COMPOSITION AND PROCESS FOR FORMING PHOSPHATE COATINGS ON TITANIUM AND ZIRCONIUM

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The present invention relates generally to adherent, protective coatings on titanium and zirconium metals. More specifically, the invention relates to the application of phosphate coatings on elementary titanium and zirconium metals themselves.

In recent years, the supply of titanium metal has been greatly increased by improvement in techniques of refinement. The extremely valuable properties of this metal have led to its use in a great variety of applications, in which the metal is worked, drawn, and otherwise shaped and shaped, in form, while not yet in full commercial development. Zirconium metal and its alloys have been found to have extremely valuable properties. As with other metals, an adherent, protective coating has been sought to facilitate the working of these metals and also to protect the metals themselves. Conventional phosphate and oxalate-type treating baths do not produce entirely satisfactory coatings on titanium or zirconium. With these solutions either the metal is not coated at all, or there is formed only a loose, dusty coating which is unsatisfactory in the drawing operation.

It has been found, in accordance with this invention, that titanium and zirconium may be provided with uniform, hard and adherent phosphate coatings by contacting a surface of the metal with a bath comprising an aqueous solution of manganese dihydrogen phosphate, the fluoride ion, and a small amount of a stable oxidizing agent. While good coatings are obtained in the treating baths of this invention which contain no dissolved titanium or zirconium, it has been found that the general quality of the coatings obtained under conditions of industrial application is improved, and more consistent operation is insured, if a very small proportion of tita

While in no wise necessary for obtaining coatings of satisfactory weight and adherency, it has been found that improved coatings and more satisfactory and reliable operation of the treating bath are obtained if there is present an ion such as ammonium, or a combination of ammonium with sodium, potassium and the like; or a combination of sodium and potassium ions, with or without ammonium ions. Thus, while the ammonium ion is always beneficial, the presence of either sodium or potassium ions, alone, seems to be without effect. In contrast, a combination of sodium and potassium ions seems to improve the action of the bath in a manner similar to that of the ammonium ion. To derive this beneficial effect only a small proportion of ammonium and/or sodium plus potassium ions are required. In general, only 0.02% of ammonium ion or its equivalent in sodium and potassium is required. Better results are obtained with 0.03 to 0.04%. While not deleterious, no further significant improvement is noted with more than 0.2% ammonium ion or its equivalent of sodium plus potassium ions.

While phosphate solutions, other than those of manganese phosphate, will produce coatings on titanium or zirconium, such coatings are not entirely satisfactory. For example, zinc phosphate coatings do not improve drawing or other working operations to nearly the same extent as do manganese phosphate coatings. Solutions in which manganese dihydrogen phosphate is the major or predominating coating constituent, however, produce harder, more tightly adherent, and heavier coatings on a wider variety of titanium and zirconium metals and their alloys. Moreover, the coatings derived from manganese phosphate solutions are of greater superior quality in metal working operations. The proportions of manganese dihydrogen phosphate in the coating solution of this invention are in no wise critical. For example, excellent, hard and tightly adherent coatings are obtained in solutions containing from as little as 0.5% to as much as saturation. A typical bath for use in this invention will contain from 2 to 10% manganese dihydrogen phosphate. The effectiveness of this action increases with increases in manganese phosphate content in the range between 3 and 9%. The phosphate solution may vary considerably in its "free acid" and "total acid" content. (The former is the number of ml. of N/10 sodium hydroxide solution required to neutralize 2 ml. of the phosphate solution to a bromophenol blue end-point while the latter is the number of ml. of N/10 sodium hydroxide solution required to neutralize 2 ml. of solution to a phenolphthalene end-point.) With typical solutions, excellent coatings are obtained when the ratio of free acid to total acid is in the range 1:4 to 1:7. Stable, concentrated stock solutions may be prepared containing at least twice the useful concentration of manganese dihydrogen phosphate and other ingredients disclosed below; these solutions merely being diluted with water before use or added as required.

