Nickel release from nickel-plated metals and stainless steels

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Nickel release from nickel-plated metals often induces allergic contact dermatitis, but, for nickelcontaining stainless steels, the effect is not well-known. In this paper, AISI 304, 316L, 303 and 430 type stainless steels, nickel and nickel-plated materials were investigated. 4 tests were performed: patch tests, leaching experiments, dimethylglyoxime (DMG) spot tests and electrochemical tests. Patch tests showed that 96% of the patients were intolerant to Ni-plated samples, and 14% to a high-sulfur stainless steel (303), while nickel-containing stainless steels with a low sulfur content elicited no reactions. Leaching experiments confirmed the patch tests: in acidic artificial sweat, Ni-plated samples released about 100 μ g/cm²/week of nickel, while low-sulfur stainless steels released less than 0.03 μ g/cm²/week of nickel, and AISI 303 about 1.5 μ g/cm²/week. Attention is drawn to the irrelevance of the DMG spot test, which reveals Ni present in the metal bulk but not its dissolution rate. Electrochemical experiments showed that 304 and 316 grades remain passive in the environments tested, while Ni-plated steels and AISI 303 can suffer significant cation dissolution. Thus, Ni-containing 304 and 316 steels should not induce contact dermatitis, while 303 should be avoided. A reliable nitric acid spot test is proposed to distinguish this grade from other stainless steels.

Key words: allergic contact dermatitis; electrochemical tests; leaching experiments; nitric acid spot test; potentiodynamic polarization; nickel; stainless steels; prevention. © Munksgaard, 1994.

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Nickel (Ni) contact dermatitis has been the subject of many medical publications (1-12). The responsibility of Ni in cases of contact between it and the skin is not doubted. However, the harmfulness of skin contact with Ni-containing stainless steel is denied by some authors (1) and, when implicated by others, the stainless steel grade is not specified (2). This point is of particular interest, since there exist many different grades of stainless steel, some of them containing Ni in significant amounts and others not (13), the corrosion resistance of which in aggressive environments may differ significantly. Moreover, when used under appropriate conditions, a stainless steel is known as "passive", as it is covered with a thin iron (Fe)-chromium (Cr) oxide film (thickness of the order of a few nanometers), which inhibits cation dissolution. Thus, the cations that can, at a very slow rate, be released towards the environment are those that are present in the passive film (Fe and Cr) and not those that, such as Ni, are contained in the steel bulk but not in the protective passive film. Under these conditions, the safety of stainless steels in contact with the skin, even those containing Ni, is insured so long as the passive film remains stable with respect to sweat. Considering the composition of human sweat (pH, chloride content, etc.), it is very likely that the commoner stainless steels obey this requirement. This is probably untrue for Ni and Niplated alloys, the passive films of which are known to be much less stable in chloride media.

It was intended in this study to shed light on these points, by assessing the skin tolerance of different stainless steels in patients allergic to Ni, and evaluating the Ni and cation release of these materials. As a reference, we first investigated a Nifree 17% Cr ferritic steel. Then, some Ni-containing austenitic grades were considered, containing or not containing molybdenum (Mo), since this element is known to improve corrosion resistance in chloride-containing media. In contrast, sulfur is known to decrease the corrosion resistance drastically. Therefore, a high-sulfur free machining steel was also characterized. The following studies were carried out:

(a) Clinical evaluation of skin tolerance of different stainless steels, using patch testing with these metallic samples.

(b) Comparative determination of Ni release from these stainless steels in artificial sweat and sodium chloride solutions of neutral or acidic pH (6.6 and 4.5), and evaluation of this release, a rate less than $0.5 \ \mu g/cm^2/week$ being considered as safe by Menné et al. (1).

(c) Dimethylglyoxime (DMG) spot test. This test is commonly used to assess the "safety" of a material with regard to Ni allergy (2, 3, 5, 10-12), but its validity is very questionable and we will show that it is not relevant in case of stainless steels.

(d) Potentiodynamic polarization experiments in deaerated chloride media, to compare qualitatively the cation release of the materials studied, the width of the passivity region and the level of the anodic current in this passivity region both being taken into consideration.

Experiments were conducted at the Ugine Research Centre, except for the patch tests, which were performed by J. F. at the Strasbourg civil hospital.

