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| RESEARCH ARTICLE

Evaluation of Chemical Glove Permeation Breakthrough Time on Biocide Glutaraldehyde Injection at PT. X Upstream Oil and Gas Production Facility

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| ABSTRACT
Microbiological contamination using biocide glutaraldehyde is one of the applications to maintain the integrity of pipelines and vessels in oil and gas production. PT. X's data on the recording of occupational illness shows an incident that occurred in 2019 due to chemical mishandling. The incident resulted in an inappropriate selection of chemical gloves and caused seven cases of irritant contact dermatitis in workers who injected biocide containing glutaraldehyde. The purpose of this study is to evaluate permeation breakthrough time on three types of glove materials used in the glutaraldehyde biocide injection process. Data taken from replacement gloves for workers who carry out the glutaraldehyde injection process, technical data on three types of gloves used in production: butyl rubber with Viton® outer layer, 100% butyl rubber, and neoprene. Simulation calculated using NIOSH permeation calculator V.3.0.0. Result from technical data for butyl rubber with Viton®, butyl rubber BT >480 minutes, and ND for Neoprene. BT field used, butyl rubber with Viton®, butyl rubber 240 minutes, and neoprene 45 minutes. Based on simulation, open-loop BDT 4.6 minutes, SBT 4.83 µg/cm2/min, SSPR 661.648 µg/cm2/min, CP 1089.67, 4108.64 and 7369.79 µg/cm2; permeation rate 385.177 µg/(cm^2*min). Closed-loop BDT 34.06 minutes, SBT 29.98 µg/cm2/min, SSPR 13.62 µg/cm2/min, CP 0.059, 356.73 and 1219.58 µg/cm2; permeation rate 10.597µg/(cm^2*min). The use of gloves made of butyl rubber with Viton® and butyl rubber at PT. X is suitable for protecting workers to >30% glutaraldehyde, while a neoprene glove is not recommended.

| KEYWORDS

Breakthrough time, glutaraldehyde, gloves, permeation, upstream oil & gas operation

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1. Introduction
In oil and gas production systems, microorganisms often challenge the integrity of pipelines and vessels. The most common problem caused by microbial contamination is Microbiologically Influenced Corrosion (MIC) which can increase the corrosion rate by producing metabolic byproducts that react with iron from the metal. The complexity of microbiological contamination is due to the possible interaction between oil and water (Turkiewicz et al., 2013); therefore, the chemical injection process needs to be carried out to prevent corrosion caused by microorganisms.

One way to discover chemical control of microbiological contamination in oil and gas is by using biocides. Biocides are compounds used to disinfect, decontaminate, and sterilize surfaces to eliminate microbial degradation. The chemicals commonly used in the chemical injection process in upstream oil and gas production facilities are glutaraldehyde and other chemicals, selected based on different interactions with microorganisms. Glutaraldehyde or OCH(CH2)3CHO or C5H8O2 is a colorless and oily liquid with a pungent odor, having a 100.12 g/mol molecular weight with a vapor density of 17mmHg. Glutaraldehyde is a type of chemical that is a contact irritant, a skin sensitizer and has the potential of a respiratory sensitizer (Wilbur et al., 2017).

Many cases of glutaraldehyde irritation occur in health workers; around 5-10% of health workers are exposed to glutaraldehyde (ATSDR, 2015). In a 5-year study at the University of Kansas on 468 patients who were patch tested for glutaraldehyde, 17 (3.6%)

of the 468 subjects were allergic to glutaraldehyde. Positive reactions were more than eight times more likely to occur in health workers than non-health workers (Shaffer & Belsito, 2000). The research found that five patients with contact dermatitis due to glutaraldehyde exposure had to change jobs due to this disease (Smith & Wang, 2006). Data obtained from PT X's recording of Occupational Illness (OI) shows there was an incident that occurred in 2019 due to chemical mishandling, i.e., inadequate information on the Safety Data Sheet (SDS) and a leak in the transfer hand pump. The incident led to an inappropriate selection of chemical gloves. It caused seven cases of irritant contact dermatitis in workers injecting glutaraldehyde biocide in production facilities upstream of oil and gas operations.

