

Chromated metal products may be hazardous to patients with chromate allergy

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Background: Hidden allergen exposure may contribute to persistence and relapse of chromate dermatitis. According to case reports, chromated metal products, such as screws, fittings, etc., may be relevant allergen sources for patients sensitized to chromate.

Objectives: To examine concomitant patch test reactivity to potassium dichromate 0.5% petrolatum (pet.) and three different types of chromated metal rings.

Patients/Methods: Patients with proven or suspected chromate allergy were patch tested with potassium dichromate 0.5% pet. and three different types of chromated metal rings (yellow, olive, and black). Hexavalent chromium Cr(VI) release from the patch tested rings was chemically analysed.

Results: Ninety-five patients were tested: 49/95 (52%) reacted to potassium dichromate and 25/95 (26%) reacted to black chromated rings. Reactions to chromated rings exclusively occurred in patients reacting to potassium dichromate. Of 20 patients with a strong reaction to potassium dichromate, 14 reacted to black chromated rings. These were shown to have a high Cr(VI) release. Only two patients reacted to the other chromated rings, which had a very low Cr(VI) release.

Conclusions: Handling chromated metal products must be regarded a hazard to chromate-sensitive patients, in particular those with a strong sensitization.

Key words: chromate; chromate dermatitis; chromated metal; contact allergy; patch test study; potassium dichromate. © Blackwell Munksgaard, 2009.

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Patients sensitized to chromate usually are advised to avoid skin contact with wet cement [as far as it still contains hexavalent chromium, Cr(VI)] or, if appropriate, not to wear chromium-tanned leather shoes in order to avoid a relapse of allergic contact dermatitis. However, it is well known that contact dermatitis in chromate-allergic patients tends to be chronic and recalcitrant, even in spite of the patients' efforts to avoid allergen contact. This may – at least in part – be due to hidden allergen exposures. Chromium-plated surfaces do not release any water-soluble Cr(VI) and are thus not regarded as a hazard (1, 2). In contrast, little is known about the role of chromated metal products. Many metal products made from iron or zinc, such as screws, fittings, and other material used in construction and do-it-yourself procedures, are chromated in order to prevent rust or surface oxidation.

Chromating is a process consisting of several steps, beginning with degreasing, followed by 'pickling' using phosphoric acid, a bath in zinc chloride (ZnCl₂) solution, and another step of 'pickling' using different acids for the different colours. Finally, the metal products are treated with chromic acid (CAS 1333-82-0) and other acids. For yellow chromating, nitric acid (CAS 7697-37-2) and sulfuric acid (CAS 7664-93-9) are added. For olive chromating, a combination of chromic acid and phosphoric acid is used. A black chromating can be achieved by the combination of chromic acid, acetic acid (CAS 64-19-7), and sulfuric acid and/or by the addition of silver. The surface of chromated metal products contains zinc chromate (ZnCrO₄ in variable amounts and other compounds) (3).

There are a few case reports of contact dermatitis caused by handling chromated metal products. Fregert et al. described hand dermatitis in five metal workers who had handled chromated metal sheets. The contents of water-soluble chromium were 0.03–0.44 µg/cm², and of this, 22–86% were hexavalent (4). Rycroft and Calnan reported the case of a metal worker who had acquired a chromate sensitization by contact with wet cement. In this patient, hand dermatitis was elicited by handling a chromated metal sheet releasing 0.03–0.10 µg/cm² of Cr(VI) (5). Hjerpe observed a small outbreak of hand dermatitis in five assembly workers in a Swedish automobile company, caused by chromated metal products. His conclusion was that yellow chromation is unsuitable for components that are manually handled (6). Wass and Wahlberg published an experimental patch test study with five patients in which they found that all the five patch tested chromate-allergic individuals reacted to chromated

metal discs releasing 0.60 µg/cm² of Cr(VI) from the surface within 20 min. Patch test with discs releasing lower amounts of Cr(VI) failed to elicit positive test reactions. Based on their results, they recommended that the mean release of Cr(VI) from chromated products should not exceed 0.30 µg/cm² (7).

As no larger study on the problem of elicitation of contact dermatitis by chromated metal products has been performed, we conducted a prospective study addressing the following questions. How many individuals sensitized to chromate do react to chromated metal products? Does reactivity to chromated metal products depend on the degree of sensitization, reflected by the intensity of the patch test reaction to potassium dichromate? Are there differences in reactivity to, and in release of Cr(VI) from, yellow, olive, or black chromated metal products?