Materials and Methods

Materials studied

6 materials were studied: pure nickel, Ni-plated steel, and 4 stainless steel grades for which chemical analyses are given in Table 1. These grades will be referred to using the AISI (American Iron And Steel Institute) standard.

Stainless steel (SS) grades are basically ironchromium alloys, this last element being added in sufficient amount to form, in aqueous solution, a protective Cr (or sometimes, Fe–Cr) oxide layer (the "passive layer"), the thickness of which is of the order of a few nanometers. As long as SS does not corrode (that is to say its passive layer is stable), the dissolution rate of the steel is negligible. Moreover, when considering the residual cation flux throughout the passive film, it is worth noting that only the cations present in the film (mostly Cr and possibly Fe) can dissolve, even if other alloying elements are present in the steel though not in the passive layer. In contrast, when SS corrodes, such as in very aggressive media, the corrosion rate depends mostly on the composition of the steel and not just on that of the passive film. The question of the safety of SS, regarding their cation release in a given environment, is therefore directly related to their corrosion resistance and thus to their passive film stability.

Other elements may also be added to stainless steels for various purposes, including Ni and Mo, which change both the metallurgical structure and the mechanical properties of the steel and improve its corrosion resistance. A typical Ni-free SS is the grade AISI 430, the crystalline structure of which is bcc (body-centered cubic) (13), referred to as a "ferritic" structure. This steel does not contain Ni in a significant amount, from the viewpoint under consideration. Adding Ni up to typically 8% wt. (grade AISI 304) makes the structure become fcc (face-centered cubic) (13), which is referred to as an "austenitic" structure. Adding Mo to such steel (typically up to 2%) does not change its crystallline structure but strongly improves its corrosion resistance. In each case, the passive film remains a Fe-Cr oxide (or hydroxide). It must be noted that the passive film formed on Ni (or Ni-plated alloys) is a Ni oxide, that is to say completely different from passive films formed on SS.

Another metallurgical point must be considered: for various reasons, industrial steels contain many minor elements or impurities. In particular, even a small amount of sulfur combines with manganese (Mn) to form Mn sulfides, which, in very aggressive chloride-containing media, act as pitting corrosion initiation sites. Furthermore, there exists a special austenitic grade(AISI 303) to which sulfur is added at a very high level (typically 0.2% to 0.3%) for free machinability purposes. It was necessary to test the behaviour of such an SS grade regarding Ni release, and to propose a simple test for determining its corrosion resistance under relevant conditions.

Table 1 shows the chemical composition of the stainless steels studied. Experiments were performed either on polished surfaces (SiC paper, grade 1200) or on surfaces as received (annealed and pickled sheets for AISI 304, 316L and 430, and machined rods for AISI 303). Prior to experiments,

Table 1. Chemical composition (wg %) of the stainless steel grades and of the nickel used in our study

Grade	Cr	Ni	Mo	С	S	Mn	Si	Ti	Nb	Р
AISI 303	17.3	8.459	0.26	0.064	0.275	1.79	0.54	0.002	0.012	0.033
AISI 304	18.2	8.65	0.26	0.036	0.007	0.82	0.49	0.002	0.004	0.023
AISI 316L	17.9	11.3	2.15	0.021	0.002	1.67	0.61	0.004	< 0.002	0.023
AISI 430	16.6	0.11	0.11	0.037	0.001	0.43	0.33	0.007	< 0.002	0.017
Nickel		99.8			0.002		0.01			

samples were cleaned ultrasonically in a solution of acetone + ethanol (50/50 in volume ratio).

Patch tests

These tests were performed in 50 patients already known to be sensitive to nickel (nickel sulfate 5% pet.), with circular samples of the 4 SS grades and of the Ni-plated steel (1.5 cm in diameter) in the asreceived condition. Prior to experiments, samples were washed with distilled water and cleaned first with ethanol and then with ether (10). Tolerance was tested with a Roc Neodermotest applied on the back and read after 2 and 3 days, according to International Contact Dermatitis Research Group recommendations (3). Sensitivity to Cr and cobalt (Co) for these patients was also known (Cr as potassium dichromate 0.5% pet. and Co as cobalt chloride 1% pet.).

Leaching experiments

These were mainly in artificial sweat solutions and in 0.05 M sodium chloride (NaCl) solutions at pH 4.5 and at ambient temperature. pH 4.5 was chosen from a paper by Hemingway & Molokhia (4) as the lowest pH value found quoted in the literature for the biological sweat. Composition of the artificial sweat solution was as follows (4): NaCl 0.3%, Na₂SO₄ 0.1%, urea 0.2% and lactic acid 0.2%. Samples of the same grade, in the as-received condition, were immersed for 1 week in 100 ml of the naturally aerated solution.

