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Contents of sensitising rubber accelerators in disposable rubber gloves: A Copenhagen market survey

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Abstract

Background: Rubber gloves contain rubber accelerators that may cause contact allergy. The content of sensitising rubber accelerators in contemporary rubber gloves is not well known.

Objectives: Identify and quantify the content of rubber accelerators in disposable rubber gloves.

Methods: Fifty-one gloves of 49 different brands were collected. Forty-eight of the gloves were disposable and three re-usable. The gloves were analysed for their content of sensitising rubber accelerators, that is, zinc dithiocarbamates, thiurams, thiazoles/benzothiazoles, diphenylguanidine, and thioureas by high-performance liquid chromatography.

Results: Rubber accelerators were identified in 43/48 (90%) of the disposable gloves. In total, 39 gloves contained zinc dibutyldithiocarbamate (ZDBC) (0.18–1.96 mg/g), 34 zinc diethyldithiocarbamate (ZDEC) (0.032–2.78 mg/g), three zinc dibenzyldithiocarbamate (0.65–1.4 mg/g), one zinc dimethyldithiocarbamate (0.23 mg/g), and one 1,3-diphenylguanidine (0.21 mg/g). 2-cyanoethyl dimethyldithiocarbamate (CEDMC) was identified in three gloves (<0.052 mg/g). The one glove labelled as accelerator free contained ZDBC (1.07 mg/g). Only few glove packages had the specific content of rubber accelerators labelled.

Conclusions: The most frequent rubber accelerators in rubber gloves are ZDEC and ZDBC. Accelerator-free gloves may contain rubber accelerators. Full labelling of

Abbreviations: CEDMC, 2-cyanoethyl dimethyldithiocarbamate; DPG, 1,3-diphenylguanidine; HPLC, high-performance liquid chromatography; MBT, mercaptobenzothiazole; MD, medical device; PPE, personal protective equipment; TETD, tetraethylthiuram disulfide; ZDBC, zinc dibutyldithiocarbamate; ZDBZ, zinc dibenzyldithiocarbamate; ZDEC, zinc diethyldithiocarbamate; ZDMC, Zinc dimethyldithiocarbamate.

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rubber gloves is needed and producers should be sure not to falsely claim that the rubber gloves are free of rubber accelerators.

KEYWORDS
allergic contact dermatitis, contact allergy, hand dermatitis, high-performance liquid chromatography (HPLC), market survey, occupational disease, rubber accelerators, rubber gloves, ZDEC

1 | INTRODUCTION

Rubber accelerators are used as vulcanization agents in the production of rubber items such as rubber gloves. Some rubber accelerators may cause contact allergy for example thiurams, dithiocarbamates, guanidines, and thiazoles.[1] Contact allergy to rubber accelerators is a frequent occupational disease affecting employees in wet work occupations as cleaning, healthcare, and the food industry.[2–5] The European baseline series includes the rubber accelerators thiuram mix, mercaptobenzothiazole (MBT), and mercapto mix.[6] Patients under suspicion of rubber accelerator contact allergy are tested with specialised rubber series with a broad spectrum of different rubber accelerators for example, individual thiurams and dithiocarbamates as tetraethylthiuram disulfide (TETD) and zinc diethyldithiocarbamate (ZDEC).[6]

The most frequent exposure for patients with contact allergy to rubber accelerators is gloves.[1] Thiurams were previously the primary accelerator in rubber gloves but may now have been replaced with dithiocarbamates.[7–9] Paradoxically, contact allergy to thiurams is most frequent and has remained stable for many years as reported by surveillance data from Denmark.[1,10,11] A new dithiocarbamate, 2-cyanoethyl dimethyldithiocarbamate (CEDMC), was recently identified in rubber gloves and has proven to be a contact allergen by causing positive reactions in patch testing.[12] CEDMC is however not a rubber accelerator added to the production of rubber gloves but a chemical that may be formed during vulcanization in the manufacturing of nitrile gloves.[12] Another rubber accelerator is 1,3-diphenylguanidine (DPG). The content of DPG in rubber gloves has probably increased in recent years, but contact allergy to DPG seems to be less frequent in Denmark than in Sweden, which may be explained by Swedish exposure to a specific brand of polyisoprene gloves.[1,8,13]

Labelling of the content of rubber accelerators in rubber gloves is not mandatory to the disadvantage of doctors and patients. Better labelling has been proposed for decades but nothing has changed.[1,10,14–17] More knowledge on the content of rubber accelerators in gloves is needed for understanding of epidemiological trends, up-to-date diagnostics, and for informing preventive measures.