In the biocide injection process, the piping system's dose is 400-500 ppm/Water, depending on the operational needs, period, and duration of 1 week/5 hour with glutaraldehyde content > 30%. The impact of using glutaraldehyde on workers in upstream oil and gas production facilities has not been widely publicized, but that does not mean it is unaffecting. Therefore, this study aims to determine the appropriate personal protective equipment (gloves) for workers exposed to glutaraldehyde. Determination of chemical gloves is carried out by evaluating the permeation breakthrough time and studying technical data on three types of glove materials, i.e., butyl rubber with Viton, butyl rubber, and neoprene used in the glutaraldehyde biocide injection process. This determines the best permeation barrier and prevents occupational skin diseases in the glutaraldehyde biocide injection process at PT. X upstream oil and gas production facility.

2. Material and Methods

The research was conducted by referring to the record of changing gloves on workers who carried out the biocide injection process with a closed and open drain system from July to December 2021. These two processes had different doses, frequencies, and durations. Meanwhile, the biocides used were BIOC31150A and MB544 with glutaral (CAS: 111-30-8) content of 30-60%.

The three gloves were used to observe the glutaraldehyde biocide injection process at PT. X included butyl rubber with Viton® outer layer (BV-06//60957), 100% butyl rubber (B-05R//60949), and Neoprene (AlphaTec®29-865). The specification of gloves for chemical permeation based on EN 374-1:2016 in one of the upstream oil and gas production facilities can be seen in Table 1.

Table 1. EN 374-1: 2016 Gloves Classification

Butyl rubber with Viton®	Butyl rubber	Neoprene
EN ISO 374-1: 2016 / Type A AFKLMN	EN ISO 374-1: 2016 / Type A ABIKLP	EN ISO 374-1:2016 Type B AKL

Type of classified chemical resistant gloves: Type A: Protective glove with permeation resistance of at least 30 (Level 2) min each for at least 6 test chemicals; Type B: Protective glove with permeation resistance of at least 30 min (Level 2) each for at least 3 test chemicals; Type C: Protective glove with permeation resistance of at least 10 min (Level 1) for at least 1 test chemical.
A: methanol; B: acetone; C: acetonitrile; F: toluene; G: diethylamine; H: tetrahydrofuran; I: ethyl acetate; K: sodium hydroxide 40%; L: sulphuric acid 96%; M: nitric acid 65%; N: acetic acid 99%; P: hydrogen peroxide 30%

The method used was taken from the technical data of the permeation of the three types of gloves. A product datasheet from the glove manufacturer was used to maintain the consistency of the permeation and penetration data in terms of thickness, manufacture, type of material, and test parameters. Data from different manufacturers for the same type, thickness, temperature, and physical quality of glove material show highly variable permeation behavior (Banaee & Que Hee, 2020; Que Hee, 1996). Breakthrough times shown in minutes represent normalized breakthrough times required by ASTM F739 Method for Permeation. Table 2 is a rating that represents the requirements of ANSI/ISEA 105-2000 American National Standard for Hand Protection Selection Criteria with a rating criteria scale of 0-6 (Chemrest, 2002).

Table 2. Chemical Resistance Ratings ASTM Breakthrough Times in Minutes

Scale	
0	< 10 minutes breakthrough time
1	> 10 minutes breakthrough time
2	≥ 30 minutes breakthrough time
3	≥ 60 minutes breakthrough time
4	≥ 120 minutes breakthrough time
5	≥ 240 minutes breakthrough time
6	≥ 480 minutes breakthrough time

In this research, the experiment of material permeation test in the laboratory is not implemented by the authors. However, the permeation process is calculated using the NIOSH permeation calculator V.3.0.0, which is compatible with Microsoft Windows. This tool is a computer-based tool for automating the analysis of permeation test data (ASTM Committee F2815-10, 2014; Gao et al., 2009). In using the tools, the open-loop permeation test menu is selected according to the tests carried out by the manufacturer (Sean Banaee, 2020) and the closed-loop permeation test on the selection of gloves for glutaraldehyde (Jordan et al., 1996).

