

Baths and process for the chemical polishing  
of stainless steel surfaces

Case S 90/02

SOLVAY (Société Anonyme)

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 (Polissage électrolytique et chimique des  
métaux [Electrolytic and chemical polishing of metals] -  
W.J. Mc G. Tegart - Dunod - 1960 - p. 122 et seq.); it  
consists in treating the metal surfaces to be polished  
with oxidising baths. Baths comprising a mixture of  
hydrochloric, phosphoric and nitric acids in aqueous  
15           solution (patent US-A-2,662,814) are generally employed  
for the chemical polishing of austenitic stainless  
steels. To improve the polishing quality, suitable  
additives are usually incorporated in these baths, such  
as surface-active agents, viscosity regulators and  
20           brightening agents. Thus, patent US-A-3,709,824 describes  
a composition of a bath for the chemical polishing of  
stainless steel surfaces, comprising, in aqueous solu-  
tion, a mixture of hydrochloric acid, nitric acid and  
phosphoric acid, a viscosity regulator chosen from water-  
25           soluble polymers, a surfactant, and sulphosalicylic acid  
as brightening agent.

30           These known polishing baths have the distinctive  
property of attacking the metal at a very high rate. A  
polishing treatment of a stainless steel surface with  
such baths generally cannot exceed a few minutes, or else  
it gives rise to localised corrosion phenomena. This high  
rate of action of the known polishing baths is a dis-  
advantage because it renders them unusable for certain  
applications, especially for polishing the inner face of  
35           the walls of large vessels such as boilers, autoclaves or  
crystallisers. Since the time required to fill and to  
drain such vessels is generally much longer than the  
duration of the optimum chemical polishing treatment, it

becomes impossible, in fact, to obtain a uniform polish of the wall, since some areas of the latter are insufficiently polished and others are deeply corroded. Furthermore, the high rate of action of the known chemical polishing baths makes the polishing difficult to control.

Document EP-A-274,776 (Solvay & Cie) describes very slow-acting chemical polishing baths which consequently avoid the abovementioned disadvantages. These known baths comprise, in aqueous solution, a mixture of hydrochloric, nitric and phosphoric acids, sulphosalicylic acid, and an abietic compound, such as an abietamine.

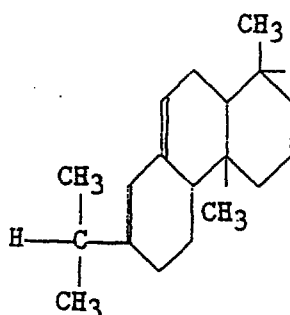
These known slow-acting polishing baths are designed to work at temperatures of at least 50°C, generally between 60 and 80°C.

The invention is aimed at providing baths designed to produce a slow and efficient chemical polishing of stainless steel surfaces at working temperatures below 50°C.

Consequently, the invention relates to baths for the chemical polishing of stainless steel surfaces, comprising, in aqueous solution, a mixture of hydrochloric acid, nitric acid and phosphoric acid, an optionally substituted hydroxybenzoic acid, an abietic compound and an additive chosen from perchloric acid and the water-soluble salts of perchloric acid.

In the baths according to the invention the hydroxybenzoic acid is used as a brightening agent. It may be unsubstituted, such as salicylic acid, or substituted, such as sulphosalicylic acid. Salicylic acid is preferred.

Within the scope of the invention, the abietic compounds are chemical compounds containing an abietyl radical of general formula:

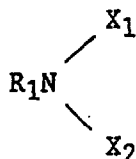


or a hydroabietyl or dehydroabietyl radical.

In accordance with the invention the abietic compound must be soluble in the aqueous solution.

Abietic compounds which can be employed in the baths according to the invention are the abietamines.

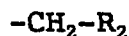
Abietamines which are especially recommended for the baths according to the invention are those of general formula:



in which:

- $\text{R}_1$  denotes an abietyl, hydroabietyl or dehydroabietyl radical defined above,
- $\text{X}_1$  denotes a radical containing at least one carbonyl group, and
- $\text{X}_2$  denotes a hydrogen atom or a radical containing at least one carbonyl group.

