GLOVE PERMEATION BY SEMICONDUCTOR PROCESSING MIXTURES CONTAINING GLYCOL-ETHER DERIVATIVES

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Results of permeation tests of several glove materials challenged with semiconductor processing formulations containing glycol-ether derivatives are described. Commercial glove samples of nitrile rubber (Edmont), natural rubber (Edmont and Baxter), butyl rubber (North), PVC (Baxter), a natural rubber/neoprene/nitrile blend (Pioneer), and a natural rubber/neoprene blend (Playtex) were tested according to the ASTM F739-85 permeation test method (open-loop configuration). The liquid formulations examined included a positive photoresist thinner containing 2-ethoxyethyl acetate (2-EEA), n-butyl acetate, and xylene; a positive photoresist containing 2-EEA, n-butyl acetate, xylene, polymer resins, and photoactive compounds; a negative photoresist containing 2-methoxyethanol (2-ME), xylene, and cyclized poly(isoprene); and pure 2-methoxyethyl acetate (2-MEA), which is the solvent used in a commercial electron-beam resist. With the exception of the negative photoresist, butyl rubber provided the highest level of protection against the solvent mixtures tested, with no breakthrough observed after 4 hr of continuous exposure at 25°C. Nitrile rubber provided the highest level of protection against the negative photoresist and reasonably good protection against initial exposure to the other solvent mixtures. Gloves consisting of natural rubber or natural rubber blends provided less protection against the mixtures than either nitrile or butyl rubber. For most of the glove samples, permeation of the glycol-ether derivatives contained in the mixtures was faster than that predicted from the permeation of the pure solvents. Increasing the exposure temperature from 25 to 37°C did not significantly affect the performance of the butyl rubber glove. For the other gloves, however, exposures at 37°C resulted in decreases in breakthrough times of 25–75% and increases in steady-state permeation rates of 80–457% relative to values obtained at 25°C. Repeated exposure of nitrile rubber samples resulted in shorter breakthrough times for all mixture components. In fact, exposure for as little as one-half of the nominal breakthrough time followed by air drying overnight resulted in measurable quantities of one or more of the component solvents at the inner surface of the gloves at the beginning of the next exposure. This effect was not observed with the butyl rubber samples. With the exception of the negative photoresist, heating previously exposed nitrile rubber samples at 70°C for 20 hr prior to retesting reduced or eliminated the effects of residual solvents, permitting reuse of the gloves. The use of thin PVC or natural rubber gloves adjacent to the nitrile gloves provided moderate increases in permeation resistance. Addition of 10% acetone to the positive photoresist resulted in shorter breakthrough times and higher permeation rates for all components through the nitrile rubber.

T he production of semiconductor devices involves a series of chemical and physical processes performed on a single crystalline wafer of silicon or some other semiconducting substrate. The fabrication of these miniaturized devices is performed in clean rooms that employ filtered supply air and high ventilation rates to minimize the levels of particles that might settle on the wafer and interfere with the formation of the circuitry. Although each type of device requires a different series of processing steps, virtually all devices are made by using various iterations of six unit processes: oxidation, microlithographic patterning, etching, junction formation, layer deposition, and metallization. Detailed reviews of the hazards associated with each of these processes have been published elsewhere.[1-5]

Considerable interest has been raised recently about the risks of adverse reproductive health effects associated with working in the semiconductor industry. Results from one study suggested an increase in spontaneous abortions among production workers

in a major U.S. semiconductor manufacturing plant.[6] However, the findings from that study were considered inconclusive because of the small size of the study population and the failure to identify any specific etiologic agents that might be responsible for the observed health effects. A number of other studies have since been initiated to examine in more detail the risks of reproductive and other health effects in the semiconductor industry.[7,8]

Relatively little is known about specific reproductive hazards in semiconductor manufacturing,[9] although certain chemicals have been linked with teratogenic effects in test animals. Most notably, the glycol ethers and their derivatives, which are used as solvents in microlithographic resist formulations, have been linked to these effects.[10,11] Recognition of the toxicity of the glycol ethers has led several resist manufacturers to develop formulations containing less toxic solvents[12,13] but the use of glycol-ether–based resists is still quite prevalent.

The limited industrial hygiene data available for this industry suggest that 8-hr time-weighted-average exposures to vapors of the most common processing solvents are typically less than 10% of recommended standards.[14] However, the potential for exposure via dermal absorption has not been examined in detail. For large-scale semiconductor manufacturing, many of the processing steps are automated, which reduces the likelihood of chronic dermal exposure; however, routine maintenance of equipment and restocking chemical source vessels still give rise to the potential for periodic employee exposure. In smaller production facilities, as well as academic and industrial research laboratories, smaller quantities of materials are used but most operations are performed manually. Thus, the potential for contact with the process chemicals remains high.

Statistics compiled by the Occupational Health System of the Semiconductor Industry Association indicate that contact with chemicals accounted for over 20% of all Occupational Safety and Health Administration (OSHA)–recordable injuries and illnesses in the industry from 1982–1986; dermatoses accounted for 45% of all OSHA–recordable illnesses among semiconductor workers over the same period.[15] Similarly, data from the Bureau of Labor Statistics Annual Reports show that "skin disorders and diseases" accounted for 28% and 41% of all illnesses in the semiconductor industry for 1984 and 1985, respectively.[16]

Although many of the reports of chemical contact and dermatoses undoubtedly involved acid splashes, the relatively high number of such incidents raises the question of whether dermal absorption may represent a significant exposure route for systemic toxicants. For glycol-ether derivatives, this exposure route may be particularly important because they are readily absorbed through intact skin.[11]

The selection of gloves for protection against dermal exposure to glycol-ether derivatives used in semiconductor processing is complicated by the use of mixtures of solvents in many of the formulations. Several reports have described the permeation of gloves by solvent mixtures,[17–19] and it has been shown that the permeation of solvents in mixtures can be significantly accelerated relative to that of the individual component solvents.[19]

Modest increases in temperature can also lead to significant increases in glove permeability.[20,21] In addition, solvents can be retained in the glove after an initial exposure and slowly permeate to the inner surface during periods of nonuse.[22,23] Predictive models of permeation based on the physicochemical properties of the solvents and glove materials are being developed[24,25] but have yet to provide any generally applicable selection rules. Thus, the confident selection of a glove material requires empirical testing by the end-user for the particular mixture involved.

