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ORIGINAL ARTICLE

RESISTANCE OF THE ISOLATIVE PROTECTIVE GARMENT DESIGNATED FOR SPECIALISTS´ PROTECTION AGAINST SELECTED CHLORINATED HYDROCARBONS

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Summary

Chlorinated hydrocarbons are very often used and are relatively dangerous substances from healthy risk point of view. While manipulating with them, mainly in large volumes, individual protective equipment (IPE) must be used in a protection position. Users are supposed to know the construction material breakthrough time especially in case of long-term usage of personal IPE and in the situation when contamination of them is real. Studying connections between a chemical compound structure and the structure of IPE characterised by barrier materials enables us to understand present body protective devices protection quality and gives us an option to choose barrier materials with targeted properties. In this article there are results of breakthrough time of isolating protection folio with a butyl rubber barrier layer in relation to chlorinated ethanes. This material is used for protection of specialists of both Fire Rescue Brigades and the Czech Armed Forces Chemical Corps. The PIEZOTEST device has been used for detection of permeated chemicals. The Quartz Crystal Microbalance (QCM) sensor is a part of PIEZOTEST device.

Key words: Permeation Rate; Lag-Time; Steady State Permeation Rate; Breakthrough Time; Toxic Industrial Chemicals; Protection Property; Construction Material.

INTRODUCTION

Within Individual Protective Equipment (IPE) employment there is an assumption that a user will know its real protective properties. Related to IPE designated for body surface protection it is the knowledge of breakthrough time of materials in relation to toxic chemical compounds and temperatures. Although, within introduction of protective equipment into the Czech Armed Forces (CAF) and to the market in accordance with the norm of ČSN EN ISO 6529 [1], determination of its resistance to selected chemical compounds is not known in case of real usage. Very often the user has no information about real protective properties of the equipment not only generally but also for a particular contaminant. In case that it is the contaminant of which chemical composition is clear the prediction of protective properties is very difficult. From this reason the study of protective materials´ resistance performed with respect to the chemical structure of test chemicals is profitable not only for the final user but also for selecting suitable

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barrier polymeric materials in a framework of a proposal of resistant equipment for body surface protection. The result of the study of constructional materials should be mainly used to achieve knowledge of its resistance for under interest chemical compounds. At the same time it can be used for determination of a relationship of material resistance on a chemical structure of test chemicals among them. Based on this knowledge it is possible to predict resistance of constructional materials for homologs, analogs and isomers.

THEORETICAL PART

Chlorinated hydrocarbons are, from the chemical composition point of view, very aggressive compounds affecting very intensively the constructional materials created from a butyl rubber barrier layer. The CAF have in their armament a decontamination mixture whose basic components are dichloramine and dichloroethane. Although, this decontamination mixture is not designated for decontamination of IPE it is prepared in a decontamination vehicle. In this case the service has to use the IPE in a protective position. Even if the service is very careful within the decontamination mixture preparation the stain of the garments can reveal. It can be, however, always accompanied by reduction or even loss of protective properties of IPE. From this reason it was interesting to verify how resistance of the equipment designated for specialists can be changed after affection of dichloroethane. Chlorinated ethanes are important as solutions as well as intermediate products for the whole range of chemical products and that is why it was efficient to study the change of resistance. These changes have been studied in relation to the change of breakthrough times of the isolative protective foil for specialists with butyl rubber polymeric barrier in a line of 1,2-dichloroethane (CAS 107-06-2), 1,1,2-trichloroethane (CAS 79-00-5) and 1,1,2,2-tetrachloroethane (CAS 79-34-5). An increasing number of chlorine atoms could show how the chlorinated hydrocarbons can behave in similar ranges.

Butyl rubber is a strongly nonpolar polymer. However, it is possible to consider that organic solutions which are either of nonpolar or weakly polar character will cause substantial changes in its structure. These changes can probably impact the loss or essential reduction of protective properties of such constructional materials where the butyl rubber is used as the barrier material. Nonpolar or weakly polar solutions can cause enormous swelling of protective materials with the butyl rubber polymeric layer in a place of a contact with the particular solution. This process undoubtedly reduces protective and product manufacture qualities of constructional materials. Furthermore, a molar volume of above mentioned chlorinated hydrocarbons can have a significant influence on permeation solution through barrier materials.

