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A Breakthrough Time Comparison of Nitrile and Neoprene Glove Materials Produced by Different Glove Manufacturers

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Specimens of similar nominal thickness from commercially available nitrile and neoprene gloves were each tested for breakthrough time against three chemicals. The null hypothesis was that the breakthrough times for the glove specimens of the same generic type but produced by different manufacturers would be the same. Breakthrough time data for each material/chemical combination were analyzed using an analysis of covariance to adjust for differences in the measured specimen thickness while testing for product differences. A significant difference in chemical breakthrough times was found among generically similar products produced by different manufacturers. The largest difference between the mean breakthrough time of two generically equivalent products, 30 *vs.* 300 min, was obtained for perchloroethylene through nitrile products. In conclusion, breakthrough time data for use in selection of chemical protective clothing or in prediction modeling for chemical protective clothing should be manufacturer and product specific.

Introduction

Chemical protective clothing (CPC) is used to reduce the risk of dermal exposure to chemicals. The selection of CPC should be based on an evaluation of a large number of factors that include the following: hazard identification, toxicity, skin exposure risk, engineering controls, CPC types, chemical permeation data for skin and CPC, fit comfort, thermal comfort, moisture transmission, dexterity, tear resistance and other job performance needs. This article focuses on evaluation of a portion of the chemical permeation factor of the selection process.

Permeation data from a variety of sources have been used as a basis for selecting CPC[1] and for correlating permeation data with other physical and chemical properties of the material and chemical for prediction modeling.[2] Most often these selection guides and prediction models are material specific, but not product specific.

One measurement used to characterize CPC resistance to permeation is known as breakthrough time. Breakthrough time is defined as the elapsed time between initial contact of the hazardous liquid chemical with the outside surface of a protective clothing material and the time at which the chemical can be detected at the inside surface of the material by means of the chosen analytical technique.[3]

Breakthrough times show a coefficient of variation of 15% to 30% when the specimens are taken from the same lot of material.[4] Breakthrough time values from different sources usually have greater variations. For example, a 0.56-mm Edmont 37-155 nitrile glove,[5] and a 0.36-mm North LA-142G nitrile glove[6] are reported in manufacturers' literature to yield breakthrough times for perchloroethylene of 5.0 and 1.3 hr, respectively. Thickness differences and interlaboratory variability may cause part of the variability in permeation data. The ASTM method, F739-81[3] for testing the resistance of protective clothing materials to permeation by hazardous liquid chemicals, does not define the analytical sensitivity of the detection system. The sensitivity of the detector used by one investigator usually is not the same as that of another investigator. This can have a significant effect on determining the breakthrough time. A more sensitive method will yield earlier breakthrough times. These factors may account for part of the variability in breakthrough times found in literature, but it most probably does not account for all the variability reported.

It is plausible to postulate that varying a glove fabrication process or raw materials used may produce variability in glove performance. The variable factors that may influence the raw materials (polymerization) and/or fabrication process are numerous. Variables include the following: formulation; temperature and pressure of reactor; type and amount of catalyst, additives, inhibitors and initiators; cure parameters; *etc.*

The purpose of this study was to determine if there is a significant difference in chemical breakthrough time among glove product materials bearing the same generic name but produced by different manufacturers. If significant variation in breakthrough times exists among generic CPC materials produced by different manufacturers, then product specific testing would be necessary to make intelligent selection decisions. If breakthrough times for different products of the same generic class of materials do not vary significantly, then selection could be based on the generic material classification.

Glove products made of nitrile and neoprene material were selected rather than other CPC materials because glove products are the protective clothing most frequently used in industry and these two materials were available with similar thicknesses from a variety of manufacturers.

Breakthrough time measurements were selected as the critical measure of product performance. Other measurements such as chemical permeation rates were considered but were found to be less meaningful to the end user because of insufficient data in the area of percutaneous absorption. In addition, overall experimental time was a key consideration. To collect steady state permeation rate data along with the breakthrough time data would have increased the time to complete each test at least fivefold as compared to collecting only breakthrough time data.

Intramanufacturer (lot-to-lot) variation was not considered in this study. Part, or all, of the variation observed in this study may have been the result of lot-to-lot variation within each manufacturer. In either case, the variation that was found is quite significant to the glove user. The null hypothesis was tested by comparing chemical breakthrough times of specimens of one lot from each manufacturer.

