

# APARATURA

## BADAWCZA I DYDAKTYCZNA

### Retention of two dialkyl alkylphosphonates and a phosphoramidate utilized as chemical weapons agents simulants in a polyurethane rubber matrix

IRMA GAVILÁN GARCÍA<sup>1</sup>, DANTE GIMENEZ<sup>2</sup>, JAVIER C. QUAGLIANO<sup>2</sup>

<sup>1</sup>DEPARTMENT OF ORGANIC CHEMISTRY, FACULTY OF CHEMISTRY, NATIONAL AUTONOMOUS UNIVERSITY OF MEXICO (UNAM), MEXICO CITY, MEXICO

<sup>2</sup>ARGENTINE INSTITUTE FOR SCIENTIFIC AND TECHNICAL RESEARCH OF THE MINISTRY OF DEFENSE (CITEDEF), VILLA MARTELLI, BUENOS AIRES, ARGENTINA

**Keywords:** chemical weapons agent simulant, polyurethane rubber, retention

#### ABSTRACT

In this article we report the retention of two dialkyl alkylphosphonates and a phosphoramidate in a polybutadiene-based polyurethane rubber matrix. Two dialkyl alkylphosphonates, which are degradation products of nerve chemical weapons agent (CWA) and a phosphoramidate, were tested in this study for penetration into the rubber matrix. They are often used as a simulant of CWA. One of the dialkyl alkylphosphonates and the phosphoramidate were synthesized and the rubber matrix was challenged with these chemicals for retention and penetration using three different thickness of barrier material. Under the experimental conditions tested, no penetration of chemical simulants on the rubber was observed. Our results suggested that this polyurethane matrix could be a potential barrier material for protection against CWA.

#### Zatrzymywanie w gumie poliuretanowej dwóch dialkiloalkilofosfonianów i fosforoamidu stosowanych jako symulanty bojowych środków trujących

**Słowa kluczowe:** symulanty bojowych środków chemicznych, guma poliuretanowa, zatrzymywanie

#### STRESZCZENIE

Opisano zatrzymywanie dwóch dialkiloalkilofosfonianów i fosforoamidu w gumie polbutadienowo-poliuretanowej. Dwa dialkiloalkilofosfoniany, które są produktami degradacji bojowych środków trujących (BST) z grupy trucizn nerwów i fosforoamidu badano pod kątem ich wnikania do gumy. Przeprowadzono syntezę jednego dialkiloalkilofosfonianu i fosforoamidu, które wraz z handlowym dialkiloalkilofosfonianem nanoszono na gumę w celu określenia ich zatrzymywania oraz przenikania stosując różne grubości gumy. W warunkach doświadczenia nie stwierdzono przenikania symulatorów przez gumę. Otrzymane wyniki pozwalają sądzić, że guma poliuretanowa może być stosowana do ochrony przed BST.

## 1. INTRODUCTION

The new international context of a potential terrorist attack has elicited the research on protection against CWA. Due to the toxicity of CWA, direct evaluation cannot be accomplished through the use of a specific agent [1]. For this reason, chemical simulants with similar physicochemical properties to CWA are utilized. Dimethyl methylphosphonate (DMMP) was chosen as a simulant for having P=O, P-CH<sub>3</sub> and P-OCH<sub>3</sub> functional groups which are also found in both Sarin (GB) and Soman (GD) [2]. Today DMMP is one of the most utilized simulant for the nerve agent chemical weapons type. Particularly, diethyl methylphosphonate (DEMP) and diisopropyl methylphosphonate (DIMP) are simulants for GB [3]. Sulfur dioxide and methyl acetoacetate were reported as Sarin simulants; bis(2-ethylhexyl) hydrogen phosphate and diethyl phtalate with a fluorescent dye tracer was used as VX simulant presumably because they behave like VX [4]. The estimation of persistence and resistance to permeation of CW simulants of sulfur mustard and Sarin through different polymeric barriers was thoroughly studied [5, 6].