Materials and Methods

Patch tests

Patients patch tested due to suspected chromate allergy (*n* = 84) or with previously positive patch test reaction to potassium dichromate (*n* = 11) were included in the study. Contact allergy to dichromate was suspected in cases of dermatitis presumably caused by cement, leather articles, e.g. shoes or gloves, or chromium in ionized form. Sixteen departments of dermatology, all of them members of the German Contact Dermatitis Research Group (DKG) and the Information Network of Departments of Dermatology (IVDK), participated in the study. After informed consent, patients were patch tested with potassium dichromate 0.5% in petrolatum (pet.) (Hermal, Reinbek, Germany) and with three chromated metal rings of different colours. The outer diameter was 9 mm, the inner diameter was 5 mm, and the rings were about 1 mm thick. These rings, obtained from Cohline, Dillenburg, Germany, had a base of a zinc/iron alloy and were chromated according to the steps mentioned above, resulting in a zinc chromate layer of estimated 8–16 µm. The rings were unused before the study, and during the study only used once for patch testing.

Patch tests were performed and read according to DKG guidelines (8, 9). Patch test exposure time was 2 days. For patch testing with chromated rings, test systems with large plastic chambers mounted on adhesive tape were used. Patch tests with standardized allergen preparations including potassium dichromate were performed with Finn Chambers[®] on Scanpor. For data evaluation, generally patch test reaction at D3 was

considered. If a D4 reading was performed instead of a D3 reading, this reaction was taken for data analysis.

Data analysis was performed at the IVDK data centre using SAS[®] 9.1 software (SAS Institute, Cary, NC, USA).

Chemical analysis of the chromate contents of the patch tested rings

Chromate analyses were performed at the BGIA – Institute for Occupational Safety and Health of the German Social Accident Insurance (DGUV), Sankt Augustin, Germany. For measuring the release of Cr(VI), of each colour, three chromated rings were incubated together in 10 ml purified water for 2 days in a glass bottle at room temperature and stirred from time to time. After 1 day, the rings were turned upside down. After 2 days, the migration solution was filtered. An aliquot of 5 ml was used for photometric analysis of Cr(VI) using the diphenylcarbazide method. Unfortunately, multiple analyses were not possible. For this, the National Institute for Occupational Safety and Health (NIOSH) method 7600 for detecting Cr(VI) in air was modified (10). Results were calculated as CrO₃, related to the metal surface.

Results

Altogether, 95 patients from 16 departments of dermatology were patch tested with chromated rings and potassium dichromate 0.5% in pet. The mean age of the study group was 48 years (range 18–81 years). A description of the test population and the groups of patients reacting to potassium dichromate and the black chromated rings, respectively, is given in Table 1. There were no significant differences in any of the MOAHLFA (M, male; O, occupational dermatitis; A, atopic dermatitis; H, hand dermatitis; L, leg dermatitis; F, face dermatitis; and A, age of 40 years or more) index items between these three groups.

Table 2. Patch test reactions to chromated rings and potassium dichromate 0.5% petrolatum

Reaction (symbol)	Chromated ring			Potassium dichromate
	Yellow <i>n</i> (%)	Olive <i>n</i> (%)	Black <i>n</i> (%)	<i>n</i> (%)
Negative (–)	92 (97)	91 (96)	67 (71)	41 (43)
Doubtful (?)	1 (1)	2 (2)	2 (2)	4 (4)
Weak positive (+)	2 (2)	2 (2)	17 (18)	29 (31)
Strong positive (++)	0 (0)	0 (0)	7 (7)	14 (15)
Strong positive (+++)	0 (0)	0 (0)	1 (1)	6 (6)
Irritant (ir)	0 (0)	0 (0)	1 (1)	1 (1)
Total	95 (100)	95 (100)	95 (100)	95 (100)

Table 3. Concomitant patch test reactions to black chromated rings and potassium dichromate 0.5% petrolatum

Potassium dichromate	Black chromated ring						Total
	Negative	?	+	++	+++	Irritant	
Negative	40	1	0	0	0	0	41
?	4	0	0	0	0	0	4
+	17	1	9	2	0	0	29
++	4	0	6	4	0	0	14
+++	2	0	2	1	1	0	6
Irritant	0	0	0	0	0	1	1
Total	67	2	17	7	1	1	95

