

UNITED STATES PATENT OFFICE

2,162,618

COATING METAL

Emmette F. Izard, Kenmore, N. Y., assignor to
E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

No Drawing. Application August 25, 1936.
Serial No. 97,795

7 Claims. (Cl. 91—68)

This invention relates to the coating of metals and, more particularly, to the provision on metal surfaces of coating films of such a character as to provide adequate protection of the metal surface against tarnishing or corrosion and at the same time as to be capable of being readily removed from the surface when desired.

It is well known that most metals such as silver, brass, copper, iron, steel, etc., tend to corrode or tarnish when exposed to atmospheric conditions. It has been proposed heretofore to protect the surfaces of metals, especially such metals as silver, copper and brass, with lacquer coatings and this expedient has been adopted to some extent in the art. The lacquers usually employed for this purpose are cellulose derivative lacquers, which in general provide a fairly good protection for metal surfaces during storage and shipment of the articles thus coated. However, most of these lacquers are somewhat brittle in nature and have a tendency to flake off in places thereby resulting in darkening or tarnishing of the unprotected portions. A further disadvantage of lacquers of this type is the fact that the ultimate purchaser of the coated article usually finds it very difficult to remove the lacquered film before using the article inasmuch as cellulose derivative lacquers are soluble only in certain special types of organic solvents.

In the case of iron and steel articles, particularly articles of the nature of cutlery, surgical and scientific instruments, razor blades, and the like, the usual practice is to apply a coating of an oil or grease to the surface of the article to prevent rusting during the period intervening between the manufacture of the article and its ultimate use. Such coatings can, of course, be readily removed when desired but they are unsightly and tend to rub off and soil any articles which come in contact with them.

It is an object of the present invention to provide a new and improved type of protective coating for metal articles; a further object is to provide coatings on metal articles characterized by a high degree of flexibility and elasticity; a further object is to provide coatings of the aforesaid type which are readily removable by solution in water. Other objects and advantages of the invention will be apparent from the ensuing description thereof.

The above objects are attained in accordance with the invention by providing metal articles with a continuous protective film comprising polyvinyl alcohol either alone or in combination with wetting agents and/or insolubilizing agents,

and/or plasticizers as will be described more particularly hereinafter.

Polyvinyl alcohol is a water soluble, resin-like material which is usually obtained by the hydrolysis of polymerized vinyl esters such as polyvinyl acetate. Polyvinyl alcohol can be made in a number of modifications of different degrees of polymerization, the degree of polymerization depending largely upon the extent to which the vinyl compound from which it is derived has been polymerized. All of these modifications of polyvinyl alcohol are, to some extent, soluble in water. The more highly polymerized forms are less soluble and produce solutions of higher viscosities for equivalent concentrations than the lower polymers. There are also a large number of the so-called partial derivatives of polyvinyl alcohol in which some of the hydroxyl groups in the molecule are replaced by other radicals such as ester radicals or acetal radicals. Such partial derivatives may be produced by the incomplete saponification of vinyl esters or by the incomplete reaction of polyvinyl alcohol with aldehydes or other compounds which react with hydroxyl groups. As would be expected, the properties of the partial derivatives of polyvinyl alcohol vary in accordance with the proportion of hydroxyl radicals that have been substituted by other groups. When the hydroxyl radicals sufficiently predominate the partial derivatives show essentially the properties of polyvinyl alcohol and, like polyvinyl alcohol itself, are soluble in water as distinguished from the esters, acetals, etc. which are soluble only in organic solvents. Consequently, the term "polyvinyl alcohol" is used herein and in the appended claims to designate generically pure polyvinyl alcohol and also such partial derivatives thereof as contain a sufficient number of unsubstituted hydroxyl groups as to render the compound soluble in water.

In spite of the fact that polyvinyl alcohol is soluble in water, I have made the surprising discovery that films of polyvinyl alcohol adequately protect metal surfaces against the action of moisture, atmospheric oxidation or corrosive gases such as hydrogen sulfide.

In coating metal in accordance with the invention, a suitable solution of polyvinyl alcohol is applied to the surface of the article and the solvent evaporated therefrom to produce a thin continuous film of polyvinyl alcohol surrounding the article. The concentration of polyvinyl alcohol in the solution used for the coating may vary within considerable limits, depending largely on the degree of polymerization of the particular

form of polyvinyl alcohol used. In general, solutions ranging in concentration of about 2% to 20% by weight may be used. I have found that a 10% aqueous solution of a relatively highly polymerized form of polyvinyl alcohol gives excellent results. In some instances it is advantageous to heat the solution to above room temperature in order to decrease its viscosity and to facilitate the removal of any entrained air bubbles which would give rise to the formation of imperfections in the resultant coating. The coating operation may be carried out by immersing the metal articles in a solution of polyvinyl alcohol at a temperature of about 50 to 80° C. However, satisfactory coatings may be obtained at higher or lower temperatures and the solution may also be applied in other ways, as for example, by spraying or by brush application.

