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APPLIED STUDIES

A Comparative Analysis of Glove Permeation Resistance to Paint Stripping Formulations

Although there is a wide variety of work gloves available to users of commercial paint stripping products, there are no published studies examining which type of gloves provide the best protection. To address this need, a multiphase study was undertaken to evaluate how several types of gloves resist multichemical-based paint stripping formulations. Due to the wide range of commercial paint stripping formulations available, seven categories of surrogate paint stripper formulations were created to evaluate glove performance initially. Twenty different glove types were identified for initial evaluation. Degradation resistance screening was carried out for each glove style and paint stripping formulation. Screening results were used to identify those glove styles least affected by the surrogate paint strippers. Those gloves were then evaluated for their resistance to permeation using continuous contact testing based on ASTM Test Method F 739. Glove styles showing extensive permeation with early breakthrough were then evaluated to see how they performed with only intermittent contact with the surrogate paint strippers using a modified form of ASTM Test Method F 1383. These results were used to select glove styles to be tested using commercially available paint stripping products. Gloves made of plastic laminate and butyl rubber were the most effective against the majority of paint strippers. More glove styles resisted permeation by N-methylpyrrolidone and dibasic ester-based paint strippers than conventional solvent products such as methylene chloride, methanol, isopropanol, acetone, and toluene. The study also found that decreased contact time caused relatively little change in permeation resistance and that the surrogate paint stripper data did not always accurately predict resistance to the commercial paint stripper formulations.

Keywords: chemical degradation resistance, chemical permeation resistance, glove testing, N-methylpyrrolidone (NMP), paint strippers, protective gloves

Consumers and industry alike commonly use paint strippers, varnish removers, and similar compounds to remove paint and other finishes from wood and other surfaces. Traditional paint strippers contain a variety of different volatile chemical compounds, including methylene chloride, methanol, isopropanol, acetone, and toluene. More recently, less volatile chemicals, such as N-methylpyrrolidone, *d*-limonene, γ-butyrolactone, and dibasic esters have been used in new paint stripper formulations.

Paint stripping often involves intimate and prolonged contact between the user's hands and the chemicals used. Although some paint stripper manufacturers provide gloves with their products, relatively little information is available to guide the end user in selecting gloves that provide the best protection for specific strippers. Selecting gloves based on individual components in specific paint stripper formulations may not account for synergistic permeation behavior observed for many different chemical mixtures.[1]

To determine which types of gloves afford the greatest protection against contact with paint strippers, an extensive program was designed to evaluate the resistance of gloves to permeation by paint stripper mixtures.

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GENERAL APPROACH

The glove testing program was designed to evaluate several gloves styles for resistance to paint strippers to identify the best gloves for wearer protection against specific paint stripper formulations. This work, as originally defined, was divided into four major phases.

- Phase I identified suitable candidate gloves and performed degradation resistance screening of 20 commercially available gloves by seven laboratory surrogates of paint strippers sold in local hardware or home center stores. Seven of the 20 gloves tested did not exhibit severe degradation.
- In Phase II the seven gloves that did not exhibit severe degradation were subjected to continuous contact permeation testing against the seven surrogate paint strippers. For gloves that showed permeation of the surrogate mixtures, breakthrough times and permeation rates were determined for individual chemical compounds.
- In Phase III those glove styles that exhibited rapid permeation of the surrogate paint stripper formulations in Phase II were tested using intermittent contact permeation testing.
- Phase IV consisted of permeation testing of the three "most successful" glove types with actual commercial paint strippers corresponding to the seven surrogate paint stripping formulations.

METHODS

Selection of Test Chemicals

Surrogate Paint Stripper Formulations

For the purpose of minimizing testing for representing a wide range of commercial paint strippers, surrogate paint stripper formulations were devised to represent the range in commercial paint stripper composition. These surrogate paint stripper formulations were based on a review of the marketplace using paint stripper composition information provided by the Consumer Product Safety Commission and the U.S. Environmental Protection Agency (EPA) together with input from a chemical manufacturer trade group. Seven different surrogate paint stripper formulations were then created using various combinations of methylene chloride; methanol; isopropanol; acetone; toluene; N-methylpyrrolidone; *d*-limonene; γ-butyrolactone; Exxate 600 solvent (oxo-hexyl acetate); Ektapro EEP (ethyl 3-ethoxy propionate); dimethyl adipate; dimethyl glutarate; dipropylene glycol methyl ester; and water. These surrogate paint stripper formulations, listed in Table I, were intended to represent both conventional solvent-based paint strippers as well as N-methylpyrrolidone or dibasic ester-based paint strippers.

Specific Commercial Paint Strippers

The original information from the Consumer Product Safety Commission and EPA was used to select two commercial paint strippers in each of the seven categories represented by the surrogate paint stripper formulations. This was accomplished for all but formulation Category VII, for which only one commercial paint stripper could be identified. The resulting list of paint strippers and their reported composition appear in Table II. The reported composition was taken from either information provided by the manufacturer or from a study performed by EPA.

A quantitative analysis of the composition of each commercial paint stripper was performed to determine which permeants should be quantified in the permeation testing. In some cases these analyses provided results that did not match the reported composition of the product.

