

Review Article

A metallurgical approach to metal contact dermatitis

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It is well-known that some metals/alloys are sensitizing on skin contact, but it is not so well appreciated that sensitization is dependent on the reaction of the metal/alloy with sweat. The first step in skin sensitization by metals/alloys is a corrosion process and the formation of soluble metal ions. The nature of this process has implications with respect to occurrence of metal contact dermatitis, to testing techniques and to classification of metals/alloys as skin sensitizers.

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In most cases, toxicity due to metals (M) in the metallic state arises only when reaction occurs with electrolytes such as body fluids or, in the case of ecotoxicity, with aqueous environmental fluids. The reaction is electrochemical in nature and it is the metal ions, formed by anodic reaction, e.g., $M = M^{++} + 2e^-$, that exert toxic behaviour. Electrons from the anodic reaction are consumed by a corresponding cathodic reaction, which most commonly is the reduction of oxygen, $O + H_2O + 2e^- = 2(OH)^-$, but may also be the evolution of hydrogen, especially in acid solutions, or the reduction of a high valency species such as ferric or cupric ions. Generally, the 2 reactions occur randomly over the metal surface. In the absence of oxygen or other reducible species, the cathodic reaction cannot occur, and the anodic formation of metal ions does not take place.

Skin contact with metals presents a special case in that at the skin/metal interface, oxygen may be excluded, whilst the thin films of sweat provide an electrolyte with high electrical resistance. Thus the shape, nature of contact with the skin and mode of use of articles that contain an allergenic metal can be critical in determining the onset of an allergic reaction. In so far as metal contact dermatitis is concerned, *pure* metals may be placed in 4 categories, '?' indicating where data are inadequate:

- I. metals that do not react with sweat or form allergenic ions: titanium, molybdenum, niobium, silver, tungsten(?);
- II. metals that do not react with sweat but can form allergenic ions (1, 2): aluminium, chromium, gold, palladium, platinum, rhodium;
- III. metals that react with sweat but do not form allergenic ions: antimony (?), cadmium (?), iron, lead (?), zinc, zirconium;
- IV. metals that react with sweat and can form allergenic ions (1, 2): beryllium, copper (?), cobalt, mercury, nickel, tin (?).

Categorization in this way, although providing a guide to possible incidence of dermatitis, has limited application in practice, primarily because pure metals are generally not of wide occurrence; alloys are of much greater significance and can have properties very different from those of the metals they contain. Secondly, a variety of ions may be formed by the metal/alloy and those formed by reaction with sweat may not have the greatest allergenic potency.

The ability of allergenic metal ions to elicit a reaction in a particular person is dependent upon their concentration, the area of skin exposed and the duration of exposure (3, 4). The concentration of ions developed by reaction of a metal with sweat is dependent on:

(i) the rate of reaction of the metal, which is governed by its electrochemical characteristics, the supply of oxygen or other reactant to the cathodic surface and the electrical resistance of the film of sweat;

(ii) the geometric configuration, which controls diffusion of reactants, e.g., oxygen, to the reacting surfaces and of corrosion products away from reacting surfaces (the reaction products may form insoluble compounds and although remaining on site, may be present in an innocuous form);

(iii) the supply of sweat and its composition.

Thus, the circumstances governing development of the critical concentration of metal ion at the metal/skin interface that is necessary to cause sensitization, can be complex and variable.

Alloys

Alloys cannot be considered as mixtures of metals. The constituent metals (i) may react with one another and form intermetallic compounds, (ii) may partially dissolve one with another and form separate phases, (iii) may completely dissolve and form a complete range of solid solutions, (iv) may form a continuous oxide film on the surface of those alloys that contain a sufficiently high content of a metal which readily forms a stable oxide, e.g., chromium or titanium, and thus be completely protected against corrosion. Even in those cases, such as lead-iron alloys, where the constituent metals do not dissolve or react one with another and remain as separate entities, they will affect each other to greater or lesser extent in the electrochemical reaction of the alloy with sweat.

Thus, there is no relationship between content of allergenic metal in the alloy and ability to cause an allergic response, but there is a close relationship between rate of formation of ions of the allergenic metal in sweat and elicitation of contact allergy (5, 6). For this reason, when assessing the allergenicity of alloys and dose/response relationships, the dose is defined not by the metal concentration in the alloy but by the rate of formation of allergenic metal ions.