Examples of such abietamines which are suitable for the baths according to the invention are those in which at least one of the radicals  $\text{X}_1$  and  $\text{X}_2$  is a radical of general formula:



in which  $\text{R}_2$  denotes a saturated or unsaturated, substituted or unsubstituted, linear or cyclic alkyl residue containing at least one carbonyl group. Among these compounds preference is given to those in which the  $-\text{CH}_2-$  group is linked to a carbonyl group of the  $\text{R}_2$  residue by a carbon atom carrying at least one hydrogen atom. Such substituted abietamines and the means for

obtaining them are described in patent GB-A-734,665. Examples of abietamines of this type which can be employed in the baths according to the invention are those in which the alkyl residue  $R_2$  is chosen from  
5 acetonyl, 2-ketobutyl, 4-methyl-2-keto-3-pentenyl, 4-hydroxy-4-methyl-2-ketopentyl, 2-ketocyclopentyl, 4-hydroxy-2-keto-3-pentenyl, 2-ketocyclohexyl, 2,5-diketohexyl and 2-phenyl-2-ketoethyl residues.

10 In the baths according to the invention it is appropriate that the respective quantities of, on the one hand, the additive chosen from perchloric acid and its water-soluble salts and, on the other hand, the abietic compound should be adjusted so as to permit a coadsorption on the surface of the steel to be polished, while  
15 avoiding exceeding their solubility product. As a general rule it is expedient that the baths according to the invention should contain, per litre, between 0.001 and 0.5 mol of the additive chosen from perchloric acid and its water-soluble salts and between 0.005 and 1 g of the  
20 abietic compound.

The appropriate weight quantities of the various constituents of the baths according to the invention depend on the grade of the stainless steel subjected to polishing and on the polishing conditions, especially on  
25 the profile of the steel object subjected to polishing, its volume, the volume of the bath, its temperature and the stirring to which it may be subjected. They must therefore be determined by routine laboratory tests in each individual case. Examples of baths in accordance  
30 with the invention which are suitable for polishing chromium and nickel alloy austenitic stainless steels at temperatures of between 25 and 50°C contain, per litre of aqueous solution:

- 35 - between 0.5 and 5 mol of hydrochloric acid (preferably 0.5-3 mol),
- between 0.005 and 1 mol of nitric acid (preferably 0.05-0.5 mol),
- between 0.005 and 1 mol of phosphoric acid (preferably 0.01-0.5 mol),

- between 0.0005 and 0.5 mol of the additive chosen from perchloric acid and its water-soluble salts (preferably 0.001-0.2 mol),
- between 0.005 and 1 g of abietic compound (preferably 0.01-0.5 g), and
- between 0.001 and 5 g of substituted or unsubstituted hydroxybenzoic acid (preferably 0.005-0.3 g in the case of the unsubstituted acid).

The polishing baths according to the invention may optionally contain additives which are usually present in the known baths for the chemical polishing of metals, for example surface-active agents, alcohols and viscosity regulators. In particular, they may contain products of the Dehyquart trademark (Henkel), which are surface-active agents chosen from alkylpyridinium salts and quaternary ammonium salts containing alkyl, phenyl or benzyl radicals, substituted or unsubstituted.

The baths according to the invention are suitable for the chemical polishing of any surfaces made of austenitic stainless steel. They are especially suited to 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 molybdenum-free 18/8 and 18/10 grades (AISI standard 304 and 304L). The baths according to the invention have the distinctive characteristic of producing the polishing of such steels at a slow rate, generally requiring a contact time of between 2 and 20 hours, generally between 5 and 12 hours. They can be employed at any temperatures between 20°C and the boiling temperature. However, they have the remarkable particular characteristic of exhibiting an excellent effectiveness at temperatures below 50°C, generally between 35 and 45°C, at normal atmospheric pressure, and this makes them easier to use and simplifies the measures to be taken to ensure the healthiness of the polishing workshops. The baths according to the invention have the additional advantage of producing good quality polishes of assemblies which are welded according to the principles of the art.

The invention also relates to a process for polishing a stainless steel surface, according to which the surface is brought into contact with a chemical polishing bath in accordance with the invention.

