NOBLE METAL-PLATED ARTICLE, ORNAMENTAL JEWELLERY AND METHODS FOR STORAGE THEREOF

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a noble metal-plated article, ornamental jewellery, methods for the storage thereof and packages accommodating the same. More particularly, it pertains to a noble metal-plated article which is treated so as to suppress the corrosion of its substrate metal and underlying metal and prevent the deterioration of its bonding properties and external appearance, ornamental jewellery which is treated so as to prevent the deterioration of its gloss and color change, a method for the storage of any of the noble metal-plated article and the ornamental jewellery for the purpose of carrying out the above-mentioned treatment and a package of any of the noble metal-plated article and the ornamental jewellery which is subjected to the above-mentioned treatment.

2. Description of the Related Arts

By the term "noble metal-plated article" as mentioned in the text of the specification is meant an article in which is employed, as the plating layer, so-called a noble metal such as gold, silver or an element belonging to the platinum group. The noble metal-plated article may be equipped, as the case may be, with a layer comprising a

metal which is baser than a plating metal, that is, a metal having an ionization tendency higher than that of the plating metal to form an underlying layer for the layer of a noble metal plating.

Both the aforesaid noble metal and the underlying metal (the metal used as an underlying layer) need not be pure, but an alloy may be used as well. The combination of the noble metal/underlying metal which constitutes the present invention is typified by but not limited to gold/nickel, silver/copper, rhodium/nickel, and palladium/nickel. The aforesaid combination is exemplified by an electrode, an electronic part having an electrode, or the like which is concerned with microjoint of an electronic part, especially a semiconductor element such as LC and LSI in an electronic industry and which comprises a thin plating layer of a noble metal and an underlying layer of a metal that is baser than the noble metal and is provided as the case may be.

On the other hand, examples of the ornamental jewellery as mentioned in the present invention include an article such as finger ring, breast pin, bracelet, earring, pierced earring, pendant, hair ornament, tie clip, cuff button, watch, clock, spectacles, crown, stick, sword and ornament for alcove, which article is ornamented with a noble metal, is combined with a jewel, a pearl, coral, ivory, tortoiseshell or the like, or is ornamented with a noble metal along with a jewel, a pearl, coral, ivory,

tortoiseshell or the like. The ornamental jewellery according to the present invention is not limited to these finished products, but includes a work in process, a part and a material for the above-mentioned article.

A noble metal is widely used as a plating metal for ornaments and electronic parts, since it is less apt to undergo a chemical change and thus is stable; and besides imparted with beautiful gloss and high electronic conductivity. However, the thickness of a noble-metal plating layer is suppressed to an irreducible minimum requirement from the economical point of view because of its expensiveness. There is no problem with a noble-metal plating layer when having a sufficient thickness owing to its being inherently stable, whereas several problems are caused when the plating layer is thinned. Specifically, as a noble-metal plating layer becomes thin, pinholes are liable to appear in the plating layer, thus increasing the exposure of a substrate metal or an underlying metal. Accordingly, even if the noble metal itself is not subjected to a chemical change, the substrate metal or the underlying metal which is exposed to the atmosphere is directly oxidized, or when the plating layer is covered with a micro water film, corrosion of the substrate metal or the underlying metal proceeds by the galvanic action between the different metals, that is, between the noble metal and the exposed substrate metal or the exposed underlying metal which is baser than the noble metal. Such

galvanic corrosion leads to discoloration of the plated surface and deterioration of the gloss thereof and, in the case of an electronic part, deterioration of bonding property between the metals.

An ordinary electrode of an electronic part is frequently composed of gold as the plated surface layer consisting of a noble metal and nickel as the underlying layer consisting of a metal baser than the plating metal. There are used, as a method for plating gold, an electroless plating method, a reduction type electroless plating method and substitutional electroless plating method (commonly called flash plating method). In industrial application of plating, it is thought that the bonding property is improved with an increase in the thickness of plated gold, and it has been generally said that an electrode plated with gold in a thickness of more than 1 μm causes no problem in bonding property. However, the electrode is directed to that having a gold plating thickness of 1 μm or less because of an economical disadvantage in using expensive gold for thick plating. Nevertheless, gold plating with a thickness of 1 μm or less is liable to be affected by the storage environment. Moreover, as the gold plating gets thinner and thinner, the underlying metal is corroded, accompanied by discoloration and deterioration of the bonding property, thereby lowering the market value of the product or sometimes making the product unable to withstand practical use. The use of a

substitutional electroless plating method enables the formation of an electrode having extremely thin gold plating of thinner than 0.1 μm at a further low cost.

However, the extremely thin gold plating is not generally put into practical application at the present time, since it accelerates the corrodible deterioration of the underlying metal and thus causes discoloration and remarkable decrease in bonding properties of the plating. Under such circumstances, it has been desired in electronic industries to realize thin inexpensive gold plating having favorable bonding properties.

With regard to an electronic industry in recent years for example, wire bonding and wireless bonding are frequently employed as a means for forming an electrical bond between a semiconductor element and an electrode plated with a noble metal in a wiring board. The material for wiring in wire bonding is usually gold or aluminum in the form of wire. For particularly high density wiring, a wire having a diameter of 25 to 30 μm is generally used in many cases. In order to realize favorable bonding properties in wire bonding, several attempts have been made as disclosed in Japanese Patent Application Laid-Open No. 74200/1995 including improvement in the wire itself; Japanese Patent Application Laid-Open No. 294474/1989 including improvement in the wire preservation system; Japanese Patent Application Laid-Open No. 95527/1989 including improvement in wire bonding equipment; Japanese

Patent Application Laid-Open No. 21437/1993 including improvement in bump forming equipment in wireless bonding procedure; and the like. Although some improvements have been made on the wire and wire bonding equipment, a sufficient improvement has not heretofore been made on the further protection of an electrode portion, since the electrode is frequently plated thereon with a noble metal less prone to be corroded such as gold. As a countermeasure against corrosion of the surfaces of electrodes, inert gas filling or drying with a desiccant is partly carried out. However, the aforesaid countermeasures suffer the disadvantages in that inert gas filling requires an expensive filling apparatus, thus causing a problem of cost, that it is difficult to completely replace the atmosphere in a vessel with an inert gas, and that a desiccant removes only moisture in the environmental atmosphere, thus leading to insufficient countermeasure against corrosion. Such being the case, there has heretofore been unavailable a noble metal-plated article which is capable of readily and sufficiently suppressing the corrosion of the substrate metal and underlying metal, preventing discoloration and deterioration of bonding properties, and thus is satisfactory in every respect.

