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(54) ELECTROLYTIC PASSIVATED TIN PLATED STEEL

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(57) ABSTRACT

An electrolyte composition for passifying tin plated steel wherein the essential ingredient consists of a mixture of organic hydroxyl acids and phenol organic acids; a method of passifying tin plate steel articles with the composition by electrolysis with a pH of about 7.0-10.0 and preferably a pH of 8.0-9.5; and providing the passified tin plated steel article produces by the method along with the passified articles having an appropriate paint thereon.

ELECTROLYTIC PASSIVATED TIN PLATED STEEL

FIELD OF INVENTION

[0001] This invention relates to an electrolytic coating composition for tin plated steel articles which provides the tin plated steel with a protective coating and improved paint adhesion.

[0002] More particularly, the present invention provides a tin plated steel coating composition having as its essential ingredients organic hydroxyl acids, both saturated and unsaturated, and phenol organic acids; the method of coating the surface of the tin plated steel articles; and the tin plated steel article electrolytically coated with the composition having as its essential ingredients organic hydroxyl acids, both saturated and unsaturated, and phenol organic acids; and the coated articles painted.

BACKGROUND OF THE INVENTION

[0003] The natural oxide film on a tin plated steel surface provides a protective barrier and acts to improve paint adhesion. Maintaining this oxide film while at the same time preventing the rapid and uncontrolled growth of the oxide to a thick, yellow and non-adhesive layer has always been the primary goal of tin plated steel producers. In addition, foods high in sulfur will stain tin plated steel surfaces not properly passified.

[0004] Initial attempts at passification all centered around the thickening of the tin's natural oxide film with an inorganic oxidant while at the same time leaving a corrosion resistant conversion coating on the surface of the metal to retard further oxide growth and prevent sulfide stains. In 1931 S. R. Mason (U.S. Pat. No. 1,827,204) patented an electrolytic process which used chromates to both thicken the oxide film and leave a film of reduced chromic oxides to retard further oxide growth and prevent sulfide stains. In 1935 a French patent (French patent 777,314) detailed a process which used sodium molybdates, an inorganic oxidant and various heavy metals to produce a passive film on the metal's surface. In the same year U.S. Pat. No. 2,024,951 described a process which used potassium permanganate to both stabilize the oxide film and reduce sulfide staining. In 1940 U.S. Pat. No. 2,215,165 described an electrolytic process which oxidized and then reduced the oxide to give a more dense oxide film and produce a more passive tin oxide. That same year R. Kerr (Kerr, R., "Protective Films on Tin Plate by Chemical Treatment", J. Soc. Chem. Ind., 59, 259, 1940) published the results of his investigations which showed that an alkaline solution of chromates would passivate tin plated steel surfaces. In 1943 W. O. Cook and H. E. Romine (U.S. Pat. No. 2,312,076) obtained patents on a process which used dichromates mixed with phosphates to passivate tin plated steel surfaces. Since that time new patents (U.S. Pat. Nos. 2,327,127 and 2,357,970) involving inorganic compounds have been issued, but they have all involved the use of dichromates or chromium in the plus three oxidation state which will naturally oxidize itself to the plus six oxidation state (U.S. Pat. No. 6,099,714) when exposed to humid conditions in the open atmosphere. The hexavalent chromium present in all of these compositions is extremely toxic and as such is banned in Europe and in many areas of the United States.

[0005] A totally organic electrolytic process of increasing paint adhesion, controlling the rate of oxidation and providing resistance to sulfide staining was described by J. W. Bibber in U.S. Pat. No. 6,830,821. Since that patent was issued, the amount of tin applied to the steel in tin plating applications has fallen off significantly due to the cost of the tin itself and competition from glass and plastic containers. In addition the stain resistant requirements and adhesion requirements of tin plated steel have all been increased.

SUMMARY OF THE INVENTION

[0006] My invention eliminates the need for hexavalent chromium and/or trivalent chromium compositions which, due to their extreme toxicity, are being removed from the work place environment. In addition my process will provide the same level of sulfide stain resistance and coating adhesion as the chromium based compositions. At the same time this process is less expensive and requires no toxic waste disposal.

