

SX34 and the decontamination effects on chemical warfare agents (CWA)

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Abstract: -The decontamination of sensible surfaces contaminated by chemical agents is a key issue for the safety of population and security of structures. SX34 is an innovative decontamination product developed for sensible surfaces decontamination from biological and chemical agents. In this work the authors present the effects of SX34 on contaminated surfaces and its effectiveness compared to classic decontaminants. The electrical insulation on sensitive equipments is analyzed as innovative possible application of this product.

Key-Words: - Chemical Warfare Agent, Decontamination, Sensitive equipment, SX34, CBRNe

1 Introduction

In order to obtain an effective CBRNe defense it is necessary to manage several complex processes at the same time. Studying real events [1-3] and using simulation technologies [4-6] are essential steps to identify the best practices to adopt in order to achieve the result of an effective and quick response to a CBRNe event. Managing a CBRNe emergency, both of terrorist and natural source, means to follow the rings of a chain. The chain starts with an alarm, carries on with identification and tracking of the dangerous substances applying the most appropriate countermeasures and it finishes with the decontamination of affected sites. The latter aspect mentioned has to be designed with the proper material and technologies to improve its resilience [7].

The practice of decontamination from chemical warfare agents (CWA) is an important step in order

to restore the initial conditions. It consists in a complex set of technologies [8] that have the common goal to ensure the safety of people and the security of the materials and the areas involved in the event. The decontamination process can be carried out by absorption, destruction, neutralization, inhibition or removal of chemical warfare agents.

The choice of one or more of these different approaches depends on both the context and the characteristics of the agents involved.

Different chemical reactions can be used to obtain chemical products less toxic than CWAs. Many chemical warfare agents undergo to significant hydrolysis reaction in alkaline conditions so both nerve agents and mustard gas, being sensible to oxidation, have been always well treated by bleach (NaClO) and others different hypochlorite-based compounds, as calcium hypochlorite (Ca(ClO)₂), lithium hypochlorite

(LiClO), or different chlorinated molecules [9]; these compounds have also been used in emulsion form [10] to increase their effectiveness.

The perfect decontaminant should be efficient, easy to prepare and use, should well adhere on surfaces but, at the same time, should be also easy to remove. Besides operators' safety, environmental friendship and low costs are required. Of course all these aspects cannot be found in the same product, so compromises are needed to obtain the best overall performance.

For these reasons new approaches have to be developed and tested. Different techniques should be used for the same agents on different supports, for example a person [11], an indoor surface of a building [12] or an environmental remediation context [13]. Particularly in this case, different approaches have to be followed, when decontamination border with remediation approach that spans from waiting a spontaneous decontamination.

A less obvious example about the complexity of the decontamination question comes from the different decontamination threshold levels used in military and civilian contexts. If the protected infrastructures are not strictly of military use, such as offices and ministries, the level of decontamination that needs to be reached is a lower level of residual pollution because the potentially exposed are not protected or trained, so the techniques potentially involved are different [14].

In this work, a new decontaminant product, SX34 [15], has been tested and investigated in order to understand its capability to remove CWAs from sensitive surfaces guaranteeing, at the same time, the integrity of the treated materials.

2 Experimental Methodology

2.1 Decontamination agent SX34

The SX34 is a decontaminant formed by a solid adsorbing medium dispersed in a volatile solvent and it acts incorporating the toxic agent in a physical manner so that it can be subsequently removed mechanically. SX34 is a multiphase decontaminant, stored in the form of pressurized aerosol, in not reusable metallic or polymeric container of reduced volume, easy to use and to introduce in confined spaces, ready for immediate employ. A gas propellant allows the application of

the product in a range of operating pressure from 3 to 6 bar.

2.2 Chemicals

Chemical warfare agents: Yperite (C₄H₈Cl₂S, Bis(2-chloroethyl) sulfide, CAS 505-60-2, NATO code HD) distilled from old chemical weapons; Soman (C₇H₁₆FO₂P, 3,3-Dimethylbutan-2-yl methylphosphonofluoridate, CAS 96-64-0, NATO code GD) and VX (C₁₁H₂₆NO₂PS, Ethyl ({2-[bis(propan-2-yl) amino] ethyl}sulfanyl)(methyl) phosphinate, CAS 50782-69-9, NATO code VX) (kindly provided by JCBRN Defence COE, Vyskov, Czech Republic).

