Contact Dermatitis 2005: 53: 107–113
Printed in Singapore. All rights reserved


CONTACT DERMATITIS

# Survey of sulfur-containing rubber accelerator levels in latex and nitrile exam gloves

G. J. Depree, T. A. Bledsoe and P. D. Siegel
Health Effects Laboratory Division, National Institute for Occupational Safety and Health, Morgantown, WV 26505-2888, USA

2-Mercaptobenzothiazole and zinc dialkyldithiocarbamates are commonly used sulfur-containing rubber vulcanization accelerators known to cause allergic contact dermatitis. Exposure to these agents occurs through clothing such as undergarments and shoes, latex medical devices and latex and nitrile gloves. A simple, inexpensive screening method for total sulfur accelerator and a high performance liquid chromatographic speciation method were developed in the present study. These methods were applied to screen and quantify the sulfur accelerator content from 38 brands of 'off-the-shelf' latex and nitrile gloves obtained from commercial vendors. It was found that accelerator levels ranged from not detectable to 7.35 mg/g in the gloves analysed. Brands were found to contain single and multiple accelerator species within the glove. Powdered gloves had significantly higher accelerator levels than powder-free gloves from the same manufacturer; however, these chemical accelerators do not preferentially partition to the powder. The present analytical methodology is suitable for both manufacturing quality validation purposes, as well as for accelerator allergy research.

*Key words:* allergic contact dermatitis; exposure analysis; rubber chemicals. 

*Accepted for publication 19 May 2005*

Latex-induced dermatological problems are common among health care, food industry and construction workers. Irritant dermatitis and allergic contact dermatitis (ACD) have been associated with chemical accelerators present in latex and nitrile gloves, clothing (eg. underwear and shoes) and other medical/personal care devices (condoms, catheter tubes, bandages, etc.). In a study of hospital employees who used gloves, 24.4% reported glove-induced symptoms (1). Over 10% of these subjects were patch test positive to rubber-related chemicals. If this is reflective of the entire health care industry of approximately 8 million workers, approximately 200 000 health care workers are sensitized to chemical accelerators from latex. Thiuram (23.3%) and 2-mercaptobenzothiazole (MBT, 20.9%) latex accelerator-induced ACD were reported to be prevalent in student athletes with eczematous skin lesions (2). Conde-Salazar et al. (3) reported that 25.9% of Spanish construction workers/patients with cutaneous lesions or a clinical history consistent with occupational dermatitis were patch test positive to latex chemicals and 23.7% specifically to thiurams.

Development of ACD occurs in two phases. The first phase, termed induction, involves antigen presentation and development of antigen-specific T-cells. It is thought that this immunological sensitization, while asymptomatic, persists for life. The second phase, termed elicitation, occurs with re-exposure to the antigen and development of ACD. Allergic contact dermatitis manifests within 24–48 h of exposure. It is treatable and usually transient. The level of exposure required to elicit an ACD response is less than that required for induction, thus reduction of exposure to levels that protect against elicitation of ACD will also protect a worker from becoming sensitized.

The accelerator content of commercially available gloves is not routinely measured and the level that can elicit ACD under normal usage conditions is not known. Emmett et al. (4) reported in a titration patch test study of rubber sensitive subjects that the highest concentration of MBT that did not elicit any reaction in ACD subjects was 1.45 $\mu g/cm^2$. A similar study of threshold determination for zinc dialkyldithiocarbamate (ZDTC) was not found in the literature.

Several issues concerning the applicability of patch testing for determination of safe accelerator levels in gloves include difference in allergic sensitivity between the back versus hands, the 48 h. occluded exposure time, effect of exposure matrix and interpretation of a positive reaction at low doses. It is also generally believed that the dose required for elicitation of ACD response is inversely related to the degree of sensitization.