Chemical warfare agents often need to be decontaminated not only in battlefields but also in production and storage sites. Furthermore, equipment surfaces and personnel may also need to be decontaminated. Hence, interactions between the surface and the agent are a major concern, together with the contamination density, decontamination time and destructivity [7]. Nerve agents can penetrate to a certain extent latex rubbers; therefore, isolation suits and butyl rubber gloves are required [8, 9].

Permeation is a complex process that involves both kinetic and thermodynamic processes. The competitive kinetic processes are droplet evaporation versus diffusion into the protective material. The thermodynamic property is the equilibrium solubility of the test liquid in the barrier material [10]. Studying permeation through barrier polymers is necessary for designing low sorption and chemical agent-resistant polymers. Active oxides such as zinc and titanate were tested for its destructive activity against nerve and mustard agents simulants and analyzed if any penetration may proceed [3].

The standard method for testing the modification of rubbers exposed to oils, greases, fuels, and

other fluids is the ASTM D471-12. It includes the measurement of several parameters such as dimensional change when exposed to liquids, mass of soluble matter extracted by these liquids and change in mechanical properties. As this test requires a large amount of data we adopted a direct methodology of challenging samples with a drop of CWA simulant for penetration. This methodology is presented as an alternative for testing in the bibliography, including the methodology of total submersion of samples in the challenging liquid. The variables to test permeability of materials in a full experimental test would include chemical nature and physical state of barrier (elastomer or thermoplastic), chemical-material interaction type and heterogeneity of material [5]. Rubbers from different chemical composition such as butyl, silicone, neoprene and others are normally used for the manufacture of personal protection equipment like gas masks. However, much less is reported for polyurethane rubbers. In this study, we report the results of challenging a polyurethane rubber matrix with three CWA simulants, utilizing attenuated total reflectance Fourier transformed infrared (ATR-FTIR) spectroscopy and X-ray energy dispersion analysis (EDAX) as analytical techniques. These results are relevant to the objective of finding novel polymer barriers to be utilized as protection layers against CWA in military and civilian equipment.

## 2. EXPERIMENTAL

Dimethyl methylphosphonate (97%) was purchased to Sigma Aldrich Co. Argentina. CWA simulants diethyl methylphosphonate and diisopropyl N,N-dimethyl di-isopropyl phosphoramidate (DIPDMP) were synthesized in our laboratory and checked for its identity and purity by <sup>1</sup>H-NMR [CDCl<sub>3</sub>: δ 1.35 (t,6H), 1.46-1.53 (d,3H), 3.81-4.3 (m,4H)] and GC-MS [MS (m/e): 211 (M+), main secondary ions at 168, 152, 126, 108, 44)], respectively.

Polyurethane (PU) rubber matrices were synthesized in our laboratory by reaction of hydroxy-terminated polybutadiene (M<sub>w</sub> 2600) and glyceryl monoricinoleate, cured with toluene diisocyanate and catalyzed with stannous dibutyl laureate (0,05% w/w). After 3 hours polyurethanes were completely cured and ready for the study.

Permeation disk specimens were challenged with a liquid drop of each of the three chemicals:

DMMP, DEMP and DIPDMP and allowed to reach a steady state. We adopted this methodology because we did not have enough volume of simulants to perform a submersion test. One barrier material and three CWA simulants were included in the experimental design. Samples were incubated for 24 h or alternatively 7 days and washed with water for 30 minutes and ethanol for 5 minutes.

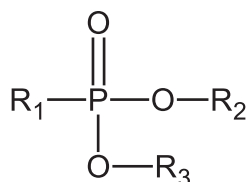
ATR (attenuated total reflectance) FT-IR spectroscopy studies were performed using a Nicolet 520 spectrometer utilizing a KBr window, utilizing a Spectra Tech ATR attachment with an horizontal ZnSe crystal. The collected spectra were analyzed using Omnic 3.0 software.

