The Most Significant Influences of Decontamination Mixtures Containing Chlorinating and Oxidizing Agents on Barrier Materials Formed by Isobutylene - Isoprene Rubber

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The influences of hypochlorite DM with oil ingredient and without it, which is introduced into the armament not only by the Czech Armed Forces Chemical Corps, but also by the chemical services specialists of the Czech Republic Fire Rescue Service, on a substrate consisting of a barrier material based on isobutylene-isoprene rubber (butyl rubber) were presented in this paper. Based on the repeated exposure of the substrate formed by the barrier layer material selected by this decontamination mixture and its subsequent rinsing, a change of the breakthrough time has been studied using the MIKROTEST method employing the chemical warfare agent of sulfur mustard and Congo red as a detecting agent.

Keywords: MIKROTEST, barrier material, butyl-rubber, decontamination mixture, breakthrough time, sulfur mustard, Congo red

The process of achieving a finished product on the market has two key factors to satisfy both the customer / beneficiary (product quality) and the producer (economic performance). In order to achieve these goals, regardless of the area of interest, information from various fields correlates, ensuring high economic parameters and optimal finite products [1-13]. Permanent evaluation of the quality of materials used by the army and the discovery of superior ones implies an efficient and sustainable management by industrial producers in the field. In this context of quality products, when it comes to the army, the problem is all the more acute [14-20]. Protecting the health of soldiers against chemical agents, pathogens, toxic or any other harmful nature is essential. Obtaining materials with protective qualities is in the forefront of the decision makers who manage the production of military equipment [21-39].

Protecting the safety of the CAF Chemical Corps specialists and the Czech Fire Rescue Brigades´ chemical specialists against the dangers associated with exposure to toxic chemical, radioactive, and biological compounds either by inhalation, skin or oral routes is the primary purpose of personal protective equipment also named as individual protective equipment (IPE) or chemical protective clothing. This equipment consists of control devices worn or used while working to protect soldiers from the category of the Chemical Corps specialists and fire rescue brigade chemical service specialists from exposure to hazards caused by chemical warfare agents (CWAs), biological agents and radioactive agents. Most of the time different classes of pesticides are extensively used in agriculture to control harmful pests and to increase the productivity (preventing crop yield losses or product damage). Being know the undesirable effects to human health and their long persistence in the environment, pesticides were used also in different combat situation as chemical warfare agents [8].

Chromatographic methods are recommended for pesticide detection [40,41]. Rapid tests as enzyme-based biosensors are also used for detection of organophosphorus and carbamates pesticides in water and soil samples [42-51].

The decontamination procedures and the use of appropriate equipment are important to prevent the accidental contamination in agro systems, generally in nature [52], and also during some specific military activities.

Decontamination of used IPE prevents further contamination with the toxic compounds from the category of CWAs and toxic industrial chemicals (TICs) that the IPE came in contact with during the course of its use within all types of both military and rescue operations. It is also a means of prolonging the product life of the particular IPE. The economic advantages are obvious. Moreover, IPE is quite expensive and the greatest advantage comes from using IPE to the fullest extent. However, no IPE is designed to last forever and should be discarded long before wearing out. This is valid mainly if chemical specialists repeatedly fulfill their operational tasks in real contamination caused by CWAs and TICs.

Individual protective equipment designated for users´ body surface protection has been produced and subsequently marketed as disposable (use one time and discard), limited-reusable (use several times prior to disposal), or reusable (multiple uses, decontaminations, repairs, and reuses prior to disposal). Products made from the butyl-rubber (hereinafter IIR) belong to the reusable IPE. They must be decontaminated adequately so that the user is not subjected to any residual contamination. Improper decontamination and handling of contaminated IPE, whether single-use or re-usable can create serious health and/or environmental consequences [53,54].