The objective of this study is to identify and quantify the content of sensitising rubber accelerators in a large sample of disposable rubber gloves randomly collected in Copenhagen, Denmark.

2 | MATERIALS AND METHODS

2.1 | Study design

We conducted a systematic market survey of contemporary disposable rubber gloves used in Copenhagen (Denmark). The gloves were analysed for their content of rubber accelerators by high-performance liquid chromatography (HPLC) at the Department of Occupational and Environmental Dermatology, Skåne University Hospital Malmö, Sweden. For sub-analysis, a few reusable gloves were similarly analysed.

2.2 | Glove collection

In June 2023, a total of 51 rubber gloves consisting of 49 different brands were randomly collected from Copenhagen professions, online retailers used by the professions, and Copenhagen physical retailers. Forty-eight gloves were disposable including one accelerator free, and three reusable.

2.2.1 | Gloves from professions

One hundred and eight shops were asked for rubber gloves in the five districts of inner Copenhagen. Thirty-two gloves (28 nitrile; four latex) representing 30 different brands were collected from 31 shops. The gloves were purchased and collected from hairdressing saloons (number of gloves [n] = 5); mechanic workshops ($n = 6$); healthcare clinics including cosmetic clinics ($n = 11$); food shops and restaurants ($n = 5$); cleaning contractors ($n = 5$). One glove was reusable.

2.2.2 | Gloves from online and physical retailers

Thirteen gloves (nine nitrile; four latex) of different brands were bought from four websites used by Copenhagen healthcare workers, mechanics, and cleaners. Two gloves were reusable. Six gloves (four nitrile; two latex) of different brands were bought from physical retailers in Copenhagen (supermarket: $n = 2$; hardware stores: $n = 2$; hairdressing store: $n = 1$; hobby shop: $n = 1$).