TABLE I. Paint Stripping Surrogate Formulations

(I) Methylene chloride based
Methylene chloride (80%), acetone (10%), toluene (4%), methanol (3%), isopropanol (3%)
(II) Methylene chloride/acetone/toluene/methanol based
Methylene chloride (30%), toluene (26%), acetone (22%), methanol (22%)
(III) Acetone/methanol/toluene based
Acetone (46%), toluene (35%), methanol (19%)
(IV) N-methylpyrrolidone based
N-methylpyrrolidone (75%), *d*-limonene (25%)
(V) N-methylpyrrolidone (≤50%)
N-methylpyrrolidone (50%), γ-butyrolactone (28%), Exxate 600 solvent (17%), Ektapro EEP (5%)
(VI) Dibasic ester/NMP based
Dibasic ester blend (55%),[A] N-methylpyrrolidone (36%), dipropylene glycol methyl ester (9%)
(VII) Dibasic ester based
Water (74%), dimethyl adipate (23%), dimethyl glutarate (3%)

Note: Composition reported as weight percentage.
[A]The dibasic ester blend is Formulation VII.

Glove Selection

Selection of Gloves for Degradation Screening

A multistage process was used initially to select a relatively large number of gloves for chemical degradation resistance screening and to use the data from each phase to select the "most successful" gloves for each successive phase.

Initial selection of candidate gloves was based on a number of factors. Reviews of chemical resistance databases and manufacturers' data identified glove materials that appeared to offer "adequate" resistance to the various chemicals used in the seven different surrogate paint stripping formulations.[2-4] The inclusion of several different types of glove materials and the ready availability of the gloves to consumers were also factors.

All of the existing chemical resistance data for gloves were for neat chemicals only; there were no data on mixtures that approximated any of the seven surrogate paint stripping formulations. In addition, there were no data at all for some of the chemicals listed in these formulations.

The final list of 20 glove styles, appearing in Table III, was created by selecting two to three glove types from selected generic classes of gloves found to offer some degree of chemical permeation resistance as determined by an examination of the two databases, discussions with glove manufacturers, and preliminary glove survey information provided by paint stripper manufacturers. Some consideration was given to glove expense; Viton and other fluoropolymer gloves were not considered due to their prohibitive cost. Other materials were eliminated from consideration based on known performance problems. Polyvinyl alcohol gloves, for example, cannot be used around water even though they have outstanding chemical resistance against several solvents.

Selection of Gloves for Continuous and Intermittent Contact Permeation Testing

Seven different gloves were selected for continuous contact permeation testing against each surrogate paint stripper formulation. Six of these gloves were selected based on their ranking in Phase I degradation resistance screening tests. These included the same

TABLE II. Selected Commercial Paint Strippers and Identified Compositions

Formulation	Paint Stripper	Identified Composition[A]
IA	Klean Strip KS-3 Premium Stripper	76% methylene chloride, 5% isopropanol, 3% methanol, 3% butyl cellosolve
IB	Zip-Strip Paint & Varnish Remover	75% methylene chloride, 8% ethanol, 3% methanol, <1% decane
IIA	Savogran Strypeeze Original	35% toluene, 22% methanol, 20% acetone, 14% methylene chloride
IIB	National Solvent Liquid Stripper	87% methylene chloride, 5% methanol <1% acetone, <1% toluene
IIIA	Klean Strip Liquid Remover	46% acetone, 42% ethyl acetate, <1% iso-octane
IIIB	Parks Furniture Remover	34% acetone, 25% isopropanol, 21% methanol, 17% toluene, <1% methylene chloride
IVA	Savogran Biodegradable Strypeeze	67% NMP, 5% *d*-limonene, 25% dimethyl adipate, 3% dimethyl glutarate
IVB	Specialty Env. Tech. Citristrip	37% NMP, 23% *d*-limonene
VA	National Solvent Liquid Ultra Safe Stripper	22% NMP, 17% ethylene glycol, 61% Exxate
VB	Klean Strip Wood Finishers Pride Varnish Stripper	20% NMP, 37% γ-butyrolactone, 20% ethyl-3-ethyoxypropionate
VIA	Pyrox Safe Stripper	15% NMP, 5% dimethyl adipate, 1% dimethyl glutarate, 50% propylene carbonate
VIB	Parks Pro Stripper II	40% NMP, 5% dimethyl adipate, 11% dimethyl glutarate, 44% ethyl-3-ethyoxypropionate
VIIA	3M Safest Stripper	18.7% dimethyl adipate, 1.8% dimethyl glutarate balance primarily water

[A]Composition reported as weight percentage.

four gloves for each surrogate paint stripper formulation, the plastic laminate glove (Style E), and the three butyl rubber glove styles (Styles J, P, and S) (see Table III). The remaining two gloves selected varied depending on the formulation. The seventh glove selected was the next best performing commercially available glove style (distributed through the hardware retail business). Intermittent contact permeation testing was conducted on those gloves that showed normalized permeation breakthrough times of less than 2 hr for one or more formulation components. Gloves selected for continuous and intermittent contact permeation testing are shown in Table IV.