The concentration of oxidizing agent does not appear to be critical providing sufficient is utilized to insure coating action. With as little as 0.7% sodium nitrate (equivalent to about 0.5% nitrate ion), a preferred oxidant in this composition, excellent, uniform and adherent coatings are obtained. It is preferred, however, to use somewhat larger quantities to insure a slight excess of oxidant. In commercial treating baths containing from 2 to 10% manganese dihydrogen phosphate, it is preferred to utilize about 1.5 to 1.75% sodium nitrate or its equivalent. Concentrations up to saturation may be satisfactorily employed. Other oxidizing agents which are somewhat weaker than sodium permanganate or potassium persulfate, for example, may be satisfactorily employed, such as for example ammonium nitrate, sodium...
chlorate, sodium nitrite, saccharin, sucrose and others.
Saccharin in amounts between 0.2 and 20% has been found

The concentration of the free fluoride ion is not critical

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Heavier, more adherent coatings are obtained when at

0.2% fluoride ion is present. It has been found that

when the fluoride ion is present in an excess at least

0.09% over that theoretically required to form TiF₄ ion or a

zirconium complex with the titanium or zirconium content of the

bath. In a bath containing about 8% manganese dihydro-

gen phosphate dihydrate, heavy, adherent and high-

quality coatings are obtained on titanium or zirconium when

the fluoride ion is present in an excess at least

0.09% over that theoretically required to form TiF₄ ion or a

zirconium complex with the titanium or zirconium dissolved in the

bath. In order to avoid frequent re-

plenishing of the fluoride content of the bath during use,

it is usually desirable to have a considerable excess of

fluoride ion present. For this latter purpose 0.15 to

2.5% free fluoride ion usually is sufficient.

The fluoride content of the bath may be derived from

any water-soluble fluoride or bifluoride such as the alkali-

metal and ammonium fluorides and bifluorides. Ammonium

bifluoride (NH₄HF₂) sodium bifluoride and potassium

bifluoride are much preferred, because they also serve as

a source of the desirable ammonium, sodium and

potassium ions.

In the method of this invention, processing temperatures

between about 190° F. and boiling may be used satisfac-

tory. As the temperature is increased above about 190°

F., the time required for coating is decreased. For ex-

ample, at a temperature of about 195° F., a satisfactorily

adherent coating is obtained in 30 minutes. At tem-

peratures of 200° F. or more, satisfactory coatings are ob-

tained in about 15 minutes.

No special pretreatment of the titanium or zirconium

metals is required before applying the coating. Generally,

however, it is desirable to subject the metal to the nitric-

acid-hydrofluoric acid activation pretreatment convention-

tially employed in connection with stainless steels,

followed by a hot water rinse. Any grease, oil, or soil

may be removed by wiping, spraying, or dipping in mineral

spirits or other solvents, or by use of an alkali cleaner,

preliminary to the nitric acid-hydrofluoric acid pretreat-

ment.

The coatings applied by the method and compositions of

this invention provide added protection to the metal

against corrosion. When the coatings are to be used as

a base for paint, it is desirable to follow the coating

formation step with the conventional chrome-acid raining

step. When the coated titanium or zirconium is deformed,

it is advantageous to follow the phosphate coating step

with the application of conventional drawing lubricants

such as stearate soaps prior to the actual deformation

operation.

By the term “titanium metal” or “zirconium metal” as

used herein, is meant any of the commercially available

forms of titanium or zirconium and any alloys thereof

in which titanium or zirconium is present in a greater

quantity than that of any other metal and preferably in a

predominating proportion. Titanium and zirconium alloy

readily with nearly all metals, including especially

copper, tin, iron, aluminum, chromium, cobalt, moly-

denum and tungsten. Titanium, zirconium and alloys

thereof, or of either with the above and other metals, par-

ticularly the commercial varieties thereof, may be worked

by swaging, hot and cold rolling and wire drawing.

Titanium metal, in particular, oxidizes and reacts with

nitrogen very readily when hot. Consequently, an ad-

herent, protective coating is of great value during the

working of this metal, especially during wire drawing.

The coating in conjunction with lubricants makes pos-

sible higher drawing speeds, greater reduction per draw

and higher finish.

The invention will now be more fully described with

reference to several specific examples. As used herein-

above and unless otherwise specified, the concentra-

tions of the various ingredients are expressed as percent

wt./vol. In other words, the density of the solution is

taken as unity.

