COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952
APPLICATION FOR A STANDARD PATENT

Henkel Kommanditgesellschaft auf Aktien, of Henkelstrasse 67, 4000 Dusseldorf, FEDERAL REPUBLIC OF GERMANY, hereby apply for the grant of a standard patent for an invention entitled:

Hard Water-Stabilizing Additive to Activating Agents for Zinc Phosphating

which is described in the accompanying complete specification.

Details of basic application(s):

Basic Applic. No: P38 14 334.8
Country: DE
Application Date: 28 April 1988

The address for service is:-

Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this TWENTY SIXTH day of APRIL 1989

Henkel Kommanditgesellschaft auf Aktien

By: [Signature]
Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 82620
S&F CODE: 55370

S007050 27/04/89
5845/3
COMMONWEALTH OF AUSTRALIA

DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITION

In support of the Convention Application made for a

[patent]

Hard Water-Stabilizing Additive to Activating Agents
for Zinc Phosphating

Full name and address of Declarant:

Dr. Georg Zeit

Falkenweg 2
4018 Langenfeld / Germany

do solemnly and sincerely declare as follows:

1. I am authorised by HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN
the applicant for the patent

(or, in the case of an application by a body corporate)

2. The basic application as defined by Section 141 of the Act was made in

Federal Republic of Germany

on the

28th day of April 1988

by

HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN

of Düsseldorf, Germany

3. Dr. Helmut Endres, of Benrodestraße 82,
4000 Düsseldorf 13 / Germany

Dr. Peter Christophliemk, of Rudolf-Breitscheid-
Straße 61, 4000 Düsseldorf 13 / Germany

Karl-Dieter Brands, of Gänsestraße 1,
4000 Düsseldorf 13 / Germany

Dr. Wolf-Achim Roland, of Spreestraße 60,
5650 Solingen / Germany

are the actual inventors of the invention and the facts upon which the applicant
is entitled to make the application are as follows:

by assignment from the actual inventors to the said applicant

4. The basic application referred to in paragraph 2 of this Declaration
was the first application made in a Convention country in respect
of the invention the subject of the application.

Declared at Düsseldorf this 3 day of January 1989

Dr. Georg Zeit

Signature of Declarant

Dr. Georg Zeit
(19) AUSTRALIAN PATENT OFFICE

(54) Title
HARD WATER-STABILIZING ADDITIVE TO ACTIVATING AGENTS FOR ZINC PHOSPHATING

(51) International Patent Classification(s)
C23C 022/80

(21) Application No.: 33782/89  (22) Application Date: 27.04.89

(30) Priority Data

(31) Number  (32) Date  (33) Country
3814334  28.04.88  DE FEDERAL REPUBLIC OF GERMANY

(43) Publication Date:  02.11.89

(71) Applicant(s)
HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN

(72) Inventor(s)
Dr. HELMUT ENDRES; Dr. PETER CHRISTOPHLIEMK; KARL-DIETER BRANDS; Dr. WOLF-ACHIM ROLAND

(74) Attorney or Agent
SPRUSON & FERGUSON

(57) Claim

1. Hard water-stabilizing additives to treatment baths for the activation of metal surfaces composed of iron, steel, zinc, galvanized or alloy-galvanized iron or steel, aluminum or aluminated iron or steel prior to the step of phosphating said surfaces with phosphating baths containing zinc ions, said additives consisting of poly-(aldehydocarboxylic acids) and/or their water-soluble alkali metal salts.
Complete Specification for the invention entitled:

Hard Water-Stabilizing Additive to Activating Agents for Zinc Phosphating

The following statement is a full description of this invention, including the best method of performing it known to me/us.
HARD WATER-STABILIZING ADDITIVE TO
ACTIVATING AGENTS FOR ZINC PHOSPHATING

Abstract of the Disclosure

The invention relates to hard water-stabilizing additives to treatment baths for the activation of metal surfaces composed of iron or steel, zinc, galvanized iron or steel, aluminum or aluminated iron or steel prior to the step of phosphating said surfaces with phosphating baths containing zinc ions, said additives consisting of poly(aldehydocarboxylic acids).
HARD WATER-STABILIZING ADDITIVE TO ACTIVATING AGENTS FOR ZINC PHOSPHATING

The invention relates to additives to treatment baths for the activation of metal surfaces composed of iron or steel, zinc or galvanized steel as well as aluminum or aluminated steel prior to phosphating said surfaces with phosphating baths containing zinc ions, and more specifically prior to so-called low-zinc phosphating wherein the ratio of zinc ions to phosphate ions in the treatment solution is less than 1:12. The invention also relates to the use of said additives.