In this paper, the permeation behavior of several common glove materials challenged with semiconductor processing mixtures containing glycol-ether derivatives is described. Comparisons are made between the permeation of the solvents in the mixtures and the individual solvents comprising the mixtures. The effects of temperature from 25 to 37°C are also determined for most of the glove/mixture pairs. Results of repeated exposure of the butyl and nitrile rubber gloves to the mixtures are presented, as well as the use of thermal decontamination to remove residual solvents in the nitrile rubber gloves. The effects of glove thickness and additional glove layers (natural rubber or PVC) on the permeation of the nitrile rubber gloves by the mixtures are also evaluated.

GLOVE USE PRACTICES

In conjunction with this study, a survey was conducted of a number of semiconductor processing facilities to assess current glove use practices.[26] In some facilities a single glove type was used for all chemicals. More typically, two types of gloves were used—one type for acids and bases and another for organic solvents. In a few facilities, up to three types of gloves were used with specific recommendations made for each type of liquid for which protection was desired. For acids and bases, the most common type of glove used was natural rubber. For organic solvents, various glove materials were used but nitrile rubber was by far the most common. Most of the users surveyed indicated that gloves were reused for up to 5 days before being replaced.

The use of thin, surgical-type gloves is mandatory in most clean rooms in order to prevent contamination of the wafers by the oils and salts on the hands of the workers. Although these gloves are not designed to serve as liquid or gaseous chemical barriers, the survey revealed a few cases where these gloves are used alone when handling chemicals. In most cases, these thin gloves are worn beneath more impervious gloves for protection against chemical exposure.

The need to minimize particulate generation within semiconductor production facilities precludes the use of flock-lined gloves. A number of manufacturers now offer gloves that have been specially treated and packaged to minimize particulate generation. It was found that these types of gloves are used extensively in the industry. The Edmont Nytek® and Puretek®, Pioneer Trionic®, and Baxter gloves included in this study are examples of such treated gloves.

In addition to considerations of current glove use practices in the industry, the choice of glove materials for this study was also based on information found in glove selection guides[21,27–30] and material safety data sheets for the solvents investigated.

EXPERIMENTAL MATERIALS AND METHODS

Table I lists the brands, models, polymer components, and mean thicknesses of the gloves tested. Individual solvents were of

reagent grade or higher purity and were used without further purification (Aldrich Chemical Co., Milwaukee, Wis.). Table II presents the compositions of the liquid formulations tested, which included a positive photoresist thinner (Microposit Thinner Type A, Shipley Co., Newton, Mass.), a positive photoresist (Microposit Photoresist S1400-17, Shipley Co.), and a negative photoresist (Negative Photoresist 747, KTI Chemicals, Sunnyvale, Calif.). 2-Methoxyethyl acetate (2-MEA), the solvent component of an electron-beam resist, was used in pure form in lieu of using the resist material itself. Additional tests were performed on a mixture of the positive photoresist and acetone to simulate operations where acetone is used to remove photoresist residues from wafers and processing equipment.

Permeation testing was performed according to the ASTM F739-85 method.[31] A 5.08-cm (2-in.) diameter test cell (Pesce Lab Sales, Kenneth Square, Pa.) was used in an open-loop configuration with dry N_2 gas being

TABLE I. Brand, Model, Polymer Component(s), and Mean Thickness of Each Glove Tested

Brand/Model	Composition	Thickness (cm)
Edmont Nytek® (49-155)	nitrile	0.036, 0.043[A]
Edmont Puretek® (30-139)	natural rubber	0.051
Pioneer Trionic®	natural rubber/ neoprene/ nitrile blend	0.046
Playtex (827)	natural rubber/ neoprene blend	0.038
North (B-161)	butyl rubber	0.038
Baxter (G7-224)	natural rubber	0.018
Baxter (G7-238)	PVC	0.018

[A]Each mean thickness represents a different lot of nitrile gloves.

TABLE II. Compositions of Liquid Formulations[A]

Formulation	Component Solvents	Weight Fraction (%)
Positive photoresist thinner	2-ethoxyethyl acetate (2-EEA)	82
	xylene	9
	n-butyl acetate	9
Positive photoresist	2-ethoxyethyl acetate (2-EEA)	68
	xylene	7.5
	n-butyl acetate	7.5
	resins/photoactive compounds	17
Negative photoresist	2-methoxy ethanol (2-ME)	<6
	xylene	80–92
	cyclized poly(isoprene)	5–15

[A]Based on material safety data sheets provided by the manufacturers.

passed through the collection side of the cell at 500 cm³/min. All downstream components of the system were constructed of Teflon® or stainless steel to avoid adsorptive losses. The test cell was immersed in a constant-temperature water bath controlled to ±0.5°C. The cell and a flask containing the challenge liquid were placed in the water bath for several minutes prior to testing to allow all system components to come to thermal equilibrium. The liquid was then transferred to the test cell either by syringe or by cannula (under a positive pressure of air). The temperature of the N_2 gas stream was also regulated to ±1.5°C with a heating mantle prior to passing it through the test cell. The N_2 temperature was monitored with a thermocouple placed just upstream from the cell. For the resist formulations, all manipulations were performed under yellow lights to avoid light-induced changes in the photoactive components of these formulations. All test mixtures were stirred with a glass rod connected to a mechanical stirrer.

Test samples cut from the gauntlet region of each glove were clamped into the cell and tightened to a constant pressure of 20 in.-lb with a torque wrench. Mean sample thicknesses were determined from measurements with a micrometer at five random locations on the sample. Intersample thickness variations were less than 0.00254 cm (1 mil) for a given glove type. For the Edmont Nytek glove, tests were performed on gloves from each of two lots, which differed in mean thickness (see Table I).

The gas downstream from the test cell was sampled periodically with a 5-mL gastight syringe and analyzed with a gas chromatograph (Model 2860, Varian Associates, Palo Alto, Calif.) equipped with a packed column (0.61-m stainless steel, 0.32-cm OD, packed with 1% SP-1000 on 60/80 mesh Carbopack B, Supelco, Bellefonte, Pa.) and a flame ionization detector. Peak areas were measured with an electronic integrator (Model 3390A, Hewlett Packard, Palo Alto, Calif.). Instrument calibrations were performed daily by using test atmospheres of the analytes diluted in air in 100-L Tedlar® bags (SKC, Eighty Four, Pa.). Wall adsorption losses were examined and found to be negligible for all solvents.

