Central Fire Brigades Advisory Council
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Joint Committee on Fire Research

Degradation of Chemical Protective Clothing

by KIRSTY BOSLEY

Research Report Number 69

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Degradation of Chemical Protective Clothing

The Fire Research and Development Group (FRDG) was asked to investigate the possible deterioration of the chemical protective qualities of chemical protective clothing with use. Chemical permeation tests were carried out on fabrics that are currently used in chemical protection suits worn by the UK Fire Service.

INTRODUCTION

In 1994 the FRDG published a report on decontaminating chemical protective suits (see Note 1). One conclusion of this work was that it is impossible to be sure that a contaminant has been completely removed from a suit by primary decontamination processes (i.e. showering or scrubbing the suit to enable the firefighter to remove it without being contaminated). Consequently, there is a possibility that chemicals may remain on the surface of, and within the matrix of, the suit. The presence of these chemicals may alter the protective characteristics of the suit the next time it is used.

The aim of the work described in this report was to look for any change in the chemical protective qualities of suits, particularly where they had been subject to contamination from known chemicals during operational use, even though there was no visible damage.

Unfortunately, it proved difficult to obtain contaminated suits from brigades because:

- There were few suits that had been heavily chemically contaminated.
- Suits that had been heavily contaminated were often returned to the manufacturer or destroyed.
- The precise histories of the chemicals to which the suits had been exposed were not always known.

Although some of the suits obtained for this work had been chemically contaminated, others were well worn but may not have been in contact with hazardous chemicals. For each old suit fabric that was obtained, a new sample of similar fabric was obtained from the suit manufacturer for comparative testing. A summary of the fabric samples that were tested is given in Table 1.

The protective qualities of the fabrics were measured in terms of the breakthrough time of a battery of chemicals (specified in the draft European standard on chemical protective clothing, see Note 2). This is a measure of the time that it takes molecules of the chemical to permeate (or break through) from one side of a sample of fabric and to be detected on the other side. The shorter the time, the poorer the protection afforded by the fabric. Twenty fabrics were tested, and each one was subjected to 15 chemicals. The breakthrough times for the used and new fabrics were compared to find out whether any change had occurred.

Each permeation test required a sample of fabric approximately 3 cm in diameter. 45 samples of each fabric were required (3 tests of each of 15 chemicals).

Samples were taken from an area of the suits just below the knees. This was considered to be an area where suits were most likely to have been exposed to chemical contamination. It also presented a difficult area to clean after an incident. Only standard fabric areas were used, i.e. seams or toughened knee patches were not used. Any visibly damaged areas were avoided.

EXPERIMENTAL METHOD

A diagram of the equipment is given in Figure 1. A piece of the sample fabric is held horizontally between two cells. The top cell contains the test chemical and the bottom cell contains a detection

Sample No	Suit Type	Made by	Fabric Type
1	Coverall liquid tight	Respirex	Neoprene
2	Non-coverall liquid tight	Beadle	PVC
3	Non-coverall liquid tight	RFD	Neoprene
4	New fabric	Respirex	Neoprene
5	New fabric	Respirex	PVC
6	Coverall gas-tight	Respirex	HNB
7	New fabric	Respire	HNB
8	New fabric	Beadle	PVC
9	Non-coverall liquid tight	Beadle	PVC
10	Non-coverall gas-tight	Beadle	Double coated PVC
11*	Coverall gas-tight	Respirex	Viton/butyl
12	Coverall gas-tight	Respirex	HNB
13	New fabric	Respirex	Viton/butyl
14	Coverall liquid tight	Respirex	PVC
15	Non-coverall gas-tight	RFD	Neoprene
16	Coverall liquid tight	Respirex	Neoprene
17	New fabric	Beadle	Double coated PVC
18	Non-coverall gas-tight	Beadle	Double coated PVC
19	New fabric	Sea Dog**	Neoprene
20	Non-coverall gas-tight	Beadle	Double coated PVC

