersion of the articles being 90 min.

The nitriding layer comprises, in composition by weight, approximately 87%  $\epsilon$  iron nitride ( $\text{Fe}_{2,3}\text{N}$ ) and approximately 10%  $\gamma'$  nitride ( $\text{Fe}_4\text{N}$ ), the remainder being iron oxides, sulphides and oxysulphides.

Structurally the nitrided layer has a thickness of 15  $\mu\text{m}$  with a compact deep sublayer 8  $\mu\text{m}$  in thickness.

On leaving the nitriding bath the articles are immersed for 20 min in a salt bath according to FR-A-2 525 637, at a temperature of  $420 \pm 15^\circ\text{C}$ . The bath was made up as follows:

1020 g of caustic potash, 510 g of sodium nitrate and 170 g of sodium carbonate are melted in a 1 litre electrically heated crucible. To this is added 85 g of a mixture of equal parts by weight of potassium permanganate and dichromate, whose normal oxidation-reduction potentials are lower than -1 volt relative to the hydrogen electrode.

The crucible is provided with an immersed nozzle connected to a source of pressurised air through a valve for controlling the flow rate and a flow meter capable of measuring flow rates of between 0.02 and 0.2  $\text{cm}^3/\text{s}$ . A sintered iron filter fitted with a heating jacket has been arranged beside the crucible, and the contents of the crucible are passed through this periodically to retain the solid particles of more than 3  $\mu\text{m}$  in size and thus to maintain the proportion of insoluble materials in the crucible at a suitable value. The air flow rate is 0.42 l/h, that is 0.12  $\text{cm}^3/\text{s}$ .

After this treatment the nitrided layer on the articles contains  $\epsilon$  nitride with 6%  $\gamma'$  nitride, whilst all the oxysulphide compounds have been converted into magnetite iron oxide ( $\text{Fe}_3\text{O}_4$ ), with oxygen inserted into the first 2 to 3 micrometres at the surface.

The resistance to corrosion in a standardised saline mist is established as 50-60 hours in the case of the nitrided articles and 200-250 hours in the case of the articles which have been nitrided and then oxidised, whereas before treatment the articles exhibit a generalised corrosion after only a few hours.

A coating of fluoroethylene-propylene (FEP) 10  $\mu$  in thickness is produced on the articles which have thus been nitrided and then oxidised, by electrostatic spraying of a powder with a particle size of 5  $\mu$ m, followed by a sintering treatment for 10 minutes at 350°C.

The resistance to corrosion in saline mist in accordance with AFNOR standard NF x 41002 exceeds 1500 hours, no pitting or separation of the FEP layer being observable at 1500 hours' exposure.

#### Example 2 - Comparative

The operation was carried out on sample pieces of steel for screw cutting (AFNOR standard 40 MF 6) 20 mm in diameter and 55 mm in height.

These pieces were subjected to various known surface treatments well known for facilitating the bonding of coatings, and were then given an FEP coating as in Example 1, 10  $\pm$  1.5  $\mu$ m in thickness (electrostatic dusting and sintering at 350°C).

After the coating a cross-shaped scratch was made using a scribe point pressing sufficiently to cut through the FEP coating; after this the specimens were subjected to the saline mist test according to AFNOR x 41002.

The test was followed by daily visual observations, to watch for the appearance of corrosion pitting and coating separations.

The test results are summarised, using averages of three samples, in Table I below.

Table I (see following page)

TABLE I

| TREATMENT BEFORE<br>FEP COATING | PERIOD OF EXPOSURE<br>TO SALINE MIST<br>(hours) | OBSERVATIONS                                              |
|---------------------------------|-------------------------------------------------|-----------------------------------------------------------|
| None                            | 24                                              | generalised corrosion<br>complete separation of the layer |
| Wet sand-blasting               | 24                                              | pits at the location of the cross                         |
|                                 | 72                                              | generalised pitting<br>separation of the layer            |
| Sulphiding                      | 24                                              | generalised corrosion<br>separation of the layer          |
| Zinc<br>phosphating             | 48                                              | pits at the location of the cross                         |
|                                 | 168                                             | generalised corrosion<br>separation of the layer          |
| Manganese<br>phosphating        | 48                                              | generalised corrosion<br>separation of the layer          |
| Oxidation                       | 24                                              | numerous pits<br>localised separations                    |
| Nitriding                       | 312                                             | initial pits                                              |

It will be noted that the oxidation and nitriding were performed on separate articles, but in the respective baths according to Example 1. Oxidation alone gives practically no improvement in corrosion resistance.