Steady-state permeation rates (PR, µg/cm²/min) were calculated by averaging five measurements obtained after the downstream solvent concentration showed no further increase with time. Breakthrough times (BT, min) were defined as the times required for the downstream vapor concentration to reach 10 mg/m³, which corresponds to a permeation rate of 0.25 µg/cm²/min for this test system. This concentration corresponds to injected masses that were well above the limits of detection for all of the vapors tested. For exposures at 37°C, the appropriate temperature correction was applied to the air concentrations of the injected samples.

For repeated exposures, samples were exposed initially, carefully removed from the test cell, patted dry to remove visible

liquid, and then allowed to air dry in an exhaust hood having a face velocity of 27–30 m/min (90–100 ft/min). Thermal decontamination tests were performed by suspending exposed gloves in a vented oven maintained at 70°C. All manipulations of unexposed glove samples were performed while wearing surgical gloves. All chemicals and preexposed gloves were handled with chemical protective gloves made of butyl or nitrile rubber.

RESULTS AND DISCUSSION

Pure Solvents versus Mixtures

Table III presents the breakthrough times and steady-state permeation rates measured at 25°C for the individual solvents. For neat 2-EEA, 2-ME, and 2-MEA, butyl rubber provided the best protection with no breakthrough being observed after 4 hr of exposure. For n-butyl acetate, butyl rubber again showed the longest breakthrough time and the lowest permeation rate. For xylene, nitrile rubber showed the highest permeation resistance. The results obtained here are in qualitative agreement with those published by the glove manufacturers[27–30] and other sources of permeation data for these solvents.[11,21] Note that for both n-butyl acetate and xylene, shorter breakthrough times and higher permeation rates were observed for all glove samples relative to the glycol-ether derivatives. On the basis of previous studies of solvent mixtures,[17–19] it was suspected that the presence of these solvents in the mixtures might compromise the resistance of the gloves to the glycol-ether derivatives.

The breakthrough times and steady-state permeation rates of the solvents in each of the mixtures measured at 25°C are presented in Table IV. Comparisons of the values for the component solvents in the photoresist thinner with those for the individual solvents (Table III) show that the xylene and n-butyl acetate permeated much more slowly in the mixture, consistent (qualitatively) with their low concentrations. For the 2-EEA in the mixture, however, the breakthrough times for all of the glove materials except butyl rubber were less than or equal to those of the neat 2-EEA (see Figure 1a), even though this solvent comprised only 82% by weight (80% by volume) of the mixture. In addition, the permeation rates for 2-EEA in the mixture for these four glove materials were greater than or equal to those for the neat 2-EEA (see Figure 1b). (Note: the difference in the 2-EEA permeation rates for the nitrile glove was negligible.)

TABLE III. Breakthrough Times (BT) and Steady-State Permeation Rates (PR) of Individual Solvents at 25°C

Solvent	Glove	n	BT (min)	PR (µg/cm²/min)
Xylene	Playtex	2	3 (0)[A]	1031 (96)[A]
	natural rubber	3	4 (0)	886 (99)
	Trionic®	3	2 (1)	837 (156)
	nitrile[B]	3	62 (6)	196 (24)
	butyl	2	9 (0)	760 (42)
n-Butyl acetate	Playtex	2	7 (1)	679 (3)
	natural rubber	3	7 (1)	844 (78)
	Trionic	3	5 (0)	789 (20)
	nitrile[B]	3	69 (5)	239 (17)
	butyl	2	82 (0)	62 (1)
2-EEA	Playtex	3	14 (1)	128 (20)
	natural rubber	3	14 (2)	85 (10)
	Trionic	3	13 (3)	88 (18)
	nitrile[B]	3	112 (5)	118 (24)
	butyl	2	>240	ND[C]
2-ME	Playtex	2	48 (0)	12 (1)
	natural rubber	2	43 (1)	4 (1)
	Trionic	2	27 (2)	6 (1)
	nitrile[B]	2	126 (8)	88 (7)
	butyl	2	>240	ND
2-MEA	nitrile[D]	2	42 (1)	250 (2)
	butyl	2	>240	ND

[A]Numbers in parentheses are standard deviations.
[B]Thickness = 0.043 cm.
[C]None detected.
[D]Thickness = 0.036 cm.

Also presented in Figures 1a and b are the breakthrough times and permeation rates, respectively, of the 2-EEA in the positive photoresist. In this case, the breakthrough times for 2-EEA in the mixture were virtually the same as those for neat 2-EEA for all of the gloves, and the permeation rates were about the same or lower for the mixture than for the neat 2-EEA. The improvements in permeation resistance relative to the resist thinner can be attributed to a combination of lower solvent concentrations and the presence of the polymer resin and photoactive compound, which comprise 17% of the mixture. The resin used in this formulation is a phenol-formaldehyde polymer and the photoactive compound is a salt of a substituted diazo naphthalene sulfonic acid. Given the large molecular sizes of these components and the ionic nature of the photoactive compound, neither would be expected to permeate the gloves to a significant extent.

A common practice in many research and production facilities is to use acetone to manually clean equipment contaminated with residual positive photoresist. To investigate the effects of small amounts of acetone on the permeation resistance of nitrile and butyl gloves, additional tests were performed at 25°C with a mixture of the positive photoresist and acetone (10% by volume). For the nitrile samples, decreases of approximately 30% in the breakthrough times and increases of 40% (2-EEA), 62% (n-butyl acetate), and 78% (xylene) in the permeation rates were observed relative to values for the positive photoresist alone. Acetone had an average breakthrough time of 81 ± 1 min and an

TABLE IV. Breakthrough Times (BT) and Steady-State Permeation Rates (PR) of the Solvents in the Mixtures at 25°C