Scanning electron micrographs (SEM) were performed using a Phillips 515 microscope at an energy of 18 kV, using the  $K\alpha$  emission line of Cu. EDAX results were processed using Genesis v.5.21 programme. The results were expressed as a percentage of the total elements captured by the microprobe (1  $\mu\text{m}$  width circumference with 1  $\mu\text{m}$  penetration into the sample).

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization and identification of n-dialkyl n-alkylphosphonates

We first synthesized diethyl methylphosphonate and diisopropyl dimethyl phosphoramidate. For obtaining the double or mixed esters such as DEMP, we made the reaction between alkyl phosphonyl dichlorides and the corresponding couple of alcohols, using triethylamine as a quencher of the hydrochloric acid produced. The chemical structure of DAAP is similar to that of nerve agents, as can be seen in the Figure 1.

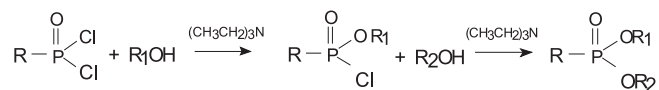


**Figure 1** General formula of the n-dialkyl n-alkylphosphonates synthesized

**Rysunek 1** Ogólny wzór zsyntezowanych n-dialkilo-n-alkilofosfonianów

For purifying the products, micro vacuum distillation was done at pressures of 0,2-1 mm Hg. The general method for preparing mixed esters is sketched as follows:

For characterizing and identifying the compounds, two techniques were utilized:  $^1\text{H}$ -RMN and gas chromatography coupled to FT-infrared spectroscopy (GC-FTIR).



**Figure 2** Reactions corresponding to the methods utilized for mixed esters n-dialkyl n-alkylphosphonate synthesis

**Rysunek 2** Reakcje odpowiadające metodzie syntezy n-dialkilo-n-alkilofosfonianów

Capillary-spiked 25  $\mu\text{l}$  drops of the three simulants were placed both on the surface of polybutadiene-based polyurethane alone and the same polymer loaded with 20% (w/w) titanium dioxide and left for one week at ambient temperature (20-25°C). After 7 days the surface was washed with distilled water during 30 minutes and with ethyl alcohol for 5 minutes. When the surfaces where the drops were placed were analyzed by ATR-FTIR no residues of the simulants were detected, as seen in the Figure 3.