Individual protective equipment produced from a polyethylene-vinyl acetate (PEVA) polymeric mixture

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contains polar chemical compounds whose molecules exhibit electrically positive characteristics at one extremity and negative characteristics at the other. This kind of IPE belongs to the group of limited-reusable IPE of the entire soldiers´ body surface protection. On the other hand, a non-polar compound, thus a non-polar polymeric mixture whose typical representative is the IIR, belonging to chemical compounds whose molecules do not have a positive or negative electric charge [55]. Chemical protective clothing based on this kind of polymeric barrier material belongs to the category of reusable IPE designated for chemical specialist body surface protection.

Regarding IPE contamination, we have to consider two cases: surface contamination and matrix contamination. Surface contamination is the consequence of a contaminant that adheres to the surface of IPE without entering any pores or the molecular matrix. This type of contamination is usually easy to remove, while matrix contamination is much more difficult to deal with because this kind of contamination has to be understood as consequence of a contaminant that permeates into the molecular matrix of the protective barrier material. It is necessary to realize that all materials are permeable to some degree; the matrix is always being contaminated, which represents a potential risk, not only for the IPE´s user but also for other people who manipulate it especially within higher temperature.

Permeation in this case is the process by which the sulfur mustard moves through a sample of the protective clothing material on a molecular level. It covers a multistep process involving the sorption of the toxic compound into the surface of the barrier material, diffusion through the barrier material, and desertion from the other surface. Properties of importance in considering this process include the solubility of the toxic compound in the barrier material as well as the diffusion coefficient [56-58].

While speaking about decontamination processes it is necessary to emphasize that they are very complex due to different parameters and effects that are involved in these systems. This became especially evident when one considers such different processes as for example military vehicles decontamination and detergency or personal care [59]. In accordance to many literature sources the decontamination must be understood as the process by which a chemical agent is partially or completely neutralized, destroyed or removed. All these processes are seldom possible in field conditions [60,61].

The year 2013 became crucial for the determination of changes in the approach to decontamination in the CAF as a whole. There was also initiated a very useful discussion, which aimed to describe the current state in support of decontamination of technical means and decontamination mixtures (DM) and set new trends that its effectiveness should be significantly promoted [62-64].

There moval of biological contaminants and / or organic pollutants can be done by using liquid and gaseous chemical reagents such as fluorine, ozone, hydrogen peroxide, potassium permanganate, hypochlorous acid, chlorine, oxygen, chlorine dioxide, etc.

The strong oxidation effects of halogens and halogenated compounds are well known. Numerous studies highlight the oxidative capacity of these species, especially hypochlorite using different chemical and electrochemical methods, such as: disinfection and sterilization processes related to water and food industry [65-69], electrochemical reduction with a passive effect on the surface of metals [70-72], paper preservation [73], disinfectant for the oral cavity [74].

The most important approaches which have been considered as the fundamental challenges were summarized as follows:

-to rationalize the system of DM in the CAF – to leave DM ODS-5 and OR-3, to establish DM of EDS;

-to solve problems of decontamination of air vehicles with the aim of developing corresponding DM and technical devices for their decontamination;

-to complete the development of compounds for the decontamination of internal surfaces and sensitive materials, including the method of application and compositions for individual protection;

-to carry out research and development in the field of detection and disposal of processed water after decontamination;

-to implement control application (spraying) specified quantity of the DM using a spray streamlines.

After particular applications of the above mentioned challenges it is possible to determine one crucial impact on problems encountered by CAF Chemical Corps specialist in a field of decontamination activities concerning implementation of such DM and their components with minimization of those organic substances which have destructive effects on the underlying barrier material made of polymeric mixture based of IIR.

Influences of DM on a IIR polymeric foil have been studied quite recently. Some results have significantly pointed to the fact that a good choice of the material either practically or potentially used in the branch of specialists´ chemical protection is a crucial part of the whole life-time processing [75-80].

