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PROCESS OF ELECTROLYTICALLY DEPOSITING IRON AND IRON ALLOYS

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This invention relates to the electrodeposition of iron and iron-nickel alloys. More particularly it resides in improvements in the process of depositing iron and such alloys from an acid solution containing ferrous sulfate.

As is well known, the electrodeposition of iron and iron alloys is desirable for many purposes, such as the production of electrolytic iron, electro forming, the plating of iron or iron alloy on many different metals or on non-metallic surfaces, the building up of worn parts such as cylinders, shafts and bearings, etc.

In the making of such deposits it is highly desirable and usually necessary that the electrodeposited metal shall be free from pits, roughness and cracks, shall have good adhesion and be free from brittleness. The plating solution should have good throwing power and should not be too critical in the pH range which will produce good results. There should be a minimum of "treeing" when high current densities and along plating times are used. It should be possible to obtain a good and firmly adherent deposit without the necessity of preparing the article to be plated by unduly complex cleaning procedures. The plating process should not produce noxious fumes.

The foregoing desiderata are attained and the process of electrodepositing iron and iron-nickel alloys is greatly improved by the present invention which resides in the use in an electrolyte comprising an acid solution of ferrous sulfate of zinc hyposulfite as a soluble reducing agent. It has been found that very small amounts of these reducing agents suffice, satisfactory results having been obtained with from 0.1 to 1.5 grams per gallon of solution.

Iron plating solutions of ferrous sulfate are of course known and have been used with fair results but have been difficult to operate with uniform success, a particular difficulty with them being pitting and roughness of the deposit, which defects have been attributed to the presence in the bath of ferric iron. Various expedients for reducing the ferric compounds to the ferrous state have been tried but pitting and roughness have nevertheless occurred in an unpredictable manner, making the process unreliable, or else the expedients are impractical to use. Complicated cleaning procedures have also been necessary to obtain good adherence of the deposited metal to the object to be plated. When using the reducing agent, zinc hyposulfite, of the present invention, however, the process operates with certainty and the deposits are uniformly good. It is also possible to obtain good adherence using only a simple cleaning cycle such as that commonly used in copper and nickel plating. The reducing agent, zinc hyposulfite, of the invention also gives the bath better throwing power (ability to deposit metal more uniformly into recesses at a rate comparable to the deposition on flat surfaces) and greater ranges of the temperature and the pH of the solution are permissible.

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In order to render the reducing agent effective to improve the process, as described above, the bath must contain free sulfuric acid in an amount (as determined by titration with sodium hydroxide and methyl orange) of from about 0.5 cc. per gallon to about 5 cc. per gallon of 66° Bé. acid. If the free acid falls below the minimum amount, the reducing agent appears to become ineffective and, if it exceeds the maximum amount, cracks are liable to form in the deposit, adhesion may become poor, and the deposit may be brittle.

The pH of the bath may range from 2 to 5, the optimum range being 3 to 3.6. The pH will of course vary during electrolysis and pH determinations or titrations should be made at regular intervals. The rate of change may be determined for any given set of conditions and sulfuric acid may be added by a suitable dropping method to maintain the desired range. If the free acid content becomes too high it may be lowered by suspending iron in the solution without current until sufficient acid has been consumed. Alkali should not be used for this purpose as it will cause a precipitate to form in the bath.

In producing iron or iron alloy deposits according to this invention the process should be carried out in a tank which contains no metal in contact with the electrolyte other than the anodes and cathodes, such as a rubber lined tank. Since the electrolyte is preferably heated, the tank should be heated from the outside as by a steam jacket. Lead heating coils suspended in the electrolyte have been found to interfere with the satisfactory operation of the process.