Closed-loop test simulation with continuous sampling used a total Volume Collection Medium (Vt in ASTM F739) of 5.64 L and a detectable permeation rate of 0.01 g/cm2/min. While in the open-loop test with constant flow rate used Volume Collection Medium (Vt in ASTM F739) 3.94 L and Analytical Method Detection Limit 0.01 - 0.025 g/cm2/min (ASTM Committee F2815-10, 2014). The program will import the ASTM F2815 test data in which file is already available in the software database and will be processed according to the instructions and standard parameters of ASTM F739, ASTM D 6978, and ISO 6529. The program then will display all the calculated permeation parameters, permeation curves, and other relevant information (Gao et al., 2009). Breakthrough Time (BT), Standard Breakthrough Time (SBT), and Steady-State Permeation Rate (SSPR) are general data used to measure the permeation resistance index of a material used for protection against specific chemicals (Anna et al., 1998; Banaee & Que Hee, 2020). The limitation of this program is that it can only project estimated cumulative permeation for 21 minutes for open-loop and 130 minutes for closed-loop, regardless of the type, chemical, type, or thickness of the glove material. Therefore, the authors will only simulate the permeation with 30, 60, and 120 minutes for closed-loop and 10, 15, and 20 minutes for open-loop.

3. Results

The type of chemical gloves used at PT. X for glutaraldehyde biocide injection work based on the technical specifications obtained were butyl rubber with Viton® with a thickness of 0.06 cm and butyl rubber with a thickness of 0.05 cm having a BT >480 min, while the neoprene type used by PT. X, authors were unable to find BT gloves technical data for glutaraldehyde from manufacture (Table 3)

Based on the data on the use and replacement of gloves in the upstream oil and gas field at PT. X (Table 4), glutaraldehyde biocide with a content >30% was used on a scheduled basis at site A, Site B, and GTS well with a recommended injection concentration of 1000 ppm/water for site A and 750 ppm/water at site B and GTS Well. The number of workers involved in this process was two people per work location.

Table 3. Gloves Technical Data Sheet

Gloves Material	Breakthrough Time (Min)	Scale	Sample Thickness (cm)
Butyl rubber with Viton®	>480	6	0.06
Butyl rubber	>480	6	0.05
Neoprene	ND	ND	0.04

Source: (Ansell, 2021; UVEX, 2021). ND = No Data.

Table 4. Glutaraldehyde Biocide Use, Duration and Glove Change at PT. X

Location	Injection Point	Chemical	Concentration (ppm/water)	Work Duration (hour)	Frequency	Number of Workers	Glove Change Duration/day (min)			Glove Consumption/day (pairs)		
							Butyl rubber with Viton®	Butyl rubber	Neoprene	*Butyl rubber with Viton®*	Butyl rubber	Neoprene
Site A	Downstream oil export pump	BIOC-31150A	1000	5	Every week	2	240	NU	NU	2	NU	NU
Site A	OD-XXX-149XX	BIOC-31150A	1000	5	Every two weeks	2	240	NU	NU	2	NU	NU
Site B	SCX Open Drain Drum	MB544	750	5	Every two weeks	2	NU	240	45	NU	2	12
Site B	SMX Slugcatcher	MB544	750	5	One time at the end of vessel cleaning	2	NU	240	45	NU	2	12
GTS Well	HP KO drum, vent KO Drum, closed drain, and other vessels	MB544	750	5	One time shock treatment and repeated after the vessel used for water containment (cleaning, offloading well service/drilling activities	2	NU	240	45	NU	2	12

NU: Not Used

Workers at site A wore butyl rubber gloves with Viton®. For five hours injection process, this type of glove could only be used for 240 minutes (4 hours), so the consumption of gloves per worker in 8 working hours was two pairs. In the injection process at sites B and GTS Well, workers used butyl rubber gloves for 240 minutes (4 hours); consumption per worker in 8 working hours was two pairs. In addition, at Site B and GTS Well, workers also used neoprene gloves which must be changed every 45 minutes, so that the consumption of gloves per worker in 8 working hours was 12 pairs.

Simulation results of chemical glove permeation time using NIOSH calculator software V.3.0.0. in Table 3, the open-loop, constant flow rate method shows no difference in the Breakthrough Detection Time (BDT) results for 10 15 20 minutes, which is 4.62 minutes. The SBT value at 0.10 g/cm2/min for 10, 15 and 20 minutes was 4.83 g/cm2/min, and the SSPR at 10,15 and 20 minutes was 661,648 g/cm2/min. The difference in the results in the open-loop simulation, the constant flow rate was only on Cumulative Permeation (CP) of 1089.67 g/cm2 in 10 minutes, 4108.64 g/cm2 in 15 and 7369.79 g/cm2 in 20 minutes.