Tests were performed on similar articles, treated according to Example 1 and subjected to the saline mist test after scratching of a cross with a scriber point. No pitting or coat separation were noted at 1500 hours.

### Example 3. Frictional properties

These tests were carried out to confirm that the improvement in corrosion resistance of the treatment according to the invention did not take place at the expense of a deterioration in the frictional properties.

This example related to articles made of XC 18 carbon steel treated by nitriding, oxidation and FEP coating as in Example 1.

### Test A - Friction-measuring instrument

The test specimens consist of pairs consisting of a 35 mm diameter ring, bearing dry on a small parallelepipedal plate 30 mm x 10 mm x 8 mm in size. The ring rotates at a speed corresponding to a sliding speed of 0.55 m/s and the bearing load increases linearly, starting with an initial value of 10 daN.

The result of the test is evaluated using 4 values: period of time before the appearance of the first incidents (binding, judder); maximum load reached, mean coefficient of friction, wear.

The same test was carried out, by way of comparison, on pairs

which had not been subjected to any treatment, nitrided pairs and pairs which were nitrided and then oxidised. The results are shown in Table II.

TABLE II

| TREATMENT OF THE PAIR SPECIMENS  | TEST PERIOD (min) | CUMULATIVE WEAR ON THE TWO PIECES ( $\mu\text{m}$ ) | MAXIMUM LOAD REACHED (dan) | COEFFICIENT OF FRICTION |
|----------------------------------|-------------------|-----------------------------------------------------|----------------------------|-------------------------|
| none                             | 0                 | i m m e d i a t e s e i z u r e                     |                            |                         |
| nitriding                        | 30                | 50                                                  | 60                         | 0.40                    |
| nitriding-oxidation              | 45                | 40                                                  | 90                         | 0.30                    |
| in accordance with the invention | 45                | 30                                                  | 90                         | 0.20                    |

It is noteworthy that the treatment in accordance with the invention reduces the wear and the coefficient of friction without affecting the load-carrying capacity when compared with the articles which are nitrided and then oxidised.

#### Test B - Flat friction

A flat shoe rubs to-and-fro on a flat slide at a speed of 0.03 m/s and under a load of 5 MPa (50 bars). The test period corresponds to 500 cycles and the test is carried out dry in air.

The evaluation values are the coefficient of friction and the wear on the slide. The comparison test was carried out on articles nitrided and oxidised as in the preceding tests. The results are shown in Table III below.

Table III

| TREATMENT                     | SLIDE WEAR ( $\mu\text{m}$ )<br>AFTER 500 CYCLES | MEAN COEFFICIENT<br>OF FRICTION |
|-------------------------------|--------------------------------------------------|---------------------------------|
| nitriding-<br>oxidation       | 7                                                | 0.48                            |
| according to<br>the invention | 6                                                | 0.43                            |

#### Test C - Fatigue in alternating flexure

Alternating flexure fatigue tests were carried out on rotating specimens made of 35 CD 4 quenched and annealed steel, which were stressed laterally. The standard specimens have an endurance limit of 630 MPa (63 hbar). After nitriding, this endurance limit rises to 820 MPa (82 hbar). The treated specimens according to the invention have the same endurance limit as the nitrided specimens.

#### Example 4 - Appropriate coating thicknesses

Articles as in Example 1 are covered with FEP coating layers by electrostatic dusting and sintering under the conditions of this Example 1, but with thicknesses ranging between 1 and 40  $\mu\text{m}$ .

In the saline mist test, the period of exposure before the appearance of signs of corrosion does not differ appreciably, in the case of thicknesses up to 3  $\mu\text{m}$ , from the period of exposure of uncoated nitrided-oxidised articles, that is 200-250 hours. This period increases with the coating thickness up to approximately 10  $\mu\text{m}$ , that is 350-400 h at 4  $\mu\text{m}$ , 800 h at 6  $\mu\text{m}$  and 1500 h in the case of 10  $\mu\text{m}$ .

