PAPER

A laboratory investigation of the effectiveness of various skin and surface decontaminants for aliphatic polyisocyanates†‡

Dhimiter Bello,[ad] Susan R. Woskie,[a] Robert P. Streicher,[b] Meredith H. Stowe,[c] Judy Sparer,[c] Carrie A. Redlich,[c] Mark R. Cullen[c] and Youcheng Liu[c]

[a] *University of Massachusetts Lowell, Work Environment Department, KI 200, One University Ave., Lowell, MA 01854, USA*
[b] *National Institute for Occupational Safety and Health, Division of Applied Research and Technology, 4676 Columbia Parkway, Cincinnati, OH 45226, USA*
[c] *Yale University School of Medicine, Occupational and Environmental Medicine Program, 135 College Street, New Haven, CT 06510, USA*
[d] *Harvard School of Public Health, Exposure, Epidemiology & Risk Program, Landmark Center, West/404F, 401 Park Drive, Boston, MA 02215, USA. E-mail: dbello@hsph.harvard.edu; Fax: 617 384 8859; Tel: 617 384 8809*

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Isocyanates may cause contact dermatitis and respiratory sensitization leading to asthma. Dermal exposure to aliphatic isocyanates in auto body shops is very common. However, little is known about the effectiveness of available commercial products used for decontaminating aliphatic polyisocyanates. This experimental study evaluated the decontamination effectiveness of aliphatic polyisocyanates for several skin and surface decontaminants available for use in the auto body industry. The efficiency of two major decontamination mechanisms, namely (i) consumption of free isocyanate groups *via* chemical reactions with active hydrogen components of the decontaminant and (ii) physical removal processes such as dissolution were studied separately for each decontaminant. Considerable differences were observed among surface decontaminants in their rate of isocyanate consumption, of which those containing free amine groups performed the best. Overall, Pine-Sol® MEA containing monoethanolamine was the most efficient surface decontaminant, operating primarily *via* chemical reaction with the isocyanate group. Polypropylene glycol (PPG) had the highest physical removal efficiency and the lowest reaction rate with isocyanates. All tested skin decontaminants performed similarly, accomplishing decontamination primarily *via* physical processes and removing 70–80% of isocyanates in one wiping. Limitations of these skin decontaminants are discussed and alternatives presented. *In vitro* testing using animal skins and *in vivo* testing with field workers are being conducted to further assess the efficiency and identify related determinants.

Introduction

Isocyanates are a group of highly reactive, low molecular weight chemicals that are extensively used in various industries and commercial products. Exposure to isocyanates can cause contact dermatitis, skin and respiratory tract irritation, respiratory sensitization and asthma, and less commonly hypersensitivity pneumonitis.[1] Respiratory sensitization and asthma remain the primary isocyanate health concern. The role of skin as an independent exposure route and risk factor for respiratory sensitization in humans is inadequately investigated. However, there is evidence, particularly from animal studies, suggesting dermal exposure could be an important route in developing respiratory sensitization and asthma.[2–12]

The need for decontamination

Workers in the auto body repair and refinishing industry use isocyanate-containing products. Both inhalation and skin contamination are important exposure routes. Isocyanates used in body shops are aliphatic polyisocyanates, based almost exclusively on aliphatic hexamethylene diisocyanate (HDI) and/or isophorone diisocyanate (IPDI). The typical monomer content of commercial formulations is $<1\%$.[13,14] Because aliphatic polyisocyanates have very low vapor pressures, aerosolization during spray painting is the primary cause of inhalation exposure.

Dermal exposure on the other hand could occur as a result of mishandling of bulk products, during formulations preparation, as a result of contact with contaminated equipment, surfaces, personal protective equipment, and possibly direct deposition of aerosol on unprotected skin areas (such as forehead, forearms, and unprotected hands) during spraying. Skin and surface contamination in auto body shops is common.[13,15,16] It is, therefore, prudent to have effective products available for decontamination and reduction of exposure.

Selection of an effective product for decontamination of aliphatic polyisocyanates for use in auto body shops is neither easy nor straightforward, because objective testing data are scarce, especially for aliphatic isocyanates. Currently used decontamination products in auto body shops are based on recommendations from manufacturers' representatives (jobbers) and anecdotal reports. The efficacy of these products in removing HDI- and IPDI-based polyisocyanates is typically not known.