Selection of Gloves for Permeation Testing Against Commercial Paint Strippers

Three different gloves were chosen for evaluation against each of the selected commercial paint strippers. Glove Style E consistently outperformed all other gloves in terms of degradation and permeation resistance. The next "best" performing group of gloves (Styles J, P, and S) were those containing butyl rubber. Of these, Glove Style J demonstrated longer breakthrough times and lower permeation rates overall. Therefore, Glove Styles E and J were chosen as the first two gloves to be tested against the commercial paint stripper in each formulation category. The third glove style was selected based on continuous contact permeation data showing the longest nonbutyl rubber glove permeation breakthrough time. This selection process permitted the inclusion of three relatively different glove styles:

- Glove Style E is a highly chemical resistant, inexpensive glove; it is not, however, a traditional glove design and does not fit as well as rubber gloves.
- Butyl rubber gloves, although comfortable to wear, are relatively expensive.
- The third glove style was a less expensive rubber glove. For all surrogate formulations, except for Surrogate Formulation VII, the third glove style chosen was Style K. For Surrogate Formulation VII, Style F was selected.

Glove Chemical Degradation Screening

General Approach

In the chemical degradation resistance screening, one side of the test material was exposed to the chemical for 4 hr and changes in weight, thickness, and appearance were recorded. A one-sided exposure was considered important because many candidate gloves were not homogeneous or had specific linings that absorb chemicals differently than the normal exposure surface. The 4-hr exposure period is commonly used by the glove industry for rating glove degradation resistance and provides adequate time for measuring changes in glove condition. Weight change and changes in thickness are generally coupled with visual observations as consistent and useful measures of glove performance against chemicals for degradation testing.

Specimen Preparation

Fisher Septa~Jar® (Chicago, Ill.) wide-mouth containers (60 mL) with Teflon® fluorocarbon resin/silicone septa were used as the exposure container. The septa were removed from each bottle because the glove specimen would act as the gasket material between the bottle and the lid. The lid of the jar contained an 18 mm diameter hole, which allowed any evidence of severe degradation in the form of dripping or seepage to be observed. Glove material disks of 50 mm diameter were taken from the glove palms, backs, and sides for evaluation. Removal of specimens from nonhomogeneous areas of the glove was avoided. A total of three specimens was used for each glove type/paint stripping formulation combination. The weight and thickness of each specimen was determined and recorded prior to evaluation. An Ohaus model CT-200-S (Pinebrook, N.J.) balance was used to weigh each specimen

TABLE III. Glove Candidates for Degradation Resistance Testing

Style	Manufacturer	Glove Identification	Thickness (mil)
A	Ansell Edmont (Conshocton, Ohio)	natural rubber style 392	22
B	Ansell Edmont	neoprene style 29-845	17
C	Ansell Edmont	nitrile style 37-165	22
D	Ansell Edmont	Snorkel PVC style 4-414	65
E	Safety 4 (Lenexa, Kan.)	4H plastic laminate	2.7
F	Pioneer (Willard, Ohio)	neoprene style N-44[A]	22
G	Pioneer	Strip&Stain style E194 (nat/neo/nit)[A]	19
H	Pioneer	Technic neoprene style NS401[A]	22
I	Pioneer	disposable vinyl[A]	5
J	North (Charleston, S.C.)	butyl rubber style B-161	16
K	Thompson & Formby (Cleveland, Ohio)	refinishing gloves[A]	30
L	Wells Lamont (Niles, Ill.)	nitrile style 178[A]	15
M	Best Manufacturing (Menlo, Ga.)	Chem Master (neoprene/nat. rub.)	26
N	Best Manufacturing	N-Dex style 9005 (thin nitrile)	6
O	Comasec (Enfield, Conn.)	Multiplus (PVC/NBR nitrile)	65
P	Comasec	Butyl Plus (butyl/neoprene overdip)	25
Q	Best Manufacturing	Nitrile Nitrosolve	15
R	Best Manufacturing	Natural Rubber Value Master	18
S	Guardian (Willard, Ohio)	Butyl-Standard	15
V	Boss (Kewanee, Ill.)	PVC style 1FP2714[A]	54

[A]Consumer product.

to the nearest 0.01 g, whereas an Ames Series 27–2 (Waltham, Mass.) thickness gauge was used to measure specimen thickness to the nearest millimeter.

Exposure Period

Investigators placed 20 mL of a formulation in an exposure jar. A glove specimen was then inserted into the lid of the jar, and the jar lid was firmly secured to the jar. The exposure period was begun by inverting the jar and bringing the liquid into contact with the glove material. The inverted jars were placed on a ventilated rack 25 mm above a piece of blotting paper. At the end of the 4-hr period, the blotter paper and jar lid were examined for evidence of chemical dripping or seepage.

Measurement of Weight and Thickness Change

Specimens were carefully removed from the jar lid and placed between two sheets of blotting paper (Georgia Pacific style HM9201, two-ply towels). A weight was then placed on top of the blotting paper to achieve a 3.4 kPa pressure on the specimen for a period of 10 sec. The specimen was then turned over and reblotted for another 10 sec using the same procedure. Immediately following the blotting procedure, the weight of the exposed specimen was measured and recorded to the nearest 0.01 g followed by measuring the specimen's thickness to the nearest millimeter. To prevent variation in experimental technique, the same test operator performed all determinations.

