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A new revision of European directive on nickel release will come into force the by the april 2013. The new norm will dramatically drop down the maximum allowed nickel release limit, leading to significant implications for the jewelry industry. This paper aims to provide an overview about how the scenarios will change after the april 2013 in comparison to the existing situation. The paper will also discuss what possibilities for materials and technologies with and without nickel will be able to provide satisfactory solutions to the jewelry market, together with a possible change in the way the white gold production is currently approached by the jewelry industry.

White gold alloys for gold jewellery and new EN1811:2011 standard on nickel: limitations and possibilities

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Summary

The new revision of the European standard on nickel EN1811:2011 will come into force on 1st April 2013. It will impose a drastic limitation on the release values, setting tighter limitations to the use of nickel in jewellery production.

In this work the authors aim to provide an overview of the current situation and the situation envisaged after the new legislation has come into force, indicating the possibilities of the new materials with and without nickel and the production technologies for the gold jewellery market, and also how the production approach of the goldsmith will have to change.

Introduction

With the introduction of the new (EC) regulation No. 1907/2006 of the European Parliament and Council (REACH) *[1]*, which came into force in 2008, the European Union carried out a substantial revision of its legislation concerning chemicals (13). Nickel is one of the substances recognised as being harmful to human health and its use has therefore been subject to precise restrictions, as specified in point 27 of Annex XVII of the REACH regulation. To determine whether an article containing nickel is in compliance with these restrictions, the REACH regulation indicates EN1811:2011 (1) as the specific reference standard. The EN1811:2011 standard describes a method for simulating the release of nickel from all items inserted into pierced parts of the ear or other parts of the human body and from objects designed to come into direct and prolonged contact with the skin.

Compared to the previous version, the new EN1811:2011 standard introduces some important new features:

- The standard is applied to all types of object designed to come into contact with pierced parts of the body *[2]*.
- The composition of the artificial sweat solution is slightly modified, making it probably more aggressive.
- The correction factor is eliminated and an uncertainty factor is introduced, determined in a sort of round robin test among laboratories.
- The standard is accompanied by a specific Annex (Annex C) in which preparation of the test samples is discussed.

([1]) On 1st June 2007 the (EC) Regulation no. 1907/2006 of the European Parliament and Council of 18th December 2006 came into force in the European Union countries, which reorganised the community laws concerning registration, evaluation, authorisation and restriction of chemicals – the so-called "REACH Regulation".
Section VIII of the Regulation (art. 67 – 73) regulates the "restrictions relative to the manufacture, placement on the market and use of certain dangerous substances, preparations and articles".
The restricted substances (both as such and as components of a preparation or article), are listed in Annex XVII.
Annex XVII, point 27, establishes that nickel cannot be used:

a) in all metal objects inserted into pierced ears and other pierced parts of the human body, unless the nickel release rate from said objects is below 0.2 μg/cm²/week (migration limit);
b) in articles designed to come into direct and prolonged contact with the skin, such as

- *earrings,*
- *necklaces, bracelets and chains, ankle bracelets,*
- *rings,*
- *watch cases, watch straps and clasps,*
- *poppers, fasteners, rivets, zips and metal logos, if applied to clothing,*

if the rate of nickel release from the parts of these objects which come into direct and prolonged contact with the skin is higher than 0.5 μg/cm²/week;

c) in articles like those listed in letter b), if they have a nickel-free coating, unless said coating is sufficient to guarantee that the rate of nickel release from the parts of said articles which are in direct and prolonged contact with the skin does not exceed 0.5 μg/cm²/week for a period of at least two years of normal use of the article.

The above articles may not be placed on the market unless they comply with the prescriptions indicated.

The standards adopted by the CEN (European Committee for Standardisation) are used as test methods to demonstrate compliance of the articles.
The CEN standards used for the purposes of nickel determination are:

- *EN 12472:2009 – Method for the simulation of wear and corrosion for the detection of nickel release from coated items*

- *EN 1811:2011 – Reference test method for release of nickel from all post assemblies which are inserted into pierced parts of the human body and articles intended to come into direct and prolonged contact with the skin.*

([2]) In the previous revision of 1998 these objects were excluded from the field of application of the standard, while for the objects designed to come into contact with pierced parts of the body, a maximum nickel content of 0.05% was established; subsequently, as from 1st April 2005, the directive 2004/96EC transformed the maximum weight limit into a maximum release limit of 0.2μg/cm²/week, considering the control of nickel release to be more closely correlated with the risk of allergies than its weight content in the alloy.

Although the release limit values remain nominally unchanged (0.5 μg/cm²/week, with the exception of objects inserted into pierced parts of the body, for which the maximum release value is 0.2 μg/cm²/week), with the application of an uncertainty factor of 46% defined by the standard, the nickel release values actually determined must not exceed the values of 0.28 and 0.11 μg/cm²/week respectively. If the release values are between 0.11 and 0.35 μg/cm²/week for objects inserted into pierced parts of the body and between 0.28 and 0.88 μg/cm²/week for all the other objects, the result of the test cannot be considered conclusive, as it is not possible to clearly establish whether the release value complies or not with the EN1811:2011 standard *([3])*. The combination of the two new elements results in reduction of the maximum limit value by over 18 times approximately, compared to the release limit permitted by the previous version of the standards (Tab. I).

Table I – Release limits according to the new EN1811:2011 standard

Ni release value	Limit according to new EN1811:2011	Result	Effective limit according to old EN1811:2008 standard
(µg/cm²/week)	(µg/cm²/week)	(With an uncertainty of 46%)	(µg/cm²/week)
<0.11 0.11 ÷ 0.35 >0.35	0.2 (for objects inserted into pierced parts of the body)	Compliant Non-conclusive Non-compliant	0.05% in weight; 2.0µg/cm²/week after 1st april 2005
<0.28 0.28 ÷ 0.88 >0.88	0.5	Compliant Non-conclusive Non-compliant	5.0

([3]) It is interesting to note that if the release values are between 0.11 and 0.35 µg/cm²/week for objects inserted into pierced parts of the body and between 0.28 and 0.88 µg/cm²/week for all the other objects, the test result cannot be considered conclusive, since it is not possible to clearly establish whether the release value complies or not with the EN1811:2011 standard. Release values that fall within this intermediate range therefore make the outcome of any possible contestation uncertain. It should also be pointed out that objects whose release values are not conclusive because they are within the above ranges, may not be placed on the market as they do not comply with the limits imposed by the standard.