A similar previous study[7] looked at two CPC glove materials, testing them both with three chemicals. The data were displayed by means of a table presenting the ratio of the product (penetrated solvent concentration times sample thickness) for the glove material that least resisted penetration to that which most resisted penetration. The largest ratio, 48, which was obtained for the nitrile/perchloroethylene combination, indicates a significant intermanufacturers' variability. This study, however, did not indicate the number of products tested, the origin of the products tested, or the thicknesses of the products tested. More importantly, it did not report the key permeation property known as breakthrough time.

Experimental

The null hypothesis of this study was that glove products bearing the same generic name but produced by different manufacturers would yield the same breakthrough times.

The material/chemical combinations were chosen to obtain reasonable breakthrough times (long enough to determine differences among products but less than one working day per test run) and to encompass several chemical functional groups. The scope of this work entailed collection of 273 breakthrough time measurements. Two generic materials, nitrile and neoprene, were exposed to three chemicals each. Eight nitrile and five neoprene glove products were selected to compare performance. Seven specimens (replicates) were tested for each product/chemical combination.

Most glove manufacturers carry glove products of different thicknesses. In this study products were procured that have the same, or close to the same, nominal thickness. All gloves were purchased from a single distributor (Industrial Products Company of Langhorne, Pa.). Most gloves were received promptly and were tested in random order to minimize time dependent errors. One glove type, Granet neoprene 2001, was received late and was tested by itself using the same test system and calibration technique.

Specimens were flat surfaced, unlined and not embossed. Test specimens were taken from the back portion of the glove, opposite the palm. When the back portion of the glove was not a smooth surface, the cuff portion of the glove was used to obtain the test specimens. The models that required that specimens be taken from the cuff were all nitrile: Uniroyal 4-15, North LA-142G, Best 727 and Surety 315R.

Five thickness measurements (±0.01 mm) were made uniformly over the surface of each glove sample within the 24.5-mm diameter permeation area. The thickness measurements were made using a Federal Products Corporation Model A6 micrometer with a 4-mm diameter presser foot.

Ambient temperature at the test site was monitored during each test run. During the testing period the temperature ranged from 21° to 25° C with the exception of two consecutive runs where the temperature reached 27° C.

The specimens were mounted into AMK permeation test cells with the outside surface facing up toward the chemical challenge and the inside surface facing the collection side of the cell. The AMK cell has been shown to be equivalent to the ASTM cell.[8] Air was used as the collection gas. With the use of Tylan flow controllers,[9] the flow rate was maintained at 200 cc/min through each test cell. In order to provide adequate flow to the detection system, 353 cc/min of air was added to the collection air downstream of the test cell.

An H-NU PI-101 photoionization detector was used to determine breakthrough time. A 10.2 eV lamp was used in all but the ethanol runs, in which case an 11.7 eV lamp was used. The use of the H-NU PI-101 enabled an automated system to be utilized to speed up data collection (see Figure 1). Four specimens were tested simultaneously for breakthrough time using a purge gas between each specimen sample and a calibration checkpoint through a diffusion tube. The automated sampling sequence was, Specimen No. 1, Purge, Specimen No. 2, Purge, Specimen No. 3, Purge, Specimen No. 4, Purge, Diffusion tube, and Purge. Then returning to Specimen 1, the process was repeated until breakthrough was reached for all test specimens. Each specimen was checked for breakthrough time every 200 seconds or less. After breakthrough was reached and the chemical concentration in the collection medium continued to climb beyond the breakthrough concentration, the specimen was no longer sampled to ensure that the manifold connecting the four test cells was not contaminated.

The recorded breakthrough time was calculated by taking the average value of the following: the time of the first sample that exceeded the breakthrough threshold concentration and the time of the sample taken just prior to the sample that exceeded the breakthrough threshold concentration. This value was rounded to the nearest minute.

The breakthrough threshold was the predetermined concentration level of contaminant in the collection medium above the limit of detection that was used to indicate breakthrough time. The breakthrough threshold was at least four times the background noise of the instrument. A diffusion tube held at constant temperature was used as the standard for calibration. From the diffusion tube output and a series of dilutions, the instrument was calibrated to determine the concentration of the contaminant at the breakthrough threshold. Table I displays the breakthrough threshold concentrations for each chemical in terms of minimum detector sensitivity and permeation rate.

Only breakthrough time was measured as a dependent variable. Additionally, any catastrophic changes in the material subsequent to breakthrough were noted.