Solvent (wt%)	Glove	n	BT (min)	PR ($\mu g/cm^2/min$)
Photoresist Thinner				
Xylene (9%)	Playtex	2	15 (0)[A]	37 (1)[A]
	natural rubber	3	13 (1)	37 (2)
	Trionic®	2	9 (0)	44 (1)
	nitrile[B]	3	106 (5)	22 (1)
	nitrile[C]	5	79 (3)	23 (1)
	butyl	1	>300	ND[D]
n-Butyl	Playtex	2	14 (0)	46 (1)
acetate (9%)	natural rubber	3	12 (1)	42 (2)
	Trionic	2	8 (0)	51 (0)
	nitrile[B]	3	103 (5)	30 (1)
	nitrile[C]	5	74 (3)	34 (2)
	butyl	1	>300	ND
2-EEA (82%)	Playtex	2	14 (1)	135 (0)
	natural rubber	3	11 (2)	128 (10)
	Trionic	2	8 (0)	154 (1)
	nitrile[B]	3	96 (4)	116 (6)
	nitrile[C]	5	64 (5)	118 (8)
	butyl	1	>300	ND
Positive Photoresist				
Xylene (7.5%)	Playtex	2	16 (3)	32 (5)
	natural rubber	2	17 (0)	25 (4)
	Trionic	2	15 (1)	30 (1)
	nitrile[B]	2	129 (1)	9 (1)
	nitrile[C]	3	107 (7)	10 (2)
	butyl	1	>240	ND
n-Butyl	Playtex	2	13 (0)	38 (8)
acetate (7.5%)	natural rubber	2	16 (0)	29 (5)
	Trionic	2	14 (1)	43 (18)
	nitrile[B]	2	120 (3)	16 (1)
	nitrile[C]	3	98 (5)	16 (2)
	butyl	1	>240	ND
2-EEA (68%)	Playtex	2	12 (0)	101 (21)
	natural rubber	2	14 (0)	78 (12)
	Trionic	2	14 (1)	90 (7)
	nitrile[B]	2	114 (4)	70 (2)
	nitrile[C]	3	89 (3)	68 (6)
	butyl	1	>240	ND
Negative Photoresist				
Xylene (80–92%)	Playtex	2	4 (1)	569 (40)
	natural rubber	2	6 (0)	669 (57)
	Trionic	2	4 (0)	604 (33)
	nitrile[B]	2	66 (7)	60 (4)
	nitrile[C]	3	49 (2)	82 (8)
	butyl	2	12 (0)	554 (35)
2-ME (<6%)	Playtex	2	5 (1)	38 (0)
	natural rubber	2	6 (0)	41 (9)
	Trionic	2	4 (0)	39 (1)
	nitrile[B]	2	77 (9)	6 (0)
	nitrile[C]	3	72 (4)	12 (2)
	butyl	2	12 (0)	26 (5)

[A]Numbers in parentheses are standard deviations. [B]Thickness = 0.043 cm. [C]Thickness = 0.036 cm. [D]None detected.

average permeation rate of 106 ± 6 $\mu g/cm^2/min$ in the mixture. Although the breakthrough times for all solvents were still greater than 1 hr, the decrease in protection caused by this small amount of acetone is of some concern. Actual cleanup operations might involve much higher relative concentrations of acetone, which might cause further reductions in permeation resistance to the photoresist solvents. No breakthrough was observed for the butyl rubber samples after 4 hr of exposure to this mixture.

For the negative photoresist, significant decreases in the breakthrough times of 2-ME were observed for the mixture relative to the neat solvent for all of the gloves, as shown in Figure 2a. This effect was most dramatic for the butyl rubber samples, which showed no breakthrough after 4 hr of exposure to pure 2-ME, but had a breakthrough time of only 12 min for the 2-ME in the mixture (<6% by weight). In contrast to the behavior seen with the positive resist and the resist thinner, xylene apparently had a significant effect on the permeation resistance of the butyl glove to the negative resist. The nitrile rubber samples, which showed the greatest resistance to pure xylene, showed the least reduction in breakthrough time for the 2-ME in the negative resist. With the exception of nitrile rubber, the permeation rates for 2-ME in the mixture were greater than those for pure 2-ME for all of the gloves (Figure 2b), although the permeation rates remained relatively low.

Comparison of the permeation of the solvent mixtures through the two nitrile rubber gloves (i.e., 0.043-cm samples versus 0.036-cm samples) shows that the breakthrough times for the 0.036-cm samples were consistently lower; however, the thickness dependence of the breakthrough times varied with
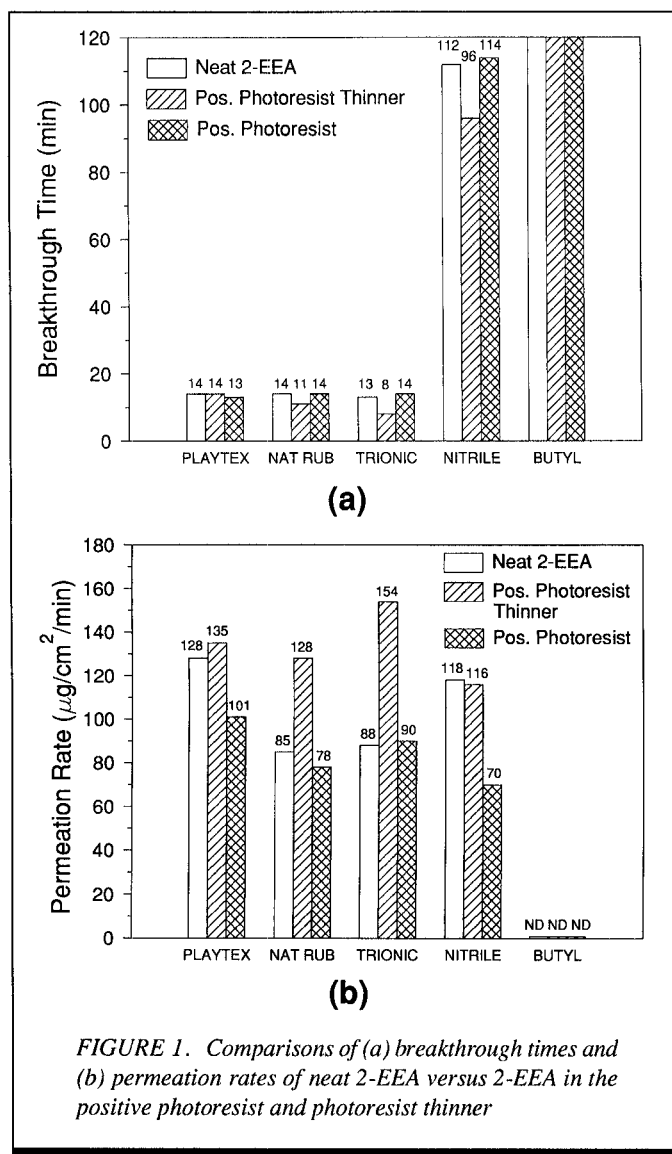
FIGURE 1. Comparisons of (a) breakthrough times and
(b) permeation rates of neat 2-EEA versus 2-EEA in the
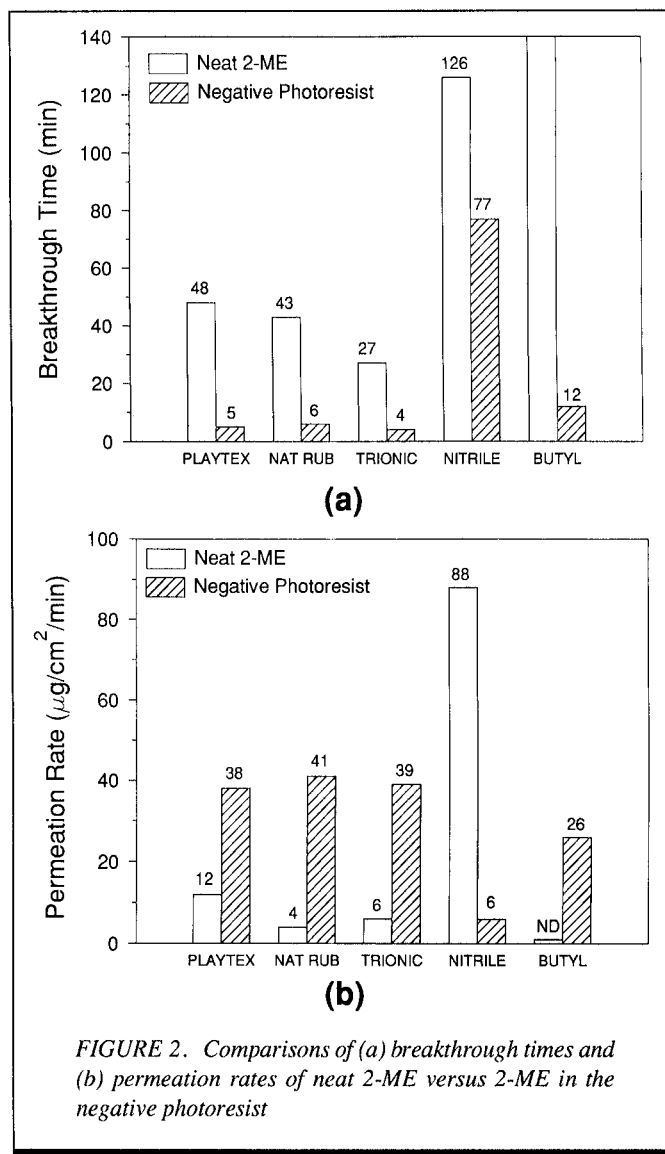positive photoresist and photoresist thinner