The device of PIEZOTEST has been used to study the breakthrough time [2]. This device uses a Quartz Crystal Microbalance (QCM) sensor with the polymeric layer for capturing harmful substances permeated through tested materials. The QCM sensor is built into a spare electrical network of a quartz resonator which is a part of a permeation cell. The PIEZOTEST device is able to measure an amount of the permeated harmful substance with high sensitivity. The change of the QCM sensor working frequency is a response on the capture of the particular substance. If we change a type of the QCM sensor polymeric layer we can then affect its sensitivity for interest groups of chemical substances. The experimentally employed device declares high sensitivity for nonpolar and weakly polar solutions [3].

The resistance of isolative protective folios expressed by a value of breakthrough time is increased by the growth of test chemical´s concentration on a back side of the folio. In the case of measurements of breakthrough times in static conditions a cumulative amount of the test chemical on the foil´s back side is measured. In case of the PIZOTEST device the growth of the amount (concentration) Δm permeated into the QCM detector diffusion area in a unit of time and captured in its polymeric layer is expressed by the difference of working frequency Δf in time t. An output curve related to dependence of cumulative permeation on time can be constructed from the dependence of Δf on time. From this dependence it is possible to read time of resistance, so called lag-time (t_l). Bronwich claims [4] that lag-time is often identified with the breakthrough time. Mainly within isolative protective folio with short time of permeation and with severe growth of test chemical´s concentration after achievement of breakthrough time (protective ability), the value of lag-time can be marked as fully the same as breakthrough time with no respect of the norm concentration of permeation. Based on the knowledge of lag-time, the value of diffusion coefficients D for different materials can be determined [5].

USED DEVICES, TEST CHEMICALS AND EQUIPMENT

For the study of resistance of barrier materials, 1,2-dichloroethane (clearness p.a., Lachema, Brno, the Czech Republic), 1,1,2-trichloroethane (96%, Sigma-Aldrich, s. r. o. Prague, the Czech Republic) and 1,1,2,2-tetrachloroethane (reagent grade, ≥ 98 %, Sigma Aldrich, Prague, the Czech Republic) have been used.

The thickness of the isolative folio has been measured with the help of the quick thickness meter of 542-401 (Mitutoyo, Japan) with the exactness of three decimal numbers. Heating of permeation cells with a sample has been performed before and during measurements in the biological incubator Friocell 111 (BMT medical technology, Ltd., Brno, the Czech Republic) with the exactness of ±1 °C. For measurement of breakthrough times the PIEZOTEST device (GRYF HB, Ltd., the Czech Republic) has been employed. The test material - the isolative protective folio of the garments for specialists´ protection OPCH-05 TP-RUB-001-06, Rubena, a. s., Hradec Králové, the Czech Republic has been produced for the final producer of the OPCH-05 garment ECO Protect spol. Ltd., Zlín, the Czech Republic. From footage of isolative folio the samples have been cut with the help of a knife and a presser (Polymertest, Zlín, the Czech Republic). Particular measurements of resistance have been performed within the temperature of 30 °C. Chlorinated ethanes have been dosed into the area of permeation cell in the volume of 2 cm^3.

RESULTS AND DISCUSSION

The thickness of samples has been measured with the help of the quick thickness meter in the middle part. Samples have been chosen in accordance to a rule to have simple sets of samples for unique test chemicals in quite similar thickness. As it is visible from the table 1, mean value of samples for 1,2-dichloroethane was 0.337 mm, for 1,1,2-trichloroethane it was 0.335 and for 1,1,2,2,-tetrachloroethane 0.349 mm. Because of the fact that in a branch of individual protection it is a custom to work with minimal values of protective parameters, we also introduced minimal values of thickness of isolative protective folio in the table. These values describe the conditions for subsequent assessment of constructive materials protective properties in a better way.

Experimental measurements of chemical resistance of samples of isolative protective folio with butyl

Table 1. Statistic evaluation of thickness of isolative protective folio OPCH-05 samples [mm] for measurement in static conditions concerning chemical resistance for selected chlorinated ethanes.