Beyond 10  $\mu\text{m}$  no further significant increase is recorded in the period of exposure before the appearance of signs of corrosion.

However, the production of thick coatings may become tricky in industrial production if thickness irregularities are to be avoided, especially if the articles are complex in shape, and high thicknesses may give rise to difficulties in fit tolerances.

In addition, thick coatings of more than 20  $\mu\text{m}$  exhibit degraded frictional performance with sticking, juddering and crumbling of the coating. In the majority of cases it will be at least prudent not to exceed thicknesses of 15  $\mu\text{m}$ .

#### Example 5 - Morphology of the nitrided layer

The tests in this example were intended to determine the morphological parameters of the nitrided layer which must be complied with in order to obtain the increase in corrosion resistance.

These tests related to XC 38 steel specimens which had been subjected to nitriding, oxidation and FEP coating operations according to Example 1, with the exception of the nitriding conditions, which were varied, by applying empirical rules, to obtain variations in the thickness of the nitrided layer and selectively of the respective thicknesses of the compact deep and porous surface sublayers, and of the diameter of the pores of the surface sublayer.

It should be remembered that, whatever the operating conditions, the nitrided outer layer comprises a compact deep sublayer and a porous surface sublayer; the operating conditions can therefore act so as to determine the respective thicknesses of the compact deep and porous surface sublayers, and the diameter of the pores of the surface sublayer.

The various operating conditions do not, of course, in isolation have a specific effect on a given morphology parameter, but act on all these parameters to different extents.

The findings obtained can be summarised as follows:

- When the compact deep sublayer has a thickness which is too small, typically less than 4  $\mu\text{m}$ , the corrosion resistance is not increased significantly; thus, with a compact sublayer 2  $\mu\text{m}$  in thickness, the first signs of corrosion in a saline mist appear at 240 hours.
- When the surface porous sublayer exceeds 20  $\mu\text{m}$  in thickness the layer is subject to rapid crumbling (after 192 hours' exposure to saline mist in the case of a sublayer 25  $\mu\text{m}$  in thickness); this result can be attributed to a non-homogeneous coating embrittled by the sintering.
- If the porous sublayer is absent or if it includes pores with a diameter of less than 100 nm in practice, the coating

separates off on exposure to saline mist after very short periods of around 24 to 48 hours.

From these tests it is inferred that the compact sublayer must be at least 4  $\mu\text{m}$  thick, that the porous sublayer must have a thickness of between 2 and 20  $\mu\text{m}$  and that the diameter of the pores of this sublayer must be greater than 100 nm.

Example 6 - Adjustment of the morphology of the nitrided layer

This example leads to the drawing up of empirical rules for adjusting the thicknesses of the sublayers of the nitrided layer.

The nitriding is carried out according to the combined disclosures of patent documents FR-A-2 171 993 and FR-A-2 271 307, under the initial conditions of Example 1, that is to say:

- |                       |                      |
|-----------------------|----------------------|
| - cyanate ion content | CNO <sup>-</sup> 37% |
| - temperature         | 570°C                |
| - treatment time      | 90 minutes           |

On a steel of type XC 38, under the conditions of Example 1, the total thickness of the nitrided layer is typically from 13 to 15  $\mu\text{m}$  with practically equal sublayer thicknesses.

Under the same conditions, with an XC 10 steel, the layer thickness changes to 15-18  $\mu\text{m}$ , and with a Z 38 CDV 5 steel to 8-10  $\mu\text{m}$ , the sublayer thicknesses remaining substantially equal.

It will be noted that the advantageous adjustments can be limited to that of the total thickness of the nitrided layer since the ratio of the sublayer thicknesses can be kept approximately equal, and that the pore diameter is not affected appreciably.

The parameters which will make it possible to adjust the total thickness of the nitrided layer without upsetting the thickness ratio of the sublayers or excessively reducing the diameter of the pores in the surface sublayer will be the content of sulphur-containing species ( $K_2S$  in this case) and the quantity of air injected into the bath.

These parameters will be adjusted as a function of the mass of the salt bath and that of the articles treated daily.

