International Conference KNOWLEDGE-BASED ORGANIZATION
Vol. XXIII No 3 2017

CHEMICAL RESISTANCE OF TEXTILE WITH A BUTYL-RUBBER POLYMERIC MIXTURE AGAINST DECONTAMINATION MIXTURE ON THE BASE OF CHLORINATED ALIPHATIC AND AROMATIC HYDROCARBONS

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***Abstract**: Used equipment for providing hermetic isolative protection of the Czech Armed Forces Chemical Corps specialists´ body surface is currently solved with the employment of a mixture based on butyl-rubber. By producers declared protective properties of used barrier material does not mention a potential influence of decontamination mixtures and their components on the change of protective properties. A paper deals with selected chemical properties of butyl-rubber and points to the destructive influences of selected decontamination mixtures on protective textile used to production of isolative hermetic protective equipment. Study of barrier material chemical resistance against permeation of selected chemical compounds and mixtures creates the base presumption for evaluation of its usability.*

Keywords: decontamination, decontamination mixture, breakthrough time, diffusion

1. Introduction

The Czech Armed Forces (CAF) Chemical Corps (CCs) specialists fulfil the most complicated tasks and precautions falling into the area of Chemical, Biological, Radiological and Nuclear Defence (hereinafter CBRN Defence) and Chemical support (CS). The primary aim of fulfilment of these tasks is to minimize the impact of effects of Weapons of Mass Destruction (WMD) and Toxic Industrial Materials (TIM) on the CAF forces. They use standardly established isolative garments of body surface protection within fulfilment of their professional activities. These garments are characterized with so called breakthrough time (BTT). This time is defined as the time for a safety stay in a protective garment. In the case of isolative garment the BTT is considered as the time during that the particular material reliably protects against a liquid Chemical Warfare Agents (CWA) [1,2]. Basically, it is the time from loading the drop on a true side of the isolative material until its permeation on a back side of the isolative material in a threshold amount in a form of the gas.

Understanding of BTT has been significantly affected with the change of a security environment and security threats [3-5]. The current time is permanently typical with problems concerning misuse of Chemical Weapons and CWA in different countries across the World. It is connected with both scientific workers´ and specialists´ permanent interest related to development of methods leading to improvement of the CAF CCs specialists´ isolative protection in relationship to Toxic Industrial Chemicals (TIC). These chemical

DOI: 10.1515/kbo-2017-0181

substances are a crucial part of the chemical industry in all countries in the whole World and at the same time they are the part of some decontamination mixtures established in the CAF [6,7].

2. Theoretical part

We expect from the CAF CCs´ garments of isolative body surface protection that they will be in a direct contact with liquid phases of CWAs and TICs. Furthermore, we expect that they will provide the high quality isolative protection of the whole body surface against these toxic chemical substances to user. The skin, as the biggest organ of the human body, can fulfil the task of the entrance gate of toxic compound into the organism in the case of imperfect isolative protection. In this connection it is necessary to admit that to transdermal toxicity and the CAF CCs specialist´ health protection has not been devoted such an interest as this problems deserve to [8,9].

In current time specialists of the NBC Defence Institute of the University of Defence in the long term deal with testing butyl-rubber polymeric mixture, thus the material which is used as the basic construction material for production of the garment OPCH-05 [10-12]. From published reports and papers it is evident that chemical resistance of used material expressed with BTT has got some significant limits just in relationship to liquid TICs which are the basic part of decontamination mixtures in the CAF. General consciousness concerning this insufficiency has become the challenge for elaborating experimental works aimed to clearly determinate the effects of liquid decontamination mixtures on the OPCH-05 garment. The experimental work has been conducted in the scope of TICs which are specified as those which are not designated for decontamination of garments of the CAF CCs´ isolative body surface protection. It is necessary to mention that the CAF CCs specialists can be in contact with liquid decontamination mixture and their components not only within their preparation during mixing components but also within fulfilment of the task connected with the thorough decontamination of the CAF on decontamination sites especially when it is performed with a stationary way with the help of streamlines and brushes. In both these cases it is not possible to accept measurements leading to prevention the contact with decontamination mixtures and their components by which some restrictions leading to either prevention or maximally limitation of the contact between the garment and the liquid phase of the decontamination mixture are known or set. If we exclude the possibility of contamination of the OPCH-05 garment with the carelessness caused by non-professional manipulation with barrels or stocks of components of liquid decontamination mixtures to stain and contamination of the surface of the garment could come within falling drops of decontamination mixtures during their mixing and mainly during pressurized spray of decontamination surfaces or during their slumping even in keeping standardized decontamination procedure. In both cases it is possible to speak of a long-term contact which can lead to destruction of the structure of a barrier polymeric layer made from a linear amorphous non-crosslink polymeric material based on the butyl-rubber. This one is typical by its expressively non-polar properties.