Table 1 : Origin of the fabrics

Notes to Table 1:
*Sample 11 — Contaminated with chlorine.
**Sea Dog & RFD — RFD were taken over by Sea Dog - thus samples 3,15 and 19 are comparable
Coverall suits go over the top of BA cylinders and the BA mask.
Non-coverall suits are worn under BA cylinders with the suit sealing around the outside of the BA mask.

medium flowing through the cell. This detection medium is regularly analysed to detect and measure the test chemical. From this the permeation rate is calculated. The breakthrough time to the nearest minute is the time when the permeation rate of the chemical reaches 1.0 $\mu g/cm^2/min$.

Gases were tested using a modified version of this method. In this, the sample chemical flowed slowly through a modified top cell at a constant pressure. The breakthrough time was calculated as shown.

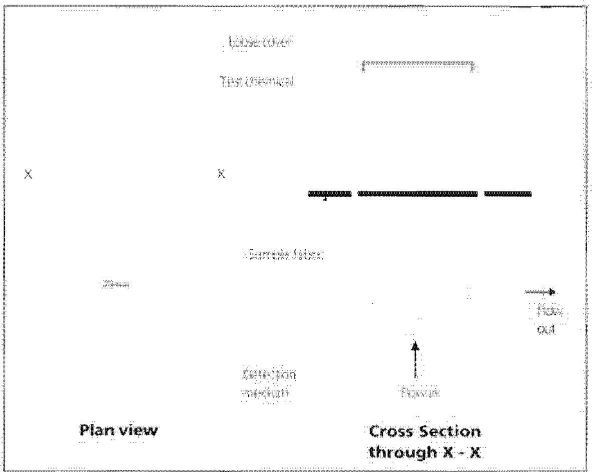


Figure 1 : Permeation Test Cell

Each fabric was tested with each chemical three times. Times were measured to the nearest minute. The breakthrough time quoted is the mean of the three tests.

The permeability of a fabric was described in terms of classes, with the breakthrough times being grouped into the classes shown below.

Class	Breakthrough Time (minutes)
6	greater than 480
5	greater than 240
4	greater than 120
3	greater than 60
2	greater than 30
1	greater than 10

Table 2 : Classification of permeation resistance

Any fabric with a breakthrough time of 10 minutes or less was not classified.

The battery of 15 chemicals that was selected for testing is shown in Table 3 below.

Chemical Name	Liquid or Gas	Class of Chemical
Acetone	L	Ketone
Acetonitrile	L	Nitrile
Ammonia	G	Basic inorganic gas
Carbon disulphide	L	Sulphur organic compound
Chlorine	G	Acidic inorganic gas
Dichloromethane	L	Chlorinated hydrocarbon
Diethylamine	L	Amine
Ethyl acetate	L	Ester
n-Hexane	L	Aliphatic hydrocarbon
Hydrogen chloride	G	Hydrochloric acid
Methanol	L	Alcohol
Sodium hydroxide 40%	L	Inorganic base
Sulphuric acid 96%	L	Inorganic acid
Tetrahydrofuran	L	Heterocyclic ether
Toluene	L	Aromatic hydrocarbon