It should be remembered that adoption of the REACH regulation by all the European Union member states prescribes sanctions in the form of fines but can also involve arrest for those who manufacture or place on the market objects not in compliance with the provisions of the regulation *([4])*.

([4]) Art. 16 –Italian Republic, Legislative Decree of 14th September 2009, no. 133
Breach of the obligations arising from article 67 of the regulation concerning restriction.
Unless the fact constitutes a more serious offence, the manufacturer, importer, sole representative or user downstream who produces, places on the market or uses a substance as such or as a component of a preparation or an article not in compliance with the restriction conditions established by Annex XVII of the regulation, outside the cases referred to in article 67 of the regulation, is punished by arrest of up to three months or a fine from 40,000 to 150,000 euro.

The spirit of the new EN1811:2011 standard

In the introductory note, the new revision of the EN1811:2011 standard is based on the premise that contact allergies caused by nickel represent the most frequent cause of contact allergy in Europe. The release limits imposed by the previous revisions of the standard have proved to be insufficient to avoid elicitation reactions in sensitised subjects, as also shown by research performed in the Legor Group R&D laboratories (2, 3). The dangerousness of nickel is related not to its content but to the quantity of nickel ions released by the object per surface unit when placed in contact with a solution of artificial sweat. No relation is therefore established between nickel content and relative release value, since the release of nickel ions depends on the composition and state of the material as a whole and is not necessarily correlated to its content. The adoption of the new release limits certainly represents a more realistic alignment between the maximum nickel release limits and the possibility of preventing the onset of allergic phenomena, although the risk of allergic reactions in particularly sensitive subjects can never be excluded even when the release values are compliant with the new revision of the EN1811:2011 standard.
The REACH regulation (Annex XVII, No. 27, point c) establishes that for all objects designed to come into direct and prolonged contact with the skin (therefore excluding objects designed to be inserted into pierced parts of the body) on the surface of which other material has been deposited *([5])* (excluding deposits containing nickel), it must be demonstrated that the release value does not exceed the limit of 0.5µg/cm²/week for a period of 2 years of "normal use" of the object before it is placed on the market.

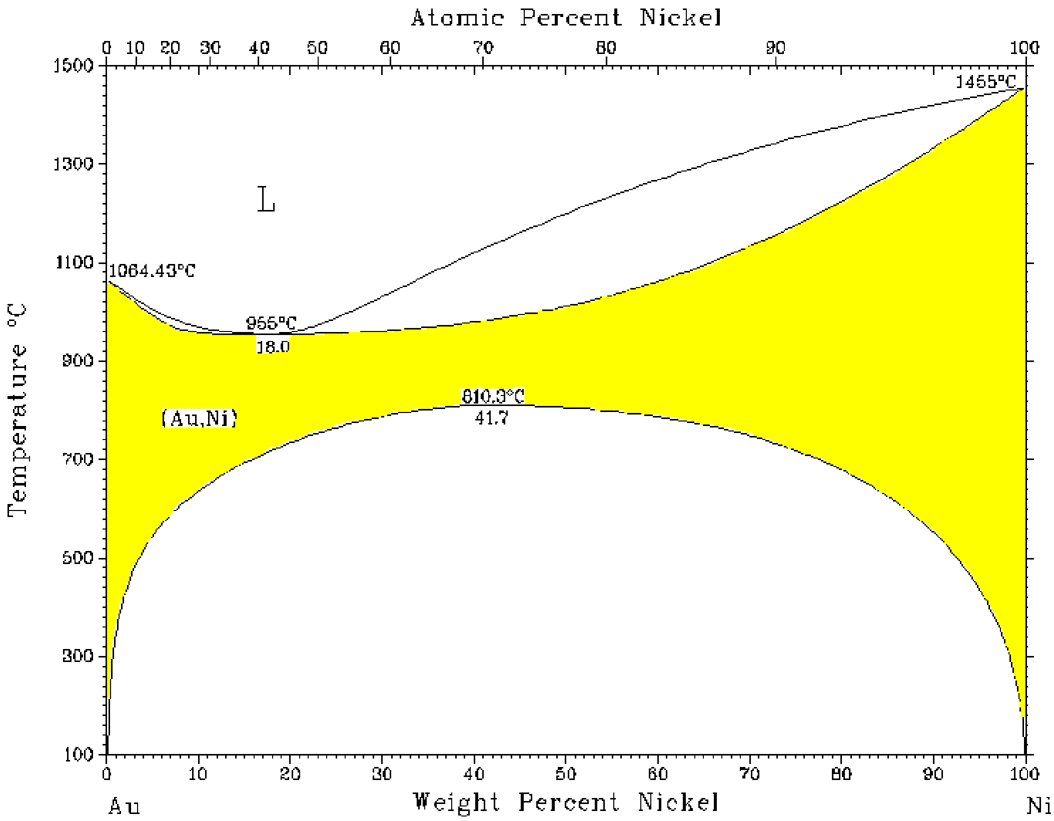
The method for simulating a level of wear corresponding to normal use of the object for a period of 2 years is defined by the EN12472:2009 standard.
Paradoxically, under the new European legislation defined by the REACH regulation, it would be possible to place on the market objects with release values higher than the limits permitted by the new EN1811:2011, on condition that they are coated with a surface deposit which is sufficiently robust to pass the EN1811:2011 release test after undergoing the wear test established by the EN12472:2009 standard.

([5]) Italian Republic, Presidential Decree of 30th May 2002, no. 150, art. 38, par. 2: non-precious metals, with the exception of iridium, osmium, rhodium and ruthenium, shall not be deposited on objects in precious metal alloy by the galvanic deposition method or similar methods.

Impact of the new EN1811:2011 on the production of white gold alloys

The metallurgical implications of the introduction of the new standard are extremely important. The miscibility gap between gold and nickel (Figure 1) creates serious limitations in the development of white gold alloys with corrosion resistance values compatible with the release limits established by the new standard.

Figure 1 – Gold-nickel phase diagram. The composition and temperature conditions at which the two elements are perfectly miscible, forming a single-phase structure, are shown in yellow. With the reduction in temperature, the structure of the alloy becomes two-phase and, as such, much more susceptible to corrosion phenomena which can result in a significant increase in the release of nickel ions.



The difficulties of obtaining alloys containing low release nickel increase dramatically with reduction in the gold content. In the current state of the art, it is reasonable to assume that the possibility of producing white gold alloys containing nickel will be limited to the highest carat titles (750/1000 or above), for which alloys with low nickel release can be successfully produced; greater difficulties are predicted in the case of medium carat titles (585/1000), while it can be realistically envisaged that the use of white gold alloys with nickel at low carat titles (333, 375, 417‰) will be fairly improbable from now on.