FIGURE 2. Comparisons of (a) breakthrough times and
(b) permeation rates of neat 2-ME versus 2-ME in the
negative photoresist

the type of solvent mixture. For the solvents in the photoresist thinner and the xylene in the negative photoresist, the ratios of breakthrough times were equal (within 9%) to the ratios of the squares of the glove thicknesses whereas for the positive photoresist, the solvent breakthrough times varied directly with the thicknesses. For the 2-ME in the negative photoresist, the breakthrough times for the two gloves were virtually the same. For both solvents in the negative photoresist, considerably higher permeation rates were observed with the thinner nitrile rubber samples. In contrast, the steady-state permeation rates of all other mixture solvents were nearly independent of glove thickness.

To put these results into perspective, it is useful to consider them briefly in the context of permeation theory. The permeation of organic solvents through polymeric glove materials is governed by the solubility and diffusion of the solvent in the glove.[21,32] In the ideal case, Fick's laws of diffusion are obeyed, the diffusion coefficient is constant, and the solubility of the solvent in the polymer is proportional to the solvent concentration in the challenge mixture. Under these conditions, the steady-state permeation rate of a solvent in a mixture should be directly proportional to its concentration. The relationship between the breakthrough time and the solution con-

centration is more complex, but the breakthrough time should also decrease as the solvent concentration decreases. For a given solvent/ glove pair, the steady-state permeation rate should vary inversely with the thickness of the glove sample. The theoretical variation in breakthrough time with thickness is approximately equal to the ratios of the squares of the thicknesses, as has been observed experimentally.[33]

The fact that the permeation rates of the glycol-ether derivatives were higher than expected and the breakthrough times lower than expected for most of the gloves challenged with the mixtures indicates that the other solvents (i.e., n-butyl acetate, xylene, and acetone) were facilitating the diffusion of glycol-ethers through the gloves, most likely by swelling the glove polymers and increasing the effective diffusion coefficients and/or solubilities of the other solvents in the gloves. The exceptionally good resistance of the butyl rubber to the positive resist and resist thinner indicates that this effect was not significant where the other solvents were present in relatively small quantities. In contrast, the results for the butyl rubber/ negative resist combination show that a high percentage of the rapidly permeating xylene had a pronounced effect on the permeation of 2-ME. The reason for the differences in the thickness

dependence of the breakthrough times is not known but may be the result of varying degrees of glove swelling or the presence of polymeric resins in the resists. A more detailed examination of these results in light of empirical and theoretical models of permeation is currently underway.

Temperature Effects

Most of the processes involving potential contact with resist formulations are performed at room temperature. Thus, the relevant temperature range over which to examine the gloves is between room temperature (i.e., 25°C) and body temperature (i.e., 37°C). To determine whether significant changes in permeation would occur over this modest temperature range, permeation tests were repeated at 37°C.

Table V presents the ratios of the breakthrough times and permeation rates observed at 37 and 25°C (i.e., 37°C/25°C) for several of the glove/solvent pairs. With the exception of butyl rubber challenged with pure 2-MEA, a decrease in permeation resistance was observed for all of the solvents at the higher temperature. Focusing on the glycol-ether derivatives, the breakthrough times decreased by as much as 73% (Trionic/2-EEA) and permeation rates increased by as much as 300% (nitrile/2-ME) between 25 and 37°C.

TABLE V. Ratios of Breakthrough Times (BT) and Steady-State Permeation Rates (PR) at 37°C and 25°C for the Mixtures and Neat 2-MEA

Solvent	Glove	n^A	BT (37°C)/BT(25°C)	PR (37°C)/PR(25°C)
Photoresist Thinner				
Xylene	natural rubber	3	0.55	1.76
	Trionic®	3	0.30	1.59
	nitrile[B]	3	0.51	1.64
	butyl[C]	2	278/>240	1.2/ND[D]
n-Butyl	natural rubber	3	0.50	1.69
acetate	Trionic	3	0.30	1.47
	nitrile	3	0.50	1.70
	butyl	2	266/>240	1.2/ND
2-EEA	natural rubber	3	0.31	2.16
	Trionic	3	0.27	1.81
	nitrile	3	0.51	2.16
	butyl	2	235/>240	4.2/ND
Positive Photoresist				
Xylene	nitrile	2	0.58	1.89
	butyl	2	296/>240	0.5/ND
n-Butyl	nitrile	2	0.59	1.75
acetate	butyl	2	284/>240	0.6/ND
2-EEA	nitrile	2	0.58	1.85
	butyl	2	246/>240	1.6/ND
Negative Photoresist				
Xylene	nitrile	2	0.64	5.57
	butyl	2	0.68	1.53
2-ME	nitrile	2	0.66	4.00
	butyl	2	0.75	1.44
Pure 2-MEA				
2-MEA	nitrile	2	0.64	1.84
	butyl	2	>240/>240	ND/ND

[A]n is the number of trials performed at 37°C.