2.3 Tested materials

Materials chosen for exposure to Yperite were selected from a range of gums and polymeric products typically used in internal part of military airplane as Eurofighter™: a) polimethyl metacrylate sheet; b) fluorinated rubber sheet type viton 6000; c) PVC sheet Ultem1668A (29) sheet; d) fluorinated rubber sheet type 6000; e) painted metal (Chemical Agent Resistant Coating - CARC paint); f) chloroprene sheet type 3012; g) fuel-resistant sheet type 2026; h) super chloroprene sheet type 3015; i) oil-resistant sheet type 2001. 25.0 cm² pieces of each material were used in each test.

Tests using Soman and VX were performed using the following materials: i) polyurethane paint, (CARC paint), applied on steel supports of 50.0 x 50.0 mm; ii) butyl rubber (minimum thickness of 1.0 mm); iii) polycarbonate (minimum thickness 2.0 mm); iiiii) fabric PES (plasticized PVC on both sides) laminated (minimum thickness of 0.5 mm).

2.4 Liquid agents exposure

All the materials were tested after an applied contamination ten times higher than the standard used for the decontamination of sensitive equipment (0.20 g/m²). A special tool to put 25 droplets equally distributed on the test surface (25.0 cm²) was used (Fig. 1). A surface contamination of around 2.0 g/m² for Yperite, Soman and VX is obtained.

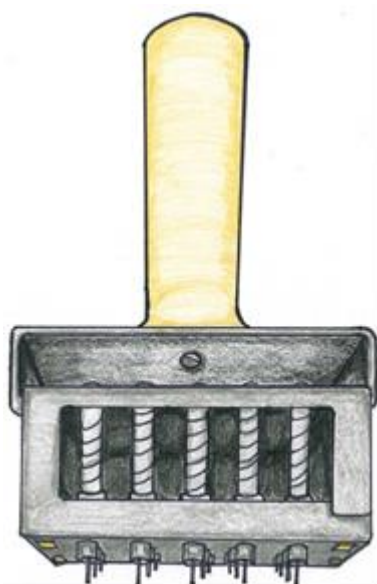


Fig. 1 - Device for the liquid agents exposure

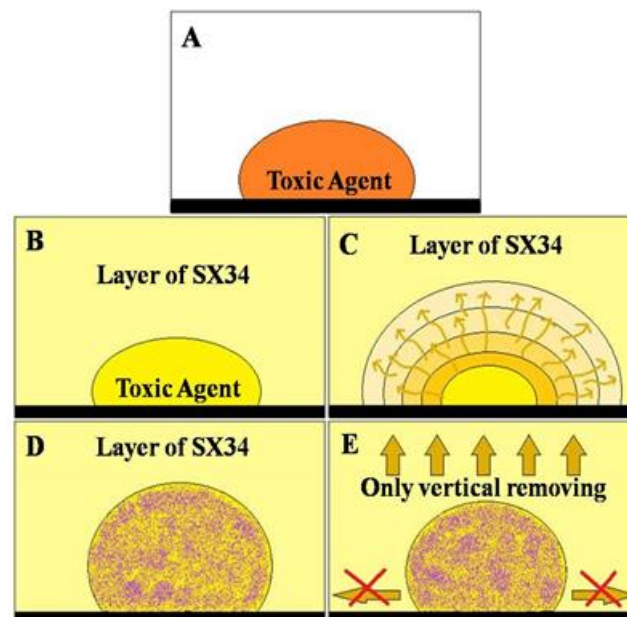


Fig. 2 - Mechanism of SX34 application and action

2.5 Decontaminant application

The decontamination process can be described by three steps (Fig. 2). In the first stage, the solvent melts and removes the CWA from the contaminated surface; in the following step, after solvent evaporation, the CWA is absorbed to the solid phase which remains on the object. Finally, in the third stage, the solid phase is mechanically removed. In figure 3, a prototype of portable decontamination equipment is shown.

In the present work, SX34 decontaminant was distributed directly on the contaminated surfaces by spraying and a thick layer was obtained. After 30 minutes the layer is removed by a suction system similar to a vacuum cleaner, which avoids the dispersion of the product in the air.

Two different decontamination protocols in two different test series were followed. During decontamination tests using Yperite, the decontaminant was applied from two to six times in order to assess the decontamination effectiveness compared to subsequent applications.

During decontamination tests using VX and Soman, only one decontaminant application was performed.



Fig. 3 - SX34 decontamination equipment prototype. A. Deco vacuum aspirator (9.5 kg - 20.9 lbs; 220 ÷ 240V – 50 ÷ 60HZ; 1200 W); B. Chest container and 10 canisters (capacity 0.75 l each) of SX34 decontaminant; C. HEPA and ULPA filters; D, H. Accessories and connections tubes; E. Brushes and maintenance accessories; F. Nozzles; G. Bags for the collection of contaminated materials; I. PSDS/1,5 MIL decontamination system-acids resistant according to STANAG 4360.