Physico–chemical properties of polyisocyanates

Physical and chemical properties of isocyanates affect their performance in decontamination efficacy. Isocyanates dissolve

† Disclaimer: Mention of company names and/or products does not constitute endorsement by the Centers for Disease Control and Prevention (CDC).
‡ Electronic supplementary information (ESI) available: Fig. S1: Surface decontamination efficiency for the HDI polyisocyanate isocyanurate (N3300) by various painters' hand cleaners. See http://www.rsc.org/suppdata/em/b5/b503807c/

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very well in a number of polar aprotic and non-polar solvents, such as acetone, butyl acetate, methylene chloride, and toluene. Isocyanates generally do not dissolve in water, but react chemically with it to form more water-soluble ureas. This reaction rate is strongly influenced by the isocyanate structure and can vary over orders of magnitude depending on other reaction conditions, such as temperature, isocyanate to water ratio, homogeneity of the reaction medium, *etc*.

The NCO functional group of isocyanates reacts (sometimes vigorously) with compounds containing active hydrogen H–X–R′ (such as amines (R′–NH_2), alcohols (R′–OH), water (H_2O), carboxylic acids, R′–COOH, *etc*.) in a nucleophilic addition reaction as depicted in eqn. (1): [17–19]

$$R–N{=}C{=}O + H–X–R' \rightarrow R–NH–CO–X–R' \qquad (1)$$

A general order of reactivity of some active hydrogen compounds with isocyanates without catalyst is as follows: aliphatic amines (primary R–NH_2 and secondary R_2NH) > aromatic amines (primary Ar–NH_2 and secondary Ar_2NH) ≫ primary alcohols (R–OH) > secondary alcohols (R–OH) > phenols (Ar–OH, Ar is an aromatic ring). Aliphatic amines react with isocyanates much faster than aromatic amines (Ar–NH_2), and reactivity is proportional to their basicity. Primary amines with the –NH_2 functionality may react orders of magnitude faster than water and primary alcohols. About an order of magnitude difference in reactivity exists between primary and secondary alcohols.[18]

Decontamination mechanisms

Decontamination of a reactive compound, such as an isocyanate, could be achieved *via* two distinct mechanisms: (i) chemical destruction or (ii) physical processes.[20] Chemical destruction of the contaminant can be achieved through a chemical reaction with the decontaminant, which destroys the N=C=O groups. The reaction product, presumably of much lower toxicity, is left on the contaminated medium (skin or surface). The second mechanism consists of physical processes such as dissolution and absorption or mechanical forces such as agitation and abrasion. The contaminant is removed from the contaminated medium without undergoing chemical changes. We will refer to the aggregate of physical and mechanical processes as physical processes, to contrast them with the chemical destruction mechanism. If removal of the contaminant from a contaminated medium is the final goal, then chemical destruction alone will likely be insufficient and should be followed by removal *via* physical processes. Such physical processes are present to some extent in all decontamination procedures. For example, emergency spill-cleanup procedures in industrial settings use a liquid decontaminant, which chemically consumes the isocyanate groups, in combination with a solid decontaminant, such as vermiculite and Kieselguhr (clay), which serves as an absorbent and carrier material.[21,22]

To date no study has been published that has investigated the individual contribution of each decontamination mechanism for surface and skin decontaminants. Moreover, no published study has investigated the decontamination efficiency of painters' hand cleaners for aliphatic isocyanates. Published studies on the decontamination efficiency for aromatic isocyanates have employed an experimental design that relied on a single mechanism; either monitoring consumption of isocyanates in a chemical reaction[22,23] or physical removal efficiency.[24]

The main objectives of this study were: to evaluate (i) the individual contribution of each decontamination mechanism and (ii) the decontamination efficiency (total contribution of both mechanisms) for some common skin and surface decontaminants; and (iii) to identify the most efficient decontaminants for skin and surface decontamination of aliphatic polyisocyanates in auto body shops.

This is tier 1 of a three-tier study, the other two being *in vitro* testing with a hairless guinea pig skin model, and evaluation of products in auto body shops, including auto body workers' subjective evaluation of product properties.

Materials and methods

Decontamination products

A list of surface and skin decontamination products was compiled from the published literature,[22–24] products in use in auto body shops in the New Haven, Connecticut area, and household cleaners available from a local supermarket.

The surface decontaminants included: water [W]; 10% w/v liquid soap (Johnson Wax Professional, Sturtevant, WI) in water [SW-10%]; 1% and 50% monoethanolamine (MEA, Aldrich Chemical Co., Milwaukee, WI) in water [MEA-1% and MEA-50%]; 10% concentrated ammonia solution in water [AMN-10%] (Clear Ammonia, DeMoulas Super Market, Inc. Tewksbury, MA); 20/5/75% tergitol® (non-ionic surfactant, Aldrich catalog # 52107-8)/isopropanol/water [TG20-IP5-W75]; a generic ammonia-based window and glass cleaner [WINDOW-SC] (DeMoulas Super Market, Inc), isopropanol [IP] (Aldrich), poly(propylene glycol) [PPG] (average M_W = 425, Aldrich catalog # 20,230-4); a proprietary ammonia-based isocyanate decontamination solution from Colormetric Laboratories (CLI) [CLI-NH3-IDS] (Des Plaines, IL); and Pine-Sol® general purpose cleaner (Clorox Co., Oakland, CA), for which the material safety data sheet (MSDS) specified that it contained <1% v/v monoethanolamine [Pine-Sol® MEA]. The SW-10%, MEA-1%, MEA-50%, AMN-10% and TG20-IP5-W75 were prepared in our laboratory using the specified ingredients and deionized water. All surface cleaners were liquids, most of them water-based and highly polar.