Visual Evaluation of Specimen Condition

Ratings of the specimen's condition were made in the following categories: swelling, discoloration, curling, delamination, and deterioration.

Three choices were provided to rate these material conditions: 0—no effect; 1—mild or moderate effect; and 2—severe effect. In addition to visual ratings, photographs were taken for comparing a "pristine" specimen to representative specimens exposed to each of the seven different formulations.

Continuous Contact Permeation Testing

Glove Specimen Preparation

Die cut samples (25 mm diameter) were taken from the glove palms, backs, and sides for evaluation. Removal of specimens from nonhomogeneous areas of the glove was avoided. Three specimens

TABLE IV. Selected Glove Styles for Permeation Testing

Surrogate Paint Stripper Formulation	Selected Glove Styles[A]						
	1	2	3	4	5	6	7
I	E	**P**	**S**	**J**	**K**	**N**	**V**
II	E	P	**S**	J	**K**	**V**	**H**
III	E	P	S	J	**K**	**I**	**R**
IV	E	P	S	J	**K**	**A**	**G**
V	E	P	S	J	**K**	**H**	**M**
VI	E	P	S	J	K	**M**	**H**
VII	E	P	S	J	K	F	**A**

[A]Glove styles correspond to gloves listed in Table III; glove styles in boldface type indicate glove styles that were also evaluated for intermittent contact permeation resistance testing.

were used for each glove type/paint stripping formulation combination. The weight and thickness of each specimen was determined and recorded prior to evaluation. An Ohaus model CT-200-S balance was used to weigh each specimen to the nearest 0.01 g for computing specimen unit area weight, whereas an Ames series 27–2 thickness gauge was used to measure specimen thickness to the nearest 0.001 inch or mil. Specimens were edge-sealed between two Teflon gaskets with the glove material acting as a barrier between the challenge and collection sides of the permeation cell.

Permeation Test Method

Permeation testing was performed in accordance with a modified version of ASTM F 739–95, *Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases.* The modification of the test method was to use a smaller diameter test cell. Use of the smaller test cell has been shown to be equivalent through previous studies and reduces the volume of test chemical consumed in testing.[5,6] Although the standard specifies procedures for conducting the test, a number of test parameters are left to the discretion of the test laboratory. These primarily include the configuration of the permeation system and detector. The selection of the detector affects how the system is set up and the operating conditions for the test. It also greatly affects the reported permeation breakthrough time, because insensitive detectors will yield longer breakthrough times.

Permeant Collection Technique

A splash-type collection was used for this testing. This approach was adopted primarily because Formulations IV through VII contained relatively nonvolatile components, which could not be easily captured using conventional permeation collection techniques. Splash-type collection has previously been demonstrated as an effective means for collecting permeant of relatively nonvolatile chemicals.[7–9] This method employed 2-ethoxyethanol or methanol as the collection solvent. The choice of solvent was based on ensuring broad solubility of formulation components while minimizing leaching of glove material additives. The solvent rinse consisted of applying 2.0 mL of 2-ethoxyethanol (or methanol) for a residence time of 2–3 sec on the collection surface of the test specimen. Solvent rinses were individually applied and collected at 15-min intervals over the 4-hr test period.

Detection Methods for Conventional Solvent-Based Formulations

Gas chromatography was used for separating and quantifying formulation components for Formulations I through III, which contained primarily volatile solvents. Gas chromatography was performed with an HP 5890 (Palo Alto, Calif.) gas chromatograph (GC) equipped with a flame ionization detector and 30 m HP-1 column. A temperature program of 40°C for 6 min with a 20°C/min ramp to 100°C with no hold time was used. This procedure yielded a 2.5 μg/mL detection limit for all compounds.

Detection Methods for N-Methylpyrrolidone (NMP)-Based Formulations

Because of the relatively nonvolatile components of Formulations IV through VII, a more sophisticated analytical technique was required: use of a GC combined with a mass spectral detector (Perkin Elmer Automated System GC with auto injector). The specific procedure used was injection of 1 μL into a Perkin Elmer (Norwalk, Conn.) Autosystem GC with auto injector equipped with a 60-m J and W Scientific (Palo Alto, Calif.) DB-VRX column and Perkin Elmer Q-Mass 910 quadrapole rod detector. An injector temperature of 250°C was used with an initial oven temperature of 100°C for 5 min and ramp temperature of 10°C/min to 240°C. Helium was used at a flow rate of 1.12 mL/min with no split.

Mass spectral identification and quantification was performed using selected ion masses for each respective formulation component. External standardization was used in calculating the analytical results. Established detection limits were calculated to be 0.1 ng/μL. The detection limits were determined by using the lowest response factor and multiplying that factor by a verified response of 1000 area counts. Quality assurance and quality control were accomplished by running a standard with every batch run (20 samples) to verify the five-point calibration curve.