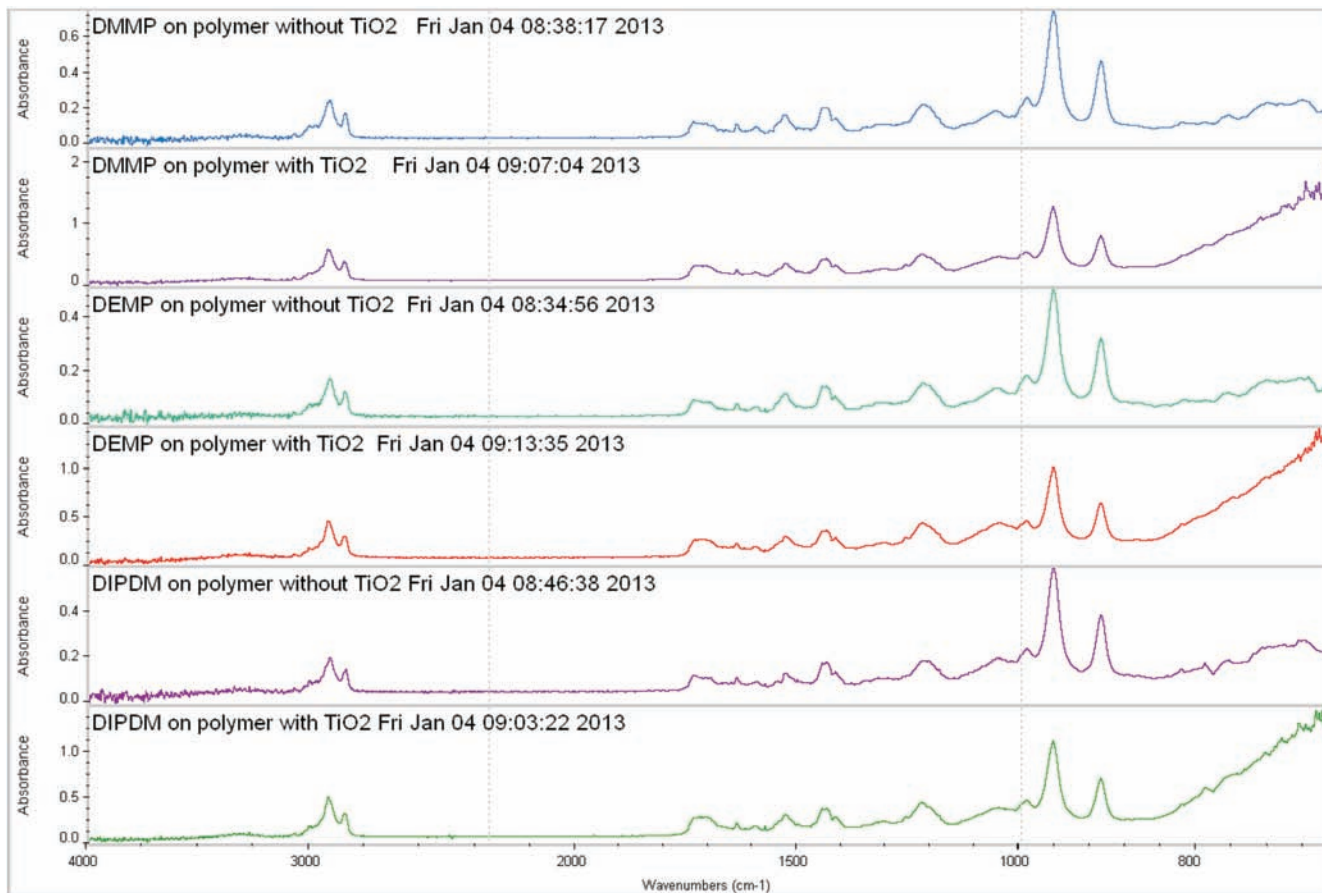
DEMP, DMMP and DIPDMP simulants were not detected on PU neither with nor without  $\text{TiO}_2$ . These results suggested that the simulants were not adsorbed into the PU matrix under the test conditions, both with and without the addition of titanium oxide. This later was added to the rubber formulation because metal oxides like titanium oxide are well known for its photocatalytic activity for the destruction of many toxic chemicals, particularly CWA [11]. At the same time, scanning electron micrographs were taken on PU alone and loaded with  $\text{TiO}_2$  and are shown in the Figure 4.

Micrographs revealed that the PU matrices are very dense, suggesting that the simulants could not easily penetrate inside the polymer. The cavity in left SEM was due to the deposition of dust particle from environmental air.