Closed-loop simulation and continuous sampling show no difference in the results of the BDT, which is 34.06 minutes for 30, 60, and 120 minutes. The SBT values at 0.10 g/cm2/min for 30, 60 and 120 minutes are 29.98 g/cm2/min, and the SSPR at 30, 60 and 120 minutes is 13.62 g/cm2/min. Similar to the open-loop simulation, the difference in the results in the closed-loop simulation, continuous sampling is only cumulative permeation of 0.059 g/cm2 within 30 minutes, 356.73 g/cm2 within 60, and 1219.58 g/cm2 within 120 minutes. The open-loop and closed-loop CP simulation graphs can be seen in Figure 1a. Figure 1b shows the permeation rate graph in the open-loop method tends to be constant from 0 – 21.1 minutes is 385.177 g/(cm²*min), and in the closed-loop method, the permeation rate graph is constant from minute 0 – 136.5, is 10,597 g/(cm²*min)

Table 5. NIOSH Permeation Calculator Software Simulation

Open Loop, Constant Flow Rate												
	Breakthrough Time Detection (BDT) in minute			**Standardize breakthrough time (SBT) at 0.10 µg/(cm²*min)**			**Steady-state permeation rate (SSPR) at µg/cm2/min**			**Cumulative Permeation (µg/cm²)**		
Gloves Material	**10**	**15**	**20**	**10**	**15**	**20**	**10**	**15**	**20**	**10**	**15**	**20**
Butyl rubber with Viton®, Butyl rubber & Neoprene	4.6	4.6	4.6	4.8	4.8	4.8	661.6	661.6	661.6	1089.7	4108.6	7369.8
Closed Loop, Continuous Sampling												
	Breakthrough Time Detection (BDT) in minute			**Standardize breakthrough time (SBT) at 0.10 µg/(cm²*min)**			**Steady-state permeation rate (SSPR) at µg/cm2/min**			**Cumulative Permeation (µg/cm²)**		
Gloves Material	**30**	**60**	**120**	**30**	**60**	**120**	**30**	**60**	**120**	**30**	**60**	**120**
Butyl rubber with Viton®, Butyl rubber & Neoprene	34.06	34.06	34.06	29.98	29.98	29.98	13.62	13.62	13.62	0.06	356.73	1219.58

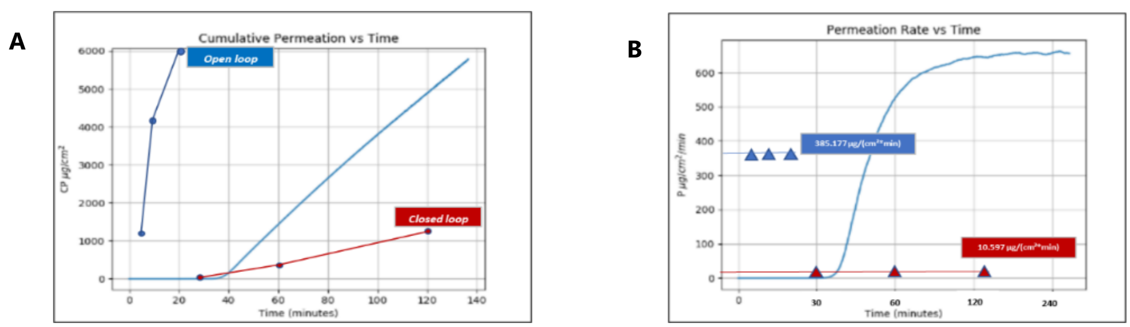

Figure 1. (A) CP vs. Time in open and closed-loop simulation and (B) Permeation Rate vs. Time in the open and closed-loop simulation

4. Discussion

According to a review of technical data on gloves used for glutaraldehyde injection, gloves made of butyl rubber with Viton® and butyl rubber with a thickness of >0.3mm (0.03 cm) have BT resistance >8 hours with direct contact for glutaraldehyde 30-70% (Forsberg & Mansdorf, 2003); this is also consistent with a test report conducted by Jordan et al., 1996 for gloves made of butyl rubber and neoprene with thickness greater than 0.3 mm (0.03 cm) have a BT resistance of >4 hours with continuous contact, but work with glutaraldehyde is not recommended for all types of gloves with a thickness less than 0.3 mm (0.03 cm) (Forsberg & Mansdorf, 2003).

