The present invention relates to alloys of palladium, platinum and silver and more particularly to a noble white alloy containing palladium, platinum and silver, substantially resistant to nitric acid.

Hitherto, high grade jewelry has been made from either cast gold alloys, or from alloys consisting almost wholly of platinum or palladium hardened by the addition of small amounts of iridium, ruthenium, or the like. It has been known that, due to its color, tarnish and corrosion resistance and other chemical and physical properties, platinum has been peculiarly well adapted for use in the production of jewelry, such as in the setting of diamonds and the like. Platinum, however, has been a rare and expensive metal, and in general the cost of platinum metal jewelry was prohibitive for large articles of jewelry and very much in excess of that of cast gold alloys, such as 12 to 14 kt. gold. Many attempts have been made to produce a precious white alloy suitable for jewelry and other purposes where high stability and moderate cost are essential. Thus, various types of white gold alloys were proposed, in which gold was present as a major constituent. Attempts have also been made to use commercially pure palladium, palladium and silver, platinum and silver, etc. These white metal alloys, however, involved certain shortcomings including a deficiency in tarnish and corrosion resistance, especially when exposed to the action of nitric acid, lack of ductility, strength or resistance to wear, a tendency to “fire” crack on annealing, and in many cases insufficient cheapness. To be satisfactory for jewelry purposes, an alloy must not only be readily workable, adequately hard and tarnish resistant, but must also be resistant to nitric acid. Thus, a mode of testing which is used by jewelers for testing alloys is conducted as follows: A drop of concentrated nitric acid is applied to the clean surface of the alloy and is allowed to remain upon the surface of the sample for a few minutes, during which time the behavior and appearance of the drop are observed. The drop is then washed off and the condition of the underlying metal is noted. The metal is considered satisfactory when neither the drop itself, nor the surface of the metal are appreciably discolored during the test. It is known that the usual white gold alloys are not completely resistant to the aforementioned nitric acid test. For instance, 14 kt. white gold alloys became discolored during the test. The staining became more intense in 12 and 10 kt. white golds, and in alloys with a lower gold content than 10 kt. alloys the attack was usually very vigorous and the drop of nitric acid turned green. It is also known that commercially pure palladium, alloys of palladium and nickel, and alloys of palladium and silver do not withstand successfully the nitric acid test and have therefore been unsuited for use in the jewelry art. Likewise, platinum silver alloys were not useful for jewelry, as they were extremely difficult to cast and to work when the platinum content was higher than about 40%, and they were not resistant to tarnish and to nitric acid when the platinum content was less than about 40%. Although many proposals have been made by those skilled in the art to provide the trade and the public with precious alloys, especially white alloys, having the requisite resistance to tarnish and nitric acid, workability and moderate cost, none as far as we are aware has been wholly satisfactory and successful in practical, commercial and industrial use.

I have discovered that the addition of relatively small percentages of platinum to certain special palladium silver alloys renders such alloys not only readily workable, but also resistant to tarnish and to nitric acid.

It is an object of the present invention to provide an alloy containing palladium, platinum and silver which is strong, adequately hard and readily workable, and which possesses adequate resistance to tarnish, to corrosion and to nitric acid.

It is another object of the invention to provide a noble white alloy containing palladium, platinum and silver, which is relatively inexpensive, and which can be cast and fabricated easily and economically.

A further object of the invention is to provide a palladium-platinum-silver white alloy which possesses the appearance, quality and the properties that make it desirable for use in the production of jewelry and other purposes where high stability and moderate cost are required.

It is also within the contemplation of the present invention to provide a noble white alloy of palladium, platinum and silver which is suitable for jewelry and similar purposes, and which contains substantially no gold, thereby offering an effective means for conserving gold and releasing it for essential monetary purposes.

The invention further contemplates the provision of a white alloy containing palladium, platinum and silver suitable for jewelry and similar purposes, which can be made on an industrial scale, which can be handled, fabricated and worked with conventional appliances and equip-
ment, and which is relatively cheap and permits wide use.

Other objects and advantages of the invention will become apparent from the following description taken in conjunction with the accompanying drawing showing a ternary diagram in which the alloys contemplated by the present invention are plotted on the basis of weight percentages. Generally speaking, the present invention contains templates providing a precious white alloy containing palladium, platinum and silver in which the palladium content may vary from about 15% to about 30% and is preferably not less than about 30% of the platinum content of the alloy. When such conditions are observed, the alloys of palladium, platinum and silver contemplated by the present invention possess excellent qualities in regard to color, strength, toughness, workability, resistance to wear, corrosion and nitric acid, etc., and are fully suitable for the production of jewelry and similar purposes. In addition, the alloys are not only less expensive than corresponding known white gold alloys but are also superior to them in several respects, such as resistance to nitric acid and workability etc., so as to be preferable to the gold alloy for jewelry and other uses where high stability and moderate cost are desirable.