500 kg molten salt bath

| - nature of the treated articles                | steel   | cast iron |
|-------------------------------------------------|---------|-----------|
| - quantity of treated articles/24 h             | 1000 kg | 1000 kg   |
| - flow rate of air to be injected into the bath | 250 l/h | 250 l/h   |
| - quantity of potassium sulphide $K_2S$ /day    | 8-9 g   | 12-13 g   |

1000 kg molten salt bath

Steel articles

Quantity of articles treated

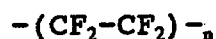
|                    |         |         |         |
|--------------------|---------|---------|---------|
| per 24 h           | 1000 kg | 2000 kg | 3000 kg |
| $K_2S$ to be added |         |         |         |
| per 24 h           | 16 g    | 19 g    | 23 g    |

#### Example 7 - Nature of the polymer coating

Besides the fluoroethylene-fluoropropylene copolymer, other polymers were tried for producing the coating; those which will be mentioned below were deposited in layers 10  $\mu m$  in thickness and exhibited standardised resistances to corrosion in the presence of saline mist of at least 1000 hours, and frictional properties equivalent to those given in Example 3.

Fluorocarbon polymers

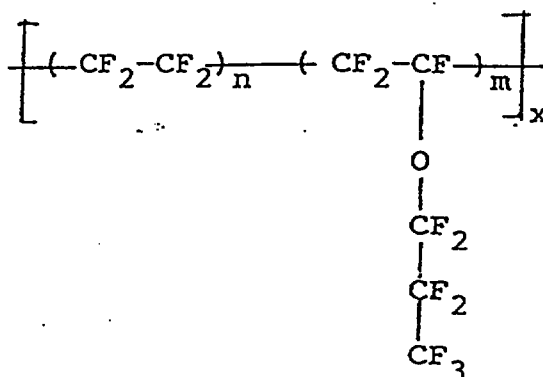
Polytetrafluoroethylene



# Fluorocarbon copolymers

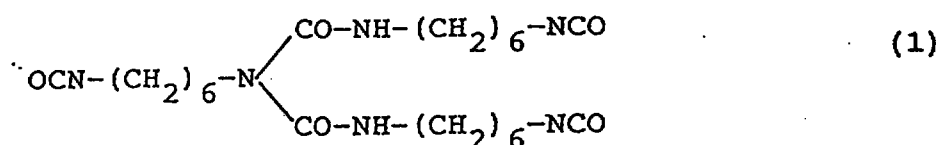
FEP already mentioned

PFA of formula

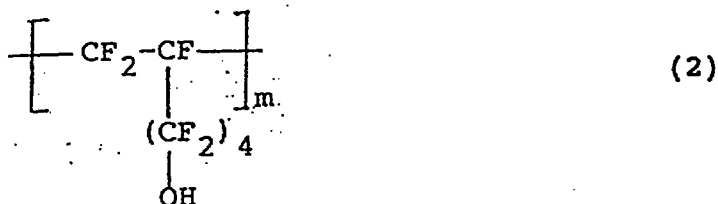


# Fluorinated polyurethanes

Products of reaction between an isocyanate of formula

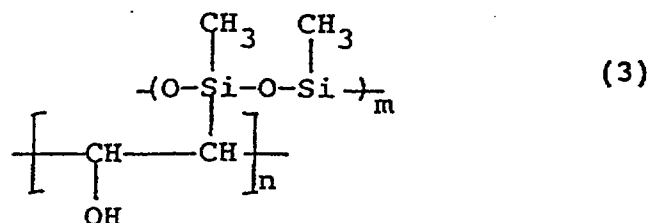


and a fluorinated polyol of formula (2)



# Silicone-containing polyurethanes

Product of reaction of the isocyanate of formula (1) and a silicone-containing polyol of formula (3)

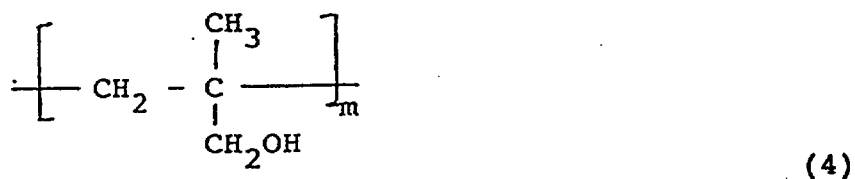


# Polyurethane copolymers

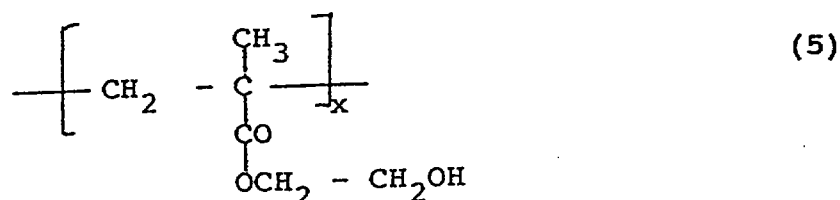
Copolymers obtained by reaction of the isocyanate of formula (1) with the fluorinated polyol of formula (2) and the silicone-containing polyol of formula (3)