Processes for producing phosphate layers on iron or steel surfaces by means of solutions of phosphoric acid containing various polyvalent metal cations and additives acting as accelerators (e.g. oxidants) have been proven prior art for long. Such processes are employed, more particularly, in the automotive industry to achieve an improved protection from corrosion of the automotive bodies. The phosphated surfaces are subsequently coated with paints, preferably by cathodic electro-dipcoating.

Phosphated are the materials conventionally used in automotive body construction, usually iron or steel
sheets, more recently also electrogalvanized or hot-galvanized steel or materials having a surface composed of zinc alloys containing, for example, iron, nickel, cobalt or aluminum as alloying elements. Phosphating such surfaces for corrosion inhibition is usual not only in automobile construction but also in the manufacture of household appliances such as washing machines or refrigerators.

Prior to the above-mentioned treatment the workpieces are cleaned, rinsed and activated in order to obtain a thin and uniform phosphate layer to be produced which is known to be one pre-requisite for a good protection from corrosion. In the "high-zinc phosphating process" used for a long time it was possible in one process step to remove adherent oils, fats and other contaminants including those due to machining from the metal surface and at the same time to activate said metal surface for the following zinc phosphating step. Treatment baths in accordance therewith have been described, for example, in the German Patent Specifications Nos. 2 951 600 and 3 213 649 within the scope of processes for pre-treating metal surfaces prior to phosphating.

Meanwhile, more recently there have been used to an increasing extent so-called "low-zinc phosphating processes" such as those set forth, for example, in the German Patent Specification No. 2 232 067. These processes in combination with the usually following electro-dipcoating procedure result in a clearly improved corrosion resistance. However, these processes more sensitively respond to changes in the process parameters and to contaminations which are introduced
into the phosphating bath with the sheets to be coated. Thereby, the step of activating the metal surface becomes much more important than before. It has proven to be particularly advantageous to carry out the activation in a separate process step subsequently to the step of cleaning and degreasing. This is all the more applicable if phosphating according to the low-zinc method is effected by a dipcoat procedure, while it is likewise relevant for zinc-phosphating according to spray or combined spray-dipcoat as well as dipcoat-spray procedures.

The activation of the metal surface has the following objectives:

Increase of the rate of formation of nuclei and, hence, the number of crystal nuclei in the start phase of zinc phosphating, which results in a layer refinement; the porosity of the desired zinc phosphate layer is reduced due to the crystals being situated closely side by side. This results in the formation of a uniform and continuous zinc phosphate layer over the entire metal surface at a low surface area weight (indicated in grams of metal phosphate per $1 \text{ m}^2$ of metal surface), low surface area weights having proven to be beneficial as primer for paints.

Reduction of the minimum phosphating time, i.e. time required to completely cover the metal surface with a continuous zinc phosphate layer.

These effects provided by the activating agent finally result in that the paint layers to be applied
will be well anchored through the dense zinc phosphate layers containing fine particles and, thus, a good protection from corrosion will be attained which is the main object of zinc phosphating.

As efficient activating agents having the demanded properties, in practice exclusively products have proven to be valuable which contain polymeric titanium(IV) phosphate, such as those already described by Jernstedt, for example in the U.S. Patent Specifications Nos. 2,456,947 and 2,310,239. Today, these activating agents are preferably used in a separate rinsing bath immediately prior to the zinc phosphating step, while, however, they may also be previously added to an - at best mildly alkaline - cleansing bath.

Since the technical production of such activating agents of a constant and high quality is difficult, there has not been a lack in attempts to develop activating agents based on materials other than titanium phosphate.

Thus, Jernstedt describes activating agents based on zirconium phosphate or on reaction products of watersoluble tin and lead compounds with disodium hydrogen phosphate in the U.S. Patent Specifications Nos. 2,456,947 and 2,462,196. In the German Patent Specification No. 29 31 712 there are described organic titanium compounds which are stable to hydrolysis as activating agents for zinc, zinc-manganese or manganese surfaces. Said compounds are obtained by the reaction of a beta-diketone titanyl acetylacetonate with gluconic acid or gluconates in the presence of a hydrogen halide salt of an aliphatic aminoalcohol.
A further option for increasing the rate of formation of nuclei on steel is the treatment of the surface with diluted aqueous copper sulfate or copper nitrite solutions as well as with oxalic acid. However, the latter is only allowed to produce weak etching of the iron surface; the activation effect will disappear if a continuous iron oxalate layer will have been formed (U.S. Patent Specification No. 2,164,024 and German Patent Specification No. 171 71924).