On the other hand, in the case where ornamental jewellery is thinly plated with a noble metal or a metal is bonded to or in contact with another metal in ornamental jewellery, corrodible deterioration due to galvanic action

between the different metals bonded to each other takes place during long-term storage. Such galvanic corrosion gives rise to discoloration of the surfaces of the noble metal and deterioration of the gloss thereof. In the case where a noble metal contains an element prone to oxidation such as copper in a K18 gold having a composition by weight consisting of 75% of gold, 15% of silver and 10% of copper, the element prone to oxidation oxidizes during long-term storage, thereby causing discoloration of the surfaces and deterioration of the gloss thereof. A pearl and coral, which contain a calcium compound as a principal component, react with oxygen and moisture in the atmospheric air at a very low rate, and finally lose the gloss of the surfaces and the values as ornamental jewellery in may cases after long-term storage. As countermeasures for preventing such quality degradation due to deterioration of ornamental jewellery, inert gas filling or drying with a desiccant is carried out. Nevertheless, the above-mentioned countermeasures suffer the disadvantages in that inert gas filling requires an exclusive filling apparatus, thus causing a problem of cost, that it is difficult to completely replace the atmosphere in a vessel with an inert gas, and that a desiccant removes nothing but moisture in the storage environment, thus leading to insufficient countermeasure against such quality degradation. It being so, there has heretofore been unavailable completely satisfactory ornamental-jewellery which is capable of

readily and sufficiently suppressing the deterioration thereof and preventing the discoloration and loss of gloss thereof.

SUMMARY OF THE INVENTION

It is general object of the invention to provide, under such circumstances, an article plated with a noble metal in a small plating thickness which article is treated so as to suppress the corrosion of its substrate metal and underlying metal and prevent the deterioration of its bonding properties and external appearance.

It is another object of the invention to provide ornamental jewellery which is treated so as to prevent the deterioration of its gloss and color change.

It is a further object of the invention to provide a method for the storage of any of the noble metal-plated article and the ornamental jewellery for the purpose of carrying out the above-mentioned treatment.

It is a still further object of the invention to provide a package of any of the noble metal-plated article and the ornamental jewellery which is subjected to the above-mentioned treatment.

As a result of intensive research and investigation accumulated by the present inventors in order to attain the above-mentioned objects, it has been found that the objects can be attained by enclosing any of an article plated with a noble metal in a thickness of at most 1 μm and ornamental jewellery together with a dehumidifying agent

and an oxygen absorbent not requiring moisture for absorbing oxygen in a vessel with gas barrier properties, and that the objects can be attained by packaging any of said article and said jewellery together with said agent and said absorbent with a packaging material with gas barrier properties. The present invention has been accomplished by the aforestated finding and information.

Specifically the present invention provides

(1) an article plated with a noble metal characterized in that said article has a plating layer in a thickness of at most 1 μm and is enclosed together with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, in a vessel with gas barrier properties;

(2) ornamental jewellery characterized in that said jewellery is enclosed together with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, in a vessel with gas barrier properties;

(3) a method for the storage of an article plated with a noble metal which comprises enclosing an article plated with a noble metal in a plating thickness of at most 1 μm along with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, in a vessel with gas barrier properties;

(4) a method for the storage of ornamental jewellery which comprises enclosing ornamental jewellery along

with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, in a vessel with gas barrier properties;

(5) a package which comprises an article plated with a noble metal in a plating thickness of at most 1 μm, said article along with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, being packaged by the use of a packaging material with gas barrier properties; and

(6) a package which comprises ornamental jewellery, said jewellery along with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, being packaged by the use of a packaging material with gas barrier properties.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic drawing showing one example of wire bonding practice, in which the symbols A, B, C, D and E are each the position relating to the fracture modes A, B, C, D and E, respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The oxygen absorbent to be used in the present invention is not specifically limited provided that it does not require moisture for absorbing oxygen, and is exemplified by an oxygen absorbent comprising an unsaturated fatty acid, a chain hydrocarbon polymer having an unsaturated group, or a thermoplastic polymer such as polyamide and polyolefin as a principal component, and an

oxygen absorption promoting substance such as a transition metal salt. Of these, is particularly preferable an oxygen absorbent comprising both or either of an unsaturated fatty acid and a chain hydrocarbon polymer having an unsaturated group as a principal compound, and an oxygen absorption promoting substance.

Examples of the unsaturated fatty acid to be used as an oxygen absorbent preferably include an unsaturated fatty acid having at least 10 carbon atoms as well as a double bond between carbon atoms, a salt of said unsaturated fatty acid and an ester thereof. The above-mentioned unsaturated fatty acid, a salt thereof and an ester thereof may each have a substituent group such as hydroxyl group and formyl group. The aforesaid unsaturated fatty acid is not necessarily required to be a single substance, but may be employed in combination with at least one other to form a mixture.

Examples of the foregoing unsaturated fatty acid include an unsaturated fatty acid such as oleic acid, linoleic acid, linolenic acid, arachidonic acid, parinaric acid, dimer acid and ricinoleic acid, an ester thereof, a metallic salt thereof, and a fat and oil each containing said ester.

As the usable unsaturated fatty acid, mention is also made of a fatty acid produced from any of an animal oil and a vegetable oil such as linseed oil, soybean oil, tung oil, bran oil, sesame oil, cotton seed oil, rapeseed oil and

tall oil.

In addition, examples of the aforesaid chain hydrocarbon polymer having an unsaturated group preferably include a polymer having at least 10 carbon atoms as well as at least one double bond between carbon atoms and a derivative thereof. The derivative may have a substituent group such as hydroxyl group, amino group, formyl group and carboxyl group. The chain hydrocarbon polymer having an unsaturated group is specifically exemplified by an oligomer and a polymer of any of butadiene, isoprene and 1,3-pentadiene, and is not necessarily required to be a single compound, but may be a copolymer or in the form of a mixture of at least two polymers. The chain hydrocarbon polymer having an unsaturated group is not necessarily required to be pure, but is permitted to contain, within a reasonable limit, a small amount of impurities such as a solvent which is possibly mixed therein at the time of production.

The aforementioned oxygen absorption promoting substance which is employed in combination with the principal component such as the unsaturated fatty acid or chain hydrocarbon polymer having an unsaturated group is exemplified by a metallic salt and a radical initiator each promoting the oxidation of an organic compound. As the metallic salt, there is preferably usable a salt of a transition metal such as Cu, Fe, Co, Ni, Cr and Mn. As the salt of a transition metal, there are preferably usable a

naphthenic acid salt of a transition metal, an unsaturated fatty acid salt of a transition metal, etc.

In the case where the principal components in the oxygen absorbent and the oxygen absorption promoting substance is in the form of liquid, it is preferable that these components be supported on a carrier substance, which is exemplified by paper made of natural pulp, synthetic paper made of synthetic pulp, nonwoven fabric, porous film, silica-gel, alumina, activated carbon, synthetic zeolite such as molecular sieve, natural zeolite such as mordenite and ericonite and clayey mineral such as perlite and activated clay. It is also a practical usage to select the carrier substance from the substances that are selected as a dehumidifying agent or an acidic gas absorbent which will be described hereinafter to impart dehumidifying or acidic gas absorbing performance to the carrier substance.

With regard to the proportion of each of the components in the oxygen absorbent, the oxygen absorption promoting substance is contained preferably in an amount of from 0.01 to 40 parts by weight based on 100 parts by weight of the principal component, and the carrier substance, when used, is contained preferably in an amount of from 1 to 1000 parts by weight based on the same.

