



Baths and process for the chemical polishing
of stainless steel surfaces

5 The present invention relates to the composition of baths for the chemical polishing of stainless steel surfaces.

10 Chemical polishing of metal surfaces is a well-known technique (Electrolytic and chemical polishing of metals - W.J. McG. Tegart - Dunod - 1960 - p. 122 et seq.); it consists in treating the metal surfaces to be polished with oxidizing baths. Baths including a mixture of hydrochloric, phosphoric and nitric acids in aqueous solution are generally employed for the chemical polishing of stainless steels. To improve the quality of the polishing it is usual to incorporate suitable additives
15 into these baths, such as surface-active agents, viscosity regulators and brightener. Thus, patent US-A-3709824 describes a bath composition for the chemical polishing of stainless steel surfaces, including, in aqueous solution, a mixture of hydrochloric acid, nitric
20 acid and phosphoric acid, a surfactant and sulphosalicylic acid as brightener.

Apart from the well-known problems concerning pollution due to phosphates when spent baths are being destroyed by a conventional physicochemical treatment,
25 the precipitation of phosphoric acid (in the form of calcium phosphates) gives rise to a large volume of sludge. This sludge is toxic and its removal is costly. Japanese Patent Application JP-A-52/72989 proposes to solve the pollution problem by employing polishing baths
30 free from phosphoric acid and including, in aqueous solution, hydrochloric acid, nitric acid, at least one derivative chosen from sulphosalicylic acid, salicylic acid and thiourea, and a cationic surfactant. However, these phosphoric acid-free baths have the disadvantage of
35 being effective only at a temperature that is higher than 80°C with the result that their rate of polishing is very high; they do not permit a slow and efficient polishing of stainless steel surfaces.



The invention aims to provide polishing baths without phosphoric acid, which are designed to produce a slow and efficient chemical polishing of stainless steel surfaces.

5 The invention consequently relates to baths for the chemical polishing of stainless steel surfaces, which are free from phosphoric acid and which include, in aqueous solution, a mixture of hydrochloric acid and nitric acid, an optionally substituted hydroxybenzoic
10 acid and a cationic surfactant, these baths being characterized in that they include ferricyanide complex ions in the aqueous solution.

 In the baths according to the invention the hydroxybenzoic acid acts as a brightener. The hydroxy-
15 benzoic acid may be unsubstituted, such as salicylic acid, or substituted, such as 5-sulphosalicylic acid or aminosalicylic acid. Salicylic acid and 5-sulphosalicylic acid are preferred.

 In the baths according to the invention the cationic surfactant advantageously includes a quaternary ammonium salt. The quaternary ammonium salt is preferably chosen from those which include at least one linear or branched long-chain alkyl radical. If appropriate, it is preferred to choose the quaternary ammonium salt from
20 those in which the long-chain alkyl group contains at least 8 carbon atoms, preferably at least 10 carbon atoms, such as, for example, the lauryl, cetyl and stearyl groups. In addition to the long-chain alkyl radical defined above, at least one other linear or
25 branched alkyl radical or a substituted or unsubstituted benzyl radical may be present. Examples are the cetyldimethylbenzylammonium, distearyldimethylammonium, lauryldimethylbenzylammonium and lauryltrimethylammonium salts. Quaternary ammonium salts which are especially
30 recommended belong to the class consisting of water-soluble alkyipyridinium, especially cetylpyridinium and laurylpyridinium, salts. The quaternary ammonium salts including a long-chain alkyl radical as defined above are preferably chosen from halides, in particular from
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chlorides. Alkylpyridinium chlorides are particularly preferred, especially laurylpyridinium chloride. Quaternary ammonium salts which can be employed in the baths according to the invention are available among the products of Dehyquart[®] trademark (Henkel).

In the baths according to the invention the ferricyanide complex ions are complex cyanides of general formula $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, also called hexacyanoferrates(III). They may be present in the aqueous solution in the form of any dissolved compounds such as, for example, hexacyanoferric(III) acid, ammonium ferricyanide and alkali metal and alkaline-earth metal ferricyanides. Preferred compounds are alkali metal ferricyanides, potassium ferricyanide being especially preferred.