[0007] Accordingly, this invention is directed towards providing a protective coating for tin plated steel surfaces which has as its essential ingredients, organic hydroxyl acids, saturated and unsaturated, and phenol organic acids. This process uses the electrolysis of various solutions of the salts of organic hydroxyl acids, saturated and unsaturated, and the salts of phenol organic acids to deposit these materials and at the same time cause them to chemically react with the steel itself and/or the tin plated on the steel. The concentration and more specifically the current density used will determine the actual amount of material applied and the degree to which these materials react with the steel and/or the tin they are attracted to during the operation of the electrolytic cell. Below 5.0 grams per liter it is not economically feasible to deposit these materials in sufficient quantity for them to be effective in preventing sulfide stain resistance or to improving the adhesion of the tin plated steel surface. Coil coating lines used to plate out tin on steel will generally not allow for more then about five seconds of exposure to any given electrochemical cell used to passivate the tin plated steel. The upper limit is the solubility limits imposed on the materials being applied. In theory any PH may be used, but tin and/or steel will dissolve in strongly acid or strongly basic solutions and the hydrogen ions must of necessity be dissociated from the acids being used to provide for the proper conductivity of the solution being employed in the electrochemical cell. The most suitable PH range extends from a PH of 7.0 to a PH of 10.0. The preferred PH is one of 8.0 to 9.5. Temperature is of no concern to the process. The voltage must of necessity be above the reduction potential of the materials in the water based solutions.

[0008] Various other materials may be added to these solutions to act as wetting agents, increase conductivity, control the PH (buffers) or prevent biological attack as long as these materials do not act to prevent the reaction of the steel and/or tin with the materials in the solution in question. The distribution of the tin on tin plated steel, the uniformity of its thickness and its corresponding density will differ from one batch of tin plated steel to another as will the iron. As an example, Tin plated steel with a "matt" finish will have a greater surface area and as a result more non uniformity in the distribution of tin over the surface of the tin plated steel. As a consequence the distribution of phenolic acid salts and/or hydroxyl organic acids salts will of necessity differ from one batch of tin plated steel to another. We find that we are able to obtain more consistent overall results by the addition of phosphates, silicates and aromatic acid salts to our hydroxyl organic acid compositions.

[0009] In the following examples a tin plated steel sheet was cleaned of oils and/or unwanted inorganic compounds (i.e. tin and/or iron oxides) by use of a non ionic detergent. The tin plated steel sheet was made the cathode of a 12 volt electrolytic cell having a current density of about 15 amps per square foot in a solution consisting of 3.0 grams per liter sodium carbonate in D.I. water for thirty seconds. The cleaned surface was then rinsed in D.I. water and treated the cleaned tin plated steel was made the cathode in a 7.5 volt electrolytic cell having a current density of 50 amps per square foot and a solution of organic hydroxyl acids and phenol organic acids. The organic hydroxyl acids preferentially form a strong protective chemical bond to the tin while the phenol organic acids prefer to bond to the iron and serve to passivate the surface of the iron. The following Examples 1, 2, and 3 will serve to illustrate this tendency and thus the need for a mixture of phenol based compounds and non phenol based organic compounds working together with each other. Examples 13 and 17 show that the hydroxyl organic acids and/or phenolic acids continue to be essential to the process. The tin plated steel panels were three inches by five inches.

[0010] The organic hydroxyl acid is selected from C_2-C_6hydroxyl acids which are preferably selected from hydroxyl acetic acid, D-gluconic acid, citric acid and lactic acid.

[0011] The organic phenol acids are preferably selected from hydrolysable tannic acid, gallic acid and dihydroxy benzoic acid.

[0012] The phosphates, silicates and aromatic acid salts are preferably selected from phosphoric acid or its salt, potassium silicate and potassium salt of 1,3,4 benzenetricarboxylic acid

EXAMPLE 1

[0013] A five percent solution of acetic acid was added to a 0.5% solution of food grade hydrolysable tannic acid and the PH of the mixture was then adjusted to a PH of 9.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which the tin plated steel was made the anode and a high grade stainless steel panel was used as the cathode. 7.5 volts and a current density of about 50 amps per square foot were passed through the cell for three seconds. The tin plated steel panel was then removed, rinsed in D.I. water, dried and then placed in a 0.6% cysteine solution adjusted to a PH of 7.0 by the use of tri sodium phosphate and boiled for one hour to remove all oxygen in accordance with testing procedures outlined by "Mittal Steel USA". The outer tin layer quickly turned a tin sulfide yellow in color indicating that it was not passivated.