Table 3 : The Chemical Test Battery

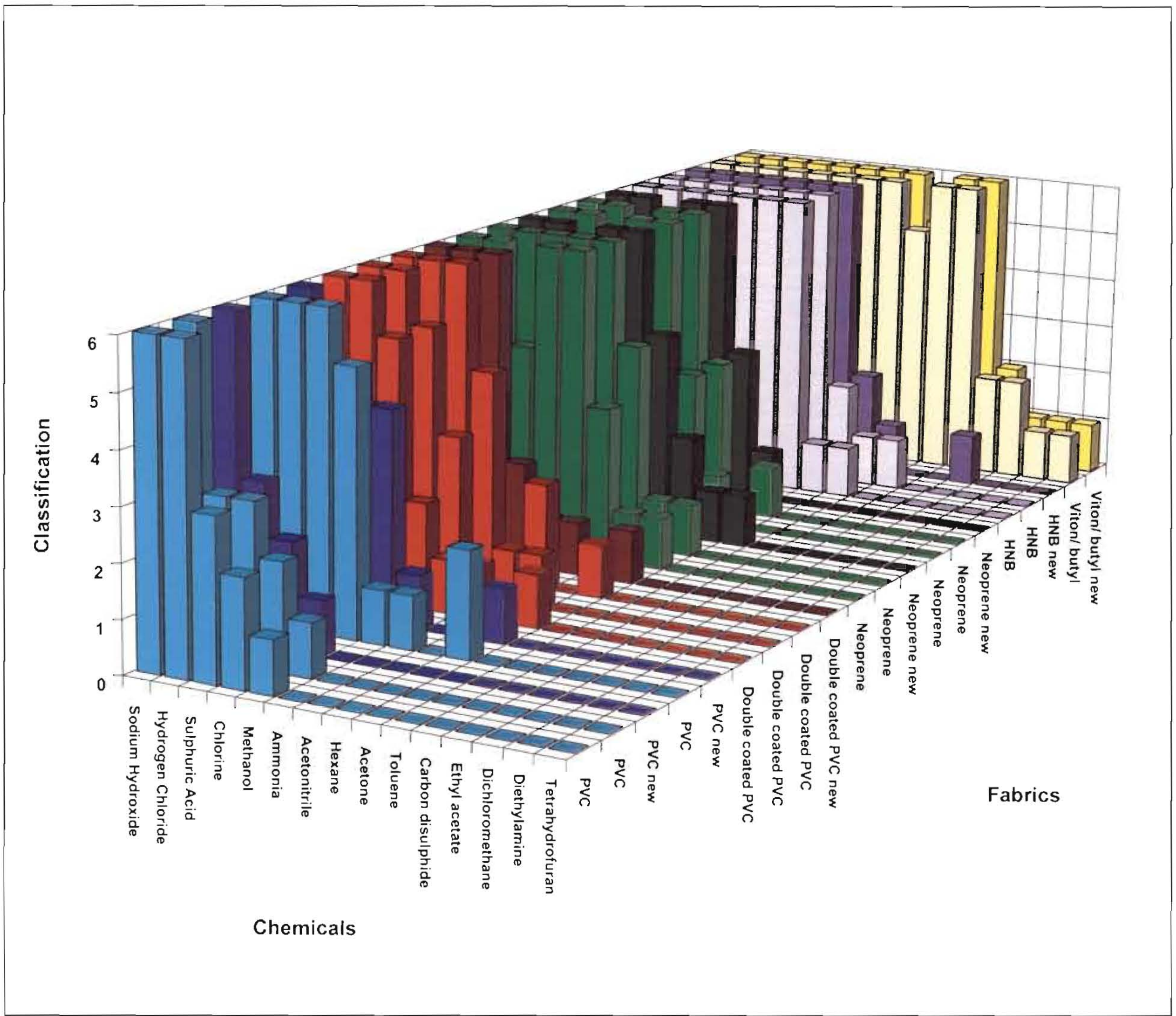


Figure 2 : Graphical summary of the permeation classification results

RESULTS

The permeation classification results are summarised in Figure 2. The actual classifications are given in Table 4 at the end of this report.

In this graph, where no column is visible, the chemical has permeated through the fabric in a time of less than 10 minutes (unclassified). The tallest columns, a class 6 pass, shows that the chemical did not permeate through the fabric, even after 8 hours.

The permeation breakthrough times were subjected to statistical analysis to compare the results from old test samples to those from the new. Not all cases could be submitted to this test as there were sometimes insufficient samples to make such a test valid. However, in 11 of the 45 cases that could be tested, there was a significant change in the permeation properties of the fabric samples.