Tests were also conducted in artificial sweat solutions, at pH 6.6 for AISI 303, 304 and the Ni-plated steel, and at pH 3.0 with NaCl concentrations of 0.05 M and 0.1 M for AISI 304 and the Ni-plated steel, to study the influence of pH and chloride (Cl⁻) concentration on the leaching of Ni. Area of specimens exposed to the above solutions were the following. AISI 303: 7.07 cm² (pH=4.5) or 10.3 cm² (pH=6.6 and 3.0); AISI 304, 316L and 430: 72 cm²; Ni-plated steel: 14.14 cm² or 28.3 cm²; nickel: 14.14 cm².

After immersion, samples were rinsed with distilled water. The test solution was added with the rinsing solution, then analysed using atomic absorption spectroscopy (detection limit = $10 \ \mu g/l$) to determine the Ni concentration, from which the leaching level (in $\mu g/cm^2/week$) was deduced.

Dimethylglyoxime (DMG) spot tests

This test is based on the complexation of Ni ions with DMG to give a chromophoric compound. In ammoniacal solution, Ni is complexed in the oxidation state +2, which develops a pink color-

ation. This coloration is characteristic of a positive reaction and thus supposedly reveals the presence of Ni. Thus, it is commonly used by determatologists to reveal the presence of Ni in alloys and so to determine if they can elicit Ni allergy in Nisensitive patients (2, 3, 5, 10-12). However, this test seems to be neither very sensitive nor relevant. For example, "false"-negative reactions, due to insufficient oxidation of Ni, can appear. It is then recommended that the alloys should be etched with a strong acid such as hydrochloric acid (HCl). This procedure leads to metal dissolution in the active state and therefore reveals the presence or not of Ni in the alloy composition. However, if the steel is used in the passive state (no corrosion), which is the normal situation if the steel is sufficiently resistant in the environment considered, its passive film forms a protection against such dissolution and then the test is probably not relevant. Moreover, "false"-positive reactions can occur because DMG is not a specific reagent for Ni. It also reacts with Fe. Thus, for alloys containing Fe, it is necessary to apply hydrogen peroxide, which decolors the complexes of Fe, but not those of Ni, with DMG.

To verify the sensitivity and validity of this test, we applied it to the Ni-plated steel and to the four SS grades, according to the method described in various papers (3, 10). Tests were conducted on asreceived samples in different ways, 3 times for each type of steel: (i) a few drops of NH₃ and of the DMG solution were placed successively or rubbed on the samples, then drops of H₂O₂ were deposited to detect "false"-positive reactions; (ii) to detect "false"-negative reactions, samples were also etched with 3N HCl before applying NH₃ and DMG.

Electrochemical investigations

Corrosion and passivity of metals and alloys are basically electrochemical processes (13). Thus, electrochemical tests enable comparison of the stability of materials, in terms of dissolution. In fact, for a given metal-solution potential difference, one obtains a current density (i) that is the sum of 2 currents: (i) the cathodic one (i_K), which is connected to the electroreduction of some ions of the solutions (for example H⁺ or OH⁻); (ii) the anodic one (i_A), which reflects the oxidation of the metal, that is to say its dissolution in deaerated media (for example Fe \rightarrow Fe²⁺ + 2 e).

Under open-circuit conditions, the total current density equals zero since $|i_K| = |i_A|$, which then represents the so-called corrosion current density. The rest potential or corrosion potential (Erest), is then the corresponding electrode potential. To study the

electrochemical behaviour of materials, it is convenient to apply the electrode potential (*E*) at values different from Erest and to record the total current density ($i=i_A+i_K$). Thus, one obtains the i=f(E) curve. Therefore, comparing the i=f(E) curves measured for several materials, enables comparison of the importance of the reaction of dissolution of the metal, and so the cation release rate. For example, for metals like Ni or Ni-plated steel, the surfaces of which are composed only of Ni, this current density reflects directly the dissolution of Ni.