The skin decontaminants were: A Colormetric Laboratories product based on high erucic acid rapeseed oil, methyl ester and poly(propylene glycol) [CLI-DTAM]; GOJO® painter's hand cleaner [GOJO-PHC] (Gojo Industries, Inc., Akron, OH); ZEP® painters partner™ hand cleaner [ZEP-PHC] (Zep Manufacturing Co., Atlanta, GA); STOKO® Cupran® special hand cleaner [STOKO-CUPRAN PHC] (Stockhausen Inc., Greensboro, NC); and a skin protection cream STOKO® Arretil® [STOKO-ARTL SPC]. Although PPG was grouped with surface decontaminants, it can be used both as a surface and skin decontaminant. The painters' hand cleaners were viscous, semi-solid complex proprietary formulations. Their MSDSs suggested that they all contained abrasives (such as pumice or silica), solvents/oils (such as dimethyl adipate, octyl stearate, and lanolin), as well as other ingredients. These products were recommended by auto body shop suppliers as effective for removing enamel, lacquer, urethane or epoxy paints, sealants, adhesives and coatings.

We studied separately the rates of chemical reaction of aliphatic isocyanates with selected decontaminants and the physical removal efficiency of each decontaminant on an isocyanate-spiked surface.

Isocyanate-decontaminant reaction kinetics

To investigate the effect of different aliphatic isocyanates on reaction rates, two model isocyanates, butyl isocyanate (Bu-NCO) and a HDI-based polyisocyanate isocyanurate (Desmodur N3300, Bayer Co., Pittsburgh, PA) were selected for testing. The monoisocyanate Bu–NCO was chosen for its simplicity in monitoring reaction products, whereas N3300 is a very common commercial aliphatic polyisocyanate product, which was also the main component of isocyanate hardeners used in auto body shops.[13,14] Comparison of the reaction rates for butyl isocyanate and N3300 would provide additional

evidence about the variability in the NCO reactivity within the broader class of aliphatic isocyanates.

Because N3300 is a very complex mixture of various HDI-based dimers, trimers and higher oligomers, studying the fate of all species is difficult. Therefore, the fate of isocyanate species was monitored *via* the main isocyanurate peak, which contributes ~65% of the total NCO content.

Five microliters (μL) of a diluted solution of each isocyanate in acetonitrile was spiked into 1 mL of each surface decontaminant to give a final NCO concentration of $\sim 1 \times 10^{-3}$ N NCO, and the reaction mixture was shaken vigorously. Under these conditions the active hydrogen species H–X–R′ in the decontaminant were expected to be in large excess compared to the NCO group, although the ratio of the sum of active hydrogen species to NCO was variable. This approach was used because (i) the chemical composition of commercial products is complex, containing active hydrogen species of variable reactivity and generally in unknown concentrations, and (ii) in our every day hand washing/cleaning experiences the amount of decontaminant used is normally limited to a practical amount of a few milliliters. One hundred microliters of the reaction solution were transferred at appropriate time intervals (1, 3, 7, 15, 30, 60 min) to a quenching vial containing 900 μL of 1.1×10^{-3} M MAP (1-(9-anthracenylmethyl)piperazine), which was later analyzed by HPLC for the MAP urea derivatives of Bu-NCO or HDI-isocyanurate following the NIOSH Method 5525.[25] Advantages of MAP as a derivatizing reagent for isocyanates include high chemical reactivity, high sensitivity, a constant response factor in the ultraviolet (UV) region that is essentially independent of the isocyanate species measured, and better chromatography.[26] Under the experimental conditions MAP reacts instantaneously with the free NCO groups converting them to MAP-ureas, thus stopping all other ongoing NCO-consuming reactions. SW-10% was not tested with N3300 because the kinetic data for butyl isocyanate suggested it reacted identically with water.