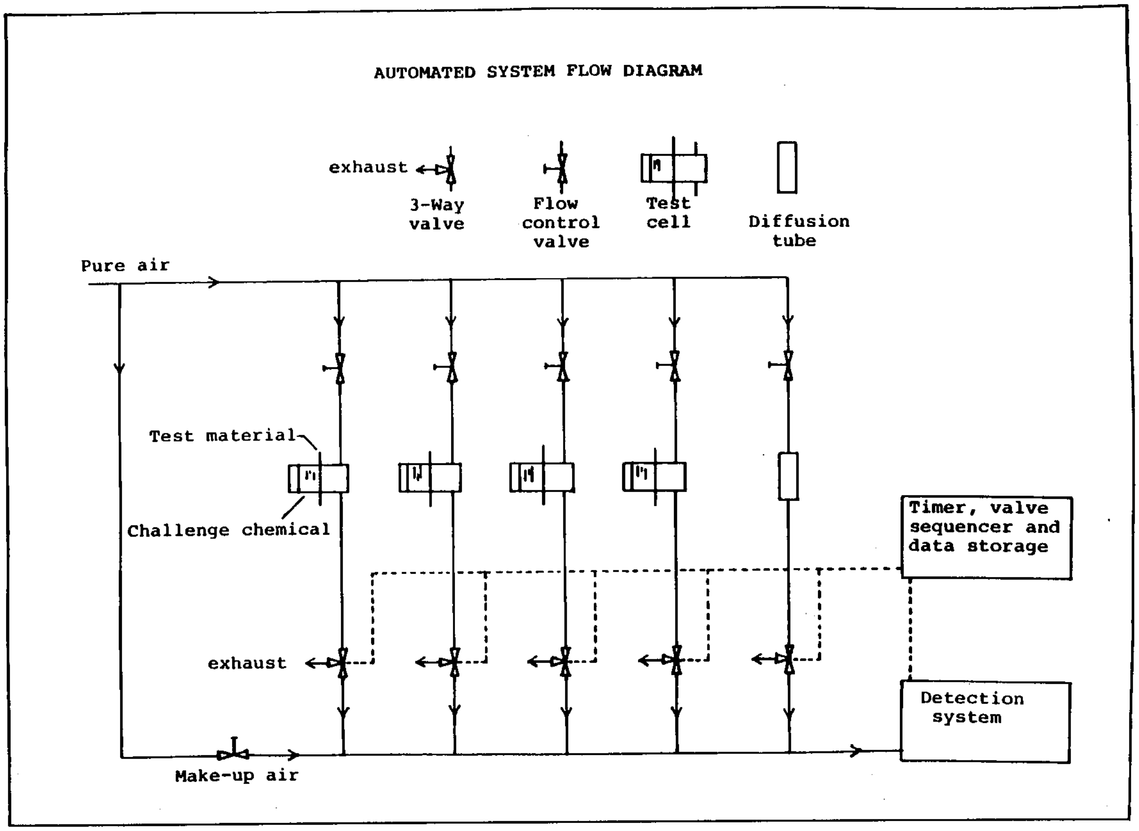

Figure 1 — Automated system flow diagram.

Raw data for each material/chemical combination were analyzed using an analysis of covariance to reduce the effect of any differences in measured thickness or temperature while testing for differences in breakthrough time. Thickness and thickness squared were used as covariates based on previous work that characterized chemical breakthrough time as a function of material thickness.[10]

Results and Discussion

The results are reported in terms of the raw breakthrough times plotted in Figures 2 through 7. Similar products were chosen based on the manufacturer material identification and nominal thickness. A consumer may be inclined to substitute freely within generic groups but would not be likely to take thickness measurements and apply appropriate calculations to compare products on a basis of common thickness. Therefore, the important comparison is among uncorrected breakthrough times, not breakthrough times corrected for thickness.

TABLE I
Breakthrough Threshold for Determining Chemical Breakthrough Times

Chemical	Minimum Detector Sensitivity ($\mu g/cm^3$)	Minimum Permeation Rate Needed for Detection ($\mu g/cm^3 \cdot min$)
Ethanol	0.0033	0.39
n-Butyl Acetate	0.0064	0.75
n-Hexane	0.0062	0.73
p-Xylene	0.0008	0.09
Perchloroethylene	0.0014	0.16

Additionally, each data point was plotted as opposed to plotting only mean values because of the need to display the large differences in the error variance among products. For example, the breakthrough time values of perchloroethylene through nitrile products were plotted in Figure 2. An estimate of the standard deviation of breakthrough times for the Pioneer and Edmont gloves was 114 and 42, respectively. The product with the higher mean breakthrough time (Pioneer) also had a much larger standard deviation. Thus, the raw data are plotted to show the differences in the spread of data as well as the differences in the mean breakthrough times.