EXAMPLE 2

[0014] A five percent solution of hydroxyl acetic acid was added to a 0.5% solution of food grade hydrolysable tannic acid and the PH of the mixture was then adjusted to a PH of 9.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which the tin plated steel was made the anode and a high grade stainless steel panel was used as the cathode. 7.5 volts and a current density of about 50 amps per square foot were passed through the cell for three seconds. The tin plated steel panel was then removed, rinsed in D.I. water, dried and then placed in a 0.6% cysteine solution adjusted to a PH of 7.0 by the use of tri sodium phosphate and boiled for one hour to remove all oxygen in accordance with testing procedures outlined by "Mittal Steel USA". The outer tin layer did not yellow after one hour of exposure to the sulfide staining solution indication that a hydroxyl organic acid was needed to passivate the tin.

EXAMPLE 3

[0015] A six percent solution of hydroxyl acetic acid and 0.5% phthalic acid was adjusted to a PH of 9.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which the tin plated steel was made the anode and a high grade stainless steel panel was used as the cathode. 7.5 volts and a current density of about 50 amps per square foot were passed through the cell for three seconds. The tin plated steel panel was then removed, rinsed in D.I. water, dried and then placed in a 0.6% cysteine solution adjusted to a PH of 7.0 by the use of tri sodium phosphate and boiled for one hour to remove all oxygen in accordance with testing procedures outlined by "Mittal Steel USA". Within a five minute period of time, the outer edges of the panel became a dark black which then spread to the rest of the panel while the outer layer of tin remained silvery in color and then began to slowly turn yellow in color. An analysis to the panel showed the presence of a thick film of iron sulfide under a thin film of tin mixed with tin sulfide. This clearly indicates that a phenol organic acid was required to passivate the iron in the tin plated steel.

EXAMPLE 4

[0016] A five percent solution of hydroxyl acetic acid was added to a 0.5% solution of food grade hydrolysable tannic acid and the PH of the mixture was then adjusted to a PH of 9.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which two tin plated steel panels were made the anode and a high grade stainless steel panel was used as the cathode. Seven point five volts and a current density of about fifty amps per square foot were passed through the cell for three seconds. The tin plated steel panels were then removed, rinsed in D.I. water and dried.

[0017] One of tin plated panels was placed in an oven at 400 degrees F. for thirty minutes in accordance with testing procedures outlined by "Mittal Steel USA". The panel showed no traces of yellow tin oxide.

[0018] The second tin plate panel was first rinsed with a one percent hydroxyl acetic acid solution to remove any unwanted alkalinity and then coated with "Valspar 6256054 GLDEPOXY" according to manufactures specifications and then tested for dry and wet adhesion according to the testing specifications outlined in ASTM D3359 and those outlined by "Mittal Steel USA". There was no loss of adhesion.

EXAMPLE 5

[0019] A seven percent solution of citric acid was added to a 1.0% solution of food grade hydrolysable tannic acid and the PH of the mixture was then adjusted to a PH of 9.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which the tin plated steel was made the anode and a high grade stainless steel panel was used as the cathode. 7.5 volts and a current density of about 50 amps per square foot were passed through the cell for three seconds. The tin plated steel panel was then removed, rinsed in D.I. water, dried and then placed in a 0.6% cysteine solution adjusted to a PH of 7.0 by the use of tri sodium phosphate and boiled for one hour to remove all oxygen in accordance with testing procedures outlined by "Mittal Steel USA". There was no yellowing of the tin due to the formation of tin sulfide after one hour and only a minor quantity of iron sulfide formed indicating the passivation of both the iron and the tin.

