

## Permeability of Organic Solvents Through Two-Layer Safety Gloves Determined by a Gravimetric Method

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Organic solvents are harmful to humans, and many of them are recognized as carcinogens. Therefore, it is necessary to protect hands from contact with them. Most methods for testing solvent resistance of gloves use gas chromatography. However, these methods are expensive and so complex that they present application problems for most glove producers and users. A simple gravimetric method to test solvent resistance of gloves was developed. It was tested by measuring the permeability of organic solvents such as white spirit, acetone, isopropyl alcohol, benzene, p-xylene, and trichloroethylene through gloves made of natural rubber, polyvinyl chloride, neoprene, perbunan, polyvinyl alcohol, and two-layer gloves made of natural rubber and neoprene. This method proved to be a simple, economical, and reliable way to examine glove permeability.

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### 1. INTRODUCTION

The major routes of entry into the human body are inhalation, ingestion, and percutaneous absorption. Close to 80% of occupational contact dermatitis involves hands. Therefore, it is not surprising that protective gloves account for the majority in the sale of industrial protective clothing. The purpose of protective gloves is to reduce or eliminate skin exposure to chemical substances by placing a physical barrier between skin and the potentially harmful environment.

From the user's point of view, the most important properties of gloves are comfort, manual dexterity, tear, puncture, and cutting resistance, and—what is most important—the ability to prevent harmful liquids from permeating and, ultimately, contacting the skin.

Organic solvents are harmful in contact with skin, because of their drying, defatting, and irritating action, and their often carcinogenic properties. Benzene, carbon tetrachloride, dioxane, ethylene dichloride, hydrazine, and some naphtha products are recognized human carcinogens. Others, such as chloroform, chloronaphthalen, kerosene, propylene oxide, or trichloroethylene are suspected carcinogens (Ansell-Edmont, 1986; Berardinelli, 1988; Rudzki, 1976).

The mechanism of solvent permeation involves the sorption of the liquid onto the outside of the glove, diffusion of the liquid through the glove, and desorption of the liquid from the inside of the glove (Krevelen, 1972).

The breakthrough time and the steady-state permeation rate are determined in permeation tests. The breakthrough time is the time required for the liquid to be transported through the glove and to be detected by the detector. The steady-state permeation rate is an equilibrium condition wherein the glove is saturated with liquid so that there is a constant flow of liquid through the glove. Both parameters are useful for selecting solvent-protective gloves.

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Breakthrough time, also known as permeation time, has been defined mathematically (Krevelen, 1972) as

$$t = \frac{x^2}{6D}$$

where  $D$  is the diffusion coefficient (length<sup>2</sup>/time) and  $x$  is film thickness.

Fick's first law of diffusion states that permeation rate,  $F$ , is inversely related to film thickness,

$$F = -D \frac{dc}{dx}$$

where  $D$  is the diffusion coefficient,  $c$  is the concentration of the diffusing substance, and  $x$  is thickness.

The permeation of harmful liquids can be tested by various methods. McFee (1964) tested 12 types of gloves made of natural rubber, neoprene, Buna N, butyl rubber, polyvinyl chloride, and polyvinyl alcohol. The gloves were filled with acetone or trichloroethylene, toluene, and other solvents. After tightening, the gloves were weighed and hung up. After 24 hr, the solvent was poured out, the gloves were reweighed (without the liquid), and the swelling of the glove was determined.

Calingaert and Shapiro (1948) tested the permeability of a mixture of lead tetraethylene and bromide ethylene through gloves made of neoprene, thiokol, saran, and PVA. They used a disk permeability test. Samples of the inert solvent were taken after 5 hr and analyzed to determine lead concentration, which indicates permeation.

Sansone and Tewari (1978) measured the differences in the solvent permeation of gloves made of the same materials but by different producers. They tested seven types of gloves made of natural rubber, against acetone, aniline, dimethyl formamide, and five types of gloves made of polyacrylonitrile, using methanol, dimethyl sulfoxide, and tetrachloroethylene. They used a two-compartment glass cell, separated by a membrane made of material cut from the glove they were testing. One compartment was filled with the tested solvent, the other with an inert solution. Samples of this solution were taken after 0.5, 1, 2, 3, 4, 6, and 8 hr and were analyzed using gas chromatography.