In Figures 2 through 7, raw data are marked by 'O' and mean breakthrough time values from each product/chemical combination are marked by a line. The largest difference between mean breakthrough times, 30 *vs.* 300 min, was obtained for perchloroethylene through nitrile products. Data such as these lead to the rejection of the null hypothesis and the conclusion that glove products bearing the same generic name may differ in their ability to resist chemical breakthrough.

Problems with the nonhomogeneous nature of the products were encountered before breakthrough testing began.

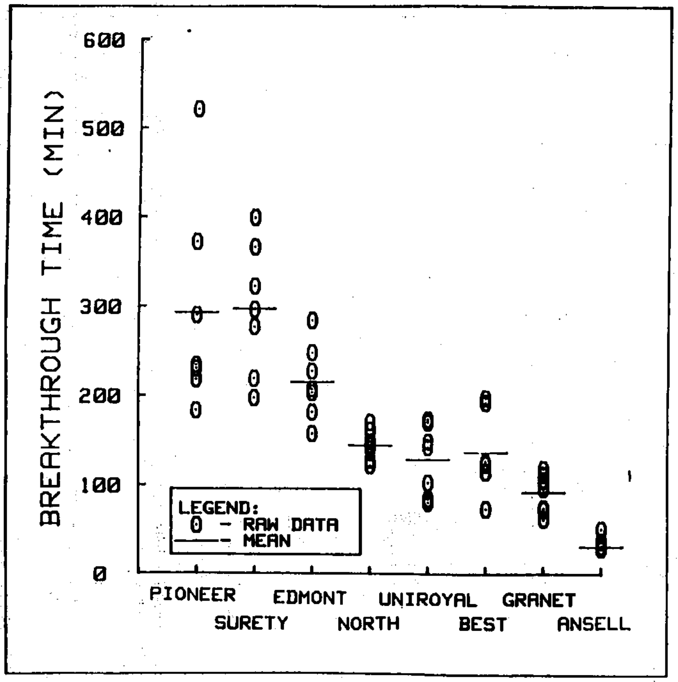

Figure 2 — Breakthrough time for nitrile *vs.* perchloroethylene.

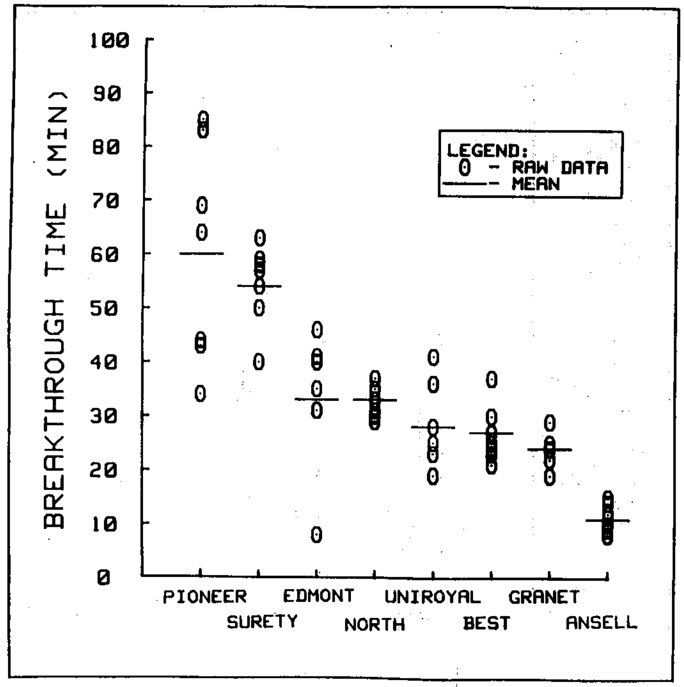

Figure 3 — Breakthrough time for nitrile *vs.* p-xylene.