The articles coated with polyvinyl alcohol solution may be dried either at ordinary or at elevated temperatures. I prefer, however, to effect the drying by heating in air at a temperature of about 50° C. to 80° C. Within this temperature range, drying is much more rapid than at atmospheric temperature and the films produced are usually more uniform and of a better quality.

In order to insure the production of completely uniform and continuous coatings, I have found it advantageous to incorporate in the polyvinyl alcohol solution an agent for reducing its surface tension, whereby a thorough and uniform wetting of the metal surface is effected. Such agents also have the advantage of decreasing the tendency for air bubbles to adhere to the metal surface. Any of the common water-soluble wetting and surface tension reducing agents known to the art which do not have a corrosive action on the metal being treated, may be used for this purpose. I have found it particularly advantageous to use the class of wetting agents comprising sulfonation products of the higher aliphatic alcohols. Compositions of this type are sold commercially under a number of proprietary trade names such as "Gardinol", "Arctic Syntex", "Igepon", "Hydralene" and others. A composition of this general type which I have found to be especially suitable for use in conjunction with polyvinyl alcohol solutions is the product sold by E. I. du Pont de Nemours & Co. under the trade name "Brilliant Aviroi". The addition of approximately 0.05% of this material to the polyvinyl alcohol solution used for coating gives excellent coverage on practically all metals.

In case that it is desired to make the coating film less sensitive to water, this can be accomplished by the use of agents which tend to coagulate or to insolubilize polyvinyl alcohol. Examples of materials which are suitable for this purpose are various inorganic compounds such as borates, perborates, silicates, chromic acid, chromates, dichromates, alum and ferric chloride; and organic hardening agents such as tannins, formaldehyde, and other aldehydes, azo dyes such as Congo red and the like. The insolubilizing agents may be applied to the metal article prior to the application of the polyvinyl alcohol coating, or the coated articles may be given a final treatment with the insolubilizing agent, or both. In some cases it is also possible to include an insolubilizing agent in the polyvinyl alcohol solution itself, although this is usually not so desirable for the reason that these materials tend to increase the viscosity of the polyvinyl alcohol solutions and to render the ap-

plication thereof somewhat more difficult. The insolubilizing treatment may be so adjusted as to impart any desired degree of water resistance to the polyvinyl alcohol film. Thus the film may be rendered sufficiently water resistant that it will not soften appreciably under conditions of extreme humidity and yet may be readily removed by solution in hot water.

If desired, the normal flexibility of the polyvinyl alcohol films may be increased by incorporating in the polyvinyl alcohol solution a suitable softening agent or plasticizer. Among the plasticizers which are suitable for this purpose, may be mentioned polyhydroxy compounds such as glycerol, polyglycerols, glycols, polyglycols, starches, sugars, gum tragacanth, gelatine; amides such as formamide and urea; and metal sulfocyanides. However, the polyvinyl alcohol film itself is very elastic and flexible and ordinarily the use of softening agents is not necessary in order to secure excellent results.

If desired, various decorative effects may be produced by incorporating in the coating composition coloring materials such as pigments or dyes. Any water-soluble dyes which are compatible with polyvinyl alcohol solutions may be used for this purpose.

The invention may be further illustrated by the following examples of specific procedures employed in coating various metals.

Example I

Two pieces of plated silverware were thoroughly cleaned and polished and one of them immersed in an aqueous solution containing 10% by weight of polyvinyl alcohol and 1% by weight of glycerol. The coated piece of silverware was dried in a slow current of air heated to a temperature of 60 to 70° C.

A lump of iron sulfide was placed in a large graduated cylinder and covered with dilute sulfuric acid to generate hydrogen sulfide. The two pieces of silverware were suspended in the cylinder and a watch glass placed over the top, thus producing a high concentration of hydrogen sulfide within the cylinder. At the end of two hours the uncoated piece of silverware was very highly tarnished while the coated piece was perfectly clean and bright. At the end of five hours the uncoated piece was completely covered with a black sulfide coating and was removed from the test jar. The piece coated with polyvinyl alcohol was allowed to remain in the test jar for a period of 72 hours, after which it was found to be entirely unaffected by the treatment with hydrogen sulfide, except for a few pin points of tarnish which were apparently due to small holes in the original coating.

Example II

A silver spoon was coated in accordance with the procedure described in Example I with the exception that the coating solution used consisted of 10% by weight of a relatively highly polymerized form of polyvinyl alcohol and 0.05% of "Brilliant Aviroi" dissolved in water.