EXAMPLE 6

[0020] A seven percent solution of citric acid was added to a 0.5% solution of food grade hydrolysable tannic acid and the PH of the mixture was then adjusted to a PH of 9.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which two tin plated steel panels were made the anode and a high grade stainless steel panel was used as the cathode. 7.5 volts and a current density of about 50 amps per square foot were passed through the cell for three seconds. The tin plated steel panels were then removed, rinsed in D.I. water and dried.

[0021] One of the tin plated panels was placed in an oven at 400 degrees F. for thirty minutes in accordance with testing procedures outlined by "Mittal Steel USA". The panel showed no traces of yellow tin oxide.

[0022] The second tin plated panel was first rinsed with a one percent hydroxyl acetic acid solution to remove any unwanted alkalinity and then coated with "Valspar 6256054 GLDEPOXY" according to manufactures specifications and then tested for dry and wet adhesion according to the testing specifications outlined in ASTM D3359 and those outlined by "Mittal Steel USA". There was no loss of adhesion.

EXAMPLE 7

[0023] A twelve percent solution of "D-Gluconic" acid was added to a 0.5% solution of food grade hydrolysable tannic acid and the PH of the mixture was then adjusted to a PH of 9.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which two tin plated steel panels were made the anode and a high grade stainless steel panel was used as the cathode. 7.5 volts and a current density of about 50 amps per square foot were passed through the cell for three seconds. The tin plated steel panels were then removed, rinsed in D.I. water and dried.

[0024] One tin plated panel was placed in an oven at 400 degrees F. for thirty minutes in accordance with testing procedures outlined by "Mittal Steel USA". The panel showed no traces of yellow tin oxide.

[0025] The second tin plated panel was first rinsed with a one percent hydroxyl acetic acid solution to remove any unwanted alkalinity and then coated with "Valspar 6256054 GLDEPOXY" according to manufactures specifications and then tested for dry and wet adhesion according to the testing specifications outlined in ASTM D3359 and those outlined by "Mittal Steel USA". There was no loss of adhesion.

EXAMPLE 8

[0026] A twelve percent solution of "D-Gluconic" acid was added to a 0.5% solution of food grade hydrolysable tannic acid and the PH of the mixture was then adjusted to a PH of 9.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which the tin plated steel was made the anode and a high grade stainless steel panel was used as the cathode. 7.5 volts and a current density of about 50 amps per square foot were passed through the cell for three seconds. The tin plated steel panel was then removed, rinsed in D.I. water, dried and then placed in a 0.6% cysteine solution adjusted to a PH of 7.0 by the use of tri sodium phosphate and boiled for one hour to remove all oxygen in accordance with testing procedures outlined by "Mittal Steel USA". There was no yellowing of the tin due to the formation of tin sulfide after one hour and only a minor amount of iron sulfide was detected on the surface of the iron attached to the tin.

EXAMPLE 9

[0027] A twelve percent solution of "D-Gluconic" acid was added to a 0.5% solution of pure gallic acid and the PH of the mixture was then adjusted to a PH of 9.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which the tin plated steel was made the anode and a high grade stainless steel panel was used as the cathode. 7.5 volts and a current density of about 50 amps per square foot were passed through the cell for three seconds. The tin plated steel panel was then removed, rinsed in D.I. water, dried and then placed in a 0.6% cysteine solution adjusted to a PH of 7.0 by the use of tri sodium phosphate and boiled for one hour to remove all oxygen in accordance with testing procedures outlined by "Mittal Steel USA". There was no yellowing of the tin due to the formation of tin sulfide after one hour.

EXAMPLE 10

[0028] A five percent solution of Lactic acid was added to a 0.5% solution of 2,4 dihydroxyl benzoic acid and the PH of the mixture was then adjusted to a PH of 9.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which the tin plated steel was made the anode and a high grade stainless steel panel was used as the cathode. Seven point five volts and a current density of about fifty amps per square foot were passed through the cell for three seconds. The tin plated steel panel was then removed, rinsed in D.I. water, dried and then placed in a 0.6% cysteine solution adjusted to a PH of 7.0 by the use of tri sodium phosphate and boiled for one hour to remove all oxygen in accordance with testing procedures outlined by "Mittal Steel USA". The outer tin layer did not yellow after one hour of exposure to the sulfide staining solution and only minor amounts of iron sulfide were found on the iron attached to the tin.

