semi-open tests with the outside of the used gloves were due to contamination with wood dust. Chemical analyses of the wood dust samples, by means of gas chromatography and Fourier transform infrared spectroscopy, identified the presence of colophonium in the wood dust, and thus confirmed this contact allergen as a relevant and occupational sensitizer. After discussing the case with the occupational physician, the patient was moved to a post without any exposure to wood dust, following which significant improvement of his skin condition occurred. The patient has given written consent to publish data and photographs.

DISCUSSION

The prevalence of colophonium allergy is 0.7% in an unselected population, and 3% in a population that had an episode of eczema the previous year.[1] Colophonium is a complex mixture containing >100 compounds derived from pine trees. It has countless applications at home,[2] and also in the work environment, and exposure to (oxidation products of) colophonium, and also to modified colophonium, is ubiquitous. We highlight this case as colophonium exposure is rather unexpected in a petrochemical industrial environment.[3–6] Querying the French database of occupational exposure (SOLVEX[4]) with the activity sector "chemical industry" and the post "storage and transport of materials" retrieved mainly aromatic compounds ("-arene"), aldehydes and acetylene black. Although colophonium is also an ubiquitous sensitizer in daily life, our patient reported no hobby or activity that made us suspect sensitization in private life. Furthermore, the timing after which the patient developed skin lesion rather favoured an (unexpected) occupational origin.

ACKNOWLEDGMENT

The authors are grateful to Nikki Sabourin-Gibbs, Rouen University Hospital, for her help in editing the manuscript.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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How to cite this article: Hamwi S, Kunst A, Boust C, Bauvin O, Tetart F. Occupational allergic contact dermatitis caused by colophonium, an unsuspected sensitizer in a petrochemical worker. *Contact Dermatitis*. 2022;87(6):548-550. doi:10.1111/cod.14211

Presence of impurities of nickel and cobalt in facial cosmetic pigments and their dissolution into artificial sweat

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Funding information
Canada Research Chairs Program (#950-233099); KTH faculty grants (#Odnevall 2019-2020); start-up funds (#Western 2020); Wolfe-Western fellowship, Canada (#2020)

KEYWORDS: allergic contact dermatitis, artificial sweat, cosmetic pigments, metals

Both nickel (Ni) and cobalt (Co) are common skin sensitizers known to cause contact allergy,[1] not only existing in alloys but also in different consumer products, such as cosmetics,[2] even though not intentionally added. Mineral pigments such as iron- (Fe), manganese- (Mn) and titanium- (Ti) oxides are often blended and used for colouring of cosmetic products.[3,4] These pigments may naturally contain different metal impurities such as Ni and Co. Repetitive use may result in skin accumulation and give rise to allergic contact dermatitis.[5] A recent report[6] on patch test results on 52 000 dermatitis patients in Europe shows 17.6% of the patients to be positive to Ni (the largest fraction) and 5.39% positive to Co. So far, it is unclear whether impurities of Ni or Co are associated with specific pigments in cosmetics. The aim of this study was to assess total amounts of Ni and Co in various inorganic pigments common in facial and powdered cosmetics (e.g., eye shadow cosmetics), and determine the extent of their dissolution into artificial sweat.

METHODS

Samples of 10 colouring pigments used in various facial cosmetic products were kindly provided by a supplier focused on cosmetics. The investigated pigments were all inorganic: (1) Unipure Yellow LC 182, (2) Unipure Red LC 381, (3) Unipure Pink LC 583, (4) Unipure Violet LC 581, (5) Unipure Black LC 990, (6) Zeosafe CL-07, (7) Mica GH 103, (8) Mica GH 108, (9) Mica GH 603 and (10) Unipure White LC 981. All pigments were supplied as dry powders and covered a range of colours (confirmed by three different people to avoid personal colour bias). Details are compiled in Figure 1.

The total Ni and Co content in the pigments were determined after complete pigment digestion in diluted aqua regia[7] (2.5 vol% HCl and 6.5 vol % HNO_3, pH <0.1). The sweat-soluble fraction of Ni and Co from the pigments were investigated after one-week extraction in artificial sweat (ASW, pH 6.5) at 30 °C, according to EN 1811:2011 + A1:2015.[8] Details are provided in section S1.1 in Appendix S1. All particle-free solution samples were analysed by means of graphite furnace atomic absorption spectrometry (GF-AAS) using a PerkinElmer AA800 analyst instrument and triplicate readings of each sample.[9] In diluted aqua regia, the limits of detection were 0.76–0.83 μg/g for Ni and 1.17–1.27 μg/g for Co. In ASW, they were 1.21–1.29 μg/g for Ni and 0.85–0.91 μg/g for Co.

The potential enrichment of Ni and Co in selected pigments were assessed by means of time of flight secondary ion mass spectrometry (ToF-SIMS), a surface-sensitive technique with a detection limit in the μg/g range. Details are given in Appendix S1.