When selecting gloves, PT. X has considered the technical data by the general chemicals used in upstream oil and gas production operations. PT. X also observed that chemical testing gloves manufactured by ISO and ASTM standards typically had met the required criteria. The glove thickness categorization system has been created for disposable, home, industrial, and special gloves, with thicknesses ranging from 0.0007 to 0.025 cm, 0.020 to 0.040 cm, and 0.036 to 0.085 cm, respectively throughout the selection process. It varied according to the application (Mellström & Boman, 1994). When selecting glove materials such as rubber, plastic, leather, textile, and combination materials, the primary classification system was based on the type of material (Banaee & Que Hee, 2020). Although the three gloves used by PT. X was technically suitable for injections of glutaraldehyde at a concentration greater than 30% PT. X had not considered the criteria for specific types of gloves for chemicals that were sensitizers or allergens, which included glutaraldehyde. ISO and ASTM standards for regular or standardized BT of 0.10 g/cm2/min at room temperature (ASTM F739: 27 1 °C) did not always cover all types of chemicals, including strong carcinogens, reproductive toxicity, and sensitizers. SSPR and BT for the same chemical and glove materials from different manufacturers might also vary (Banaee & Hee, 2019).

Based on data on the use and replacement of gloves at PT. X in Table 4, BT gloves made of butyl rubber with Viton® and butyl rubber were 4 hours or 240 minutes, and BT Neoprene was only 45 minutes. Many factors influence the occurrence of BT in the use of gloves in the glutaraldehyde injection process at PT. X upstream oil and gas production field. The first factor is the use of glutaraldehyde 30-60%. Research conducted by Vo & Zhuang, 2009., which used the Thermo-Hand method on a 50% glutaraldehyde solution which was carried out for non-latex gloves, showed BT for the hands of gloves using metricide, was 150 min + 6 min and palm-cuff indicator BT was 125 min + 5 min. Meanwhile, the BT of the hand glove using the wavicide tended to be slower, which was 300 min + 8 min, and the BT palm-cuff indicator was 125 min + 5 min. Jordan et al., in their research, says BT in glutaraldehyde 50% occurred very quickly and has a significantly higher permeation rate than glutaraldehyde 2 – 3.4%, butyl rubber, and nitrile butyl rubber has an excellent resistance (> 8 hours). At the same time, neoprene quickly absorbs glutaraldehyde solution (Jordan et al., 1996).

The second factor is that the glove permeation testing time in the laboratory is at room temperature (ASTM F739: 27 ± 1 °C). The temperature of the upstream oil and gas operation area of PT. X ranged from 30 – 35°C with 60 – 80% relative humidity. Differences in glove temperature when handling hot and cold objects, entering hot and cold areas, whether gloves are firmly attached or not, and worn for different times affected BT acceleration (Boeniger & Klingner, 2002; Gunh A. Mellstrom, Magnus Lindberg, 1992). Flexibility can also play a role in temperature, thickness variability, and continuous use (Anna et al., 1998). In addition, ASTM F739 does not consider the relative humidity at the test temperature (27 ± 1 °C) (Banaee & Hee, 2019). In a field study by Banaee and Que Hee, 2019., monitoring the air between the skin and the glove detected a breakthrough in the inner air space of the glove removed at rest to the presence of a mixture of three chemical components, which possibly occurred if the relative humidity involved in the process.

The third factor is the composition in BIOC-31150A and MB544. This is not just a single chemical; if the chemical of interest is part of a mixture, the composition must be known to determine whether the analyte BT should be shorter or longer than the BT of the other mixture chemicals on the same chemical resistance chart. The lower the concentration, the less likely an effect will occur. A chemical with a shorter BT can be significant at high concentrations. The SSPR for a donned glove (within the expiration date of a disposable glove) that has not been degraded or penetrated by a chemical is generally greater than those calculated using the standards due to factors such as temperature (except ASTM D6978-based data) and the forces experienced by the hand gloved during work. The same marks that apply to BT are also used in the mixture mentioned above situations. A chemical with a higher SSPR tends to increase the SSPR at high concentrations and may have no effect at low concentrations. When used in high concentrations, a chemical with a lower SSPR will tend to lower the analyte's SSPR but may have no effect when used in low concentrations (Banaee & Hee, 2019).

Other factors that affect the acceleration of glove permeation are the pressure during donning and doffing, flexion, and extension movements after wearing. In addition, other mechanical and physical activities such as pushing, pulling, lifting, pressing objects, and stretching the hands while performing tasks, will increase the pressure on the gloves, which can result in the formation of holes and thinning of the gloves at the pressure points so that seepage will occur when exposed with other liquid chemicals, cross-contamination can happen when gloves are donned and doffed (Mellström & Boman, 1994).