EXAMPLE 11

[0029] A five percent solution of hydroxyl acetic acid was added to a 0.5% solution of food grade hydrolysable tannic acid and the pH of the mixture was then adjusted to a pH of 8.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which two tin plated steel panels were made the anode, one panel had a matt finish while the other was polished steel. A high grade stainless steel panel was used as the cathode. Seven point five volts and a current density of about fifty amps per square foot were passed through the cell for three seconds. The tin plated steel panels were then removed, rinsed in D.I. water and dried. Both of them were placed in an oven at 400 degrees F. for thirty minutes in accordance with testing procedures outlined by "Mittal Steel USA". The matt finish panel showed traces of yellow tin oxide while the polished panel showed no traces of yellow tin oxide.

EXAMPLE 12

[0030] A five percent solution of hydroxyl acetic acid was added to a 0.5% solution of food grade hydrolysable tannic acid containing 0.5% phosphoric acid and the pH of the mixture was then adjusted to a pH of 8.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which two tin plated steel panels were made the anode, one panel had a matt finish while the other was polished steel. A high grade stainless steel panel was used as the cathode. Seven point five volts and a current density of about fifty amps per square foot were passed through the cell for three seconds. The tin plated steel panels were then removed, rinsed in D.I. water and dried. Both of them were placed in an oven at 400 degrees F. for thirty minutes in accordance with testing procedures outlined by "Mittal Steel USA". The panels showed no traces of yellow tin oxide.

EXAMPLE 13

[0031] A five percent solution of acetic acid was added to a 0.5% solution of food grade hydrolysable tannic acid containing 0.5% phosphoric acid and the pH of the mixture was then adjusted to a pH of 8.0 by the addition of potassium hydroxide. This solution was then used in an electrolytic cell in which two tin plated steel panels were made the anode, one panel had a matt finish while the other was polished steel. A high grade stainless steel panel was used as the cathode. Seven point five volts and a current density of about fifty amps per square foot were passed through the cell for three seconds. The tin plated steel panels were then removed, rinsed in D.I. water and dried. Both of them were placed in an oven at 400 degrees F. for thirty minutes in accordance with testing procedures outlined by "Mittal Steel USA". Both panels showed extensive amounts of yellow tin oxide.

EXAMPLE 14

[0032] A five percent solution of hydroxyl acetic acid was added to a 0.5% solution of food grade hydrolysable tannic acid and the pH of the mixture was then adjusted to a pH of 8.0 by the addition of potassium hydroxide. To this solution was added 0.5% potassium silicate and the pH was again adjusted to 8.0. This solution was then used in an electrolytic cell in which two tin plated steel panels were made the anode, one panel had a matt finish while the other was polished steel. A high grade stainless steel panel was used as the cathode. Seven point five volts and a current density of about fifty amps per square foot were passed through the cell for three seconds. The tin plated steel panels were then removed, rinsed in D.I. water and dried. Both of them were first rinsed with mild acid solution to remove any unwanted alkalinity and then coated with "Valspar 6256054 GLDEPOXY" according to manufactures specifications and then tested for dry and wet adhesion according to the testing specifications outlined in ASTM D3359 and those outlined by "Mittal Steel USA". There was no loss of adhesion on either panel. Repeating this procedure with the exception of leaving out the silicate, resulted in a loss of adhesion to the matt finish panel.

EXAMPLE 15

[0033] A five percent solution of hydroxyl acetic acid was added to a 0.5% solution of food grade hydrolysable tannic acid and the pH of the mixture was then adjusted to a pH of 8.0 by the addition of potassium hydroxide. To this solution was added 1.0% of the potassium salt of 1,3,4 Benzenetricarboxylic acid and the pH was again adjusted to 8.0. This solution was then used in an electrolytic cell in which two tin plated steel panels were made the anode, one panel had a matt finish while the other was polished steel. A high grade stainless steel panel was used as the cathode. Seven point five volts and a current density of about fifty amps per square foot were passed through the cell for three seconds. The tin plated steel panels were then removed, rinsed in D.I. water, dried and then placed in a 0.6% cysteine solution adjusted to a PH of 7.0 by the use of tri sodium phosphate and boiled for one hour to remove all oxygen in accordance with testing procedures outlined by "Mittal Steel USA". There were no signs of any black iron sulfide formation on either panel after one hour of exposure to this solution. Repeating the above experiment but leaving out the 1,3,4 Benzenetricarboxylic acid resulted in traces of black iron sulfide on the matt finished panel.

