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ZINC PLATING

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This invention relates to the electrodeposition of zinc from a cyanide solution and more particularly to the production of bright zinc electrodeposits.

Many steel articles are commonly electroplated with zinc, not only to provide rust protection but also to provide a pleasing appearance to various hardware articles such as small tools, machine parts, bolts, screws, and the like. For such purposes it is generally desirable to produce a bright, white electrodeposit and bright deposits having a blue cast are most generally desired.

The electrolysis of a zinc cyanide solution tends to produce a somewhat dull electrodeposit and the desired brightness is generally obtained by the addition of a small amount of a brightening agent. One such brightening agent which has been utilized is polyvinyl alcohol. Heretofore the difficulty with this addition agent has been that the bright electrodeposits thereby produced have a yellowish film giving the bright plated articles a yellowish cast instead of the desired blue-white bright finish. The yellowish color can be removed by treating the electroplated parts with a dilute nitric acid solution followed by washing; but such additional step in the process adds to the expense and it is desirable to utilize a brightening agent in the plating bath which directly produces the desired blue-white finish. Certain aromatic aldehyde zinc brightening agents can be used to produce the desired result but these are relatively expensive as compared with polyvinyl alcohol.

An object of the present invention is to provide an improved zinc electroplating brightening agent which is relatively inexpensive and which will produce a bright zinc electrodeposit free from yellow color. The invention includes the novel brightening agent which is believed to be a new chemical substance. Other objects of the invention will be apparent from the following description.

I have discovered that by sufficiently oxidizing an aqueous solution of polyvinyl alcohol with hydrogen peroxide or equivalent oxidizing agent, a solution is produced which contains an organic peroxide. The nature of the organic peroxide is not fully understood but since apparently peroxide groups enter at least part of the polyvinyl alcohol molecules present I have termed it "polyvinyl alcohol peroxide." I have found that the addition of a small amount of this oxidized polyvinyl alcohol solution to a conventional zinc cyanide electroplating solution causes the electrodeposition of brilliant bright bluish zinc with no trace of yellow color.

I have further discovered that the addition of a small amount (e.g. 0.1 to 1 g./l.) of potassium permanganate (or sodium permanganate or other water soluble permanganate) to the electroplating bath, preferably followed by filtration, further enhances the brightening effect of the oxidized polyvinyl alcohol.

In order to obtain the above indicated result I have found that in oxidizing the polyvinyl alcohol, the latter must be contacted with at least about 8.5% of its weight of hydrogen peroxide. If a smaller proportion of peroxide is used the resulting bright zinc electrodeposit generally will have the yellowish color characteristic of that produced by using untreated polyvinyl alcohol. The proportion of hydrogen peroxide in the oxidation process can be stated in another way, in terms of 35% hydrogen peroxide solution, which is a staple article of commerce. The weight ratio of 35% hydrogen peroxide to the polyvinyl alcohol being oxidized should be not less than about 0.25 to 1. A larger ratio may be used, as desired, such as around 1 to 1 or higher; but generally there is no advantage in exceeding a 1 to 1 ratio.

The new addition agent may also be defined in terms of the extent of oxidation achieved by the treatment of the polyvinyl alcohol, that is, by measuring the organic peroxide content of the polyvinyl alcohol solution. An organic peroxide content equivalent to at least about 2.0% by weight of H_2O_2 based on the dry weight of the polyvinyl alcohol is required.

While hydrogen peroxide is the preferred oxidizing agent because of its relative cheapness, availability and absence of chemical elements other than hydrogen and oxygen, other oxidizing agents can be used to produce the same result. Examples of such are first the other peroxygen compounds such as organic and inorganic peracids and their salts and metallic peroxides such as sodium peroxide or barium peroxide and other strong oxidizing agents, for example, potassium permanganate.

In oxidizing the polyvinyl alcohol, the concentration of the hydrogen peroxide or other oxidizing agent is of importance only to obtain the required degree of oxidation within a reasonable period of time. I generally prefer to have an initial peroxide concentration in the reaction mixture equivalent to at least 0.9% by weight of H_2O_2 and, if desired, this may be as high as 2 or 3%. Still higher concentrations can be used but generally are not desirable. The time required to oxidize the polyvinyl alcohol may be shortened if desired by heating the solution for a time from a few minutes to several hours at temperatures, e.g., of from 40 to 90° C. but if a sufficiently high concentration (for example, around 1% of peroxide) is utilized, heating is usually unnecessary. The reaction also can be accelerated by adding a small amount of acid, either organic or inorganic, to the reaction mixture sufficient to reduce the pH to a value of say 2–4. I generally prefer to oxidize under acidic conditions.