The European Patent Specification No. 0 056 675 describes a process for the pre-treatment of steel wire prior to zinc phosphating using a bath containing sodium salts of oxalic, tartaric or citric acids as activating agents.

The phosphate-containing activating agents are rapidly rendered unusable by the hardness elements of water. Therefore, in practice it is necessary to employ the activating agents at least in partially de-salted water, better effects being attained in fully de-salted water. This is as costly as is the alternative of replenishing the activating baths with fresh activating mixture after only a short period of use.

As one possible solution to this problem there has been proposed in the European Patent Application No. 0 180 523 the use of phosphonic acids for complexing the water hardness or for hard water-stabilizing the activating agents. In application tests the process resulted in a well satisfactory activation at a markedly extended bath use-life as compared to activating baths containing no phosphonic acid. However, said process has the drawback of that the waste water to be disposed
of is additionally contaminated by the organophosphorus compounds which are biodegradable only with great difficulty.

The German Unexamined Patent Application 36 15 294 describes the use of anionic copolymers from unsaturated carboxylic acids and acrylic acid derivatives, isobutylene and/or styrene as well as anionic condensation products of naphthalenesulfonic acid and formaldehyde for "stabilizing" activating baths. This is understood to mean the delay of "ageing" of the baths, i.e. the phenomenon that activating baths once prepared will rapidly lose their activity even upon use of fully de-salted water, irrespectively of whether or not they will have been used. As a side-effect due to the use of polymers there has been indicated that for the preparation of the activating baths water of a lesser grade than so far usual may be used. As a parameter for the grade of the water there is used the specific conductivity. However, said parameter which is commonly used in practice for characterizing the water quality by nature fails to tell anything about the presence of hardness elements in the water. Appropriate tests using hard water even proved the inefficiency of the described polymers for stabilizing in hard water. Similar copolymers which also do not contain any aldehyde groups have been claimed in the German Unexamined Patent Application 21 25 963 as additives to cleaning baths containing grain-refining titanium compounds to extend the pH range as required for the activating effect.

In contrast thereto, it is the object of the present invention to achieve a stabilization of the activating agents with respect to the hardness elements
of water by using complexing agents which only contain the elements carbon, hydrogen and oxygen which under ecological aspects involve less problems.

Surprisingly it was found that polymers bearing aldehyde groups in addition to carboxyl groups offset the sensitivity to hard water of the activating agents without adversely affecting the activating effect.

The invention relates to hard water-stabilizing additives to treatment baths for the activation of metal surfaces composed of iron, steel, zinc, galvanized or alloy-galvanized iron or steel, aluminum or aluminated iron or steel prior to the step of phosphating said surfaces with phosphating baths containing zinc ions, said additives consisting of poly(aldehydocarboxylic acids) and/or their water-soluble alkali metal salts.

According to one embodiment of the present invention there are obtainable poly(aldehydocarboxylic acids) and/or their water-soluble alkali metal salts by the reaction of hydrogen peroxide, acrolein and acrylic acid, which have:

- a viscosity number within the range of from 5 to 50 ml/g,
- an acid value within the range of from 450 to 670,
- an acid equivalent weight within the range of from 125 to 70,
- a setting point of less than 0 °C,
- a content of carboxyl groups within the range of from 55 to 90% by mole, and
- a molecular weight within the range of from 1,000 to 20,000.
While according to the invention the poly(aldehydocarboxylic acids) are employed in the acid form, one embodiment of the present invention consists of that the poly(aldehydocarboxylic acids) are employed as alkali metal salts, the sodium salts being particularly preferred.

Furthermore, the present invention relates to the use of the additives according to the invention in treatment baths for the activation of metal surfaces in an amount of from 0.05 to 3 g/l.

One preferred embodiment of the present invention consists of that the poly(aldehydocarboxylic acids) are employed in an amount of from 0.5 to 1 g/l in treatment baths for the activation of metal surfaces.

While basically the additives according to the present invention may be employed in any conventional phosphating process, one further preferred embodiment of the present invention consists of that the additives are employed prior to a low zinc-phosphating procedure.