The dehumidifying agent to be used in the present invention is exemplified by paper made of natural pump, synthetic paper made of synthetic pulp, silica-gel, alumina, activated carbon, synthetic zeolite such as molecular sieve,

natural zeolite such as mordenite and ericonite, perlite, activated clay, quick lime, barium oxide, calcium chloride, barium bromide, calcium hydride, calcium sulfate, magnesium chloride, magnesium oxide, magnesium sulfate, aluminum sulfate, sodium sulfate, sodium carbonate, potassium carbonate and zinc chloride.

It is also a practical usage to select the dehumidifying agent from the substances that are selected as an oxygen absorbent carrier or an under-mentioned acidic gas absorbent to impart dehumidifying performance thereto. The above-mentioned carrier substance or acidic gas absorbent, when selected from substances imparted with dehumidifying function, does not make it always necessary to freshly incorporate a dehumidifying agent. The dehumidifying agent is not necessarily required to be a single substance, but may be used in combination with at least one other to form a mixture.

The acidic gas absorbent, which may be used, when desired, along with the aforesaid oxygen absorbent and dehumidifying agent in the present invention needs only be a substance capable of absorbing or adsorbing an acidic substance present in a hermetically sealed atmosphere without specific limitation, and is exemplified by paper, synthetic paper, a synthetic resin, porous material including synthetic zeolite such as molecular sieve, natural zeolite such as mordenite and erionite, and activated carbon, an oxide, hydroxide, carbonate or organic

acid salt of an alkali metal or an alkaline earth metal, and an organic amine.

It is also a practical usage to select the acidic gas absorbent from the substances that are selected as an oxygen absorbent or a dehumidifying agent to impart acidic gas absorbing performance thereto. The aforesaid oxygen absorbent carrier or dehumidifying agent, when selected from substances imparted with acidic gas absorbing function, does not make it always necessary to freshly incorporate an acidic gas absorbent. The acidic gas absorbent is not necessarily required to be a single substance, but may be used in combination with at least one other to form a mixture.

The amount of the oxygen absorbent to be used in the present invention need only be an amount capable of absorbing at least the oxygen in the space volume of a hermetically sealed vessel having gas barrier properties, preferably an amount 1.1 to 10 times the said amount. Likewise, the amount of the dehumidifying agent to be used therein need only be an amount capable of absorbing at least the moisture in the space volume of the aforesaid vessel, preferably an amount 1.1 to 500 times the said amount, and is suitably selected according to the gas barrier performance of the hermetically sealed vessel having gas barrier properties.

It is possible in the present invention to use the oxygen absorbent, dehumidifying agent and acidic gas

absorbent each individually or as a mixture with one another in the form of powder, granule, tablet, sheet or the like in accordance with the situations. It is unfavorable to bring any of the oxygen absorbent, dehumidifying agent and acidic gas absorbent into direct contact with the material to be preserved in the vessel. Accordingly, it is usually used in the form of package in which the absorbent or the agent is packed with a well known air permeable packing material composed of, for example, paper or nonwoven fabric as a base material. The oxygen absorbent may be packed in part or in whole along with either or both of the dehumidifying agent and the acidic gas absorbent, or may be individually packed. The package is not specifically limited in its form, packaging material and constitution, but may be in the form of small bag, sheet or blister (bubble) package according to the purpose of use. In addition, it is possible as a dust-proof measure to duplicate the package by further covering the aforementioned package with a dust-proof packaging material which does not hinder the permeability of oxygen, moisture and acidic gas nor discharge the dust generated from the package outside the duplicate package. However, in the case where dust-proof measure is taken for the package itself, the package need not be covered with a dust-proof packaging material.

The article plated with a noble metal according to the present invention is constituted of an article plated

with a noble metal which article is enclosed along with the above-mentioned oxygen absorbent and dehumidifying agent, and the acidic gas absorbent when desired, in a vessel having gas barrier properties. The method for the storage of the article plated with a noble metal according to the present invention comprises enclosing said article along with the above-mentioned oxygen absorbent and dehumidifying agent, and the acidic gas absorbent when desired, in a vessel having gas barrier properties. The package of the article plated with a noble metal according to the present invention comprises a package in which the aforesaid article along with the above-mentioned oxygen absorbent and dehumidifying agent, and the acidic gas absorbent when desired, are packaged with a packaging material having gas barrier properties.

The aforestated article plated with a noble metal is an article having a plating layer comprising a noble metal such as gold, silver or an element belonging to the platinum group on a substrate metal or an underlying metal which is placed thereon as necessary. Both the noble metal and the underlying metal which is placed as necessary need not be pure, but an alloy may be used as well. The combination of the plating metal/underlying metal in the present invention need only be constituted of a plating metal and an underlying metal which is baser than the plating metal, and is exemplified by but not limited to gold/nickel, silver/copper, rhodium/nickel and

palladium/nickel. The article plated with a noble metal according to the present invention has a plating layer of the noble metal in a thickness of at most 1 μm, preferably at most 0.1 μm.

The article plated with a noble metal as mentioned above need only be imparted with the aforesaid properties without specific limitation, and is exemplified preferably by an electrode and an electronic part having an electrode.

In the article plated with a noble metal, the method for the storage thereof and the package thereof each according to the present invention, the article plated with a noble metal along with the oxygen absorbent and the dehumidifying agent, and the acidic gas absorbent as desired is enclosed in a vessel with gas barrier properties, or is packaged with a packaging material having gas barrier properties. It is preferable in this case that the article be enclosed therein or packaged therewith immediately after the plating step in particular. The oxygen concentration during the storage in the vessel or the package is preferably at most 5%, more preferably at most 1%, still more preferably at most 0.1%. In addition, the moisture in terms of relative humidity during the storage in the vessel or the package is preferably at most 10%, more preferably at most 5%, still more preferably at most 1%.

In the case where the oxygen concentration or the moisture is higher than the above higher limit, respectively, corrodible deterioration is liable to take

place in the substrate metal and/or the underlying metal which is baser than the noble metal as the plating layer, whereby the color change and deterioration of bonding properties of the article are brought about, thus causing a fear of lowering in the product value and/or incapability of no longer standing the practical use.

As the above-mentioned enclosed vessel or packaging material each having gas barrier properties, there are preferably used according to the purpose of use, for example, a plastics vessel, a film bag, a metallic vessel, a glass vessel and the like each having high gas barrier properties. In the case of sufficiently long enclosing or packaging period, there is no denying that during storage, oxygen and water vapor permeate in the enclosed vessel or package each having gas barrier properties, thereby increasing the concentrations of oxygen and moisture in the vessel or package. With regard to a film bag as an example, there is usable a material having poor gas barrier properties such as polyethylene, polypropylene and nylon thread, provided that the enclosure period of time is relatively short. On the other hand in the case of long-term enclosure, there is need for the use of a material enhanced in gas barrier properties such as aluminum foil and silicon oxide vapor deposited material. The value of the gas barrier properties of the hermetically sealed vessel having gas barrier properties is usually preferably 10 mL (milliliter)/m^2 · day · atm or less expressed in terms

of oxygen permeability at 25°C, 60% RH (relative humidity) and 1 g/m^2 · day or less expressed in terms of water vapor transmission rate at 40°C, 90% RH. At the time of enclosing a noble metal-plated article in a vessel by hermetically sealing the vessel, or packaging the article with a packaging material, the atmosphere in the vessel or package may be replaced with a dry inert gas such as nitrogen and argon, as the replacement with the gas preferably leads to a decrease in the use amounts of the oxygen absorbent and dehumidifying agent, especially the use amount of the oxygen absorbent.