The following specific example will illustrate in detail the practice of the process of the invention in electrodepositing iron: A suitable tank is filled about half full with clean cold water acidified by the addition of 2 cc. per liter of sulfuric acid (66° Bé.) and the temperature brought to 190° F. Ferrous sulfate is added in the amount of 64 oz. per gallon with constant stirring until completely dissolved. The working level is adjusted by adding water and the pH is adjusted, by addition of acid if necessary, within the range 2.5 to 4. Reducing agent is then added, for example zinc hyposulfite in the amount of 0.1 g. per gal, of solu-

tion and the solution stirred. A titration for free acid is then made, as the salt will neutralize some acid, and if below 0.5 cc. per gal, more acid is added to bring the acid within the range 0.5 to 5 cc. per gal.

Iron anodes, contained in canvas or specially treated filterpaper bags in known manner, and the object or objects to be plated are suspended in the bath. At the temperature of 180° F. the anode and cathode terminal bars are connected to an electroplating generator of suitable capacity.

The reducing agent, zinc hyposulfite, is preferably dissolved in water and added to the electrolyte as a solution. It should be added promptly after being dissolved for if allowed to stand there will be a considerable loss of effectiveness. Direct addition of the reducing agent in dry form is possible but is liable to produce roughness in the deposit.

In electrodepositing an iron-nickel alloy an electrolyte is used containing nickel sulfate in addition to the ferrous sulfate and, as in electrodepositing iron, as above described, the reducing agent for such a bath is zinc hyposulfite. As an example of such an alloy depositing bath, there may be used ferrous sulfate 48 to 72 oz. per gal., nickel sulfate 2–3 oz. per gal., and zinc hyposulfite from 0.1 to 1.5 g. per gal. The pH should be between 2.5 and 4. Such a bath will produce a deposit having 3% metallic nickel. Higher concentrations of nickel sulfate will produce deposits having correspondingly higher nickel content.

Zinc hyposulfite, which is the described reducing agent for bath iron and iron-nickel deposits is not commonly known but is available as the commercial products sold as "Decroline soluble concentrate" which is stated by the manufacturer to be formed by the condensation of sodium hyposulfite and zinc formaldehyde.

In addition to the metal salt, sulfuric acid and reducing agent in the iron or iron-nickel alloy plating baths described above, sodium fluoride may be used, as taught in the patents of William A. Crowder, Nos. 2,118,395 and 2,131,427. When used in conjunction with this invention, the addition of sodium fluoride improves the appearance of the electrodeposited metal, giving it a silvery grey crystalline appearance.

The amount of ferrous sulfate in the iron and iron-nickel plating baths of this invention is not critical. They will operate as well with 48 oz. per gal. as with 72 oz. per gal. but at the lower concentrations lower current densities must be used. At 48 oz. per gal. one may operate the bath at from 5 to 30 amps. per square decimeter.

It is to be understood that the invention is not to be limited to the specific details given above by way of explanation or illustration but may be practiced in other ways within the purview of the following claims.

What is claimed is:

1. The process of electrolytically depositing iron-nickel alloy which comprises electroplating through a solution of ferrous sulfate and nickel sulfate, sulfuric acid in an amount equivalent to from about 0.5 cc. to 5 cc. per gallon of 66° Bé. acid, and zinc hyposulfite in an amount sufficient to reduce any ferric iron in the solution to the ferrous state.

2. The process of electrolytically depositing iron and iron-nickel alloys which comprises electroplating through a solution containing ferrous sulfate where iron alone is deposited and ferrous sulfate and nickel sulfate where iron-nickel alloy is deposited, free sulfuric acid in an amount equivalent to from about 0.5 cc. to about 5 cc. per gallon of 66° Bé. acid, and a reducing agent consisting of zinc hyposulfite in an amount sufficient to reduce any ferric iron in the solution to the ferrous state.

3. The process of electrolytically depositing iron which comprises electroplating through a solution containing ferrous sulfate, free sulfuric acid in an amount equivalent to from about 0.5 cc. to about 5 cc. per gallon of 66° Bé. acid, and zinc hyposulfite in an amount sufficient to reduce any ferric iron in the solution to the ferrous state.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,131,427	Crowder	Sept. 27, 1938
2,157,699	Hardy et al.	May 9, 1939

OTHER REFERENCES

Trans. Electrochem. Soc., vol. XLIII (1923), page 120. (Copy in Division 56.)