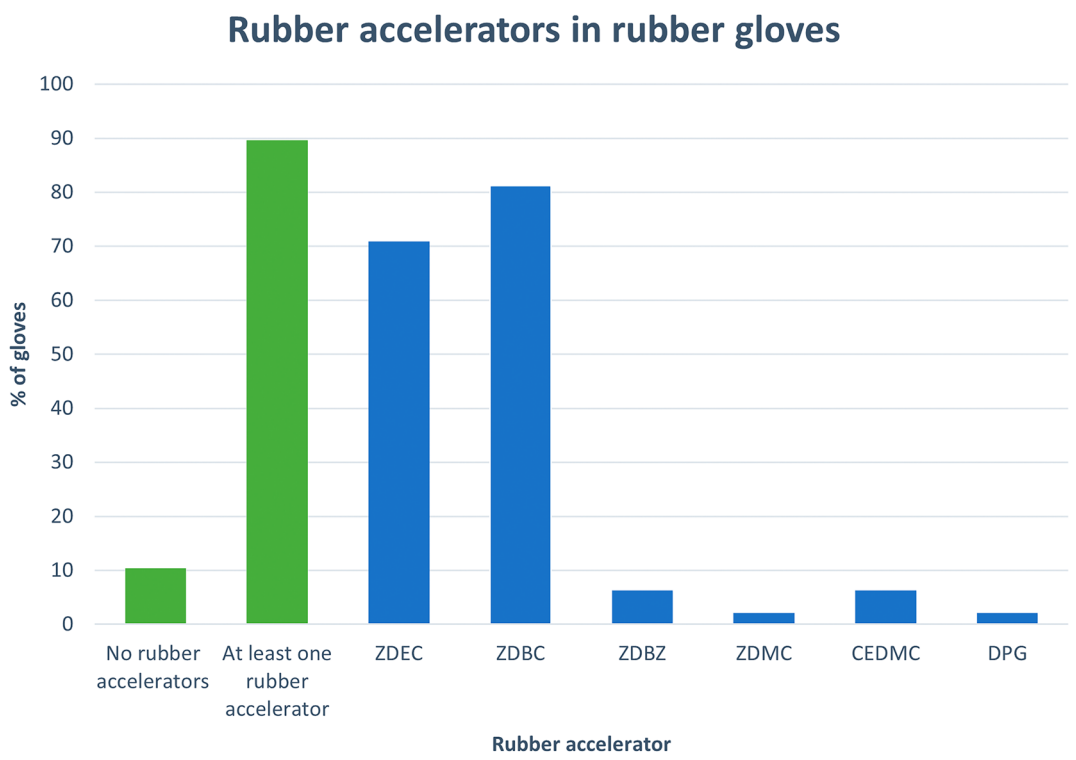

FIGURE 1 The distribution of rubber accelerators in disposable rubber gloves. A single glove can contain more than one rubber accelerator. CEDMC, 2-cyanoethyl dimethyldithiocarbamate; DPG, 1,3-diphenylguanidine; ZDBC, zinc dibutyldithiocarbamate; ZDBZ, zinc dibenzyldithiocarbamate; ZDEC, zinc diethyldithiocarbamate; ZDMC, zinc dimethyldithiocarbamate. CEDMC is not a rubber accelerator added to the production of rubber gloves but a chemical that may be formed during vulcanization in the manufacturing of nitrile gloves.[12]

2.3 | Chemicals

Acetone (CAS no: 67-64-1) used for the extractions of analytical grade and acetonitrile (CAS no: 75-05-8) of HPLC grade were obtained from Labscan Ltd. (Dublin, Ireland). 95% ethanol (CAS no: 64-17-5) was obtained from Kemetyl (Haninge, Sweden).

2.4 | Analysis of the content of rubber accelerators by HPLC

A sample (~0.5 g) of a glove was cut into smaller pieces and placed in a 10 mL-test tube with screw. Five millilitres acetone was added, and the tube was shaken for 10 min using a shaker. The glove extract was transferred to a round-bottomed flask and under vacuum evaporated to dryness. The dry extract was hereafter dissolved with acetonitrile (1 mL) and filtered into a HPLC-vial followed by injection on the HPLC-column. Chromatograms of the samples were compared with reference chromatograms. Duplicate analyses were conducted for each glove type.[7,12,18] This method describes analysis of zinc dithiocarbamates, thiurams, CEDMC, thiazoles/benzothiazoles, and thioureas with limits of detection estimated to 10 µg/g for zinc dithiocarbamates and 1 µg/g for the other.

2.5 | Analysis of 1.3 DPG

For the analysis of DPG, gloves were extracted as above but in 95% ethanol instead. The extracts were not evaporated, but instead filtered directly and the ethanol extracts were analysed as described by Dahlin et al.[19] by HPLC with a limit of detection estimated to 2 µg/g.

3 | RESULTS

The contents of sensitising rubber accelerators in each of the collected rubber gloves are presented in Table S1.

3.1 | Contents of rubber accelerators in disposable rubber gloves

The distribution of rubber accelerators in the disposable rubber gloves is seen in Figure 1.

Rubber accelerators were identified in 90% (43/48) of the disposable gloves. The most frequent rubber accelerator was zinc dibutyldithiocarbamate (ZDBC) identified in 81% (39/48) of the gloves (0.18–1.96 mg/g, 0.018%–0.20%) followed by ZDEC identified in

71% (34/48) of the gloves (0.032–2.78 mg/g, 0.0032%–0.278%). In total 6% (3/48) of the gloves contained zinc dibenzyldithiocarbamate (ZDBZ) (0.65–1.4 mg/g, 0.065%–0.14%), 6% (3/48) contained CEDMC (<0.052 mg/g, <0.0052%), and 2% (1/48) contained zinc dimethyldithiocarbamate (ZDMC) (0.23 mg/g, 0.023%). DPG was identified in 2% (1/48) of the gloves with a content of 0.21 mg/g (0.021%). No thiurams were identified. The content of rubber accelerator per area glove was as the following: ZDBC: 0.0010–0.025 mg/cm^2; ZDEC: 0.00017–0.035 mg/cm^2; ZDBZ: 0.0039–0.0093 mg/cm^2 glove; ZDMC: (0.0014 mg/cm^2); DPG: 0.0013 mg/cm^2. The content of CEDMC per area glove was $<6.14 \times 10^{-4}$ mg/cm^2.