Experimental part

Testing protective suits is performed in the CAF in a stage of their development thus before their introduction into the armament. Testing for the sulfur mustard uses a two-stage chemical reaction between the sulfur mustard and indication treatment agents. Hygroscopic cellulose paper colored by the Congo red color (pH-indicator) is used as a sulfur mustard indicator. The paper is activated after its exsiccation with CNITI-8 chloramide [*N*-chlor-*N*-(2-tolyl)benzamide]. An indication principle lies on CNITI-8 chloramide reaction with sulfur mustard. During this reaction hydrogen chloride is released, which changes an alkali form of the acid basic indicator to an acid one. It is revealed with a change of the Congo red color which alternates from red color into the blue one by the way of the azo-hydrazone tautomery. The indicator paper is in a direct contact with a tested material. The blue-change reveals the place of the sulfur mustard permeation (fig.1). A moment of a threshold amount of the sulfur mustard (0.005 mg.cm^{-2}) permeation is signalized with the first visible blue spot which has an average of 1 mm. This working principle uses the MIKROTEST method in illustrated in figure 2.

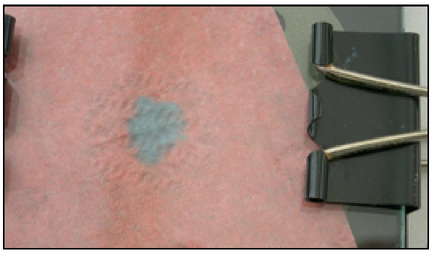

Fig. 1. The blue spot on indicator paper created after sulfur mustard passage through a sample of material

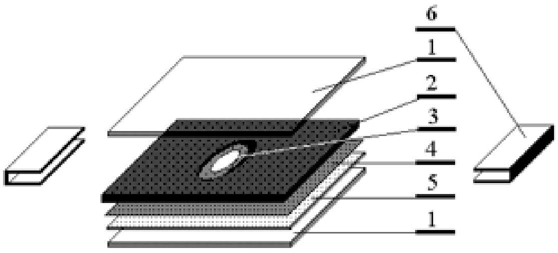

Fig. 2. Arrangement of individual layers when measuring breakthrough time(BT) using the "MIKROTEST" method (1-underlay and covering glass, 2-rubber mask with a cut medial loophole, 3-cut of filtration paper, 4-IPE foil sample, 5-indicator paper, 6-closing clincher)

Table 1

DECONTAMINATION MIXTURES ESTABLISHED IN THE CAF AND THE CZECH REPUBLIC FIRE RESCUE BRIGADES DESIGNATED FOR DECONTAMINATION OF MILITARY VEHICLES, TERRAIN, AND OBJECTS

DM	Composition	Time of Application [min]	Consumption $[dm^3.m^{-2}]$
Hypochlorite DM	2 % $Ca(ClO)_2$, 0.5 % detergent ALFA, 1 % oil, rest water	15 – 30	2.5 – 3.0 warmed 1.5
DM No 1	10% mixture of dichloroamine in dichloroethane	10 – 15	0.5 – 0.6
DM OR - 3	30 % cyclohexylamine, 40 % monoethanolamine, 30 % ethanole, on each liter 98 g KOH	15	0.1 – 0.25
DM OR - 3M	40% diethylentriamine, 30% natriumethanolate, 25%dimethylsulfoxide, 5% xylene	15	0.1 – 0.25
DM ODS-4	3 % detergent LINKA 1, 2 % NaOH, rest water	5	0.5
	0.15 % detergent LINKA 1, 0.1 % NaOH, rest water	immediately	2.5
Emulsion DM	85 volume parts of 10% water suspension of $Ca(OCl)_2$ and 15 volume parts of emulsion oil EO 04	30	0.6 – 1.0
Peroxide DM	30 volume parts of30% hydrogen peroxide and 70 volume parts of organic component of peroxide mixture	30	0.5

Material

The tested material is represented by the isolative protective folio of the chemical specialists garments marked as TP-RUB-001-06 (Rubena, a. s., Hradec Kralove, Czech Republic).For detection of permeated sulfur mustard the cellulose paper with the neutral leach has been used. This paper has been (for purposes of this test) gradually impregnated with 1% solution of the Congo red (pH-indicator) and after its drying with 1.5% solution of *N*-chloro-*N*-(2-tolyl)benzamide [chloramide CNITI-8] in chloroform. For covering this component on cellulose paper the aerosol sprayer DESAGA SG-1 (DESAGA GmbH, Wiesloch, Germany) has been used. Samples of the test material have been put into the set of the MIKROTEST device (fig. 2). The set has been completed and put into the biological incubator of FRIOCEL 111 (Brnenska medicinska technika, CZ).

