United States Patent [19]
Kurosaki et al.

[11] **3,787,294**
[45] **Jan. 22, 1974**

[54] **PROCESS FOR PRODUCING A SOLID LUBRICANT SELF-SUPPLYING-TYPE CO-DEPOSITED METAL FILM**

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[22] Filed: **Dec. 7, 1971**

[21] Appl. No.: **205,726**

[52] **U.S. Cl.** **204/16,** 204/181
[51] **Int. Cl.** **C23b 7/00,** B01k 5/00
[58] **Field of Search** ... 204/16, 181; 252/9, 12, 12.2, 252/18

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[57] **ABSTRACT**

A process for producing a solid lubricant self-supplying-type co-deposited metal film in which fine powder of inorganic polymer of graphite fluoride is dispersed in a metal plating bath in the presence of a co-deposition assisting surfactant having C - F bond in molecules selected from the group comprising cationic surfactants, nonionic surfactants and amphoteric surfactants which exhibit cationic characteristic at the pH value of a particular plating bath employed with or without levelling and brilliance imparting agents and a metal coating or film is deposited on a substrate so as to co-deposit graphite fluoride in the metal coating. A mechanical part having a graphite fluoride co-deposited metal coating thereon produced by the process. A metal plating bath employed in the process.

4 Claims, No Drawings

PROCESS FOR PRODUCING A SOLID LUBRICANT SELF-SUPPLYING-TYPE CO-DEPOSITED METAL FILM

BACKGROUND OF THE INVENTION

This invention relates to novel and improved metal plated products having thereon inorganic polymer-codeposited coatings or films of solid lubricant self-supplying-type and processes producing the same.

There have been proposed a number of processes for producing plated products having thereon inorganic polymer-co-deposited coatings or films of solid lubricant self-supplying-type. For example, there are disclosed in Japanese Patents Nos. 419,801 and 521,020 processes for producing such plated products wherein a metal substrate is deposited in a metal plating bath with the addition of an insoluble inorganic salt in a fine powder form in plating bath so as to have the deposited metal coating or film uniformly incorporate the fine particle inorganic salt therein.

However, either of the processes of these Japanese patents referred to above is performed by the addition of fine powder of salt of aluminum, magnesium or strontium or an oxide of any of the materials to an acidic nickel plating bath. Although there is described in either of the Japanese patents that by the addition of such salts or oxides, nickel coatings or films can be formed on the substrate surfaces having fine powdery material uniformly dispersed therein, the prior arts disclosed in these Japanese patents exclusively direct to decorative "satin-like" coatings or films or undercoats for corrosion resistance chromium platings, but do not direct to co-deposited metal coatings of films of solid lubricant self-supplying-type to which the present invention pertains. Of late, the technology for co-depositing fine powder of molybdenum disulfide on the metal-deposited substrate surfaces to provide lubricative plated products has been proposed (for example, see the "Co-Deposited Nickel Molybdenum Disulfide Metal Finishing" by C.E. Vest & D.F. Baggarre, November 1967 and more particularly, pages 52–58 thereof). Molybdenum disulfide has been employed as a solid lubricant because molybdenum disulfide has the layer structure in which each of molybdenum atoms is sandwiched between sulfur atoms, each molybdenum atom slides between the surfaces of the sulfur atoms and the molybdenum has a low shearing strength. However, it has been known that molybdenum disulfide is a hydrophilic compound and has disadvantages with respect to chemical-resistant properties and lubricating characteristics at elevated temperature and therefore, molybdenum disulfide is not a satisfactory co-deposition material.

SUMMARY OF THE INVENTION

We have found that although graphite fluoride is quite hard to be dispersed in both water and oil, the compound has excellent properties as a solid lubricant. And on the basis of the discovery, we have exerted our efforts toward the utilization of the properties of the compound as a solid lubricant in the field of co-deposition plating and have reached the present invention which pertains to the production of plated products having co-deposited coatings of films of solid lubricant self-supplying-type.