Copolymers obtained by reaction of the isocyanate of formula

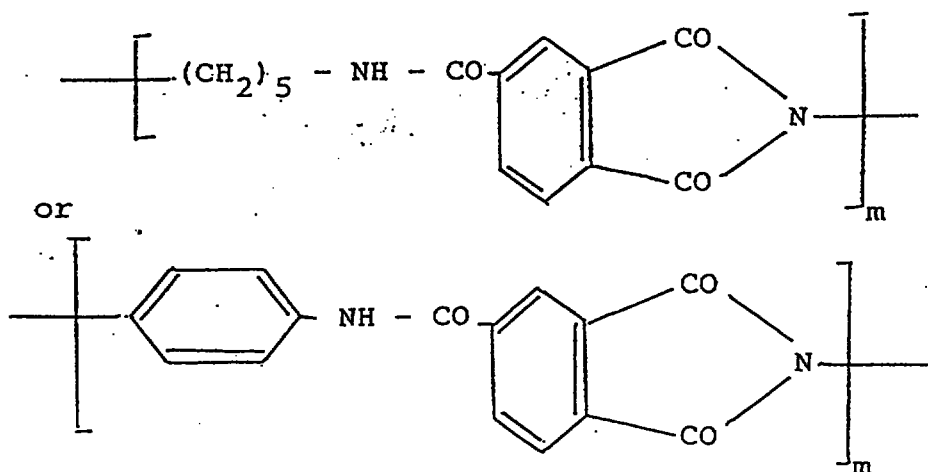
(1) with the fluorinated polyol of formula (2) and a polyol of formula (4)



Copolymer obtained by reaction of the isocyanate of formula (1) with the fluorinated polyol of formula (2) and an acrylic polyol of formula



#### Polyamides-imides



#### Example 8 - Coating processes

Apart from the production of the coating by electrostatic dusting and sintering, this coating may be produced by dipping.

The starting point is articles made from X 38 steel which are nitrided and oxidised according to Example 1.

#### 8-1 - Dip-coating with FEP

An FEP powder with a particle size close to 5  $\mu\text{m}$  is suspended in a solvent consisting of a mixture of methyl isobutyl ketone (MIBK) and N-methylpyrrolidone (NMP). The proportions of FEP and of the solvent components are adjusted experimentally to bring the viscosity of the suspension to a suitable value so that, after immersion and subsequent treatment, the final thickness of the FEP coating is 8-10  $\mu\text{m}$ .

The articles are immersed in the suspension and are taken out and drained, after which the articles are stoved at 350°C for 10 minutes to sinter the FEP.

When exposed to saline mist, no sign of corrosion is visible at 600 hours.

#### 8-2 - Dip-coating with polyurethane

A polyisocyanate and a polyol are reacted and solvents are added to adjust the viscosity to a suitable value for the required coating thickness and to slow down the polyurethane condensation reaction.

The articles are immersed in the reaction medium and are then taken out and drained. They are then stoved at 60°C until the solvent has completely evaporated, which allows the condensation to be completed.

A polyurethane layer thus deposited with a thickness of 5-6  $\mu\text{m}$  gives the articles a corrosion resistance such that after 500 hours' exposure to saline mist no sign of corrosion can be seen.

Example 9 - Nitriding and oxidation in an ionised atmosphere

The starting point is X 38 steel articles similar to those used in Example 1.

The articles are nitrided in a leakproof vessel under reduced pressure, in an atmosphere consisting of 60% nitrogen and 40% hydrogen and ionised by a cathode discharge.

