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ELECTROCHEMISTRY

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This invention relates to electrochemistry and more particularly to the deposition of metals and to a novel electrolyte.

The principal object of the invention is to provide an electrolytic bath having new and improved properties adapting it for use as an electrolyte in the plating of metals, and to provide a simple and inexpensive method of making the bath.

It is a further object to provide a process by means of which alloys of two or more metals can be successfully plated; it is also an object to provide novel coatings either of single metals or of alloys.

It is a further object to provide a method of treating metal surfaces to remove constituents therefrom to provide predetermined surface characteristics; and it is likewise an object to provide articles which have been subjected to such treatment.

Further objects and advantages will be apparent from the description and the appended claims.

In the process of electroplating, as generally practiced, a plating bath is provided in which is dissolved a suitable salt of the metal to be plated. An anode and a cathode are positioned in the bath and an electric current is passed through the bath to cause a deposition of the cation, usually a metallic ion, from the bath upon the base material which is usually connected to the cathode.

The present invention relates to such a process but involves the use of a novel electrolyte having very desirable properties by means of which entirely new platings can be obtained. Through the use of this electrolyte there is a great increase in the degree of ionization of the bath. Its resistance is materially decreased and likewise the separation potential of the metallic ions therein is reduced, both of these factors contributing to permit a lower plating voltage and consequently to decrease the power consumption. A bath formed according to the invention has much greater throwing power than ordinary baths so that an article having pockets, corners, and recesses can be successfully plated. Moreover the coatings are not brittle, loosely adhering, and flaky but on the contrary the deposits obtained according to the invention are so attached to the base metal that they are deformable with the base metal with no distinct line of cleavage occurring and the two metals acting as if intermolecularly bonded together at their adjacent faces. As a further important advantage the

invention provides for the successful plating of alloys of two or more metals in any desired proportions. A further advantage of the present electrolyte lies in the fact that it can be used with any desired degree of acidity from highly acid to highly alkaline and it is now possible to plate many metals from acid baths where previously it had always been considered necessary to have an alkaline bath; and similarly other metals which have always required an acid bath can now be plated from an alkaline bath. As a result entirely novel coatings not known heretofore are obtained and the coatings of known materials are greatly improved in physical and chemical properties. Good surface coatings may be obtained in certain cases by merely dipping the article in the bath without the use of any external current.

Through the use of the invention it becomes possible to remove certain surface constituents and to produce predetermined surface characteristics with respect to metals. For example the surface of a metal may be prepared to receive a coating either of a metallic or a non-metallic material, the treatment including the removal of matter detrimental to either the reception of the coating or its retention, all such matter being referred to as an impurity. Following the treatment the metal is in a highly receptive condition and its surface has been freed of the non-metallic film so that a close bond can be obtained.

The material which is utilized for producing the electrolyte which makes possible the practicing of the present invention has been heretofore produced as a waste product in the paper making industry. The woody or fibrous material used in that industry consists of cellulose fibers and of non-cellulosic material—such as lignins. In making the better grades of paper all of the non-cellulosic and some of the cellulosic material is removed during digestion. In some of the other grades of paper, paperboard, etc. only part of the non-cellulosic material is removed. For example, in the more complete cooks used in the paper industry, such as the so-called "sulfit" cook which utilizes calcium sulfite as the digestion material, a substantial portion of the cellulose is removed in the waste liquor along with the non-cellulosic portion. In so-called "semi-chemical" pulping processes the cooking is so carried on that only a part of the non-cellulosic material is removed, the fibrous material being softened, and then converted into pulp by a mechanical treatment. In such cooking processes the digestion liquor comprises an alkali

metal sulfite and sodium bicarbonate in a substantially neutral cook. The waste digestion liquor contains the removed non-cellulosic materials but practically none of the cellulosic portion is present.

It has been found that the presence of cellulose is objectionable in connection with the electrolyte according to the present invention; but if an objectionable proportion of cellulose is present, the digestion liquor may be treated to remove it or to reduce the quantity thereof to an objectionable or negligible amount. This may be done in one of the known manners. The spent digestion liquor resulting from the mild or semi-chemical cook or a similar cook in which the spent liquor does not contain an objectionable amount of cellulose is directly usable without preliminary refining.