Tests were conducted in 0.05 M NaCl solutions at pH 4.5 and 6.6, and in artificial sweat solutions at pH 4.5. They were performed on circular samples (diam. = 30 mm except for AISI 303: diam = 15 mm). The holder was designed so as to avoid any risk of crevice corrosion, which was verified throughout the testing procedure. Test solutions were maintained at 23°C and deaerated with $N_2 + 3\%$ H₂ flux for 2 h before and throughout the experiment. After 15 min at the rest potential, polarization curves were obtained from the rest potential to the pitting potential, using a 10 mV/min scanning rate. SS were tested in the as-received condition and polished (followed by 24 h ageing in air), except in NaCl at pH 4.5 in which they were tested only in the as-received condition. Niplated steel was tested as received and Ni after polishing.

Results

Patch tests

Results of the patch tests are presented in Table 2. They clearly reveal that the low sulfur SS studied here, including austenitic SS, elicited no allergic reactions in Ni-sensitive patients. In contrast, 96% of the patients reacted to Ni-plated metal and 14% to the resulfurized austenitic stainless steel (AISI 303), which has the lowest corrosion resistance among SS studied here, as will be seen below.

Leaching experiments

Results obtained for the tests run in artificial sweat solutions are shown in Fig. 1. They are averaged over several tests, the number of which is given in parentheses. (Ni)_{Re} is the Ni quantity leached in the test solution by the metallic samples during the 1-week experiment. For each type of solution, a blank was also analysed by atomic absorption spectroscopy and, when traces were found, values obtained for the test solutions were corrected.

It appears from these results that leaching levels of Ni from Ni or Ni-plated steel are very high, of the order of $100 \,\mu\text{g/cm}^2/\text{week}$, while they are much

Table	2.	Results	of	the	patch	tests	performed	in	50	patients
alread	y :	sensitive	to	nick	el					

	Patch test results (reading at D2)							
Sex	Ni	Cr	Со	AISI 430	AISI 304	AISI 316L	AISI 303	Ni-plated Steel
F*	+	1222			_	_		+
М	+	_	+		—	_	+	++
F*	+	_			_			++
F	+	_	+			_		++
F*	+				_			++
F*	+				_	_		++
F*	+	_	+		_	_		+
F	+	_		_	_	_		+
F	+	_						_
F*	+	-	—	-	-	-	—	++
F	+ +	_			_			++
Μ	++		-		—	_	++	++
F^*	++	<u>_</u>						+ + +
F*	++	-		-		-	+	+ +
F^*	++	_	0.00		-			++
F^*	++	_	++		—	-		++
F*	++		_					+ +
F	++	—				_		+ +
F^*	++	—			_	<u></u>		+ +
F*	++	—	—	_	-	-	—	+ + +
F*	++	_	-	-	_	—	-	++
F*	++	_			_	—		++
F	++	_	+		_	_		++
F^*	++	_				—		++
F	++	—			_	-		++
F	++	_		_	_	—	+	++
F^*	++	_			_	—	-	+ + +
F*	++	_	—	-	_	—		++
F	++					—		+
F*	++		+ + +	-	_	-	-	+
F*	+ +	_		-		-		++
F	++	_						++
F*	++	_	_			_	+	++
Μ	++	-			_	_		++
F	++	+	_		_	-		++
F*	++	_	_		_	_		+ +
F	++	_	_		—			+
F	++	-	_		_		+	++
F.*	++	-	—					++
F	++	-		-	-	_	+	++
F*	+ + +	+	+		—	—		++
F*	+ + +	_	+	2002		1000		+ + +
F*	+ + +	_	_	—	—	—		+
F*	+ + +		+	_	-		_	+ + +
F*	+ + +	—	-	-	-	_		++
F	+ + +	-	_		_	- 	-	+ + +
F*	+ + +	-	++	-		_		++
F	+++	-	—	_		_		+ + +
F*	+ + +	-	++	-		—		++
Μ	+ + +	-	—		_		-	—

* Previous contact dermatitis from costume jewellery.

lower for the low-sulfur-containing SS studied here: around 0.1 μ g/cm²/week in the most corrosive solutions and often beyond the detection limit of 1.4 10⁻² μ g/cm²/week (for AISI 304, 316L and 430). Besides, the AISI 303 grade exhibits a higher (Ni)_{Re} value than the other SS, though well below



Fig. 1. Amounts of Ni released, $(Ni)_{Re}$ ($\mu g/cm^2/week$), from AISI 304, 316L, 430, 303, pure Ni and Ni-plated steel, after a 1-week immersion in artificial sweat solutions of variable pH, at 23°C.

those observed on pure nickel and Ni-plated steel. Nickel release is close to the value of 0.5 μ g/cm²/ week, which is currently considered as being a sensitization limit, below which only weak reactivity in Ni-sensitive patients is expected (1).

