

Review Article

New developments in jewellery and dental materials

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This communication reviews the latest alloys introduced in the fields of jewellery and dental prostheses. For this we have scanned current patents and others to which we have access, and it is evident that, although not always correctly used, the words "antiallergic", "hypoallergic", "non-allergic", "to avoid allergies", etc., now appear frequently, indicating manufacturers' awareness of the problems that nickel can cause. On the other hand, the problems that may be associated with other sensitizing metals, such as cobalt and palladium, are not yet addressed.

Key words: metals; alloys; jewellery; dental prostheses; nickel; cobalt; palladium; allergic contact dermatitis; prevention. © Munksgaard, 1998.

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One of the principal obligations in contact dermatology should be to keep patch test series up to date. For this reason, we have reviewed the latest alloys introduced in the fields of jewellery and dental prostheses (1). We are pleased to see the recent appearance of words on patents such as "antiallergic", "hypoallergic", "non-allergic", "to avoid allergies", etc., even though they are sometimes incorrectly used. Manufacturers appear to have realized the problem caused by nickel, though they do not yet take into account other sensitizing metals, such as palladium and cobalt.

Firstly, we mention patent WO 9717479 A1 970515-9725*JA, which shows a way to produce a metal for watchmaking and ornamentation. It is based on titanium and aluminium and has exceptional hardness and non-allergic capacity. Another such patent shows the way to produce a material suitable for prostheses, dental implants, rings, bracelets, watchstraps, etc., based on a noble metal, such as palladium, platinum, etc., and treatment of the surface with titanium at high temperatures, forming a layer of titanium oxide which prevents the underlying metal from provoking allergy (JP 09125223 A 970513). In patent JP 09075116 A 970325, the decorative part and the fastener in contact with the earlobe are covered with acrylic resin or silicone resin, to prevent allergy to metals

in earrings. For people allergic to metals, patent JP 09070305 A 970318 proposes covering gold with selenium.

We find patent JP 09053159 A 970225 very interesting. It is proposed for the manufacture of watch cases, watch chains and spectacles by pulvimetal-lurgic injection with chrome, molybdenum, titanium, niobium, vanadium, zirconium and iron. Patent EP 751231 A 970114 proposes an alloy, based on aluminium, magnesium, iron and copper, and hard and shiny enough to be used in the manufacture of necklaces, watches, etc., but not producing allergies. Patent DE 19625807 A1 970102 explains how the addition of small quantities of titanium to a quaternary alloy on a basis of gold, silver, copper and zinc, and which also contains small quantities of iridium, ruthenium, silicon, beryllium and indium, gives great hardness and shine in the manufacture of high-quality articles. In jewellery, a way of uniformly covering any surface with a mixture of calcium phosphate and silver by electrodeposition is described. This achieves shine, colour, good appearance, etc. This patent (JP 08120496 A 960514) guarantees that the surface has antibacterial qualities and is safe for humans in that it does not provoke allergy.

Another patent that should be mentioned is JP 08066210 A 960312, which proposes the creation

of articles of jewellery on a titanium base, covered by different layers of oxides of this metal through electrodeposition. It is attested that, when UV light impinges, it penetrates through the said layers, reacting with the titanium oxides, generating positive and negative ions. The positive ions react with the oxygen in the atmosphere forming hydroxyl radicals, which at the same time break down the chemical products into hydrogen and carbon dioxide gas, permitting autosterilization by breaking down certain chemical substances and allowing the production of pieces of various colours (earrings, pins, etc.).

In jewellery, patent JP 08013132 A 960116 claims that it can prevent allergy to metals by manufacturing stainless steel or brass items and, through electrodeposition, covering them with a fine layer of an alloy that contains 94% gold, 3% iron and 3% palladium. In EP 693261 A1 960124, a way to manufacture ornamental items, such as bracelets, belts, earrings, zips, hooks, etc., with the appearance of nickel yet not containing nickel is explained. This is done on a basis of zinc with layers of copper, zinc and finally chrome through electrodeposition. It is claimed that this achieves the appearance of nickel, prevents the possibility of producing allergy, and is resistant to corrosion.

Occasionally, we have observed how the join or solder of the fastener of an earring presents a rough and oxidized surface, with consequential increase in the possibility of freeing metallic ions, basically nickel. Patent CH 68616136 A5 960115 proposes an alloy based on gold, manganese, copper and silver, with the addition of zinc, gallium, and indium. It is pointed out that this is a solder ideal for use in contact with skin, with the advantage of not containing nickel, and therefore eliminating the possibility of causing allergies. The colour is also similar to gold.

Patent E 678586 A1 951025 is interesting in that it proposes an alloy based on copper, which also contains manganese, zinc and aluminium, which can be worked cold and allows the manufacture of hollow buckles, buttons, kitchen pans, drills and any piece of costume jewellery which comes into contact with the skin, such as brooches, fasteners, zips, etc., with resistance to corrosion and not causing contact dermatitis. We find patent JP 07188945 A 950715 less promising due to its content of palladium on the surface, placed there by electrodeposition onto an underlying alloy of copper and tin.

Patent EP 641868 A1 950308 proposes a nickel-free, non-magnetic alloy resistant to corrosion. It is easy to work and can be used in objects in contact with the skin such as watch chains and boxes,

spectacles, material for implants, kitchen items, etc.. The approximate composition can present slight variations in %s of basic metals, the rest of its composition being iron:

Cr	Mn	Co	C	N	Si	W	Mo	V	Y	Nb	Ti
20	30	35	0.5	0.5	2	5	5	3	0.5	1	1

Al	S	Se	Te	Zr	Ca	Pb	Ag
1	0.2	0.2	0.2	0.2	0.2	0.2	2

Patent AT 9201393 A 931215 proposes another alloy that can safely be in contact with the skin. It has a low content of nickel and an approximate composition of:

C	S	Mn	Cr	Mo	N	V	Nb	Ta
0.10	1	11 to 25	10 to 20	1.6	0.5	1	1	1

W	Al	Ti	Cu	B	Fe
1	1	1	1	2	rest

It is guaranteed that the nickel content is less than 0.5%. This alloy is recommended for the manufacture of watch chains and boxes, spectacles and prostheses, and it is assured that it does not cause allergic reactions.

Patent WO 9703227 A1 970130 has been designed for the electrical and jewellery industry, as it proposes a new method of obtaining plated items without having to use a previous chrome bath, in this way avoiding the toxic effect of materials used in chroming in the industry. It is a simple and cheap method, consisting of treating the surface of the alloy with 10% sodium hydroxide for 15 min at a temperature of 55°C, the surface later being treated with nitric acid and finally passivated with sulfuric acid.

Concerning metallic dental prostheses, the developments which appear most interesting to us are those proposed by Lloyd (4), where he explains that titanium's high melting point (1660°C) creates a major disadvantage when working it. Through the addition of 25% cobalt a lower melting point (600°C) is achieved, but a large part of its resistance to corrosion is lost. This can be avoided by the addition of 5% nickel, but this metal has a bad reputation from the biological point of view. The now classical alloy Ti6Al4V is questioned due to possible toxic effect of aluminium and vanadium, and for this reason 2 alternative alloys are being tested on the basis of titanium, zirconium, niobium, tantalum and palladium, and titanium, tin, niobium, tantalum and palladium, respectively. From the dermatological point of view, the addition of palladium to these alloys could mean more sensitization to this metal in the future.

Nickel-chromium and nickel-chromium-beryllium blasted with sand at high pressure, so that the roughness formed helps to retain resin, continue to be proposed with reference to metal alloys joined with resins.

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