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3,738,858

METHOD OF PRODUCING LOW-SCATTER SURFACES ON METAL SUBSTRATES

Robert M. Elwell, Merrimac, Jurgen M. Kruse, Lincoln, and Leon Michelove, Lexington, Mass., assignors to Itek Corporation, Lexington, Mass.

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ABSTRACT OF THE DISCLOSURE

A method for producing low-scatter or ultrasmooth surfaces of metal substrates is disclosed. The method comprises contacting and polishing the metal substrate in the presence of both a source of the metal in a zero-valent or latent zero-valent state and a source of the metal in an ionic state. The metal substrate is preferably polished with a soft, smooth, resilient cloth. Low-scatter surfaces are useful on certain optical components including mirrors.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a method for producing uniform, highly-polished, low-scatter surfaces on metal substrates.

(2) Description of the prior art

Many techniques for forming smooth, metallic coatings on metal substrates are known. Some of those which have been described in the patent literature and which are believed representative of existing processes are as follows:

U.S. Pat. 915,415, to Cowper-Coles, describes electrolytic techniques for coating cast metal mirrors on their back with metals such as copper, and on their front with metals such as silver, nickel or cobalt. The front reflecting surface is subsequently ground and polished to a mirror finish.

U.S. Patent 3,097,117, issued to Grunwald, describes an electroless plating method for producing black nickel coatings on metallic nickel substrates by immersing the substrate in an aqueous solution containing an oxidizing agent belonging to the family of aromatic nitro derivatives and an inorganic salt of thiocyanic acid, together with a sufficient amount of a strong inorganic acid to lower the pH under 2.0 at a temperature of above 100° F. This method is stated to be limited to metallic nickel substrates, and is also stated to be inoperative with electroless nickel coated substrates.

U.S. Pat. 3,216,845, issued to Brown, teaches a method of depositing nickel, cobalt, cadmium, tin or lead coatings on substrates by heating a metal alkoxide. For example, nickel alkoxide of ethylene glycol is heated to a temperature around 200° C. to break the nickel oxide bond homolytically and thereby deposit nickel in a powdery film or mirror-like film on a substrate.

U.S. Pat. 3,472,665, to Prueter et al., describes a process for depositing a continuous film of cobalt or nickel by contacting a metallic or non-metallic substrate with an electroless coating bath comprising a solution of 0.01-50% of a cobalt or nickel salt in liquid 2-oxazolidone.

While some of these various patented methods are described as depositing mirror-like metallic finishes, they do not produce "low-scatter" or "ultrasmooth" surfaces. For purposes of this invention, these terms are used as explained below.

When a beam of light is incident on a theoretically smooth mirror surface, it is reflected according to the laws of geometrical optics into the specular direction. Scattered light is that fraction of the incident beam which

is diffusely reflected or diffracted from a real surface in a direction other than that of the specular beam. This is a function of the residual surface roughness of the mirror, which is in turn dependent on the material and its interaction with the polishing process. Optical surfaces polished by traditional optical shop practices exhibit a characteristic level of scattered light, described here as the normal scattering. Mirror surfaces with considerably improved (decreased) scattering may be described as ultrasmooth or low-scatter surfaces. Such low-scatter surfaces may have scattered light reduction of as much as three (3) orders of magnitude in energy. They also exhibit reflectance equivalent to the theoretical reflectance of the bulk material, and absorption equivalent to that of a theoretically uniformly smooth surface.

Those skilled in the art are familiar with the above. To avoid any ambiguity, however, the following quantitative definitions are provided.

A "low-scatter" surface is one which, upon being illuminated from the normal direction with a laser source (He-Ne) at 6328 Å., scatters less than 100 p.p.m., and preferably less than 20 p.p.m., of the incident energy, measured by a detector subtending no more than 0.03 steradian solid angle from the surface when the midpoint of the detector is located at 17° from the specular beam. In contrast, typical mirror-surfaced nickel coatings scatter between about 1000 to 10,000 p.p.m. under this test.