ID	INCI	Color	Chemical composition (wt%)
(1)	CI77492	Yellow	$Fe_2O_3 \cdot nH_2O$
(2)	CI77491	Red	Fe_2O_3
(3)	CI77742	Pink	$MnNH_4P_2O_7$
(4)	CI77742	Purple	$MnNH_4P_2O_7$
(5)	CI77499	Black	$FeO \cdot Fe_2O_3$
(6)	ZEOLITE	White	SiO_2 67-72%, Al_2O_3 11-14%, CaO 3-6%, K_2O 1-4%, MgO 0.5-1.5% Na_2O 0.2-1.5%, Fe_2O_3 0.8-1.7%
(7)	MICA	White	SiO_2 ≤54%, Al_2O_3 ≥25%, K_2O ≥ 8%, MgO 1.5-1.6%, Fe_2O_3 2-3%
(8)	MICA	White	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
(9)	MICA	White	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
(10)	CI77891	White	TiO_2

Total and ASW-soluble amounts (μg/g) of Ni and Co in pigments

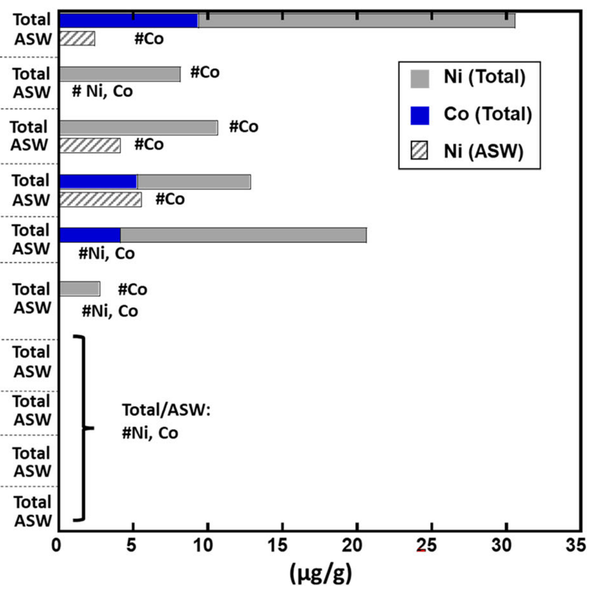

FIGURE 1 Summary of the investigated pigments (pigment ID number, International Nomenclature Cosmetic Ingredient (INCI) name, colour, chemical composition (supplier information)), and total and artificial sweat (ASW)-soluble amounts (μg/g) of Ni and Co from each pigment (by means of graphite furnace atomic absorption spectrometry, raw data in Table S1 in Appendix S1) compared with the total content. #Ni or #Co denotes a concentration below the limit of detection (see "Methods" section)

RESULTS

Results on soluble amounts of Ni and Co released into artificial sweat from the pigments compared to their total content are summarized in Figure 1. All coloured pigments (IDs 1–5), and one of the white pigments (ID 6), contained detectable amounts of Ni, whereas only the yellow, purple and black pigments (IDs 1, 4, 5) also contained Co. The Co contents were for these pigments lower than the corresponding Ni contents. Only Ni was dissolved into ASW. The ASW-soluble fractions of Ni were lower than the total contents and were only observed for three pigments (yellow (ID 1), pink (ID 3) and purple (ID 4)), in amounts ranging from 2.4 to 5.5 μg Ni/g pigment. Ni was only soluble into ASW for pigment ID 1, containing $Fe_2O_3 \cdot nH_2O$, but not Fe_2O_3 (ID 2) or $FeO \cdot Fe_2O_3$ (ID 5). This can be explained by different solubilities of these Fe oxides, also influencing the dissolution of impurities.[10,11] The coloured pigments (IDs 1–5) were all rich in Fe or Mn and contained clearly higher total amounts (7.6–21.2 μg/g) of Ni compared with the white pigments (2.7 μg/g—ID 6, <1.17 μg/g—IDs 7–10). Co was an identified constituent in the Fe- and Mn-rich pigments (the yellow, purple and black pigments, IDs 1,4,5), ranging from 4.1 to 9.4 μg/g (total content), though no Co was released into ASW. To further gain insights in the location and distribution of the Co and Ni impurities, investigations were performed on the yellow and black pigments of highest Ni and Co content (IDs 1 and 5) by means of ToF-SIMS. Neither Ni nor Co was observed (see Figures S1 and S2). This implies that Ni and Co were not locally enriched but rather evenly distributed within the pigments.