One hundred milligrams (~0.2 mL) of each of the skin decontaminant were carefully placed on the bottom of a 2 mL vial forming a nearly uniform 1–2 mm thick layer. Five microliters of the isocyanate solution in methylene chloride were carefully spiked on the skin decontaminant, and at appropriate time intervals (1, 3, 7, 15, 30, 60 min) 1 mL of 1.1×10^{-3} M MAP in acetonitrile (ACN) was added to quench the reaction. Due to the very viscous nature of the skin decontaminants, mixing was not possible. The samples were then cleaned through solid phase extraction (SPE) on a Supelco LC-Si 500 mg/6 mL cartridge (Bellefonte, PA) and analyzed by HPLC (NIOSH Method 5525). A heterogeneous reaction medium between the semi-solid skin decontaminant and liquid isocyanates would be more prone to higher variability; nevertheless, this is more similar to the normal cleaning process.

Surface physical removal efficiency

Aluminium foil was chosen as the model surface due to its low porosity. It is anticipated that high porosity surfaces such as in the auto body shop workplace will adversely affect physical removal efficiency as a result of limited contact of the decontaminant with isocyanates trapped inside the pores. Five hundred microliters of a diluted solution of N3300 in acetonitrile were spiked on the cup-shaped 10 cm diameter foil (area = 78.5 cm^2) to give a relatively uniform distribution of the isocyanate concentration on the surface. The acetonitrile was evaporated in the hood under a gentle flow of nitrogen. Butyl isocyanate was not suitable for these experiments because of its high volatility. No other suitable monoisocyanate (such as octyl isocyanate) was tested, in part to reduce the high workload of this experiment and because it was believed that N3300 alone would suffice. All experiments were conducted in an air-conditioned laboratory environment at a temperature of 22–24 °C, and low relative humidity (20–30)%. After reviewing the reaction kinetic data for butyl isocyanate and N3300 some products were excluded from subsequent testing with N3300 in the surface physical removal efficiency experiments because they would not provide any significant new information. For example, the MEA-50% and MEA-1% solutions were not tested because their reaction with isocyanates was instantaneous and Pine-Sol MEA would suffice. Similarly, the water and 10% soap/water reacted at identical rates with butyl isocyanate and water was excluded because isocyanates do not dissolve in water. AMN-10% was also excluded because it was not significantly different from WINDOW-SC.

Two spike levels were tested, each in triplicates. The low spike equaled 4 μg NCO/surface area (0.051 μg NCO cm^{-2}), whereas the high concentration spike was 0.51 μg NCO cm^{-2}. These isocyanate contamination levels are realistic for auto body shops and in the range of exposures we have found during our extensive evaluation of surface and skin contamination in these settings.

Five hundred microliters of the surface decontamination solution (optimal volume based on preliminary tests) were spiked on a 2.5 × 2.5 cm cotton sterile gauze, which was obtained by folding an eight-ply 5 × 5 cm gauze (USP Type VII, Medline Industries, Inc. Mundelein, IL). The surface was wiped with the pad in decreasing concentric circles, by applying maximum pressure with the fingertip of the nitrile-gloved index finger. A second dry pad was used in a similar manner to collect the solvent left behind. Both pads were immediately transferred to a scintillation vial containing 10 mL 5×10^{-4} N MAP in acetonitrile (ACN). The surface was then rinsed with 10 mL of 5×10^{-4} N MAP in ACN and the rinse was collected in a separate scintillation vial for subsequent SPE and analysis. The first fraction determines removal efficiency, whereas the second one serves to determine the fraction of total unreacted NCO remaining on the surface. Surface wiping with both pads lasted typically 60–80 s, with ~5 min lag time between the wiping and rinsing. The residence time of isocyanates on the surface prior to wiping was 3–5 min, which includes the time for solvent drying with N_2 and the preparation time for wiping. Recovery at each spike level was tested in a similar manner. Samples were analyzed by HPLC as described for the reaction kinetics testing for N3300.

The skin decontaminants (CLI-DTAM, GOJO-PHC, ZEP-PHC, STOKO-CUPRAN PHC, PPG) and the barrier cream (STOKO-ARTL SPC) were tested in the same design as the liquid surface decontaminants, except that this time 0.5 g of each skin decontaminant was deposited on the gauze. The timing and duration of events was the same as that used for the surface decontaminants. Samples were cleaned through SPE and subsequently analyzed by HPLC as previously described.

