

Preventing nickel allergy using various topcoats for decorative items

Allergic contact dermatitis (ACD) is a form of skin reaction that can be aggravated by nickel causing the skin to become red and itchy. Clive Whittington (Managing Director of C.M. Whittington & Associates Ltd) and Dr W. Y. Lo (Secretary General, Hong Kong Surface Finishing Society) have tested a range of coatings over nickel-based decorative articles such as costume jewellery and watches, to prevent ACD. The aim of these coatings is to keep the concentration of nickel comfortably under the REACH (the EU Commission's Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals) safety restrictions and thus minimise the risk of nickel allergy. Nickel-containing decorative alloys were also evaluated.

If you have a nickel allergy, something as simple as wearing a watch can trigger an allergic reaction. Nickel can be found in everyday decorative items, including costume jewellery and watches, which can make it difficult for those with an allergy to avoid. A collaboration between Dr William Y. Lo and Clive Whittington aims to improve the use of nickel in the marketplace and help prevent nickel allergy.

When a part of the body is consistently in contact with nickel, sweat can liberate nickel ions which are absorbed by the skin. That area of skin can become easily irritated and prone to an allergic reaction. This phenomenon is called Allergic Contact Dermatitis (ACD), but it is also colloquially referred to as nickel allergy. The skin turns red and itchy

as a response to the allergen (nickel). Allergic sensitisation, leading to ACD, can often be triggered when the skin is in contact with nickel-plated watches, items such as clothing hooks, clasps and zippers, costume jewellery, and body piercing items.

WHAT CAUSES ACD?

It's difficult to tell who will become allergic to nickel or what can trigger contact dermatitis. In the UK, contact dermatitis affects 9% of the population and can be caused by many irritants. Nickel is a common allergen, but nickel allergy mostly affects females, in particular young women – often as a result of wearing more jewellery.

ACD does not occur upon first contact between the skin and nickel (the allergen).

A reaction to wearing nickel can be itchy and uncomfortable. Watches and jewellery often contain nickel.



Sweat from the skin can liberate nickel ions which are absorbed by the skin and initiate an allergic response

Instead, the body becomes sensitised, but may not react immediately. When the skin is further exposed to nickel, the now-sensitised body treats it as an allergen and the immune system reacts. The response to the nickel causes the skin to become red and itchy. Once the item containing nickel is removed, ACD symptoms will start to dissipate. The degrees of allergic response differ greatly from person to person.

Clive Whittington and Dr William Lo evaluated non-nickel surface coatings which enable nickel-containing consumer products to be safely placed on the market without concern for nickel release. Such products must comply with specific regulations covered by the EU 'Nickel Restrictions' which impose limits on the amount of nickel released from articles intended to come into direct and prolonged contact with skin (like the back of a watch).

In the tests run by Whittington and Lo, each coating was measured for nickel release according to the CEN (Comité Européen de Normalisation, European Committee for Standardization) nickel tests for coated items: EN 12472 (for wear and corrosion) and EN 1811 (for the determination of nickel release). The CEN tests require that nickel release should not exceed $0.5 \mu\text{g cm}^{-2} \text{ week}^{-1}$ after two years of normal use. However, because of measurement uncertainty

an article is compliant if nickel release is $< 0.88 \mu\text{g cm}^{-2} \text{ week}^{-1}$ after two years and can be placed on the market.

Since costume jewellery is usually made from cheaper metals and plated with nickel, these items are more likely to trigger nickel ACD in sensitised persons. Therefore, there is a need for efficient topcoats to prevent nickel release from these decorative items in particular.

COATINGS FOR NICKEL-BASED DECORATIVE ITEMS

In their ongoing research, Whittington and Lo look at using different coatings that prevent the release of nickel from nickel-based decorative items on the market. They tested non-nickel surface coatings including gold alloys, coloured and uncoloured topcoats against nickel release and found most coatings succeeded in preventing nickel release well within the CEN nickel-release limits.

CHROMIUM TOPCOATS

In their initial tests, the authors found that regular chromium deposited from a hexavalent electrolyte, microporous trivalent chromium from a chloride electrolyte, and ultraviolet (UV) cured

polyurethane electrophoretic coatings prevent nickel release when applied according to the relevant International Organization for Standardization (ISO) specifications. However, hexavalent chromium electrolytes are constrained in many jurisdictions due to environmental concerns. Trivalent chromium electrolytes therefore present an effective alternative.