There are therefore three possible solutions to the problem of production of white gold objects:

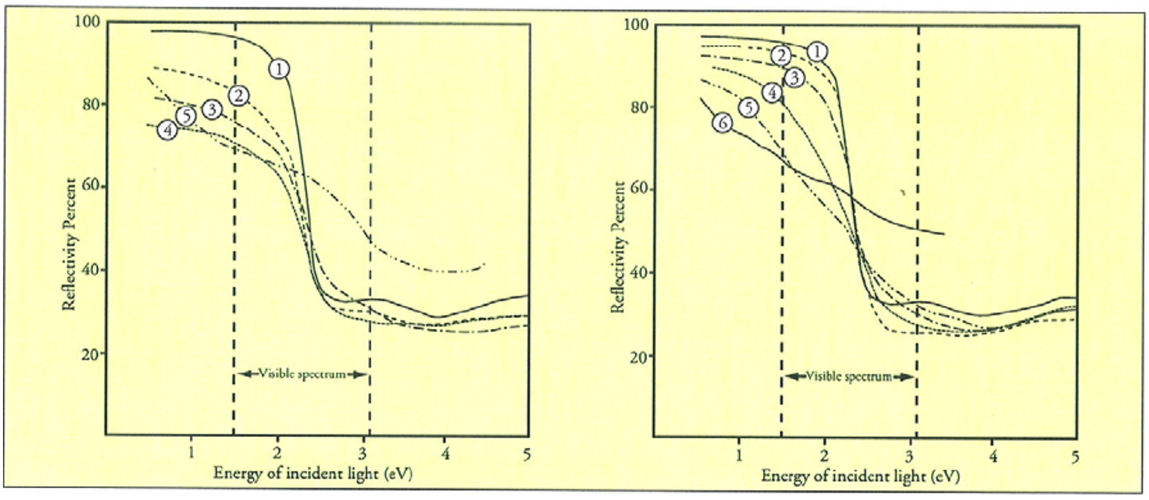
1. Production of nickel-free white gold alloy objects with zero nickel allergy risk also for hypersensitive subjects.
2. Production of coated white gold alloy objects containing "standard" type nickel with appropriate deposits able to demonstrate compliance with the release limits established by the new EN1811:2011 standard after wear treatment according to the EN12472:2009 standard. This would allow the use of white gold alloys with release limits prior to the covering deposit not necessarily in compliance with the release limits established by EN1811:2011. This solution, while formally complying with the release limits established by the REACH regulation, would not exclude the possibility of allergic phenomena in susceptible subjects after natural removal of the protective coating as a result of wear due to use of the object.

3. Production of coated white gold alloy objects containing very low release nickel. This third solution, if possible, would allow compliance with the release limits established by the new legislation even after removal of the protective coating as a result of normal wear. Here again, the risk of possible allergic reactions can never be totally excluded, but the risk is nevertheless significantly reduced compared to solution no. 2 due to the low release of nickel ions by the object even after removal of the protective coating.

Possibility of use of nickel-free white gold alloys

In this situation of uncertainty the obvious question is: what are the possible alternatives to nickel as gold whitening metals?
In the last fifteen years, the possible use of various whitening metals as alternatives to nickel have been explored (10, 11, 12). In the current state of the art a whitening element alternative to nickel able to offer the same versatility of use as nickel at a limited cost has not yet been identified. There are, however, several other elements which in certain circumscribed conditions of use can represent a possible, albeit partial, alternative to nickel as gold whitening elements.
The whitening effect depends on the ability of an element to lower the reflectivity level of the light in the region of the visible light spectrum with longest wavelength (red-yellow area). Figure 2 shows the reflectivity profiles of pure gold (curve 1) and the reflectivity profiles of gold alloys with increasing nickel content (left-hand graph) and palladium content (right-hand graph). It can be seen that increasing additions of the two elements produce a flattening in the reflectivity profile throughout the visible light region, which is perceived as an increase in the whiteness degree of the object observed.

Figure 2 – Reflectivity curves for gold alloys containing nickel (left) and palladium (right).
Left: 1-Au pure, 2-Au2at%Ni, 3-Au5at%Ni, 4-Au10at%N, 5-Ni pure.
Right: 1-Au pure, 2-Au5at%Pd, Au10at%Pd, 4-Au20at%Pd, Au30at%Pd, 6-Pd pure (6, 13).



Assessment of the degree of whiteness of an alloy can be performed via the Yellow Index *(6)* (YI) which is a scalar number calculated from spectrophotometric data (in the same way as the CIELab coordinates). The Yellow Index derives from an index used for plastic (Standard D-1925).
The white quality scale has been drawn up by Chris Corti in collaboration with MJSA (Manufacturers of Jewelry Society of America). On the basis of this type of classification, white gold is classified in the following categories:

1. Premium white, with YI below 19 (rhodium-plating not necessary).

2) Standard white, with YI between 19 and 24.5 (rhodium-plating optional).

3) Off white, with YI between 24.5 and 32 (the piece must be rhodium-plated).

4) *Yellow alloy,* with YI above 32. The gold can no longer be considered white.

*(6) Yellow Index calculation formula: YI = 100 * (1.274641506 * X - 1.057434092 * Z) / Y - 4.5, where X, Y, Z represent the three tristimulus values: X = (Coordinate_L + 16) / 116 + (Coordinate_a / 500); Y = (Coordinate_L + 16) / 116; Z = (Coordinate_L + 16) / 116 - (Coordinate_b / 200).*

Although not yet officially acknowledged by any standards body, this classification is considered in practice a reference recognised by the majority of operators in the sector. The adoption of this white gold definition system therefore excludes the possibility of using yellow gold alloys as a base for the production of white gold objects even if they undergo rhodium-plating treatment (Figure 3).

Figure 3 – Rhodium-plated bronze key ring after 4 years of use. The red colouring of the alloy below due to progressive surface wear and removal of the surface rhodium layer is clearly visible.

Many elements have gold whitening properties. One of the possible alternative whitening agents to nickel is obviously palladium, which currently represents the best and most “noble” alternative to the use of nickel; as is known, the main drawback of palladium is its high cost. Palladium is used mainly as a whitening agent for 750‰ gold alloys, where it is added in a concentration range of between 10 and 15% of the gold alloy. Palladium is also used for the production of 585‰ white gold alloys, in which it is added in concentrations normally between 8 and 15% of the gold alloy.
Palladium has a whitening effect slightly lower, but anyway rather similar in terms of intensity to that of nickel, with excellent mechanical deformability properties. As it is a high-melting metal (1555°C), it gives gold alloys higher melting temperatures on average than nickel. As regards mechanical properties, 750‰ palladium gold alloys have lower hardness values than the corresponding nickel white gold alloys, unlike 585‰ palladium white gold alloys, which are on

average harder and have poor deformability compared to the nickel-based alloys. The main properties of nickel and palladium-based white gold alloys are summarised in Table II.