An "ultrasmooth" surface is defined using the interferometric technique based on white light fringes, or Fringes of Equal Chromatic Order (FECO) as described by Bennett and Bennett (Physics of Thin Films 4, 1, 1967). To be "ultrasmooth," the surface must exhibit an R.M.S. surface roughness below about 20 Å., and preferably below 10 Å. Typical metal surfaces referred to in the art as having mirror smooth surfaces have R.M.S. surface roughnesses of 50 Å. or more.

SUMMARY OF AN EMBODIMENT OF THE INVENTION

This invention relates to the production of low-scatter or ultrasmooth surfaces on metal substrates. In this process, the substrate is polished in the presence of a source of the metal in either a zero-valent or latent zero-valent state, and also in the presence of a source of the metal in its ionic state. Both are necessary. Polishing is accomplished with a soft, smooth, resilient polishing pad, and is continued until the desired low-scatter surface is obtained.

The method described herein has many advantages. One is that it is the only process known to the inventors for obtaining low-scatter coatings which is both practical and economical. Additionally, low-scatter surfaces can be produced on optical elements without disturbing the optical figure thereon, and it might even be possible to simultaneously form low-scatter coatings and perform optical figuring on such surfaces using this process. Further, the process is not limited by the sample size, as is true with the various electrochemical and electroless plating methods for forming coatings. The most important advantage, however, is the superior low-scatter or ultrasmooth surfaces which can be obtained by this method.

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

A variety of metallic substrates can be treated by the method described herein to produce low-scatter surfaces. Some examples include, but are not limited to, substrates of nickel, cobalt, molybdenum, iron, beryllium, aluminum, tungsten, chromium, manganese, rhenium, vanadium, ruthenium and rhodium. Also substrates comprising alloys such as copper alloys, steel, inconel, etc. can be used.

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Multi-layered substrates can be used as long as the top layer is one of the metals which can be used with the process described herein.

It has been empirically found that two different sources of metal are required for this process. The first is a source of the metal in a zero-valent or latent zero-valent state. The second is a source of the metal in an ionic form.

The source of zero-valent metal should be a compound or compounds which, under the experimental conditions, easily liberates the desired species. This source can be compounds which contain the metal at zero-valent state initially, such as metal carbonyls, or compounds such as organometallics which contain the metal in an ionic form, but also contain potential strong reducing agents which can be liberated to reduce the ionic metal to a zero-valent state. In all cases, the source of zero-valent metal must be decomposable at a temperature below about 250° C., and preferably at a temperature below about 155° C., so that the zero-valent metal will be liberated during processing, especially polishing. Some specific examples of compounds suitable as the source of zero-valent metal are given below.

The first group is compounds containing metals at the zero-valent state, such as metal carbonyls. Some suitable metal carbonyls include nickel carbonyl, indium carbonyl, manganese carbonyl, rhenium carbonyl, ruthenium carbonyl, vanadium carbonyl, molybdenum hexacarbonyl, chromium carbonyl, cobalt carbonyl, dicobalt carbonyl, iron pentacarbonyl, iron nonacarbonyl, iron dodecacarbonyl, molybdenum carbonyl, tungsten carbonyl, acetylene dicobalt nonacarbonyl, butadiene iron tricarbonyl, 1,3-pentadiene iron tricarbonyl, bis(triphenylphosphine) nickel dicarbonyl, cobalt nitrosyl tricarbonyl, dicobalt octacarbonyl, anilinechromium tricarbonyl, anisolechromium tricarbonyl, benzenechromium tricarbonyl, chromium hexacarbonyl, tris(triphenylphosphine)rhodium carbonyl, triphenylphosphine cobalt tricarbonyl dimer, mesitylenechromium tricarbonyl and toluenechromium tricarbonyl. Other compounds containing zero-valent metals include dibenzenechromium, bis(acrylonitrile) nickel, tetrakis(triphenylphosphine) platinum and dibenzenevanadium.