SULPHUR-CONTAINING BRIGHT NICKEL WITH FLASH GOLD DEPOSITS

Whittington and Lo also tested electrodeposits of sulphur-containing bright nickel on pieces of costume jewellery and determined that nickel ions were released at a rate exceeding acceptable CEN limits. A thin, porous flash topcoat of gold applied over the same items also failed the tests, since the thin coating of gold significantly accelerated the release of nickel to figures exceeding the CEN limits. On the other hand, an uncoated gold alloy containing 6% nickel passed the CEN nickel-release tests.

METAL SURFACE COATINGS

Costume jewellery and watch cases



Costume jewellery often contains nickel which can cause an allergic reaction.

Nickel allergy often occurs where nickel-containing jewellery, like a ring, has been worn in close contact with the skin.



WHAT'S A PVD TIN COATING AND HOW IS IT APPLIED?

PVD TiN refers to a Titanium Nitride (TiN) coating applied by a process called Physical Vapour Deposition (PVD). This coating is the most commonly applied PVD coating because it is durable, inert, adherent and can be easily stripped and recoated if needed. A PVD TiN coating has several uses and

COATINGS CAN BE COLOURED TOO...

As well as looking at the different coatings that prevent nickel release, Whittington and Lo also tested different colours that could be applied to topcoats to give the effect needed. For example, organic non-nickel topcoats may be dyed to produce a variety of colours in the surface finish of the item. The results from these tests showed that most coatings passed the CEN tests and did not exceed the nickel release limits.

Nickel is one of the most common metals used in costume jewellery and watch cases. As nickel allergy is so widespread, research to discover which coatings could be used to prevent nickel release is extremely significant.

The researchers found regular hexavalent chromium, microporous trivalent chromium from a chloride electrolyte, ultraviolet (UV) cured polyurethane electrophoretic coatings

having an electrodeposited palladium barrier coating (either as a topcoat or an intermediate layer over bright nickel) prevented nickel release and kept it within CEN limits successfully.

NICKEL-CONTAINING AUSTENITIC STAINLESS-STEEL WATCH CASES

For this test, Whittington and Lo utilised watch cases made of nickel-containing stainless steel (Grades 304 and 316). They masked off the areas of the watch case that did not come into contact with skin and tested for nickel release when uncoated and also coated with a very thin Physical Vapour Deposition Titanium Nitride (PVD TiN) coating. Both the uncoated and coated watch cases passed the CEN nickel release tests comfortably.

is currently used on many expensive tools, medical (implanting and surgical) instruments, food processing and decorative applications. TiN is applied by vaporising the material from a solid source in the form of atoms/molecules and then transporting it in the form of vapour through a vacuum, low-pressure gas or plasma to the substrate (e.g. a watch case) where it condenses and coats the item.

and an electrodeposited palladium barrier all prevent nickel release. Additionally, nickel-containing stainless steel with or without a PVD TiN coating readily passed the CEN nickel release tests. The results of this work mean these coatings and alloys can be used for decorative articles that are sold in the market without concerns about nickel release exceeding the recommended limits.

The EU 'Nickel Restrictions' impose limits on the amount of nickel released from articles.



Nickel containing austenitic stainless-steel watch cases were submitted to the approved CEN nickel release tests, with nonsignificant surfaces masked as shown in accordance with the specified test method.

Behind the Research



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Dr William Lo

Research Objectives

Clive Whittington and Dr Lo's work looks at ways to prevent nickel allergy.

Detail

Bio

Clive is a Chartered Professional Engineer, Fellow of the Institute of Materials Finishing (UK) and Managing Director of C. M. Whittington and Associates Ltd in Hong Kong and Melbourne, distributing nickel to manufacturers in Asia. He undertakes original research on the better use of nickel and provides technical consulting services to end-users.

Dr William Lo is focused on industrial surface finishing, materials technology and testing, especially applied R&D, technology transfer in production and waste minimisation technology. He is a Fellow of the Institute of Materials Finishing (UK) and has worked as a technical adviser and industrial consultant in the surface finishing industry for more than 20 years.

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Personal Response

What first sparked your interest in nickel allergy and the prevention of ACD?

Manufacturers in Asia are major suppliers of costume jewellery, watch components and decorative consumer items to Europe, and if independent testing identifies that nickel release exceeds the CEN test limits, they cannot be placed on the market. To ensure product designers, manufacturers and merchandisers of nickel-containing articles are able to export to Europe, this work was undertaken to provide peer-reviewed guidelines to industry.

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