All tests were run in triplicate for a period of 4 hr at room temperature (25 + 2°C). Temperature control was managed by placing the test cells in a permeation testing box that had a thermostat and series of lamps and a fan to control temperature within the chamber. In addition to three replicates, a blank consisting of test glove material without challenge chemicals was run. Measurements of the blank were used to establish baseline measurements.

The measured concentration of each component was determined for each solvent-rinse and reported at the end time of the interval evaluated. For example, when a solvent rinse collection was performed at the end of 30 min, the resulting concentrations of formulation components were reported for 30 min but actually included all permeant that passed through the material from 15 to 30 min. In determining actual breakthrough time, the time preceding the reported time when chemical was first detected became the actual breakthrough time for the specific component using the limit of detection for the particular analytical approach. Normalized breakthrough time was based on the time preceding the reported time where a permeation rate equal to or greater than 0.1 $\mu g/cm^2 min$ was determined.

Intermittent Contact Permeation Testing

The same specimen preparation, collection technique, and detection strategies were used for intermittent contact permeation testing as for continuous contact permeation tests. Differences in permeation testing for intermittent contact tests were based on the selected test method.

Permeation testing was instead performed in accordance with a modified version of ASTM F 1383–92, *Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Intermittent Contact* using Condition B. Condition B involves cycling the formulation's exposure to the glove specimen over the duration of the test (4 hr) using the following technique:

- 5 min of chemical (formulation) exposure; and
- removal of the chemical (formulation) from the test cell (by pouring it out) and purging of the test cell with "dry" air for 10 min.

Normalized breakthrough time was based on the time preceding the reported time where a cumulative permeation equal to or greater than 0.05 $\mu g/cm^2$ was determined.

RESULTS AND DISCUSSION

Degradation Resistance Screening Testing

Results for degradation resistance screening testing are summarized in Table V, which compares percentage changes in weight

TABLE V. Summary of Degradation Resistance Testing Results

Glove Style[A]	Percentage Weight Change by Surrogate Paint Stripper Formulation						
	I	II	III	IV	V	VI	VII
A	96.2	39.1	32.7	58.6	22.5	9.5	6.4
B	105.8	50.9	44.1	210.0	109.7	58.7	23.2
C	120.5	139.0	101.4	258.0	188.7	122.4	46.4
D	49.0	45.9	45.0	80.2	78.4	80.1	14.3
E	0.0	2.4	2.4	0.0	0.0	0.0	0.0
F	57.7	34.0	36.8	105.0	37.3	26.6	5.9
G	72.2	34.5	35.4	70.0	22.7	12.0	7.2
H	64.9	33.9	37.2	83.0	14.4	10.3	7.9
I	47.1	−5.0	23.1	−100.0[B]	−100.0[B]	−100.0[B]	48.2
J	30.2	13.9	8.7	23.4	0.8	0.7	0.8
K	70.1	36.4	27.9	49.9	11.7	6.7	5.2
L	295.2	137.2	142.5	229.8	296.8	153.0	82.6
M	51.4	49.9	33.0	65.3	20.6	8.4	7.5
N	12.7	138.4	152.7	456.6	434.8	268.2	86.0
O	52.4	33.9	38.2	63.4	72.5	52.2	22.5
P	32.0	16.2	8.6	17.2	1.6	0.6	0.0
Q	110.4	97.3	113.4	308.8	205.7	159.8	51.6
R	98.1	43.0	27.7	84.4	22.9	11.4	10.2
S	26.2	14.7	8.3	31.6	2.3	1.1	0.7
V	29.8	10.0	34.7	97.5	83.5	76.0	37.1

[A]See Table III for definitions of glove styles.
[B]Glove dissolved completely during chemical exposure.

and thickness, overall degradation rating, and pass/fail performance relative to proposed acceptance criteria. Gray boxes indicate results falling outside those criteria. Study acceptance criteria consisted of the following:

- Percentage weight change ≤25%
- Percentage thickness change <25%
- Overall rating ≤3
- No dripping (as the result of degradation)

These degradation test results showed that no glove met all the performance criteria for every surrogate paint stripping formulation. The "better" performing gloves included gloves failing against one formulation—Glove Style E (Safety 4 4H plastic laminate glove), Glove Style J (North Butyl Rubber style B-161), and Glove Style P (Comasec Butyl Plus); gloves failing against two formulations—Glove Style S (Guardian Butyl-Standard); and gloves failing against four formulations—Glove Style G (Pioneer Strip&Stain), Glove Style H (Pioneer Technic neoprene style NS 401), and Glove Style K (Thompson & Formby Refinishing Gloves).

The majority of failures were due to weight gains in excess of 25%. Of the seven formulations, Formulations I (methylene chloride, methanol, isopropanol, and toluene) and IV (>50% NMP-based) were found to be the most "aggressive." The greatest weight gains were generally observed for formulations containing NMP. This is likely due to the lower volatility of NMP and dibasic esters as compared with organic solvents used in other formulations, such as methylene chloride, acetone, toluene, methanol, and isopropanol, which have higher vapor pressures. Fewer failures were observed on the basis of thickness; however, large weight gains were usually accompanied by swelling and significant changes in thickness.

