Chromium (Cr) is the third most common (1, 2) metal allergen, affecting 1–3% of the general population in Europe (3). Common sources of exposure are chromium-tanned leather (4, 5), Cr(VI) (chromate) in cement (5, 6), work tools (5), and protective layers or sprays on metals and wood (7, 8). Although Cr(VI) is a more potent allergen, both Cr(III) and Cr(VI) are important causes of chromium contact dermatitis (4, 9). The amount of Cr released from Cr-tanned leather, and the oxidation state (Cr(III) or Cr(VI)), is largely dependent on exposure factors, such as relative humidity during storage, and contact with alkaline solutions (10, 11). We report here the scenario of combined exposure to Cr-tanned leather and alkaline cooling fluid, resulting in chromium dermatitis.

CASE REPORT
A 55-year-old man working in a major metal industry in Sweden was referred due to dermatitis. He had no previous history of skin diseases or atopy, and he had been working on the production line for 28 years. Three years previously he had started working in the maintenance department, with the task of grinding and polishing the cylinders used to produce rolled iron. During this process he was mainly in contact with the cylinders, the cooling fluid, protective leather gloves, which were generally soaked with cooling fluid, and detergents for skin cleansing. He also used protective leather shoes. Within 2 months, he started to develop hand dermatitis with hyperkeratosis, scaling and fissures. This was followed by foot dermatitis. Patch-testing with the Swedish baseline series revealed a positive reaction (+++) to 0.5% potassium dichromate. The shoes and gloves were changed to products that were chromium-free according to the manufacturer. The patient’s foot dermatitis improved. Since it was not possible to avoid exposure of the hands to cooling fluid, a change in working tasks was planned and the patient was first given sick leave. After 6 months of sick leave, his hand dermatitis had improved significantly and he was appointed another job within the factory.

METHODS

Analysis of leather
Five gloves used with the coolant fluid, and 5 unused protective leather gloves (“Tegera by ejendals”, Style 103 (Svinnarv), Leksand, Sweden), the type used when the dermatitis started, and triplicate samples of a previously characterized Cr-tanned leather sample (the same as analysed in (10, 12), denoted “Cr leather”, and in (11) “leather (cattle)”), were analysed. All leather samples (approximately 0.5–1 g) were exposed to 20% relative humidity at 70°C for 24 h in a climate chamber prior to extraction, as in (11). The extraction was performed in 50 ml of 22.8 g/l K2HPO4 •3H2O, adjusted to pH 8.0 ± 0.1, in closed vessels in a dark incubator controlled to 25°C and bilinear shaking (12°, 22 cycles/min) for 3 h. Total Cr in the extraction solutions was analysed by means of atomic absorption spectroscopy (AAS), with a detection limit of 0.08 mg/l, and Cr(VI) by means of spectrophotometry (detection limit of 0.026 mg/l). Details are given in (11).

Analysis of coolants
Three samples were taken at the same time from the patient’s work-place. The coolant had not been changed for 6 months. Three samples of unused cooling fluid were also collected at the same time. All samples were analysed for total Cr by means of AAS (detection limit 0.054 mg/l) and spectrophotometry (no measurement possible due to interferences).

RESULTS
Released total Cr, Cr(III), and Cr(VI) from the gloves and the reference leather are shown in Fig. 1, Fig. S11 and Table SI1. The total Cr concentration was below the limit of detection in the unused cooling fluid. The concentration in the used cooling fluid (0.5 ± 0.2 mg/l) was similar to the extraction solutions of the leather gloves (0.7 ± 0.2 mg/l).

DISCUSSION
The majority of Cr released from leather is in the form of Cr(III) (10–12). Although total Cr and Cr(III) released from the leather gloves in this case are smaller compared with the reference leather (previously found to be a worst-case leather (12)), released Cr(VI) is in the same range or higher and exceeds the restriction limit of 3 mg/kg for some of the unused and all used gloves. The used gloves had been in contact with the cooling fluid (pH 9.8). It has been shown previously that alkaline solutions can increase the amount of total Cr or Cr(VI) released from leather (11), and we consider it likely that

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the high pH contributed to the relatively high release of Cr(VI) from the used gloves. However, based on this limited study, we cannot exclude possible contamination by Cr(VI) from the cooling fluid. Cr detected in the used cooling fluid might derive from contact surfaces of chromium-containing alloys in the cooling system during the 6-month period, particles (as judged from the darker colour of used fluid compared with new fluid), or chromium-tanned leather gloves (fibres were visible in the used fluid). A pH above 9 is skin irritating and may, in combination with released Cr from the protective leather gloves, cause Cr sensitization and dermatitis. A similar combined effect of Cr and alkaline pH is well-known for cement (6).

This case demonstrates that care must be taken in occupations where protective chromium-tanned leather gloves are used in combination with alkaline solutions.

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Fig. 1. (a) Chromium Cr(III), Cr(VI) and total Cr released from used (n = 5) and unused (n = 5) gloves, and the Cr-tanned reference sample (n = 3) (11, 12), normalized to the dry mass of the leather (mg/kg leather). (b) Magnification of the Cr(VI) values in (a), dotted line indicates restriction limit of 3 mg/kg (13) in comparison with released Cr(VI). The error bars show the standard deviation between samples. Corresponding values normalized to the surface area and single values are shown in Fig. S1 and Table S1.