The implementation of the specific chemical, biological, radiological and nuclear (CBRN) defense measures, as well as the chemical support of the CAF CCs specialists (ie decontamination in depth), is accomplished through the engagement of the established DM, the survey of which is summarized in table 1. Information concerning other used chemicals is summarized in table 2.

Table 2

THE SURVEY AND SPECIFICATION OF USED CHEMICALS

Chemical	Specification, clearness	Producer
Calcium hypochlorite	Universal degassing set UOS-1M, series of 071211	ORIMEPEX, ltd, Prague, CZ
Detergent ALFA	-	Rakona Rakovnik, CZ
Bis(2-chlorethyl)sulfide sulfur mustard	92.7 % distilled sulfur mustard	VOP 072 Zemianske Kostoľany, SK
Oil	NM-35	Distributed network of petrol stations, CZ

Note: The percentage of active chlorine was found using a iodometric method. To find BT, only mixtures containing at least 60% active chlorine were used.

Methods

Test samples (size 6.5x6.5 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 contained 10 samples) have been separates. Every set has been created in accordance with the principle of obtaining samples with approximately the same thickness. The samples have been wiped with ethanol in order to remove mechanical impurity and grease. Two milliliters of the DM have been dosed to the middle of each sample at common laboratory temperature. The volume of the DM has been immediately spread with circle movements of a paintbrush on the whole area of the sample (42 cm^2). The DM has worked 15 min. After this time the sample has been dried. The surface of the sample has been wetted with the DM just in the amount to reach the state when the sample has been constantly damp on its whole area during the test. The samples have been rinsed three times in a beaker with distilled water after 15 min and put on filtration paper. After approximately 3 h has been performed the next stage, 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 consisting of 100 samples 5 days were needed.

Results and discussions

No changes on the surface of the tested material have been observed after the performance of the 1st, 2nd and 3rd decontamination cycle. Test material was not changed and from the point of view of its appearance it was possible to identify it with the original unused fabric (fig. 3a). After the performance of the 4th decontamination cycle has been found that the surface of the sample of the tested material revealed mechanical changes only within hypochlorite DM with oil whereas samples decontaminated with hypochlorite DM without oil have remained the same. The surface of samples repeatedly decontaminated by using hypochlorite DM with oil showed marks of the beginning of swelling (fig. 3b). This fact is possible to be observed only based on the occurrence of stains of darker coloration than the original color of the sample. The appearance of stains is mainly visible in the middle of the sample and on its left side.

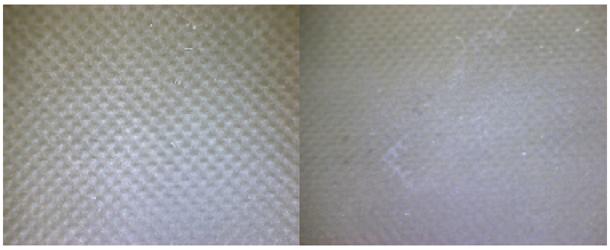

Fig. 3. Appearance of samples of the tested material (a) at the beginning of the measurement, b) after 4 cycles of decontamination with the employment of the hypochlorite DM with oil)

Swelling on the surface of the tested material is with the biggest probability caused by a mutual interaction of IIR with oil. With an increasing number of performed decontamination cycles using hypochlorite DM with oil, the swelling destructive effects have been more intensive (fig. 4b a 5b). The intensity of swelling has been more serious after the performance of the 6th, 8th and the 10th decontamination cycle. It is very probable that samples decontaminated after the 6th cycle revealed effects of continuing destruction of samples which have been exposed in former decontamination cycles. Based on findings, it is possible to suppose that disruption of the polymeric barrier layer has been irreversible and further increasing of the contamination time only deepened the effect of the hypochlorite DM. It has been shown that samples denary exposed with hypochlorite DM with oil not return to the original state.