When the content of allergenic metal in the alloy is low, the rate of formation of metal ions may be insufficient to allow a concentration to be achieved which will initiate an allergic response in the person concerned. The ion concentration actually achieved will be dependent on the nature of the alloy and the factors stated above for metals. However, if the duration of exposure is long and the area of alloy exposed to the skin is large, a low concentration of allergenic metal in the alloy could be sufficient to elicit a response. Thus, it is not possible to define a lower limit for the content of

allergenic metal in an alloy, below which there could be no possibility of eliciting contact dermatitis. The European Union (7) arbitrarily classifies alloys as skin sensitizers if they contain more than 1% of an allergenic metal. However, that classification refers to the ability to induce sensitization and not to its elicitation in an already sensitized person. It would be more exact for classification of alloys as skin sensitizers to be based, not on alloy composition, but on the rate of formation of allergenic ions when the alloy is exposed to an artificial sweat solution.

Metals and Alloys in Massive and Powder Forms

Transient contact with an allergenic metal or alloy in massive form is rarely damaging, because the duration of contact is too short for reaction with sweat to occur, assuming surface contamination is not present. This may not be the case with powdered metals/alloys, partly because the surface area of powders is so very large that significant reaction may occur in a short time, and partly because very fine powders can cling to the skin and may be difficult to remove. Powders of allergenic metals/alloys containing particles of size less than 50 μm and, especially, less than 10 μm , have a particularly high potential to cause reaction.

Patch Testing and Metal Release

The results from the patch testing of metals/alloys require more care in interpretation than do those from the testing of solutions of metal compounds. Consideration has to be given to the time required for the metal to react with sweat and provide sufficient ions to cause an allergic response. The metal patch, tightly strapped to the skin for a period generally of 2 days, provides a crevice which limits the access of oxygen required to sustain the cathodic reaction. Oxygen within the crevice, derived by diffusion from the atmosphere or from the body, is soon consumed since the crevice is narrow. The cathodic reaction is then confined to the area outside the crevice that is wetted by sweat. The extent of sweating can thus be a significant factor in determining the rate at which ions are produced. Clearly the dimensions of the test specimen and tightness of the strapping govern the dimensions of the crevice and hence the concentration of metal ions developed in the solution in contact with the skin.

Furthermore, acidity may develop in the film of sweat between metal and skin and cause corrosion which otherwise would not occur (8). This is particularly the case with metals/alloys that form surface oxide films. Thus, it is possible for a discrep-

ancy to arise between patch test results and metal release data obtained from a sample of the metal freely exposed to artificial sweat solution. An example is reported in tests made on a nickel base alloy containing 15% Cr and 8% Fe, which gave 54% positive reactions in the patch test but nickel release values of only 0.3, 0.04 and 0.05 $\mu\text{g}/\text{cm}^2$ /week after 1, 3 and 6 weeks exposure to artificial sweat (5), i.e., values which are below those considered necessary for significant response to be obtained (9). Apart from this instance, the rate of release of nickel from nickel containing alloys shows good correlation with patch test results on nickel sensitized persons.

When it is required to assess the allergic response of a particular individual to a metal/alloy, it is evident that the patch test will give specific results of direct significance. However, for the purpose of ranking alloys of a particular allergenic metal in order of metal release, and hence probability of causing an allergic reaction, the metal release test is much to be preferred to the patch test, since errors arising from the variable allergic susceptibilities of the test subjects and from uncontrolled differences in test environment are obviated.

Sweat

The composition of sweat is very variable depending on the person, activity, diet and other factors. Major constituents are chloride (average values 0.44–1.4 g/l); sodium (av. 0.33–1.28 g/l); potassium (av. 0.29–0.39 g/l); urea (range 0.26–1.22 g/l); ammonia (range 0.06–0.11 g/l); amino acids (av. 0.48–1.4 g/l); and lactic acid (range 0.4–3.6 g/l). Minor constituents include iron, copper, manganese, zinc, phosphate, sulfate, creatinine (10). The pH value can range from 2.1 to 6.9 and averages 5.3 (11). The 2 factors most important in corrosion of metals by sweat, assumed fully aerated, are chloride and pH value. The significance of the amino acids (including serine, glutamic acid aspartic acid, arginine, threonine, alanine, leucine, glycine and histidine) is difficult to assess. Some may act as inhibitors by adsorption on metal surfaces. Those that complex metal ions would promote corrosion.