BT simulation using NIOSH permeation calculator software shows that the BDT in the open-loop method was 4.6 minutes and 34.06 minutes in the closed-loop method. These results show the time of chemical seepage into the inner surface of the glove material. Meanwhile, the SBT time when the permeation rate is 4.83 g/cm2/min (standard 0.10 g/cm2/min) in the open-loop method and 29.98 g/cm2/min (standard 0.25 g/cm2/min) in the closed-loop method is achieved within a minimum time window of 5 minutes. The SSPR of the open-loop method of 661,648 g/cm2/min shows the maximum constant permeation rate, with the measured concentration being directly proportional to the permeation rate. When the measured concentration becomes constant, it indicates a stable condition for the method. For the closed-loop method, the SSPR 13.62 g/cm2/min represents the linear portion of the accumulated mass of accumulated mass/exposed area versus the time curve defining the steady-state period of the permeation rate.

Cumulative permeation is the mass trans at the end of the permeation test period, usually a maximum of 2, 4, or 8 hours for an 8-hour work exposure (Banaee & Hee, 2019). The ASTM F739 standard also requires reporting cumulative permeation (μg/cm), but there is no maximum limit. The simulation results show a significant increase in the open-loop method are 1089.67 g/cm2 in 10 minutes, 4108.64 g/cm2 in 15 minutes and 7369.79 g/cm2 in 20 minutes, and 0.059 g/cm2 in 30 minutes, 356.73 g/cm2 in 60 minutes and 1219.58 g/cm2 in 120 minutes in the closed-loop method. If the cumulative permeation time of the test chemical exceeds 0.25 and 1.0 g/cm, the permeation rate's uncertainty becomes large, estimated at 21% at the 95% confidence level (Mäkelä et al., 2014). The dose per unit area (μg/cm) is considered the most critical factor in skin sensitization (Monica R. Upadhye, 1993). Thus, cumulative permeation is helpful for chemical safety assessments when the appropriate type of protection is selected for different kinds of exposure scenarios (ECHA, 2016). In contrast to BT, which is intended only to assess the ratio of permeation time, cumulative permeation can roughly estimate the received skin exposure to sensitizing chemicals. It can also be used to determine BT limits for gloves and chemical protective clothing (Mäkelä et al., 2014) with the condition that the information during the simulation must be valid according to the level of exposure. Based on the simulation results, it is assumed that the cumulative permeation of glutaraldehyde, which may be capable of sensitizing the skin according to EN 374-3:2003, can occur through the protective agent before the permeation rate of 1.0 g/min is reached. It is also possible at cm2 that the ASTM F739 standard limit of 0.1 g/min/cm becomes unsafe. Therefore, the standards EN 374-3 and ASTM F739 do not provide information on the comparison of safe protective materials (Mäkelä et al., 2014)

Even if the NIOSH simulation calculator compared to laboratory tests has shortcomings and has the potential to bias in its results, the calculation of all permeation parameters related to the standard ASTM F739, ISO 6529, and ASTM D6978 test methods using a computer program is allowed to compare the results of the test analysis (ASTM Committee F2815-10, 2014; Gao et al., 2009). The use of these simulation tools is quite beneficial. It helps companies identify the selection of chemical gloves for the glutaraldehyde biocide injection process in PT. X's upstream oil and gas operations.

5. Conclusion

The use of gloves made of butyl rubber with Viton® and butyl rubber at PT. X is entirely appropriate for protecting workers' skin exposure to glutaraldehyde >30%, while the existing neoprene gloves at PT. X is not recommended for use. The permeation breakthrough time of the glove must be selected using proper calculations without neglecting other factors that can affect the permeation of the glove, such as chemical composition and concentration, temperature, humidity, working method, application, etc. Optimizing gloves based on actual workplace conditions is one way to protect workers from glutaraldehyde exposure. Observation and monitoring of the use of glutaraldehyde and its changes must be carried out. BT calculation using NIOSH calculator has shortcomings and has the potential to bias; therefore, further research with different methods is needed to determine glove selection criteria based on potential health effects, the relative toxicity of agents, objective measurement, and performance of use, not just on laboratory-generated kinetic data.

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