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UNITED STATES PATENT OFFICE

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METAL PROTECTED AGAINST CORROSION AND MODE OF PRODUCING SAME

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5 Claims. (Cl. 117—127)

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The present invention has for its object a composition and process for protecting metal surfaces against corrosion.

It is known that gelatin can be made insoluble by various chemical agents, such as tannin, formal, salts of chromic acid, and so forth. Such substances will hereinafter be termed "tanning agent." This property is used, in particular, for tanning skins, for obtaining anti-mist coatings on glass, and for the manufacture of objects of plastic material.

It has been found, according to the present invention, that gelatin which has been rendered insoluble by an appropriate agent in the form of a coating on metal surfaces, forms an excellent means for protecting metal surfaces against corrosion. It enables smooth, waterproof protecting films to be obtained which, being impervious to liquid water and liquids generally, atmospheric water vapor, carbonic acid an other corrosive agents, constitutes an obstacle to their coming into contact with the metal and hence such coating constitutes an obstacle to the oxidation or the dissolution of said metal.

The formation of a film of this kind, composed of gelatin which has been rendered insoluble by a particular type of tanning agent, can be effected, according to the invention, in any appropriate manner.

It is possible, in particular, to apply to the metal a coating of a solution of gelatin, or any other chemically similar substance, dry the gelatin or equivalent, and then apply a tanning agent to the said layer of gelatin. This method of proceeding has various drawbacks in practice, in particular, the multiplicity of the steps in this operation, the large quantity of water retained by the layer of gelatin thus solidified, and the superficial character of the tanning which may allow a part of the untanned portion of the gelatin, which is therefore soluble and putrescible, to remain in direct contact with the metal, thereby causing corrosion rather than preventing it.

The preferred manner of obtaining a protecting layer according to the present invention, in more practical conditions and which offers greater safety (i. e. greater certainty), consists in using a solution containing both gelatin (or any other chemically similar substance) and the tanning agent, insolubilization taking place without any other addition thereto, owing in particular, either to an action of substances located at the surface of the metal (i. e. a pickling with an accelerating agent, such as an acid), or

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by evaporation of the water contained in the gelatinous layer.

I have referred above to the use of "gelatin or other chemically similar substances." The substances in question, which I use are those which have a chemical composition and chemical properties similar to those of gelatin. According to the literature such substances would include, from a practical standpoint, (*a*) bone gl hide glue or fish glue. On the other hand such so-called glues as (*b*) starch glue or vegetable glue, gluten glue, chitin glue, keratin glue, synthetic resin glue or mineral glue, all have chemical composition and chemical properties very different from those of gelatin. Accordingly, by the term "gelatin" as used in the appended claims, I include herein, bone glue, hide glue, fish glue, but not the others above given.

It has, in fact, been found that the insolubilization of gelatin by tanning agents is a function of three factors: the pH of the solution, the concentration of the geletin or chemically similar substance and the concentration of the tanning agent in the solution. When these three factors are suitably chosen, stable solutions can be obtained which can be kept a very long time without precipitation or insolubilization occurring but which, however, set throughout their mass and produce a plastic substance which is insoluble even in hot water if the pH is lowered. or if the concentration of the solution, with respect to the gelatin or the tanning agent is increased, e. g. by evaporation of water.

The insolubilization of the coatings can be effected, after the mixture containing the gelatin has been applied to the metal, either by a change of concentration of the constituents obtained by natural evaporation at ordinary temperature of a major part or all of the water of the solution applied, or by oven-drying the part, or again by a change of the pH due to the presence of acid ions remaining at the surface of the metal owing to a previous scouring with acid; or again, by the chemical transformation of the tanning agent, causing a modification of the pH; or again by any other means.

It has been found, according to the present invention that good results can be obtained in the preparation of a stable solution of this kind, containing gelatin or the like, by choosing as a tanning agent a compound containing the ions Cr_2O_7— or CrO_4— such as, in particular, a soluble bichromate of zinc or of manganese. In these conditions, using an ordinary commercial gelatin or chemically similar substance as defined above,

the solution remains stable if a pH of about 4 is adopted. On the other hand, certain bichromates such as manganese bichromate, decomposes of their own accord after the solution has been applied, with the formation of MnO_2 and concomitant lowering of the pH and a part of the Cr_2O_7 ions is reduced to Cr_2O_3, thereby ensuring the maximum tanning effect. Furthermore, when these compounds are used as tanning agents, a layer of insolubilized gelatin or glue is obtained which is intimately combined with oxides or salts of chromium which are, as known, excellent "passivating agents" for metals, in particular for iron and magnesium.