It has been found that when fine powder of an inorganic polymer of graphite fluoride (the material will be referred to simply as "graphite fluoride" herein below) is dispersed into a conventional plating bath (the bath will be referred to as "fundamental plating bath or composition" herein below) together with a surface active agent or surfactant selected having fluorine-carbon bond in their molecules (F-C bond) selected from the group comprising water soluble cationic surfactants, nonionic surfactants and amphoteric surfactants which exhibit cationic characteristics at the pH value of a particular plating bath employed, these surfactants perfectly wet graphite fluoride of high water repellent property, disperse the graphite fluoride in the plating bath with stabilization and cause the fine particles of the graphite fluoride to become positively charged.

It has been experimentally determined that when a metal plating operation is conducted with the thus prepared plating bath, the positively charged fine particles of graphite fluoride exhibit an electrophoresis phenomenon subject to the force from the electric field developed between electrodes and move toward and onto the cathode or workpiece whereby the graphite fluoride particles are uniformly co-deposited in the deposited metal coating or film on the workpiece.

It has been also determined that when a metal plating is conducted using the plating bath in which fine powder of graphite fluoride is uniformly dispersed in the presence of such a co-deposition agent having C–F bond in their molecules selected from the group comprising cationic surfactants, nonionic surfactants and amphoteric surfactants which exhibit cationic characteristics at the pH value of a particular plating bath employed under mechanical agitation such as screw-, liquid recycling- or air agitation, the graphite fluoride is not only perfectly wetted, but the dispersion state of the graphite fluoride is quite stabilized. Furthermore, since the thus obtained co-deposited coating or film is free of brittleness and has an excellent electrification property and even if the plating bath contains graphite fluoride in a low concentration, the co-deposited coating may contain a great mount of graphite fluoride as much as possible therein.

Since solid lubricant self-supplying metal coated products of the present invention have a high sliding property with less friction, they can find their application in inner walls of cylinders, inner walls of engines, piston rings, piston rods, bearings and slidable parts of other machines and are reliable in their functions throughout the service life. Thus, the present invention provide useful mechanical parts or members.

According to one aspect of the present invention, there is provided a process for producing a metal plated product having thereon a co-deposited coating or film of solid lubricant self-supplying-type which comprises the steps of dispersing fine powder of inorganic polymer of graphite fluoride into a metal plating bath in the presence of a fluorocarbon surfactant having fluorine - carbon bond (F–C bond) in their molecules selected from the group comprising water soluble cationic surfactants, nonionic surfactants and amphoteric surfactants which exhibit cationic characteristics at the pH value of a particular plating bath employed, and depositing a metal coating or film on a substrate so as to co-deposite graphite fluoride in the metal coating.

According to another aspect of the present invention, there is provided a plated product having a co-deposited metal coating or film of solid lubricant self-supplying-type produced by the process referred to above.

According to a still further aspect of the present invention, there is provided a metal plating bath which comprises a conventional fundamental metal plating bath composition, fine powder of inorganic polymer of graphite fluoride and a fluorocarbon surfactant having fluorine - carbon bond in their molecules (F–C bond) selected from the group comprising water soluble cationic surfactants, nonionic surfactants and amphoteric surfactants which exhibit cationic characteristics at the pH value of a particular metal plating bath composition employed.

The graphite fluoride of the present invention can be prepared by causing carbon or graphite to react with fluorine or a fluorine compound at a temperature below 550°C and is powder of an inorganic polymer of a fluoride having the structure in which fluorine is introduced between carbon layers or layers constituting a lattice structure and the layers having the fluorine therebetween are bonded together by covalent bond with the valence electron of one free extra atom of the carbon atoms which can be represented by the molecular formula $(CF)_n$. Therefore, in the graphite fluoride referred to above, the molar ratio of fluorine to carbon is 1:1 and is a solid usually having a white or gray crystal structure and a specific gravity of 2.45.