[B]Thickness = 0.043 cm for all nitrile samples.

[C]For the butyl rubber samples, actual values of breakthrough time (min) and steady-state permeation rate (μg/cm^2/min) are presented for those tests where the ratios could not be determined.

[D]None detected.

The temperature effect was least significant for the butyl rubber. For the photoresist thinner, breakthrough of the 2-EEA through the butyl rubber samples was observed after about 4 hr, but the steady-state permeation rate (4.2 μg/cm^2/min) remained quite low. It is interesting to note that pure 2-EEA did not break through the butyl rubber material at 37°C (data not shown). Thus, the other solvents apparently did affect the permeation of 2-EEA in the photoresist and photoresist thinner through butyl rubber, but the effect is of little practical significance.

Considered in terms of the absolute change in temperature (i.e., 310 K/298 K = 1.04, or a 4% increase) the effects on the permeation values for most of the gloves are quite large and reflect the positive exponential (i.e., Arrhenius) temperature dependence of the permeation process. Vahdat and Bush[34] reported similar temperature effects for toluene and trichloroethane permeation through commercial glove samples.

Because the temperature of a glove while being worn is likely to be somewhere in the range of 25 to 37°C, the permeation rates and breakthrough times to be expected in practice (under similar exposure conditions) would be between the values reported in this paper.

Double Glove Layers

As mentioned previously, workers in semiconductor clean rooms typically wear thin, surgical-type gloves made of natural rubber or PVC beneath thicker chemically protective gloves. To determine whether these gloves provided any additional protection against dermal exposure, experiments were performed with the photoresist thinner by using samples of such thin gloves placed behind samples of the nitrile rubber gloves.

Table VI shows the effects on the permeation of the photoresist thinner of combining nitrile samples with the Baxter PVC or natural rubber samples. From the ratios of the permeation parameters with and without the added layers, it is seen that these gloves do provide a modest increase in permeation resistance with the effect most significant for 2-EEA. The nitrile/PVC combination provides slightly greater protection than the nitrile/natural rubber combination. Exposure of the PVC or natural rubber samples alone at 37°C resulted in breakthrough almost immediately and, in the case of the PVC, disintegration of the sample. Clearly, these gloves should not be used alone when working with these chemicals.

Repeated Exposure and Thermal Decontamination

A series of experiments was then performed to determine the effects of repeated exposure of the nitrile and butyl rubber gloves to the solvent mixtures. Table VII presents the results for the 0.043-cm nitrile rubber gloves rechallenged with the photoresist thinner at 25°C. The mean breakthrough times and steady-state permeation rates for "normal exposures" of previously unexposed gloves (i.e., continuous exposures performed until steady-state permeation was achieved) are included for reference (from Table IV). Re-exposure of nitrile samples following air drying overnight resulted in much lower breakthrough times for all solvents (Trial 2, Table VII). In fact, measurable levels of all solvents were observed in the initial background air samples taken before filling the test cell with solvent for the re-exposure. The largest reduction in breakthrough time occurred for 2-EEA. The consistency of the steady-state permeation rates indicates, however, that the structural integrity of the glove was not measurably affected. For Trial 3, an initially exposed glove sample was allowed to air dry for 5 days before re-exposure. Again,

TABLE VI. Breakthrough Times (BT, min) and Steady-State Permeation Rates (PR, $\mu g/cm^2/min$) of the Photoresist Thinner through Nitrile Rubber with and without Additional Layers of PVC or Natural Rubber Glove Samples at 37°C

Trial/Sample	n	Xylene BT	Xylene PR	n-Butyl acetate BT	n-Butyl acetate PR	2-EEA BT	2-EEA PR
1 Nitrile	3	54 (2)	36 (5)	52 (1)	51 (2)	49 (2)	251 (5)
2 Natural rubber	2	<2	105 (1)	<2	140 (1)	<2	321 (3)
3 Nitrile/natural rubber (double layer)	2	65 (3)	32 (2)	61 (1)	40 (1)	60 (1)	179 (9)
Ratio 3/1		1.20	0.92	1.17	0.80	1.22	0.71
4 PVC[A]	1	—	—	—	—	—	—
5 nitrile/PVC (double layer)	2	75 (3)	31 (0)	72 (3)	41 (0)	69 (2)	183 (6)
Ratio 5/1		1.39	0.86	1.38	0.80	1.41	0.73

[A]This sample disintegrated within a few minutes of exposure.

TABLE VII. Repeated Exposure and Thermal Decontamination of 0.043-cm Nitrile Rubber Samples Challenged with Photoresist Thinner[A]

Trial/Conditions	n	Xylene BT	Xylene PR	n-Butyl acetate BT	n-Butyl acetate PR	2-EEA BT	2-EEA PR
1 Normal exposure	3	106 (5)	22 (1)	103 (5)	30 (1)	96 (4)	116 (6)
2 Normal exposure, air dry 20 hr, re-exposure	2	33 (9)[B]	19 (3)	50 (12)[B]	27 (1)	4 (0)[B]	110 (7)
Ratio 2/1		0.31	0.86	0.49	0.90	0.04	0.95
3 Normal exposure, air dry 5 days, re-exposure	1	82	24	79[B]	32	60[B]	140
Ratio 3/1		0.74	1.14	0.73	1.07	0.59	1.24
4 50-min exposure, air dry 20 hr, re-exposure	2	60 (7)[B]	23 (1)	46 (16)[B]	32 (1)	8 (3)[B]	115 (9)
Ratio 4/1		0.57	1.04	0.45	1.07	0.08	0.99
5 70°C 20 hr, normal exposure	1	113	17	108	26	101	98
Ratio 5/1		1.07	0.77	1.05	0.87	1.05	0.84
6 50-min exposure, 70°C for 20 hr, re-exposure	2	103 (6)	18 (1)	98 (4)	29 (0)	91 (1)	109 (1)
Ratio 6/1		0.97	0.82	0.95	0.97	0.95	0.94

[A]BT = breakthrough time in min, PR = steady-state permeation rate in $\mu g/cm^2/min$.