Table II – Comparison of main properties of white gold alloys with nickel and palladium as whitening elements.

	750‰ gold alloy			585‰ gold alloy		
Whitening element	% in alloy	Melting range	Hardness range	% in alloy	Melting range	Hardness range
Nickel (Ni)	3-12	880-970	160-240	5-12	810-960	140-200
Palladium (Pd)	10-17	970-1300	100-170	8-15	1000-1100	160-230

Lastly, the possibility of developing "hybrid" alloys containing both nickel and palladium represents a possible and interesting development for white gold alloys, even though this configuration is not widely used in the current state of the art. In-house studies would appear to show that white gold alloys containing both nickel and palladium have intermediate physical-mechanical properties and that the inclusion of palladium reduces the nickel release level.

One of the most significant gold whitening elements is zinc, which is normally always present as a secondary whitening element in white gold alloys containing nickel. Zinc reduces the liquidus temperature, improves flowability of the alloy and has a moderate anti-oxidising effect (5). However, it cannot be used as a single whitening agent due to the rapid deterioration in its mechanical properties as its concentration in gold alloy increases beyond 4-5%. Increasing concentrations of zinc also tend to increase the level of surface porosity in lost wax cast objects, increasing the risk of hot cracks, and reduce the brightness of the alloy. As the concentration of zinc in alloy increases, there are problems with excessive fume production and production of residues during melting, with increase in the final loss.
Gallium (7,8) has been recently studied as a possible alternative to nickel and palladium due to its marked whitening properties and relatively limited cost. Gallium-based white gold alloys have shown excellent properties in terms of surface quality on lost wax cast objects and particular suitability for lost wax casting with stones, due to the low casting temperatures which minimise thermal shocks even on the most sensitive stones. Nevertheless, the possible use of gallium is limited by various contra-indications, of which the most problematic is the very low initial melting temperature of the gold alloys obtained, in particular 750‰ gold alloys ($T_{solidus} \approx 400°C$), a characteristic which makes it practically impossible to use these alloys in torch soldering processes, and allowing their use only in laser soldering or self-soldering. At 585‰ carat title ($T_{solidus} \approx 710°C$) their use is less problematic. Gallium-based white gold alloys have a tendency to yellowing, and therefore final rhodium-plating treatment is required.
Manganese (Mn) has a certain, albeit restricted, field of application in the production of white gold alloys, in particular in machining processes. It is nevertheless a problematic element in use due to its high reactivity and substantial production of scrap. It has an excellent whitening action, but white gold alloys with manganese tend to rapidly tarnish after exposure to the air and have poor resistance to corrosion.
Manganese does not appear to have allergenic properties, but its possible involvement in the onset of Parkinson's diseases has been reported (9).
Chromium (Cr) has been recently studied due to its high whitening properties and its ability to give gold alloys excellent resistance to corrosion (10). However, its high reactivity with the graphite of the crucibles and the formation of oxides which are extremely difficult to remove by means of normal pickling makes the use of chromium unsuitable for the gold jewellery sector. There are currently no known industrial applications in which chromium is used as a whitening element for white gold.
Cobalt (Co) has a modest whitening power. Gold alloys containing cobalt have a high degree of segregation in two different phases, high hardness and low deformability. As cobalt is also an element with allergenic properties, it cannot be considered a possible alternative to nickel (11).
Silver is considered an element with moderate whitening properties. It is used in the production of nickel-free gold alloys with low carat title (375‰), where it is used in concentrations typically in the order of 45-58% of the gold alloy. These are moderately low-melting alloys which have excellent mechanical deformability but are characterised by fairly modest hardness values (≈ 100 HV).
Iron (Fe) has excellent whitening properties and in general confers good mechanical deformability. However, it is contra-indicated due to the poor corrosion resistance of the gold alloys obtained.
Lastly, the following are also whitening elements: indium (In), tin (Sn), aluminium (Al), platinum (Pt), titanium (Ti), tantalum (Ta), niobium (Nb) and vanadium (V) but, for various reasons, are of little practical interest for the gold jewellery sector. For further information, please refer to the existing scientific literature.

The use of protective coatings and their impact on the final release value

In order to verify the protective effect of galvanic deposits on the release of nickel after wear treatment, comparative tests were performed using a 750‰ gold alloy containing nickel (4.25% Ni in the final alloy). The release levels of plates of alloy as is (without galvanic deposit) in the different states (as cast, cold-worked, annealed, homogenized) and in two different finishing states (polished and lapped) were determined; the non-coated samples were compared with sheets on which galvanic deposits of various types were performed, which underwent the wear test according to the EN12472:2009 standard before determining the nickel release. The tests were performed in three different independent laboratories to evaluate the reproducibility of the data obtained.
The results are given in Table III.

Table III – Results of release tests performed on a 750‰ white gold alloy containing nickel (4.25% in final alloy). Key to abbreviations: Unc: sample as is (without galvanic deposit); Coat: with galvanic deposit; Ann.: sample annealed at 720°C x 20 min; Hom.: sample solubilised at 820°C x 40 min.; Coldw.: sample in cold-worked state after 70% reduction by rolling, AsC: as cast sample obtained by lost wax casting; Lap: sample incorporated in epoxy resin, with surface finish to 1 µm with metallographic cloths ; Pol: bench finish with rotary cloths; PdFesp+Rh: thick galvanic deposit of palladium + iron (0.8 µm) followed by rhodium galvanic deposit (0.3 µm); Agsp+Rh: thick silver galvanic deposit (0.8 µm) followed by rhodium galvanic deposit (0.3µm); Agsp+PdFe+Rh: thick silver galvanic deposit (0.8 µm) followed by thick palladium + iron (0.8 µm), followed by rhodium galvanic deposit (0.3 µm); Ptsp+Rh: thick platinum galvanic deposit (0.8 µm) followed by rhodium galvanic deposit (0.3 µm); Rhsp thick rhodium deposit (0.5 µm); Avg: mean referring to group of values considered (between the two horizontal lines); Sd: standard deviation; CV%: variability coefficient (sd/Avg,) expressed as a percentage.