It is preferable that the noble metal-plated article be enclosed or packaged from the time immediately after the plating treatment with a noble metal to the time immediately before the use of the article, for example, the time immediately before carrying out bonding or the like.

On the other hand, the ornamental jewellery according to the present invention is constituted of ornamental jewellery which is enclosed along with the above-mentioned oxygen absorbent and dehumidifying agent, and the acidic gas absorbent when desired, in a vessel having gas barrier properties. The method for the storage of the ornamental jewellery according to the present invention comprises enclosing said ornamental jewellery along with the above-mentioned oxygen absorbent and dehumidifying agent, and the acidic gas absorbent when desired, in a vessel having gas barrier properties. The package of the ornamental

jewellery according to the present invention comprises a package in which the aforesaid ornamental jewellery along with the above-mentioned oxygen absorbent and dehumidifying agent, and the acidic gas absorbent when desired, is packaged with a packaging material having gas barrier properties.

Examples of the ornamental jewellery as mentioned above include an article such as finger ring, breast pin, bracelet, earring, pierced earring, pendant, hair ornament, tie clip, cuff button, watch, clock, spectacles, crown, stick, sword and ornament, which article is ornamented with a noble metal, is combined with a pearl, coral, ivory, tortoiseshell, an expensive jewel or the like, or is ornamented with a noble metal along with a jewel, a pearl, coral, ivory, tortoiseshell or the like. The ornamental jewellery according to the present invention is not limited to these finished products, but includes a work in process, a part and a material for the above-mentioned article.

The ornamental jewellery comprises one or more components from among a noble metal, a pearl, coral, ivory, tortoiseshell and a jewel, which component alone or in combination with one another, is used or processed for ornament. Examples of the noble metal to be employed include gold, silver, platinum and rhodium. The noble metal need not be pure, but may be an alloy or in the form of a noble metal-plated article. The jewel need only be a mineral serviceable as an ornament (natural jewel) which is

provided simultaneously with external beauty, physical hardness and rareness in production. The jewel may also be an artificial jewel which is made from the same substance as in the natural jewel satisfying the above-mentioned requirements. The jewel is typified by diamond, ruby, sapphire, emerald, topaz, alexandrite, garnet, opal, zircon, and the like.

In the ornamental jewellery, the method for the storage thereof and the package thereof each according to the present invention, the ornamental jewellery along with the oxygen absorbent and the dehumidifying agent, and the acidic gas absorbent as desired is enclosed in a vessel with gas barrier properties, or is packaged with a packaging material having gas barrier properties. The oxygen concentration in the vessel or the package is preferably at most 5%, more preferably at most 1%, still more preferably at most 0.1%. In addition, the moisture in terms of relative humidity in the vessel or the package is preferably at most 10%, more preferably at most 5%, still more preferably at most 1%. In the case where the oxygen concentration or the moisture is higher than the above higher limit, there arises a fear of causing discoloration of the ornamental jewellery and the deterioration of the product value.

As the above-mentioned vessel or packaging material each having gas barrier properties, there are preferably used according to the purpose of use, for example, a

plastics film bag, a plastics bag, a metallic vessel, a glass vessel and the like. In the case of long-term storage, the vessel and the packaging material are preferably enhanced in gas barrier properties. In addition, it is desirable that the vessel and the packaging material be made of a transparent material with gas barrier properties so that the ornamental jewellery as the content therein can be visually confirmed from the outside thereof. It is also a practical usage in the case of an opaque material to combine it partially with a transparent material having gas barrier properties.

Suitable materials for plastics film bags include metallic foil such as aluminum foil and a laminate film having high gas barrier properties onto which silicon oxide or aluminum oxide is vapor-deposited. For example, silicon oxide vapor-deposited laminate film is useful as it is enhanced in gas barrier properties and transparent, thereby enabling visual confirmation of the content therethrough. In the case where it is necessary to visually confirm the content in an opaque bag such as a bag made of an aluminum foil film, it is also a practical usage to combine it partially with a transparent material having gas barrier properties. The film bag may be hermetically sealed by heat sealing the openings or by sealing the internal edges of the opening by the use of an adhesive, which has preferably favorable gas barrier properties. On the other hand, in the case where a film bag is repeatedly used owing

to ornamental jewellery being frequently taken out and put back, the film bag may be hermetically sealed by using a clip.

Preferably the plastics film bag has gas barrier properties of 20 $mL/m^2 \cdot day \cdot atm$ or less expressed in terms of oxygen permeability at 25°C, 60% RH and 5 $g/m^2 \cdot day$ or less expressed in terms of water vapor transmission rate at 40°C, 90% RH.

In the case of using a plastics vessel, a metallic vessel or a glass vessel other than a film bag, the form or shape of the vessel is not necessarily limited, but may be circular or rectangular in the cross section. The vessel is enclosed preferably by putting a lid on the vessel opening, more preferably by tightly fitting a lid with the opening. The constructional material of the vessel may be different from that of the lid. Examples of the vessel include a tea canister, a lidded metallic canister, a screwed metallic canister, a lidded plastics vessel, a screwed plastics vessel, a lidded glass vessel and screwed glass vessel. In order to maintain airtightness at the hermetically sealed portion of the vessel, it is also a practical usage to apply a gasket, an O-ring, a packing or the like each for airtightness to the sealed portion; to stick metallic foil or a sealing tape having as the substrate, a metal vapor deposited plastics film; or to hermetically seal with an adhesive. Likewise, in the case of a vessel made of an opaque material such as a metallic

canister, it is a practical usage to combine such material partially with a transparent material having gas barrier properties so as to facilitate the visual confirmation of the ornamental jewellery in external appearance.

The gas barrier properties to be imparted to the plastics vessel, metallic vessel and glass vessel depend upon gas permeation through the vessel itself, leakage from the fitted part between the vessel body and its lid. Preferably the aforesaid vessels have each gas barrier properties of 5 mL/liter · day · atm or less expressed in terms of the amount of oxygen permeation into the vessel per unit volume thereof at 25°C, 80% RH and 0.3 g/liter · day expressed in terms of water vapor transmission.

In the case of enclosing a tray, cloth or paper material with the ornamental jewellery to be hermetically sealed in a vessel or packaged with a packaging material, it is preferable to use a material which has low hygroscopicity or is thoroughly dry. Moreover, the atmosphere in the vessel or package may be replaced with a dry inert gas such as nitrogen and argon, as the replacement with such a gas preferably leads to a decrease in the use amounts of the oxygen absorbent and dehumidifying agent, especially the use amount of the oxygen absorbent.

According to the present invention, it is made possible to readily provide, by means of a simplified treatment, an article plated with a noble metal in a small

plating thickness which article is suppressed in the corrosion of its substrate metal and underlying metal and is free from the deterioration of its bonding properties and external appearance as well as ornamental jewellery free from the deterioration of its gloss and color change.

In the following, the present invention will be described in more detail with reference to comparative examples and working examples, which however shall not limit the present invention thereto.