For some plating results the liquor for use as the plating bath, in which the metallic salts are to be dissolved, is subjected to additional processing. Satisfactory commercial results, in this respect, are secured from subjecting the waste digestion liquor with its non-cellulosic, or lignin-containing, materials to the action of an oxidizing agent. A satisfactory method of preparation consists in mixing a small quantity of hydrogen peroxide with the liquor. With spent digestion liquor from the semi-chemical cook $\frac{1}{2}$ to 1% of 30% hydrogen peroxide, based on the weight of the liquor, will ordinarily be sufficient to produce the desired effect. A greater quantity of hydrogen peroxide will speed up the reaction, but with decrease in economy, as with larger amounts of hydrogen peroxide more oxygen is lost by bubbling up through the solution. It has also been found, in practice, that there should be a catalyst present for this reaction to be carried to the desired degree of completion. Such catalyst may be a small amount of iron, chromium or osmium, or other metal or metal salt, iron being preferred because of its cheapness. When this type of liquor is used ordinarily there will be present sufficient iron salt as an impurity in the liquor to function as a catalyst without additional catalyst being added.

Instead of using a metal as a catalyst it is also possible to carry the reaction of the organic material with the oxygen bearing material, such as the hydrogen peroxide mentioned, to the desired degree of completion by carrying on the oxidation in the presence of such an enzyme as peroxidase which belongs to the class known as desmolases, and which has the power of oxidizing or transferring oxygen and therefore transfers the oxygen from the hydrogen peroxide to the organic material. A method of preparing peroxidase in commercial quantities has been disclosed in applicant's copending case Serial No. 349,010 filed March 21, 1929, being commercially unavailable theretofore. Where using peroxidase as produced in that application, approximately one gram of extract per kg. of liquor will suffice to produce the desired reaction.

Supplementing the action of the hydrogen peroxide, the liquor is subjected either simultaneously or following the treatment with hydrogen peroxide to the action of a halogen such for instance as chlorine. This treatment may be effected by bubbling chlorine gas through the mass until such time as the acidity of the mixture requires 40 to 45 grams of sodium hydroxide per liter to neutralize. This may be determined by titration but it has been found in actual operations that it takes approximately 3% by weight

of chlorine based on the weight of the spent liquor to arrive at this acidity. The liquor is next subjected to a purifying treatment in which it is first heated sufficiently to coagulate the precipitate that is formed and is then filtered in the ordinary manner thus removing certain impurities including stray cellulosic matter. The bath is then ready to receive the metallic salts which may be immediately dissolved therein. In some cases it has been found that a sufficiently complete reaction or oxidation of the lignin-containing matter is obtained with chlorine alone, though in a longer period of time.

The liquor may be conveniently concentrated or even evaporated to dryness to facilitate storage or shipping and it is found that its desirable properties are not destroyed. The requisite amount of water is added to restore the material to its original condition when desired.

An important characteristic of the liquor is that its pH value or the concentration of the hydrogen ion may be varied to suit any conditions. It has been found that certain metals plate better in highly acid baths while with others the reverse is the case. The liquor can be made to have a wide range of pH values by adding a suitable acid or base, such as sulphuric acid or sodium hydroxide in the desired amount. The liquor can thus be used in regular commercial operations in both acid and alkaline plating baths and over a much wider range than is possible with other known electrolytes. It is possible to neutralize the liquor and to keep it in this condition until ready for use, or to ship it, and then adjust its pH value to suit the conditions of the particular plating operation.

If it is found that the halogen compounds are detrimental in working with certain metals these compounds may be removed or rendered inactive in any known manner.

Instead of the above described treatment it has been found that similar results can be obtained through the action of an electric current passing through the liquor. It is believed that an oxidation takes place at the anode through the action of nascent oxygen which is liberated there. This treatment by electrolysis may be performed as a separate operation prior to the plating operation or it may be carried out simultaneously therewith and in the same bath. If spent digestion liquor of the character described and a metallic salt are placed in the bath and current passed through the bath, the reaction with the non-cellulosic material will occur simultaneously with the deposition of the metal at the cathode. Thus plating can be effected very easily and inexpensively in this manner.

When it is desired to have a highly acid bath it has generally been found more satisfactory to pretreat the lignin-containing substance and to adjust its pH to the proper value following the oxidizing treatment as it has been found difficult to obtain the proper oxidation by electrolysis alone where the liquor is highly acid. Complete oxidation may be effected solely by electrolysis however, where a highly acid condition is not essential, this method being preferred for pH values above approximately 6, including slightly acid, neutral, and basic baths.

It has also been found that similar results can be obtained and an oxidation of the lignin-containing material effected through the reduction of certain metallic atoms. Thus if metallic salts of high valency such as the ic salts are dissolved in spent digestion liquor obtained as described

herein, a reduction of the metal atom and a loss of valency will occur with the formation of an ous salt, resulting in an oxidation of the organic matter and the production of an electrolyte material with which results can be obtained similar to those obtained with the liquor treated in the manner described above.