2.6 Standard method comparison

The decontamination protocol using SX34 was compared to the reference method described in Stanag 4653 AEP-58. This method involves washing with isopropyl alcohol 99.8% HPLC grade (Sigma Aldrich).

2.7 Solvent extraction

In order to evaluate the performance of the new approach versus the standard one, it is necessary to refer to the true value of the contaminant (C₀). For this aim, a drastic extraction method, which allows to obtain the initial quantity of the contaminant or the amount remaining in the sample after the decontamination, was used. This method involves the use of a mixture of heptanes/acetone (molar ratio 9:1) (for trace analysis, Sigma Aldrich) and an ultrasonication for 40 min at the temperature of 20°C.

2.8 Analytical methods

Quantitative chemical analysis on Yperite contaminated materials were performed using a gas chromatograph (Thermo Trace) coupled with a ion trap mass spectrometer (Polaris Q) and an electron ionization (EI) under the following experimental conditions: a) injected sample volume: 1.0 µl; b) injection mode: PTV splitless; c) inlet temperature program: initial temperature 70°C, rate 140°C/min till 250°C, then hold for 1 min.; d) split flow: 20 ml/min.; e) splitless time: 1 min; e) column RTX WAX: 30.0 m x 0.25 mm x 0.25 µm; f) carrier gas: He, 1.0 ml/min.; g) oven temperature program: initial temperature 50°C hold for 1 min, ramp 20°C/min., till 235°C and then hold 235°C for 2 min.; h) source temperature: 250°C; i) solvent delay: 6.8 min.; l) scanning mass range: 45-250 uma. 3.0 µg/ml LoD (Limit of Detection) was calculated as ten times the average noise on single mass extracted from chromatogram.

Quantitative chemical analysis on Soman and VX contaminated materials were performed using a gas chromatograph (Agilent 6890) connected with a FID (Flame Ionization Detector) under the following experimental conditions: a) injected sample volume: 1 µl; b) injection mode: splitless mode; c) inlet temperature: 300°C; d) splitless time: 1 min; e) column HP5: 30.0 m x 0.25 mm x 0.25 µm; f) carrier gas: He, 1.2 ml/min; g) oven temperature program: initial temperature 80°C hold for 1 min, ramp 20°C/min., till 300 °C and then hold 300°C for 15 min; h) detector temperature: 300°C; i) detector gas flow H₂ 40 ml/min, N₂ 40.0 ml/min, Air 450 ml/min.

2.8 Decontamination yield

The decontamination yield (η_{dec}) is defined as the difference between the initial concentration of contaminant C₀ and its concentration measured after the application of the decontaminant C_{fin}, divided by C₀ and multiplied by a factor of one hundred. It

is an indicator of the goodness of decontamination process, against a specific contaminant, expressed in percentage points.

The decontamination yield can be used to quantify both the washing with isopropanol and the decontamination using SX34 [1]:

$$\eta_{dec} = [(C_0 - C_{fin})/C_0] \times 100 \quad (1)$$

During the tests using Yperite, a number between 4 and 8 samples were contaminated and subsequently treated. CWA on sample n.1 was immediately recovered to quantify the C₀ value. Sample n. 2 was decontaminated by isopropyl alcohol treatment as previously described in materials and methods section and the residual CWA was determined to obtain the C_{fin} value.

The other specimens were treated sequentially with the decontaminant SX34 and then extracted with solvent. The values obtained (again C_{fin}) compared with the first extract directly allow to quantify the yields η_{dec} of decontamination of the SX34 for successive applications.

During the tests using nerve agents, five materials samples were contaminated; the first sample was used to calculate C₀, the second one was extracted using isopropanol and the remaining were used for the decontamination with SX34.

The decontamination performances obtained by SX34 on Yperite and nerve agents contaminated materials are shown in tables 1 and 2 respectively.

3 Results and discussion

3.1 Decontamination results

Data obtained from Yperite contaminated materials (Table 1) show that SX34 removes CWA at a higher yield than standard solvent already after the first decontamination cycle, especially for materials easy to permeate by CWA, such as nitrile rubber or chloroprene. In the case of residual contamination on the surface of tested material, repeating the decontamination cycle a strong decrement of contamination was obtained. For material hard to permeate by CWA as CARC or PVC, there was virtually no difference between efficiency of SX34 and solvent (isopropyl alcohol).

The results obtained using GD and VX as contaminants (Table 2) show that the efficiency of the SX34 is higher than the standard solvent even after only one decontamination cycle.