Example 1

(1) Preparation of gas absorbent package

A gas absorbent package (hereinafter referred to simply as "gas absorbent") was prepared by packing a mixture of 5 g of an oxygen absorbent which had been formulated in the following manner and 2.5 g of quick lime as a dehumidifying agent and acidic gas absorbent in a small paper bag laminated inside with a polyethylene film having many eyes of needle (inside dimension of 5 cm by 7.5 cm) and by covering the bag containing the mixture with a dust-free packaging material not hindering the permeation of oxygen and moisture. The aforesaid oxygen absorbent had been prepared by mixing 100 parts by weight of soybean oil selected as an unsaturated organic compound as well as the principal component and 2 parts by weight of cobalt naphthenate having a cobalt content of 8% by weight selected as an oxygen absorption promoting agent to form a mixture, adding 350 parts by weight of natural zeolite

(mordenite) to the resultant mixture, blending the resultant product with a blender and allowing the blended product to stand at 25°C for 10 minutes to produce powdery granule having fluidity.

(2) Preservation of gold-plated test pieces

A gold-plated test piece was prepared for use as a simulation product of an electronic part having a gold-plated electrode by subjecting a tough pitch copper substrate having a size of 10 mm × 60 mm × 0.5 mm to electroplating with nickel in 2 μm thickness and then to flash plating with gold in 0.05 μm thickness. The gold-plated test piece thus prepared and one pack of the gas absorbent prepared in the above item (1) along with 500 mL of air (25°C, 75% RH) were placed in a packaging bag having a size of 220 mm × 300 mm made of a laminate material of aluminum foil (oriented polypropylene/aluminum foil/polyethylene) (hereinafter referred to as "aluminum bag"). The aluminum bag was hermetically sealed by sealing its opening and allowed to stand for one month in an atmosphere at 60°C and 95% RH. Measurements were made of the oxygen concentration and humidity in the aluminum bag which had been preserved for a period of one month by means of gas chromatography. As a result, it was confirmed that the preservation system had been maintained in a state substantially free from oxygen and moisture.

(3) Evaluation of wire bonding

Wire bonding was carried out on the aforesaid gold-

plated test piece after the preservation by the use of a ball bonder (Model 4124, produced by Kulicke & Soffa Industries Inc.) under the conditions including a temperature of 120°C, a bonding load of 80 g, a supersonic wave output of 0.5 W, a bonding time of 50 msec and gold wire of 30 μm in diameter. Then, evaluations were made of the bonding properties of 20 numbers of wire bonding results by the measurement of the vertical tensile strength of wires, which was carried out by the use of a wire bond pull tester (Model UP-1, measurable range of from 2 g to 15 g, produced by Think Corp.) to evaluate the features of the fractured bonding wire portion (fracture mode) and the strength at the time of fracture.

Features of fractured portion	Fracture mode	Evaluation of bonding properties
peeling from the interface of 1st bond	A	×
fracture at loop rising portion	B	△
cut of loop midway	C	○
cut at 2nd bond neck	D	△
peeling from 2nd bond	E	×

Remarks: ○: good bonding
△: somewhat poor bonding
×: poor bonding

The evaluation results are given in Table 1. The

results of all the 20 numbers of wire bonds after one month of preservation were same as the results of bonds at the initial stage prior to the preservation (tensile strength of at least 15 g, and fracture mode of C). Thus it has been confirmed that the bonding properties of the gold-plated surfaces were maintained.

Examples 2 and 3

The procedure in Example 1 was repeated to carry out preservation and wire bonding evaluation thereof except that the thicknesses of gold plating in gold-plated test pieces were altered, respectively as shown in the following:

	Thickness of gold plating	
Example 1	0.05 μm	flash plating
Example 2	0.5 μm	electroplating
Example 3	3.0 μm	electroplating

The evaluation results are given in Table 1. The results of all the 20 numbers of wire bonds in each example after one month of preservation were same as the results of the bonds at the initial stage prior to the preservation (tensile strength of at least 15 g, and fracture mode C). Thus it has been confirmed that the bonding properties of gold-plated surfaces were maintained.

Comparative Examples 1 to 3

Gold-plated test pieces same as those that had been

used in Examples 1 to 3 were each allowed to stand for one month in an atmosphere at 60°C and 95% RH without being housed or enclosed in a vessel having gas barrier properties, and subjected to the evaluation tests same as those in Example 1. The results are given in Table 1. In much of the bonds in Comparative Example 1 were observed decrease in strength, fracture mode "E" and deterioration of bonding properties. In Comparative Example 3, no problem was found on account of the gold plating as thick as 3 μm, the results of wire bonds after the preservation were same as those at the initial stage prior to the preservation, and thus it has been confirmed that the bonding properties of gold-plated surfaces were maintained. On the contrary, in Comparative Example 2 in which the gold-plating was 0.5 μm thick, much of the bonds were evaluated as fracture mode "B" and besides tensile strength was somewhat lowered.

Table 1-1

		Initial value	Example 1	Example 2	Example 3
Gold plating thickness (μm)		-	0.05	0.5	3.0
Bag inside after one month					
Oxygen concentration (%)		-	0.03	0.03	0.03
Humidity (% RH)		-	<1	<1	<1
Vertical tensile strength					
Number of accepted wire bonds (number)		20	20	20	20
Average strength of rejected pieces (g)		-	-	-	-
Fracture mode	A	0	0	0	0
(distribution from among 20 pieces)	B	0	0	0	0
	C	20	20	20	20
	D	0	0	0	0
	E	0	0	0	0
Evaluation for bonding properties		○	○	○	○
External appearance after preservation		-	unchanged	unchanged	unchanged

Remarks: ○ good bonding

△ somewhat poor bonding

× poor bonding

Initial value is common to each of test pieces.

Table 1-2

		Initial value	Comparative Example 1	Comparative Example 2	Comparative Example 3
Gold plating thickness (μm)		-	0.05	0.5	3.0
Bag inside after one month Oxygen concentration (%) Humidity (% RH)		 - -	Exposed to preservation atmosphere	Exposed to preservation atmosphere	Exposed to preservation atmosphere
Vertical tensile strength Number of accepted wire bonds (number) Average strength of rejected pieces (g)		 20 -	 0 5	 5 10	 20 -
Fracture mode (distribution from among 20 pieces)	A	0	0	0	0
	B	0	1	9	0
	C	20	0	5	20
	D	0	3	4	0
	E	0	16	2	0
Evaluation for bonding properties		○	×	△	○
External appearance after preservation		-	gloss deterio-ration	unchanged	unchanged

Remarks: ○ good bonding

△ somewhat poor bonding

× poor bonding

Initial value is common to each of test pieces.

Comparative Examples 4 to 6

By the use of the gold-plated test pieces same as that which had been used in Example 1, the procedure in Example 1 was repeated to enclose test pieces in aluminum bags, and carry out preservation and wire bonding evaluation thereof except that in Comparative Example 4, a gold-plated test piece along with 10 g of silica-gel type A (produced by Fuji Davison Chemical Co., Ltd.) and 500 mL of air was enclosed in the bag; in Comparative Example 5, a gold-plated test piece along with a self-reaction type powdery iron-based deoxidizing agent capable of retaining moisture required for oxygen absorption reaction (Ageless Z-100PT, produced by Mitsubishi Gas Chemical Co., Inc.) and 500 mL of air was enclosed in the bag; and in Comparative Example 6, a gold-plated test piece along with 500 mL of air was enclosed in the bag without the use of a gas absorbent. The results are given in Table 2. In much of the bonds in Comparative Examples 4 to 6 were observed decrease in strength, fracture mode "E" and deterioration of bonding properties.