The concentration of organic peroxide in the polyvinyl alcohol solution at the completion of the oxidation treatment should be not less than that equivalent to about 2% by weight of H_2O_2 based on the dry weight of the polyvinyl alcohol present, as determined by the standard permanganate titration procedure for determination of peroxide. The peroxide content (on the above basis) may be made as high as around 40%; the preferred concentration is within the range of 10 to 30%. Some decomposition of the organic peroxide generally tends to occur on standing but this can be inhibited by adding a stabilizer. Stabilizers which are generally useful for stabilizing hydrogen peroxide are effective. For example, I have obtained good results by using phosphates or stannates in the conventional stabilizing quantities. If no stabilizer is utilized, it is preferable to initially produce a higher peroxide content than that required so that on standing the resulting lowered peroxide content will be at least 5% by weight. I have found that on standing for periods of 100–200 days the rate of decomposition of an unstabilized solution of polyvinyl alcohol peroxide becomes very low.

The concentrations of the polyvinyl alcohol in the aqueous solution during the oxidation reaction may be varied over a wide range from the limit of its solubility down to dilute solutions of the order of around 1% by weight concentration. A preferred range of polyvinyl alcohol concentration during oxidation is about 5% to

10% by weight. After oxidation, the resulting solution of polyvinyl alcohol peroxide may be diluted (or not), as desired, to make the solution to be employed as addition agent.

The amount of the addition agent to be added to the zinc plating bath will vary widely, depending on the composition of the plating bath, the plating conditions and the brightening effect desired. In most cases, the maximum brightening effect will be obtained with an amount equivalent to about 0.1 to 5 grams of polyvinyl alcohol per liter of plating bath.

Polyvinyl alcohol is made by hydrolysis (or alcoholysis) of polyvinyl acetate; and the different grades of polyvinyl alcohol will contain varying amounts of unhydrolyzed acetate groups. Where 90% or more of the acetate groups have been hydrolyzed to hydroxyl, the resulting polyvinyl is generally termed a "completely hydrolyzed" grade; if less, it is denoted as "partially hydrolyzed." For the purpose of the present invention, either the completely hydrolyzed grades or partially hydrolyzed grades which are water soluble are suitable. I generally prefer to use the completely hydrolyzed grades.

In common with conventional zinc plating processes, the best results are obtained in the present invention when the plating bath is free from impurities, particularly heavy metal compounds such as lead compounds. The conventional purification treatment, the addition of a small amount of a sulfide, followed by filtration is useful in practicing this invention. In addition, I have discovered that a greater degree of purification, and enhanced brightening effect is obtained by adding to the plating bath a small amount of a soluble permanganate. Potassium or sodium permanganates are preferred for this purpose; but any soluble permanganate which will not introduce objectionable impurities may be employed. Amounts equivalent to about 0.1 to 1 g./l. are suitable. The permanganate may be used in conjunction with sulfide treatment, if desired; and preferably the bath is filtered after adding the permanganate.

The following examples illustrate the invention.

Example 1

An aqueous solution of a low viscosity, completely hydrolyzed grade of polyvinyl alcohol was made containing 400 grams of the polyvinyl alcohol in 3000 cc. of water. To this was added 100 grams of 35% hydrogen peroxide solution and the mixture was heated for 6 hours at 85–90° C. The solution was cooled and diluted with water to 4000 cc. (each cc. contained 0.1 g. of oxidized polyvinyl alcohol). Analysis showed that the solution contained organic peroxide equivalent to 0.5 gram per liter H_2O_2.

A zinc cyanide plating bath was made according to the formula:

	G./l.
Zinc cyanide	60
Sodium cyanide	45
Sodium hydroxide	75
Sodium sulfide ($Na_2S \cdot 9H_2O$)	0.5
Potassium permanganate	0.5

The bath was filtered to remove impurities precipitated by the sodium sulfide and permanganate.

With the addition of 2 cc./l. of the above-described peroxide treated polyvinyl alcohol solution, the plating bath was used in conventional barrel plating equipment to electroplate steel screws and bolts, under the following conditions.

Current, 7.5 amperes
Bath temperature, 25–28° C.
Anodes, high purity (99.99%) zinc
Speed of barrel rotation, 2 r.p.m.
Plating time, 30–60 minutes

The resulting zinc electrodeposits were brilliant and bluish in color.

For comparison the same process, but without addition of the oxidized polyvinyl alcohol solution, yielded a dull gray electrodeposit.