EXAMPLE 16

[0034] A five percent solution of hydroxyl acetic acid was added to a 0.5% solution of food grade hydrolysable tannic acid and the pH of the mixture was then adjusted to a pH of 8.0 by the addition of potassium hydroxide. To this solution was added 1.0% of the potassium salt of 1,2,3,4 Benzenetetracarboxylic acid and the pH was again adjusted to 8.0. This solution was then used in an electrolytic cell in which two tin plated steel panels were made the anode, one panel had a matt finish while the other was polished steel. A high grade stainless steel panel was used as the cathode. Seven point five volts and a current density of about fifty amps per square foot were passed through the cell for three seconds. The tin plated steel panels were then removed, rinsed in D.I. water, dried and then placed in a 0.6% cysteine solution adjusted to a PH of 7.0 by the use of tri sodium phosphate and boiled for one hour to remove all oxygen in accordance with testing procedures outlined by "Mittal Steel USA". There were no signs of any black iron sulfide formation on either panel after one hour of exposure to this solution. Repeating the above experiment but leaving out the 1,2,3,4 Benzenetetracarboxylic acid resulted in traces of black iron sulfide on the matt finished panel.

EXAMPLE 17

[0035] A five percent solution of hydroxyl acetic acid was adjusted to a pH of 8.0 by the addition of potassium hydroxide. To this solution was added 1.0% of the potassium salt of 1,3,4 Benzenetricarboxylic acid and the pH was again adjusted to 8.0. This solution was then used in an electrolytic cell in which two tin plated steel panels were made the anode, one panel had a matt finish while the other was polished steel. A high grade stainless steel panel was used as the cathode. Seven point five volts and a current density of about fifty amps per square foot were passed through the cell for three seconds. The tin plated steel panels were then removed, rinsed in D.I. water, dried and then placed in a 0.6% cysteine solution adjusted to a PH of 7.0 by the use of tri sodium phosphate and boiled for one hour to remove all oxygen in accordance with testing procedures outlined by "Mittal Steel USA". There were extensive signs of any black iron sulfide formation on both panels after one hour of exposure to this solution.

EXAMPLE 18

[0036] A five percent solution of hydroxyl acetic acid was added to a 0.5% solution of food grade hydrolysable tannic acid and the pH of the mixture was then adjusted to a pH of 8.0 by the addition of potassium hydroxide. To this solution was added 1.0% of the potassium salt of 1,2,4 Benzenetricarboxylic acid, 0.5% potassium phosphate and 0.5% of a potassium silicate solution and the pH was again adjusted to 8.0. This solution was then used in an electrolytic cell in which three tin plated matt finish steel panels and three polished tin plated steel panels were made the anode. A high grade stainless steel panel was used as the cathode. Seven point five volts and a current density of about fifty amps per square foot were passed through the cell for three seconds. The tin plated steel panels were then removed, rinsed in D.I. water and dried. One polished tin plated steel panel and one matt tin plated steel panel were placed in a 0.6% cysteine solution adjusted to a PH of 7.0 by the use of tri sodium phosphate and boiled for one hour to remove all oxygen in accordance with testing procedures outlined by "Mittal Steel USA". There were no signs of any black iron sulfide formation or tin sulfide formation on either panel after one hour of exposure to this solution. one of the matt finished panels and one of the polished steel panels were coated with "Valspar 6256054 GLDEPOXY" according to manufactures specifications and then tested for dry and wet adhesion according to the testing specifications outlined in ASTM D3359 and those outlined by "Mittal Steel USA". There was no loss of adhesion on either panel. One matt finish panel and one polished steel panel were baked for one half hour at 400 degree F. in accordance with testing procedures outlined by "Mittal Steel USA". Both panels showed no signs of yellow tin oxides or black iron oxides due to this baking procedure.