When results from the new fabrics were compared to those from the old the following changes in permeation resistance emerged:

- Single coated PVC improved with age against two chemicals.
- Double coated PVC worsened with age against one chemical.
- Respirex neoprene worsened with age against three chemicals.
- Beadle neoprene worsened with age against one chemical.
- HNB worsened with age against four chemicals.

DISCUSSION

General

The results of the tests are discussed in the context of the draft European standards for gas-tight and liquid tight chemical protective clothing (see Note 2) in order to identify whether a loss in permeation performance during use has occurred.

It should be borne in mind that the standards for emergency teams are only at a draft stage and have yet to be circulated for public comment. Therefore these drafts will be the subject of discussion and probable amendment before publication as European standards.

Furthermore, the materials tested during this work, with perhaps the exception of viton/butyl, have not been developed and produced on the basis of the performance requirements contained in the draft European standards.

In theory, any of the fabrics that were tested could be used in a liquid tight suit. In practice, hypalon/neoprene/butyl (HNB) and viton/butyl are used almost exclusively in gas-tight suits. PVC (single and double coated) and neoprene are the most common liquid tight suit fabrics. Fabrics for use in liquid tight suits only need to be tested against the liquid test chemicals in the battery (i.e. not chlorine, ammonia or hydrogen chloride) and a Class 1 pass (greater than 10 minutes) is acceptable without any qualification. Fabrics for use in gas-tight suits should be tested against all the chemicals in the test battery.

Additionally it is recognised that the chemical permeation test used in this work, whilst being a satisfactory test method, does not replicate what is likely to occur at operational incidents. While it may be less likely for suits to be exposed to continuous contact with chemicals (as they are in these tests), when they are in operational use they are more likely to be stretched, wrinkled, scuffed or imperfect in some way. Work is currently in hand in Europe to develop a reproducible 'splash permeation test' in an attempt to replicate, in a test environment, the conditions of real life situations.

The results in Table 4, giving the permeation classes, show that many of the fabrics tested would be unclassified (less than or equal to 10 minutes breakthrough time) against most of the chemicals. An unclassified result is represented by a 0 in Table 4. For several of the chemicals, most fabrics do not even achieve a Class 1 classification. For example, against tetrahydrofuran all fabrics are unclassified except viton/butyl which only provides a Class 1 pass.

In the following sections, the performance of individual suit fabrics is discussed. The overall change in permeation performance is found by using the statistical tests described in the Results section above.

Single Coated PVC

Single coated PVC has been one of the most commonly used suit fabrics. It is relatively cheap, but is becoming less popular as brigades opt for fabrics with a higher degree of permeation resistance. The single coated PVC is held on one side of a polyester base. Samples of single coated PVC from Beadle and Respirex suits were tested.

One new sample of single coated PVC failed to achieve a classification against 11 of the 15 chemicals. The other sample failed against 9 of them. Both of these new samples withstood only one chemical for more than 480 minutes (Class 6 pass).

Single coated PVC was unclassified against 8 of the 15 chemicals for all old and new fabrics.

The older samples of single coated PVC showed an increased permeation resistance against some of the chemicals. This improvement in permeation resistance occurs when elastomers in the surface of the fabric evaporate. This makes the PVC brittle and prone to cracking, but also increases its permeation resistance.

Double Coated PVC

Double coated PVC has both sides of a polyester base coated with PVC. It offers a slightly improved performance over single coated PVC. The used samples in these trials were all from non-coverall gas-tight suits.

New, double coated PVC failed to achieve a classification against 8 chemicals, but withstood 3 of them for more than 480 minutes to gain a Class 6 pass.

All old and new samples of double coated PVC failed to gain a classification against 7 of the 15 chemicals.

Statistically, the old fabric performed worse than the new against one chemical, but gave a similar performance against all others.

Neoprene

Neoprene is a commonly used fabric for suits. It offers a compromise between cost and performance. Samples of neoprene from Respirex and RFD suits were tested.

