

LEACHING OF NICKEL FROM STAINLESS STEEL CONSUMER COMMODITIES

S. A. Katz and M. H. Samitz

From the Department of Dermatology, School of Medicine, University of Pennsylvania, Philadelphia, Pennsylvania, USA

Abstract. Sweat and household detergents were shown to have the capacity to release nickel from stainless steel. This finding substantiates the thesis that the American-style stainless steel kitchen and other stainless steel commodities can be sources of skin contact allergy with nickel. Furthermore, a negative spot test (DMG) does not reflect the "safety" of a nickel alloy.

Key words: Nickel; Metals; Stainless steel; Contact dermatitis; Occupational dermatoses; Leaching of metals

Malten & Spruit (8) reviewed the relative importance of various sources of environmental exposure to nickel in causing contact hypersensitivity. They attribute the primary localization and increased incidence of nickel dermatitis of the hands to the fact that there are two principal nonoccupational sources of contact with nickel: nickel commodities and nickel-containing detergents.

In women there are three main source of rather continual exposure to nickel during the day: jewelry, nickel-plated garment appliances, and stainless steel kitchens. Reactions to nickel from jewelry have been well documented; the principal cause of nickel dermatitis is now probably costume jewelry, with earrings being the most frequent offender (2). Since the advent of panty hose, with which garter clips are not used, the incidence of garter-belt or suspender dermatitis has markedly decreased.

Malten & Spruit implicated the American-style stainless steel kitchen as a source of skin contact with nickel. Studies were not carried out to determine whether nickel is released from such stainless steel commodities by reaction with sweat or sweat in combination with detergents. Samitz & Pomerantz (10) demonstrated the leaching of nickel from American coins through the action of human sweat or human sweat in combination with sodium lauryl

sulfate. On the basis of these and other experiments, in which patch tests made with quantitative dilutions of nickel sulfate prepared with water and with sodium lauryl sulfate solution were compared, they proposed that sweat and detergents improve contact with skin and increase permeability. Inasmuch as sweat and detergent exposure in association with stainless steel kitchens and flatware is common in the home, these findings may explain the frequency and ease of sensitization by nickel. On the other hand, Fisher (4), commenting on the potential of nickel to cause dermatitis from stainless steel prostheses, rejected the possibility of such reaction on the grounds that the "nickel is so firmly bound physically in the alloy that body fluids and perspiration cannot leach out the nickel to make it available to produce an allergic reaction". His thesis, however, is not tenable as, in our *in vitro* solubilization studies, we showed that nickel is indeed released from stainless steel prostheses by the action of sweat, blood, and physiological salt solution (11).

To further assess this hypothesis we carried out experiments to determine the ability of sweat and household detergents to release nickel from stainless steel.

METHODS

Samples of ferrous and nonferrous, nickel-containing alloys and samples of nickel-plated objects with which there is frequent or probable contact were obtained from a variety of sources. Large objects were cut to a convenient size.

The test specimens had surface areas ranging from 2 to 10 cm². They were placed in 50 ml polycarbonate beakers and treated with 5 or 10 ml of "leaching medium" (physiological saline solution, synthetic sweat (1), 1% Ivory liquid¹ in tap water or 1% Palmolive dishwashing liquid² in tap water). Blanks containing leaching medium only, and controls consisting of the leaching medium with addition of 10-30 µg Ni were similarly prepared. The beakers were closed with waxed paper covers and allowed to stand for 7 days at room temperature (20-24°C). After this time, the leaching media

¹ Proctor & Gamble Co., Cincinnati, Ohio 45202, USA.

² Colgate Palmolive Co., New York, N.Y. 10022, USA.