As a specific example of one composition which has been found to give entirely satisfactory results, the following is mentioned. To 70 kg. of spent digestion liquor resulting from the semi-chemical cooking process containing about 12% of dry substance is added .5 kg. of 30% hydrogen peroxide, the mass is stirred and allowed to stand for a short time. After this 4.2 kg. of chlorine are bubbled through the liquor. Following the chlorination, the mass is heated until a coagulation of the precipitate is obtained, the precipitate is removed by filtering and the liquor is ready for use. It may be neutralized if desired. In plating with this substance a suitable quantity of metallic salt is dissolved in the liquor. This amount may vary over a wide range in accordance with the plating desired, an example of a satisfactory quantity being 10 kg. of zinc chloride, tin chloride, nickel ammonium sulphate, copper chloride, cadmium sulphate or other salts of similar value dissolved in 40 kg. of neutralized liquor. Plating may be carried on at room temperatures using a current density of 60 amperes per square foot or above. It will be understood however that the above values are illustrative only and may vary within wide limits.

If it is desired to work without a preliminary treatment of the organic material, one part of the metal salt, for instance zinc sulfate, may be dissolved in four parts of spent digestion liquor resulting from the semi-chemical cooking process. This provides a bath suitable for plating with high current densities. If a low current density is used the bath may be diluted to one part of metal salt to ten parts of liquor. Generally it has been found that the proportion of metal to liquor should be within the limits of one to four and one to ten, but it is possible to plate successfully with more dilute and also more concentrated baths. In some cases equal parts of metal and liquor may be used though in such cases it is usually necessary to apply heat to the bath to maintain the salt in solution.

It has been found that entirely satisfactory coatings may be obtained by dipping the article to be plated into a bath containing the treated organic material described herein and a dissolved metal salt without the use of any external current. For instance good coatings of copper on iron may be obtained by simply dipping the iron in the bath containing the oxidized organic matter and a copper salt. As one example, oxidation may be effected by dissolving a cupric salt in spent digestion liquor of the character described and platings obtained by dipping the article into the bath.

Hydrogen seems to behave differently than it does in the customary bath and apparently is not present in such a condition as to interfere with effective plating. The coating adheres tightly to the article and does not scale off such as occurs in the previously known processes where there is apparently a film of metallic hydride or other foreign material between the article and the coating.

The use of an electrolyte formed in the manner described above has been found to be of particular importance in the plating of alloys.

When the salts of two or more metals are dissolved in the usual bath, it is found that the salts have different solution potentials and that usually one or the other salt is precipitated out of the bath. If not precipitated it is generally difficult to plate out both metals on account of their difference in potential. The present invention however solves these problems and makes it possible to plate a large number of alloys without difficulty. When two or more metals are dissolved in the electrolyte made according to the present invention the solution potentials are apparently brought closer together, there is no precipitating action of one salt by the other, and it is possible to obtain good deposits of certain metals which stand high in the potential column with other metals which are low in the column. Thus it is possible to obtain good coatings of copper and zinc, zinc and tin, zinc and lead, zinc, tin and copper, and many other alloys. A further characteristic feature of the present invention is that the electrolyte can be given any desired pH value by adding suitable quantities of an acid or a base and plating operations can be carried on under all these conditions. Successful coatings are obtained with current densities of the order of 120 amperes per square foot without the formation of trees or spongy deposits.

A specific example of an alloy plating process that has been successfully performed is as follows. In 40 kg. of the organic material produced in the manner described in the previous example, 5 kg. of zinc chloride and 5 kg. of tin chloride were dissolved and plating carried on as above. In another case 100 kg. of the reaction product was rendered strongly alkaline by the addition of potassium hydroxide and then mixed with 10 kg. of sodium plumbate and 2 kg. of sodium zincate. In another case 5 kg. of zinc chloride and 5 kg. of tin chloride were added to 50 kg. of spent digestion liquor without preliminary treatment and the plating current then passed through the bath. In all the above cases good, flexible, closely-adhering deposits of the alloy were consistently obtained.

The invention also provides for giving the article a preliminary treatment in order to remove impurities from the surface thereof and better to prepare it for receiving a surface coating. In order to do this the article, after having been degreased in the usual manner, is made the anode in a suitable bath and current passed therethrough for a short time so as to remove undesirable material from the surface thereof to obtain a clean metallic surface free of impurities. In this process the material of the cathode is of little importance and it can if desired take the form of a carbon cathode or an iron cathode.