Example 2

Example 1 was repeated, except that the oxidized polyvinyl alcohol solution was made by reacting 200 grams of polyvinyl alcohol dissolved in 1500 grams of water with 30 grams of 35% hydrogen peroxide, followed by dilution to 2000 cc.; and adding 4 cc./l. of the solution to the plating bath. The electrodeposits in this case were bright but had a distinct yellowish film. This example illustrates the use of an insufficient quantity of hydrogen peroxide in oxidizing the polyvinyl alcohol.

Example 3

A series of solutions of oxidized polyvinyl alcohol were made as in Example 1 but using different proportions of hydrogen peroxide, as shown in the table below. The addition of these solutions (in the amounts indicated in the table) in the plating process of Example 1 produced bright bluish zinc electrodeposits.

Oxidized Polyvinyl Alcohol Solutions	Weight Ratio 35% H_2O_2 to Polyvinyl Alcohol	Organic Peroxide Content (H_2O_2 Equiv.), g./l.	Amount Added to Plating Bath, cc.
A	0.4		2
B	0.5		1.25
C	1.0		1
D	1.0		2
E	1.0	1.8	1.25

NOTE.—In preparing solutions B, D and E, the solutions were acidified before reacting with peroxide; in B and D by adding 0.04 cc. of glacial acetic acid per gram of polyvinyl alcohol and in E 0.05 gram of 66° Bé. sulfuric acid per gram of polyvinyl alcohol. Also in the preparation of B, D and E the heating time was 40 to 60 minutes, while in A and C the solutions were heated 5 to 6 hours.

Example 4

The procedure of Example 1 was repeated, except that permanganate was not used in purifying the electroplating bath. The resulting electrodeposits were bright and free of yellow film, but slightly darker than the bright plate of Example 1.

Example 5

Example 4 was repeated, except that solution A of Example 3 was used as the plating addition agents. The result was the same as in Example 4.

Example 6

An aqueous solution of a low viscosity, completely hydrolyzed grade of polyvinyl alcohol was made containing 10 g. of the polyvinyl alcohol in 100 cc. of water. This solution was now acidified by the addition of 4 g. of glacial acetic acid. To the resulting solution there was now added 30 cc. of a hot 10% solution of potassium permanganate with stirring. The solution turned black and heated itself to a temperature of 54° C. No precipitation of manganese hydrate occurred even after standing for several days.

An addition of 26 cc. of the above oxidized polyvinyl solution which contained 2 g. of the polyvinyl alcohol was now made to an 8-liter zinc cyanide barrel plating solution prepared and operated as disclosed under Example 1. The zinc electrodeposits now produced were brilliant and had a bluish color.

Example 7

In this run 50 cc. of a 10% aqueous solution of poly-

vinyl alcohol was mixed with 10 cc. of a 20% sodium hydroxide solution. This was now oxidized by the addition of 30 cc. of a hot 10% potassium permanganate solution with stirring. The solution turned black and jellied but became fluid again after about 5 minutes. A small amount of a black precipitate was filtered off.

The addition of 2 g. of the oxidized polyvinyl alcohol to an 8-liter zinc cyanide solution prepared and operated as in Example 1 yielded brilliant, bluish colored zinc coatings.

Example 8

A 100 cc. batch of a 10% polyvinyl alcohol solution was acidified with 4 cc. of glacial acetic acid. To this there was now added 10 cc. of 35% hydrogen peroxide with stirring. The resulting solution was now heated in a hot water bath to 85° C. for 40 minutes and then cooled. It had a pH of 3.75 and contained organic peroxides equivalent to 34.5 g./l. of hydrogen peroxide, equal to 34.5% of the dry weight of the polyvinyl alcohol.

A zinc plating test in a 8-liter barrel zinc cyanide plating solution prepared as in Example 1 and treated with 10 cc. of the above oxidized polyvinyl alcohol solution was now made. The resulting zinc deposits duplicated the brilliance and bluish color secured in Example 1.

I claim:

1. The reaction product of the substantially complete reaction of polyvinyl alcohol and a peroxygen compound wherein the amount of said peroxygen compound in the reaction mixture is sufficient to supply a quantity of peroxygen at least equal to that supplied by 8.5% by weight H_2O_2 based on the weight of polyvinyl alcohol present in said reaction mixture.

2. The reaction product of the substantially complete reaction of polyvinyl alcohol and H_2O_2 wherein the amount of said H_2O_2 is at least 8.5% by weight of the polyvinyl alcohol present in the reaction mixture.

3. The process of preparing a zinc brightening agent comprising reacting in a dilute aqueous solution, at least 1% by weight of polyvinyl alcohol, and an amount of H_2O_2 at least equal to 8.5% by weight of the polyvinyl alcohol present in the reaction mixture, said reaction being carried out for a time sufficient to permit the substantially complete reaction of said alcohol and said H_2O_2.

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