Visible changes were also useful in rating the gloves' resistance. Swelling and curling were most often reported, whereas many gloves showed various stages of deterioration. Few gloves exhibited delamination owing to their homogeneous composition. Overall ratings were used to assess material performance. In nearly all cases high cumulative ratings (those greater than 3) indicating poor resistance were observed when significant weight and thickness changes were measured.

Evidence of dripping was coupled with visual ratings to determine glove material performance. Several gloves deteriorated to the point at which liquid penetrated. Other glove styles degraded to an extent that caused failure of the seal in the exposure jar, resulting in chemical seepage.

Although only a few gloves of the same representative glove material were evaluated in this study, it was apparent that certain glove types were wholly unsuitable against these formulations. Both nitrile and PVC gloves exhibited severe degradation to more mixtures. Differences were noted in the performance of the three neoprene gloves, which illustrates how performance of nominally the same generic glove material is affected by glove compound formulation differences.

Continuous Contact Permeation Testing

Table VI summarizes continuous contact permeation resistance testing as determined by a combination of actual breakthrough time, normalized breakthrough time, and permeation rate for each surrogate formulation. Tests in which no breakthrough was detected are indicated by a normalized breakthrough time of >240 min and a permeation rate of <0.1 $\mu g/cm^2/min$. Only three replicates were performed, so no attempt was made to average results. The shortest breakthrough time and highest permeation rate are used to represent a particular glove-formulation permeation test.

The test results showed a number of formulation (mixture) components that permeated many of the selected glove styles. In general, glove permeation resistance closely followed the findings from Phase I: gloves that demonstrated the best degradation resistance also showed longer breakthrough times and lower permeation rates. Only one glove style (Style E, 4H plastic laminate)

TABLE VI. Summary of Permeation Resistance Data for Continuous Contact Tests Against Surrogate Paint Stripper Formulations[A]

		Permeation Resistance Test Data by Glove Style[A,B]									
		Glove E		Glove P		Glove S		Glove J		Glove K	
Formulation	Chemical	NBT	PR	NBT	PR	NBT	PR	NBT	PR	NBT	PR
I	methylene chloride	>240	<0.1	30	85	30	35	60	61	15	60
	methanol	>240	<0.1	30	3.0	45	1.2	60	1.4	15	3.9
	isopropanol	>240	<0.1	60	0.7	60	1.4	120	0.9	30	10
	acetone	>240	<0.1	30	9.2	45	2.4	60	4.6	15	19
	toluene	>240	<0.1	30	6.8	45	2.9	60	4.3	15	12
II	methylene chloride	>240	<0.1	150	26	120	50	150	11	<15	27
	methanol	>240	<0.1	150	34	60	22	150	14	15	63
	acetone	>240	<0.1	150	7.2	120	3.9	180	2.5	<15	16
	toluene	>240	<0.1	150	5.4	90	3.8	150	1.8	15	17
III	acetone	>240	<0.1	180	7.9	150	13	>240	<0.1	15	190
	toluene	>240	<0.1	180	61	180	7.9	>240	<0.1	15	110
	methanol	>240	<0.1	180	0.8	180	1.2	>240	<0.1	15	23
IV	NMP[C]	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	60	94
	d-limonene	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	90	275
V	NMP	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	90	7.7
	γ-butyrolactone	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	90	1.4
	Exxate 600 solvent	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	120	1.5
	Ektapro EEP	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	90	1.4
VI	dibasic ester blend[D]	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1
	NMP	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	180	0.19
	DPGME[E]	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	90	10
VII	water	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1
	dimethyl adipate	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	210	0.1
	dimethyl glutarate	>240	<0.1	>240	<0.1	>240	<0.1	>240	<0.1	210	1.3

Note: Permeation resistance test data are provided for the same five glove styles evaluated against each of the seven surrogate paint stripper formulations.
[A]Permeation resistance test data include normalized breakthrough time (NBT) reported in minutes and permeation rate (PR) reported in micrograms per square centimeter per minute. The normalized breakthrough time is defined as the time at which the permeation rate equals 0.1 $\mu g/cm^2/min$. The reported permeation rate is the maximum permeation rate observed over the duration of the test (4 hr).
[B]The reported normalized breakthrough time is the shortest of the three measured breakthrough times. The reported permeation rate is the largest of the three measured permeation rates.
[C]NMP = N-methylpyrrolidone.
[D]The dibasic ester blend is Formulation VII.
[E]DPGME = dipropylene glycol methyl ester.

showed resistance to permeation by all chemicals with the exception of two replicates showing 150-min actual breakthrough times against methanol for Formulation I. The three butyl gloves (Styles P, S, and J) demonstrated the next best permeation resistance. In nearly all cases, permeation resistance of the other glove styles was relatively poor for all formulations, with the exception of Formulation VII.

Gloves generally performed better against Formulations IV to VII as compared with Formulations I to III, which contained principally volatile compounds. Selected glove candidates performed best against Formulation VII, the water-based surrogate paint stripping formulation.