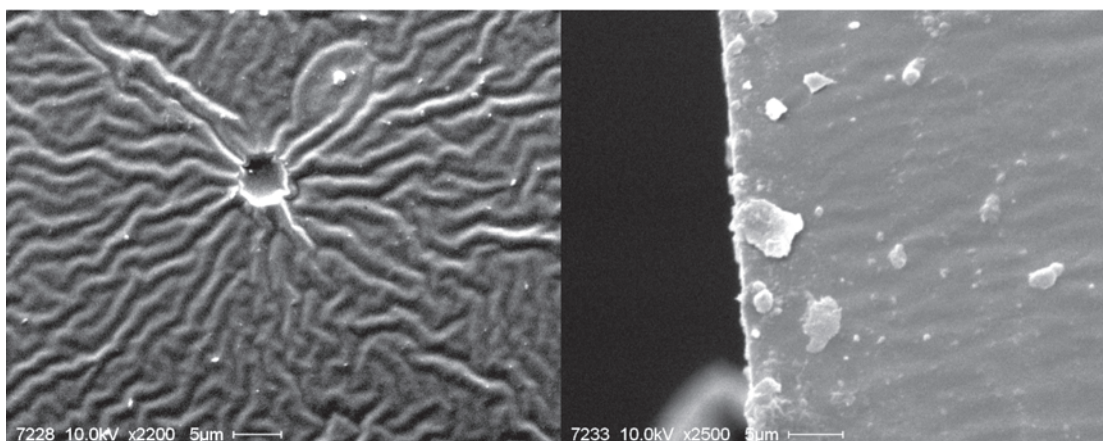
#### 3.2 Evaluation of penetration by EDAX

To further evaluate the extent of simulants retention in the polyurethane rubber matrix, an EDAX study was performed. One drop of each simulant was placed over the rubber, and left overnight at ambient temperature (around 20°C). This incubation period was selected as it was reported that breakthrough times of less than 24 hours are experimentally convenient and are less likely to require addition of more liquid to prevent evap-





**Figure 3** ATR-FTIR spectra of polyurethane rubber spiked with DEMP, DMMP and DIPDMP  
**Rysunek 3** Widma ATR-FTIR gumy poliuretanowej, na którą naniesiono DEMP, DMMP i DIPDMP



**Figure 4** Micrographs of polyurethane rubber. Left: surface. Right: transversal cut  
**Rysunek 4** Mikrografy gumy poliuretanowej, lewe – powierzchni, prawe – przekroju poprzecznego

oration to dryness [5]. Then the samples were submerged in water for 30 minutes and later with ethanol for 5 minutes. EDAX results showed that 12% of phosphorus was retained in the 500 µm rubber film when this was challenged with DMMP. When rubber films of three different widths (20, 220 and 500 µm) were inverted and analyzed for full penetration no phosphorus signal was detected. Similar results were found with

DEMP and DIPDMP. Results are shown in the following Table 1.

Even when incubation time was extended to 7 days, no traces of phosphorus were found with any of the three investigated simulants after performing the washing procedure. When protecting against hazardous chemicals, glove material thickness was reported as an important factor in determining breakthrough time and permeation



**Table 1** Retention of CWA simulants in a polyurethane matrix under the experimental conditions

**Tabela 1** Zatrzymywanie symulatorów BST w gumie poliuretanowej w warunkach doświadczenia

PU barrier material thickness ( $\mu\text{m}$ )	Retention of CWA simulant (%)		
	DMMP	DEMP	DIPDMP
20	0.2	0.2	0.1
220	0.5	0.05	0.5
500	12	2.4	0.6

rate. However, a thinner glove was more resistant to challenge than a thicker of other material [6], thus no generalizations can be made.

#### 4. CONCLUSIONS

CWA simulants tested in this work did not penetrate into polyurethane rubber matrices after 7 days of exposition at room temperature up to the detection limits of ATR-FTIR and EDAX techniques. However, from the state of the art we are aware that other more sophisticated techniques not utilized in this work could detect chemicals up to a much lower detection limit [12]. For example, thermal desorption ion mobility spectrometry (TD-IMS) demonstrated much lower detection limit for simulants, in the order of nanograms, offering clearer advantages of speed, high throughput and versatility over chromatographic methods of analysis for detecting CWA