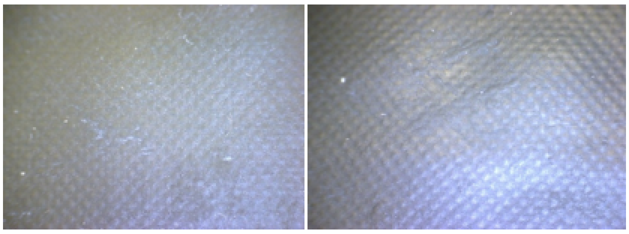

Fig.4. Appearance of samples of the test material of the isolative foil of OPCH-05 after repeated decontamination with hypochlorite DM (a) after 7 cycles, b) after 8 cycles with usage of the hypochlorite DM with oil)

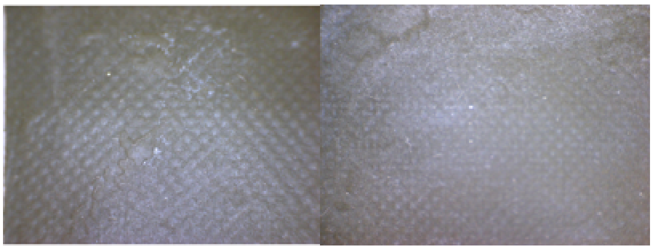

Fig. 5. Appearance of samples of the test material of the isolative foil of OPCH-05 after repeated decontamination with hypochlorite DM within finishing of the examination (a) after 10 cycles, b) after 10 cycles with usage of the hypochlorite DM with oil)

Moreover, after finishing the 6th decontamination cycle, white stains have been observed on the surface of samples of test material. These stains have been probably caused by the presence of the crystalline form of the calcium hypochlorite. The solid phase of the calcium hypochlorite was revealed on the samples surface within all followed decontamination cycles, however, its appearance has been more intensive with increasing number of decontamination cycles regardless a triple rinse of samples after each decontamination cycle. Figure 5 shows the final state of the samples of tested material at the end of the test.

In the same figure on the left and at the top right are shown disturbed structures of sample which were at the beginning of the test fully homogeneous. It is very likely that this situation will not change and the tested material samples were deformed permanently. The results of the measurements show that the solid crystalline phase of calcium hypochlorite is likely to cause disruption of the internal structure of the linear chains, which have lost their elasticity and consequently the ability to achieve the most energy-efficient state. It can also be assumed that the destructive effects caused by disruption of the internal structure of the linear polymer material create more efficient space for repeated and intense permeation of organic components hypochlorite DM (oil). Repeated exposure of tested material samples to oil has caused bigger space to be formed, it has been used for permeation

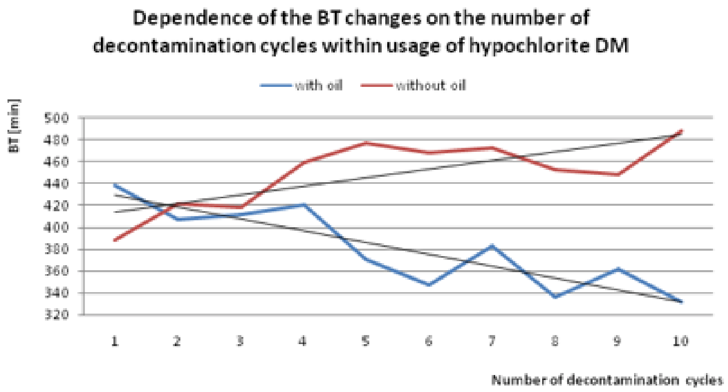

Fig. 6. Duration of dependence of the BT change of tested material after repeated decontamination with hypochlorite DM with oil and without it

of other melted components of hypochlorite DM (polar phase) which could affect bigger areas and thus even bigger volume.