The accelerator-free gloves contained ZDBC (1.07 mg/g, 0.107%; 0.0059 mg/cm^2).

One of the gloves did not contain any rubber accelerators but probably phthalates.

3.1.1 | Labelling of the disposable gloves

A total of 29 glove packages were labelled as potentially allergy-causing, including four of the packages of gloves without identified rubber accelerators. The content of specific rubber accelerators, for example, dithiocarbamates, was labelled on 10 glove packages. Three of these glove packages did not contain the stated rubber accelerator. The five gloves without identified rubber accelerators were not labelled as accelerator free: Three of these gloves were labelled as nitrile and two were labelled as latex; one was labelled as a medical device (MD), one was labelled as a personal protective equipment (PPE), and three was labelled both MD and PPE; one glove was purchased from a healthcare clinic, one from a food shop, one from a hairdressing saloon, one from a hobby store, and one from a website used by mechanics.

A total of 6% (3/48) of the gloves were classified as MDs, 10% (5/48) as PPE, 68.8% (33/48) as both MDs and PPE, and 14.6% (7/48) were not classified according to regulations on medical device/personal protection equipment standards.

The glove that probably contained phthalates was marked as both nitrile glove and MD but visually looked like a vinyl glove.

3.2 | Contents of rubber accelerators in reusable rubber gloves

The sub-analysis identified rubber accelerators in one of the three reusable gloves, that is, ZDEC (1.43 mg/g glove, 0.143%; 0.064 mg/cm^2). This glove was a latex glove used for cleaning purchased from a website used by cleaners. The two reusable gloves without identified rubber accelerators were also latex gloves used for cleaning and they were purchased directly from a cleaning contractor and from a website used by cleaners.

4 | DISCUSSION

In this study, we analysed the contents of sensitising rubber accelerators in 48 disposable rubber gloves and three reusable rubber gloves.

In summary, most of the 48 disposable gloves contained dithiocarbamates, that is, primarily ZDBC (81% of the gloves) and ZDEC (71%). Additional dithiocarbamates identified were ZDBZ (6%), CEDMC (6%), and ZDMC (2%). A single glove contained DPG. No thiurams were identified in any of the gloves.

Several studies in the period from 2000 to 2010 have analysed the content of rubber accelerators in rubber gloves.[7,8,20,21] The studies identified ZDEC, ZDBC, zinc-dipentamethylendithiocarbamate, MBT, and to a lesser extent zinc-mercaptobenzothiazole, tetrabutylthiuram-disulfide, zinc-diisobutyl-dithiocarbamate, tetramethylthiuram disulfide, TETD, and DPG.[7,8,20,21]

The production of rubber gloves may for the majority be localised in Southeast Asia and thereafter imported to retail users in European countries; of the 48 disposable gloves, 35 were produced in Southeast Asia, and 13 did not state the country of origin. Therefore, and to the best of our knowledge, we do not anticipate that any significant differences in the content of rubber accelerators in rubber gloves exists between western countries. However, the extensive use of dithiocarbamates in the analysed rubber gloves in this analysis is in contrast to the previous studies, that also identified other rubber accelertors,[7,8,20,21] which may be ascribed changes in rubber accelerators during the vulcanization process. It would be interesting to analyse gloves from different countries and regions of the world to get evidence of the external validity of this Danish market survey.