Gas chromatography is often used to determine the rate of glove permeation (Schorope, Goydan, & Entholt, 1992; Stull & Pinette, 1990; Zellers et al., 1992). Details of the analytical routine are described in Deutsches Institut für Normung (1993). However, there are problems with the tightness of the chemical permeation cell used in this method. The steady-state permeation rates between the two cells using the same direct reading instrument are statistically different (Berardinelli, 1988; Jencen & Hardy, 1989), and there is no easy way to overcome this problem.

In Poland, a method described in Polski Komitet Normalizacyjny (1974) is used to test gloves. It consists of swelling glove materials in liquids. Samples are cut from the glove and weighed. They are immersed in the solvent for 8, 24, or 48 hr, then they are dried and reweighed. However, this method cannot be used to test two-layer gloves, because of the delamination of the two layers. Each layer has different chemical resistance and different swelling, so foliation occurs. Therefore, a new method had to be developed.

Following, we present a simple and economical method for testing and evaluating the permeability of organic solvents through safety gloves. This method is used to determine permeability as a function of the chemical nature of the solvent, the chemical nature of the tested glove material, the thickness of the glove material, and the duration of contact between the solvent and the glove material.

## 2. EXPERIMENTAL MATERIALS AND METHOD

Gloves (No. 10) and materials tested in this study were prepared in the laboratories of the Institute of Rubber Industry, Warsaw, Poland, according to the procedure described by Liwkowicz (1986). The glove specifications are given in Table 1.

TABLE 1. Kinds of Tested Gloves and Materials

Type of Glove Material	Thickness (mm)
Natural rubber	0.35; 0.50; 0.70; 0.97
Perbunan (polyacrylonitrile)	0.37
Polyvinyl chloride	0.80
Polyvinyl alcohol (PVA)	0.18; 0.21; 0.31
Neoprene (polychloroprene)	0.34; 0.58; 0.75; 0.93
Natural rubber covered with PVA (twice)	0.93
Natural rubber covered with PVA (three times)	1.00
Natural rubber covered with perbunan	0.37; 0.45; 0.74

Mass-produced gloves were tested, too. They were natural rubber gloves certified by the Central Institute for Labour Protection (No. 800) 0.40 mm thick and Solvex (Ansell-Edmont, Belgium) gloves, 0.27 and 0.67 mm thick.

To test permeability, Polish technical and analytical grade solvents were used: acetone, white spirit, naphtha, isopropylalcohol, ethylacetate, benzene, p-xylene, chlorobenzene, and cyclohexane.

The penetration of solvents through the glove material in a given period of time was determined using three middle fingers cut from the gloves. All samples had the same length and diameter. The thickness of the tested glove finger was determined with the use of a micrometer.

The testing was performed in a laboratory, where the temperature was 23 °C ( $\pm 2$ ), and the relative humidity was 50% ( $\pm 5$ ). The fingers were weighed together with a 25-cm<sup>3</sup> beaker (30 mm in diameter, height: 55 mm). Next, the beaker was filled with 20 cm<sup>3</sup> of the tested solvent, and the finger was stretched over the beaker and weighed again. The accuracy of weighing was  $\pm 0.0002$  g.

The permeability of a given solvent was determined in the following way: The beaker was turned upside down, so that the finger was filled with the tested solvent. Before testing, fingers were turned inside out, to assure contact of the external layer of the glove with the solvent (see below). This structure was supported on a rack. It was weighed every 30 min during the first 6 hr, and then after 24 and 48 hr, to determine losses of the solvent due to permeability.

Permeability,  $P$ , after each period of time, was calculated as

$$P = \frac{m_1 - m_2}{m_1} \cdot 100\%$$

where  $m_1$  is the mass (grams) of the used solvent and  $m_2$  is the mass (grams) of the solvent after a given time.

### 3. RESULTS AND DISCUSSION

Results show that the permeability of acetone through natural rubber after 48 hr is above 26%, through perbunan 100%, through polyvinyl chloride 100%, and through polyvinyl alcohol 9% (Figure 1). The permeability of benzene, p-xylene, trichloroethylene, chlorobenzene, and ethyl acetate through natural rubber and perbunane is 100%. Only polyvinyl alcohol films are resistant against aromatic and chlorinated solvents (Figure 2). These results are in step with previous literature reports (Berardinelli, 1988; Jencen & Hardy, 1989).