[B]Low vapor concentrations (i.e., <10 mg/m³) observed in background samples prior to re-exposure.

levels of *n*-butyl acetate and 2-EEA were detected in the initial background samples, and significant decreases in the breakthrough times for all of the solvents were still observed. The increase in permeation rate for 2-EEA suggests that some degradation of the glove may also have occurred, although the permeation rates for the other solvents did not change appreciably.

For Trial 4 in Table VII, a fresh nitrile rubber sample was exposed for about one-half of the time required for breakthrough of all of the solvents (i.e., 50 min) and allowed to air dry overnight. Again, measurable levels of the solvents were found in the background air samples the next day upon replacing the sample in the test cell, indicating that the solvents continued to diffuse through the glove after exposure had ceased.

Several reports have shown that protective clothing containing residual amounts of organic solvents can be decontaminated by moderate heating.[22,23] On the basis of the results from one of these studies,[23] a temperature of 70°C was selected for decontamination treatment. Pretreatment of a nitrile sample at 70°C overnight showed no indications of physical degradation. Exposure of this sample to the photoresist thinner resulted in slightly longer breakthrough times and lower permeation rates than observed for untreated samples (see Trial 5, Table VII), but the changes were minor. Exposure of a fresh nitrile rubber sample to the photoresist thinner for 50 min followed by treatment at 70°C overnight and retesting (Trial 6, Table VII) gave breakthrough times for all of the solvents that were within 5% of the values observed for the previously unexposed samples.

Results of similar tests performed on the 0.036-cm nitrile rubber samples are shown in Table VIII. As with the thicker nitrile gloves, the steady-state permeation rates were unaffected by repeated exposure, but retention of the solvents was evident from the shorter breakthrough times. Re-exposure following an initial normal exposure again resulted in measurable levels of the solvents in the background samples the next day. For the longer drying period (Trial 3, Table VIII) or the shorter exposure period (Trial 4, Table VIII), reductions in the breakthrough times were still observed, but residual solvent levels were not detected in the initial background samples.

In contrast to the thicker nitrile rubber gloves, thermal treatment of the thinner samples following a normal exposure or an exposure for one-half of the nominal breakthrough times resulted in only partial recovery of the permeation resistance (Trials 6 and 7, Table VIII). Subsequent breakthrough time values ranged from 86–90% of the initial values. The reason for the lack of a full recovery for the thinner samples is not clear. However, from a practical standpoint, the thermal treatment was effective enough to afford good protection upon reuse of the gloves.

A similar series of experiments performed on the butyl rubber material showed no evidence of persistent permeation and no degradation in the level of protection afforded upon re-exposure to the photoresist thinner.

Table IX presents the results of repeated exposure of the 0.036-cm nitrile rubber gloves to the positive photoresist. Again, there is evidence for retention of the solvents in the glove samples. The decreases in breakthrough times upon re-exposure following a normal exposure and air drying overnight were generally greater than those observed for the photoresist thinner under similar conditions. Traces of all of the solvents were

TABLE VIII. Repeated Exposure and Thermal Decontamination of 0.036-cm Nitrile Glove Samples Challenged with Photoresist Thinner[A]

Trial/Conditions	n	Xylene		n-Butyl acetate		2-EEA	
		BT	PR	BT	PR	BT	PR
1 Normal exposure	5	79 (3)	23 (1)	74 (3)	34 (2)	64 (5)	118 (8)
2 Normal exposure, air dry 20 hr, re-exposure	1	35[B]	27	34[B]	32	4[B]	127
Ratio 2/1		0.44	1.17	0.46	0.94	0.06	1.08
3 Normal exposure, air dry 5 days, re-exposure	1	56	20	53	30	46	121
Ratio 3/1		0.71	0.87	0.72	0.88	0.72	1.02
4 35-min exposure, air dry 20 hr, re-exposure	1	55	23	46	33	12	121
Ratio 4/1		0.70	1.00	0.62	0.97	0.19	1.02
5 70°C 20 hr, normal exposure	1	80	24	74	35	65	110
Ratio 5/1		1.01	1.04	1.00	1.03	1.02	0.93
6 35-min exposure, 70°C 20 hr, re-exposure	1	69	24	64	35	56	126
Ratio 6/1		0.87	1.04	0.86	1.03	0.88	1.07
7 Normal exposure, 70°C 20 hr, re-exposure	1	68	25	65	36	60	129
Ratio 7/1		0.86	1.09	0.88	1.06	0.94	1.09

[A]BT = breakthrough time in min, PR = steady-state permeation rate in μg/cm²/min.

[B]Low vapor concentrations (i.e., <10 mg/m³) observed in background samples prior to re-exposure.

TABLE IX. Repeated Exposure and Thermal Decontamination of 0.036-cm Nitrile Glove Samples Challenged with Positive Photoresist[A]

Trial/Conditions	n	Xylene		n-Butyl acetate		2-EEA	
		BT	PR	BT	PR	BT	PR
1 Normal exposure	3	107 (7)	10 (2)	98 (5)	16 (2)	89 (3)	68 (6)
2 Normal exposure, air dry 20 hr, re-exposure	1	21[B]	11	18[B]	18	4[B]	71
Ratio 2/1		0.20	1.10	0.18	1.12	0.04	1.04
3 45-min exposure, air dry 20 hr, re-exposure	1	61	16	58	20	43[B]	76
Ratio 3/1		0.57	1.60	0.59	1.25	0.48	1.12
4 Normal exposure, 70°C 20 hr, re-exposure	1	67	14	64	19	55	72
Ratio 4/1		0.63	1.40	0.65	1.19	0.62	1.06
5 45-min exposure, 70°C 20 hr, re-exposure	1	80	13	74	19	71	85
Ratio 5/1		0.75	1.30	0.76	1.19	0.80	1.25

[A]BT = breakthrough time in min, PR = steady-state permeation rate in $\mu g/cm^2/min$.

[B]Low vapor concentrations (i.e., <10 mg/m^3) observed in background samples prior to re-exposure.

observed in the background samples prior to re-exposure. For an initial exposure of 45 min followed by air drying overnight, only 2-EEA was observed in the background samples the next day. Permeation rates were slightly higher for the re-exposed samples as well, although the increases are not considered significant.