Most rubber gloves contained ZDBC, often in quantities greater than ZDEC. However, surveillance data indicates a significantly lower occurrence of patients reacting to ZDBC in patch testing compared with both thiurams and ZDEC.[1,10] The potentially lower sensitization potential as described by the EC3-value of ZDBC compared with other rubber accelerators may explain this.[22] It would be of interest to further investigate the EC3-value of ZDBC as this rubber accelerator could prove as a first choice in glove production in terms of its probably low allergenicity.

The analysed accelerator-free glove contained rubber accelerators in the form of ZDBC. Rubber accelerators in rubber gloves otherwise labelled as accelerator free were also recently identified in a German study, that is, ZDBC, ZDEC, and an unclassified benzothiazole derivate.[17] The producer elaborated that the finding might be due to contamination in the glove production.[17] Accelerator-free gloves are often recommended by doctors for allergic patients. It therefore highly problematic if rubber gloves are falsely labelled as accelerator free and clinicians should be aware of this when advising patients.

Only 10 of the 48 gloves had labelled the content of specific rubber accelerators on the package. There is an urgent need for greater transparency regarding rubber accelerators in rubber protective gloves. This transparency will enhance preventive measures for example by enabling doctors and allergic patients to select appropriate

gloves. Changes in the composition of rubber accelerators occur in the vulcanization process, for example, the conversion of thiurams to dithiocarbamates.[23] Labels and datasheets should ideally provide comprehensive information regarding the content of rubber accelerators in the finished glove, rather than solely focusing on the ingredients added during manufacturing. Further, better quality control of accelerator free gloves is needed, and producers should be sure not to falsely claim that the rubber gloves are free of rubber accelerator.

One glove was even labelled as a nitrile glove and MD but did not contain any rubber accelerators but probably phthalates. The glove looked like a vinyl glove, and this emphasises the importance of overall better regulation and control of protective glove.

The newly discovered rubber chemical CEDMC was identified in three of the analysed gloves. A few patients have reacted to CEDMC in patch testing but the sensitising potential of CEDMC is not yet known.[12] CEDMC should therefore be implemented in rubber patch test series for further epidemiological analyses.

Our results are consistent with the hypothesis of the use of dithiocarbamates as rubber accelerator in favour of thiurams in the production of rubber gloves. As gloves are the most frequent exposure for patients with contact allergy to rubber accelerators, our results further raise the question why patients much more often react to thiurams than dithiocarbamates in patch testing.[1,10] Cross-reactivity between ZDEC and TETD has been observed in mice which together with their relation as redox-pair may explain this paradox.[1,10,24] ZDEC should be included in standard series for better diagnosis and surveillance. Further, it is important that patients using disposable rubber gloves are tested with several rubber accelerators using supplementary rubber series.

The strengths of the study are (i) the large amount of analysed gloves, (ii) the systematic sampling of gloves, and (iii) the precision of the method used for the glove analysis. Future studies should warrant analysing rubber gloves 'free of rubber accelerators' to investigate the extent of rubber accelerators in this type of glove and investigate the time trend of frequency of contact allergy to ZDEC and ZDBC. Further, the doses of rubber accelerators causing contact allergy should be investigated clinically to establish threshold values for the content of rubber accelerators in rubber gloves.

5 | CONCLUSION

Rubber gloves contain primarily ZDEC and ZDBC. Rubber gloves labelled as accelerator free may not necessarily be accelerator free. Full labelling of gloves is highly needed.

AUTHOR CONTRIBUTIONS

Christoffer Kursawe Larsen: Conceptualization; investigation; writing—original draft; funding acquisition; methodology; formal analysis; project administration. **Jakob F. B. Schwensen:** Funding acquisition; conceptualization; methodology; writing—review and editing; supervision. **Claus Zachariae:** Funding acquisition; conceptualization; writing—review and editing; methodology; supervision. **Cecilia Svedman:** Supervision; writing—review and editing; conceptualization; methodology; resources. **Jeanne D. Johansen:** Funding acquisition; conceptualization; methodology; supervision; writing—review and editing. **Ola Bergendorff:** Conceptualization; methodology; formal analysis; supervision; writing—review and editing; investigation; project administration; resources.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available upon reasonable request.

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SUPPORTING INFORMATION

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

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