Sample	Laboratory	Coated/Uncoated	State	Finish	Release	Avg	Sd	CV
A1	A	Unc	Ann	Lap	0,231	0,221	0,035	16%
A2	A	Unc	Ann	Lap	0,175			
A3	B	Unc	Ann	Lap	0,225			
A4	B	Unc	Ann	Lap	0,183			
A5	C	Unc	Ann	Lap	0,250			
A6	C	Unc	Ann	Lap	0,260			
A7	A	Unc	Ann	Pol	0,203	0,170	0,053	31%
A8	A	Unc	Ann	Pol	0,262			
A9	B	Unc	Ann	Pol	0,133			
A10	B	Unc	Ann	Pol	0,131			
A11	C	Unc	Ann	Pol	0,160			
A12	C	Unc	Ann	Pol	0,130			
A13	A	Unc	Hom	Lap	0,182	0,169	0,018	11%
A14	A	Unc	Hom	Lap	0,142			
A15	B	Unc	Hom	Lap	0,175			
A16	B	Unc	Hom	Lap	0,175			
A17	A	Unc	Hom	Pol	0,150	0,115	0,047	41%
A18	A	Unc	Hom	Pol	0,162			
A19	B	Unc	Hom	Pol	0,080			
A20	B	Unc	Hom	Pol	0,069			
A21	A	Unc	Coldw	Pol	0,153	0,130	0,029	23%
A22	A	Unc	Coldw	Pol	0,157			
A23	B	Unc	Coldw	Pol	0,115			
A24	B	Unc	Coldw	Pol	0,096			
A25	A	Unc	AsC	Pol	0,180	0,190	0,034	18%
A26	A	Unc	AsC	Pol	0,240			
A27	B	Unc	AsC	Pol	0,165			
A28	B	Unc	AsC	Pol	0,174			
B29	B	Coat	Ann	PdFe+Rh	0,016	0,030	0,016	53%
B30	B	Coat	Ann	PdFe+Rh	0,034			
B31	B	Coat	Ann	Agsp+Rh	0,046			
B32	B	Coat	Ann	Agsp+Rh	0,027			
B33	B	Coat	Ann	Agsp+PdF	0,020			
B34	B	Coat	Ann	Agsp+PdF	0,027			
B35	B	Coat	Ann	Ptsp+Rh	0,018			
B36	B	Coat	Ann	Ptsp+Rh	0,034			
B37	B	Coat	Ann	Rhsp	0,038			
B38	B	Coat	Ann	Rhsp	0,025			
B39	C	Coat	Ann	Rhsp	0,010			
B40	C	Coat	Ann	Rhsp	0,070			

Although the available data was not sufficient to allow any particular statistical processing, the results shown in Table III nevertheless highlight some interesting findings, the most important of which are summarised below:

- There is a certain variability in comparison of the results between the various laboratories. In particular, the data obtained from laboratory B are almost systematically inferior compared to laboratories A and C; despite this, the sample groupings between the separation lines are relatively uniform and comparable.
- From comparison of the samples in the annealed state, a lower release value was identified in the polished samples compared to the lapped samples; a possible explanation could be closure of part of the surface porosity caused by the cloth polishing in the former compared to the latter, with consequent reduction in the release.
- The homogenization treatment appears to result in greater reduction of the release values of the annealed samples;
- The cold-worked samples show release values below those hypothesised.
- The samples obtained from the lost wax casting process show limited release values not significantly different from the samples obtained by machining.
- The samples treated with galvanic deposit show a significant reduction in release of approximately 7 times compared to the mean of the annealed and polished samples (samples A1…A6). Due to the small number of samples tested, it is not possible to establish whether there are significant relations between the release values and the type of galvanic deposit applied.

In general, it is interesting to observe that as the state of the material varies, the variations in the release data remain within acceptable limits. An overview of the surface conditions found on the coated samples is given in Figure 4.
In the light of the tests performed, the galvanic deposit of metals on samples of white gold has significantly contributed to reducing the release and therefore to achieving compliance with the European legislation.
Recent studies have furthermore evaluated the effect of one or more further galvanic deposits on white gold elements already rhodium-plated, in order to assess whether the additional deposit could further contribute to reduction in nickel release. The reason behind this series of tests was the need to find possible solutions for the recovery of warehouse stocks which may not be complaint after 1st April 2013. The data on the work carried out, presented last December in Vicenza (13), considered the effect of different types of multi-layered galvanic deposits on an object obtained by lost wax casting and a second object obtained by machining, starting from the same alloy formulation. The results highlighted that it was possible to obtain a further reduction in nickel release on the lost wax cast object by means of both multi-layer deposits of palladium + rhodium and silver + rhodium, deposited over the existing rhodium plating layer.
In the case of the lost wax casting, the object studied consisted of an assembly of different components, combined by laser and torch soldering techniques. The complexity of the assembled part resulted in fairly high release values, on which the galvanic treatments best demonstrated their barrier effect, although not in all cases guaranteeing compliance with the values established by the standard. As regards the machined pieces, the superior process control provided by the annealing and oven soldering resulted in improved emissivity values in the piece as is. The protective effect of the overlayers was always confirmed, even though precise figures cannot be provided due to the uncertainty of the measurements.

Figure 4 – Observations on the surface conditions of some coated samples described in Table III after abrasion treatment and nickel release test performed according to EN12472:2009 and EN1811:2011 standards. Figure 4a: central surface erosion area on sample B29 (PdFe + Rh); Figure 4b: erosion area on plate edge on sample B32 (Ag + Rh); Figure 4c: delamination area on sample B35 (Pt + Rh); Figure 4d: erosion area and scratching area on sample B37 (Rh); Figure 4e: detachment area and surrounding corrosion area on sample B38 (Rh); Figure 4f: emergence of underlying porosity on sample B38 (Rh).