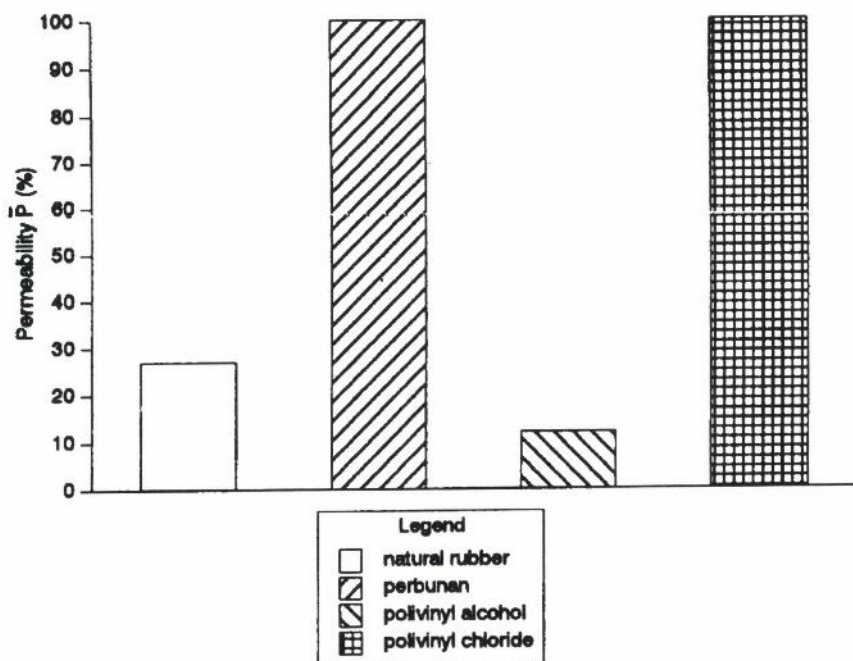


Figure 1. Permeability  $\bar{P}$  of acetone through gloves made of various materials: after 48 hr, at 23 °C (± 2).

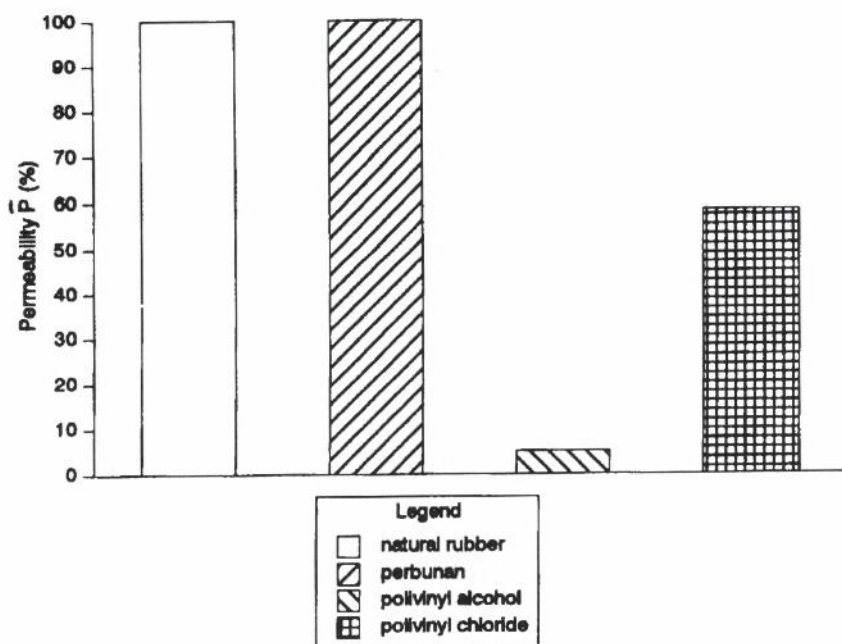


Figure 2. Permeability  $\bar{P}$  of benzene through gloves made of various materials: after 48 hr, at 23 °C (± 2).

Gloves made of natural rubber covered with polyvinyl alcohol (PVA) have significant resistance against organic liquids; permeation of white spirit after a 3-hr exposure is 0.6% for gloves covered three times with a thin film of PVA, and 2.2% for gloves covered with polyvinyl alcohol twice (Figure 3).