Influences incurred after repeated decontamination with hypochlorite DM with oil and without it being significantly reflected on the changing chemical resistance expressed with BT, which is evident from figure 6.

When comparing results relative to the value of BT of the pure sample, which has been in average 399 min, it can be concluded that after tenfold repeated decontamination of tested material with hypochlorite DM without oil the BT increased to 488 min, adding about 89 minutes. It turned out that hypochlorite DM penetration into the inner structure of the sample of material is associated with the crystalline phases of calcium hypochlorite and causes closure of the IIR polymer structure not only on its surface, but probably also inside. It was found that the closure of the polymeric structure of the crystalline phase of calcium hypochlorite favors BT of the test material.

It has further been demonstrated that the crystalline zones created are likely to act as a retaining volume for the sorption processes of the test chemicals which significantly slows down diffusion processes. It is likely that due to creation of detention zones of the barrier the material becomes less permeable. From the course of the red curve (fig. 6) it may be further noted that repeatedly decontaminated fabric with hypochlorite DM without oil has a higher resistance (higher value of BT) for the passage of the test chemicals (sulfur mustard). It can also be noted that it is likely to affect the rate of diffusion due to reduced mobility of the polymer chains in the amorphous part whereas the end of the string is mounted in the side of crystalline lamellas, which necessarily leads to a higher activation energy of diffusion. All these facts were confirmed by performing linear regression analysis.

An opposite effect on change of BT was observed in the study of repeated decontamination of the tested material of the isolative protective folio using hypochlorite DM with oil. When comparing the BT of the sample, which was decontaminated with hypochlorite DM with oil the value of BT determined after the 10th decontamination cycle was a significant decrease in BT from 399 min to 332 min, about 67 min. The decrease of the value of BT is noticeable based on the curve, which is the result of a linear regression analysis. This decrease of BT was caused by the relatively significant swelling effects, which were discussed for figure 4. It was confirmed that oil due to its non-polar nature intensively permeates into the internal structure of samples of the tested material. Based on a very high boiling point of oil, which is given in the literature of about 180°C, it is possible to believe that oil permanently affect samples of the tested material or the reason that from the structure of the sample, it diffuses into the surrounding environment.

Taking into account the results, it can be assumed that its effect is repeatedly multiplied with the number of decontamination cycles (during which appears the swelling and a significant number of damaged sites into the inner structure of the samples).

The hypochlorite DM contains an oxidizing agent. It means that this mixture contains oxygen and chlorine that will readily take on electrons. When using protective material based on IIR polymeric materials repeatedly manipulated with this MD it could be claimed that it provides protection against hazardous chemical, however, some destructive effects can occur and subsequently reduce it. These protective materials have served their purpose well over the years. However, in order to complete certain tasks concerning all activities in the scope of partial and thorough decontamination, preparing, transportation and dividing this kind of DM, greater attention is required. Furthermore, protective garments made of IIR polymeric material is very susceptible to be attacked by petroleum products and is inherently flammable. This fact has been clearly verified with decreasing BT. Care must be therefore taken in using IPE containing IIR in this presence of these latter hazards.

Conclusions

Following changes of BT of materials used for providing isolative protection to the CAF CCs specialist after repeatedly performed decontamination (with hypochlorite DM with oil and without) it has been found that it comes to the significant changes of the chemical resistance of the tested material, which has not been comprehensively studied recently. It was confirmed that for studying the changes of the resistance of the particular tested materials of the isolative type after performed decontamination, the method MIKROTEST can be used. The results demonstrate that the relationship between the particular material being tested and this DM must continuously be studied. It turns out that the effects of this DM are necessary to be studied very carefully and in the long run. The performed experimental measurements referred to certain aspects of the destructive influence of hypochlorite DM on test material and confirmed previously acquired theoretical and practical knowledge.

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