In 0.05 M NaCl solution of pH 4.5, $(Ni)_{Re}$ values for SS are similar to those obtained in artificial sweat solutions of pH 4.5, while the Ni-plated steel shows a lower $(Ni)_{Re}$ value in NaCl (20 $\mu g/cm^2/$ week), though still higher than the limit mentioned above.

In artificial sweat of pH 3.0 with a 0.1 M NaCl concentration, results are similar for the Ni-plated steel, while (Ni)_{Re} is slightly higher for the AISI 304 grade (0.1 μ g/cm²/week).

Thus, we observe an increase in Ni release from SS when the corrosivity of the leaching solution increases (lower pH and/or higher Cl⁻ concentration). In contrast, pH and Cl⁻ concentrations have no noticeable influence on Ni release from Ni-plated steel, because of the low corrosion resistance of that material in each of the leaching solution used.

Dimethylglyoxime (DMG) spot tests

The DMG test applied to Ni-plated metal samples, without acid etching, is always positive. A pink coloration appears and remains when we apply H_2O_2 . Applied to SS, the test is negative: without acid etching, no coloration appears; with acid etching with HCl, a pink coloration occurs on each sample, but disappears with H_2O_2 . This shows, then, that the coloration is due to complexation of Fe with DMG, and not of Ni with DMG.

Results obtained show that this test does not

differentiate between the SS studied here, while they do not release Ni in the same amount and while their harmfulness regarding Ni allergy is very different: for example, according to this test, theAI-SI 303 grade should be harmless, which does not agree with what was observed. Moreover, to detect false-negative reactions, it is recommended that the samples be etched with a strong acid. For an SS, such an attack results in destruction of the passive film and in the loss of its corrosion resistance. Thus, the test is then applied on the bulk of the alloy, but no longer on the surface which is actually in contact with the skin.

The irrelevance of this test led us to propose another test that would differentiate between SS, that is to say SS susceptible to release, in a corrosive environment, low or high quantities of metallic elements, Ni among them. Since, among austenitic SS, sulfur content is the main parameter that exerts an influence on corrosion resistance, we applied a very simple test with nitric acid, which reveals the presence of sulfur. We used a solution of 3N HNO₃ and applied a drop of it on each SS grade for 5 min. The AISI 304, 316L and 430 grades showed no reactions, while, on the AISI 303 samples, a black coloration appeared that indicated the presence of a high quantity of sulfur.

Electrochemical investigations

Curves obtained in deaerated artificial sweat solutions of pH 4.5 are shown in Fig. 2: SS and Niplated steel are in the as-received condition, Ni is polished. A large domain of passivity is shown for the 2 austenitic grades (AISI 304 and 316L), with a low passive current density (less than 1 μ A/cm²) in each case, while AISI 430 presents only a very



Fig. 2. Polarization curves of AISI 303, 304, 316L and 430, and of Ni-plated steel and pure nickel, measured in a deaerated synthetic sweat solution of pH 4.5 ($T = 23^{\circ}$ C). Samples are in the as-received condition except pure Ni which is polished with SiC paper (grade 1200).

small passivity domain (from 227 mV/SCE until 247 mV/SCE), not visible in Fig. 2 because of the scale used for the y axis. Finally, for AISI 303 no passivity domain is seen.

The Ni-based materials present a peak of activity at about -225 mV/SCE (SCE: saturated calomel electrode) followed by a short passive domain characterised by a "high" current density (10 μ A/ cm² for Ni, $\approx 200 \mu$ A/cm² for Ni-plated steel). From these results, it follows that AISI 304 and 316L have a much higher passivation ability than the other materials in that solution.