Of the two new samples of neoprene, one failed to achieve a classification against 6 chemicals, while the other failed against 8 of them. Both samples withstood 4 chemicals for more than 480 minutes.

All old and new samples of neoprene failed to gain a classification against 6 of the chemicals. All samples of neoprene resisted permeation of 4 of the chemicals for more than 480 minutes to gain class 6 passes.

Statistically, all used samples of neoprene (RFD and Respirex) showed a significant decrease in permeation resistance against one chemical, while used Respirex neoprene (samples 1 and 16) also showed significantly reduced permeation resistance against a further two chemicals.

Hypalon/Neoprene/Butyl (HNB)

HNB is a rubber based multi-coated fabric. It is durable and tough and provides a higher degree of protection than neoprene alone. It is commonly used as a fabric for gas-tight suits.

New HNB was unclassified against 5 chemicals, but withstood 7 of them for more than 480 minutes.

All old and new samples of HNB resisted permeation for over 480 minutes against 7 of the chemicals. However, they all failed to gain a classification against 4 of the chemicals.

Statistically, samples of used HNB performed significantly worse than new fabric in four cases.

Viton/Butyl

Viton/butyl is a relatively new and expensive, multi-coated, rubber based fabric, with good protective qualities. It is available on a nomex or polyester backing. The viton/butyl samples that were tested were on nomex backing. The used sample came from a suit that was relatively new, but that had been exposed to contamination by chlorine.

This sample offered the opportunity to consider whether the permeation resistance of a suit was reduced by exposure to a chemical that had previously been encountered. Both the new and used fabrics resisted permeation to chlorine for greater than 480 minutes.

Viton/butyl was the least permeable fabric tested. All old and new samples were classified against all 15 chemicals, and resisted permeation for more than 480 minutes against 10 of them. In every case it performed as well as, or better than the other fabrics.

Because there were only two samples of viton/butyl, statistical tests could not be carried out on the results. However the results of old and new samples were close enough to imply that there was little or no change in the permeation performance of the fabrics.

CONCLUSIONS

Although some chemical protective clothing fabrics may sometimes suffer a deterioration in their permeation resistance that might not be detected by visual examination, the majority of the permeation tests revealed no significant differences between the performance of new fabrics and that of used fabrics.

In two cases, the permeation resistance of single coated PVC significantly improved with age, but since old PVC is prone to a reduction in flexibility, and therefore an increased risk of the fabric cracking, it was not considered advantageous overall.

In a few cases there were significant reductions in the permeation performance of the used fabrics. These significant reductions showed no pattern (they were not for example all caused by one chemical, or on one fabric), except that they occurred where the original permeation performance of the new fabric was relatively low. In only one case did a significant reduction happen where the new fabric had a Class 2 rating. All others were Class 1 or less. This suggests that although there may be a reduction in the permeation qualities of used suit fabrics, it does not occur unless the permeation performance of the original new material is relatively low.

It must be remembered that none of the fabrics which were tested were designed to comply with the draft European standard. Of the fabrics tested only viton/butyl would comply with this standard. No other fabric achieved a rating of Class 1 or higher against all the chemicals in the test battery used, with a number of fabrics being unclassified.

ACKNOWLEDGEMENTS

Acknowledgements are due to all the brigades and manufacturers who co-operated in these tests by providing fabrics, advice and assistance.

NOTES

1. FRDG Publication number 9/94, "An Assessment of Fire Service Methods of Decontamination", J. Rimen, 1994.

2. Draft European Standard prEN 943 part 2. Protective clothing for use against liquid and gaseous chemicals, including liquid aerosols and gaseous particles. Performance requirements for "gas-tight" (Type 1) protective clothing for emergency teams (ET)

and

Draft European Standard prEN 466 Part 2 . Protective clothing for use against liquid chemicals, Performance requirements for chemical protective clothing with liquid tight connections between different parts of the clothing for emergency teams (Type 3 ET)