Knudsen et al. (5) developed a complex high performance thin layer chromatography method (HPTLC) analysis of accelerator content in latex gloves. This method involves acetone extraction, evaporation, reconstitution in chloroform, sample spotting and application of hexane/toluene ethyl acetate eluent to the HPTLC plate and subsequent development for analyte detection by sequential spraying of the plate with dithizon and then 2,6-dichloroquinone-4-chlorimide. Additional plates were run for confirmation of thiurams using development with copper sulfate. Gloves were selected for analysis based on manufacturers' indicated accelerator content. Multiple accelerator contents were reported from their analyses, with the major (>1 μmol/g glove) accelerants being zinc dipentamethylene dithiocarbamate, zinc diethyldithiocarbamate (ZDEC), zinc dibutyldithiocarbamate (ZDBC) and zinc mercaptobenzothiazole (ZMBT). Quantification was based on gas chromatographic mass-spectrometric detection following derivatization with trifluoroacetic anhydride. Total accelerant levels from <1–15.9 μmol/g glove were found in the gloves analysed.

The present study describes a modification of a simple quantitative spectrophotometric screening method for total sulfur accelerant and speciation of the native individual accelerants by high performance liquid chromatography (HPLC) that was described previously (6). Accelerant content of commercially available 'off-the-shelf' medical exam latex and nitrile gloves and several latex gloves from a local hardware store were assessed.

## Methods

### *Materials and reagents*

Zinc diethyldithiocarbamate, zinc dimethyldithiocarbamate (ZDMC), sodium diethyldithiocarbamate (NaDEC), cobalt chloride hexahydrate and HPLC grade acetonitrile (ACN) were obtained from Aldrich (Milwaukee, WI). Zinc dibutyldithiocarbamate, tetraethylthiuram disulfide (TETD) and 2-Mercaptobenzothiazole were acquired from Chem Service (West Chester, PA). Distilled water used throughout was purified by a Millipore MilliQ system (Molshiem, France). All solvents used for HPLC were filtered (0.22 μm membrane) and degassed by sonication under vacuum for 10 min at ambient temperature. Cobalt chloride was prepared as a 420-mmol/l solution in water. A 500-μg/ml ZDMC solution was prepared in ACN.

Stock solutions (1000 μg/ml) of TETD and MBT were prepared in ACN and ZDBC in 500 μg/ml ZDMC-ACN solution. Stock solutions of ZDEC (1000 μg/ml) were prepared in each ACN and ZDMC-ACN. Combined 1:1 ZDEC/ZDBC, ZDMC/TETD and ZDEC working standard solutions were prepared by the appropriate dilutions in ACN and/or 500 μg/ml ZDMC-ACN to yield final concentrations of 31.3, 62.5, 125, 250 and 500 μg/ml. 2-Mercaptobenzothiazole standard solutions were prepared in an analogous way using ACN to give final concentrations of 1.95, 3.91, 7.81, 15.63, 31.25, 62.5 and 125 μg/ml (additional standards, 0.24, 0.49 and 0.98 μg/ml were prepared for low level MBT determinations using a 100 μl HPLC injection). Visible chromatographic peaks below the lowest standards were not quantified by extrapolation but are noted as not quantifiable (NQ). 38 brands of gloves from 17 different manufacturers were purchased from commercial vendors.

### *Instrumentation*

Absorbance measurements of cobalt(III) dialkyldithiocarbamate (DTC) complexes were carried out on a Beckman DU 800 Spectrophotometer at 320 and 370 nm.

The HPLC methodology for determination of ZDTCs from latex has been previously reported (6). HPLC analysis was performed on a Shimadzu system consisting of two LC-600 pumps, SIL-10AD auto-injector, LPI–6B interface and SPD-M10A Diode Array Detector. An injection volume of 10 μl was used and separations performed on a 5-μm particle size, 250 × 4.6-mm Supelco Discovery $C_{18}$ column (Bellefonte, PA) at a flow rate of 1 ml/min. An absorbance at 260 nm was used for the UV detection of ZDTC complexes and 320 nm for MBT. The elution gradient profile started at 85% ACN/water and was increased at a rate of 5%/min for 3 min before being held at 100% ACN for 11 min.

### *Extraction of whole gloves*

Each glove was weighed before being cut into approximately 1-cm strips then extracted using ACN (10 ml/gram glove) for 17 h on a shaker (250 r.p.m) at room temperature. Glove powder was removed from extracts by centrifugation at 1000 × *g* for 10 min. Extraction efficiency was determined using 5 different brands of latex and nitrile gloves, each. The percent extraction efficiency is 99.6 ± 4.6% and 94.7 ± 13.1 for latex and nitrile, respectively. Extraction efficiency correction factors were not applied to accelerator content measurements presented due to the excellent observed partitioning into the ACN.