In addition, the graphite fluoride is characterized by that the compound exhibits a high electric insulation, is almost free from attack from chemicals, is not wetted with water and oil (contact angle of 145°C) and has water and oil repellence and lubricity at elevated temperature. Furthermore, the graphite fluoride is stable in both acidic and basic metal plating baths without sacrificing its characteristics as a solid lubricant. The graphite fluoride is further characterized by that the compound can maintain its lubricity at elevated temperatures on the order of 500°C at which other solid lubricants would lose their lubricity and is stable against friction heat and environmental conditions present in boundary lubrication. However, it has been known that when such graphite fluoride is dispersed and co-deposited in deposited metal film or coating, the greater the volume percentage of the compound is, the lower the adhesion of the compound to the deposited metal film is. Thus, it is preferably to limit the amount of graphite fluoride to be co-deposited in the solid lubricant self-supplying type deposited metal coating or film of the present invention to the volume fraction up to 80 percent at the most.

When the deposited metal coating or film is required to have a high mechanical strength or a metal deposited product having such a coating is employed as a friction member or part such as a piston ring or bearing, co-deposition of graphite fluoride in a substantial amount is objectionable and it is preferably to limit the co-deposition amount of such a compound to a value up to 10 percent at the most.

And particles of graphite fluoride to be added to a metal plating bath composition are preferably in a finely divided powder so that the particles may have good adhesion to the deposited metal coating. The diameter of such particles is usually smaller than 10μ and it is preferable that such particles contain about 80 percent of fine particles having diameters smaller than 0.5μ. The amount of graphite fluoride to be added to the fundamental metal bath composition is usually less than 50 g/l with preference concentration within the range of 0.1–10 g/l.

As to fluorocarbon surfactants to be suitably employed as assistants in the present invention, any member having fluorine - carbon bond (C–F bond) in their molecules selected from the group comprising cationic surfactants, nonionic surfactants and amphoteric surfactants which exihibit cationic characteristics at the pH value of a particular electroplating bath composition employed and for example, cationic surfactants sold under the trade name FC–134 (a perfluorinated quaternary ammonium compound) by Minesota Mining & Manufacturing Company in the United States of America are preferably employed. However, when nonionic surfactants having C–F bond are employed as assistants, graphite fluoride particles are positively electrified only when the metal plating bath employed is of an acidic one.

On the other hand, when anionic surfactants having C–F bond in their molecules or amphoteric surfactants which exhibit anionic characteristics at the pH value of a particular electroplating bath composition are employed as assistants, graphite fluoride particles are negatively charged and these assistants obstruct co-deposition of the graphite fluoride particles to the deposited metal coating or film and therefore, both of these types of surfactants cannot be suitable employed in the present invention.

As to the amount of the fluorocarbon surfactant to be added to the fundamental metal plating bath composition as an assistant for co-deposition, the amount of such a surfactant is preferably within the range of 5 mg/l to 5 g/l with respect to the bath composition with most preferable range of 10 mg/l to 500 mg/l. In carrying out the process of the invention, it has been found that the co-deposition operation is efficiently effected under mechanical agitation such as screw-, air- or liquid recycling agitation. It has been also found that even when powder of graphite fluoride is dispersed in water in a different way from co-deposition, the use of any one of the above-enumerated fluorocarbon surfactants having the same chemical bond as that of graphite fluoride or the fluorine - carbon bond (C–F) in its hydrophobic group is suitably employed as dispersion agent. Therefore, the present invention can be also applicable to chemical platings in which particles of graphite fluoride are suspended in water or chemical plating baths by the use of the surfactants of the invention different from electroplatings.

As to metals in the coatings or films of which graphite fluoride can be suitably co-deposited according to the present invention, as appreciated from the principle of the invention, all metals which can be deposited on cathodes or substrates by electroplating are useful. These metals include copper, nickel, chromium, zinc, cadmium, tin, iron, lead, noble metals and alloys thereof, for example. The pH of a particular plating bath employed is not related to whether the bath is acidic or alkaline.

PREFERRED EMBODIMENT OF THE INVENTION

The present invention will be now in detail described by way of specific example of the same, but it should be understood that the invention is not limited to such examples in any way and rather limited by the appended claims only.