**EXAMPLE 1**

The following materials were added to sufficient water to
make a total volume of 600 ml.:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(H₃PO₄)₂·2H₂O</td>
<td>25.5 grams</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>4 grams</td>
</tr>
<tr>
<td>NH₄HF₂</td>
<td>6 grams</td>
</tr>
</tbody>
</table>

A panel of commercially pure titanium was immersed in
this bath for 15 minutes while maintaining the tempera-
ture at 200° F. An excellent practical coating was ob-
tained. On continued use of the bath, it was necessary to
replenish the fluoride ion by small increments of

NH₄HF₂. Full bath activity is easily maintained, on con-

tinuous or extended use, by periodic replenishing with
the other ingredients.

**EXAMPLE 2**

A concentrated stock solution was prepared containing

the following ingredients:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(H₃PO₄)₂·2H₂O</td>
<td>2,000 grams</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>340 grams</td>
</tr>
<tr>
<td>NH₄HF₂</td>
<td>170 ml</td>
</tr>
</tbody>
</table>

The final volume was 7,000 ml. This solution was

stored for a moderate period with only slow precipita-

tion. This stock solution may be diluted with water un-

til the resulting solution contains about 8% manganese
dihydrogen phosphate and used to provide excellent coa-

tings on titanium as in Example 1.

**EXAMPLE 3**

To demonstrate the operation of the process in a con-

tinuous manner, a large 150 gallon bath was made up

for intermittent commercial scale use as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(H₃PO₄)₂·2H₂O</td>
<td>112 grams</td>
</tr>
<tr>
<td>NH₄HF₂</td>
<td>9 grams</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>12 grams</td>
</tr>
</tbody>
</table>

H₂O to total 150 gals.

The bath was aged by dissolving therein 1.1 lbs. of

titanium sponge prior to the initial coating attempt.
The analysis of this bath at this point was F. A.-3.7; T.

A.-17.3 and ratio F. A./T. A.-1:4.7. When it was

desired to coat titanium the bath was heated to 260 to

210° F. and then cooled down at the end of the day.
The bath continued to produce uniform, adherent coatings on titanium over the course of many months. From time to time small additional quantities of NH₄H₂PO₄ were added to maintain the desired fluoride level. Had a greater volume of metal been processed replenishment of the other ingredients would have been required. The bath amply demonstrated that it was stable over long periods.

**EXAMPLE 4**

The effect of ammonium ion was effectively demonstrated by the use of the following bath:

<table>
<thead>
<tr>
<th>Component</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(H₂PO₄)₂·2H₂O</td>
<td>125</td>
</tr>
<tr>
<td>NaH₂F₂</td>
<td>10</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>10</td>
</tr>
<tr>
<td>H₂O to 1,500 ml.</td>
<td></td>
</tr>
</tbody>
</table>

Panels of commercially pure titanium processed 70 minutes at 200°-210° F. in this solution received almost no coating. At this point, the solution analyzed as having F. A.-4.5; T. A.-18.5; ratio 1:4.1. When only 5 grams of (NH₄)₂HPO₄ were added to this solution a subsequent panel received an excellent, heavy, hard and adherent coating in 15 minutes at 200°-210° F.

**EXAMPLE 5**

A bath was made up to have the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent w/vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(H₂PO₄)₂·2H₂O</td>
<td>8.3</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.67</td>
</tr>
<tr>
<td>NH₄HF₂</td>
<td>0.67</td>
</tr>
</tbody>
</table>

This bath was heated to 200° F. and maintained at 200° F.-210° F. for 2 to 3 hours. A tube of commercially pure zirconium was pretreated in HNO₃-HF, rinsed in hot water, immersed for 15 minutes in the bath at 200° F., rinsed again in hot water and dried. The tube received a thin coating by this treatment. At this point the analysis of this bath was free acid—2.8 ml., total acid—12.6 ml., ratio F. A.:T. A.—1:4.5. Further processing of the same tube resulted in considerable improvement in the coatings. The finally coated zirconium tube was lubricated with stearate soap and subjected to drawing. Drawing operations were found to be definitely improved over the drawing of uncoated zirconium.