### *Determination of approximate total sulfur-containing accelerator content*

Aliquots (600 μl) of the extracts and ZDEC standards were treated with $CoCl_2$ (6 μl 420 mmol/l), mixed then incubated in a water bath for 2 h at 50°C. Samples of the derivatized solutions (100 μl) were then taken and diluted with ACN (1:20) prior to measuring their absorbance on a UV spectrophotometer.

### *Combined extraction and determination of total accelerator content from glove finger tips (modified screening procedure)*

2½ cm of the glove finger tip of the middle finger was trimmed from the glove, weighed, cut into small pieces and transferred into a 3.6-ml polypropylene tube. Acetonitrile (2.5 ml) containing 4.2 mmol/l $CoCl_2$ was added to each tube and the extraction/reaction was allowed to proceed for 2 h. An aliquot was removed, placed into a microcentrifuge tube and centrifuged for 5 min to remove powder. Samples of the derivatized solutions (100 μl) were then taken and diluted with ACN (1:20) prior to measuring their absorbance on a UV spectrophotometer as above.

### *HPLC determination of sulfur-containing accelerator levels*

Filtered glove extract samples were subjected to a preliminary HPLC run (conditioned by two 50 μl injections of a saturated ZDMC solution in ACN to complex and prevent interference from nickel in hardware components) to screen for the presence of ZDMC and other target accelerator species. Zinc dimethyldithiocarbamate was not detected in any of the sample extracts.

To determine ZDEC and ZDBC levels, 600 μl aliquots of the glove extracts were taken and added to tubes containing 300 μg ZDMC(600 μl aliquots of 500 μg/ml ZDMC taken down to dryness under a constant stream of nitrogen at 30°C). The tubes were then shaken until ZDMC redissolved. Prior to analysis, samples were then filtered and the HPLC conditioned by three 50-μl injections of a saturated ZDMC solution in ACN. Levels of MBT were determined from fresh aliquots of glove extract in the absence of any added ZDMC. All determinations were made in duplicate from 2 separate gloves from the same lot for each brand tested.

### *Accelerator distribution study*

Samples (1 g) were taken from 3 different areas of several brands of glove (wrist, palm and fingers) and extracted in ACN (10 ml) as described above. Extracts were then treated with cobalt chloride to determine total sulfur-containing accelerator content as previously described (with the exception that results were quantified using a 1:1 ZDMC/TETD standard curve).

### *Time course study for extraction of accelerators from latex and nitrile gloves*

Approximately 20 g of glove material from the fingers was obtained from each brand of glove investigated and cut into approximately 3 mm strips. Duplicate 2 g samples were than taken and extracted in 20 ml ACN at room temperature for 1, 2, 4, 8 and 23 h. At each time point 600 μl aliquots of extract was taken and treated with cobalt chloride and accelerator content determined as mentioned above. The combined ACN-Co(III) solvent finger tip-extraction time course was run but with time points between 5 and 240 min. For the combined ACN-Co(III) extraction latex glove finger tips were cut into small pieces, all pieces pooled and mixed. Two, 250 mg, finger tip samples were weighed out from the pooled lot for analyses at each time point.

## Results

### *Analytical methodology*

The present methodology utilizes both an initial quantitative screening method for the presence of sulfur accelerators followed by HPLC speciation and quantification. Extraction of the sulfur accelerators proceeded rapidly in ACN with >85% partitioning to the solvent by 1 h at room temperature and >95% within 4 h. Similar results were obtained when ACN-Co(III) was used as the extraction solvent (Fig. 1). An exhaustive time course study on gloves of different thicknesses and textures was not performed and some inter-brand variation may be expected.

Figure 2 is the absorbance spectra of ZDEC, TETD and MBT following reaction to Co(III). Cobalt(III)-DTC complexes formed rapidly in the presence of ZDTCs, but Co(III) complexed very slowly to thiurams. Complexation of thiurams by Co(III) was accomplished by incubation at 50°C for 2 h. The spectra for Co(III)-ZDEC and Co(III)-ZDBC were identical (data not shown).