The electrolyte for use in the anodical treatment comprises the organic material which has been subjected to the action of an oxidizing agent as described above. Following the treatment of the spent digestion liquor with hydrogen peroxide and with a halogen, it has a decided acid reaction, with a pH value of approximately 3. When the article is placed in this bath and connected to the anode, an etching thereof will take place which in certain cases may be highly desirable.

In other cases, it is desired only to remove surface impurities and not to obtain an etching of the base and in such cases it is necessary to reduce the acidity of the bath, the following

being a preferred method of doing so. The bath is first treated with a base such as sodium hydroxide to effect a neutralization of the greater part of the acidity. The amount of base to completely neutralize the liquor is computed and then approximately two-thirds of this quantity of base is added, thereby leaving the liquor still with an acid reaction. In order to neutralize the greatest part of the inorganic acids, a material such as manganese dioxide is added in excess which will react with and decompose all or practically all of the inorganic acid material. Certain organic acids however remain and are not decomposed by the addition of the manganese salt. The presence of these organic acids is highly desirable and they should be present to such an extent that after the treatment described immediately above, the bath has a pH value of from 4 to 5, represented practically entirely by the organic acid.

The article is immersed in this bath and connected to the anode for a short period of time during which its surface impurities will be removed. The time will vary with the density of the current but even with a relatively low current density, it is found that a sufficient action is obtained within a period of one minute. The adhering liquid can be easily washed off with water and the surface is then neutral and ready to receive a coating either electrolytically or in some other manner. The surface does not rust quickly and will retain its clean character for a considerable period of time.

When an etching is desired the liquor is used in the state in which it exists following the oxidizing treatment, the article is immersed in the liquor and connected so as to constitute an anode. After passage of the current for a brief time not only will surface impurities be removed but also an etching of the surface will occur, resulting in the production of minute irregularities thereof. A simple washing operation with water serves to remove the electrolyte and leaves the surface neutral, and in a high state of purity.

Articles which have been subjected to anodical treatment appear to be in a highly receptive condition for receiving coatings which adhere better than they do to untreated surfaces, presumably because there is a close bond with no intervening film of metallic compounds or other impurities between the base and the coating. Not only is this the case with metallic coatings but unusually good results are obtained when non-metallic coatings such as paints, varnishes, lacquers and similar materials are applied to an anodically treated surface. These coatings likewise adhere closely and do not deteriorate as rapidly as other types of coating.

It is also possible to obtain coatings upon a base which has been subjected to anodical treatment of metals heretofore considered very difficult to plate, the coatings being soft and of good quality, ductile, and easily workable showing a

close bond between the metals. Such is the case for example in the plating of cadmium which has always been attended with considerable difficulty and has been accomplished with any degree of success only with an alkaline cyanide bath. According to the present invention however when a ferrous base for example is given the anodical treatment as described above it is found that good coatings of cadmium can be obtained from an aqueous solution of cadmium salts either acid or alkaline and that the coatings do not flake off but the metal is in the desired soft condition. Particularly good results are obtained by plating cadmium from the organic bath described above, which can preferably be given a slightly acid reaction and it will be found that a coating will be obtained which is different from any heretofore known, the cadmium apparently being in a softer and more malleable condition than has been obtained in the past.

As another example, the invention provides for a preliminary treatment of such metals as aluminum to enable a coating of metal to be successfully plated thereon, aluminum being particularly difficult to prepare by reason of the overlying coating of aluminum oxide. According to the present invention the aluminum article is first given a cleaning treatment which may comprise the well known process in which the article is immersed in a solution of sodium hydroxide and sodium chloride and allowed to remain therein until the evolution of hydrogen visibly takes place. The article is then given an anodical treatment similar to that described above with respect to a ferrous article after which it will be found that at least portions of the surface of the article have been freed of oxide and other impurities and the pure surface of the metal exposed. This enables coatings to be made quite readily which are tightly adhering by reason of the metal bond. The process is extremely simple and inexpensive and does not require the use of strong reagents in removing the impurities.

While the articles and methods herein described constitute preferred embodiments of the invention, it is to be understood that the invention is not limited to these precise forms, and that changes may be made in either without departing from the scope of the invention which is defined in the appended claims.

What is claimed is:

1. As a new product for use in electroplating and the like and serving as a solvent for the metal or metal compounds to be plated, a lignin material which has been subjected to an oxidizing treatment.

2. As a new product for use in electroplating and the like, in which the salt of the metal to be plated is directly dissolved, a lignin material which has been subjected to the action of an oxidizing agent and a halogen.

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