Table II displays each glove product's nominal thickness, mean thickness of the 21 specimens taken from different gloves of the same lot, standard deviation from the mean, and the percent difference between the nominal and mean thickness. The Ansell 632 and the North LA-142G had a smaller nominal thickness than the other nitrile gloves. The neoprene products were all the same nominal thickness.

The Ansell 632 was the only nitrile product to have a mean thickness larger than the reported nominal thickness. Although this was nearly the thickest nitrile product, it was also the least resistant to all three chemical challenges.

Numerous statistical manipulations were performed on these data (*i.e.*, log transformation to stabilize the variance and analysis of covariance to adjust for thickness or thickness squared and/or temperature). Upon analysis, the addition of covariates to the model did not reduce the breakthrough time differences among products. Therefore, as mentioned earlier, the raw data are compared graphically.

Whether because of differences in raw materials or because of differences in the fabrication process, the end products yield significantly different breakthrough times when exposed to chemicals.

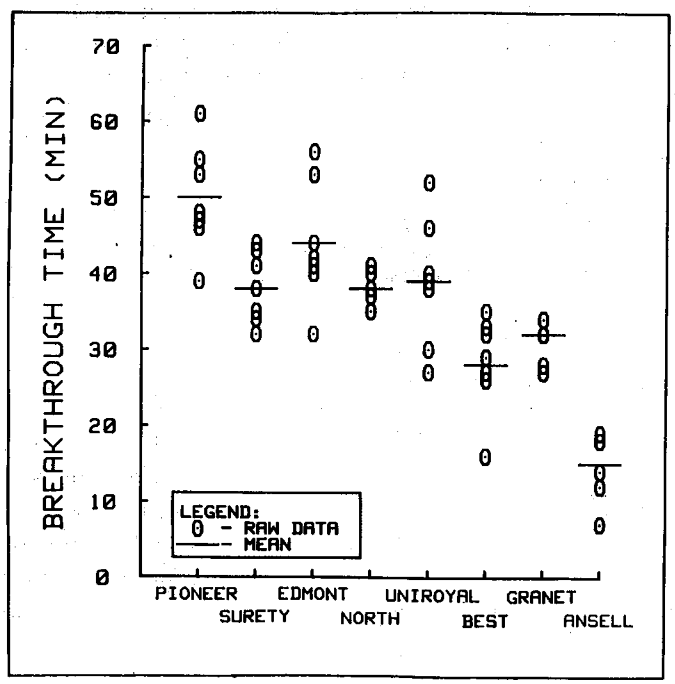

Figure 4 — Breakthrough time for nitrile *vs.* n-butyl acetate.

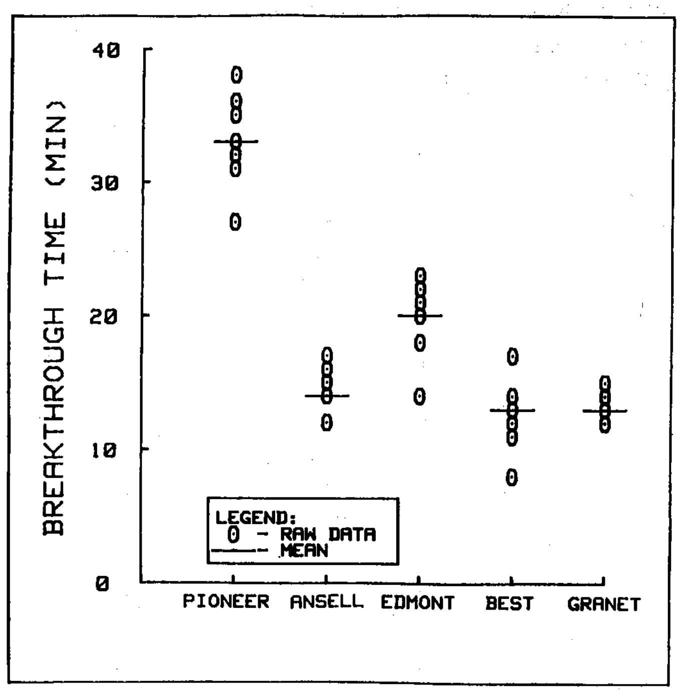

Figure 5 — Breakthrough time for neoprene *vs.* n-butyl acetate.