Prevention of the long-term contact with decontamination mixtures, respectively with their liquid components can be difficult even from the length of specialists´ operational deployment point of view within fulfilment of the professional task in different conditions of military operations leading in various climatic conditions. Furthermore, in accordance with valid rules of forces deployment it is planned that forces will be used in operational shifts running from 8 to 12 hours in dependence on the type of military operation. It will be very complicated to run own decontamination with the aim to prevent negative long-term influence of the particular decontamination mixtures within time of fulfilment of operational tasks [13]. Destructive effects of some decontamination mixtures can significantly influence provided specialists´ isolative protection in the time of one shift. This can be the challenge mainly in the current time when the level of available supply of these garments can cause problem within repeated fulfilment of professional tasks [14].

The CWA of the type of sulfur mustard [yperite, bis(2-chloroethyl) sulfide] is traditionally used for testing of constructive materials of the individual protection. This toxic CWA has got a relatively simple chemical structure, from the group of CWA is the least toxic, it is relatively available, it has a small molar volume in comparison with other persistent CWAs and it is well detected with the help of simple detection kits and devices. This kits and devices can be employed for detection of permeated test chemical through constructive materials [15]. The method of MIKROTEST has been used for finding influences of decontamination mixtures which destructive effects can be assessed as non-devastating. This method was developed at the former Military Technical Institute of Protection in Brno [16,17]. Nonetheless, in the case of considering destructive effects of decontamination mixtures the employment of MIKROTEST method has been purposely abandoned from the reason of significant effects on test material. Moreover, employment of the sulfur mustard could be judged as uneconomical and basically useless. Effects of mentioned decontamination mixtures have been so significant that visual consideration has been enough for description of achieved results.

3. Used chemicals and material

3.1 Used chemical

The decontamination mixture No 1 has been used for studying destructive effects on the isolative folio. Its basic data are summarized in table I. Selected properties of its components which are its parts are introduced in table II [18].

Table 1: Basic data related to decontamination mixture No 1

Mixture	*Composition*	*Time of applica-tion [min]*	*Consump-tion [$dm^3.m^{-2}$]*	*Usage*
OS č. 1	10 % mixture of dichloramine in dichloroethane	10 – 15	0,5 – 0,6	Stationary way of decontamination of vehicles

Table 2: The survey and specification of used chemicals

Name of the chemical	*Specification, clearness*	*Producer (provider)*
N,N-dichlorobenzensulfonamide (trade mark dichloramine)	55,0 % of active chlorine	ORIMPEX, Ltd, Praha
1,2- dichloroethane	p.a.	Lachema, state public enterprise Brno, plant Neratovice

Samples have been cleaned with ethanol before they usage.

3.2 Used material

Basic polymeric material that has been used to the construction of garment for specialists OPCH-05 consists on isolative protective textile of TP-RUB-001-06, polyamide textile both-sided with coating from the butyl-rubber (Rubena, public limited corporation, Hradec Králové, Czech Republic). The final product it means OPCH-05 is completed by the ECOPROTECT, Ltd, Zlín, Czech Republic. For production of samples the a cutter of samples (Marbach, limited company, Brno, Czech Republic) and a hydraulic press (Polymertest, limited company, Zlín, Czech Republic) have been used. All samples have been measured from the point of their thickness view with the help of a quick thickness meter Mitutoyo, typ 542-401 (Mitutoyo Corporation, Japan). Decontamination mixture has been dosed on samples with plastic a Pasteur´s pipette - volume 3 ml (Merci, Czech Republic) and sliced with a school paintbrush – hardness No 4 (Spokar, Spojené kartáčovny, Inc. Pelhřimov, Czech Republic). After each decontamination cycle pictures with the help of USB mikroskopem DigiMicro 2.0 Scale (Drahtlose Nachrichtentechnik, GmbH, Ditzenbach, Germany) have been made.