Statistical value	Test chemical		
	1,2-dichloroethane	1,1,2-trichloroethane	1,1,2,2-tetrachloroethane
Mean value	0.337	0.335	0.349
Mean value error	1.17E-03	1.17E-03	1.80E-04
Median	0.337	0.336	0.349
Standard deviation	4.68E-03	4.69E-03	7.19E-04
Variance	2.19E-05	2.2E-05	5.17E-07
Kurtosis	-0.403	-1.289	-0.541
Skewness	0.713	-0.136	0.731
Minimum	0.331	0.327	0.348
Maximum	0.346	0.342	0.348
Valid number	16	16	16
Reliability level (95 %)	2.49E-03	2.50E-03	3.83E-04
Minimal value	0.335	0.332	0.348

Table 2. Statistic evaluation of results concerning measurements of chemical resistance of isolative folio OPCH-05 for chlorinated ethanes [min] for the temperature of 30 °C.

Statistical value	Test chemical		
	1,2-dichloroethane	1,1,2-trichloroethane	1,1,2,2-tetrachloroethane
Mean value	9.9	21.9	50.5
Mean value error	1.2	1.6	1.8
Median	7.8	20.2	51.3
Standard deviation	4.8	6.2	7.0
Variance	23.1	37.9	49.6
Kurtosis	2.3	-0.1	3.9
Skewness	1.7	0.5	-1.5
Minimum	5.4	11.3	30.3
Maximum	22.7	33.4	60.0
Valid number	16	14	16
Reliability level (95 %)	2.6	3.6	3.8
Minimal value	7.3	18.3	46.8

rubber barrier layer have shown that material of OPCH-05 is less resistant against chlorinated ethanes. 1,2-dichloroethane permeated within a short period time through this folio and its breakthrough time expressed by so called lag-time value is less than 10 minutes (table 2). Minimal value for the set of samples was only 7.3 minutes, thus this material does not even reach the 1st degree of the chemical resistance in accordance with ČSN 943-1 [6] for a liquid phase. Permeation of 1,2-dichloroethane through examination material is very quick as proved by a quick increase of the values of QCM sensor working frequency in time (Figure 1), thus concentration of test chemical grew on the back side of isolative protective folio in dependence on time. The isolative protective folio very quickly loses its protective properties and in relatively short time from the beginning of permeation it is not able to protect the user against outer contamination. Middle value for 1,1,2-trichlotoethane was 21.9 minutes and for 1,1,2,2-tetrachloroethane 50.5 minutes. Corresponding minimal values

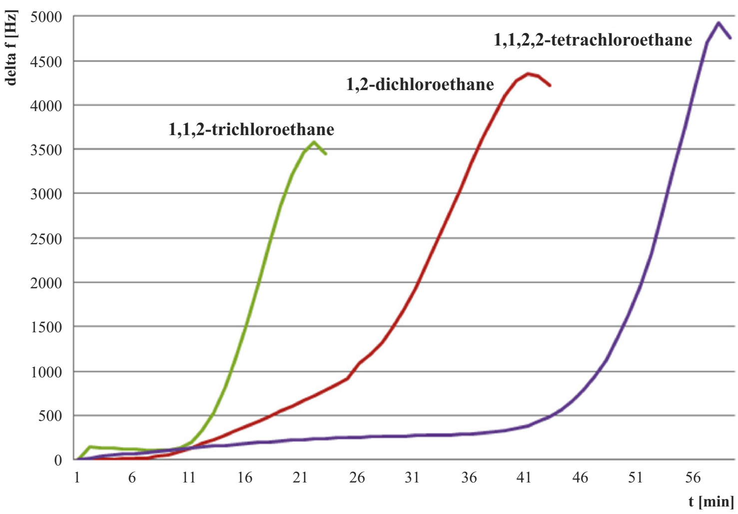

Figure 1. Dependence of growth of QCM sensor working frequency in time for chlorinated ethanes.

of breakthrough times for tested material were 18.3 minutes for 1,1,2-trichloroethane and 46.8 minutes for 1,1,2,2-tetrachloroethane. Therefore, even these two test chemicals are perceptible on the back side of the examined material.