Figure 4a

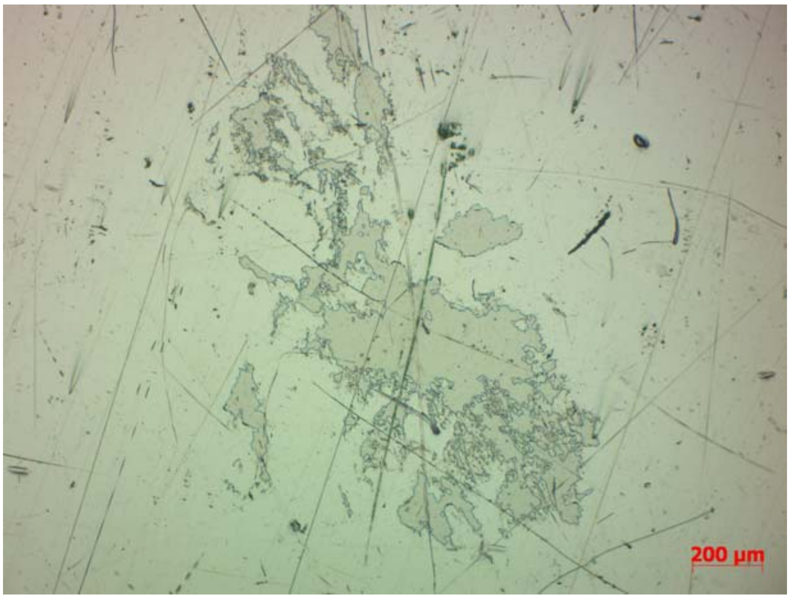


Figure 4b

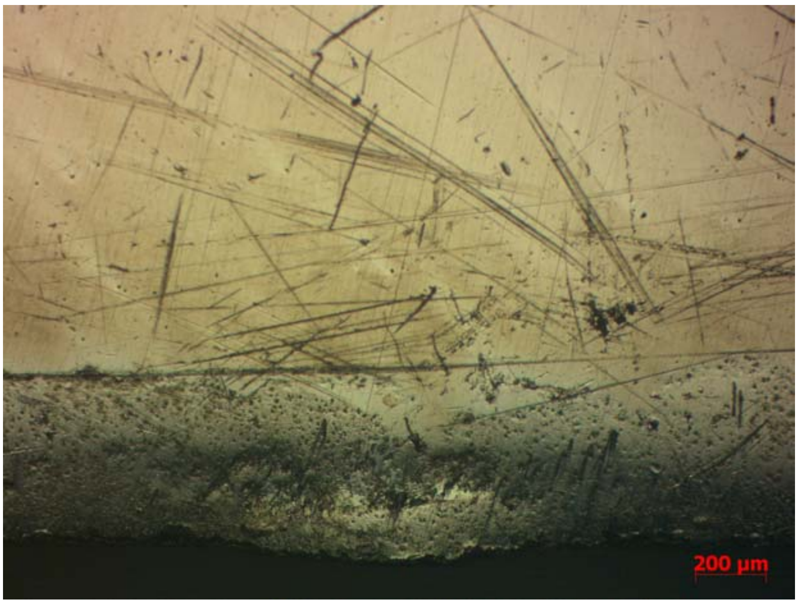


Figure 4c

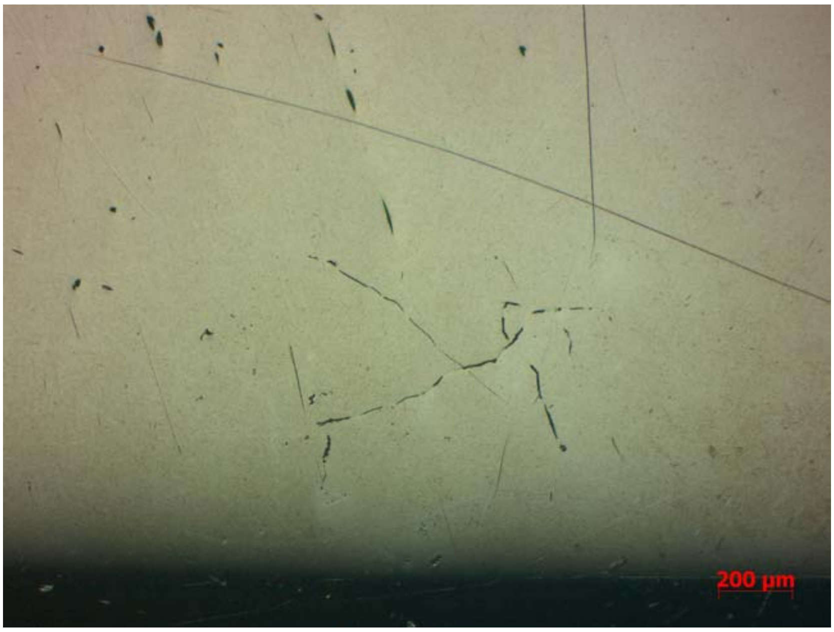


Figure 4d

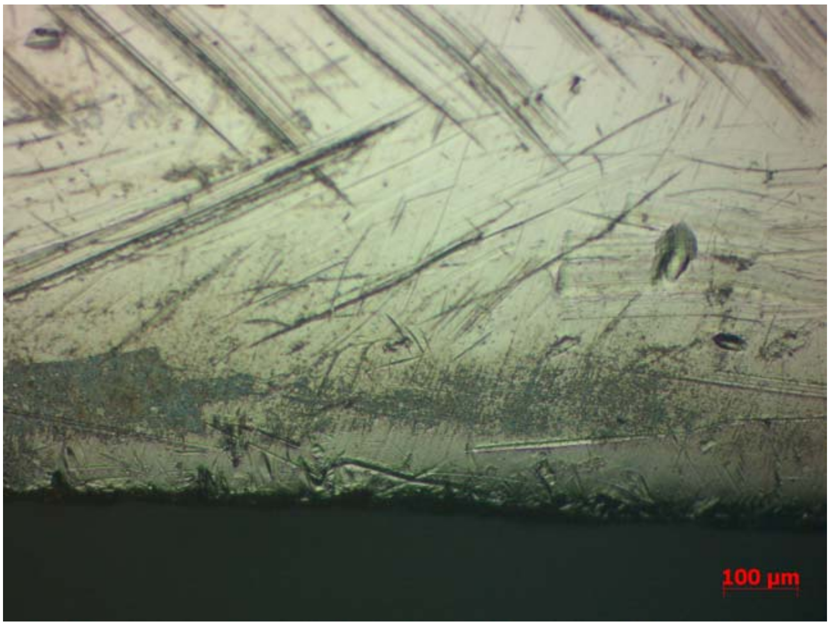


Figure 4e

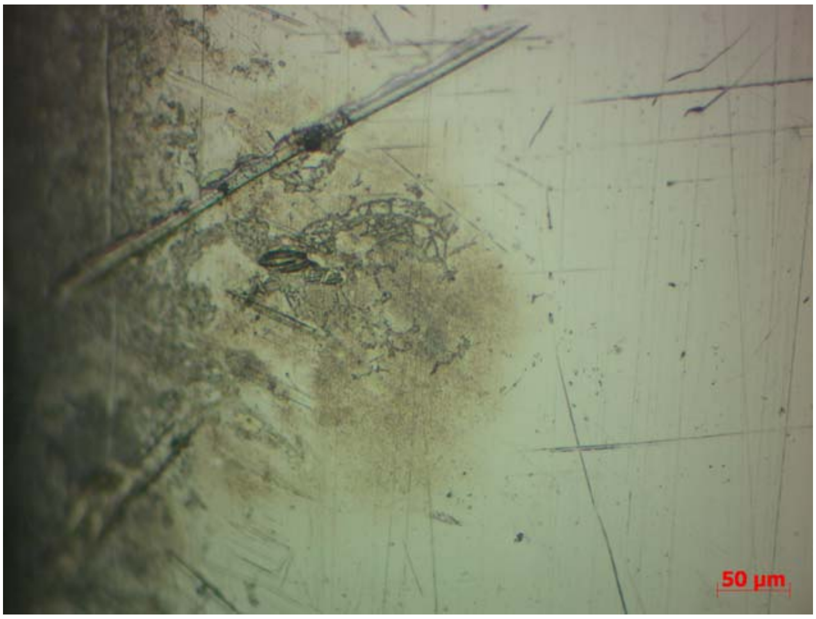
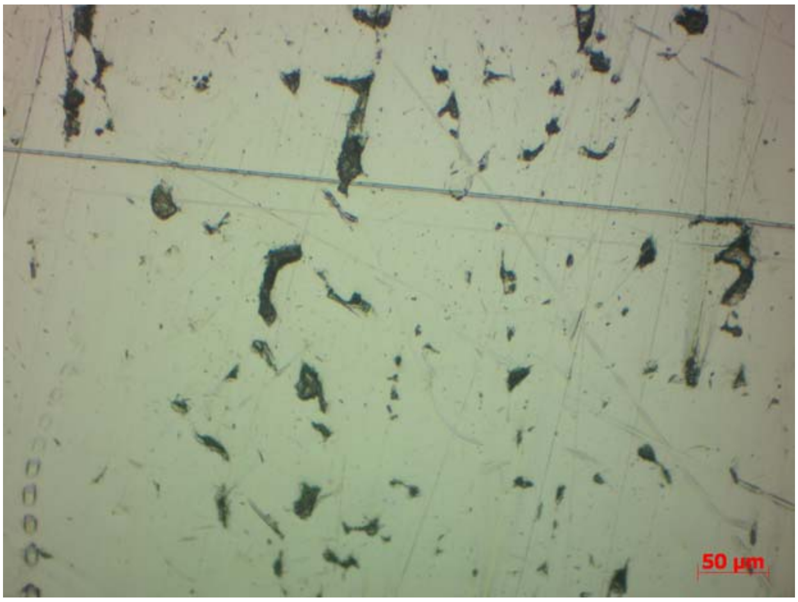


Figure 4f

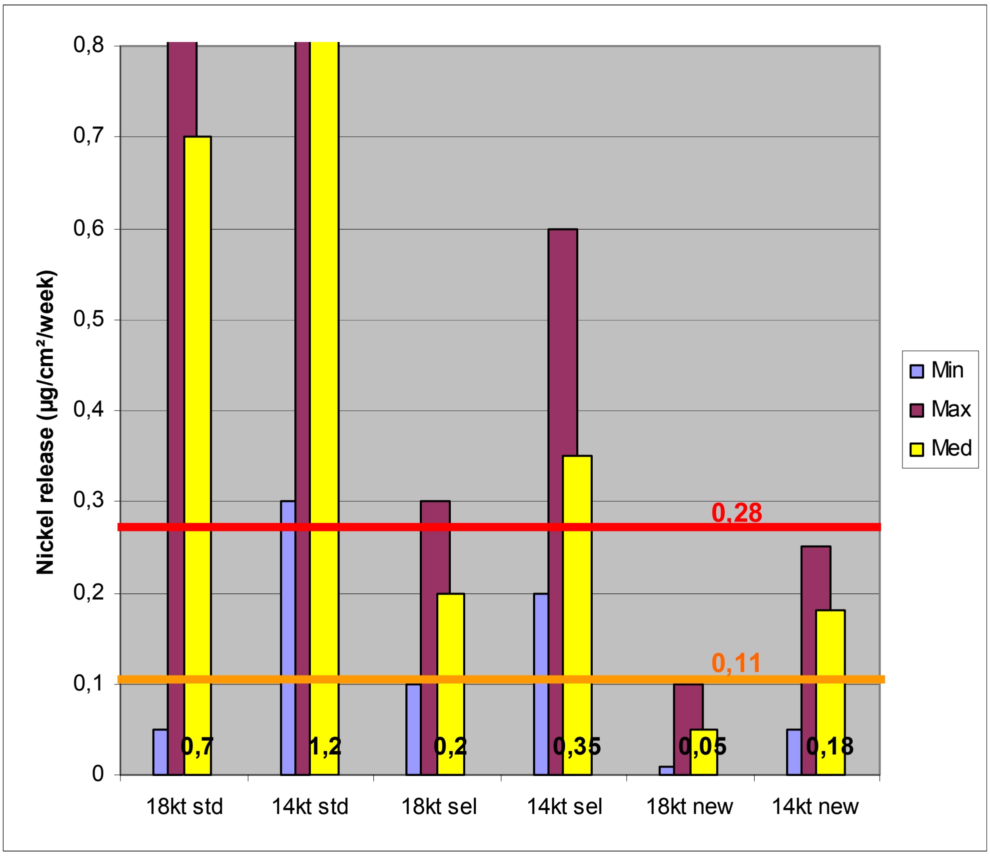


Possibility of improvement in white gold alloys containing nickel

In the current state of metallurgical knowledge, it is reasonable to envisage new formulations with nickel release below the limits established by the new EN1811:2011 standard.
Likewise, it can be assumed that the range of formulations that will be available as from April 2013 will probably be more limited than the current one, since some types of formulation will no longer be compatible in metallurgical terms with the obtaining of gold alloys with low release values.
The improvement actions that will permit the development of a new generation of alloys containing low-release nickel are based on metallurgical pre-conditions, the contents of which are beyond the scope of this discussion. Of these, the importance of the use of grain refiners and the ratio between the content of nickel and the other alloy elements should be underlined.
On the basis of these pre-conditions, studies performed in the Legor Group Research and Development laboratories have led to the identification of "new generation" white gold alloys with the following main characteristics:

- Release values reduced to approximately 20-25% compared to the best nickel-based white gold alloys currently available on the market (Figure 5);
- Greater stability during variation in the state of the material and its form, with fluctuation of the release values over a more limited range compared to the conventional alloys.