The effect of the glove material thickness on the permeation characteristics is shown in Figures 4, 5, and 6. Gloves made of natural rubber, neoprene, and perbunan with the thickness from 0.35 mm to 0.97 mm have different permeability rates. Gloves made of natural rubber with the thickness of 0.35 mm have the permeability rate (after 1.5 hr) of nearly 44%, whereas the permeability rate of a 0.97 mm thick film is nearly 44% (Figure 4). The permeability of solvent through neoprene film (0.34 mm thick) after a 3-hr exposure is 7.5%, whereas the permeability of a film 0.93 mm thick is 0.4% (Figure 5). The same results were obtained for perbunan and polyvinyl alcohol films (Figures 6, 7).

Figure 6 shows the relationship between the permeability of perbunan gloves 0.37 mm thick

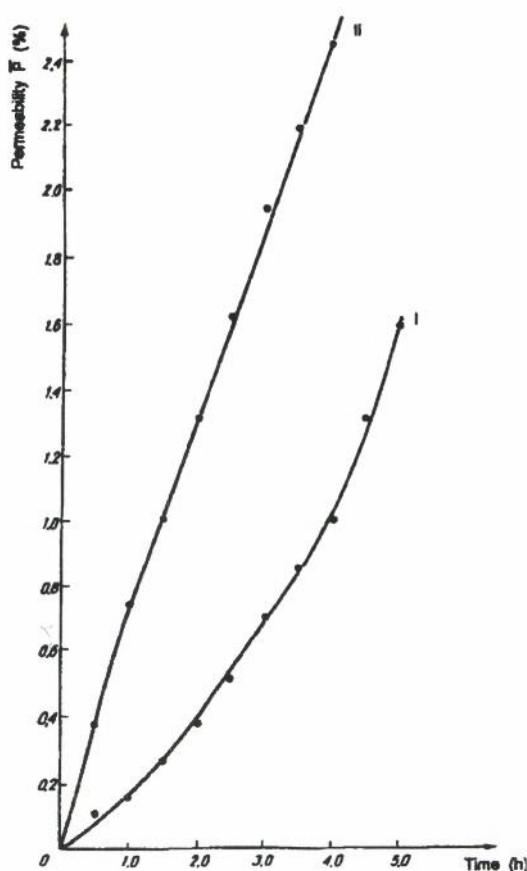


Figure 3. Permeability  $\bar{P}$  of white spirit through natural rubber gloves covered with polyvinyl alcohol.

I—natural rubber gloves covered with polyvinyl alcohol three times, 1 mm thick  
 II—natural rubber gloves covered with polyvinyl alcohol three times, 0.93 mm thick

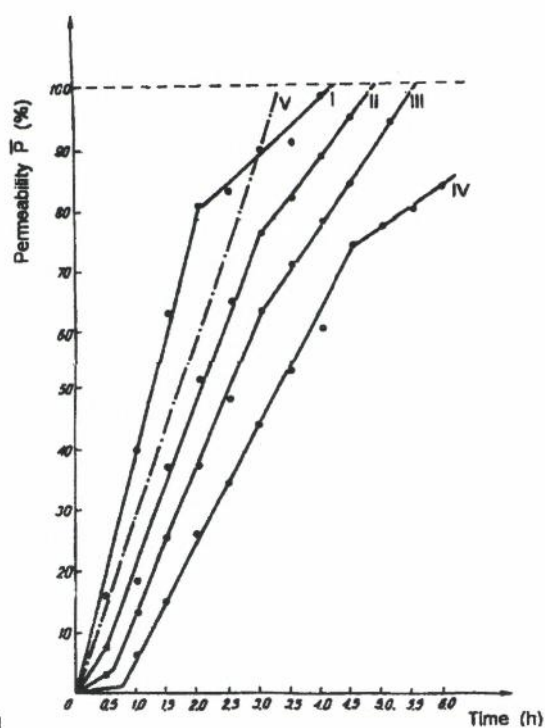


Figure 4. Permeability  $\bar{P}$  of white spirit through gloves made of natural rubber prepared in a laboratory and in normal production.