Table I. Summary of leaching studies

| Material | Leaching medium | Range | No. of samples | $\mu\text{g Ni}$ mean |
|--------------------------|-----------------------|--------------------|----------------|-----------------------|
| Flashlight case | 5 ml pss ^a | 0.42-2.75 (3/5) | 5 | 1.50 |
| Flashlight case | 5 ml 1% Ivory Liquid | None-2.23 | 5 | 0.51 |
| Flashlight case | 5 ml 1% Palmolive | 0.68-1.03 | 5 | 0.80 |
| Flashlight case | 5 ml synthetic sweat | 139-197 | 5 | 175 |
| EKCO knife (flatware) | 5 ml pss | 2.13-9.82 (4/5) | 5 | 4.94 |
| EKCO knife (flatware) | 5 ml 1% Ivory Liquid | None-1.25 | 5 | 0.25 |
| EKCO knife (flatware) | 5 ml 1% Palmolive | 0.27-0.74 | 5 | 0.48 |
| EKCO knife (flatware) | 5 ml synthetic sweat | 11.9-21.6 (4/5) | 5 | 15.2 |
| Spigot handle | 5 ml 1% Ivory Liquid | None-1.25 | 5 | 0.25 |
| Spigot handle | 5 ml 1% Palmolive | 0.47-3.37 | 5 | 1.19 |
| 302 s/s ^b | 5 ml pss | None-none (1/4) | 4 | None |
| 302 s/s | 5 ml 1% Ivory Liquid | None-1.38 | 4 | 0.37 |
| 302 s/s | 5 ml 1% Palmolive | 0.10-0.47 | 5 | 0.33 |
| 302 s/s | 5 ml synthetic sweat | 1.14-2.88 (1/3) | 5 | 1.80 |
| 303 s/s ^b | 5 ml pss | None-13.76 | 3 | 5.97 |
| 303 s/s | 5 ml 1% Ivory Liquid | 0.18-0.81 | 3 | 0.41 |
| 303 s/s | 5 ml 1% Palmolive | 0.40-1.67 | 5 | 1.00 |
| 303 s/s | 5 ml synthetic sweat | 27.7-85.6 | 5 | 51.1 |
| US 5 ϕ coin (1969) | 5 ml pss | 395-508 | 4 | 453 |
| US 5 ϕ coin (1964) | 5 ml synthetic sweat | 5 430-5 740 | 4 | 5 637 |
| US 10 ϕ coin (1972) | 5 ml pss | 190-337 | 4 | 268 |
| US 10 ϕ coin (1972) | 5 ml synthetic sweat | 2 700-3 730 | 4 | 3 348 |

^a Physiologic salt solution.

^b Used in coffee urns and cooking ware.

were transferred to separate test tubes and analysed for nickel.

The test solutions were treated with 100 mg of citric acid, 0.1 ml of iodine solution (1.3 g I₂ and 2.5 g KI/100 ml), 1 ml of concentrated ammonia and 0.5 ml of 1% dimethylglyoxime in alcohol. The test solutions were diluted to 10 ml with distilled water and transferred to test tube cuvettes. Five minutes after dilution, per cent T at 535 nm was measured, and the nickel contents were calculated by reference to a calibration curve prepared by treating standards in the same manner.

Blank values for a given leaching medium (ranging in the case of sweat from 0.5 to 1 $\mu\text{g Ni}$) were subtracted from the nickel contents of the corresponding test solutions. Recoveries from the nickel-containing samples ranged from 85 to 110%.

The results of leaching studies are tabulated in Table I.

Fisher (4) has advocated the use of a highly selective and sensitive spot test (DMG) to determine if nickel is leached from metallic objects. The DMG test is adopted from Feigl (3). Dimethylglyoxime as an inactivating agent and spot test in metal-skin experiments has been reported previously by Samitz & Pomerantz (10) and more recently by Lucas (7). Westwood Pharmaceuticals, Inc. has made this test available in kit form for clinical and field use. We have used one of

these kits to test a variety of metallic objects. The results are tabulated in Table II.

DISCUSSION

Malten & Spruit (8) suggest an "eliciting safety limit" of 1 $\mu\text{M Ni/l}$ which is approximately 0.06 ppm Ni, or equivalent to approximately 0.5 $\mu\text{g Ni}$ in our studies. In many instances, our data (Table I) show that it is possible to leach nickel from metallic objects in amounts far in excess of 0.5 μg . Our experiments were carried out over a 7-day period at room temperature. Actual exposure conditions are quite different from this, and we do not interpret our findings as reflecting actual exposures. There is little doubt, however, that nickel is leached from many metallic objects by the action of sweat and detergents.