4. Working Procedures

Test samples (size 6,5 x 6,5 cm) have been cut from the protective textile with the help of the cutter and the hydraulic press. Samples have been cut in two versions, thus the protective foil without a seam and with the seam. All samples have been marked for their better identification. The thickness has been measured in the middle of samples with the accuracy of 3 decimal places with the help of the quick thickness meter. The sets of samples (each contented 10 samples) have been separates. Every set has been created in accordance to the principle to obtain samples with approximately same thickness. Samples have been wiped with ethanol in order to remove mechanical impurity and grease. Two milliliters of the decontamination mixture have been dosed to the middle of each sample within common laboratory temperature. The volume of the mixture has been immediately sliced with circle movements of the school paintbrush on the whole area of the sample (42 cm^2). The decontamination mixture has worked 15 minutes. After this time the sample has been dried. The surface of the sample has been wetted with the mixture just in the amount to reach the state when the sample has been constantly damp on the whole its area within the whole time of the test. Samples have been rinsed three times in a beaker with distilled water immediately after 15 minutes and put on filtration paper. After approximately 3 hours has been performed next, thus the second decontamination cycle, however, the number of contaminated sets has been reduced. Two sets of samples have been prepared in one day in this way. The total number of decontamination cycles was 10. It means that for preparation of all sets consists of 100 samples 5 days were needed.

5. Results of tests and their discussion

At the beginning of the test all samples have been coloured in a standard way. In the case of samples cut out from the part of the garment with the seam the colour or samples was light green. In some cases the colour was grey-green. This coloration has been considered as normal (figure 1 and 2). It was visible that the thickness of the butyl-rubber mixture has been different. On the figure 1 (left) there is visible texture of the polyamide foil. It can predict lower thickness of butyl-rubber on the sample with the seam than on the sample without it. Generally it is supposed that the seam can cause leakage of the garment and from this reason it is furnished with thicker layer of butyl-rubber in order to prevent of permeation of harmful substances through relatively inhomogeneous connection of two or more parts of the garment.

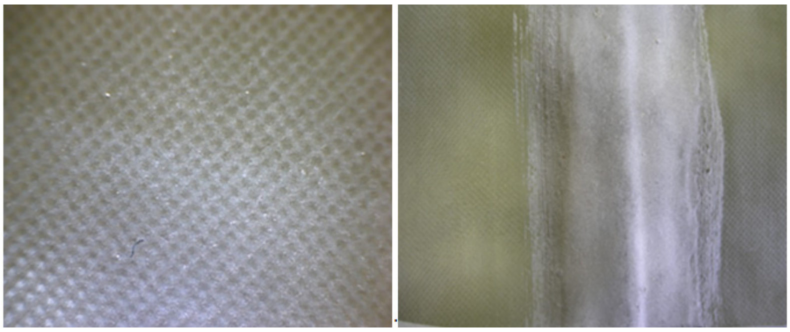

Figure 1: The foil of OPCH-05 at the beginning of the test (on the right sample with the seam)

In accordance to the above mentioned procedure the decontamination mixture has been deposited on samples. The time of contamination (15 minutes) corresponds the time during which the decontamination mixture must actively effect on the decontaminated surface of military vehicles. Based on this fact there is no direct connection between the lengths of the time of real affection of the decontamination mixture with the garments. Just after one cycle to significant changes of both samples of tested material has come. The most significant change has been recorded in coloring. Both samples have diverged from original green, respectively grey-green color to brown one. This change is visible on figure 2.