FURTHER INFORMATION

The following report provides more details of the work carried out in this project:

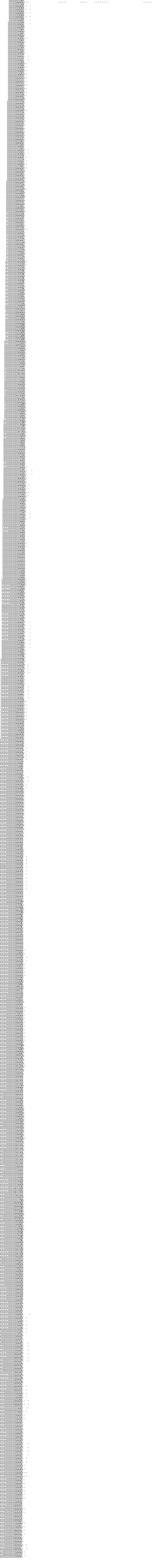
FRDG Publication number 9/96, "Degradation of Chemical Protective Clothing", K. Bosley, 1996

Fabric Type	Sample No	Manuf	Acetone	Aceto-nitrile	Ammonia	Carbon disulphide	Chlorine	Dichloro-methane	Diethyl-amine	Ethyl acetate	Hexane	Hydrogen Chloride	Methanol	Sodium Hydroxide	Sulphric Acid	Tetrahydro-furan	Toluene
PVC	2	Beadle	0	0	0	0	2	0	0	0	0	6	1	6	3	0	0
PVC	9	Beadle	0	0	0	0	2	0	0	0	0	3	1	6	3	0	0
PVC new	8	Beadle	0	0	0	0	1	0	0	0	0	3	0	6	2	0	0
PVC	14	Respirex	0	0	1	0	5	0	0	0	2	6	1	6	6	0	0
PVC new	5	Respirex	0	0	0	0	4	0	0	0	1	2	1	6	4	0	0
Double coated PVC	10	Beadle	0	0	1	0	2	0	0	0	1	6	1	6	5	0	0
Double coated PVC	18	Beadle	0	1	1	0	3	0	0	0	0	6	0	6	5	0	0
Double coated PVC	20	Beadle	0	0	2	0	4	0	0	0	1	6	0	6	6	0	0
Double coated PVC new	17	Beadle	0	0	1	0	2	0	0	0	1	6	1	6	6	0	0
Neoprene	1	Respirex	0	1	3	0	6	0	0	0	1	6	6	6	4	0	0
Neoprene	16	Respirex	0	1	4	0	6	0	0	0	1	6	6	6	6	0	0
Neoprene new	4	Respirex	1	2	4	0	6	0	0	0	1	6	6	6	5	0	0
Neoprene	3	RFD	0	1	3	0	6	0	0	0	0	6	6	6	3	0	0
Neoprene	15	RFD	0	0	3	0	6	0	0	0	1	6	6	6	4	0	0
Neoprene new	19	RFD	0	1	3	0	6	0	0	0	0	6	6	6	4	0	0
HNB	6	Respirex	1	6	6	0	6	0	0	0	1	6	6	6	6	0	0
HNB	12	Respirex	1	6	6	0	6	0	0	0	2	6	6	6	6	0	1
HNB new	7	Respirex	1	6	6	0	6	0	0	1	2	6	6	6	6	0	0
Viton/ butyl	11	Respirex	5	6	6	6	6	2	1	2	6	6	6	6	6	1	6
Viton/ butyl new	13	Respirex	5	6	6	6	6	1	1	2	6	6	6	6	6	1	6

Table 4 : Permeation classifcations

Summary key: 0 : unclassified (breakthrough within(10 minutes) 1 : lowest classification 6 : no breakthrough within 480 minutes

The fabrics are grouped into types, i.e. all PVC fabrics are at the top of the table etc. The types of fabrics are separated by a bold line. In any group of fabric types, the shaded row is the new and unused fabric of that type.



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