Brilliance imparting agents employed in Examples 1, 2, 6 and 7 as described hereinbelow (these agents are sold under the trade names "Asahilight" SN–1 and SN–2) are added to electroplating baths so that the surfaces of deposited coatings of films can be not only smoothened, but also the hardness of the coatings or films is increased sufficient to enhance its wear resistance property.

EXAMPLE 1

An electroplating bath was prepared employing the following composition ingredients:

Fine powder of graphite fluoride (average particle diameter of 0.2μ) — 5 g/l
Water soluble fluorocarbon cationic surfactant FC—134 (the trade name of a product sold by Minesota Minning & Manufacturing Company in the United States of America) — 20 ppm
$NiSO_4 \cdot 6H_2O$ — 280 g/l
$NiCl_2 \cdot 6H_2O$ — 45 g/l
H_3BO_3 — 40 g/l
Asahilight SN–1 (the trade name of a commercially available brilliance imparting agent) — 20 cc/l
Asahilight SN–2 (the trade name of a commercially available brilliance imparting agent) — 2 cc/l

The pH of the plating bath was adjusted to 4.2 using sulfuric acid. A steel test piece (30 mm in outer diameter, 16 mm in inner diameter and 8 mm in thickness) for a Nishihara-type wear-resistance testing machine was employed as the cathode and a nickel plating operation was performed under conditions such as bath temperature of 50°C and current density of 5 A/dm^2 for about 50 minutes until the cathode was deposited thereon a graphite fluoride-codeposited coating up to the thickness of 50 μ. For comparison purpose, a control test piece of the same material was electroplated using the same plating bath as that employed in the above plating operation except for the elimination of the graphite fluoride powder and surfactant under the same plating conditions. Wear resistance tests were conducted on these plated test-pieces and the results of the tests are given hereinbelow.

Wearing procedure — Rolling including 29.73 percent of sliding
Load — 30 kg
Rolling rate — 613 r.p.m.
Environment — Dry wearing in the atmosphere
Mating piece — Annealed carbon tool steel SK 5

TEST RESULTS

TABLE 1

Test piece Item for measurement	Graphite-co-deposited test piece	Control
Number of rollings required for wearing up to 50 mg	15,000	3,000

From the above Table 1, it will be appreciated that the wear-resistance of the graphite fluoride-codeposited metal coating or film of the invention is substantially higher than that of the not co-deposited metal coating or film.

EXAMPLE 2

An electroplating bath was prepared employing the following composition ingredients:

Fine powder of graphite fluoride (the average diameter of 0.2 μ) — 5 g/l
Water soluble fluorocarbon cationic surfactant FC–134 — 20 ppm
$NiSO_4 \cdot 6H_2O$ — 280 g/l
$NiCl_2 \cdot 6H_2O$ — 45 g/l
H_3BO_3 — 40 g/l
Asahilight SN–1 — 20 cc/l
Asahilight SN–2 — 2 cc/l

The pH value of the plating bath was adjusted to 4.2 using H_2SO_4. Eight SUJ–2 steel test pieces (in a doughnut form (40 mm in outer diameter and 8 mm in thickness) for a roller-type friction testing machine were employed as cathodes and a nickel plating operation was performed under screw agitation using plating conditions such as bath temperature of 50°C and current density of 5 A/dm^2 for about 50 minutes until the cathodes were deposited thereon graphite fluoride-co-deposited nickel coatings or films of 50μ. For comparison purpose, the corresponding number of control test pieces identical with those employed in the co-deposition plating operation mentioned just above using the same nickel plating bath except for the elimination of the above-mentioned graphite fluoride and fluorocarbon surfactant. All the thus treated test pieces were subjected to comparison tests for their coefficients of friction in No. 1 additive turbin oil (JIS K 2213) under load of 60 kg/mm^2. The results of these are given hereinbelow.

TABLE 2

Test piece Item for measurement	Graphite fluoride co-deposited nickel coated test pieces	Control
Average coefficient of friction	0.0340	0.0530

From the above Table 2, it will be understood that the average coefficient of the graphite fluoride-co-deposited nickel coatings of the invention is smaller than that of the control nickel coatings having no graphite fluoride co-deposited therein.