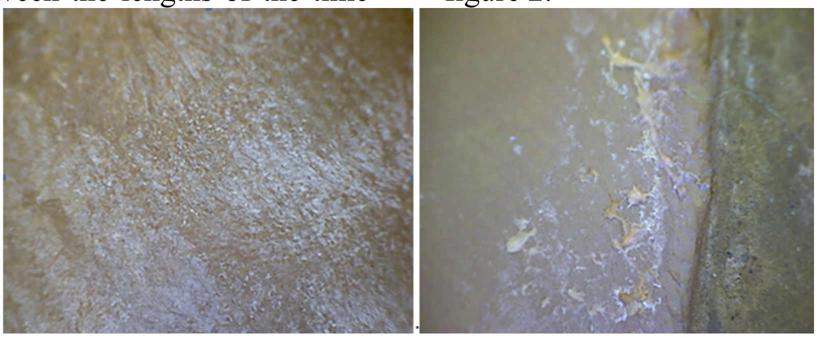

Figure 2: Foil OPCH-05 after one cycle of contamination with decontamination mixture No 1 (on the left the fabric, on the right the seam after the effect of decontamination mixture)

The change of coloration will probably cohere with mutual interaction of a chlorine-oxidation reagent with a color admixture of tested polymeric material. With regard to the fact that N,N-dichlorobenzenesulfonamide (dichloroamine) is a white crystalline matter which does not embody any discoloring effects in combination with liquid 1,2-dichloroethane proceeds into the mixture and discoloring effects are probably multiplied. By the effect of the liquid phase of the decontamination mixture comes to elution of colors and its transfer on the surface of tested material. Here comes to a chlorine-oxidation reaction which is typical with the change of color into brown one. It can be supposed that discoloring effects of dichloroamine will be probably minimal in spite of the fact that it releases chlorine within a contact with organic compounds. Very significant phenomenon which appears even after the first decontamination cycle is swelling of a polymeric coat. It has to be stressed that the butyl-rubber is a strongly non-polar solvent. It keeps this very important property in spite of the fact that for production of OPCH-05 garment it is used in combination with many addition agents. A principle influence on swelling of the polymeric coat will have 1,2-dichloroethane. Hydrogen halogenide non-polar solvents based on chlorinated linear non-saturated hydrocarbons with a short hydrocarbons chain have high ability to permeate with the help of diffusion processes into the structure of sparsely crosslink amorphous polymers. Within employment of prepared decontamination mixture No 1 it is possible to expect that diffusion of larger molecules of dichloroamine will be slower than in case of molecules of 1,2-dichloroethane. It is not excluded that molecules of 1,2-dichloroethane will create the effective area among linear chains of macromolecules of butyl-rubber. To permeation of bulkier molecules of dissolved dichloroamine can come though this area. Moreover, it was observed that samples of tested material have wrested due to significant swelling. Changes of shapes of samples are caused due to change of conformation of polymeric chains within filling gaps among them with the liquid phase of the mixture.

Intensity of the color composition of tested material has been visible continuously even after running other decontamination cycles. It is perceptible from figure 3. On this figure there are photos of samples after six decontamination cycles.

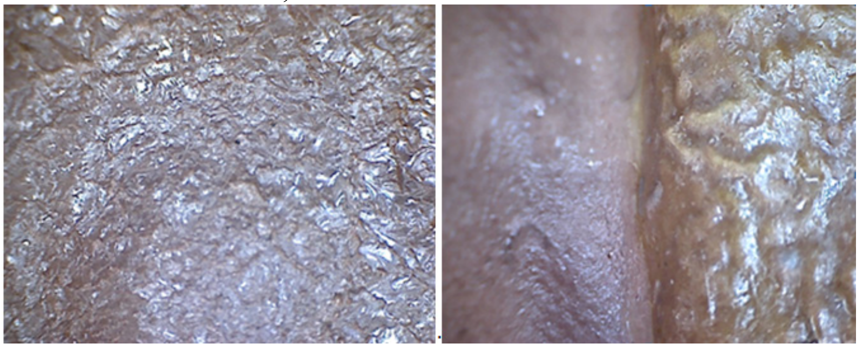

Figure 3: Folio of OPCH-05 after one cycle of contamination with decontamination mixture No 1

It is perceptible from the figure that swelling has reached its peak. It can be supposed that into inner structure of the tested material the decontamination mixture has penetrated and its desorption back on the surface was not possible. Regarding the fact that samples have been almost dry after the time of the measurement it is possible to assume that chains of butyl-rubber has closed and decontamination mixture has affected the material only from the inside. This consideration has shown to be real mainly in case of the sample with the seam which has had wider coat of butyl-rubber than another one.