[0037] While this invention has been illustrated and described in the preceding disclosure, it is recognized that variations and changes may be made therein without departing from the invention as set forth in the claims.

What is claimed is:

1. A tin plated steel passificating composition wherein the essential ingredient consists of a mixture of organic hydroxyl acids and phenol organic acids.

2. The composition of claim **1** wherein the organic hydroxyl acid is selected from C_2-C_6hydroxyl acids.

3. The composition of claim **2** wherein the C_2-C_6hydroxyl acids are selected from the group consisting of hydroxyl acetic acid, D-gluconic acid, citric acid and lactic acid; and the phenol organic acids are selected from the group consisting of hydrolysable tannic acid, gallic acid and dihydroxy benzoic acid.

4. The composition of claim **3** wherein the composition is an electrolyte composition having a pH of 7.0 to 10.0 and preferably a pH of 8.0-9.5.

5. The composition of claim **4** wherein the composition contains less than 4.0 % of a compound or mixture of compounds selected from the group consisting of phosphates, silicates and aromatic acid salts.

6. The composition of claim **5** wherein the phosphate is phosphoric acid or its salt, the silicate is potassium silicate and the aromatic acid is potassium salt of 1,3,4 benzenetricarboxylic acid.

7. A passified tin plated article which has been passified by a composition wherein the essential ingredient of the composition is selected from a mixture consisting of mixture of organic hydroxyl acids and phenol organic acids.

8. The passified tin plated article claim **6** wherein the organic hydroxyl acid is selected from C_2-C_6hydroxyl acids.

9. The passified tin plated article claim **6** wherein the C_2-C_6hydroxyl acids are selected from the group consisting of hydroxyl acetic acid, D-gluconic acid, citric acid and lactic acid;

and the phenol organic acids are selected from the group consisting of hydrolysable tannic acid, gallic acid and dihydroxy benzoic acid.

10. The passified tin plated article claim **7** wherein the composition is an electrolyte composition having a pH of 7.0-10.0 and preferably a pH of 8.0-9.5.

11. The passified tin plated article claim **10** wherein the composition contains less than 4.0 % of a compound or mixture of compounds selected from the group consisting of phosphates, silicates and aromatic acid salts.

12. The passified tin plated article of claim **11** wherein the phosphate is phosphoric acid or its salt, the silicate is potassium silicate and the aromatic acid is potassium salt of 1,3,4 benzenetricarboxylic acid.

13. The passified tin plated steel article of claim **10**, wherein the article has a layer of an appropriate paint to provide a paint protected zinc, zinc plated, or steel article that passes the ASTM-D3359 paint adhesion test.

14. A method of preparing a passified tin plated steel article comprising electrolytically passifating a cleaned tin plated steel article with an electrolyte composition wherein the essential ingredient consists of a mixture of organic hydroxyl acids and phenol organic acids.

15. The method of claim **10** wherein the organic hydroxyl acid is selected from C_2-C_6hydroxyl acids.

16. The method of claim **11** wherein the C_2-C_6 hydroxyl acids are selected from the group consisting of hydroxyl acetic acid, D-gluconic acid, citric acid and lactic acid; and the phenol organic acids are selected from the group consisting of hydrolysable tannic acid, gallic acid and dihydroxy benzoic acid.

17. The method of claim **12** wherein the electrolyte composition having a pH of 7.0-10.0 and preferably a pH of 8.0-9.5.

18. The method of claim **17** wherein the composition contains less than 4.0% of a compound or mixture of compounds selected from the group consisting of phosphates, silicates and aromatic acid salts.

19. The method of claim **18** wherein the phosphate is phosphoric acid or its salt, the silicate is potassium silicate and the aromatic acid is potassium salt of 1,3,4 benzenetricarboxylic acid.

20. The method of claim **17**, comprising the further steps of drying the passified tin plated steel article, and painting the dried article to provide paint protected tin plated steel article that will pass the ASTM-D3359 paint adhesion test.

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