Table 2

		Initial value	Comparative Example 4	Comparative Example 5	Comparative Example 6
Gold plating thickness (μm)		-	0.05	0.05	0.05
Treatment of bag inside		-	non-treated	enclosed with desiccant	enclosed with moisture retention type powdery iron-based deoxidizing agent
Bag inside after one month					
Oxygen concentration (%)		-	21	21	0.05
Humidity (% RH)		-	70	5	85
Vertical tensile strength					
Number of accepted wire bonds (number)		20	0	0	0
Average strength of rejected pieces (g)		-	5	6	6
Fracture mode (distribution from among 20 pieces)	A	0	0	0	0
	B	0	2	2	3
	C	20	0	0	0
	D	0	3	4	3
	E	0	15	14	14
Evaluation for bonding properties		○	×	×	×
External appearance after preservation		-	gloss deterioration	gloss deterioration	gloss deterioration

Remarks: ○ good bonding △ somewhat poor bonding × poor bonding

Initial value is common to each of test pieces.

Examples 4 to 6

Gas absorbents were prepared in the same manner as in Example 1 except that the combination of the oxygen absorbent as the principal component and the oxygen absorption promoting substance was altered, respectively as shown in the following:

	Principal component in oxygen absorbent (100 parts by weight)	Oxygen absorption promoting substance (2 parts by weight)
Example 1	soybean oil	cobalt naphthenate
Example 4	fatty acid from tall oil	cobalt salt of fatty acid from tall oil 2)
Example 5	soybean oil	cobalt salt of fatty acid from tall oil
Example 6	soybean oil + liquid polyisoprene 1)	cobalt naphthenate

Remarks 1) mixture of soybean oil and liquid polyisoprene (produced by Japan Synthetic Rubber Co., Ltd. under the trade name Dinaclean R113 at a ratio by weight of 6:4.

Remarks 2) cobalt salt of fatty acid from tall oil having cobalt content of 6% by weight.

By the use of each of the above-prepared gas absorbents each having different combination of the oxygen absorbent as principal component and oxygen absorption promoting substance the procedure of Example 1 was repeated to carry out the preservation of the gold-plated test piece

and evaluation thereof. The evaluation results are given in Table 3. The results of all 20 numbers of wire bonds in each example after one month of preservation were same as the results of bonds at the initial stage prior to the preservation as is the case with Example 1. Thus it has been confirmed that the bonding properties of gold-plated surfaces were maintained.

Table 3

		Example 1	Example 4	Example 5	Example 6
Gold plating thickness (μm)		0.05	0.05	0.05	0.05
Oxygen absorbent					
Organic compound as principal component		Soybean oil	Fatty acid from tall oil	Soybean oil	Soybean oil+liquid polyisoprene
Oxygen absorption promoting substance		Cobalt naphthenate	Cobalt salt of fatty acid from tall oil	Cobalt salt of fatty acid from tall oil	Cobalt naphthenate
Bag inside after one month					
Oxygen concentration (%)		0.03	0.03	0.04	0.03
Humidity (% RH)		<1	<1	<1	<1
Vertical tensile strength					
Number of accepted wire bonds (number)		20	20	20	20
Average strength of rejected pieces (g)		-	-	-	-
Fracture mode (distribution from among 20 pieces)	A	0	0	0	0
	B	0	0	0	0
	C	20	20	20	20
	D	0	0	0	0
	E	0	0	0	0
Evaluation for bonding properties		○	○	○	○
External appearance after preservation		unchanged	unchanged	unchanged	unchanged

Remarks: ○ good bonding △ somewhat poor bonding × poor bonding

Initial value is common to each of test pieces.

Examples 7 & 8

Silver-plated test pieces were prepared for use as simulation products of electronic parts each having a silver-plated part by subjecting tough pitch copper substrates each having a size of 10 mm × 60 mm × 0.5 mm to electroplating with silver, while the thicknesses of silver plating were altered as shown in the following:

	Thickness of silver plating	
Example 7	0.9 μm	electroplating
Example 8	5.0 μm	electroplating

Then, the procedure in Example 1 was repeated to carry out preservation and wire bonding evaluation test thereof. The results are given in Table 4. The results of all wire bonds in each example after one month of preservation were same as the results of the bonds at the initial stage prior to the preservation (tensile strength of at least 15 g and fracture mode C). Thus it has been confirmed that the bonding properties of silver-plated surfaces were maintained.

Comparative Examples 7 & 8

Silver-plated test pieces same as those that had been used in Examples 7 & 8 were each allowed to stand for one month in an atmosphere at 60°C and 95% RH without being housed or enclosed in a vessel having gas barrier properties, and subjected to the evaluation tests same as

those in Example 1. The results are given in Table 4. In Comparative Example 8, no problem was found on account of the silver plating as thick as 5 μm, the results of wire bonds after the preservation were same as those at the initial stage prior to the preservation, and thus it has been confirmed that the bonding properties of silver-plated surfaces were maintained. On the contrary, in Comparative Example 7 in which the silver-plating was 0.9 μm thick, much of the bonds were evaluated as fracture mode "D", and besides tensile strength was lowered.

Table 4

		Initial value	Example 7	Example 8	Comparative Example 7	Comparative Example 8
Silver plating thickness (μm)		-	0.9	5.0	0.9	5.0
Bag inside after one month					Exposed to preservation atmosphere	Exposed to preservation atmosphere
Oxygen concentration (%)		-	0.03	0.03		
Humidity (% RH)		-	<1	<1		
Vertical tensile strength						
Number of accepted wire bonds (number)		20	20	20	3	20
Average strength of rejected pieces (g)		-	-	-	6	-
Fracture mode (distribution from among 20 pieces)	A	0	0		0	0
	B	0	0	0	2	0
	C	20	20	20	3	20
	D	0	0	0	10	0
	E	0	0	0	5	0
Evaluation for bonding properties		○	○	○	×	○
External appearance after preservation		-	unchanged	unchanged	gloss deterio-ration	unchanged

Remarks: ○ good bonding
△ somewhat poor bonding
× poor bonding
Initial value is common to each of test pieces.

Example 9

(1) Preparation of gas absorbent package

In the exactly the same manner as in Example 1, a gas absorbent package (gas absorbent) was prepared.

(2) Preparation of a transparent laminated film bag

A transparent vapor-deposited film composed of a 12 μm thick polyethylene terephthalate (PET) film on one side of which is formed a silicon oxide thin film layer (produced by Mitsubishi Chemical Industries Ltd. under the trade name Techbarrier) was coated, on the deposited side, with a urethane-based adhesive (produced by Toyo Moton Ltd.) to form an adhesive layer of 3.3 g/m^2 in coating amount. The resultant adhesive layer was laminated with a linear low density polyethylene (LLDPE) film of 100 μm in thickness (produced by Toasero Co. Ltd. under the trade name TUX-FCD) to obtain a film one side of which is laminated with the duplex layer of transparent deposited film/LLDPE film and the other side of which is PET itself. The three sides of the resultant film were heat-sealed to form a bag (gas barrier vessel) having a size of 220 mm × 300 mm with the inside surfaces of LLDPE (hereinafter referred to as transparent laminated film bag).