The experimental conditions are:

|                             |                  |
|-----------------------------|------------------|
| Temperature of the articles | 570°C            |
| Gas pressure                | 10 kPa (10 mbar) |
| Cathode discharge voltage   | 1500 volts       |
| Treatment time              | 2 hours          |

A nitrided layer consisting essentially of  $\epsilon$  iron nitride ( $\text{Fe}_{23}\text{N}$ ) between 10 and 12  $\mu\text{m}$  in thickness is thus obtained.

When the nitriding operation is finished the vessel is purged and oxygen is then introduced into it at a pressure of 100 pa (0.1 mbar).

The articles are raised to a negative DC voltage of 1500 volts relative to the vessel for approximately 30 min. Iron oxides and oxynitrides form at the surface of the articles.

When the oxidation is finished the articles are covered with a coating of FEP with a thickness of approximately 10  $\mu\text{m}$  as in Example 1.

The corrosion resistance corresponds to an exposure to saline mist for at least 1000 hours before signs of corrosion appear.

By way of comparison, on leaving the vessel the nitrided and oxidised articles exhibit signs of corrosion after 250-300 hours' standardised exposure to saline mist.

The invention is, of course, not limited to the examples described but includes all the variant embodiments within the scope of the claims.

## CLAIMS

1. Process for conferring excellent corrosion resistance on articles made from ferrous metal, with good friction properties, a low coefficient of friction and resistance to wear and seizing, a process in which the articles are nitrided and then oxidised either in a bath of molten oxidising alkaline salts or by means of an oxidising ionised atmosphere, so that the articles have a nitrided outer layer with a compact deep sublayer and a porous surface sublayer, characterised in that the nitriding and oxidation are effected so that the deep sublayer has a thickness of at least 4  $\mu\text{m}$  and the surface sublayer has a thickness of between 2 and 20  $\mu\text{m}$ , the diameter of the pores being at least 100 nm, and in that, after the oxidation stage, the nitrided/oxidised layer is coated, to a thickness of between 3 and 20 micrometres, with a polymer selected from amongst fluorocarbon polymers and copolymers, polyurethane polymers and copolymers which are either silicone-treated or fluorinated and which are used alone or mixed with each other or with hydrocarbon polyurethanes, urethane and acrylic copolymers, and polyamides-imides.

2. Process according to Claim 1, characterised in that the thickness of the coating is between 3 and 15 micrometres.

3. Process according to one of Claims 1 and 2, characterised in that the articles are nitrided in a bath of molten salt consisting essentially of carbonates and cyanates of alkali metals, Na, K and Li, the  $\text{CO}_3^{--}$  being present at 1 to 35% by weight and the  $\text{CNO}^-$  anion at 35 to 65% by weight whilst, with respect to the mass of alkali metal ions, the proportions by weight are 25 - 42.6% in the case of  $\text{Na}^+$ , 42.6 - 62.5% in the case of  $\text{K}^+$  and 11.3 - 17.1% in the case of  $\text{Li}^+$ .

4. Process according to Claim 3, characterised in that the



nitriding salt bath also contains a sulphur-containing substance in such a quantity that the proportion by weight of the elemental sulphur in the bath is between 0.001 and 1%.

5. Process according to any one of Claims 1 to 4, characterised in that the nitrided articles are then oxidised in a bath of molten salts comprising, by weight, from 99.5% to 85% by weight of a mixture consisting of 25 to 35% by weight alkali nitrates, 8 to 15% alkali carbonates and the remainder, to 100%, alkali hydroxides, and from 0.5 to 15% oxygen-containing salts of alkali metals whose normal oxidation-reduction potential relative to the hydrogen reference electrode is lower than or equal to -1.0 volt, a gas containing oxygen being bubbled into the bath at a flow rate sufficient for the bath to be saturated with dissolved oxygen, and the content by weight of insoluble particles therein is maintained at less than 3%.

6. Process according to Claim 5, characterised in that the temperature of the oxidising bath is between 350° and 450°C.

7. Process according to Claim 1, characterised in that the nitriding is carried out in a sealed chamber containing an atmosphere of nitrogen and hydrogen at reduced pressure, ionised by a cathodic discharge, the articles being raised to a temperature of at least 550°C.

8. Process according to Claim 1, characterised in that the oxidation is carried out in a sealed chamber in an ionised oxygen atmosphere at reduced pressure, the articles being cathodic relative to the vessel.