The respective contents of hydrochloric, nitric and hydroxybenzoic acids, of cationic surfactant and of ferricyanide complex ions in the chemical polishing baths according to the invention are chosen as a function of the grade of the stainless steel subjected to the polishing and of the polishing conditions, especially of the profile of the steel object subjected to the polishing, of its volume, of the volume of the bath, of its temperature and of the stirring to which it may be subjected. They must consequently be determined by routine laboratory tests in each particular case.

In the baths conforming to the invention the hydrochloric acid content of the aqueous solution is advantageously at least 1, preferably 2, moles per litre and generally does not exceed 6, preferably 5, moles per litre. The nitric acid content is advantageously at least 0.001, preferably 0.005, moles per litre of the aqueous solution and generally does not exceed 0.3, preferably 0.03, moles per litre of the aqueous solution. The hydroxybenzoic acid content is advantageously at least 0.1, preferably 1, mg per litre of the aqueous solution and generally does not exceed 15,000, preferably 7000, mg per litre of the aqueous solution. The cationic surfactant content is advantageously at least 0.1, preferably 1, mg per litre of aqueous solution and

generally does not exceed 1000, preferably 100, mg per litre of aqueous solution.

5 The content of ferricyanide complex ions in the chemical polishing baths according to the invention is preferably at least 1×10^{-7} moles per litre of aqueous solution and, particularly preferably, the content of ferricyanide complex ions is at least 1×10^{-5} moles per litre. A content of at least 3×10^{-5} moles per litre is very particularly preferred. The content of ferricyanide
10 complex ions preferably does not exceed 1 mole per litre and, particularly preferably, the content of ferricyanide complex ions does not exceed 1×10^{-3} moles per litre. A content which does not exceed 3×10^{-4} moles per litre is very particularly preferred.

15 Baths conforming to the invention which are suitable for ensuring the chemical polishing of surfaces made of austenitic stainless steel alloyed with chromium and nickel, in a period of time varying from 1 to 24 hours and at a temperature of between 20 and 80°C are
20 those in which the aqueous solution includes, per litre,
- from 2 to 5 moles of hydrochloric acid,
- from 0.005 to 0.03 moles of nitric acid,
- from 1 to 7000 mg of hydroxybenzoic acid,
- from 1 to 100 mg of cationic surfactant, and
25 - from 1×10^{-5} to 1×10^{-3} moles of ferricyanide complex ions.

In a particular embodiment of the polishing baths according to the invention, these contain, in the aqueous solution, an additive capable of decomposing nitrous
30 acid. The function of this additive is to decompose at least a part of the nitrous acid which is formed during the polishing of a steel surface as a result of an oxidation of ferrous ions released into the bath during the polishing. The additive capable of decomposing
35 nitrous acid is preferably chosen from urea and its derivatives, such as thiourea and urea homologues. The optimum content of additive capable of decomposing nitrous acid is from 0.01 to 5 g per litre of the aqueous solution. The baths conforming to this embodiment of the

invention are especially suited for the polishing treatments in which the ratio of the area in contact with the bath to the volume of the latter is higher than 10 m^{-1} .

5 The baths according to the invention may optionally contain additives usually present in the baths for chemical polishing of metals, for example surface-active agents other than the cationic surfactant defined above, alcohols and viscosity regulators.

10 The baths according to the invention may additionally contain other inorganic acids commonly present in chemical polishing baths, for example sulphuric acid. However, they are essentially free from phosphoric acid and phosphate ions.

15 The baths according to the invention are suitable for the chemical polishing of stainless steel surfaces. They are well-suited for the polishing of austenitic steels containing between 16 and 26 % by weight of chromium and between 6 and 22 % by weight of nickel, such as the steels of 18/8 and 18/10 grades. The baths according to the invention are especially well suited for the
20 polishing of austenitic steels containing molybdenum. Austenetic steels, with or without molybdenum, are typically the AISI 304, 304L, 316, 316L, 904 and 904L steels. The baths according to the invention have the
25 special property of effecting the polishing of such steels at a slow rate. They may be employed at any temperatures lower than the boiling temperature of the bath. However, they exhibit the remarkable special property of exhibiting an outstanding effectiveness at
30 temperatures lower than 80°C , more particularly lower than or equal to 70°C , at normal atmospheric pressure, and this facilitates their use and simplifies the measures to be taken to ensure the salubriousness of the polishing shops. The baths according to the invention
35 have the special property of allowing a slow polishing, and this makes them suitable for the polishing of large industrial equipment. The baths according to the invention have the additional advantage of producing polishes of good quality on assemblies welded according to the

rules of the art.