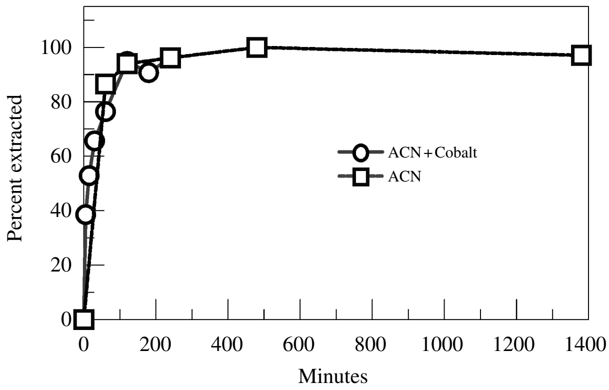


*Fig. 1.* Accelerator latex extraction time course using acetonitrile (ACN) or ACN-Cobalt. Latex glove material was extracted for up to 23 h. Accelerator content was assessed by measuring the absorbance of the Co(III)DTC at 320 nm against a zinc diethyldithiocarbamate standard plot ($n = 2$/time point).

Both ZDTC- and thiuram-Co(III) turn the solution to concentration-dependent shades of green. Thiurams can qualitatively be distinguished from ZDTC by their slow complexation (slow colour formation and increasing absorbance at 320 nm over time). Mercaptobenzothiazole does not complex to Co(III), however, it absorbs highly at 320 nm. It can be distinguished from both ZDTCs and thiurams by its lack of absorbance at 370 nm (Fig. 2) and lack of visible green colour. ZDEC, ZDBC, TETD, TMTD and NaDEC standard curves had relatively similar slopes [0.0023 ± 0.0003 absorbance units/(μg/ml)]. Mixtures produced spectrophotometric absorbances in between that of the individual components (data not shown).

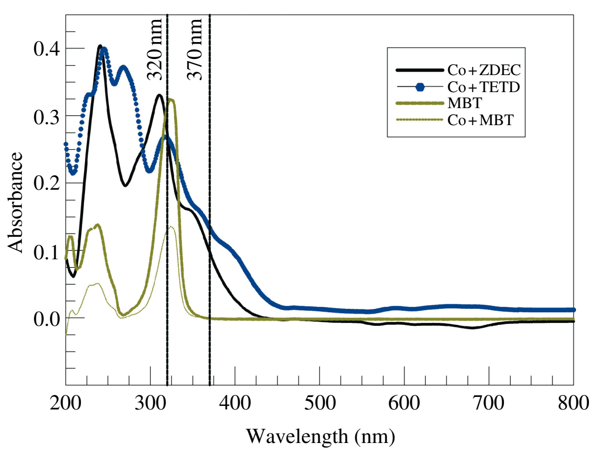


*Fig. 2.* Spectral analyses for Co(III) + tetraethylthiuram disulfide (TETD), Co(III) + zinc diethyldithiocarbamate (ZDEC) and 2-mercaptobenzothiazole (MBT). Thiurams and zinc dialkyldithiocarbamates (ZDTCs) cobalt complexes absorb at 320 nm. Mercaptobenzothiazole does not react with cobalt, but has a strong native absorbance at 320 nm. Thiurams and ZDTCs can be distinguished from MBT by MBT's lack of absorbance at 370 nm.

2-Mercaptobenzothiazole absorbance at 320 nm was 3.22–4.58 times higher than the Co(III) complexes.

Distribution of accelerator within 4 different gloves (2 latex and 2 nitrile) was examined. A gradient in accelerator content (per gram of material) was noted in only one of the four gloves (Fig. 3). Although the average accelerator content was similar (2.29 versus 2.26 mg accelerator/g latex) for the duplicates of the gloves displaying a concentration gradient from the wrist to fingers, considerable variation was noted in the relative accelerator distribution within these two gloves from the same lot.

A modified screening method in which the extraction and derivatization steps were combined (2 h, room temperature) was evaluated. A finger tip (2.5 cm, middle digit) was used to reduce solvent and $CoCl_2$ requirements. Figure 4 is a comparison of screening gloves by assaying only the middle digit finger tip using the modified screening procedure versus the whole glove extraction method. A strong correlation of $r^2 = 0.89$ was found between whole glove versus finger-tip analyses. Partitioning of $CoCl_2$ was noted into the matrix of several nitrile gloves, presumably due to the particular dye content. This altered the visual appearance of the extract (shade of green) but did not alter the spectrophotometric measurement of the Co(III)-DTC complex.