In NaCl solution at pH 4.5, results are basically similar. For AISI 304, 316L and 430, we observe a higher rest potential ($\Delta E_{\text{rest}} \approx 80 \text{ mV}$ for AISI 304, $\Delta E_{\text{rest}} \approx 20 \text{ mV}$ for AISI 316L and around 10 mV for AISI 430) and a lower pitting potential $(\Delta E_{\rm p} \approx 160 \text{ mV for AISI 304 and } \Delta E_{\rm p} \approx 90 \text{ mV for}$ AISI 316L). Thus, the width of the passivity potential range is smaller than in artificial sweat, but the passive current density, which varies as the cation release rate throughout the passive film, remains of the same order of magnitude. For the AISI 303 grade and Ni-plated steel, there is no noticeable development of passivity. For pure Ni, the maximum anodic current density is significantly larger than in artificial sweat (850 μ A/cm² instead of 50 $\mu A/cm^2$). Thus, the chemical components added to the NaCl solution to form the artificial sweat seem to improve the corrosion resistance of some of the materials, which can be explained by an inhibitory effect.

pH effect: acidification of the NaCl solution from pH 6.6 to 4.5 has the following consequences: (i) an increase in the rest potentials for all the metals, due to an increase of the redox potential of the solution; thus, for AISI 304, 316L and 430 grades, the passive domain is reduced and it disappears for AISI 303; (ii) an increase in the passive and in the active current density for the AISI 303 grade and the Ni-based materials.

Mechanical polishing decreases the rest potential with respect to the as-received condition, in neutral NaCl solution as well as in acid artificial sweat solution (in NaCl, $\Delta E_{\text{rest}} = -130$ mV for AISI 304, -290 mV for AISI 316L, -280 mV for AISI 304, and -100 mV for AISI 303. In artificial sweat, $\Delta E_{\text{rest}} = -630$ mV for AISI 304, -570 mV for AISI 316L, -790 mV for AISI 430 and -70 mV for AISI 303), while pitting potentials seem fairly unchanged. It results in a larger passive domain, but with a higher passive current density.

Thus, it appears from these results that AISI 304 and 316L have the highest corrosion resistance, AISI 430 shows an intermediate behaviour, and AISI 303 and the Ni-based materials have the lowest corrosion resistance. Qualitatively, this is well correlated with the respective level of Ni release measured previously. However, it is difficult to quantitatively relate Ni release and anodic current measured in electrochemical test, since the Ni release rate probably decreases with time during the leaching experiment.

Discussion

The maximum amount of nickel that can be released in a corrosive environment is proportional to the anodic current density, which corresponds to the cationic current flowing from the metal to the corrosive solution. This current density, i, depends on the rest potential Erest, which is itself determined by the cathodic reaction that is effective at the metal-solution interface. In aerated neutral media, the cathodic reaction is that of oxygen reduction, which roughly determines the rest potential. This remains true at lower pH (such as pH 4.5), when the rest potential is not controlled by the hydrogen evolution reaction. Thus, studying the current density i(E) versus electrode potential E, in deaerated media, allows estimation of the current density in aerated media as being roughly $i(E_{rest})$. Finally, the polarization curves in deareated media allow a qualitative comparison of the cation release tendency of the various materials, taking into consideration both the width of the passivity region and the level of the anodic current in this passivity region.

From this viewpoint, the polarization curves obtained in various chloride solutions (artificial sweat of pH=4.5 and NaCl of pH=4.5 and 6.6), show a much better behaviour of the SS 304, 316L and 430 grades compared to pure nickel or Ni-plated metal. This can be attributed to the stability of the passivation of SS in those solutions, while Ni passivity is clearly destroyed in such conditions. Thus, using SS in conditions where the passive film remains stable should not lead to any risk of contact dermatitis.

The case of the high-sulfur grade AISI 303 must be considered in a different way. It is well-known that manganese sulphide inclusions, while highly favourable to free machinability, are very detrimental to corrosion resistance. Our studies show that the corrosion resistance of AISI 303 is not sufficient in the considered solutions to avoid any risk of contact dermatitis, even if the risk is much lower than for Ni-plated steels. Thus, the use of Ni-containing SS in prolonged contact with the skin should be restricted to low-sulfur-containing SS (typically less than 0.03%, while AISI 303 contains of the order of 0.3%). The nitric acid spot test proposed in this paper allows distinction between the 2 types of steel. Conversely, the DMG spot test appears irrelevant in determining which alloys can elicit nickel intolerance, because it includes acid etching. In fact, in the case of SS, this attack destroys their passive film and so greatly reduces their corrosion resistance, a fundamental property that enables them to be safe with regard to nickel allergy. To be valid, the test must be applied to the surface that really comes into contact with the skin and not to the bulk of the alloy. Thus, instead of this test, it seems more appropriate to apply a test that allows differentiation between SS with regard to their corrosion resistance, such as the nitric acid spot test.