Results

Isocyanate-decontaminant reaction kinetics

Surface decontaminants. Reaction progress for butyl isocyanate and N3300 with surface decontaminants is presented in Figs. 1 and 2, respectively. Reaction rates varied noticeably and ranged from instantaneous to very slow. Decontaminants fell in three distinguishable groups: fast, moderate and slow. The fast group of decontaminants includes all MEA solutions (MEA-1%, MEA-50%, Pine-Sol® MEA) and the CLI ammonia-based product (CLI-NH3-IDS). The two ammonia based-solutions, namely AMN-10% and Window-SC reacted instantaneously with butyl isocyanate, but slower with N3300. The second group, which includes water (W), 10% soap in water (SW-10%) and ammonia solution in water (AMN-10%), reacts at an appreciable rate (>50% consumption of the total isocyanate group in the first 5 min). The rest of the decontamination solutions fell in the slow category of reaction time

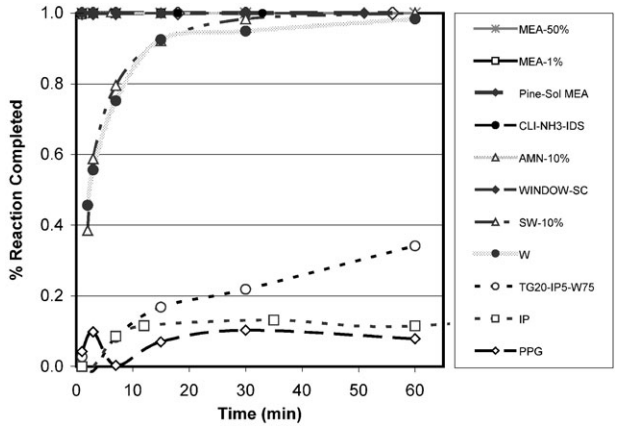

Fig. 1 Reaction rates for butyl isocyanate and various surface decontaminants. MEA-50% and MEA-1% are 50% and 1% v/v monoethanolamine (MEA) in water; Pine-Sol MEA is a Pine-Sol® general purpose cleaner containing <1% v/v monoethanolamine; CLI-NH3-IDS is a proprietary ammonia-based isocyanate decontamination solution from Colormetric Laboratories Inc. (Des Plaines, IL); AMN-10% is a 10% concentrated ammonia solution in water; WINDOW-SC is a generic ammonia-based glass cleaner; SW-10% is a 10% w/v liquid soap in water; W water; TG20-IP5-W75 is 20/5/75% tergitol® (non-ionic surfactant)/isopropanol/water; IP isopropanol; PPG poly(propylene) glycol. Lines for MEA-50%, MEA-1%, Pine-Sol MEA, CLI-NH3-IDS, AMN-10% and SW-10% overlap.

(>1 h). Most notable in this group are poly(propylene glycol) (PPG), isopropanol (IP) and the 20% tergitol/5% IP/75% water mixture (TG20-IP5-W75). For these decontaminants, the amount of NCO consumed during the first 15 min was <40%. With a very few exceptions, the reaction rates and the overall order of products was maintained when the isocyanate was changed from butyl isocyanate to N3300, suggesting that these reaction rates are applicable to the wider class of aliphatic isocyanates.

Skin decontaminants

The skin decontamination products generally reacted slowly with isocyanates, consuming from ~10% to 60% NCO in the first 15 min (Figs. 3 and 4). The reaction rates for N3300 were generally higher, especially initially, and more variable than for Bu–NCO. This can be attributed to two factors: (i) non-homogeneity (solid–liquid phases) of the reaction medium, and (ii) the consumption of the isocyanurate molecule as a surrogate for the reaction of NCOs in N3300. The N3300 material is expected to exhibit poorer solubility than butyl isocyanate, thus leading to greater inhomogeniety in the reaction medium and greater variability in the data. Also, since the isocyanurate molecule contains three NCO groups, reaction of a single group would suffice for it to be accounted as fully

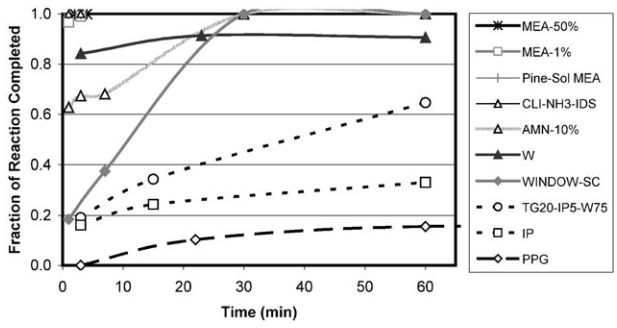

Fig. 2 Reaction rates for the polyisocyanate HDI isocyanurate (Bayer Desmodur N3300) and various surface decontaminants. See Fig. 1 text for abbreviations. SW-10% was not tested. Lines for MEA-50%, MEA-1%, Pine-Sol MEA and CLI-NH3-IDS overlap.