## *Glove survey*

Table 1 lists the results of the survey of accelerator content from 'off-the-shelf' non-powdered latex, powdered latex and nitrile gloves. Three

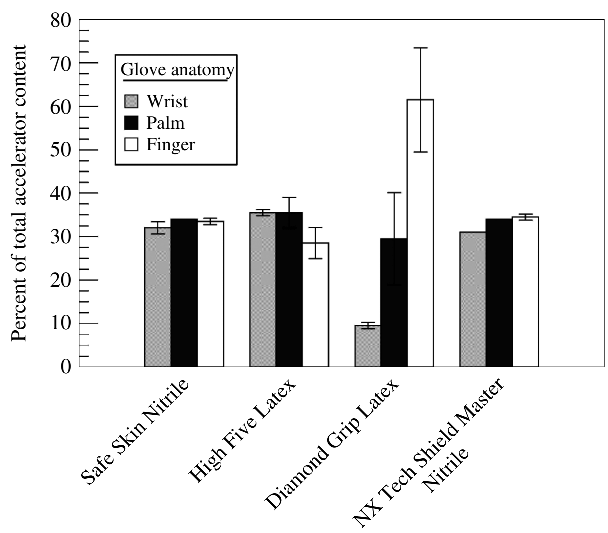


*Fig. 3.* Accelerator distribution within nitrile and latex gloves. Material from the wrist, palm and fingers of 4 brands of gloves were assessed in duplicate for accelerator content. Only the Diamond Grip Latex gloves displayed an accelerator content gradient across the glove.

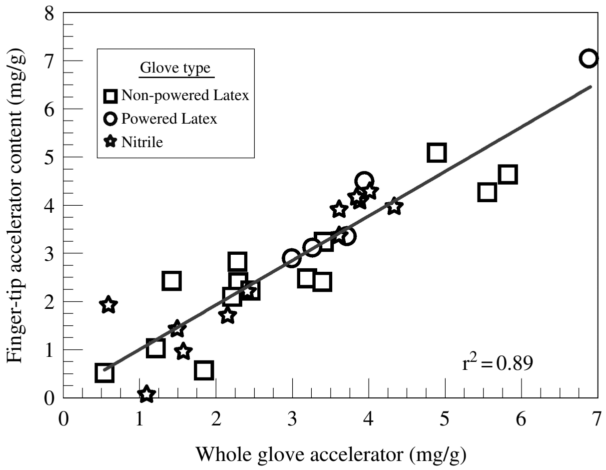


*Fig. 4*. Comparison of screening total sulfur accelerator content from the middle digit finger tip versus whole latex and nitrile gloves.

non-exam gloves, purchased at a local hardware store are also included (Stanley HandHelpers, Bag O'Gloves and latex gloves). Total accelerator content extrapolated from a ZDEC/absorbance standard plot and specific accelerator type and amount from HPLC analyses are provided. Each analysis was run in duplicate (2 gloves from the same box). Mercaptobenzothiazole, ZDEC and ZDBC, alone or in combination, were found in measurable levels. Levels ranged from non-detectable to 1.31, 5.17 and 4.59 mg/g latex for MBT, ZDEC and ZDBC, respectively. The relative amount of accelerator content between powdered and powder-free gloves from the same manufacturer was examined (Table 2). The amount of accelerator found in powder-free gloves was less than in powdered gloves from every manufacturer ($P = 0.0456$). Powder (>5 mg each) was vacuumed off Safe Skin LPE and Micro One gloves (3 each) onto preweighed 37 mm, 0.45 μm pore Telflon filters. Powder amount was determined by the difference between pre- and post-filter weight. Powder from Safe Skin LPE did not have measurable levels of accelerator (<14.6 μg accelerator/mg powder). Micro One powder contained 15 μg accelerator/mg powder.