Of course, the composition of the alloy permits wide variations and a wide range of physical and chemical properties may be obtained by properly varying the proportion of the ingredients of the alloy and especially by controlling the ratio of the palladium to platinum content thereof. In general, the tarnish and nitric acid resistance of the new alloy improves with increases in the combined content of palladium plus platinum in the alloy. When the palladium content is not less than about 60% of the platinum content, the nobility of the alloy varies with the combined palladium plus platinum content in a manner analogous to that of commercial gold alloys, and is equal or superior to that of a corresponding white gold alloy, or an alloy having a gold content approximately equal in weight to the combined palladium plus platinum content of the new alloy. For instance, the palladium-silver-platinum alloys containing more than 35% of palladium attain a resistance to nitric acid equal to that of a corresponding white gold alloy when 5% or more of platinum is present. Likewise, palladium-silver-platinum alloys containing between 15% and 35% of palladium exhibit a similar resistance to nitric acid when the combined palladium plus platinum content of the alloy is 40% or more.

Referring more particularly to the drawing, the most useful alloys of the palladium-silver-platinum system exhibiting a resistance to nitric acid equal or superior to that of a corresponding white gold alloy are shown in the area A—D—G—K. The composition of the alloys expressed in weight percentages may vary from about 15% to about 30% palladium, from about 15% to about 30% silver, and from about 5% to about 54% platinum.

The new alloys having a resistance to nitric acid comparable with that of 10 kt. gold and suitable for replacing 10 and 12 kt. gold alloys in the jewelry art or the like are shown in the field A—D—J—K. Expressed in weight percentages, the composition of these alloys may vary from about 15% to about 50% palladium, from about 45% to about 60% silver, and from about 5% to about 34% platinum. These alloys have in the annealed state a Rockwell B hardness of about 38 to about 75.

Those alloys having a resistance to nitric acid comparable to 14 kt. gold and suitable as replacement alloys for 12 and 14 kt. gold alloys are shown in field B—C—H—J, which comprises the alloys containing from about 21% to about 65% palladium, about 30% to about 45% silver, and about 5% to about 44% platinum. These alloys have a Rockwell B hardness, when annealed, of about 48 to about 80.

The alloys included in area C—D—G—H exhibit excellent resistance to nitric acid and tarnish and are suitable for the replacement of 14 and 18 kt. gold alloys. These alloys have the annealed state a Rockwell B hardness of about 63 to about 90 and may contain from about 26% to about 82% palladium, about 13% to about 30% silver and about 5% to about 54% platinum.

These alloys containing more than about 55% palladium plus platinum with a platinum content preferably of 9% or more possess excellent tarnish and nitric acid resistance, have high melting point and hardness, and are suitable for replacing gold alloys for jewelry, dental, electrical, and other uses where it is desirable to secure the abovementioned properties at a moderate cost. These alloys are included in area B—D—F—Q of the drawing.

When the total palladium plus platinum content is more than 55% and the platinum is preferably 15% or more, the alloys possess extraordinary resistance to tarnish, to nitric acid, and increased resistance to hypochlorite antiseptics and have higher hardness and melting point. These alloys are indicated by the area B—D—E—N of the diagram and are most suitable for dental use where very severe conditions may be encountered.

As hereinafore more fully explained when the palladium content of the alloys is not less than about 60% of the platinum content thereof, the nobility of the alloy and especially its resistance to nitric acid is superior to that of gold alloys having a gold content equal to the palladium plus platinum content of the new alloy. The nobility of the alloys may further be increased by increasing the total palladium plus platinum content. For instance, alloys containing about 31 to 50% palladium, about 5 to 9% platinum and not more than 60% silver, possess a higher resistance to nitric acid than the usual 10 kt. gold alloys. By raising the platinum content to about 9 to about 15%, the palladium content ranging from about 25% to about 45%, the alloys show better resistance to nitric acid than 14 kt. gold alloys. If the alloys contain 5 to 9% platinum, about 46 to 65% palladium and the silver is not in excess of 45%, the alloys show better resistance to nitric acid than 14 kt. gold alloys. Likewise, alloys containing 40% to 61% palladium, about 9% to 15% platinum, the silver content being not more than 45%, offer a resistance to nitric acid equal to that of 18 kt. gold alloys.