One further preferred embodiment of the present invention consists of that the additives are employed in treatment baths for the activation of metal surfaces in activating baths having a pH value of from 5 to 9.

The poly(aldehydocarboxylic acids) used according to the invention are commercially available and are marketed by the company DEGUSSA AG, Frankfurt (West Germany), for example under the designations POC OS 20, POC HS 0010, POC HS 2020, POC HS 5060, POC HS 65 120 and POC AS 0010, POC AS 2020, POC AS 5060 or POC AS 65 120. Herein the designation HS refers to the acid form, and
the designation AS refers to the sodium salt form of the poly(aldehydocarboxylic acids). They may be prepared by a specific process developed by the company Degussa, the "oxidative polymerization" of acrolein. In said process, acrolein alone or in admixture with acrylic acid in an aqueous solution is treated with hydrogen peroxide. The $\text{H}_2\text{O}_2$ acts as a polymerization initiator and a molecular weight modifier. At the same time part of the aldehyde groups of the acrolein is oxidized by hydrogen peroxide to form carboxyl groups. Thereby polymers are formed which have pendant aldehyde and carboxyl groups, namely the poly(aldehydocarboxylic acids).

Indications on the above-described preparation of the poly(aldehydocarboxylic acids) and on possible uses thereof are found in a company brochure by DEGUSSA AG under the title "POC-Umweltfreundliche Polycarbonsäuren mit vielfältigen Anwendungsmöglichkeiten" (Print note: CH 215-3-3-582 Vol). In accordance therewith, the poly-(aldehydocarboxylic acids) may be used, for example, as hardness stabilizers with respect to an inhibition of a crystallization of calcium and other alkaline earth metal salts, as inhibitor of deposit formation in sea water de-salting, as dispersing agent for aqueous pigment dispersions which are rich in solids, and as matrix material (builder) for washing and cleansing agents. Furthermore in said company brochure there may be found indications on respectively relevant patent literature, for example the German Patent Specification No. 10 71 339 (preparation), German Unexamined Patent Application No. 19 04 940 (complex-forming agents), German Unexamined Patent Application No. 19 04 941 (polyoxycarboxylic acids), German Patent Specification

The free poly(aldehydocarboxylic acids) can be neutralized with alkali solutions to form the corresponding salts, e.g. with NaOH to form sodium poly(aldehydocarboxylates).

The contents of carboxyl and carbonyl groups and the average molecular weight of the various grades of poly(aldehydocarboxylic acids) may be varied by selecting suitable reaction conditions. The general formula (I) represents the fundamental structure of the poly(aldehydocarboxylic acids) to be used according to the invention.

\[ \text{HO}[(\text{CH}_2-\text{CH})_x (\text{CH}_2-\text{CH})_y]_p \text{-OH} \quad \text{COOH} \quad \text{CHO} \]  

The poly(aldehydocarboxylic acids) are poly(aldehydocarboxylic acids) which have been mostly linearly linked via carbon-carbon bonds and comprising many pendant carboxyl groups and a few pendant carbonyl groups and terminal hydroxyl groups. The chemical constitution thereof is more specifically characterized by the general formula (I).

The average degrees of polymerization are indicated by the viscosity numbers. These are usually between 5 and 50 ml/g, based on 100% solids, measured as a 2% solution in 0.1N NaBr at 25 °C and a pH of 10 in an
Ubbelohde viscosimeter, capillary No. 0a. The steric linkage of the monomer constituents may be assumed to be atactic, the sequence of linkage may be assumed to be at random.

The content of carboxyl groups, expressed as \% by mole of COOH, may be calculated from the acid value (DIN 53402) of the dried polymers. The acid value of aqueous poly(aldehydocarboxylic acids) is unsuitable for calculating the molar percentage of COOH, since the technical grades contain minor amounts of formic acid, acetic acid and \( \beta \)-hydroxypropionic acid as by-products.

The sodium poly(aldehydocarboxylates) will have to be converted into the H form prior to the determination of the acid value by ion exchange.

Whereas upon use of commercially available activating agents in hard water (city tap water of hardness 18 °d) in the subsequent zinc phophation coarse crystals are immediately formed due to an insufficient activation, the addition of the poly(aldehydocarboxylic acids) according to the invention produces phosphate layers having values of the area-based mass ("area weights") which otherwise are obtained only if fully de-salted water is used in the preparation of the baths of activating agents. Under the hardness conditions as investigated, the addition of an amount of polymer of 0.5 g/l proved to be sufficient, whereas higher amounts resulted in a coarse appearance of the phosphate layers. In the individual case, the optimum amount of complexing agents will have to be determined for the local hardness conditions of the used (tap) water by way of a test series.
In the preparation of the ready-to-use activating bath the amount to be employed may be flexibly adapted to the water hardness available at the respective site of use by the addition of the poly(aldehydcarboxylic acids) according to the invention.