simulants [13]. Anyway, it is not likely that a surface giving negative results for the presence of simulants by ATR-FTIR and EDAX could be toxic to first responders or decontamination personnel, respect to the amount of hazardous chemical that could penetrate. These preliminary results suggest that this matrix could be useful as a protection layer for different surfaces in equipment utilized for defense and protection against CWA. Moreover, it could be easily applied by brushing or aspersion onto metal, glass or plastic surfaces, and normally cheaper than nitrile rubber. Only one barrier material and three CWA simulants were included in this experimental design. We should point out that a full experimental design might include a number of CWA compounds, simulants and different barriers. However, the chosen methodology attempts to simulate severe exposure conditions through controlled accelerated testing, although any direct correlation with actual performance as a barrier is concluded, since service conditions vary too widely. In this respect, the very detailed report of Rivin and coworkers has concluded that the data found using different test methods and conditions were not consistent with each other [5]. Thus, experimental conditions should be specified to the details. Overall, our results suggested that this polyurethane matrix rubber could be a potential barrier material for protection against CWA, although more investigations are needed to establish performance and to specify service conditions of this barrier.

#### REFERENCES

- [1] Glaser J. Chemical warfare agent simulants. *Clean Technologies and Environmental Policy*, 2008, 10, 4, 319-321.
- [2] Kanua A., Haigh P. and Hill H. Surface detection of chemical warfare agent simulants and degradation products. *Analytica Chimica Acta*, 2005, 553, 148-159.
- [3] Ramaseshan Z., Ramakrishnan, Z., and Ramakrishnaz S. Zinc Titanate Nanofibers for the Detoxification of Chemical Warfare Simulants. *J. Am. Ceram. Soc.*, 2007, 90 [6] 1836-1842.
- [4] Croddy J. and Wirtz J. *Weapons of mass destruction: an encyclopaedia of worldwide policy, technology and history*. 2005, ABC-CLIO, Santa Barbara, California.
- [5] Rivin D., Wendel J., Shuely Palya F., Jr., Lindsay R., Rodriguez A. and Bartram P. Estimation the Persistence Resistance of Non Barrier to Sulfur Mustard (HD) and Sarin (GB) Chemical Warfare Agents using Liquid Simulants. 2008, National Institute for Occupational Safety & Health (NIOSH).

- [6] Daugherty, M., Watson A. and Vo-Dinh T. Currently available permeability and breakthrough characteristics of chemical warfare agents and their simulants in civilian protective clothing materials. *Journal of Hazardous Materials*, 1992, 30, 243-267.
- [7] Kim D., Gweon B., Moon S. and Choe W. Decontamination of the chemical warfare agent simulant dimethyl methylphosphonate by means of large-area low-temperature atmospheric pressure plasma. *Current Applied Physics*, 2009, 9, 1093-1096.
- [8] Noeller T. *Biological and Chemical Terrorism: Technology and Management*. Cleveland Clinic Journal of Medicine 2001, 68, 12.
- [9] Report on Penetration of CWA on different matrices. 2004-2005. Research Project held for the Organization for the Prohibition of Chemical Weapons (OPCW) at the Department of Applied Chemistry of the Argentine R&D Institute for the Defense, Buenos Aires, Argentina (in spanish and english).
- [10] Söderstrom M. and Ketola R. Identification of nerve agents and their homologues and dialkyl methylphosphonates by gas chromatography/Fourier transform infrared spectrometry (GC-FTIR). *Fresenius J. Anal. Chem.*, 1994, 350: 162-167.
- [11] Vorontsov E., Smirniotis P. and Kozlova A. Comparative study on photocatalytic oxidation of four organophosphorus simulants of chemical warfare agents in aqueous suspension of titanium dioxide. *Journal of Photochemistry and Photobiology A: Chemistry* 2004, 162, 503-511.
- [12] Brickhouse M., Creasy W., Williams B., O'Connor R., Dupont Durst H. Multiple-technique analytical characterization of a mixture containing chemical-weapons simulant from a munition. *Journal of Chromatography A*, 2000, 883, 185-198.
- [13] Kanu A., Haigh P. and Hill H. Surface detection of chemical warfare agent simulants and degradation products. *Analytica Chimica Acta* 2005, 553, 148-159.