The solution of this kind containing gelatin or equivalent can be applied to the metal either by immersion, or with a spray gun, or with a brush, or by any other known means.

A first coating operation can be followed, after complete drying of the coating by a second coating operation (or several of such) the thickness of the coating and its protecting power will thus be increased.

As indicated hereinbefore, the oven-drying of this coating, effected for example in an oven at 100–180° C., enables a quicker and more complete evaporation of the water to be effected and, consequently, an insolubilization of practically all the gelatin or equivalent applied to the metal.

Finally, substances performing an auxiliary function, such as wetting agents like sulforicinic acid (i. e. sulphonated castor oil), plastifying agents like glycerin, and/or colored pigments or dyes, can be added to the solution, if desired.

The four examples given hereinafter show how such solutions containing gelatin can be obtained and used.

Example 1

A solution is prepared from 1.5 kg. of gelatin in 50 litres of water, on the other hand a solution is prepared from 4 kg. of chromic acid in 50 litres of water and in which are dissolved 2.5 kg. of zinc carbonate (pH of this solution=4). Allow both solutions to stand for 24 hours and pour the first solution into the second. The pH of the mixed solution is about 4.25. 24 to 48 hours later the solution thus obtained is filtered to remove any precipitate from the clear solution. Such final solution will contain about 1.5% of gelatin and about 5.3% of zinc bichromate.

The metal to be protected is immersed in this solution and the metal is thereafter dried by exposing it to sunlight or preferably to the light of an electric lamp.

Example 2

A solution is prepared, on the one hand of 1 kg. of gelatin in 50 litres of water, and on the other hand of 3 kg. of chromic acid in 50 litres of water in which 1.95 kg. of manganese carbonate are dissolved and which is filtered after preparation. This solution has a pH about 4.9.

Pour the first solution into the second. This mixed solution will contain about 1% of gelatin and about 4.3% of manganese bichromate.

This mixed solution is applied, e. g. by means of a spray gun to the metal (e. g. iron or steel) surface to be protected.

Allow the coated article to dry in the air. After 4 hours drying, a second coating is applied and the whole is dried in an oven at 130° C. for 10 to 15 minutes.

When the solutions contain gelatin and manganese bichromate, the coats thus obtained are

of dark brown color, which may range to black, are very resistant to corrosion, are insoluble in boiling water, are very resistant to sea water and can be used as a sole protection of the metal against corrosion.

It is possible, however, if desired, to add to this coat a coat of paint which may be air-dried or oven-baked.

Example 3

Prepare, on the one hand, a solution of 2 kg. of gelatin in 50 litres of water; on the other hand, a solution of 8 kg. of chromic acid in 50 litres of water and add 4.4 kg. of zinc carbonate, which will dissolve, and filter the solution.

The pH of this second solution (zinc bichromate) is 2.05.

Pour slowly, while stirring, into the first solution. The pH of the mixture is 3.9. This mixed solution will contain about 2% of gelatin and about 9.4% of zinc bichromate (which later contains, in combined condition, an amount of chromic acid equal to about 8% of the solution).

Dip the metal to be protected into this solution and allow it to dry in the air.

Example 4

Prepare, on the one hand, a solution of 2.1 kg. of gelatin in 50 litres of water; on the other hand a solution in 50 litres of water, of 4 kg. of chromic acid, in which 2.2 kg. of manganese carbonate are dissolved and which is filtered after preparation.

The pH of this second solution is 1.9.

Pour the second solution slowly, while stirring, into the first solution. The pH of the mixture is 4.0. This final solution will contain, in 100 litres of water, 2.1 kgs. (=about 2.1%) of gelatin and about 5.2 kgs. (=about 5.2%) of manganese bichromate.

The solution is applied, e. g. by means of a brush to the surface of the metal to be protected, and allowed to dry in the air.

The concentrations of the solutions as given in the above examples are very satisfactory. But the proportions can be varied somewhat, from those given in the examples, while still giving good results. Thus the amount of gelatin can be between 0.1% and 2.1%, and the amount of the tanning agent can be between 1% and 10% (both based on the entire solution). Preferably the amount of gelatin or equivalent in the solution is between 1% and 2.1% or more e. g. about 2.5%. With this is used a larger percentage of bichromate. The latter component (the bichromate) may contain up to 8% (preferably about 3% to about 8%) of chromic acid in combined form, i. e. as bichromate. The amount of the tanning agent is several times the amount of the gelatin. The mixed solutions (gelatin plus bichromate) should best have a pH above 3 and not above 5.

In the above examples gelatin was used. The gelatin can be substituted by an equal weight (dry basis) of high glue, bone glue or fish glue, with the production of practically as good results. The gelatin can be of any of the commercial grades, it does not have to be highly pure (i. e. it does not have to be edible gelatin).