After being subjected to the action of hydrogen sulfide as in Example I, the spoon coated with polyvinyl alcohol retained its initial polish and brilliance and was entirely free from any pin points of tarnish. Evidently due to the presence of the "Brilliant Aviroi" in the coating solution, perfect coverage of the metal surface was obtained, thus avoiding the formation of any microscopic holes in the coating such as were evidently

responsible for the slight pin points of tarnish produced in the test of Example I.

Example III

5 Silver spoons were coated as in Example II with the exception that, before application of the polyvinyl alcohol-"Brilliant Avicol" solution, the spoons were first immersed in a 1% aqueous solution of borax. The resultant coating showed
10 the same resistance to the action of hydrogen sulfide as the coating of the previous example; in addition, it exhibited less tendency to soften under conditions of extreme humidity but could still be dissolved readily by the application of
15 hot water.

Example IV

Silver spoons were coated with polyvinyl alcohol as in Example II; the coated spoons were then immersed in a 1% borax solution and dried.
20 The resultant film was similar to that obtained in Example III and showed a similar degree of resistance to extreme humidities.

Example V

25 Several lengths of steel strips were carefully cleaned free from scale and rust, and polished. Each of the strips was coated over a part of its area, utilizing the same solution and the same procedure as in Example II.

30 The strips were then exposed to the atmosphere in a chemical laboratory for a period of three weeks. Finger stains were noticed on the uncoated portions of the strips within four days. In one week rust spots had appeared on the uncoated portions and in three weeks the uncoated
35 portions were substantially completely covered with rust. The coated parts retained their original lustre with no traces of finger stains or rust spots.

40 Articles of copper, brass, zinc and other metals coated and tested in the same manner as described in the above examples, were similarly protected from tarnishing and corrosion by films of polyvinyl alcohol.

45 Polyvinyl alcohol films produced in accordance with the invention are characterized by a high degree of elasticity and flexibility. They adhere well to metal surfaces and have practically no tendency to flake or chip off on handling. They
50 are normally colorless and transparent and lustrous, and thus provide an attractive finish for polished metal surfaces. They can, however, be made opaque and/or be colored to any desired hue by the use of suitable pigments and/or dyes.
55 They provide excellent protection of metal surfaces against tarnishing, rusting and corrosion. By appropriate treatment with insolubilizing agents, the films may be rendered resistant to highly humid atmospheres and yet retain the im-
60 portant advantage of being readily removable by solution in hot water.

The coating of metal articles in accordance with the invention is particularly advantageous for such purposes as coating of silverware, copper cooking utensils, hardware, cutlery, surgical

and scientific instruments, razor blades and the like, where it is desired to provide adequate protection against tarnishing, corrosion or rust and at the same time to be able to remove the coating merely by the application of warm water without the use of special solvents. The coatings of the invention also may be used to advantage for lining the interiors of metal containers, especially containers for materials which are corrosive to metals but which are non-solvents for polyvinyl alcohol.

It is to be understood that the invention is not limited to the specific embodiments thereof described herein above, but includes all such modifications, variations and equivalents as fall in the scope of the appended claims.

I claim:

1. The method of coating a metal article which comprises applying to the surface thereof a solution of water soluble polyvinyl alcohol and drying the coated article to form a surrounding film of polyvinyl alcohol which is readily removable by solution in water.

2. The method of coating a metal article which comprises applying to the surface thereof an aqueous solution of polyvinyl alcohol and drying the coated article to form a surrounding film of polyvinyl alcohol which is readily removable by solution in water.

3. The method of coating a metal article which comprises treating the surface thereof with a coagulant for polyvinyl alcohol, applying to said treated surface a solution of water soluble polyvinyl alcohol, and drying the article to form a surrounding film of polyvinyl alcohol which is readily removable by solution in water.

4. The method of coating a metal article which comprises treating the surface thereof with a borax solution, applying to said treated surface a solution of polyvinyl alcohol and drying the article to form a surrounding film of polyvinyl alcohol which is readily removable by solution in water.

5. The method of coating a metal article which comprises applying to the surface thereof an aqueous solution of polyvinyl alcohol containing an agent for reducing the surface tension thereof, and drying the coated article to form a surrounding film of polyvinyl alcohol which is readily removable by solution in water.

6. The method of coating a metal article which comprises applying to the surface thereof an aqueous solution of polyvinyl alcohol containing a small amount of a wetting agent comprising a sulfonated derivative of a higher alcohol, and drying the coated article to form a surrounding film of polyvinyl alcohol which is readily removable by solution in water.

7. A metal article coated with a film of water soluble polyvinyl alcohol, said film being readily removable by solution in water and being adapted to protect the surface of the metal from corrosion and tarnishing.

EMMETTE F. IZARD.