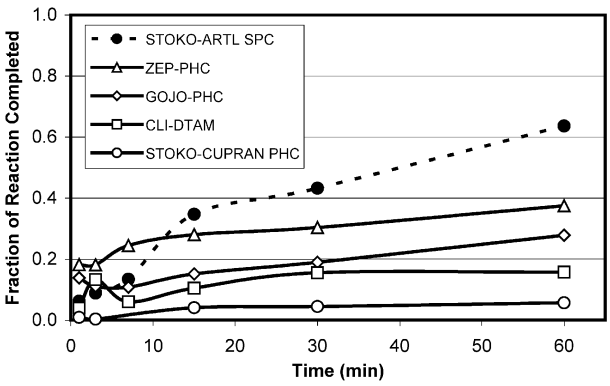

Fig. 3 Reaction rates for butyl isocyanate and various skin decontaminants. STOKO-ARTL SPC is the STOKO® Arretil® skin protection cream (Stockhausen Inc., Greensboro, NC); ZEP-PHC is the ZEP® painters partner™ hand cleaner (Zep Manufacturing Co., Atlanta, GA); GOJO-PHC is the GOJO® painter's hand cleaner (Gojo Industries, Inc., Akron, OH); CLI-DTAM is an isocyanate skin decontaminant from Colormetric Laboratories (Des Plaines, IL); STOKO-CUPRAN PHC is the STOKO® Cupran® special hand cleaner (Stockhausen Inc., Greensboro, NC).

reacted. There is a three times higher probability for the first NCO group of isocyanurate to react compared to butyl isocyanate and this may explain the initial higher reaction rates for N3300. The skin barrier cream (STOKO-ARTL SPC) performed similarly to painters' hand cleaners with regard to isocyanate consumption.

Physical removal efficiency

NCO mass balance. The mass balance requires that:

Spiked NCO amount = unreacted NCO amount removed + unreacted NCO amount remaining + reacted NCO amount during wiping + other losses during sample preparation.

The first two components (unreacted NCO amount removed + unreacted NCO amount remaining) are measured directly as MAP-NCO derivatives (eqns. (2) and (3) below) and are presented as percent of the spiked NCO amount in Fig. 5. The total reacted NCO amount and other losses can be calculated by the difference (eqn. (4)).

$$\%\ \text{Unreacted NCO removed} = (\text{NCO-MAP derivative amount on wipe/spiked NCO amount}) \times 100; \quad (2)$$

$$\%\ \text{Unreacted NCO remaining} = (\text{NCO-MAP derivative amount in rinse/spiked NCO amount}) \times 100; \quad (3)$$

$$\%\ \text{Reacted NCO + other losses} = 100 - (\%\ \text{unreacted NCO removed} + \%\ \text{unreacted NCO remaining}); \quad (4)$$

A separate recovery study at both concentration levels revealed that losses occurred mostly during the rinse phase. Thus, no absorption losses were observed on the cotton pad (recovery at both levels was > 99.3%, $n = 2$ each). In contrast, the average

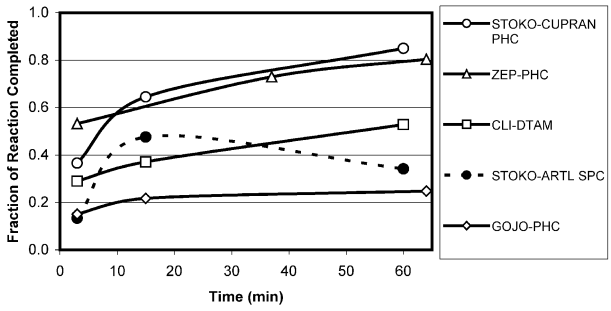

Fig. 4 Reaction rates for the polyisocyanate HDI isocyanurate (N3300) and various skin decontaminants. See Fig. 3 text for abbreviations.