The composition of the artificial sweat most commonly used for determining rate of metal release (5, 12) is 0.5% sodium chloride, 0.1% lactic acid, 0.1% urea, adjusted to pH 6.5 by addition of ammonia. Whilst the higher values of chloride and pH may not be of significance, the absence of amino acids could affect the release rate of those metals with ions that form complexes (see section on gold).

Specific Metals that Form Allergenic Ions

Aluminium

Although aluminium would be expected, from its electrochemical characteristics, to react strongly with sweat, in practice it has good resistance to corrosion by chloride solutions due to the surface film of aluminium oxide. The protection provided is greater with increasing purity and can be enhanced by anodizing, which thickens and strengthens the oxide film. Anodizing is an electrolytic process conducted in sulfuric or chromic acids followed by sealing of the film in steam or boiling water. A cold sealing process, involving the use of nickel fluoride solution, requires that the sealed surface is rinsed thoroughly, otherwise nickel ions are retained on the surface and may cause nickel contact dermatitis on subsequent handling (13). The resistance of aluminium to corrosion is also improved by immersion treatment in solutions containing chromates. The resulting surface films, grey or greenish in colour, are largely of oxide/hydroxide with some chromate which may be slowly released in subsequent exposure.

The alloys with magnesium are equally as resistant to corrosion as the pure metal, but those containing copper, nickel and iron can suffer pitting corrosion in chloride solution and thus generate aluminium ions.

Dermatitis due to contact with aluminium metal/alloys is of rare occurrence but has been reported in employees at an aircraft manufacturing plant (14). Positive results from patch tests made with aluminium Finn Chambers and also exposure to soluble aluminium compounds have been reported (15–17).

Beryllium

Beryllium metal is similar to aluminium in forming an oxide surface film that very largely gives protection from corrosion. It has light weight, high melting point, exceptional high stiffness/weight ratio, high permeability to X-rays, good electrical conductivity, and has been used in structural components for spacecraft and missiles. The main use of the metal is when alloyed in small amounts with copper, nickel or aluminium. The 2% Be alloy with copper is the most important and combines high strength with excellent electrical and thermal conductivities. It is widely used for high performance, high reliability electrical connectors. The corrosion-resistant properties of these alloys are similar to those of the major metal component.

Nickel-chromium-beryllium alloys, containing about 11–14% Cr, 1.5–2.0% Be, sometimes also with 1–4% Mo, are used in dental prostheses. The

beryllium content of dental, base metal, casting alloys is limited to 2% maximum by standards, e.g., BS3366 1988.

Although the allergenic properties of soluble beryllium compounds are well recognized, it is very doubtful if contact of the metal or its alloys with the skin can generate sufficient soluble compound to elicit an allergic reaction. Elution tests in artificial sweat, in accordance with the procedure developed for nickel (12), on 0.5% Be and 2% Be-Cu alloys show a low release of about 0.8 and 1.3 $\mu\text{g Be/cm}^2/\text{week}$, respectively. Patch tests on workers using beryllium metal and the 2% and 4% Be-Cu alloys have given negative readings. Handling of pure beryllium or its alloys does not affect the skin (18). Early reports (prior to 1950) of acute dermal reactions in workers handling beryllium were subsequently found to be due to the presence of beryllium fluoride trapped within the structure of the metal (19).

Guinea pigs which had been sensitized to beryllium by intradermal injection of beryllium sulfate, gave positive readings in patch tests conducted with 0.4% Be-Cu, 2% Be-Cu, 50% Be-Al and metallic beryllium. No reaction was shown by control animals that had not been pre-sensitized (20).

The Ni-Cr-Be dental alloys, partly as a result of chromium contents that are generally not much above the level required to obtain passivity and partly as a result of segregation of alloying constituents when in the cast condition (21), may suffer corrosion when in use. Dental alloys are subjected to a wide variety of corrosive media, often acidic, and this combined with concomitant abrasion increases the probability of breakdown of protective, oxide, surface films and the likelihood of formation of soluble beryllium and nickel ions. Contact dermatitis from Ni-Cr-Be dental alloys has been reported (22) and (23) and, in the latter case, specifically ascribed to beryllium.

It is evident that skin contact with the low beryllium alloys with copper, nickel or aluminium in persons not previously sensitized to beryllium does not result in dermatitis, and the satisfactory experience recorded by operators in the alloy producing and using industries confirms that view. Further, since the rate of release of beryllium from the low beryllium alloys is low, it is very unlikely that even beryllium-sensitized persons would suffer from contact with the alloys in normal handling and use. Sensitization to beryllium could arise from exposure to soluble beryllium compounds or from the use of dental alloys containing beryllium.