This application is a continuation-in-part of my copending application Serial No. 636,067, filed Dec. 19, 1945, now abandoned, (corresponding to a patent application filed in France on Dec. 28, 1944).

It will be understood that the gelatin or chem-

ically similar substance can be used (in preparing the solution) in the dry condition or in the form of a solution of any desired concentration, containing the above mentioned amount of gelatin or equivalent. Thus fish glue, which commonly comes on the market as a viscous solution can be conveniently used in that form, and the amount of actual glue in the solution is to be figured as equivalent to that same amount of dry gelatin or dry similar substance. The hereinafter given example shows how such glue can be employed.

Example 5

A solution is prepared from one liter of a 5% fish glue solution and one liter of a solution previously prepared from 100 grs. of CrO_3 and 60 grs. of $MnCO_3$ (that is to say, a manganese bichromate solution). It will be understood that in making this solution, the 100 grs. of CrO_3 unite with water to give 118 grs. of H_2CrO_4 in the solution, which latter then acts on the $MnCO_3$ to produce bichromate of manganese. In the 2 liters of the mixed solution, the 118 grs. of H_2CrO_4 represents approximately 5.8% of H_2CrO_4. The glue represents approximately 2.5% of actual glue in the 2 liters of mixed solution, and the manganese bichromate in said mixed solution is about 6.5%.

The pH of the final solution thus obtained is 4.2. This solution is applied, e. g. by means of a spray gun to the surface to be protected, which surface is allowed to dry in an oven at 110° C. for 10 minutes.

As will be observed from the foregoing formulas, the amount of the specific tanning agent (zinc bichromate or manganese bichromate) is several times greater than the amount of gelatin or glue used.

I am of course aware that coating compositions containing gelatin or glue with bichromate of alkali metal or with chromic acid have been proposed. These bichromates or chromic acid are not the equivalents of the zinc bichromate or manganese bichromate used in the present invention. The prior art compositions do not become so completely insoluble in both hot and cold water, and do not give coatings which are so completely resistant to water and do not so well prevent iron or steel from rusting, under severe service conditions, as do the compositions of the present case.

Besides, such previous compositions are very sensitive to light, and when exposed to light (as occurs when the container is left open) they set throughout their mass and are to be thrown away. On the contrary my compositions would remain stable in such conditions, being only affected, as described, by a substantial increasing of their concentration, or other substantial lowering of their pH.

The invention is applicable in the prevention of corrosion of articles made (wholly or partly) of iron, steel or aluminium.

Throughout the specification and claims, the figures as to gelatin or equivalent are given on the dry basis (i. e. free from water). And the

references to chromic acid are based on H_2CrO_4 (which can be made, if desired, by dissolving CrO_3 in water).

The composition of matter used for coating the metal, namely the solution of a gelatinous material with the specified bichromates, is not claimed herein, but is claimed in my copending application Serial No. 688,336 filed August 3, 1946.

I claim:

1. Process of protecting a metallic surface against corrosion which consists in applying to said surface a coat of a solution which is stable at normal atmospheric temperature and stable when exposed to light, and containing at least about 1% of a gelatinous substance selected from the group consisting of gelatin, bone glue, hide glue and fish glue, and containing a substantially greater amount of a tanning agent which is a soluble bichromate of a metal selected from the group consisting of zinc and manganese, and has a substantially acid pH, which is not below 3, and producing on said surface an irreversible insolubilization of said gelatinous material by drying said solution on said surface, while being exposed to light.

2. A process as claimed in claim 1, in which the pH of the solution of the said gelatinous material and bichromate is between 3 and 5.

3. A process as claimed in claim 1, in which the coated article is baked at a temperature above 100° C.

4. A process as in claim 1, in which the amount of said gelatinous material in the coating solution is between 1% and 2.5% and the amount of combined chromic acid in said bichromate is between 3% and 8%, said percentages being based on the whole solution.

5. A metal article composed of a metal which is, in the unprotected condition, subject to corrosion by the continued exposure to both air and moisture, such metal article carrying a wholly dried protective coating, which coating is resistant to the action of both cold water and boiling water, and produced according to the process of claim 1.

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Certificate of Correction

Patent No. 2,505,734 April 25, 1950

HERBERT MANFRED FREUD, also known as JEAN FRASCH

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 2, line 9, for the indistinct word after "bone" read *glue*; line 52, for "Cr_2O_7—or CrO_4—" read $Cr_2O_7^{--}$ *or* CrO_4^{--}; column 4, line 65, for "high" read *hide*; and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of November, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.