From the above it is clear that the presence of zirconium ion in the bath improves the coating action of the solution on zirconium to a noticeable extent. When zirconium panels are processed in a similar bath which had been used to coat titanium, a heavy, uniform coating was obtained which was not as adherent as those prepared in the presence of zirconium ion.

**EXAMPLE 6**

The efficiency in metal drawing of zinc phosphate coated titanium was compared to that of manganese phosphate coated titanium. The zinc phosphate solution and procedure utilized were as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(H₂PO₄)₂·2H₂O</td>
<td>13.1</td>
</tr>
<tr>
<td>NaClO₃</td>
<td>3.6</td>
</tr>
<tr>
<td>NH₄HF₂</td>
<td>4.0</td>
</tr>
<tr>
<td>Sodium salt of ethylene-diamine tetracetic acid</td>
<td>1.0</td>
</tr>
<tr>
<td>H₂O to 700 ml.</td>
<td></td>
</tr>
<tr>
<td>Processing temp.—130°—150° F.</td>
<td></td>
</tr>
</tbody>
</table>

The above procedure formed a phosphate coating on tubes of commercially pure titanium. A manganese phosphate coated tube, prepared according to the procedure of Examples 1 to 3 was utilized in the comparison. Both tubes were lubricated with sodium stearate before drawing. The zinc phosphate coated tube did not draw as satisfactorily as the tube coated with manganese phosphate. The latter is suitable for commercial drawing operations while the former is not.

**EXAMPLE 7**

For commercial coating of titanium a two package composition was developed, one solution for original make-up and the other a concentrated replenisher solution for replenishing a bath made from the make-up solution. The materials of the two solutions were mixed in the following proportions:

<table>
<thead>
<tr>
<th>Solution</th>
<th>Weight—grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(H₂PO₄)₂·2H₂O</td>
<td>80.00</td>
</tr>
<tr>
<td>HNO₃ (42° Baumé)</td>
<td>3.00</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>10.90</td>
</tr>
<tr>
<td>NaH₂F₂</td>
<td>0.90</td>
</tr>
<tr>
<td>K₂TiF₆</td>
<td>2.10</td>
</tr>
<tr>
<td>Water</td>
<td>94.9</td>
</tr>
</tbody>
</table>

Total | 191.8 (133 ml. vol.)

**Replenisher**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Weight—grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(H₂PO₄)₂·2H₂O</td>
<td>80.00</td>
</tr>
<tr>
<td>Nitric acid (42° Baumé)</td>
<td>7.70</td>
</tr>
<tr>
<td>KNO₃</td>
<td>3.70</td>
</tr>
<tr>
<td>Water</td>
<td>94.80</td>
</tr>
</tbody>
</table>

Total | 186.2 (135 ml. vol.)

In the above formulations the nitric acid or other mineral acid was added to keep the ingredients in solution. Before use, the acidity of the make-up was reduced to a desired value by adding a small amount of manganese carbonate. The acid content of the replenisher as given above is such as to maintain correct acidity in the make-up bath throughout its period of use. Since sodium bifluoride is of limited solubility when cold, a sufficient amount cannot be incorporated in either of the make-up or replenisher solutions. This ingredient must be added periodically by itself. The above proportion of bifluoride, however, is stable on storage, lesser or greater amounts seemingly favoring the formation of a precipitate. The make-up contains both sodium and potassium ions and also titanium ions. The replenisher contains potassium ions in sufficient concentration to combine with the sodium bifluoride additions to maintain a satisfactory sodium-potassium level and obtain the above-discussed accelerating and improvement action.

In use the make-up solution is first diluted with water, each 175 lb. portion of make-up being diluted with sufficient water to make 100 gals. of solution. The diluted solution is then heated in 200°-210° F. and 1.7 lbs. of manganese carbonate is added to reduce the acidity. Two pounds (2 lbs.) of sodium bifluoride are finally added and the bath is ready for use.

As the bath is utilized the total acidity will gradually decline due to depletion. The addition of 10 pounds of replenisher for every 100 gals. of the bath will raise the total acidity of the make-up solution by one point. On continued use small portions of sodium bifluoride are added as needed to maintain the free fluoride level and bath activity. The above formulas produce consistent, excellent coatings on commercially-pure titanium metal. The formulas can be varied in strength and in proportion, it being understood that the solutions should be dilutable to produce final solutions having concentrations within the ranges of proportions given herein.