Experimental data have confirmed that with the growth of the number of chlorinated atoms in basic molecule of ethane there is prolongation of breakthrough time. Butyl rubber is a nonpolar linear polymer and that is why we can expect that nonpolar compounds will permeate quicker through this material. When we compare polarities of test chemicals expressed by values of their relative permittivity (dielectric constants), which is a quantity expression of solution´s polarity (Table 3), all these compounds have comparable polarities. In accordance to Lowery and Richardson [7], solutions with values of dielectric constants lesser than 15 are considered as nonpolar. Based on this division all above mentioned test chemicals can be ordered in a group of nonpolar compounds. Therefore, comparable polarity of test chemicals does not create more favorable conditions to permeation of some of them through the barrier created by butyl rubber.

Permeation of compounds through barrier materials also depends on their thickness. Earlier performed experimental work has shown that the shorter the breakthrough time of materials, the lower the influence of increasing of barrier material thickness concerning isolative protective folio resistance. This dependency is valid even in contrary, too. Significant differences among breakthrough times for simple test chemicals could thus not be caused by differences in thickness of samples of isolative protective folio. For tempering of permeation cells with samples we used the biological

Table 3. Basic physical data of test chemical.

Test chemical	Molar weight M_r, g.mol^{-1}	Relative permittivity [8] $\varepsilon_r(T)$	Molar volume V_M, [cm^3.mol^{-1}]	Density ρ, [g.cm^{-3}]
1,2-dichloroethane	98.96	10.42 (293.2)	79.168	1.25
1,1,2-trichloroethane	133.41	7.1937 (298.2)	92.638	1.44
1,1,2,2-tetrachloroethane	167.85	8.50 (293.2)	105.566	1.59

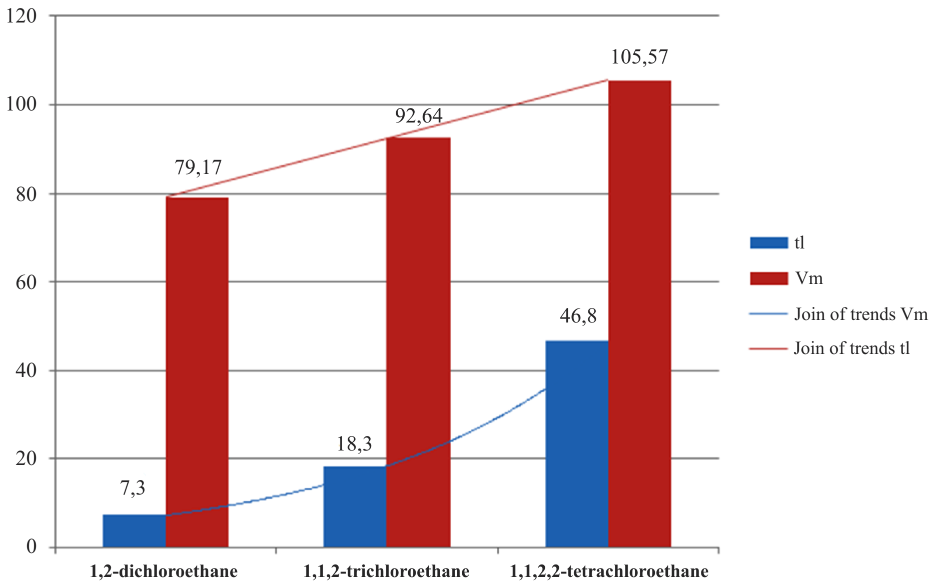

Figure 2. Comparison of increasing of breakthrough time of isolative protective folio and molar volumes for test chemicals.

incubator Friocell 111 which is able to measure and keep temperature very exact with the exactness of ± 1 °C. Due to this fact, oscillation of temperature can be excluded.

Based on the analysis of factors which can affect resistance of isolative protective folio, it is possible to suppose that prolongation of breakthrough time in the line of 1,2-dichloroethane < 1,1,2-trichloroethane < 1,1,2,2-tetrachloroethane is caused by increasing of the molar volume of chlorinated ethanes in mentioned orders. If the growth of molar volume between 1,2-dichloroethane and 1,1,2-trichloroethane is 17 % and between 1,1,2-trichloroethane and 1,1,2,2,-tetrachloethane is 13.95 %, then increasing of breakthrough time between 1,2-dichloroethane and 1,1,2-trichloroethane is 2.5 multiple, similarly as between 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane, where it came to increasing of breakthrough time by the multiple of 2.56 (Figure 2). Growth of breakthrough time in dependence on molar volume of test chemicals is not possible to use automatically, however, it is always necessary to take into account also the relationship between a structure of the chemical compound and polymeric material creating the barrier layer of isolative protective folio. Earlier performed measurements [9,10], however, show that for estimation of resistance of the isolative protective folio it is possible to take the change of molar volume as one of the crucial criteria. Nonetheless, consideration is needed to perform in a scope of not only homological lines and analogs but also for isomers.