The hardness of the new alloys is largely dependent upon the combined percentages of the palladium plus platinum and in general it increases with the platinum content of the alloy. For instance, the hardness reaches a value of about 63 Rockwell B at about 70% palladium and 5% platinum. On further increasing the platinum content, the alloy becomes harder and the rather high hardness of 94 Rockwell B may be attained when the alloy contains about 40% palladium and about 40% platinum.

I have discovered that higher hardness values may be imparted to the new palladium-silver-
platinum alloy by the addition of a small percentage of copper, nickel and/or cobalt, for instance, in amounts varying from about 2% to about 10%. When the palladium plus platinum content of the alloys containing nickel or copper is not less than about 60% and the palladium plus platinum content of the new alloy, while their properties, especially resistance to tarnish and to nitric acid, are superior to those of the gold alloys. By virtue of the lower density of the new alloy, the cost per unit of volume becomes even more attractive when compared on the same basis with corresponding gold alloys.

The following table sets forth by way of example, a comparison between a new palladium-platinum-silver alloy and a corresponding 14 kt. white gold alloy.

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<tr>
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<tbody>
<tr>
<td>Pt-Pt-Ag alloy (percent)</td>
<td>Complete</td>
<td>$15.00</td>
<td>$5.74</td>
</tr>
<tr>
<td>Pt-10.00 Ag-41.67.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14 kt. white gold alloy (percent)</td>
<td>Good, but yellow stain results.</td>
<td>$20.00</td>
<td>$8.36</td>
</tr>
</tbody>
</table>

High-grade jewelry can be made from the solid alloy, but the less expensive grades can be made from laminated stock, variously called clad, rolled, plated or filled stock, in which the outer surface may be composed of a layer of the new alloy welded or soldered to a nickel or other suitable core. Composite material of this nature composed of an outside surface layer of the new palladium, platinum, silver alloy and a core of a suitable base alloy has been manufactured successfully by methods similar to those employed in the production of gold filled wire. I have found that alloys containing about 26% to 64% palladium, about 6% to 14% platinum, and about 30% to 60% silver are especially suitable for cladding purposes.

It is to be observed that the present invention provides a new white precious alloy containing palladium, platinum and silver which is relatively inexpensive, easy to cast and to work, and which has sufficient hardness, strength, good wearing qualities and resistance to tarnish, corrosion and to nitric acid, as to be fully adapted for use in the production of jewelry or other purposes where high stability and moderate cost are essential.

It is further to be observed that by varying and controlling the proportion and/or ratios of the ingredients of the new palladium-platinum-silver alloys, as hereinabove more fully described, the alloy can have imparted thereto such a wide range of properties as to resistance to corrosion, hardness, strength, melting point, wearing qualities, etc., as to enable them to be adapted for a large and diversified number of uses and applications.

Furthermore, it is to be noted that the palladium-platinum-silver alloys provided by the present invention are not only less expensive, but are also superior in regard to resistance to tarnish and to nitric acid and other properties to known white gold alloys having a gold content substantially equal to the combined palladium plus platinum content of the new alloy.

Moreover, it is to be noted that the invention provides a new white precious alloy of moderate cost and suitable for use in the jewelry and other arts, which contains substantially no gold, thereby offering an effective means for conserving gold and releasing it for essential monetary purposes.

Although the present invention has been described in conjunction with preferred embodiments, it is understood that modifications and variations may be resorted to without departing
from the spirit and scope of the invention, as those skilled in the art will readily understand. Thus, the alloy may be used for other purposes other than jewelry where high stability, high corrosion and erosion resistance, coupled with moderate cost, are essential, such as electrical, chemical, artistic applications and the like.

I claim:

1. An alloy, substantially resistant to nitric acid, consisting of 15% to 82% palladium, 5% to 54% platinum, the palladium content always being at least 60% of the platinum content, and the balance consisting of silver, the said silver content being not less than 13% nor more than 60%.

2. An alloy, substantially resistant to nitric acid, consisting of 15% to 50% palladium, 5% to 34% platinum, the palladium content always being at least 60% of the platinum content, and the balance consisting of silver, the said silver content being not less than 45% nor more than 60%.

3. An alloy, substantially resistant to nitric acid, consisting of 21% to 65% palladium, 5% to 44% platinum, the palladium content always being at least 60% of the platinum content, the balance consisting of silver, the said silver content being not less than 30% nor more than 45%.

4. An alloy containing from 35 to 70% of palladium and platinum of which 5 to 10% is platinum, the remainder of the alloy being silver.

5. An alloy consisting of about 45% of palladium, about 50% of silver and about 5% of platinum.

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