The invention consequently also relates to a process for the polishing of a stainless steel surface, according to which the surface is placed in contact with a chemical polishing bath conforming to the invention.

In the implementation of the process according to the invention the metal surface may be brought into contact with the baths in any suitable manner, for example by immersion. The period of contact of the surface to be polished with the bath must be sufficient to produce an effective polishing of the surface. It may not, however, exceed a critical value beyond which the bath loses its polishing properties. The optimum contact time depends on many parameters such as the steel grade, the geometry and the initial roughness of the surface to be polished, the composition of the bath, the working temperature, stirring of the bath in contact with the surface and the ratio of the area of the surface to be polished to the volume of the bath; it must be determined by routine laboratory work in each particular case. The period of contact of the surface to be polished with the bath is generally at least 1 hour, preferably at least 2 hours. In general the contact time does not exceed 24 hours, preferably 12 hours.

In the implementation of the process according to the invention the temperature at which the bath is used is generally lower than its boiling temperature. The working temperature is preferably lower than 80°C. Good results are obtained with a temperature lower than or equal to 70°C. The temperature at which the bath is used is generally at least equal to the ambient temperature. The temperature is preferably at least 35°C.

In a preferred embodiment of the process according to the invention the bath is used at normal atmospheric pressure, at a temperature of 35 to 70°C and the surface to be polished is kept in contact with the bath for a period of between 2 and 12 hours.

The advantage of the invention will become evident on reading the examples set out below.

In each of the examples whose description follows, a stainless steel panel was immersed in a polishing bath maintained at an appreciably constant temperature and subjected to moderate stirring. At the end of the immersion period the panel was withdrawn from the bath, rinsed with demineralized water and dried. The following parameters were measured:

- the arithmetic mean roughness R_a , which was the mean deviation in relation to the mean surface of the panel [Encyclopedia of Materials Science and Engineering, Michael B. Bever, Vol. 6, Pergamon Press, pages 4806 to 4808]:

$$R_a = \frac{1}{L} \int_0^L |y(x)| dx$$

- the measurements being performed with a sensor fitted with a point 10 μm in diameter and corresponding to a cut-off value of 0.25 mm;
- surface brightness at an incidence angle of 20 degrees (according to ASTM standard D523).

Example 1 (conforming to the invention)

A panel of austenitic stainless steel of the AISI 316 type was immersed in a polishing bath conforming to the invention, including, per litre:

- 2.7 moles of hydrochloric acid,
- 0.01 mole of nitric acid,
- 10 mg of salicylic acid,
- 2 mg of the product Dehyquart[®] C which contains laurylpyridinium chloride as main constituent,
- 40 mg of $\text{K}_3\text{Fe}(\text{CN})_6$.

The operating conditions were the following:

- bath volume: 725 cm^3 ,
- area of the panel subjected to polishing: 43 cm^2 ,
- bath temperature: 50°C,
- immersion period: 5 h 30 min.

The following results were recorded:

- arithmetic mean roughness (R_a):
 - before the polishing: 0.28 μm ,
 - after the polishing: 0.13 μm ,

- brightness: 25 %.

Example 2 (conforming to the invention)

A panel of austenitic stainless steel of the
AISI 904L type was immersed in a polishing bath conform-
ing to the invention, including, per litre:

- 4 moles of hydrochloric acid,
- 0.01 mole of nitric acid,
- 5 g of 5-sulphosalicylic acid,
- 10 mg of the product Dehyquart® C which contains
laurylpyridinium chloride as main constituent,
- 20 mg of $K_3Fe(CN)_6$.

The operating conditions were the following:

- bath volume: 1000 cm³,
- area of the panel subjected to polishing: 65 cm²,
- bath temperature: 65°C,
- immersion period: 5 h.

The following results were recorded:

- arithmetic mean roughness (R_a):
 - before the polishing: 0.17 μ m,
 - after the polishing: 0.11 μ m,
- brightness: 15 %.