5 In the implementation of the process according to the invention the contact between the metal surface and the bath may be brought about in any suitable manner, for example by immersion. The contact time between the sur-  
10 face to be polished and the bath must be sufficient to produce an effective polishing of the surface. However, it must not 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  
15 polished, the bath composition, the working temperature, any stirring of the bath in contact with the surface, and the relationship between the area of the surface to be polished and the volume of the bath; it must be determined by routine laboratory work in each individual case.

20 In a preferred embodiment of the process according to the invention the bath is used at a temperature of between 20 and 50°C, preferably between 35 and 45°C at normal atmospheric pressure, and the surface to be polished is kept in contact with the bath for a period of  
25 between 5 and 12 hours.

The advantage of the invention will be revealed on reading the examples which are set out below.

The stainless steel panels which were employed in the examples whose description follows were of 18/10  
30 grade [chromium (18.0 %) and nickel (10.0 %) alloy steel, molybdenum-free].

In each example the panel was immersed in the polishing bath which was maintained at a substantially constant temperature and was subjected to moderate  
35 stirring. At the end of the immersion period the panel was taken out of the bath, rinsed with demineralised water and dried. The following parameters were measured:  
- the average depth of corrosion of the metal, defined by the relationship

$$\Delta e = 10^4 \times \Delta P / S \times d$$

where S denotes the area of the panel (in cm<sup>2</sup>),

d denotes the density of the metal (in g/cm<sup>3</sup>),

$\Delta P$  denotes the loss in weight (in g) of the panel during the immersion in the bath,

$\Delta e$  denotes the depth of corrosion ( $\mu$ m);

- the arithmetic mean roughness  $R_a$ , which is the mean deviation relative to the mean surface of the panel (Encyclopedia of Materials Science and Engineering, Michael B. Bever, Vol. 6, 1986, Pergamon Press, pages 4806 to 4808 (page 4806):

$$R_a = (1/L) \int_0^L |y(x)| dx$$

the measurements being performed with a feeler equipped with a 5  $\mu$ m-diameter point and corresponding to a cutoff value of 0.25 mm;

- the surface brightness.

Example 1 (in accordance with the invention)

A polishing bath in accordance with the invention was used, containing, per litre:

- 2.0 mol of hydrochloric acid,
- 0.2 mol of nitric acid,
- 0.2 mol of phosphoric acid,
- 0.1 mol of perchloric acid,
- 0.1 g of sulphosalicylic acid,
- 0.1 g of the product Rodine 213, which is a mixture of substituted abietamines, isopropanol and surface-active agents (Rodine being a registered trademark of Amchem Products Inc.).

The operating conditions were as follows:

- bath volume : 1940 cm<sup>3</sup>,
- area of the surface subjected to polishing : 87 cm<sup>2</sup>,
- temperature : 35°C,
- immersion period : 11 hours.

The following results were noted:

- average depth of attack : 27  $\mu$ m;
- arithmetic mean roughness:

- before polishing :  $0.3 \pm 0.1 \mu\text{m}$
- after polishing :  $0.11 \pm 0.02 \mu\text{m}$ .

The surface has a satin finish.

Example 2 (in accordance with the invention)

5 A polishing bath in accordance with the invention was used, containing, per litre:

- 1.5 mol of hydrochloric acid,
- 0.1 mol of nitric acid,
- 0.2 mol of phosphoric acid,
- 10 - 0.02 mol of perchloric acid,
- 0.1 g of salicylic acid,
- 0.15 g of the product Rodine 213 defined in Example 1.

The operating conditions were as follows:

- bath volume :  $970 \text{ cm}^3$ ,
- 15 - area of the surface subjected to polishing :  $43 \text{ cm}^2$ ,
- temperature :  $35^\circ\text{C}$ ,
- immersion period : 12 hours.

The following results were noted:

- 20 - average depth of attack :  $25 \mu\text{m}$ ;
- arithmetic mean roughness
  - before polishing :  $0.3 \mu\text{m}$ ,
  - after polishing :  $0.11 \mu\text{m}$ ,
- brightness [at an angle of 30 degrees (according to
- 25 ASTM standard E430)]: 28 %.