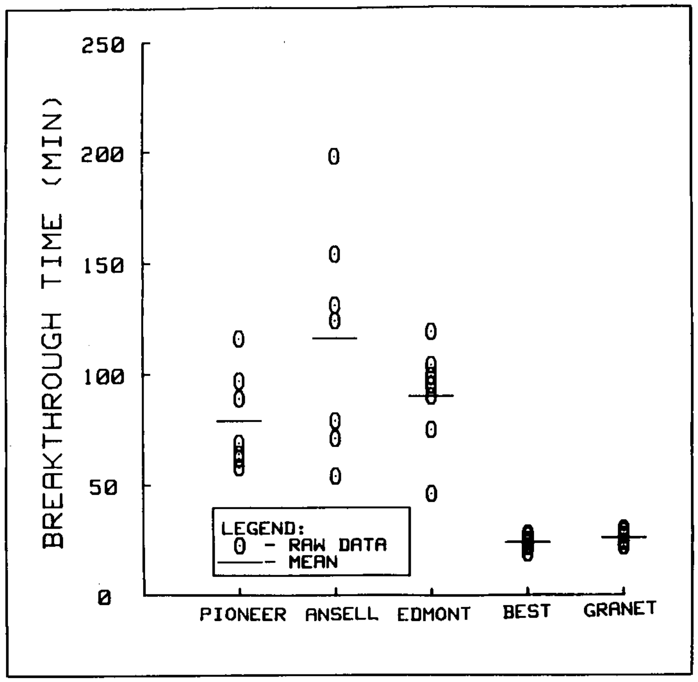

Figure 6 — Breakthrough time for neoprene *vs.* n-hexane.

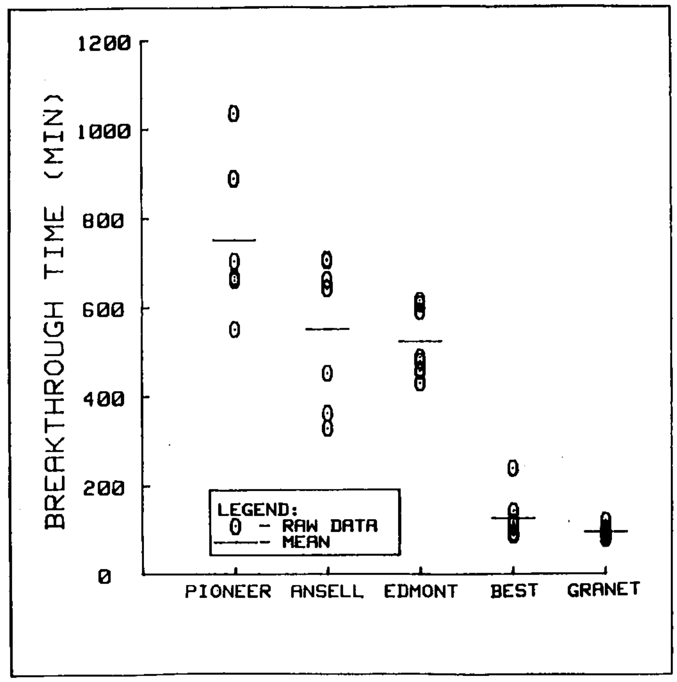

Figure 7 — Breakthrough time for neoprene *vs.* ethanol.

When considering the nitrile products' performance for all three chemicals, some trends appear. Although the rank order in which the different products resisted breakthrough varied from one chemical to another, evident by a statistical interaction between chemical type and product type during the analysis of variance, there were no major changes in rank order such as the best performer against one chemical being the worst performer against another chemical. For example, the Pioneer A-15 was in the highest (most resistant) group for all three chemicals. The North LA-142G was in a middle group for all three chemicals and the Ansell 632 was the least resistant for all three chemicals. Bearing in mind the small number of chemicals used, these trends may not hold for other chemicals.

Similar to the nitrile products, the neoprene products that resisted chemical breakthrough the longest for one chemical tended to perform well for the other chemicals and the products that resisted breakthrough the shortest length of time for one chemical tended to breakthrough earlier for the other chemicals.

After the tests were completed there were no holes or other catastrophic defects found in any of the test specimens. All the specimens suffered minor deformation because of swelling but no attempt was made to measure this effect.

A follow-up study into the compositional dependency of permeation through nitrile polymers has been proposed. Details of this follow-up study are being formulated.