Laboratory practice shows that the removal of the chemical aggressive by decontaminant should preferably be orthogonal to the application direction, in order to avoid that the solutions produced after the application of the decontaminant could penetrate into the interstices. This condition is important especially during the treatment of sensitive equipment.

MATERIAL	Decontamination yield (%)*						
	η_{10}	η_1	η_2	η_3	η_4	η_5	η_6
1. Polimethyl metacrylate sheet	99.5	99.3	100				
2. Fluorinated rubber sheet type viton 6000	99.0	93.5	98.7	99.8			
3. PVC sheet	98.7	99.9	100				
4. Uitem1668A(29) sheet	98.5	98.6	99.8	99.9			
5. Fluorinated rubber sheet type 6000	97.9	98.5	99.2	99.5			
6. Painted metal (CARC paint)	92.2	93.1	98.1	99.4			
7. Chloroprene sheet type 3012	43.9	66.1	78.5	87.1	89.0	93.2	
8. Fuel-resistant sheet type 2026	9.3	32.1	58.9	73.8	77.3	86.4	
9. Super chloroprene sheet type 3015	1.8	44.3	80.7	89.2	90.7	93.2	
10. Oil-resistant sheet type 2001	1.4	31.8	44.8	63.3	73.0	80.0	83.9

Level of Contamination of mustard gas (HD): 2 g/m²
 LOD (Limit of Detection) = 2.4 ppb
 * where C₀ = initial concentration of HD agent (ppm) (Sample A)
 C_n = concentration of HD agent (ppm) after one or plus decontamination cycles (from 1 to 6), or after washing with solvents (Sample B)

Table 1 - Results of the test carried out using Yperite as a contaminant

Single decontamination cycle with SX34:								
AGENT	CONTAMINATION LEVEL							
- Soman (GD) - VX - Yperite (HD)	2 g/m ² and 10 g/m ² (*)							
	MATERIALS							
	- poliuretanic paint (CARC) - butyl rubber (for masks and gloves) - polycarbonate - PVC laminated on both sides							
(*) From 10 to 50 times higher than the 2 g/m ² level, in NATO Document – STANAG 4653-AEP 58 Ed.1 (2005)								
Single treatment cycle								
CHEMICAL AGENT	Decontamination yield η_{dec} (%) on painted metal (CARC paint)		Decontamination yield η_{dec} (%) on butyl rubber		Decontamination yield η_{dec} (%) on polycarbonate		Decontamination yield η_{dec} (%) on laminated PVC (PVC/Polyester/PVC)	
	SOLVENT	SX34	SOLVENT	SX34	SOLVENT	SX34	SOLVENT	SX34
Soman (GD)	-	99.7 99.9	69.5 63.3	96.7 97.1	-	99.6 99.9	31.3 53.0	83.1 76.8
VX	-	98.5 99.8	53.2 59.4	98.5 97.4	83.4 78.3	99.8 99.9	-	99.8 93.2
Yperite (HD)	-	99.7 99.8	25.5 40.6	72.2 70.9	64.2 63.8	67.7 66.2	35.8 31.9	51.3 63.5

Table 2 - Results of the test carried out using Soman (GD) VX and Yperite.

3.2 Undamaged electrical components

The maintenance of the dielectric strength between the electrodes and the voltage between them, before and after the application of SX34, was also measured [16]. Several measurements on metal surfaces, after the application of different voltages, were performed. The application of the decontaminant has shown that this does not cause loss of electrical insulation on sensitive equipment (Table 3):

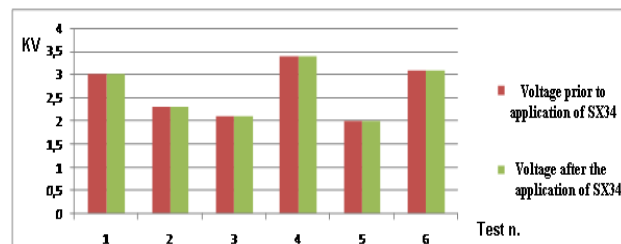


Table 3 - Voltage comparison before and after SX34 application

4 Conclusions

The results obtained from the decontamination tests carried out using HD, GD and VX show that the decontamination values were higher respect to the ones reached using classical decontaminant solvent like isopropyl alcohol. In case of a little residual contamination it is necessary only re-apply for one or few cycle the decontaminant. The harmless of the SX34 against electrical insulation and integrity of electrical circuits was also demonstrated.

The SX34 was successfully tested also in case of a radiological contamination with good results. The authors can conclude that the SX34 therefore represents a promising decontaminant for sensitive materials in military and civilian contexts

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