Of the 95 patients tested, 49 (52%) reacted positively to potassium dichromate and 25 (26%) reacted to the black chromated rings. Only two patients reacted to the yellow and olive rings. Details of the patch test results with the chromated rings and potassium dichromate are listed in Table 2. As shown in Table 3, all 25 patients with positive reactions to the black chromated rings also reacted to potassium dichromate. Among patients with a strong patch test reaction (++ or +++) to potassium dichromate, the proportion of patients reacting to the black chromated rings was found to be significantly higher (14 of 20, i.e. 70%) than among those with a weak positive reaction to potassium dichromate (11 of

Table 1. MOAHLFA index of the test population (*n* = 95), patients reacting to potassium dichromate (*n* = 49), and patients reacting to black chromated rings (*n* = 25)

Item		Test population		Dichromate positive		Black ring positive	
		Patient count	Percent	Patient count	Percent	Patient count	Percent
Male	M	52	54.7	26	53.1	10	40.0
Occupational dermatitis	O	30	31.6	14	28.6	6	24.0
Atopic dermatitis	A	25	26.3	10	20.4	7	28.0
Hand dermatitis	H	43	45.3	17	34.7	9	36.0
Leg dermatitis	L	7	7.4	5	10.2	1	4.0
Face dermatitis	F	9	9.5	4	8.2	2	8.0
Age ≥ 40 years	A	67	70.5	35	71.4	17	68.0

Table 4. Reaction pattern in four patients reacting to yellow and olive chromated rings

Reaction to	Patient 1	Patient 2	Patient 3	Patient 4
Yellow ring	?	+	+	–
Olive ring	?	+	+	?
Black ring	+	++	+++	+
Potassium dichromate	+++	++	+++	+

29, i.e. 38%) ($P = 0.04$; Fisher's exact test). Reactions to the yellow and olive chromated rings were only seen in patients reacting to both, the black rings and potassium dichromate. The reaction patterns of four patients with positive or doubtful reactions to the yellow or olive rings are depicted in Table 4.

Results of the Cr(VI) analyses were calculated as chromium trioxide (CrO_3) and related to the surface area. The respective amounts were yellow rings – $0.18 \mu\text{g}/\text{cm}^2 \text{CrO}_3$; olive rings – $0.23 \mu\text{g}/\text{cm}^2 \text{CrO}_3$; and black rings – $11.2 \mu\text{g}/\text{cm}^2 \text{CrO}_3$. This means that the Cr(VI) release from the black rings was about 55 times as high as the release from the yellow or olive rings. The Cr(VI) concentration of the supernatant of the yellow and olive rings was close to the detection limit.

Discussion

Our results confirm that the release of Cr(VI) from chromated metal products may be high enough to elicit allergic reactions in patients sensitized to chromate. Particularly, those patients with a strong patch test reaction to potassium dichromate, indicating a high degree of sensitization, are at risk. Fourteen of 20 patients with a ++ or +++ reaction to potassium dichromate also reacted to the black chromated rings. Unspecific, irritant reactions to the chromated rings can be excluded as only chromate-allergic patients reacted to the rings, but no patients without reaction to potassium dichromate.

Of course, the Cr(VI) exposure in a closed patch test with a chromated ring is different from the Cr(VI) exposure by handling a chromated metal part at work. In the latter situation, the contact is not as intense and prolonged as in the 2-day occlusive patch test. However, repeated contact to chromated products at work may contribute to the persistence or relapse of a chromate dermatitis localized at the hands or fingers. A similar situation was described in the case reports by Fregert et al. (4), Rycroft and Calnan (5), and Hjerpe (6).

Cr(VI) release from chromated products obviously varies within a broad range. While the Cr(VI) concentration of the supernatant of the yellow and olive rings was close to the detection

limit, the concentration was about 55 times as high in the supernatant of the black rings. Due to different chemical methods, our data concerning the Cr(VI) release cannot be directly compared with the data mentioned in the papers cited in the introduction. However, it is evident that an elicitation threshold exists. Only a few of our patients reacted to the rings with the lower release, and all these reacted more intensely to the black rings and to potassium dichromate.

Cr(VI) release does not necessarily depend on the colour of the chromated metal part nor is the colour necessarily an indicator of a certain Cr(VI) release. The release of Cr(VI) depends on other factors in the chromating process than the colour. Therefore, in every day life or in occupational settings, handling chromated metal products generally must be regarded as a hazard to sensitized patients. In particular, patients with a high degree of sensitization to chromate should be advised to be careful when handling chromated metal products and to be aware of adverse reactions.

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