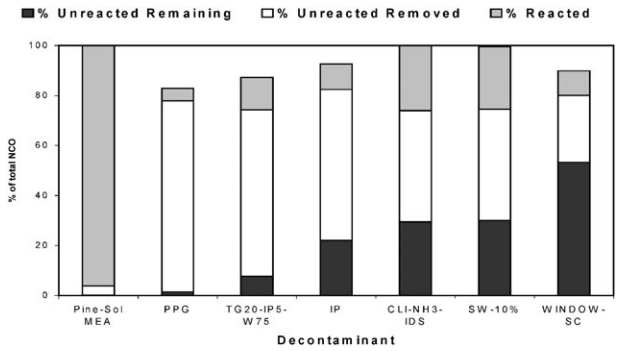

Fig. 5 Physical removal efficiency for the HDI polyisocyanate isocyanurate (N3300) by various surface decontaminants. % Unreacted remaining is the mean ($n = 3$) isocyanate fraction remaining on the surface after wiping and measured as NCO-MAP; % removed is the mean ($n = 3$) isocyanate fraction physically removed during wiping and measured as NCO-MAP; % reacted is a calculation of the isocyanate fraction consumed by chemical reactions during the first minute of wiping. This fraction could not be measured directly. The difference to 100% is made up of other losses. Pine-Sol MEA is a Pine-Sol® general purpose cleaner containing <1% v/v monoethanolamine; PPG poly (propylene) glycol; CLI-DTAM is an isocyanate skin decontamination solution from Colormetric Laboratories Inc. (Des Plaines, IL); TG20-IP5-W75 is 20/5/75% tergitol® (non-ionic surfactant)/isopropanol/water; IP isopropanol; CLI-NH3-IDS is a proprietary ammonia-based isocyanate decontamination solution from Colormetric Laboratories Inc. (Des Plaines, IL); SW-10% is a 10% w/v liquid soap in water; WINDOW-SC is a generic ammonia-based glass cleaner. Four products from the kinetic study experiment in Fig. 2 (MEA-50%, MEA-1%, AMN-10% and W water) were considered of no interest in this experiment and not tested.

rinse recovery was 74% (range 70.4–77.4, $n = 3$) for the low spike and 88.6% (range 71.9–100.1, $n = 3$) for the high spike. Appropriate corrections were made for the incomplete rinse recovery. Small isocyanate losses also occur in the sample preparation/cleanup step.[26] Therefore, large NCO losses can be attributed to the reacted NCO component. % Reacted NCO is the amount of NCO lost to chemical reactions with the decontaminant during wiping and between wiping and rinsing. An accurate account of NCO losses during each of these events is not possible because of the differences in important factors such as variable experimental time scales, concentration, and homogeneity of the reaction medium. However, an approximate estimate of NCO losses can be calculated from the kinetic data as follows.

The first data points in Figs. 2 and 4 are a good starting point for the %NCO consumed in chemical reactions. This is based on the assumption that most of the NCO on the surface (50–100%, from Fig. 5) will be diluted immediately in all (0.5 mL) of the decontamination solution, giving ~1.0 to 2.0 × 10^{-3} N NCO, which is comparable to 1.0 × 10^{-3} N NCO in the reaction vial in Figs. 2 and 4. Thus, the fraction of isocyanate reacted during ~1 min wiping would be approximately %NCO reacted during the first 1 min in Figs. 2 and 4 for the faster reactions and 1/3 %NCO reacted in the first 3 min for slower reactions. Similar calculations were made for the skin decontaminants. This calculated % reacted NCO consumed in the chemical reactions is also plotted in Fig. 5, instead of the total (% reacted + % NCO losses). This allows for a better understanding of other losses. The fact that the total NCO recovered by this approach for most products does not differ significantly from 100% reassures that this is a reasonable estimation.

Surface decontaminants

Physical removal efficiency from the aluminium foil surface at the high spike level (0.51 μg NCO cm^{-2}) for various surface decontaminants is presented in Fig. 5. The low spike level closely resembled the high spike in the overall decontaminant ranking and is, therefore, not presented. A relatively larger percentage of isocyanates was consumed by chemical reactions at the low spike for both surface and skin decontaminants.

The average % unreacted NCO remaining on the surface at 0.51 μg NCO cm^{-2} and measured as NCO-MAP (after correcting for rinse recoveries) ranged from ~2% for PPG to 53% for the WINDOW-SC. The average % unreacted NCO removed from the surface and measured as NCO-MAP ranged from ~27% for the generic window surface cleaner (WINDOW-SC) to ~76% for PPG.

The calculated % reacted NCO varied from ~5% for PPG to ~100% for Pine-Sol® MEA. Therefore, other losses ranged from ~0% for Pine-Sol® MEA to ~17% for PPG, with in-between values for other decontaminants.

Skin decontaminants

The physical removal efficiency was very comparable among various skin decontaminants. The % unreacted NCO removed from the surface at the high spike of 3.3 μg NCO in^{-2} ranged from ~67% for ZEP-PHC to ~80% for STOKO-CUPRAN PHC. The average % unreacted NCO remaining on the surface ranged from 0 for ZEP-PHC and STOKO-CUPRAN PHC to ~7% for STOKO-ARTL SPC. The calculated % reacted NCO consumed in chemical reactions during wiping varied from 9% (STOKO-ARTL SPC) to 33% (ZEP PHC). Other losses accounted for 0 to 13%. Higher losses for the slower reacting skin and surface decontaminants, in particular those with lower physical removal efficiency, can be explained in part with a larger NCO amount lost to chemical reactions on the surface during the 3–5 min interval between the wiping and rinsing steps. The reproducibility of the wiping method was satisfactory, having standard deviations for triplicates in the range <1 to 8% for all surface and skin decontaminants. The only exception was PPG with a SD 18.1%. The performance of surface and skin decontaminants at the lower spike was similar, except that the recovered fraction (% unreacted NCO removed) of isocyanates was 20–50% lower.