Chromium

Chromium-plated articles are constantly handled but it is doubtful if they ever give rise to chromium

contact dermatitis. The chromium plate, generally of average thickness about 0.2 μm but varying greatly over the contour of an intricately shaped article, is almost invariably deposited on a nickel substrate. The chromium is likely to be porous in low thickness areas and cracked in the thicker regions, thus allowing access of sweat to the nickel undercoat (24). Thus, dermatitis arising from contact with a chromium-plated object is almost certainly due to nickel ions from the undercoat, and not to the presence of trivalent or, even more doubtfully, to hexavalent chromium ions. Although chromium coatings on a nickel substrate can greatly reduce the amount of nickel release, they cannot be relied upon to give complete protection (6, 25).

Chromium is widely used in iron, nickel and cobalt based alloys and to much lesser extent in aluminium and copper base alloys. The term stainless steel is generally applied to iron base alloys containing not less than 10%Cr, and that level of chromium confers similar "stainless" characteristics to the nickel and cobalt base alloys. The most commonly used stainless steel contains 18%Cr and 9% Ni and in most situations does not react with sweat. Hence negative readings are obtained in patch tests. Nevertheless, corrosion of this steel may occur if it is used in crevice conditions for a long period of time (8). Those steels containing molybdenum and higher levels of chromium and nickel, e.g., those used in surgical implants, have much increased resistance to corrosion by chloride solutions under crevice conditions. The resistance to corrosion of stainless steels is impaired if they are low in chromium content or are enriched in sulfur in order to obtain machinability (26). Such steels can give positive readings in patch tests.

Chromium forms a variety of ions, the most common being the trivalent cation and the hexavalent chromate anion. The former has mild skin sensitizing properties but the latter is a very potent skin sensitizer. Low chromium stainless steels and nickel base alloys, if corroded by artificial sweat or by saline solutions, generate trivalent but not hexavalent chromium ions (27). Thus allergic reaction arising from direct and prolonged contact of stainless steel with the skin is more probably due to nickel ions than to those of chromium.

The hexavalent chromate ion is a powerful inhibitor of corrosion and immersion treatments in acid dichromate solutions have been developed to provide protective films of metal oxide containing chromate on metal surfaces. Such chromate passivation treatments are particularly valuable for zinc, magnesium and their alloys but are also used for aluminium, cadmium and for iron which has been given a phosphate treatment. Since the chro-

mate in the film is slightly soluble it will leach out in sweat and may cause contact dermatitis. Wass & Wahlberg (28) have devised a test technique for determining the release of chromate from passivated articles in artificial sweat solution. They concluded that the mean release of hexavalent chromium from chromated parts immersed for 20 min in artificial sweat solution should not exceed $0.3 \mu\text{g}/\text{cm}^2$ in order to reduce the risk of chromate allergy.

Cobalt

Cobalt metal reacts slowly with sweat and neutral saline solutions to provide the divalent ion which is a potent skin allergen (the trivalent ion is unstable in solution and is unlikely to be able to cause allergy). Despite the potency of the cobalt ion, dermatitis due to cobalt alone is rare, although cobalt associated with nickel allergy is more common, perhaps because cobalt alloys often also contain nickel. The cobalt content of refined nickel is generally very low, e.g., $< 0.1\%$, but low grades of primary nickel used in the production of alloys may contain up to 1.5% cobalt. Cobalt compounds are used extensively in paints and inks as driers; as adhesives in the bonding of rubber and steel in tyres; as catalysts; and in pigments. The soluble forms can be a cause of dermatitis.

Ultra-fine cobalt metal powders are used as binders in the manufacture of carbide-tipped tools and diamond grinding wheels and saws. There are few other applications for cobalt metal; however, the alloys are used extensively and have many specialized applications. Cobalt alloys with more than 10% chromium are resistant to corrosion and, when further alloyed with molybdenum, find application as, surgical implants and dental prostheses. The cobalt-chromium alloys are also used in jet-engine components and in wear-resistant applications, especially as coatings. High speed steels often contain up to about 10% Co, whilst magnetic alloys may contain as much as 50% Co; the low expansion alloys with iron and nickel contain less than 20% Co.

Thus, except for dental prostheses, exposure of the cobalt-containing alloys to the skin is minimal and it is only in the production and industrial use of the alloy that significant exposure may occur.