A second group comprises compounds containing latent zero-valent metal. These are compounds which contain the metal in an ionic form, but which also liberate upon dissociation, a reducing agent capable of easily reducing the ionic metal to its zero-valent state. Such compounds include metallocenes such as nickelocene and ruthenocene. Others are cyclopentadienylnickel carbonyl dimer, dicyclopentadienylnickel, tris(ethylenediamine) nickel (II) sulfate, tris(triphenylphosphine)rhodium carbonyl, triphenylphosphine cobalt tricarbonyl dimer, dicyclopentadienylcobalt, etc.

The source of metal in an ionic state should be chosen so as not to leave a residue upon the substrate. For that reason, metallic carbonates, oxides, hydroxides, oxalates, formates and acetates are preferred. Compounds which might be corrosive to the surface being polished, such as certain halides, are not suitable.

Some specific compounds suitable for the source of metal in an ionic state are as follows: nickel acetate, nickel formate, nickelic hydroxide, nickelic oxide, nickelous hydroxide, nickel oxide, chromic acetate, chromic formate, cobaltous acetate, cobaltous carbonate, cobaltous formate, manganese acetate, manganese oxalate, molybdenum dioxide, molybdenum trioxide, ferric oxalate, vanadium pentoxide, vanadium trioxide.

It should be clear that the specific compounds given above are only intended to be exemplary of the many compounds containing zero-valent, latent zero-valent, and ionic metal which can be used with this process. Those skilled in the art will know, or be able to ascertain using no more than routine experimentation, many other suitable compounds.

Some of the compounds specified above are toxic, air-flammable, or water flammable. Those skilled in the art

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will know, however, the proper care to be used with such compounds.

As mentioned, one way to apply the sources of metals to the substrate is in the form of emulsions. One very suitable emulsion can be formed which contains minor amounts of nitrobenzene in water. Others will be readily apparent, or easily ascertainable with no more than routine experimentation by those skilled in the art. To form emulsions, it is necessary that the metal sources be soluble to some degree in either the aqueous or organic phase. This solubility need not be great, however, and solubilities as low as 1% at 72° F. are useful.

Alternatively, pastes or suspensions of the metals can be formed for application to the substrate.

The metal substrate can be polished by hand or machine. For the best results, it has been found that a soft, smooth, resilient cloth should be used. Abrasive cloths should be avoided since they scratch the surface. Suitable polishing cloths include those formed from reinforced porometric materials, such as those sold under the trademarks Politex Supreme and Politex Pix by Geoscience Instruments Corp. Natural materials, such as leather, are also suitable. If desired, the cloth can be lap mounted. It is important, however, to apply a very light pressure so that a minimum of scratches and streaks are formed.

The order of applying and polishing each of the required metal forms has not been found to be critical.

In most instances, the low-scatter surfaces desired can be obtained in one cycle of applying and polishing each form of metal into the substrate. If the desired surface is not obtained with the first cycle, however, the process is merely repeated until a satisfactory low-scatter surface is obtained.

While the theory of how the low-scatter surfaces are obtained is not well understood, it is believed to be due to a rearrangement of the metal ions accomplished through redox-type reactions. The rearrangement of metal ions appears to remove metal from the high spots and to fill in low spots or streaks on the metal surfaces. Despite the lack of understanding of this process, it has been repeatedly observed that the substrate must be polished in the presence of both zero-valent and ionic metals. Attempts to use either alone have failed.

Low-scatter surfaces produced by the method described herein are particularly useful for optical components requiring highly reflecting surfaces, i.e. where as much of the incoming energy as possible should be reflected into the specular direction; or low-scatter characteristics, i.e. where as little energy as possible must be scattered; or, low absorption surfaces, i.e. where as little energy as possible must be absorbed; or, ultrasurface surfaces.

The following examples further illustrate the invention. All parts and percentages are by weight, unless otherwise specified.

EXAMPLE I

A disc-shaped piece of aluminum (diam.=1½") coated to a thickness between 0.004 and 0.005 inch with a nickel coating, formed by the process known and practiced under the trademark "Kanigen," was used. After coating, the sample was heat treated at 250° F. for one hour.

Nickel nitrate crystals, Ni(NO₃)₂·6H₂O, were used as both a source of zero-valent nickel (Ni⁰) and a source of ionic nickel (Ni⁺⁺).