(3) Storage of K-18 made test piece

A test piece was prepared which was made of K-18 having chemical composition by weight consisting of 75% of gold, 15% of silver and 10% of copper and which had a size of 10 mm × 30 mm × 0.5 mm for use as a simulation product

of ornamental jewellery. The K-18 test piece in one number and one pack of the gas absorbent as prepared in the preceding item (1) along with 500 mL of air at 25°C and 75% RH were placed in the transparent laminate film bag, which was hermetically sealed by heat sealing the opening part of the bag. The resultant transparent laminate film bag thus sealed was allowed to stand for 4 weeks in an atmosphere of 40°C and 95% RH. Measurements were made of oxygen concentration and moisture inside the transparent laminate film bag after the storage of 4 weeks by means of gas chromatography. The results are given in Table 5. It has been confirmed that the inside of the storage system was maintained in a state substantially free from oxygen and moisture. The bag was unsealed to visually check the test piece for any discoloration. As a result, no change in color or gloss was observed, thus maintaining the initial state.

Comparative Example 9

A K-18 made test piece same as that which had been used in Example 9 was allowed to stand for 4 weeks in an atmosphere at 40°C and 95% RH without being housed or enclosed in a vessel having gas barrier properties, and thereafter was visually observed in the same manner as in Example 9. The results are given in Table 5. The test piece was tinged with red as a whole, thus revealing deterioration of gloss.

Comparative Examples 10 to 12

By the use of the K-18 made test pieces same as that which had been used in Example 9, the procedure in Example 9 was repeated to enclose the test pieces in the transparent laminate film bags and carry out storage and visual evaluation thereof except that in Comparative Example 10, a K-18 made test piece along with 10 g of silica-gel type A (produced by Fuji Davison Chemical Co., Ltd.) and 500 mL of air was enclosed in the bag; in Comparative Example 11, a K-18 made test piece along with a self-reaction type powdery iron-based deoxidizing agent capable of retaining moisture required for oxygen absorption reaction (Ageless Z-100 PT, produced by Mitsubishi Gas Chemical Co., Inc.) and 500 mL of air were enclosed in the bag; and in Comparative Example 12, a K-18 made test piece along with 500 mL of air was enclosed in the bag without the use of a gas absorbent. The results are given in Table 5. As shown in the table, color change and gloss deterioration were observed.

Table 5

	Example 9	Comparative Example 9	Comparative Example 10	Comparative Example 11	Comparative Example 12
Treatment of bag inside	Enclosed with gas absorbent of the invention	Exposed to preservation atmosphere	Enclosed with desiccant	Enclosed with moisture retention type powdery iron-based deoxidizing agent	Non-treated
Bag inside after 4 weeks					
Oxygen concentration (%)	0.03	-	21	0.05	21
Humidity (% RH)	<1	-	2	85	75
External appearance after 4 weeks					
Color	Unchanged	Turned reddish yellow	Tinged somewhat with yellow	Tinged somewhat with yellow	Yellowish hue deepened
Gloss	Maintained	Deteriorated	Deteriorated	Deteriorated	Deteriorated
Evaluation after storage	○	×	×	×	×

Remarks: ○ good

× poor

Examples 10 to 12

Gas absorbents were prepared in the same manner as in Example 9 except that the combination of the oxygen absorbent as the principal component and the oxygen absorption promoting substance was altered, respectively as shown in the following:

	Principal component in oxygen absorbent (100 parts by weight)	Oxygen absorption promoting substance (2 parts by weight)
Example 9	soybean oil	cobalt naphthenate
Example 10	fatty acid from tall oil	cobalt salt of fatty acid from tall oil [2]
Example 11	soybean oil	cobalt salt of fatty acid from tall oil
Example 12	soybean oil + liquid polyisoprene [1]	cobalt naphthenate

Remarks 1) mixture of soybean oil and liquid polyisoprene (produced by Japan Synthetic Rubber Co., Ltd. under the trade name Dinaclean R113 at a ratio by weight of 6:4.

Remarks 2) cobalt salt of fatty acid from tall oil having cobalt content of 6% by weight.

By the use of each of the above-prepared gas absorbents each having different combination of the oxygen absorbent as principal component and oxygen absorption promoting substance, the procedure in Example 9 was repeated to carry out the storage and visual evaluation

thereof. The evaluation results are given in Table 6. The results of all the test pieces in each example after 4 weeks of preservation were same as the results at the initial stage prior to the preservation as is the case with Example 9. Thus, the effect on preventing the discoloration of K-18 was confirmed.

Table 6

	Example 9	Example 10	Example 11	Example 12
Oxygen absorbent				
Organic compound as principal component	Soybean oil	Fatty acid from tall oil	Soybean oil	Soybean oil+liquid polyisoprene
Oxygen absorption promoting substance	Cobalt naphthenate	Cobalt salt of fatty acid from tall oil	Cobalt salt of fatty acid from tall oil	Cobalt naphthenate
Bag inside after 4 weeks				
Oxygen concentration (%)	0.03	0.03	0.04	0.03
Humidity (% RH)	<1	<1	<1	<1
External appearance after 4 weeks				
Color	Unchanged	Unchanged	Unchanged	Unchanged
Gloss	Maintained	Maintained	Maintained	Maintained
Evaluation after storage	○	○	○	○

Remarks: ○ good

× poor

Example 13

Storage of pearl:

Spherical pearls in 10 numbers each having a diameter of 4 mm that had been prepared as ornamental jewellery and one pack of the gas absorbent as prepared in Example 9 (1) along with 500 mL of air at 25°C and 75% RH were placed in the transparent laminate film bag as prepared in Example 9 (2). The bag was hermetically sealed by heat sealing the opening part thereof. The resultant transparent laminate film bag thus sealed was allowed to stand for 4 weeks in an atmosphere of 40°C and 95% RH. Measurements were made of oxygen concentration and moisture inside the transparent laminate film bag after the storage of 4 weeks by means of gas chromatography. The results are given in Table 7. It has been confirmed that the inside of the storage system was maintained in a state substantially free from oxygen and moisture. The bag was unsealed to visually check the pearls for any discoloration. As a result, no change in color or gloss was observed, thus maintaining the initial state.

Comparative Example 13

Ten pieces of pearls same as those which had been used in Example 13 were placed in a PE-made cage with fine mesh and the cage was allowed to stand for 4 weeks in an atmosphere at 40°C and 95% RH without being housed or enclosed in a vessel having gas barrier properties. Thereafter the pearls were visually observed in the same

manner as in Example 13. The results are given in Table 7. The pearls were tinged with red as a whole, thus revealing deterioration of gloss.