After finishing of eight decontamination cycle the transfer from light brown color to more intensive brown has been recorded, however, the shade was the same.

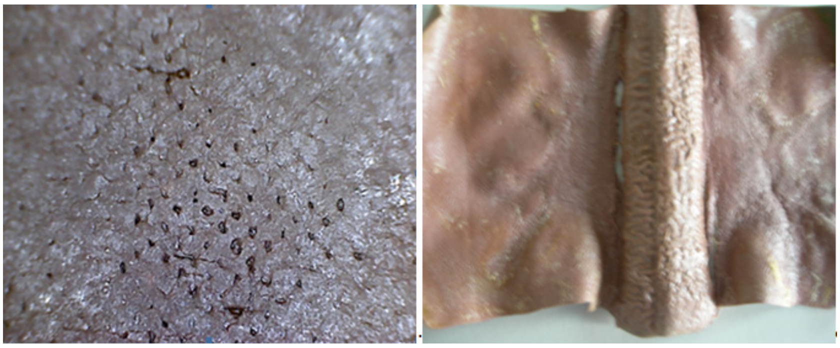

Figure 4: Folio of OPCH-05 after one cycle of contamination with decontamination mixture No 1

From the figure it is visible that destructive effects have caused irreversible changes in the structure of tested polymeric material. Measurement of the thickness of test material has not been done in this phase from the reason of strong failure of the homogeneity. Multiple and relatively long contact of decontamination mixture with tested material has caused the fenestration of samples. In this way characterized samples the transport phenomenon cannot be described with the help of diffusion processes on a molecular level but with processes of penetration. These processes are characterized with penetration of the harmful substance in its liquid phase. In this case the barrier material does not fulfil its protective function. In a practice live it means that it does not come to capture of toxic compounds either on the surface or in the structure of polymeric material. In the case of penetration of tested material comes into the direct penetration of the liquid phase into the area behind the barrier, thus to the direct contact with user´s body surface. Medical risks caused due to affection of liquid phase of chlorine hydrocarbons respectively their saturated steams in a tight contact with user´s skin can be very significant at time when steams of toxic compounds either cannot permeate back or only very slowly. Rigidity of the material significantly has increased due to presence of mixture. At the same time its firmness has decreased and within bend has come to its cracking. All these effects has caused that ta fabric has become inapplicable for providing any protection.

To total destruction of samples tested materials has come during completing the tenth, thus the last decontamination cycle (figure 5). By the affection of very weak mechanical force has come to rupture of the sample of the tested material. In this case has come to very intensive mutual interaction of the decontamination mixture not only with the coat made from butyl-rubber but also with relatively non-reactive fabric made from polyamide. Its structure has been strongly disrupted by the affection of chlorinated hydrocarbons.

Figure 5: Folio of OPCH-05 after ten cycle of contamination with decontamination mixture No 1

6. Conclusions

Provision of constant the CAF CCs´ isolative protection against the affection of toxic compounds is one from conditions for long-term and trouble-free fulfillment of obligations in all types of military operations. Fulfillment of tasks concerning thorough decontamination is one from the typical tasks falling into the CAF CCs responsibility. Current equipment of decontamination units and formations of the CAF CCs is always based on fulfillment of tasks of decontamination with the employment of liquid decontamination mixtures. The CAF CCs specialists´ protection against the affection of single components is very limited. Based on practical negative affection of the decontamination mixture No 1 on barrier material made from polymeric rubber it is possible to claim that it is necessary to study influences of established decontamination mixtures on providing specialist´ isolative protection.

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