A source of zero-valent nickel was prepared by placing nickel nitrate crystals in an evaporating dish on a Lab-Line, Pyromagnestr, Ser. No. 1168, hot plate set at its highest setting. Heating was continued to the point where the crystals went through a transition in appearance from a crystalline material to a viscous liquid. At this point, evolution of a nitrogen dioxide began. Heating continued, and as the material became harder, it was crushed with a pestle until a fine black powder resulted. At this point, the hot plate was turned off and the powder allowed to cool.

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About 25 cubic centimeters of the black powder, 3-4 drops of nitrobenzene, and 15-20 drops of distilled water were combined to form a black suspension which was used for application to the nickel coating substrate.

A source of ionic nickel (Ni^{++}) was produced by filling a 300 ml. beaker half full with nickel nitrate crystals and covering them with distilled water. The mixture was placed on the hot plate and heated until the liquid boiled. As the mixture continued to boil, more nickel nitrate crystals were added. It was noted that a haze formed on top of the viscous liquid. A viscous, green liquid was formed, and subsequently became a hard residue. Heating and stirring continued until a granular paste formed, which was removed from the hot plate and cooled. A hard, green residue resulted. This residue was in turn placed in distilled water and boiled down again. Approximately 50 cubic centimeters of the resulting green residue was added to 25 ml. of distilled water in a beaker. Upon mixing, a yellowish suspension formed which was suitable for application to the substrate.

Three to four drops of the black suspension were placed on the sample's surface. Polishing began, using a Politex Supreme cloth, and continued for about ten minutes. Light finger pressure was used to move the cloth across the sample's surface at approximately two revolutions per second. During polishing, the surface was kept wet by applying small amounts of distilled water, as required.

Subsequently, 3-4 drops of the yellowish suspension were applied to the sample, and the same type of polishing began. After approximately ten minutes, a low-scatter coating was obtained.

The low-scatter surface was evaluated and found to scatter 20 p.p.m. of incident light in the test as defined above.

EXAMPLE II

The procedure of Example I was used to form a black suspension of ionic nickel.

A suspension of latent zero-valent nickel was prepared by combining 20 ml. of distilled water, 15-20 drops of nitrobenzene, and one gram of nickelocene. The mixture was agitated and heated to 150-160° F. to expedite formation of the emulsion.

The remaining procedure was that of Example I.

A low-scatter nickel surface was obtained which scattered 6 p.p.m. of incident light in the test defined above.

EXAMPLE III

A molybdenum substrate might also be used. The procedure of Example I would be followed using molybdenum hexacarbonyl as a source of latent zero-valent molybdenum. Similarly, molybdenum oxalate would be used as

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a source of ionic molybdenum. Because molybdenum hexacarbonyl decomposes at a relatively high temperature, it is advantageous to heat the sample while it is being polished with this material.

What is claimed is:

1. A method for producing a low-scatter or ultra-smooth surface on a metal substrate, comprising:
 - (a) polishing the surface of said metal substrate in the presence of a source of the substrate metal in zero-valent or latent zero-valent state;
 - (b) also polishing the surface of said substrate in the presence of a source of the substrate metal in an ionic state; and,
 - (c) continuing said polishing until the desired surface is obtained.
2. A method of claim 1 wherein said metal substrate comprises nickel.
3. A method of claim 2 wherein said source of metal in a zero-valent or latent zero-valent state comprises nickel nitrate or nickelocene.
4. A method of claim 3 wherein the source of metal in an ionic state comprises nickel nitrate.
5. A method of claim 4 wherein said substrate is polished with a soft, smooth, resilient polishing cloth.
6. A method of claim 1 wherein said metal substrate comprises molybdenum.
7. A method of claim 6 wherein said source of metal in a zero-valent state comprises molybdenum hexacarbonyl.
8. A method of claim 7 wherein said source of metal in an ionic state comprises molybdenum oxalate.

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RALPH S. KENDALL, Primary Examiner

J. R. BATTEN, JR., Assistant Examiner

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