Influence of solution on changes of isolative protective folio has been observed in duration of measurements. From the figure 3 it is clear that solutions cause rather important swelling.

Swelling reveals with emphasis of the structure of a polyamide carried fabric. It is also visible in a form of deformation (twisting) of the sample.

Test chemicals which have been in margin on the isolative protective folio were colored with resolved colors from the examined material. This effect was observed mostly by 1,1,2,2-tetrachloroethane which had been in contact with the tested material for the longest time period. It was observed that colors rinse from the polymeric material away and moreover, the polymeric material changes its composition. From the reproducibility of the employment of garments point of view, it would be quite undoubtedly interesting to study what swelling and rinsing of colors and others compounds can cause in the scope of evaluation of protective and mechanical properties of protective garments.

CONCLUSION

The study of the relationship of a pair of both substances represented by polymeric barrier layer – solution has not only theoretical but mainly also practical importance. The possibility of prediction of constructive materials resistance against chemical

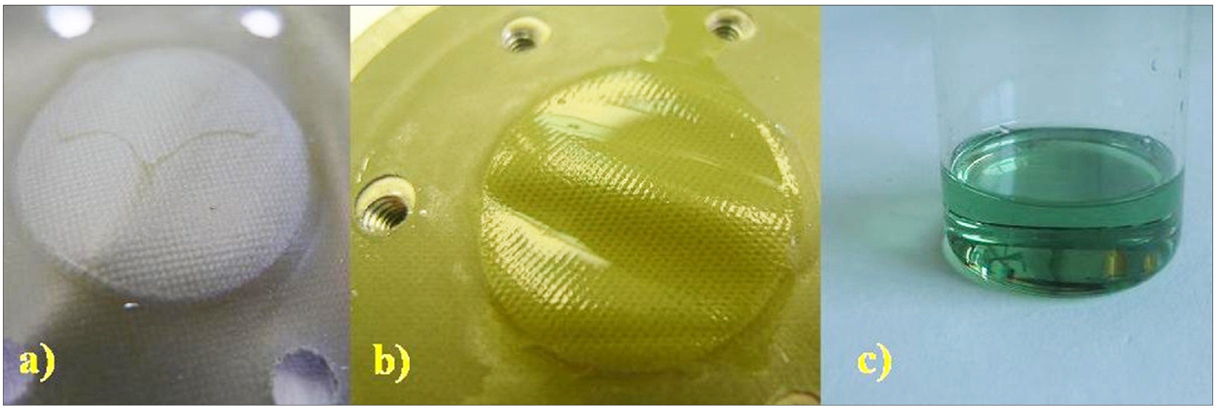

Figure 3. Swelled samples of isolative protective folio and coloration of solution after measurements of breakthrough time.

a) sample of material after exposition of 1,2-dichloroethane
b) sample of material after exposition of 1,1,2,2-tetrachloroethane
c) 1,1,2,2-tetrachloroethane after finishing of the probe

compounds based on their chemical structure is important mainly when it is not possible to perform selection of protective equipment and when people performing the activities in contaminated areas or with chemical substances, mainly of the organic type, have only available one type of the garment for themselves. Moreover, repeated contamination with these solutions can cause non-recurring changes and gradual damage of material´s construction. It can finally lead to total limitation of breakthrough time, thus to a health threat.

Knowledge of either breakthrough times or their qualified estimation is the basic condition for fulfillment of tasks in contaminated areas or for work within a period of time when a protective garment must surely protect and it cannot cause damage of health to its user. Health protection should be first-rate tasks. Excellent protection of health is not fulfilled by wearing protective garments and other protective aids but by perfect knowledge of their protective properties and influences which can significantly change them especially in the area where very dangerous contaminants like chlorinated hydrocarbons occur. They are dangerous mainly due to their toxicological properties and very wide employment in industrial technologies.

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