I—gloves, 0.35 mm thick  
 II—gloves, 0.50 mm thick  
 III—gloves, 0.70 mm thick  
 IV—gloves, 0.97 mm thick  
 V—gloves, CIOP No. 800, 0.40 mm thick

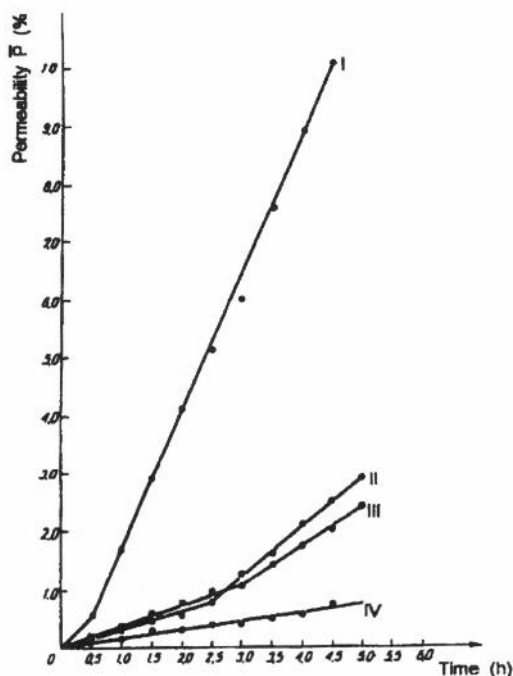


Figure 5. Permeability  $\bar{P}$  of white spirit through neoprene gloves prepared in a laboratory.

- I—gloves, 0.34 mm thick
- II—gloves, 0.53 mm thick
- III—gloves, 0.75 mm thick
- IV—gloves, 0.93 mm thick

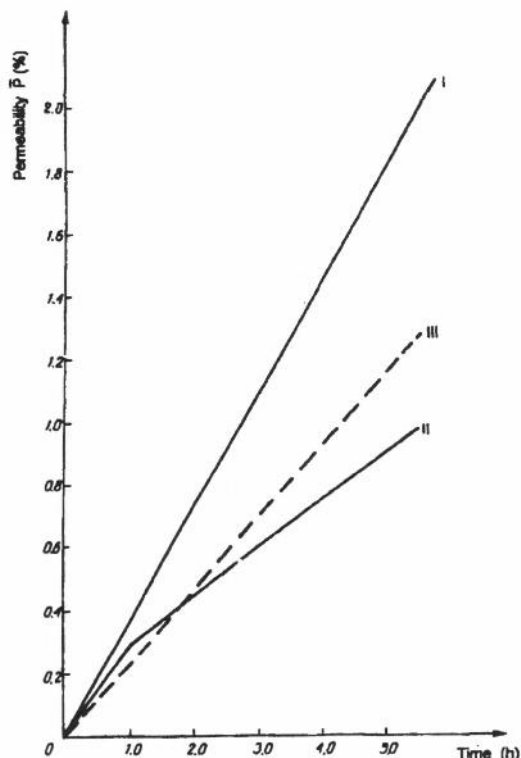


Figure 6. Permeability  $\bar{P}$  of white spirit through gloves made of perbunan and two-layer gloves made of natural rubber and perbunan.

- I—perbunan 0.37 mm thick
- II—perbunan 0.74 mm thick
- III—natural rubber 0.20 mm + perbunan 0.40 mm thick (actual thickness: 0.45 mm)

and the permeability of a two-layer glove (0.45 mm thick) made of natural rubber covered with perbunan. The permeability of the two-layer glove is lower (curve III) than the permeability of the perbunan glove (curve I), but tensile strength and tearing strength of two-layer gloves are much better. This is also true in the case of two-layer gloves made of natural rubber polyvinyl alcohol and natural rubber perbunan (Figure 6).

Figure 7 shows differences in permeation as a function of thickness of the polyalcohol film (the thickness of the layers ranges from 0.18 mm to 0.31 mm). The permeability measured after 4 hr is 5% for the layer 0.18 mm thick and 2.2% for the PVA layer of 0.31 mm.

The permeability of solvent through the tested membranes is obviously related to exposure time. Figure 8 shows the effect of exposure time on the permeability of white spirit through the gloves made of natural rubber (0.40 mm thick), neoprene (0.34 mm thick), perbunan (0.37 mm thick), and polyvinyl alcohol (0.21 mm thick). After 3 hr, the solvent completely penetrated through natural rubber, that is, the permeability equalled 100%, whereas the permeability of the PVA film was below 1%. After 72-hr exposure, the permeability rate of the solvent through the PVA film was 5.5%, whereas for perbunan it was 11.0% and for neoprene it was 81.0%. It should be noticed that the PVA film, although the thinnest, was the most resistant to permeation by organic solvents.