Patch tests and leaching experiments confirm these conclusions. Results of the patch tests showed that no allergic reactions occurred with low-sulfur SS, while some of the patients (14%) reacted to the AISI 303 grade and most of them were intolerant to Ni-plated metal (96%). It is also interesting to compare the Ni release value in artificial sweat solution to the sensitization limit of 0.5 $\mu g/cm^2/$ week. According to that limit, the low sulfur SS should elicit no reactions in Ni-sensitive patients, while the AISI 303 grade should provoke reactions only in patients with an acid sweat, since in the acid leaching solution (pH = 4.5) we found a (Ni)_{Re} value of 1.4 μ g/cm²/week, but at pH=6.6, it was below 0.5 μ g/cm²/week (0.3 μ g/cm²/week). Finally Ni-plated steel, as well as pure nickel, should elicit strong reactions in the majority of patients. Patch test results confirm these assumptions and thus validate the value of 0.5 μ g/cm²/week as a sensitization limit.

Thus, a good correlation appears between corrosion resistance in neutral or slightly acid NaCl solutions, Ni release levels in the same solutions, and the probability that the material will elicit allergic reactions in Ni-sensitive patients. Our main conclusion is that the AISI 304, 316 and 430 grades can be used without any problem in prolonged contact with skin, while Ni-plated metals and, a fortiori, pure nickel, should be prohibited. Finally, the use of an appropriate nitric acid spot test allows selection of an appropriate low-sulfur-containing SS, while the dimethylglyoxime test is irrelevant for this purpose.

The results presented in this paper can be generalized to various uses of Ni-containing SS in biological applications or in the food industry. (i) So long as the steel remains passive in the actual environment, a Ni-containing stainless steel does not release Ni, since it is protected by a Ni-free passive film. (ii) Tests to be used for deciding whether a steel is safe or not should be carefully evaluated. It is meaningless to use a test that gives information on the alloying elements that are contained in the steel: chemical analysis does the same, and more accurately. The relevant question to know the answer to is whether these elements dissolve or do not dissolve in the environment under consideration.

References

- Menné T, Brandrup F, Thestrup-Pedersen K, Veien N K, Andersen J R, Yding F, Valeur G. Patch test reactivity to nickel alloys. *Contact Dermatitis* 1987: 16: 255–259.
- Fischer T, Fregert S, Gruvberger B, Rystedt Y. Nickel release from ear percing kits and ear rings. *Contact Dermatitis* 1984: 10: 39-41.
- 3. Cavelier C, Fousserau J, Massin M. Nickel allergy: analysis of metal clothing objects and patch testing to metal samples. *Contact Dermatitis* 1985: *12*: 65–75.
- Hemingway J D, Molokhia M M. The dissolution of metallic nickel in artificial sweat. *Contact Dermatitis* 1987: 16:99–105.
- Fisher A. Contact dermatitis, 3rd edition. Philadelphia: Lea and Febiger, 1986: 752–755.
- Emmett E, Risby T, Jiang L, Ket S, Feinman S. Allergic contact dermatitis to nickel: bioavailibility from consumer products and provocation threshold. J Am Acad Derm 1988: 19: 314–322.
- Christensen O B, Möller H. Release of nickel from cooking utensils. *Contact Dermatitis* 1978: 4: 343-346.
- Katz S A, Samitz M H. Leaching of nickel from stainless consumer commodities. *Acta Dermato-venereologica* 1975: 55: 113–115.
- Romaguera C, Grimalt F, Vilaplana J. Contact dermatitis from nickel: an investigation of its sources. *Contact Dermatitis* 1988: 19: 52–57.
- Foussereau J. Les eczémas allergiques cosmétologiques, thérapeutiques et vestimentaires. Paris: Masson, 1987: 64–65; 130–132.
- Dion C, Gaumeton A, Martin P. Réflexions sur la mise en évidence par spot test du nickel dans les objets métalliques. Actualités en Dermato-Allergie 1982: 6: 3–12.
- Menné T, Andersen K E, Kaaber K, Osmundsen P E, Andersen J R, Yding F, Valeur G. Evaluation of the dimethylglyoxime stick test for the detection of nickel. *Dermato*sen 1987: 35: 128–130.
- Lacombe P, Baroux B, Beranger G. Les aciers inoxydables. Les Ulis, France: Editions de Physique, 1990.

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