EXAMPLE 3

A plating bath was prepared employing the following composition ingredients:

Fine powder of graphite fluoride (average particle diameter of 0.2μ) — 10 g/l
Water soluble fluorocarbon cationic surfactant FC–134 — 20 ppm
Sodium cyanate — 147 g/l
Copper cyanate — 150 g/l
Sodium hydroxide — 40 g/l
Potassium soda tartrate — 211 g/l
Lead acetate — 75 g/l

A brass bearing material was employed as the cathode and a pure copper piece was employed as the anode. The cathode was deposited thereon a copper - lead alloy coating or film in which graphite fluoride was deposited under screw agitation thickness using plating conditions such as bath temperature of 60°C and current density of 5 A/dm^2 for about 50 minutes up to 50μ.

The thus treated bearing material was found suitable as a bearing. The torque of the thus treated bearing material was found 32 percent less than that of the control which was treated in the same plating bath except for the elimination of the above-mentioned graphite fluoride and fluorocarbon surfactant and accordingly, the copper-lead alloy coating on the control had no graphite fluoride co-deposited therein.

EXAMPLE 4

An electro-plating bath was prepared employing the following composition ingredients:

Fine powder of graphite fluoride (average particle diameter of 0.2μ) — 10 g/l
Water soluble fluorocarbon cationic surfactant FC–134 — 20 ppm
Lead borofluoride — 243 g/l
Fluoboric acid — 23.3 g/l
Boric acid — 23.3 g/l
Gelatine — 0.2 g/l

The pH value of the plating bath was adjusted to 1.5 using fluoboric acid. A brass bearing material was employed as the cathode a lead piece was employed as the anode and the cathode was deposited thereon a lead coating or film in which graphite fluroride was co-deposited under air agitation using plating conditions such as bath temperature of 30°C and current density of 5 A/dm^2 for about 20 minutes up to the coating thickness of 50μ. The thus treated brass bearing material was found suitable as a bearing. A control bearing material formed of the same material was treated in the same plating bath except for the elimination of the above-mentioned graphite fluoride and fluorocarbon surfactant therefrom. The two bearing materials were subjected to abrasion test in which the time required to wear the material to a predetermined amount was determined and it was found that the time required to wear the inventive material having the graphite fluoride co-deposited coating was about 4.5 times long as that for the control. This means that a machine or apparatus having the bearing with the lead coating in which graphite fluoride is co-deposited has a service life at least 4 times as long as the corresponding machine or apparatus having the control bearing.

EXAMPLE 5

An electroplating bath was prepared using the following composition ingredients:

Fine powder of graphite fluoride (average particle diameter of 0.2μ) — 10 g/l
Water soluble fluorocarbon cationic surfactant FC–134 — 20 ppm
Silver cyanate — 38 g/l
Potassium cyanate — 50 g/l
Potassium hydroxide — 125 g/l
Potassium carbonate — 44 g/l

A pure silver piece was employed as the anode and a brass bearing material was employed as the cathode. A silver plating operation was performed under screw agitation using plating conditions such as bath temperature of 35°C and current density of 5 A/dm^2 for about 16 minutes to deposit a silver coating on the cathode in which graphite fluoride was co-deposited up to the thickness of 50μ. The thus treated bearing material was found suitable for a bearing as in the case of the products in Examples 3 and 4. When employed under light load conditions, the wear of the graphite-co-deposited silver coating was one fifth as less as that of the control which had been treated in the same plating bath except for the elimination of the above-mentioned graphite fluoride and fluorocarbon surfactant therefrom.