## Discussion

Residual vulcanization accelerators are known to produce latex glove-associated ACD; however, threshold levels associated with this hypersensitivity response are not known. A major obstacle in determining acceptable levels of accelerators within gloves has been the lack of a widely acceptable analytical chemical measurement method. Simple, inexpensive screening methods have been developed in this study for total sulfur accelerator content in latex and nitrile gloves. Acetone has been commonly used for extraction of accelerators from the latex matrix, but accelerator stability is very limited in this solvent (5, 7). Acetonitrile was used as the extraction solvent due to its compatibility with analytes and analytical methods. Approximately 95% of the accelerator(s) are extracted within the first 2 h. Interestingly, it takes an extended time to recover the last few percent of residual accelerator. It is not known whether this reflects surface accelerator versus that trapped within the latex matrix.

The present methodology represents an expansion over that which we previously reported for assessment of ZDTCs from latex condoms (6). Both cobalt and copper have been used as reagents in qualitative spot test for dithiocarbamates (8). Copper salts may provide an alternative reagent to $CoCl_2$ for spectrophotometric quantitative screening of total accelerator content; however, solvent compatibility, adduct stability and spectral characteristics have not been evaluated for thiurams and ZDTCs. Two variations of the total sulfur accelerator screening spectrophotometric method were evaluated. Extraction of the latex or nitrile material by ACN, followed by derivitization with $CoCl_2$ allowed for assessment of the average accelerator content within the glove and ability to speciate the accelerator from the same extract. Extraction and derivitization can be combined; however, several limitations apply to this modification. In this combined procedure only finger tips were analysed to limit the amount of $CoCl_2$ required. Speciation by HPLC would require a separate ACN extract. Measurement of thiurams would require an extended reaction time or the application of heat to the latex and nitrile materials to facilitate reduction of the disulfide bond. It was also noted that several of the nitrile gloves adsorbed the cobalt. This did not interfere with accelerator extraction or the formation of Co(III)DTC complexes but did alter the colour appearance (shade of green).

Interestingly, thiurams, the most commonly reported cause of latex accelerator ACD, were not detected in any of the recently manufactured gloves. Mercaptobenzothiazole, ZDEC and ZDBC were found alone or in multiple combinations in nitrile, medical latex exam and non-medical latex gloves. Latex accelerators were measured in the part per thousand (by weight) range from many of the gloves. Food and Drug Administration (FDA) regulations require that accelerators not exceed 1.5% by weight of rubber medical devices (9). The glove with the highest accelerator content had approximately ½ the maximally allowed accelerator content as free, extractable accelerator. It must be noted that lot to lot variation in accelerator levels were not assessed, and the levels found in each particular brand may vary

*Table 1.* Accelerator content of powdered latex, powder-free latex and nitrile gloves