For the majority of tests, results were consistent in terms of both breakthrough times and permeation rates for the three replicates tested. However, there were some combinations where wide ranges of permeation behavior were observed; it is believed that these variances are due to differences in glove thickness and composition.

Intermittent Contact Permeation Resistance Data

All of the selected glove-surrogate formulation combinations that had demonstrated rapid breakthrough under continuous contact test conditions also showed intermittent permeation breakthrough times of less than 2 hr for all components.

Table VII provides a comparison of normalized breakthrough times for both continuous contact and intermittent contact permeation resistance tests for selected glove styles and surrogate formulation chemicals. In many cases there were no changes in normalized breakthrough time for continuous contact and intermittent contact tests; however, a number of test results showed both shorter and longer normalized breakthrough times. Many of the longer intermittent testing breakthrough times were measured for the surrogate formulations containing volatile chemicals, whereas many of the shorter breakthrough times were measured for NMP and other less volatile chemicals.

Permeation rates were measured at the time of breakthrough for intermittent contact tests, so these rates were generally high compared with continuous contact data. However, the data presented in continuous contact tests were based on the steady state or ending permeation rates recorded at the end of the 4-hr tests. When continuous and intermittent contact data are presented on the same basis, performance was equivalent, as shown in the examples in Table VIII.

These examples demonstrate how much permeation rates can vary. The reasons for these variations are based on the overall permeation behavior for all glove styles with the exception of Glove Style E (Safety 4 4H plastic laminate glove). This permeation behavior is classified as Type D, as defined in ASTM F 739 (permeation that goes through a maximum and then levels off at some steady-state rate). Type D permeation behavior is

TABLE VII. Comparison of Normalized Breakthrough Times for Continuous and Intermittent Contact Permeation Resistance Tests for Selected Glove Style Surrogate Formulation Combinations

Chemical	Formulation	Glove Style	Normalized Breakthrough Time (min) Continuous Contact	Intermittent Contact
Methylene chloride	I	P	30	60
		S	30	30
		J	60	75
		K	15	15
	II	S	120	75
		K	<15	15
		V	<15	15
Acetone	I	P	30	60
		S	45	45
		J	60	75
		K	15	15
Toluene	II	S	60	90
		K	15	15
		V	<15	15
NMP	IV	K	60	15
		A	30	15
	V	K	90	45
		H	45	15
		M	30	30
	VI	H	60	15
		M	90	45

attributed to exposures in which there is moderate to heavy swelling of the material specimen, during which time the permeation rate achieves a maximum level and then stabilizes as the amount of swelling stays constant.[9] The degradation test data bear out this phenomenon because some swelling was noted with all rubber glove styles.

The overall finding for this phase is that glove performance was no better for intermittent exposure than for continuous exposure; that is, the same relative amount of permeation can be expected to occur with repetitive 5-min exposures every 15 min as with continuous chemical contact. This is likely the result of chemical driving forces that remain in effect due to wetting of the gloves' outer surfaces by the formulation itself. This phenomenon has been reported by other researchers in this field.[10–12] As a consequence of this testing, no other glove styles were qualified as "acceptable" from applying the 2-hr breakthrough time to intermittent contact permeation test results.

Permeation Testing Against Commercial Paint Strippers

Tables IX and X provide a comparison of the normalized breakthrough times and permeation rates by chemical for two of the surrogate formulations and the representative commercial paint strippers. For the most part, permeation test results for evaluation of the three selected gloves against each commercial paint stripper showed performance consistent with continuous contact permeation testing with surrogate paint stripper formulations. Glove performance was ranked similarly:

- Glove Style E (the 4H glove) provided the "best" permeation resistance for commercial paint strippers tested. No permeation was detected for any commercial paint strippers except for those that contained relatively high levels of methylene chloride (Formulation I). Composition analysis of Commercial Paint Stripper II-B shows relatively high levels of methylene chloride. This commercial paint stripper would have been more appropriately classified as a Formulation I paint stripper.
- The next "best" glove was a butyl rubber glove (Glove Style J). This particular glove did well against most NMP-based paint strippers and paint strippers with relatively low levels of methylene chloride.
- The third glove, usually the Thompson & Formby natural rubber glove, generally showed rapid permeation for solvent-based commercial paint strippers and only achieved breakthrough times greater than 2 hrs for the dibasic ester-based paint stripper. All of the volatile solvent-based paint strippers permeated at or before 15 min.

In many cases the permeation rates of the three glove styles differed by an order of magnitude. This was particularly evident in examining commercial paint strippers corresponding to Formulations I–III.

In comparing glove performance against commercial paint strippers with performance against the surrogate formulations, poorer permeation resistance was generally noted for gloves in the commercial paint stripper permeation tests against surrogate Formulations I–III. Permeation resistance testing of gloves against the commercial NMP-based and dibasic ester formulations showed performance in line with surrogate formulation testing.

Differences in results between surrogate formulations and corresponding commercial paint stripper formulations are believed to be caused by deviations in the composition of commercial paint strippers compared with the surrogate formulations or to the synergistic effects of additional mixture components not accounted for in the surrogate formulations.