**EXAMPLE 8**

A second type of concentrated make-up and replenisher solutions, which employ the ammonium ion as an accl-
erator in place of the sodium-potassium combinations of Example 7, was made up as follows:

<table>
<thead>
<tr>
<th>Make-Up, Grams</th>
<th>Replenisher, Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(H₂PO₄)₂ · 2H₂O</td>
<td>90.0</td>
</tr>
<tr>
<td>Nitric Acid Conc.</td>
<td>14.0</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>10.8</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>2.9</td>
</tr>
<tr>
<td>H₂O</td>
<td>85.9</td>
</tr>
<tr>
<td>Total</td>
<td>191.4</td>
</tr>
</tbody>
</table>

The treating bath was made by diluting the make-up solution as in Example 7. The replenisher solution was used periodically to restore bath strength. Sodium bifluoride also was added periodically to maintain an excess over the titanium or zirconium in the bath. The bath of this example was slightly superior in coating efficiency to that of Example 7.

**EXAMPLE 9**

A single concentrated solution which is useful both as a make-up and as a replenisher was made up as follows:

<table>
<thead>
<tr>
<th></th>
<th>Pounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(H₂PO₄)₂ · 2H₂O</td>
<td>80.0</td>
</tr>
<tr>
<td>70% nitric acid</td>
<td>7.5</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>3.4</td>
</tr>
<tr>
<td>KNO₃</td>
<td>3.7</td>
</tr>
<tr>
<td>Water</td>
<td>105.4</td>
</tr>
<tr>
<td>Total</td>
<td>200</td>
</tr>
</tbody>
</table>

This stock solution was made by mixing the acid and water and then adding the solid chemicals thereto. The solution was stirred for about 1.5 hours and then filtered. After 27 days storage in glass bottles at room temperature, only a slight, light-weight precipitate formed which did not in any way affect the utility of the solution. For analysis, 60 grams of the above solution was diluted to 1000 ml. with distilled water and 10 ml. aliquots of the resulting solution analyzed for free acid and total acid using bromophenol blue and phenolphthalein indicators, respectively. The free acid of the solution was 3.03 ml. the total acid 23.17 ml. and the specific gravity at 85° C. was 1.365.

The treating bath was made up by adding 175 lbs. of the above solution to enough water to make 100 gallons. The solution was then heated to 200–210° F. and 4.3 lbs. of manganese carbonate, 1.8 lbs. of K₂FeF₆, and 2.85 lbs. of NaH₂PO₄ added for every 100 gallons of solution. Commercially pure titanium, pretreated for one minute at room temperature in a solution containing 3% HF and 10% HNO₃, processed for 15 minutes in the resulting bath acquired uniform, excellent coatings weighing an average of about 104 mg./ft.

**EXAMPLE 10**

Other oxidizing agents useful as replacements for sodium nitrate were added to a bath containing about 8.3% manganese dihydrogen phosphate, about 0.7% ammonium bifluoride, and about 0.1% titanium ion. Baths containing from 0.2 to 20% of saccharin, 0.7 to 2.5% sodium chlorate, or 0.2 to 2% sucrose yielded uniform adherent coatings at 200–210° F. A dilute solution of sodium nitrite was slowly trickled into a similar bath at a rate to maintain a concentration estimated to be of the order of 0.01%. With this bath, satisfactory coatings on titanium also were obtained.

While there have been disclosed certain preferred ways of carrying out the invention, it is desired not to be limited solely thereto, and it will be appreciated that the invention is susceptible to modification, variation and change without departing from the proper scope or fair meaning of the subjoined claims.

What is claimed is:

1. The process of producing an adherent, protective coating on a surface of titanium and zirconium metals which comprises contacting a metal surface with an aqueous solution consisting essentially of manganese dihydrogen phosphate, at least about 0.05% by weight of at least one ion selected from the group consisting of titanium ions and zirconium ions, an oxidizing agent in an amount having an effect on the coating-forming ability of said solution equivalent to about 0.5% to about 1.5% of the nitrate ion and the fluoride ion in an amount in excess of the concentration of the ion selected from the group consisting of titanium and zirconium ions.