Example 3 (reference test)

The test of Example 2 was repeated with a chemical polishing bath not in accordance with the invention, containing neither perchloric acid nor the abietic

30 compound. The bath contained, per litre:

- 1.5 mol of hydrochloric acid,
- 0.1 mol of nitric acid,
- 0.2 mol of phosphoric acid,
- 0.1 g of salicylic acid,

35 The operating conditions were as follows:

- bath volume :  $970 \text{ cm}^3$ ,
- area of the surface subjected to polishing :  $43 \text{ cm}^2$ ,
- temperature :  $35^\circ\text{C}$ ,

- immersion period : 9 hours 30 minutes.

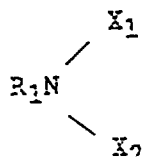
The following results were noted:

- average depth of attack : 25  $\mu\text{m}$ ;
- arithmetic mean roughness
  - before polishing : 0.23  $\mu\text{m}$ ,
  - after polishing : 0.27  $\mu\text{m}$ ,
- An increase in roughness is observed.



# CLAIMS

1. Baths for the chemical polishing of stainless steel surfaces, comprising, in aqueous solution, a mixture of hydrochloric acid, nitric acid and phosphoric acid, a brightening agent chosen from optionally substituted hydroxybenzoic acids and an abietic compound, which are characterized in that they comprise an additive chosen from perchloric acid and the water-soluble salts of perchloric acid, in a quantity of between 0.001 and 0.5 mol per litre of the solution, the abietic compound being present in a quantity of between 0.005 and 1 g per litre of solution.
2. Baths according to Claim 1, characterized in that the hydroxybenzoic acid is salicylic acid.
3. Baths according to Claim 1, characterized in that the substituted hydroxybenzoic acid is sulphosalicylic acid.
4. Baths according to any one of Claims 1 to 3, characterized in that the abietic compound is a substituted abietamine of general formula:



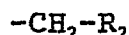
in which:

- $R_1$  denotes an abietyl, hydroabietyl or dehydroabietyl radical,
- $X_1$  denotes a radical containing at least one carbonyl group, and



-  $X_2$  denotes a hydrogen atom or a radical containing at least one carbonyl group.

5        5.        Baths according to Claim 4, characterized in that at least one of the radicals  $X_1$  and  $X_2$  is a radical of general formula:



where  $R_2$  denotes a saturated or unsaturated, substituted or unsubstituted, linear or cyclic alkyl residue containing at least one carbonyl group.

10       6.       Baths according to Claim 5, characterized in that the alkyl residue  $R_2$  is chosen from acetonyl, 2-ketobutyl, 4-methyl-2-keto-3-pentenyl, 4-hydroxy-4-methyl-2-ketopentyl, 2-ketocyclopentyl, 4-hydroxy-2-keto-3-pentenyl, 2-ketocyclohexyl, 2,5-diketohexyl and 2-phenyl-  
15       2-ketoethyl residues.

7.       Baths according to any one of Claims 1 to 6, characterized in that they comprise, per litre of aqueous solution,

- between 0.5 and 5 moles of hydrochloric acid,
- 20       -       between 0.005 and 1 mole of nitric acid,
- between 0.005 and 1 mole of phosphoric acid,
- between 0.0005 and 0.5 mole of the additive chosen from perchloric acid and its water-soluble salts,
- between 0.005 and 1 g of abietic compound, and
- 25       -       between 0.001 and 5 g of substituted or unsubstituted hydroxybenzoic acid.

8.       Baths according to any one of Claims 1 to 7, for the chemical polishing of surfaces made of austenitic steels.

30       9.       Baths according to Claim 8, for the chemical polishing of surfaces made of austenitic steels alloyed with chromium and nickel and free from molybdenum.

10.       Process for the polishing of a stainless steel surface, according to which the surface is brought into  
35       contact with a chemical polishing bath, characterized in that a bath in accordance with any one of Claims 1 to 10 is employed, and is maintained at a temperature of between 20 and 50°C.