DISCUSSION

Findings of this study reveal that impurities of both Ni and Co can be present in inorganic metal oxide pigments used in cosmetics. Their presence was associated with metal oxides rich in Fe and Mn. These pigments are usually darker and/or more colourful compared with less coloured or white pigments containing silicon-(Si) and Ti-rich pigments. A similar trend was observed in a recent study on tattoo inks[3] showing a strong correlation between the content of impurities of Ni and Co from the ink with several metal constituents, including Fe and Mn, and also between each other. Both Ni and Co had considerably lower solubility in artificial sweat than the corresponding total impurity content. The dissolution of Ni into artificial sweat was primarily observed for Fe- and Mn-oxide pigments at a concentration above 1 μg/g, a level that may increase the risk for the development of allergies in sensitized subjects.[4,5] Note that the used concentration of these pigments in some facial cosmetic products, such as eye shadow, can be a significant fraction (a few to more than 50%) of the ingredients. Consistent with a previous study on cosmetic pigments,[12] no dissolution of Co was observed in artificial sweat, which suggests Co in these pigments to be present in insoluble forms or in too low concentrations to be detected.

AUTHOR CONTRIBUTIONS

Xuying Wang planned and conducted the study, and drafted the manuscript; Yolanda S. Hedberg supervised the study and revised the manuscript; Inger Odnevall supervised the study and revised the manuscript.

ACKNOWLEDGEMENTS

We thank Dr. Jonas Hedberg, Dr. Heng-Yong Nie and Kwang Soak Gabriel O'Donnell, all at the University of Western Ontario, Canada, for ToF-SIMS measurements and discussions.

FUNDING INFORMATION

This work was supported by Wolfe-Western fellowship, Canada (#2020); the Canada Research Chairs Program (#950-233099); start-up funds (#Western 2020); KTH faculty grants (#Odnevall 2019-2020).

CONFLICT OF INTEREST

The authors declare they have no conflicts of interest.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Wang X, Hedberg YS, Odnevall I. Presence of impurities of nickel and cobalt in facial cosmetic pigments and their dissolution into artificial sweat. *Contact Dermatitis*. 2022;87(6):550-553. doi:10.1111/cod.14212

Sensitization to modified colophonium in glucose sensors: Another problem for diabetes patients

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KEYWORDS: allergic contact dermatitis, case report, colophonium, diabetes mellitus, FreeStyle Libre, hydrogenated methyl abietate, isobornyl acrylate, methyl abietate, methyl dehydroabietate, modified colophonium

We report two diabetes type 1 patients with allergic contact dermatitis (ACD) from modified colophonium in glucose sensors.

CASE REPORTS

Case 1

A 12-year-old boy developed dermatitis on his arms following the application of a FreeStyle Libre I glucose sensor (Abbott Diabetes Care), a few months after starting its use. Replacement by a Dexcom G6 sensor (Dexcom) resulted in an immediate relapse of the eczema. Patch tests were performed with the European baseline, plastics and glues, and a (meth)acrylate series (Chemotechnique Diagnostics) including IBOA 0.1% pet. and N,N-dimethylacrylamide (DMAA) 0.1% pet. (both in-house prepared; raw materials from Sigma-Aldrich) mounted on IQ Ultra chambers. Additionally, three types of modified colophonium (provided by a manufacturer of adhesive bandages) were tested: methyl ester of rosin (CAS 68186-14-1), hydrogenated rosin ester (CAS 8050-15-5), and hydrogenated methyl abietate (CAS 30968-45-7) (all 20% pet.). Pieces of the adhesives from the two glucose sensors were patch tested 'as is', as well as a hydrocolloid dressing (Duoderm Extra Mince, ConvaTec), which he regularly placed between the devices and the skin to prevent skin reactions. All tests were occluded for 2 days with Oper tape (Iberhospitex, Innovative Health Technologies) and were read on day (D)2, D4 and D7 according to ESCD guidelines.

Positive reactions (D4) were observed to IBOA 0.1% pet. (+++), sesquiterpene lactone mix (SLM) 0.1% pet. (+), and linalool hydroperoxides 1% pet (+). Colophonium 20% pet. gave a doubtful reaction (?+) on D4, whereas the three modified rosins were positive (++). The adhesive from FreeStyle Libre I gave a doubtful (?+) reaction, whereas the piece of the hydrocolloid dressing was positive (++). The adhesive of Dexcom G6 as well as abietic acid and hydroabietyl alcohol (Abitol) remained negative.

Case 2

A 56-year-old male developed eczema from his FreeStyle Libre I during the first few weeks after starting its use. In order to improve the skin adhesion, the patient had used Skin Tac wipes (Torbot Group Inc.), containing colophonium, which further aggravated his skin symptoms. Stopping the use of these wipes, and changing the device to the IBOA-free FreeStyle Libre II sensor resulted in no improvement; another attempt by using the Dexcom G5 sensor brought no amelioration either. Patch tests, performed as in Case 1, showed sensitizations (D4) to nickel (+++), cobalt (?+), colophonium (++), abietic acid (+), Abitol (+), and also to the modified colophonium methyl abietate (CAS 127-25-3) 5% pet. (++) (Figure 1), as well as to several fragrances (*Myroxylon pereirae* resin, Fragrance mix