| Sample | Manufacturer | Lot number | Preliminary assay Total DTC (ZDEC equivalent) (mg/g glove) | HPLC Analysis (mg/g glove) | | | |
|---|---|---|---|---|---|---|---|
| | | | | ZDEC | ZDBC | MBT | Total |
| Powder-Free Latex Gloves | | | | | | | |
| Conform XT | Ansell | 0308004659 | 2.29 | 1.58 | 0.58 | ND | 2.16 |
| InstaGard | Allegiance | 4L02J084 | 3.41 | 2.63 | 0.81 | ND | 3.43 |
| Positive Touch | Allegiance | PE03E617 | 2.21 | ND | 2.63 | ND | 2.63 |
| Fisherbrand | Fisher Scientific | 03123205 | 1.21 | 0.83 | 0.36 | 0.01 | 1.20 |
| High Five Egrip | High Five Products | OC 22921 | 4.89 | 2.84 | 1.95 | ND | 4.78 |
| High Five Aloe | High Five Products | DYSH 22077 | ND | ND | ND | ND | ND |
| Safeskin PFE | Kimberly Clark | SC3243-1 | 1.42 | 0.91 | 0.43 | ND | 1.33 |
| Safeskin PFE-XTRA | Kimberly Clark | SC3297-2 | 0.54 | 0.38 | ND | ND | 0.38 |
| KleenGuard | Kimberly Clark | SO3202-A01 | ND | NQ | ND | ND | NQ |
| Aloetouch | Medline | AKA301826084 | 3.19 | 3.05 | ND | 0.03 | 3.09 |
| Diamond Grip | Microflex | 301297018 | 2.28 | 1.43 | 0.61 | ND | 2.04 |
| Evolution One | Microflex | 03000157HL 10831107 | 5.82 | 4.99 | 0.81 | 0.17 | 5.96 |
| Synetron | Microflex | 01000062HL 10930917 | 5.55 | 4.53 | 0.80 | 0.12 | 5.45 |
| Health Aid | Latexx Manufacturing SDN.BHD | 10738088 | ND | NQ | ND | ND | ND |
| Qualatex Miracle Grip | QRP | 19053203 | 2.45 | 1.66 | 0.43 | ND | NQ |
| Life Guard | Southern Pacific Coast Corp | C3BG | ND | ND | ND | ND | 2.09 |
| Stanley HandHelpers | Magla Products | Not given | 3.39 | 2.48 | 0.67 | ND | 3.15 |
| Bag O'Gloves | Hand Care Inc. | Not given | 1.84 | 0.81 | 0.75 | 0.03 | 1.58 |
| Latex Gloves | Great American Manufacturing Inc. | Not given | 2.07 | 0.99 | 0.97 | ND | 1.95 |
| Powered Latex Gloves | | | | | | | |
| Conform | Ansell | 0311000379 | 3.71 | ND | 4.59 | ND | 4.59 |
| Flexam B | Allegiance | 4Y02P006 | 3.26 | 1.62 | 1.24 | ND | 2.85 |
| Fisherbrand | Fisher Scientific | 02123015 | 2.99 | 2.13 | 0.81 | ND | 2.94 |
| Safeskin LPE | Kimberly Clark | SH3290-313 | 3.94 | 1.82 | 2.43 | ND | 4.25 |
| Micro One | Microflex | 031223663 | 6.88 | 5.17 | 2.18 | ND | 7.35 |
| Power-Free Nitrile Gloves | | | | | | | |
| TNT Blue | Ansell | 04011294AU | 2.15 | 1.05 | 1.35 | ND | 2.40 |
| Insta Touch Dental | Allegiance | 4B02L502 | 1.49 | 1.51 | ND | ND | 1.49 |
| Esteem Stretchy Nitrile | Allegiance | 4W03L001 | 3.88 | 4.03 | ND | 0.03 | 4.05 |
| N-DEX | Best Manufacturing Company | 701181 | 1.09* | ND | ND | 1.31 | 1.31 |
| N-DEX Free | Best Manufacturing Company | 702174AL | ND | ND | ND | 0.01 | 0.01 |
| Genskin | Daigger & Company Inc. | X20830 | 0.59* | ND | ND | 0.75 | 0.75 |
| Fisherbrand | Fisher Scientific | SM3069-1 | 3.84 | 3.93 | ND | ND | 3.93 |
| High Five Aloe | High Five Products | DYSH 1107 | 1.57 | 1.27 | ND | ND | 1.27 |
| Safeskin Nitrile | Kimberly Clark | 1138S-1 | 3.61 | 3.70 | ND | ND | 3.70 |
| Safeskin Purple Nitrile | Kimberly Clark | SM3307-3 | 4.33 | 4.36 | ND | ND | 4.36 |
| KleenGuard | Kimberly Clark | SM3153-2 | 4.01 | 4.24 | ND | 0.02 | 4.26 |
| Aloetouch | Medline | A000795922 | ND | ND | ND | ND | ND |
| FreeForm SE | Microflex | 01000055HL11230911 | 3.61 | ND | 2.87 | 0.97 | 3.84 |
| Life Guard | Southern Pacific Coast Corp. | M3EDA | 2.41 | ND | 3.09 | ND | 3.09 |

ND = not detected; NQ = detected, but too little to quantify; *MBT Equivalent

*Table 2.* Comparison of latex accelerator content in powdered and powder-free gloves from the same manufacturer

| Manufacturer | Powdered (mg/g) | Powder-Free (mg/g) | Difference* (%) |
|---|---|---|---|
| Ansell | 3.71 | 2.29 | 16.6 |
| Allegiance | 3.26 | 2.81 | 13.8 |
| Fisher | 2.99 | 1.21 | 59.5 |
| Kimberly Clark | 3.94 | 0.065 | 83.5 |
| Microflex | 6.88 | 4.55 | 33.9 |

*$P = 0.0456$ paired $T$-test

considerably between different lots. In addition, the measured values represent extractable accelerator content but can not be interpreted as an exposure dose. Exposure dose may vary greatly with pattern of glove use and use conditions. The survey of 'off-the-shelf' gloves does demonstrate the wide range of residual accelerator levels in gloves and that it is possible to find both powder-free latex and nitrile gloves that do not contain detectable residual accelerator.