Copper

Although copper is widely used in the home for plumbing and electrical purposes, contact with the skin is not extensive. With the demise of copper kitchen utensils, copper metal is rarely handled but copper alloys, such as brass, nickel silver and bronze, are frequently handled in applications such

as door fittings, knobs, taps, switches, coinage, etc. Copper and alloys react slowly with chloride solutions and readily form insoluble basic compounds. Thus, formation of soluble cupric ions in significant amounts in sweat is unlikely unless the sweat is particularly acidic. It is not surprising that the incidence of contact dermatitis from copper metal or alloys is rare although cases have been described (29–31).

Gold

The electrochemical nobility of gold ensures that the pure metal is unlikely to react with sweat or saline solutions unless these are contaminated with complexants or powerful oxidising agents. Alloys of gold containing less noble metals, such as zinc, nickel and copper, may undergo “de-alloying” whereby the less noble metal is preferentially dissolved from the gold matrix. “De-alloying” has been most extensively studied for copper/zinc alloys and it is known that brasses containing less than about 15% (atomic) zinc are not subject to dezincification. In an alloy having a face-centred cubic structure, such as α brass, that composition corresponds approximately to 1 atom zinc per unit cube. On that basis, gold alloys (with Cu, Zn, Ni) containing less than about $85 \text{ at}\%$ Au (plus other noble alloying metals Pt, Pd, Ag), i.e., about $95 \text{ wt}\%$ Au, could show preferential dissolution. The phenomenon of “de-alloying” with particular regard to Cu-Au alloys has been studied by Pickering and Wagner (32), especially as to the transport mechanisms whereby atoms of the less noble metal reach the reacting surface.

The results of elution tests on gold and gold alloys in artificial sweat given in Table 1 show that the release of active metals (Cu, Zn) increases as the content of noble metals (Au+Ag) in the alloy decreases. The tests carried out by the CEN working group (6, 33) refer only to nickel, but their results also indicate that the proportion of nickel positives in patch tests and of nickel release in sweat tests increases as the noble metal content (Au, Ag, Pd) of white gold decreases. The results in Table 1 show that, despite its nobility, some slight release of gold was detected but this decreased with decrease in gold content of the alloy. Thus, reported incidences of contact allergy from gold jewellery appear more likely to be due to alloying constituents than formation of gold ions.

Reports of allergy due to gold arising from skin contact with the metal or its alloys are infrequent. There have been a number of reports of gold alloys causing allergic reaction in dentistry or from the piercing of ears (34, 35), but the corrosive media involved in these cases could be distinctly, different

Table 1. Metal release from gold and gold alloys

Alloy	Au	Ag	Cu	Ni	Zn
fine gold					
composition %	99.99				
release	0.02, 0.02	<0.002,	0.02, 0.18	0.014, 0.032	0.04, 0.04
($\mu\text{g}/\text{cm}^2/\text{week}$)		<0.002			
18 ct gold					
composition %	75.0	16.0	9.0		
release	0.01, 0.02	0.003, 0.004	0.05, 0.10	<0.004,	0.03, 0.04
($\mu\text{g}/\text{cm}^2/\text{week}$)				<0.004	
14 ct gold					
composition %	58.5	5.4	30.5		5.6
release	0.005,	0.05, 0.09	0.29, 0.27	<0.004,	0.07, 0.07
($\mu\text{g}/\text{cm}^2/\text{week}$)	0.014			<0.004	
9 ct gold					
composition %	37.5	10.3	44.5		7.7
release	<0.005,	0.18, 0.06	0.80, 0.38	<0.004,	0.16, 0.07
($\mu\text{g}/\text{cm}^2/\text{week}$)	<0.005			<0.004	
9 ct gold white					
composition %	37.5		37.7	12.4	12.4
release	<0.005,	0.005, 0.004	2.9, 2.2	0.95, 0.75	0.86, 0.66
($\mu\text{g}/\text{cm}^2/\text{week}$)	<0.005				
detection limit for rate of release	<0.005	<0.002	<0.01	<0.004	<0.03
($\mu\text{g}/\text{cm}^2/\text{week}$)					

Nominal compositions as % (wt).