TABLE VIII. Comparison of Continuous and Intermittent Contact Permeation Rates for Selected Glove Style Surrogate Formulation Combinations

Glove Style	Rep. No.	Methylene Chloride Permeation Rate (μg/cm²/min) Continuous Steady State	Continuous Maximum	Intermittent Maximum
Glove K, Thompson & Formby Refinishing Glove	1	60	421	400
	2	57	381	360
	3	34	486	480
Glove V, Boss PVC Style 1FP2714	1	130	671	310
	2	190	579	380
	3	180	1052	372

Note: Both the steady-state and maximum permeation rate are reported for continuous contact permeation resistance tests, whereas the maximum permeation rate is reported only for intermittent contact permeation resistance tests.

TABLE IX. Comparison of Permeation Test Results for Surrogate Formulation I and Representative Commercial Paint Strippers

Challenge[A]	Mixture Component Percentage	Normalized Breakthrough Time[B] (min)			Permeation Rate[C] (μg/cm^2/min)		
		Glove E (Plastic)	Glove J (Butyl)	Glove K (N. Rub.)	Glove E (Plastic)	Glove J (Butyl)	Glove K (N. Rub.)
Methylene chloride							
Formulation I	80	>240	60	15	<0.1	61	60
Stripper I-A	76	15	<15	<15	3.9	91	520
Stripper I-B	75	15	15	<15	3.4	160	380
Methanol							
Formulation I	3	150	60	15	0.06	1.4	3.9
Stripper I-A	3	30	<15	<15	0.45	2.8	25
Stripper I-B	3	>240	30	15	<0.1	2.6	14
Isopropanol (IPA) or ethanol							
Formulation I	3 (IPA)	>240	120	30	<0.1	0.9	20
Stripper I-A	5 (IPA)	120	15	<15	0.15	3.3	35
Stripper I-B	8 (ethanol)	180	15	<15	0.07	1.8	4.4

[A]Three chemicals from the formulation were selected for comparison purposes.
[B]Shortest of three normalized breakthrough times recorded.
[C]Largest of three reported permeation rates.

CONCLUSIONS

This testing has demonstrated the usefulness of a multistage approach to evaluating glove permeation resistance against paint strippers. The use of surrogate paint stripper formulations representing categories of commercially available paint strippers allowed for screening tests that identify suitable gloves types for a wider range of commercial products. This study further showed the value of degradation testing for eliminating unsuitable glove types. However, paint stripper formulations represent varying multichemical mixtures and, ultimately, commercial paint strippers must be individually evaluated for permeation resistance against selected gloves.

These results show that the relatively small-molecule, volatile, chemical-based solvents cause somewhat more degradation and considerably more permeation of glove types as compared with NMP and dibasic ester-containing formulations against the same gloves. Most rubber gloves appear to show relatively rapid permeation by volatile solvent mixtures as represented by surrogate paint stripper formulations. Only a plastic laminate glove resisted permeation by the majority of surrogate formulations and commercial paint strippers. Butyl rubber gloves provide the next best level of permeation resistance, but still showed rapid permeation for some mixture components, notably methylene chloride. On the other hand, formulations containing NMP and/or dibasic esters showed less rapid permeation of butyl gloves and in many cases showed no detectable permeation for the selected butyl and natural rubber glove styles.

An important finding of this study is that glove permeation did not improve with intermittent contact time. As long as the contact is repetitive and sustained over the same period of time as used in continuous contact tests, permeation results will be similar. This type of permeation performance indicates that wetting of the glove surface by the paint stripper will provide a sufficient driving force to continue permeation, even when the bulk of liquid is removed. Therefore, shortened exposures may not be an acceptable practice for extending glove service life or for improving the marginal chemical resistance offered by some glove types. The data provided in this study should be useful for establishing appropriate glove types for different commercial paint strippers by matching the composition of the nearest surrogate formulation with the composition of

TABLE X. Comparison of Permeation Test Results for Surrogate Formulation IV and Representative Commercial Paint Strippers

Challenge[A]	Mixture Component Percentage	Normalized Breakthrough Time[B] (min)			Permeation Rate[C] (μg/cm^2/min)		
		Glove E (Plastic)	Glove J (Butyl)	Glove K (N. Rub.)	Glove E (Plastic)	Glove J (Butyl)	Glove K (N. Rub.)
NMP							
Formulation IV	75	>240	>240	60	<0.1	<0.1	94
Stripper IV-A	67	>240	>240	90	<0.1	<0.1	6.6
Stripper IV-B	37	>240	180	60	<0.1	0.3	14
d-limonene							
Formulation IV	25	>240	>240	90	<0.1	<0.1	280
Stripper IV-A	5	>240	>240	90	<0.1	<0.1	3.8
Stripper IV-B	23	>240	180	60	<0.1	0.6	17

[A]Three chemicals from the formulation were selected for comparison purposes.
[B]Shortest of three normalized breakthrough times recorded.
[C]Largest of three reported permeation rates.

the respective commercial paint stripper. Nevertheless, because of several potential synergistic effects well established in the literature and in this study for mixture permeation, it is highly recommended that glove selection decisions be based on testing of the commercial paint stripper against the specific glove in question.

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