2. The process of treating a surface of titanium and zirconium metals to produce an adherent, protective coating thereon, which process comprises contacting said surface with a solution consisting essentially of manganese dihydrogen phosphate, at least about 0.05% by weight of at least one ion selected from the group consisting of titanium and zirconium ions, an oxidizing agent in an amount having an effect on the coating-forming ability of said solution equivalent to about 0.5% to about 1.5% of the nitrate ion, about 0.02% to about 0.2% of at least one ion selected from the group consisting of ammonium, sodium and potassium ions, and the fluoride ion in an amount in excess of the concentration of the ion selected from the group consisting of titanium and zirconium ions.

3. A process of producing an adherent, phosphate coating on the surface of titanium and zirconium metals, which process comprises contacting a surface of said metal with an aqueous solution comprising manganese dihydrogen phosphate, fluoride ion, ammonium ion, a metal ion selected from the class consisting of titanium and zirconium, and saccharin; wherein the fluoride ion is in excess of said metal ion, said ammonium ion is present to the extent of at least 0.02%, said metal ion is present to the extent of at least about 0.05%, and said saccharin is present in amounts between 0.2 and 20%.

4. A composition for the phosphate coating of titanium and zirconium metals which comprises an aqueous solution of a coating phosphate comprising predominantly manganese dihydrogen phosphate, a stable oxidizing agent in an amount having an effect on the coating-forming ability of said solution equivalent to about 0.5% to about 1.5% of the nitrate ion, at least about 0.05% by weight of at least one ion selected from the group consisting of titanium and zirconium ions, and the fluoride ion in an amount in excess of the concentration of the ion selected from the group consisting of titanium and zirconium ions.

5. A composition for producing an adherent, phosphate coating on titanium and zirconium metals which consists essentially of an aqueous solution of manganese dihydrogen phosphate, at least about 0.05% by weight of at least one ion selected from the group consisting of titanium and zirconium ions, an oxidizing agent in an amount having an effect on the coating-forming ability of said solution equivalent to about 0.5% to about 1.5% of the nitrate ion, about 0.02% to about 0.2% of at least one ion selected from the group consisting of ammonium, sodium and potassium ions, and the fluoride ion in an amount in excess of the concentration of the ion selected from the group consisting of titanium and zirconium ions.

6. A process in accordance with claim 1 wherein the said surface is titanium and the fluoride ion is present in an excess of at least about 0.09% over that which is required to form a titanium ion complex with the titanium ions in said solution.

7. A process in accordance with claim 1 wherein said surface is zirconium and the fluoride ion is present in an excess of at least about 0.09% over that which is required to form a zirconium ion complex with the zirconium ions which are present in the solution.
8. A process in accordance with claim 1 wherein said oxidizing agent is selected from the group consisting of about 0.5 to about 1.3% nitrate, about 0.5 to about 1.9% chlorate, about 0.01% nitrite, about 0.2% to about 20% saccharin and about 0.2 to about 2% sucrose.

9. A composition in accordance with claim 4 wherein the said fluoride ion is present in an amount in excess of at least about 0.09% over that which is required to form a titanium ion complex with the titanium ions in said solution.

10. A composition in accordance with claim 4 wherein the said fluoride ion is present in an amount in an excess of at least about 0.09% over that which is required to form a zirconium ion complex with the zirconium ions in said solution.

11. A process in accordance with claim 1 wherein said oxidizing agent is selected from the group consisting of about 0.5 to about 1.3% nitrate, about 0.5 to about 1.9% chlorate, about 0.01% nitrite, about 0.2% to about 20% saccharin and about 0.2 to about 2% sucrose.

12. A process in accordance with claim 8 wherein said oxidizing process is nitrate.

13. A composition in accordance with claim 11 wherein said oxidizing agent is nitrate.

14. An article of manufacture having a surface at least of a metal selected from the class consisting of titanium, zirconium, and alloys thereof and an adherent manganese phosphate coating on said surface derived from an aqueous acidic solution comprising manganese dihydrogen phosphate.

15. An article of manufacture as claimed in claim 14 and further characterized in that said surface is a titanium metal.

16. An article of manufacture as claimed in claim 4 and further characterized in that said surface is a zirconium metal.

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