A "sensitizing safety limit" for nickel has not yet been defined. Extension of our animal model for chromium sensitization (5) and Jansen et al.'s

Table II. Results of "Fisher's Spot Test"

| Metal tested | Result | Metal tested | Result |
|--------------|--------|------------------------------|--------|
| 17-4 s/s | Neg. | Monel | Pos. |
| 17-7 s/s | Neg. | "Coin silver" | Neg. |
| 286 s/s | Neg. | "Nickel silver" | Pos. |
| 302 s/s | Neg. | US 5 ¢ coin | Pos. |
| 303 s/s | Neg. | US 10 ¢ coin | Pos. |
| 304 s/s | Neg. | US 25 ¢ coin | Pos. |
| 316 s/s | Neg. | Spigot handle | Pos. |
| 410 s/s | Neg. | Nickel-plated brass screw | Pos. |
| 416 s/s | Neg. | Flashlight | Pos. |
| 440 s/s | Neg. | s/s knife | Neg. |
| "Zimaloy" | Neg. | | |
| Invar | Neg. | | |

report on induction of nickel sensitization indicate that the eliciting dose is one-tenth of the sensitizing dose (6). The "sensitizing safety limit" for nickel can then be approximated at 10 $\mu\text{m Ni/l}$ or 0.6 ppm Ni. Within the time and temperature limitations cited above, the possibility of exceeding this limit (5 $\mu\text{g Ni}$) cannot be discounted, especially in the cases of cupro-nickel alloys used in current US and foreign coinage.

Although a positive "Fisher Spot Test" always indicates a nickel hazard, our data show that a negative test does not reflect the safety of a given metallic object. Both 302 s/s and 303 s/s gave negative spot tests (Table II), but our data (Table I) show that nickel is indeed leached from these alloys.

The use of nickel commodities is increasing by 10% per year (9), and the nickel-containing articles that a person can contact are legion. The use of stainless steel kitchens and flatware is continuously increasing. The solubilization of nickel by sweat and detergents person can contact are legion. The use of stainless steel kitchens and flatware is continuously increasing. The solubilization of nickel by sweat and detergents from these commodities is definitive and exposures to these materials can account for nickel dermatitis.

ACKNOWLEDGEMENT

This research was supported by Grant HO 00303. National Institute for Occupational Safety and Health, Public Health Service, Department of Health, Education and Welfare.

REFERENCES

- Colin-Russ, A.: A new form of reagent against perspiration effects on shoe materials. *J Hyg* 44: 53, 1945.
- Cronin, E.: Contact dermatitis. The significance of nickel sensitivity in women. *Br J Dermatol* 84: 96, 1971.
- Feigl, F.: *Qualitative Analysis by Spot Tests*, p. 114, 3rd ed. Elsevier, Amsterdam, 1946.
- Fisher, A. A.: Safety of stainless steel in nickel sensitivity. *JAMA* 221: 1282, 1972.
- Gross, P. R., Katz, S. A. & Samitz, M. H.: Sensitization of guinea pigs to chromium salts. *J Invest Derm* 50: 424, 1968.
- Jansen, L. H., Berrens, S. L. & Van Delden, J.: Contact sensitivity to simple chemicals: The role of intermediates in the process of sensitization. *Naturwissenschaften* 51: 387, 1964.
- Lucas, J. B.: Common industrial dermatoses. *Cutis* 13: 533, 1974.
- Malten, K. E. & Spruit, D.: The relative importance of various environmental exposures to nickel in causing contact hypersensitivity. *Arch Dermatovener (Stockholm)* 49: 14, 1969.
- Nickel consumption is increasing. *Chem Weekblad* 63: B4, 1967 (in Dutch).
- Samitz, M. H. & Pomerantz, H.: Studies of the effects on the skin of nickel and chromium salts. *Arch Ind Health* 18: 473, 1958.
- Samitz, M. H. & Katz, S. A.: Nickel dermatitis hazards from prostheses. II. In vivo and in vitro solubilization studies. *Br J Dermatol*, unpubl. data.

Received June 17, 1974

M. H. Samitz, M.D.
Duhring Laboratories
Hospital of the University of Pennsylvania
Philadelphia, Pennsylvania 19104
USA