Example 3 (not conforming to the invention)

A panel of austenitic stainless steel of the
AISI 316 type was immersed in a polishing bath including,
per litre:

- 2.7 moles of hydrochloric acid,
- 0.01 mole of nitric acid,
- 10 mg of salicylic acid,
- 2 mg of the product Dehyquart® C which contains
laurylpyridinium chloride as main constituent.

The bath used is therefore different from the
bath of Example 1 in the absence of potassium
ferricyanide.

The operating conditions were the following:

- bath volume: 725 cm³,
- surface of the panel subjected to polishing: 43 cm²,
- bath temperature: 50°C,
- immersion period: 6 h.

The following results were recorded:

- arithmetic mean roughness (R_a):
 - before the polishing: $0.27 \mu\text{m}$,
 - after the polishing: $0.31 \mu\text{m}$,
- brightness: 2 %.

5 A comparison of the results obtained in Example 1 (conforming to the invention) with those obtained in Example 3 (not conforming to the invention) reveals the progress provided by the invention insofar as the roughness and the brightness obtained at the end of the polishing are concerned.

10 Example 4 (conforming to the invention)

 Three panels of austenitic stainless steel of different grades, AISI 304L, AISI 316L and AISI 316Ti respectively, were immersed together in a polishing bath conforming to the invention, including, per litre:

- 15 -
- 2.3 moles of hydrochloric acid,
 - 0.01 mole of nitric acid,
 - 3 g of 5-sulphosalicylic acid,
 - 0.1 g of the product Dehyquart[®] LDB which contains
 - 20 lauryldimethylbenzylammonium chloride as main constituent,
 - 100 mg of $\text{K}_3\text{Fe}(\text{CN})_6$.

 The operating conditions were the following:

- 25 -
- bath volume: 1050 cm^3 ,
 - area of each panel subjected to polishing: 63 cm^2 ,
 - bath temperature: 50°C ,
 - immersion period: 4 h 30 min.

 The following results were recorded:

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Steel	Arithmetic mean roughness (R _a)		Brightness
	before the polishing	after the polishing	
AISI 304L	0.31 μm	0.17 μm	9 %
AISI 316L	0.35 μm	0.15 μm	15 %
AISI 316Ti	0.27 μm	0.17 μm	22 %

CLAIMS

1. Baths for the chemical polishing of stainless steel surfaces, which are free from phosphoric acid and which include, in aqueous solution, a mixture of hydrochloric acid and nitric acid, an optionally substituted hydroxybenzoic acid and a cationic surfactant, characterized in that they include ferricyanide complex ions in the aqueous solution.
2. Baths according to Claim 1, characterized in that the hydroxybenzoic acid is chosen from salicylic acid and 5-sulphosalicylic acid.
3. Baths according to Claim 1 or 2, characterized in that the cationic surfactant includes a quaternary ammonium salt including at least one alkyl radical containing at least 8 carbon atoms.
4. Baths according to Claim 3, characterized in that the quaternary ammonium salt is chosen from halides.
5. Baths according to Claim 4, characterized in that the quaternary ammonium salt is alkyipyridinium chloride.
6. Baths according to any one of Claims 1 to 5, characterized in that the ferricyanide complex ions are present in the solution in the form of potassium ferricyanide.
7. Baths according to any one of Claims 1 to 6, characterized in that the concentration of ferricyanide complex ions is from 1×10^{-5} to 1×10^{-3} moles per litre of solution.
8. Baths according to any one of Claims 1 to 7, characterized in that the aqueous solution includes, per litre,
 - from 2 to 5 moles of hydrochloric acid,
 - from 0.005 to 0.03 moles of nitric acid,
 - from 1 to 7000 mg of substituted or unsubstituted hydroxybenzoic acid,
 - from 1 to 100 mg of cationic surfactant,
 - from 1×10^{-5} to 1×10^{-3} moles of ferricyanide complex ions.
9. Baths according to any one of Claims 1 to 8, characterized in that they include, in the aqueous

solution, an additive capable of decomposing nitrous acid.

10. Process for polishing a stainless steel surface, according to which the surface is placed in contact with
- 5 a chemical polishing bath, characterized in that a bath conforming to any one of Claims 1 to 9 is used at a temperature of 35 to 70°C for a period of between 2 and 12 hours.