Determination of the rate of release of metal in artificial sweat solution was made by the Laboratory of the Government Chemist, Teddington, UK, using a method based on that described in (11) and analysis by ICP MS.

from that of sweat. Other reports give inadequate descriptions of the gold test-piece or article involved. On the other hand, there are numerous instances of the negative result obtained from patch testing with gold leaf. On the basis of electrochemical potential, Pickering & Wagner (32) considered that dissolution of gold from a 10 at% Au-Cu was not feasible. However, their measurements were made in an oxygen-free, $\text{CuSO}_4/\text{H}_2\text{SO}_4$ solution.

Gold is readily complexed, the complex with cyanide ($\text{Au}(\text{CN})_2^-$) being of importance in the refining and electrodeposition of gold. This complex proved positive in patch tests (36, 37). However, the complex gold sodium thiosulfate reacts almost as positively as the dicyanoaurate in patch tests (37) and is commonly used for determining sensitivity to gold. Gold sodium thiomalate, used for treatment of rheumatoid arthritis, also gives positive patch test readings but only at very high concentrations (38). The complex of gold with chloride (AuCl_4^-) gives a marked reaction in patch tests (34, 35) and was considered (37) to cause persistent allergic reactions more often than other gold compounds. Dissolution tests on gold foil or colloidal gold in amino acids, sometimes in the presence of hydrogen peroxide, were made by Brown (39), and although the data presented do not allow determination of the rate of release it is evident that amino acids could affect reaction of gold with sweat.

The conclusion is that gold present in solution as complex ions can cause contact dermatitis and that possibly the chlor-auro ion is the most potent. However, it is not clear that metallic gold or gold alloys could react with sweat at a rate sufficient to elicit an allergic reaction in gold-sensitized persons. In practice, it is evidently uncommon, having in mind the infrequent occurrence of allergy due to gold arising from contact of the skin with gold alloy jewellery. Further tests in artificial sweat containing amino acids are desirable in order to assess the possibility of a significant reaction.

Nickel

Nickel metal reacts only slowly with sweat to form the divalent nickel ion that can cause contact allergy. (The trivalent and tetravalent ions are of industrial significance but are unlikely to come into contact with the skin). Transient contact of the skin with the metal is rarely damaging and direct prolonged contact is necessary to cause a reaction in an already sensitized person (9). Thus (40) showed that handling of 25% nickel copper coins for 6 min followed by a 2-h rest period did not result in exacerbation of hand eczema in nickel-sensitized patients. A concentration of >100 ppm nickel (as nickel chloride) has been found necessary to elicit an allergic reaction in nickel-sensitized individuals (41). Time is necessary for this concen-

Table 2. Major nickel alloys

Alloying elements (Y)	% typical content		Probability of causing contact allergy	Applications
	(Y)	(Ni)		
Al	50	50	B	Raney nickel catalyst
Au	37–75	2–12	B*	white gold jewellery
Be	2	97	A	springs
Co	25	14	A	magnet alloys
Cr	20	79	C*	heating elements: jet engines
Cr/Fe	18/72	9	C*	stainless steels
Cr/Mo	16/15	54	C	chloride-resistant alloy
Cu	70–90	10–30	A	marine uses: coinage
Cu/Zn	65/20	15	A	architecture: domestic goods
Fe	80–97	0.5–18	A	engineering steels/cast iron
Fe	63	36	A	low expansion alloy
Mn	5	95	A	sulfur-resistant alloy
Mo	28	62	B	chloride-resistant alloy
Si	10	85	B	corrosion-resistant alloy
Sn	65	35	B	corrosion-resistant coating
Ti	45	55	B	shape memory alloy
Zn	88	12	B	corrosion-resistant coating

A alloys that behave similarly to nickel.

B alloys that react very slowly with sweat and are unlikely to cause contact allergy.

C alloys that only in exceptional circumstances will react with sweat and are most unlikely to cause contact allergy.

* consult text.

+ information provided by the Nickel Development Institute (see also (2)).

tration to be reached by reaction of the metal with sweat.

The induction of sensitization in an unsensitized person generally requires quite prolonged contact. A well-known cause of primary sensitization is the stud, often thinly gold-plated on a nickel substrate, that is used in pierced ears during the epithelialization process – a process which could entail several weeks continuous exposure.

Homogeneous articles of nickel (other than some coinage) are seldom encountered, but numerous articles in everyday use are electroplated with nickel. Examples are tools, keys, toys, nuts, bolts and domestic equipment. Bright nickel plate contains sulfur that renders the nickel more active and more likely to generate nickel ions than the wrought nickel used in coinage, which often exhibits semi-passive behaviour. Black nickel plate, used on photographic equipment, is even higher in sulfur and gives a strong reaction in the dimethylglyoxime test. Often the nickel plate is provided with a top coat, such as chromium, silver or gold, that, at conventional thicknesses, will reduce but is unlikely to eliminate formation of nickel ions when in contact with sweat.