EXAMPLE 6

An electroplating bath was prepared using the following composition ingredients:

Fine powder of graphite fluoride (average particle diameter of 2 μ) — 5 g/l
Water soluble fluorocarbon non-ionic surfactant FC–170 (the trade name of a product sold by Minesota Minning & Manufacturing Company in the United States of America) — 30 ppm
$NiSO_4 \cdot 6H_2O$ — 280 g/l
$NiCl_2 \cdot 6H_2O$ — 45 g/l
H_3BO_3 — 40 g/l
Asahilight SN–1 — 20 cc/l
Asahilight SN–2 — 2 cc/l

The pH value of the plating bath was adjusted to 4.2 using H_2SO_4. The test piece employed in this example was a steel piece identical with that employed in Example 1 and a nickel plating operation was conducted under liquid recycling agitation using plating conditions such as bath temperature of 50°C and current density of 5 A/dm^2 about for 50 minutes to deposit a nickel coating or film up to 50μ thickness on the cathode having graphite fluoride co-deposited therein. A control formed of the same type material was treated in the same plating bath except for the elimination of the above-mentioned graphite and fluorocarbon surfactant and accordingly, the resultant control had thereon a nickel coating in which no graphite fluoride co-deposited. The two types of test pieces were subjected to wear resistance test to find that the inventive test piece had a wear resistance 3 times as high as that of the control.

EXAMPLE 7

An electroplating bath was prepared using the following composition ingredients:

Fine powder of graphite fluoride (average particle diameter of 0.5 μ) — 10 g/l
Water soluble fluorocarbon amphoteric surfactant FC–172 (the trade name of a product sold by Minesota Minning & Manufacturing Company in the United States of America) — 0.1 g/l
$NiSO_4 \cdot 6H_2O$ — 280 g/l
$NiCl_2 \cdot 6H_2O$ — 45 g/l
H_3BO_3 — 40 g/l
Asahilight SN–1 — 20 cc/l
Asahilight SN–2 — 2 cc/l

The pH value of the plating bath was adjusted to 4.2 using H_2SO_4 and the test piece employed as the cathode in this example was a steel piece identical with that employed in Example 1. A nickel plating operation was performed on the cathode under liquid agitation using plating conditions such as bath temperature of 50°C and current density of 5 A/dm^2 for about 50 minutes to deposit a nickel coating or film on the cathode up to 50 μ thickness having graphite fluoride co-deposited therein. A control test piece formed of the same type of material as that employed in this example was treated in the same plating bath as that employed in Example 7 except for the elimination of the graphite fluoride and fluorocarbon surfactant to deposit a nickel coating thereon which had no graphite fluoride co-deposited therein. The two types of test pieces were subjected to wear resistance test using the same procedure and conditions as mentioned in connection with Example 1. The result of the test are given in Table 3 hereinbelow.

TABLE 3

Test piece Item for measurement	Inventive test piece	Control test piece
Number of rolling required for wearing up to 50 mg	17,500	3,000

As clear from the above Table 3, the graphite-co-deposited nickel coating exhibits a higher wear resistance than the control in which no graphite fluoride.

While there have been described what are at present considered to be the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and it is aimed, therefore, in the appended claims to cover all such changes and modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. A process for producing a solid lubricant self-supplying-type co-deposited metal coating or film comprising the steps of dispersing fine powder of inorganic polymer of graphite fluoride having an average particle diameter less than 10 μ in a metal plating bath in the presence of a cationic surfactant having fluorine - carbon bond in the molecule, said surfactant being water soluble, said surfactants perfectly wetting said graphite fluoride which has a high water repellent property and dispersing said graphite fluoride in the plating bath with stabilization thereof and causing the fine powder of said graphite fluoride to become positively charged, and electrically depositing a metal coating or film on an electrically conductive substrate so as to co-deposit less than 80 percent by volume of graphite fluoride in said metal coating.

2. The process for producing a solid lubricant self-supplying-type co-deposited metal film as set forth in claim **1**, in which the amount of said surfactant is less than 5 g/l and in which the amount of said graphite fluoride is less than 50 g/l.

3. The process for producing a solid lubricant self-supplying-type metal film as set forth in claim **1**, in which said surfactant is a perfluorinated quaternary ammonium compound.

4. The process for producing a solid lubricant self-supplying-type metal film as set forth in claim **1**, in which said metal plating bath further contains additive agents such as levelling and brilliance imparting agents.

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