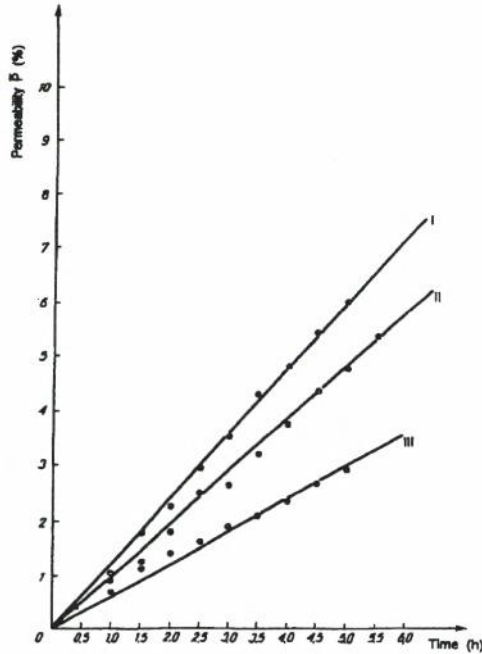


Figure 7. Permeability  $\bar{P}$  of white spirit through gloves made of polyvinyl alcohol.  
 I—gloves dipped twice, 0.18 mm thick  
 II—gloves dipped three times, 0.21 mm thick  
 III—gloves dipped four times, 0.31 mm thick

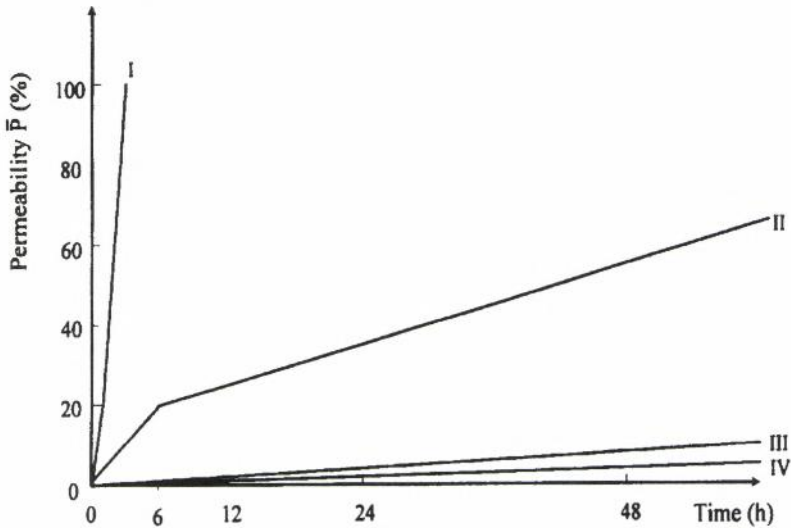


Figure 8. Permeability  $\bar{P}$  of white spirit through gloves made of various materials of nearly the same thickness.  
 I—natural rubber, 0.40 mm thick  
 II—neoprene, 0.34 mm thick  
 III—perbunan, 0.37 mm thick  
 IV—polyvinyl alcohol, 0.21 mm thick

These results are reproducible to within 5%. Although homogeneous materials were tested, variance coefficient  $V$  was low. For example, when Solvex gloves (Ansell-Edmont, Belgium) were tested using toluene,  $V$  was 4.6%.

For the evaluation of glove chemical resistance, permeability after 4 hr may be used, because after that time little change in permeability is observed. On the basis of the resistance criterion, it may be suggested that very good resistance is indicated by permeability below 5%, average resistance by permeability of 5 to 20%, and no resistance by permeability of above 20%.

#### 4. CONCLUSION

Results obtained by the gravimetric method confirm that the permeability of organic solvents depends upon the chemical nature of the glove material, the chemical nature of the solvent, thickness of the glove, and exposure time.

Glove material seems to be the most important factor. Polyvinyl alcohol was found to be most resistant against the majority of the tested organic solvents.

The gravimetric method used in this study is an easy, convenient, and reliable way to estimate both one- and two-layer gloves. By using this method, the permeability of different glove materials can be established in about 4 hr. Because it was shown that after 4 hr solvent permeates completely through nonresistant material ( $P = 100\%$ ), testing for a longer period of time is not necessary.

Two-layer gloves, especially natural rubber covered with neoprene and natural rubber covered with polyvinyl alcohol, are very good to protect hands against common organic solvents. Also, gloves made of these materials have good mechanical properties and are relatively inexpensive.

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