Accelerator content was significantly lower in powder-free gloves versus powdered gloves from the same manufacturer. This is most likely attributable to differences in manufacturing processes between the two types of gloves. Manufacturing processes to eliminate surface tack in powder-free gloves may vary considerably between manufacturers. Halogenation of the glove surface is commonly used for powder-free gloves. Gloves are processed in either chlorinated or brominated water followed by an ammonia water or aqueous sodium thiosulfate neutralization and water rinses (8). Such processing may conceivably leach out and/or oxidize accelerators. The powder recovered from the highest accelerator-containing powdered glove did have measurable accelerator in the powder fraction. The fraction of the total accelerator content found in the powder fraction of that glove, assuming 100 mg powder/glove, was a calculated 2.3%. This suggests that these hydrophobic vulcanization accelerators do not selectively partition to the powder, as do the water-soluble latex protein allergens (10).

In conclusion, simple and inexpensive latex accelerator screening and speciation methodologies presented are applicable for both industrial quality control and health research purposes. A survey of 'off-the-shelf' medical exam and hardware store latex and nitrile gloves demonstrated a wide range of accelerator levels ranging up to several parts per thousand by weight.

## Acknowledgements

The authors thank Dr Frank Perrella for his counsel with respect to rubber accelerator assay essential requirements.

This study was funded, in part, through an inter-agency agreement between NIOSH and NIEHS.

The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

## References

1. Nettis E, Assennato G, Ferrannini A, Tursi A. Type I allergy to natural rubber latex and type IV allergy to rubber chemicals in health care. *Clin Exp Allergy* 2002: 32: 441–447.
2. Ventura M T, Dagnello M, Matino M G, Di Corato R, Giuliano G, Tursi A. Contact dermatitis in students practicing sports: incidence of rubber sensitization. *Br J Sports Med* 2001: 35: 100–102.
3. Conde-Salazar L, Gatica M E, Barco L, Iglesias C, Cuevas M, Valks R. Latex allergy among construction workers. *Contact Dermatitis* 2002: 47: 154–156.
4. Emmett E A, Risby T H, Taylor J, Chen C L, Jiang I, Feinman S E. Skin elicitation threshold of ethylbutyl thiourea and mercaptobenzothiazole with relative leaching sensitizing products. *Contact Dermatitis* 1994: 30: 85–90.
5. Knudsen B B, Hametner C, Seycek O, Hesse A, Koch H-U, Peters K-P. Allergologically relevant rubber accelerators in single-use medical gloves. *Contact Dermatitis* 2000: 43: 9–15.
6. Depree G J, Bledsoe T A, Siegel P D. Determination of zinc dialkyldithiocarbamates in latex condoms. *J Chromatogr Sci* 2004: 42: 80–84.
7. Hansson C, Bergendorff O, Ezzelarab M, Sterner O. Extraction of mercaptobenzothiazole compounds from rubber products. *Contact Dermatitis* 1997: 36: 195–200.
8. Mausser R F. *The Vanderbilt Latex Handbook*, 3rd edn. Norwalk, CT: RT Vanderbilt Company Inc, 1987.
9. Tinkler J, Gott D, Bootman J. Risk assessment of dithiocarbamate accelerator residues in latex-based medical devices: Genotoxicity considerations. *Food Chem Toxicol* 1998: 36: 849–866.
10. Beezhold D, Horton K, Hickey V, Daddona J, Kostyal D. Glove powder carrying capacity for latex protein: Influence of glove powders in the ASTM ELISA test. *J Long Term Effects Med Implants* 2003: 13: 21–31.

Address:
*Paul D. Siegel, PhD*
*Allergy and Clinical Immunology Branch, M/S L4020*
*HELD/NIOSH*
*1095 Willowdale Road*
*Morgantown*
*WV 26505-2888*
*USA*
*Tel: +1 304 285 5855*
*Fax: +1 304 285 6126*
*e-mail: psiegel@cdc.gov*