EXAMPLES

In order to determine the activating effect provided by the agents prepared according to the invention and by products used for comparison, the surfaces of steel specimens (material St 1405, dimensions 10 cm x 20 cm, about 1 mm in thickness) were phosphated by means of standardized phosphating processes according to Table 1 (dipcoat phosphating, normal-zinc process).

The "area weight" of the metal phosphate layer is understood to mean the mass relative to the area, in grams per square meter, determined according to DIN 50 492. For the determination of the bath capacity, two liters each of a 0.2% aqueous preparation of the activating agent was loaded with test sheets which were subsequently phosphated. The average area weights of four subsequent test specimens were determined initially and after each tenth test sheet. The average values calculated therefrom are set forth in Table 3. The baths were considered to have been exhausted, if ten sheets in a series upon being zinc phosphated exhibited defects or coarsely crystalline regions. The bath capacity is expressed as square meter of activatable area per two liters of activating bath.
Comparative Example 1

As product for comparison there was employed a commercially available product of the company Collardin, Cologne (Fixodine®). The results of activation obtained thereby are set forth in Table 3.

Comparative Example 2

An ethylene-maleic anhydride copolymer EMA 1103 of the company MONSANTO according to the German Unexamined Patent Application 36 15 294 was employed in the same molar amount as the additive according to the invention. The result (see Table 3) shows the inefficiency of this polymer for hard water-stabilization.

Examples 1 to 6

The Examples furnish evidence of the efficiency of the additive according to the invention in combination with differently formulated activating agents. Employed were the poly(aldehydocarboxylic acids) POC HS 5060, POC HS 0010 and POC HS 65 120 of the company DEGUSSA AG, Frankfurt, which are characterized in greater detail in Table 2. The obtained results are also summarized in Table 3.
Table 1

Treatment steps in the course of the standard phosphating process

<table>
<thead>
<tr>
<th>Stage</th>
<th>Treatment step</th>
<th>Treatment with</th>
<th>Concentration % by weight</th>
<th>Temperature (°C)</th>
<th>Period of Treatment (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mechanical cleansing and degreasing</td>
<td>bibulous paper</td>
<td>-</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Chemical cleansing and degreasing</td>
<td>Ridoline(R) C 1051 ¹</td>
<td>5</td>
<td>80-90</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Rinsing</td>
<td>Tap water²</td>
<td>-</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>Mordanting</td>
<td>Chemapix(R) ACM ³</td>
<td>30</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>Rinsing</td>
<td>Tap water²</td>
<td>-</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>Activation</td>
<td>Activating agent according to Table 3</td>
<td>0.2</td>
<td>20</td>
<td>2</td>
</tr>
</tbody>
</table>

¹

Continued
<table>
<thead>
<tr>
<th>Stage Treatment step</th>
<th>Treatment with</th>
<th>Concentration % by weight</th>
<th>Temperature (°C)</th>
<th>Period of Treatment (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 Phosphating</td>
<td>Granodine(R) 4)</td>
<td>3.0</td>
<td>60-70</td>
<td>5</td>
</tr>
<tr>
<td>8 Rinsing</td>
<td>VE water 5)</td>
<td>-</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>9 Drying</td>
<td>Compressed air</td>
<td>-</td>
<td>20</td>
<td>to dryness</td>
</tr>
</tbody>
</table>

1) Commercially available strongly alkaline phosphate-containing immersion cleaner, of the company Collardin, Cologne.
2) Untreated city water of 18 °d.
3) Commercially available rust-removing and descaling agent containing hydrochloric acid and inhibitor, of the company Collardin, Cologne.
4) Commercially available nitrate/nitrite accelerated phosphating agent, of the company Collardin, Cologne.
5) Fully desalted (demineralized) water.
**Table 2**