TABLE II
Evaluation of Specimen Thickness

Glove Manufacturer and Cat. No.	Nominal Thickness (mm)	Mean Thickness (n=21; mm)	Standard Deviation of Mean	% Difference of Measured Thickness From Nominal
Nitrile:				
Ansell 632[11]	0.33	0.36	0.03	8
Best 727[12]	0.38	0.28	0.01	-25
Edmont 37-155[5]	0.38	0.32	0.01	-15
Granet 490[13]	0.38	0.32	0.01	-17
Uniroyal 4-15[14]	0.38	0.37	0.04	-5
Surety 315R[15]	0.38	0.28	0.02	-25
North LA-142G[6]	0.36	0.32	0.01	-10
Pioneer A-15[16]	0.38	0.33	0.01	-15
Neoprene:				
Ansell 520	0.46	0.38	0.02	-16
Best 723	0.46	0.64	0.06	40
Edmont 29-870	0.46	0.46	0.03	0
Granet 2001	0.46	0.55	0.02	21
Pioneer N-36	0.46	0.55	0.02	20

Subsequent to this study, the authors received notice from Ansell Incorporated that the Nitrile Product No. 632 has been discontinued and a new product line has taken its place.

Because of changing product lines, and differences among manufacturers' products, product-specific data reporting is essential.

Summary

A significant difference in chemical breakthrough times was found among generically similar products produced by different manufacturers. Because the null hypothesis was rejected, the permeation results of one product cannot be extended to other manufacturers' products bearing the same generic material name. Substituting generically equivalent gloves for gloves that have been shown to protect the worker may lead to unexpected exposures because of earlier chemical breakthrough times through the substitute glove material.

Each product needs to be tested independently. A more comprehensive study on CPC inter- and intra-manufacturer performance variability may be warranted.

Acknowledgments

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2 July 1986; Revised 1 May 1987

Comments from Manufacturers

Editor's Note

Following usual practice, pre-publication copies of this manuscript, "A Breakthrough Time Comparison of Nitrile and Neoprene Glove Materials Produced by Different Manufacturers", were sent to the eight manufacturers identified by the authors. Four of these responded. Excerpts from their letters follow. One manufacturer had no comments to offer other than that "the test result numbers speak for themselves". The other three objected to the manuscript on the grounds that the study included only one quality or property of gloves and therefore could be improperly or unfairly interpreted. These three manufacturers stressed that various other factors besides breakthrough time should be considered in the selection of gloves.

We agree with the three manufacturers that all pertinent factors should be considered in the selection of protective gloves. The same should apply in the selection of all protective equipment. On the other hand, where performance data are not available on all such factors, it is important that such data as are available be made known to those responsible for selection of such protective equipment and that the data be made available in a timely manner.

The authors certainly have made it clear that their study and evaluation were limited to breakthrough time only. They have not suggested that selection of gloves be based on this one criterion alone.

Our readers generally are industrial hygienists and safety personnel who are quite aware of the significance of tests involving only one performance factor. The authors state their correct hypothesis and actual conclusions several times in their paper. For those few readers who possibly may not be fully aware of the limitations of tests of one performance factors only, we offer a word of caution that all pertinent factors as pointed out by the manufacturers should be considered. On the other hand, the data presented by the authors, properly interpreted as intended, should prove of value to those practicing in the field.

Editor

Excerpts from Letters Received from Manufacturers

- "Manuscript is one-sided and therefore, we request that you abstain from publishing your incomplete conclusions"

  ". . . refers only to three organic solvents"

  ". . . does not address other properties of gloves: puncturing and cutting resistance; elongation; swelling; abrasion; and tearing and tensile strength."
- "No comments on the test results. The test numbers speak for themselves."
- "It [the paper] sheds light on a simple reality: you still can't judge a book by its cover or as it relates to product selection, not all nitriles are created equal.

  . . . each of the changes which are incorporated to aid one *need situation* may have a negative effect on some other characteristic in a different application. As the paper points out, the only viable solution to this dilemma, is to evaluate a specific product in specific situations and avoid generalities."
- "While we agree with the study's conclusions that each product should be tested independently, we feel that methodology, as presented could be misinterpreted as a recommendation for a particular name brand of gloves

  . . . chemical resistance considerations must be combined with those of cut, snag, puncture and abrasion resistance, plus the need for dexterity, tactility and comfort. Obviously a glove film's chemical resistance is irrelevant if the glove itself has a tear or hole in it

  . . . it is important for a glove manufacturer to balance their compound formulation and manufacturing process to produce a glove that maximizes both durability and chemical resistance."