Comparative Examples 14 to 16

By the use of the pearls same as those which had been used in Example 13, the procedure in Example 13 was repeated to enclose the pearls in the transparent laminated film bags and carry out storage and visual evaluation thereof except that in Comparative Example 14, 10 pieces of pearls along with 10 g of silica-gel type A (produced by Fuji Davison Chemical Co., Ltd.) and 500 mL of air were enclosed in the bag; in Comparative Example 15, 10 pieces of pearls along with a self-reaction type powdery iron-based deoxidizing agent capable of retaining moisture required for oxygen absorption reaction (Ageless Z-100PT, produced by Mitsubishi Gas Chemical Co., Inc.) and 500 mL of air were enclosed in the bag; and in Comparative Example 16, 10 pieces of pearls along with 500 mL of air were enclosed in the bag without the use of a gas absorbent. The results are given in Table 7. As shown in the table, color change and gloss deterioration were observed.

Table 7

	Example 13	Comparative Example 13	Comparative Example 14	Comparative Example 15	Comparative Example 16
Treatment of bag inside	Enclosed with gas absorbent of the invention	Exposed to preservation atmosphere	Enclosed with desiccant	Enclosed with moisture retention type powdery iron-based deoxidizing agent	Non-treated
Bag inside after 4 weeks					
Oxygen concentration (%)	0.03	-	21	0.05	21
Humidity (% RH)	<1	-	2	85	75
External appearance after 4 weeks					
Color	Unchanged	Yellowish hue deepened	Tinged somewhat with yellow	Tinged somewhat with yellow	Yellowish hue deepened
Gloss	Maintained	Deteriorated	Deteriorated	Deteriorated	Deteriorated
Evaluation after storage	○	×	×	×	×

Remarks: ○ good

× poor

Examples 14 to 16

Storage in a variety of vessels:

In the case of enclosing each of the K-18 made test pieces same as those that had been used in Example 9 along with the gas absorbent same as that in Example 9 and air and carrying out storage by allowing the same to stand for a period of 1 week in an atmosphere of 40°C and 90% RH, there were used different vessels for storage, different number of packs of the gas absorbent and different volume of air at the constant ratio of 500 mL of air/one pack of the gas absorbent per each example. Specifically, in Example 14, one test piece along with 6 packs of the gas absorbent and air was enclosed in an about 3L transparent hard glass-made greaseless atop lidded desiccator (available from Iuchiseieidoh Co., Ltd.); in Example 15, one test piece along with 24 packs of the gas absorbent and air was enclosed in an about 12L transparent acrylic resin-made vacuum desiccator (available from the same); and in Example 16, one test piece along with 3 packs of the gas absorbent and air was enclosed in an about 1.5L tight box (available from the same). Measurements were made of oxygen concentration and moisture inside each of the vessels after the storage of 1 week by means of gas chromatography. The results are given in Table 8. It has been confirmed that each of the storage systems was maintained in a state substantially free from oxygen and moisture (oxygen of at most 3% and RH of at most 1%). Each

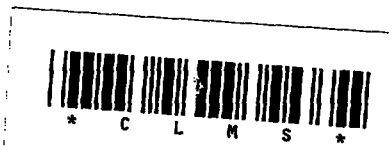
of the vessels was unsealed to visually check the test piece for any discoloration. As a result, no change in color or gloss was observed, thus maintaining the initial state in every test piece.

Table 8

	Example 14	Example 15	Example 16
Preservation vessel	Atop lidded desiccator	Vacuum desiccator	Tight box
Bag inside after 1 week Oxygen concentration (%) Humidity (% RH)	 0.07 <1	 0.04 <1	 0.09 1
External appearance after 1 week Color Gloss	 Unchanged Maintained	 Unchanged Maintained	 Unchanged Maintained
Evaluation after storage	○	○	○

Remarks: ○ good

× poor



WHAT IS CLAIMED IS:

1. An article plated with a noble metal characterized in that said article has a plating layer in a thickness of at most 1 μm and is enclosed together with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, in a vessel with gas barrier properties.

2. Ornamental jewellery characterized in that said jewellery is enclosed together with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, in a vessel with gas barrier properties.

3. The article plated with a noble metal according to Claim 1 which comprises an electrode or an electronic part having an electrode.

4. The article plated with a noble metal according to Claim 3 wherein the electrode or the electronic part having an electrode is enclosed, immediately after being plated, in a vessel with gas barrier properties.

5. The article plated with a noble metal according to Claim 1 wherein the oxygen absorbent not requiring moisture for absorbing oxygen comprises both or either of an unsaturated fatty acid and a chain hydrocarbon polymer having an unsaturated group as a principal component, and an oxygen absorption promoting substance.

6. The ornamental jewellery according to Claim 2 wherein the oxygen absorbent not requiring moisture for absorbing oxygen comprises both or either of an unsaturated fatty

* C L M S *

acid and a chain hydrocarbon polymer having an unsaturated group as a principal component, and an oxygen absorption promoting substance.

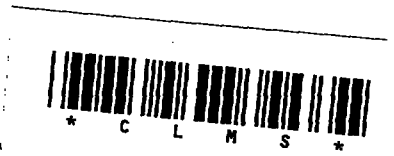
7. A method for the storage of an article plated with a noble metal which comprises enclosing an article plated with a noble metal in a plating thickness of at most 1 μm along with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, in a vessel with gas barrier properties.

8. A method for the storage of ornamental jewellery which comprises enclosing ornamental jewellery along with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, in a vessel with gas barrier properties.

9. The method for storage according to Claim 7 wherein the article plated with a noble metal comprises an electrode or an electronic part having an electrode.

10. The method for storage according to Claim 9 wherein the electrode or the electronic part having an electrode is enclosed, immediately after being plated, in a vessel with gas barrier properties.

11. The method for storage according to Claim 7 wherein the oxygen absorbent not requiring moisture for absorbing oxygen comprises both or either of an unsaturated fatty acid and a chain hydrocarbon polymer having an unsaturated group as a principal component, and an oxygen absorption promoting substance.



12. The method for storage according to Claim 8 wherein the oxygen absorbent not requiring moisture for absorbing oxygen comprises both or either of an unsaturated fatty acid and a chain hydrocarbon polymer having an unsaturated group as a principal component, and an oxygen absorption promoting substance.

13. A package which comprises an article plated with a noble metal in a plating thickness of at most 1 μm, said article along with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, being packaged by the use of a packaging material with gas barrier properties.

14. A package which comprises ornamental jewellery, said jewellery along with a dehumidifying agent and an oxygen absorbent not requiring moisture for absorbing oxygen, being packaged by the use of a packaging material with gas barrier properties.

15. The package according to Claim 13 wherein the article plated with a noble metal comprises an electrode or an electronic part having an electrode.

16. The package according to Claim 15 wherein an electrode or an electronic part having an electrode is packaged therein immediately after plating.

17. The package according to Claim 1 wherein the oxygen absorbent not requiring moisture for absorbing oxygen comprises both or either of an unsaturated fatty acid and a chain hydrocarbon polymer having an unsaturated group

* C L M S *

as a principal component, and an oxygen absorption promoting substance.

18. The package according to Claim 14 wherein the oxygen absorbent not requiring moisture for absorbing oxygen comprises both or either of an unsaturated fatty acid and a chain hydrocarbon polymer having an unsaturated group as a principal component, and an oxygen absorption promoting substance.