Nickel-containing alloys are numerous, widely used and extensively handled both in industry and in the home. Their resistance to corrosion varies greatly according to alloy composition and nature of the environment. In so far as contact dermatitis and sweat are concerned, the alloys may be placed in 3 categories as listed in Table 2. Alloys with cop-

per or iron behave similarly to nickel, but below about 10% Ni dilution effects become of some significance. Those containing more than about 10% chromium show passivity and when in this state behave in a distinctly different manner from nickel (see section on chromium).

Platinum, palladium and rhodium

There are no reports of dermatitis arising from skin contact with platinum metal, despite its extensive use in jewellery and the high potency of some platinum compounds as respiratory and skin sensitizers. The result is to be expected in view of the noble character of platinum and consequent freedom from corrosion by sweat and neutral chloride solutions. The allergy-eliciting compounds are confined to a small group of ionic complexes containing reactive halogen ligands, e.g., the hexachloroplatinates and tetrachloroplatinates. Neutral complexes and those containing more strongly bound ligands, e.g., tetramineplatinum (II) dichloride, are totally inactive (42).

Palladium is used as a catalyst in hydrogen reduction processes; for contacts in electrical relays; in high temperature brazing alloys; in dental alloys; and in jewellery, often alloyed with gold.

Although not as resistant to corrosion as platinum, palladium does not react with sweat or chloride solutions unless strong oxidants or complexing agents are present. Thus negative results were obtained in patch tests when pure palladium foil was

used on patients who were sensitive to palladium chloride (43, 44). Nevertheless, a number of cases have been reported of allergy arising from the use of dental alloys containing palladium (45–49).

Palladium dental alloys may also contain gold, silver, copper, tin and nickel; the alloy studied in (49) contained 5% Pd but the precise composition of other alloys associated with the allergy were not reported. De-alloying of palladium alloys could be expected as with gold alloys. Wataha & Hanks (50) were of the view that "the risk of using palladium in dental casting alloys appears to be extremely low because of the low dissolution rate of palladium ions from these alloys." The nature of the exposure suffered by dental alloys is more arduous than that of alloys in contact with the skin. Contact allergy from the wearing of palladium jewellery has not been reported.

Contact of rhodium with the skin may occur through its use as an electrodeposited coating on silver to prevent tarnishing and as a finish on metallic reflectors and electrical contacts. The alloy with platinum is exceptionally resistant to corrosion and is used as a lining in autoclaves and reactors. A further use is in high temperature thermocouples. The resistance of rhodium to corrosion is such that reaction with sweat is not feasible and metallic rhodium is not known as a sensitizer. However, soluble rhodium compounds are considered as potent sensitizers (1).

Tin

Contact of the skin with tin may occur through its use as a coating, notably as tin plate. Localized corrosion of tin can occur in chloride solutions but the reaction is slow. However, a low incidence of 8% positives in patch tests conducted on tin-plated copper was reported in patients who were also sensitized to nickel (5). Well-known alloys of tin are pewter, bronze, solders and bearing alloys, but there are no reports of contact allergy from their handling and use.

Conclusions

The risk of inducing and eliciting contact allergy from metals and alloys is dependent upon their reaction with human sweat and the development of a concentration of allergenic metal ions per unit area of exposed skin for sufficient time to provoke an allergic response. It is not reasonable to conclude from positive results of patch tests on soluble metal compounds that the metal itself will also be sensitizing to the skin. Even when reaction of a metal/alloy does occur, it may be so slow as to be incapable of developing a concentration of ions

sufficient to initiate an allergic response. Thus the particular circumstances (time, contact area, geometrical configuration) may be decisive in distinguishing between safe and unsafe uses of a metal/alloy.

Alloys are not mixtures of metals and their reaction with sweat may be quite different from those of the metals of which they are composed. This is particularly the case with alloys containing metals which can form protective oxide films, e.g., stainless steels. Hence, it is necessary to determine the rate of release of allergenic metal ions when an alloy is exposed to sweat in order to assess its potential for causing dermatitis. The concentration of an allergenic metal in an alloy bears no relationship to this potential.

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