Discussion

In this study, tested surface decontaminants had variable rates of reaction with the NCO group. The group of decontaminants with high physical removal efficiency (PPG, TG20-IP5-W75) left the smallest amount of contaminant on the surface, but they had very low reaction rates with isocyanates. The physical removal efficiency of decontaminants with high chemical reaction rates (MEA solutions, Pine-Sol® MEA) could not be evaluated.

When combining the two decontamination mechanisms for all surface decontaminants Pine-Sol® MEA, contrary to the first impression from Fig. 5, performed the best and operated primarily through the chemical reaction with the NCO groups. Because monoethanolamine in Pine-Sol® MEA reacted almost instantaneously with isocyanate groups, only traces of NCO were found in each fraction (removed and remaining on the surface). Pine-Sol® MEA is used as a general-purpose household cleaner. However, recently the manufacturer of Pine-Sol® has discontinued the use of MEA and substituted it with triethanol amine, a change that will render the product ineffective with regard to NCO consumption. CLI-NH3-IDS was expected to behave in a similar manner to Pine-Sol® MEA based on the kinetic data (Figs. 1 and 2), but its reaction rate with isocyanates is apparently slower than that of Pine-Sol® MEA, which resulted in a larger amount of NCO in each fraction. The 10% soap/water solution (SW-10%) and isopropanol performed comparable to CLI-NH3-IDS within the very short time frame of wiping in this experiment. Nevertheless, the efficiency of CLI-NH3-IDS would be expected to improve by

increasing the contact time with the isocyanate on the surface, proportionally more than the remainder of decontaminants such as isopropanol and the SW-10% solution, due to its higher reaction rates with NCO. CLI-NH3-IDS performed notably better than IP and TG20-IP5-W75 at the low spike level consuming 85% of NCOs and more like Pine-Sol® MEA. One drawback to CLI-NH3-IDS as a surface cleaner, however, is that it requires very good ventilation; otherwise high ammonia vapor exposure can be generated during its use. Similarly, ethanolamines such as MEA and diethanolamine (DEA) are irritating to the skin, eyes, and respiratory tract and readily absorb through the skin.[27] The SW-10% solution is a decontaminant of limited efficiency as judged by the smaller fraction of NCO removed and the larger NCO fraction remaining on the surface.

The skin decontaminants were very similar. They all had high physical removal efficiency and generally low chemical reaction rates. Therefore, no one product could be recommended over the other, and factors, such as cost, odor, perceived product effectiveness and comfort could be important determinants. These aspects are investigated in a follow-up study in auto body shops. Our results on the physical removal efficiency of previously tested skin (PPG and CLI D-TAM™, soap and water) or surface decontaminants (MEA and ammonia solutions) are in good agreement with published findings.[22]

It is our opinion that an ideal isocyanate decontaminant for skin (surface decontaminants have fewer restrictions) should possess the following qualities: (i) high decontamination efficiency by both mechanisms-chemical reaction to produce non-toxic reaction products and physical processes; (ii) low toxicity; (iii) minimal alteration of the skin barrier, thus minimizing the risk of increased penetration on subsequent exposures; and (iv) preferably low cost, ready availability, and no undesirable odors.

Our experimental data suggest that the highest skin decontamination efficiency can be achieved with an oily/lipophilic product (such as PPG and D-TAM™), which has high mechanical removal efficiency, and amine groups incorporated in the polymeric backbone of the decontaminant, such as poly glycol amines or a poly fatty amines. The concept was tested with poly (propylene glycol) bis(2-aminopropyl ether) (average M_W = 4000, Aldrich catalog # 40,669-4), for which we studied its chemical reaction with isocyanates and its physical removal efficiency. As predicted, the product reacted very fast with NCOs, and no free NCOs were detected in any of the wipe fractions. This product, however, was designated by Aldrich as an 'irritant' and even though this large molecule is not expected to be absorbed through the skin, it should be tested for its dermal effects.

Conclusion

This study design allowed us to distinguish between the two major decontamination mechanisms for reactive chemicals—chemical destruction and physical removal—and to evaluate their individual contribution. Therefore, the data provided a more rational basis for comparing different decontaminants and selecting the most promising ones for further field testing and evaluation. One major limitation of this study is that it could not measure directly the reacted fraction of isocyanates with the decontaminants during wiping. In addition, workplace acceptance and the potential of decontaminants to interfere with the quality of finished product, such as the spray finish, will need to be considered and evaluated in the field before final recommendations can be made. It is worth reminding that, in particular with reactive materials such as isocyanates, prevention should be the most prudent practice.

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