Figure 5 – Comparison of nickel release values. Std: mean release values found in a generic sample in 750‰ (18kt std) and 585‰ (14kt std) alloys respectively; 18kt sel, 14kt sel: mean (Med), maximum (Max) and minimum (Min) release values found in objects produced with low-release white gold alloys currently available on the market; 18kt new, 14kt new: mean, maximum and minimum release values found in objects produced with "new generation" white gold alloys with very low release.



These interesting possibilities can provide greater guarantees of safety in terms of compliance with the limits established by the new EN1811:2011 standard, despite the inevitable fluctuations in release values depending on the specific situations of use.
The introduction of “new generation” nickel-based white gold alloys has, as already mentioned, been made possible by the introduction of innovative elements with high crystalline grain refinement capacity. The marked reduction in dimensions of the crystalline grain must be related to the significant reduction in the segregation effect and therefore in the generation of galvanic couples responsible for the corrosive phenomena at the origin of nickel release. A comparative example of a 750‰ gold alloy currently on the market characterised by a low nickel release level (RIF.) and some examples of “new generation” alloys are given in Table IV and Figure 6.

Table IV – Comparison of 750‰ white gold alloys containing nickel. RIF.: conventional white gold alloy; A, B, C, “new generation” alloys. The difference in the dimensions of the crystalline grain and the release values can be clearly seen.

	RIF.	A	B	C
Crystalline grain (µm)	185±75	32±9	26±6	16±4
Nickel release (µg/cm2/week)	0.2	0.045	0.036	0.025

Figure 6 – Crystalline grain of conventional 750‰ white gold alloy containing nickel (Sample RIF, Figure 6a) compared with “new generation” (sample A, Figure 6b)”. The difference in the dimensions of the crystalline grain and the release values can be clearly seen.

Figure 6a

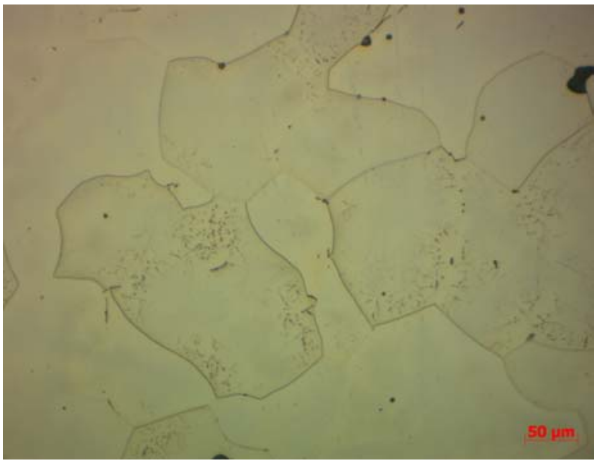


Figure 6b

Having said this, the use of appropriate formulations must go hand in hand with the adoption of correct procedures for use in standardised production processes; without these, it is not possible to produce high carat white gold jewellery.
The process control must be rigorously standardised, especially as regards all the process steps involving modifications to the microstructure, such as annealing, plastic deformations or soldering. If it is not possible to carry out a repeatable control on the microstructural characteristics of a piece, compliance with the standard cannot be guaranteed.
Lastly, the systematic performance of a quality control on the production batches on a representative number of samples grouped per object type is essential in order to obtain realistic statistics of the release values. The EN1811:2011 standard recommends performing the release test on at least three samples for each uniform batch of objects (point 8.3.4.).

In this regard it should be underlined that the jewellery producer or person who places the product on the market is solely responsible for compliance with the standard vis-à-vis the end customer.

It should always be remembered that, given the same composition, the release of nickel is linked to the following important factors:

1. State of the material: plays a fundamental role in the emissivity of the nickel. Although the difference between the various states is greatly influenced by the specific composition and crystalline grain, objects in a cold-worked state or not correctly homogenized (two-phase structures) may be subject to an increase in nickel release by as much as 100 times! It is therefore always advisable to check the state of the material and where possible perform homogenization of the pieces before final polishing with a heat treatment at temperatures from 640°C to 820°C for 30-40 minutes, in a reducing atmosphere. The higher the treatment temperature, the greater the probability of reducing the nickel release.
2. Surface roughness: polished, flat, mirror-finished surfaces generally have a lower emissivity. Since nickel release is to all intents and purposes a process of corrosion, every pointed shape, every sharp edge, every rough surface increases the release of nickel due to the so-called “shape effect”. In this regard, the standard establishes that the release test must be performed on the parts in direct and prolonged contact with the skin. The release of nickel on an entire object with considerable surface complexity in the decorative part (e.g. ring with griffe, pavé, etc.) may therefore be much higher than on the same object in which all the parts not in direct and prolonged contact with the skin are masked. This aspect should no longer be under-estimated, in our opinion, in view of the extremely low limits imposed by the new EN1811:2011 on producers. The laboratory that performs the release test should document in the test report (for example by means of photos) the sample preparation methods and the area considered for the test, as required by the EN1811:2011 standard in points 10c and 10d, relative to the preparation of the test report.
3. Surface porosity: similarly to roughness, an object without porosity generates a lower release of nickel ions compared to a porous piece. This indicates once again how important it is to obtain high quality compact surfaces free from surface defects.

Lastly, the importance of standardisation of the production process conditions must be considered, paying particular attention to the uniformity of the heat, mechanical and finishing treatments performed on the objects.

Conclusions

The study has attempted to provide a general overview of the problems and possible solutions connected with introduction of the new European standard EN1811:2011. The considerations made highlight a difficult situation as regards the production of white gold jewellery. In terms of materials, the use of palladium-based nickel-free white gold alloys still represents the most versatile (and costly) alternative to the use of white gold alloys containing nickel. The possible alternatives represented by metals other than palladium and nickel for the production of white gold may offer partial solutions limited to particular applications. One possible solution is represented by the so-called “new generation” alloys containing nickel with very low release, the introduction of which appears to be realistic for 750‰ gold jewellery production and, albeit to a lesser extent, also for 585‰ gold jewellery.
The use of specific galvanic deposits of one or more elements able to significantly lower the release values is also of great interest.
Lastly, it is fundamental to remember the decisive importance of the gold jewellery manufacturer in the production of an object with release limits in compliance with the European legislation. For producers who intend to use white gold alloys

containing nickel, standardisation and effective control of the production process represent an essential condition for achievement of the new standards imposed by the new EN1811:2011.

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