<table>
<thead>
<tr>
<th>Solids</th>
<th>pH Value</th>
<th>Density (g/ml)</th>
<th>Viscosity at 20 °C (mPa.s)</th>
<th>Setting point (°C)</th>
<th>Color Value</th>
<th>Viscosity DIN 6162 number (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POC HS 5060</td>
<td>40</td>
<td>1.3</td>
<td>240</td>
<td>-9</td>
<td>2</td>
<td>28</td>
</tr>
<tr>
<td>POC HS 0010</td>
<td>50</td>
<td>1.0</td>
<td>115</td>
<td>-9</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>POC HS 65 120</td>
<td>35</td>
<td>1.7</td>
<td>380</td>
<td>-9</td>
<td>3</td>
<td>47</td>
</tr>
</tbody>
</table>

*The viscosity number was based on 100% solids, measured with a 2% solution in 0.1N NaBr at 25 °C and pH 10; Ubbelohde viscosimeter, capillary 0a.*
### Table 3
Influence of additives for the hard-water stabilization of activating baths

<table>
<thead>
<tr>
<th>EX-AMPLE Activating Agent&lt;sup&gt;a)&lt;/sup&gt;</th>
<th>Additive (1 g/l)</th>
<th>Area Weight g/m²</th>
<th>Capacity&lt;sup&gt;b)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative FIXODINE® 6&lt;sup&gt;c)&lt;/sup&gt;</td>
<td>NONE</td>
<td>d)</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comparative same EMA 1103</td>
<td></td>
<td>4.5-7.5&lt;sup&gt;d)&lt;/sup&gt;</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 same POC HS 5060</td>
<td>2.9</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>2 same POC HS 0010</td>
<td>2.4</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>3 same POC HS 65 120</td>
<td>2.6</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>4&lt;sup&gt;e)&lt;/sup&gt; same POC HS 5060</td>
<td>2.4</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>5&lt;sup&gt;f)&lt;/sup&gt; same POC HS 5060</td>
<td>2.5</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>6&lt;sup&gt;e)&lt;/sup&gt; POC HS 5060</td>
<td>2.5</td>
<td>3.3</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a)</sup> Batch 0.2% by weight in city water of 18 °d.

<sup>b)</sup> Activatable area in m² per 2 liters of activating bath.

<sup>c)</sup> Test substance: Activating agent containing titanium phosphate by the company Collardin, Cologne.

<sup>d)</sup> Coarse crystals due to an insufficient activating effect.
Activating agent containing titanium phosphate, prepared with 1.7% by weight of POC HS 5060.

Activating agent containing titanium phosphate, prepared with 2.4% by weight of 1-amino-1-phenyl-methane-1,1-diphosphonic acid.

The activating agents containing titanium phosphate used in the Examples 4, 5 and 6 (cf. the annotations e) and f) have been described in the German Patent Application No. P 38 14 287.2 which has not been previously published.
CLAIMS
CLAIMS:
The claims defining the invention are as follows:

1. Hard water-stabilizing additives to treatment baths for the activation of metal surfaces composed of iron, steel, zinc, galvanized or alloy-galvanized iron or steel, aluminum or aluminated iron or steel prior to the step of phosphating said surfaces with phosphating baths containing zinc ions, said additives consisting of poly-(aldehydocarboxylic acids) and/or their water-soluble alkali metal salts.

2. Additives according to claim 1, characterized in that the poly(aldehydocarboxylic acids) or their water-soluble alkali metal salts by the reaction of hydrogen peroxide, acrolein and acrylic acid, to have
   - a viscosity number within the range of from 5 to 50 ml/g,
   - an acid value within the range of from 450 to 670,
   - an acid equivalent weight within the range of from 125 to 70,
   - a setting point of less than 0 °C,
   - a content of carboxyl groups within the range of from 55 to 90% by mole, and
   - a molecular weight within the range of from 1,000 to 20,000.

3. Additives according to claims 1 and 2, characterized in that they contain the sodium salts as the alkali salts of the poly(aldehydocarboxylic acids).

4. Use of the additives according to claims 1 to 3 in treatment baths for the activation of metal surfaces in an amount of from 0.05 to 3 g/l.
5. Use of the additives according to claim 4 in an amount of from 0.5 to 1 g/l.

6. Use of the additives according to claims 4 and 5 prior to a low zinc-phosphating procedure.

7. Use of the additives according to claims 4 to 6 in treatment baths for the activation of metal surfaces in activating baths having a pH value of from 5 to 9.

DATED this SIXTH day of JANUARY 1989
Henkel Kommanditgesellschaft auf Aktien

Patent Attorneys for the Applicant
SPRUSON & FERGUSON
END