Thermal treatment improved the permeation resistance but recovery of the initial values was not achieved. Breakthrough times after thermal treatment ranged from 62–80% of the initial values and permeation rates remained slightly elevated. One explanation for the lack of recovery in the permeation resistance is that the resin in the photoresist inhibits offgassing of the residual solvents by forming a thin film at the glove surface (note: the glove samples were noticeably stained after exposure to the resist). Upon re-exposure, this film could then redissolve in the resist solvents to allow normal permeation to proceed. In any case, even with only partial recovery of the permeation resistance, reuse of the gloves following thermal decontamination would afford reasonably good protection.

Results of repeated exposure of the nitrile rubber samples (0.036 cm and 0.043 cm) to the negative photoresist are presented in Table X. For both glove thicknesses, exposure for about one-half of the breakthrough times followed by air drying overnight and re-exposure resulted in reductions in the breakthrough times and, for the 0.043-cm sample, rather large increases in the steady-state permeation rates of 2-ME and xylene. Re-exposure of the 0.036-cm samples following an initial normal exposure also resulted in increased permeation rates. In this case, levels of xylene in the background samples taken before re-exposure were already above 10 mg/m^3. These data indicate significant retention of the solvents as well as irreversible changes in the structure of the glove upon exposure to the negative photoresist. Attempts to restore the permeation resistance of the 0.036-cm samples by thermal treatment were unsuccessful (Trials 6 and 7, Table X).

For pure 2-MEA, the results of repeated exposure of the nitrile glove were similar to those for the photoresist thinner.

Initial exposure for about one-half of the breakthrough time followed by air drying overnight and re-exposure resulted in measurable quantities of 2-MEA in the background samples before the next exposure (Table XI). Although there was a large decrease in the breakthrough time, the permeation rate was not affected. Treatment of the exposed glove overnight at 70°C restored the original permeation resistance to the 2-MEA. Butyl rubber samples showed no evidence of persistent permeation for the pure 2-MEA after repeated exposures for 4 hr.

SUMMARY AND CONCLUSIONS

The results presented in this paper should serve as a basis for improving glove use practices in semiconductor processing facilities where formulations containing glycol-ether derivatives are used. Coupled with information on prevalent work practices, these results should also aid in ongoing efforts to assess chemical exposures (past or present) in the semiconductor industry and, in turn, to establish meaningful risk estimates for adverse health effects.

Of the gloves tested in this study, the North Model B-161 butyl rubber glove provided the best protection against the pure glycol-ether derivatives, the photoresist thinner, and the positive photoresist. Breakthrough times for these solvents and formulations were all greater than 4 hr, and there was no evidence of persistent permeation or significant temperature effects from 25–37°C. The resistance of the butyl rubber gloves to the negative photoresist was much lower with breakthrough times of 12 min observed for the component solvents, 2-ME and xylene.

Although butyl rubber gloves are generally more expensive than the other types of gloves investigated, the ability to reuse them safely tends to offset the initial cost. It is unfortunate that these gloves are not suitable for clean room environments: according to the manufacturer, adhesion problems necessitate the use of powder during glove packaging. Still, these gloves would be useful for emergency spill response or for handling

TABLE X. Repeated Exposure and Thermal Decontamination of Nitrile Rubber Samples Challenged with Negative Photoresist[A]

Trial/Conditions	n	2-ME		Xylene	
		BT	PR	BT	PR
1 Normal exposure (0.043-cm sample)	2	77 (9)	6 (0)	66 (7)	60 (4)
2 40-min exposure, air dry 20 hr, re-exposure (0.043-cm sample)	1	68	10	50[B]	109
Ratio 2/1		0.88	1.67	0.76	1.82
3 Normal exposure, (0.036-cm sample)	3	72 (4)	12 (2)	49 (2)	82 (8)
4 30-min exposure, air dry 20 hr, re-exposure (0.036-cm sample)	1	43	10	20[B]	76
Ratio 4/3		0.60	0.83	0.41	0.93
5 Normal exposure, air dry 20 hr, re-exposure (0.036-cm sample)	2	24 (6)	22 (4)	—[C]	208 (39)
Ratio 5/3		0.33	1.83		2.54
6 30-min exposure, 70°C 20 hr, re-exposure (0.036-cm sample)	2	44 (8)	26 (13)	35 (5)	182 (64)
Ratio 6/3		0.61	2.17	0.71	2.22
7 Normal exposure, 70°C 20 hr, re-exposure (0.036-cm sample)	2	36 (6)	26 (2)	32 (0)[B]	220 (22)
Ratio 7/3		0.50	2.17	0.65	2.68

[A]BT = breakthrough time in min, PR = steady-state permeation rate in $\mu g/cm^2/min$.

[B]Low vapor concentrations (i.e., <10 mg/m³) observed in background samples prior to re-exposure.

[C]Background vapor concentration was >10 mg/m³ prior to re-exposure.

TABLE XI. Repeated Exposure and Thermal Decontamination of 0.036-cm Nitrile Rubber Samples Challenged with Neat 2-MEA[A]

Trial/Conditions	n	2-ME	
		BT	PR
1 Normal exposure	2	42 (1)	250 (2)
2 25-min exposure, air dry 20 hr, re-exposure	1	4[B]	256
Ratio 2/1		0.10	1.02
3 25-min exposure, 70°C 20 hr, re-exposure	1	40	252
Ratio 3/1		0.95	1.01

[A]BT = breakthrough time in min, PR = steady-state permeation rate in $\mu g/cm^2/min$.

[B]Low vapor concentrations (i.e., <10 mg/m³) observed in background samples prior to re-exposure.

microlithographic solvent formulations in service areas where higher particulate levels could be tolerated.

The Edmont Nytek nitrile rubber gloves provided moderately good resistance to the pure glycol-ether derivatives and the processing mixtures for continuous exposures. For the negative photoresist, the Nytek gloves provided better protection than the butyl rubber gloves. For the photoresist thinner tested, the use of thin natural rubber or PVC glove layers beneath the nitrile gloves further improved their permeation resistance. The Edmont Puretek (natural rubber), Pioneer Trionic (natural rubber/nitrile/neoprene blend), and Playtex Model 827 (natural rubber/neoprene blend) gloves showed significantly lower levels of protection than the nitrile and butyl rubber gloves against all of the solvent mixtures.

The permeation resistance of the Nytek gloves, however, decreased markedly from 25–37°C. The presence of small amounts of acetone also reduced the permeation resistance of these gloves to the solvents in the positive photoresist. In addition, solvents persisted in the gloves for up to several days following exposure. For all of the formulations tested, breakthrough times were significantly shorter for previously exposed gloves allowed to air dry overnight, even after relatively short initial exposures. For the negative photoresist, repeated exposure also resulted in increased steady-state permeation rates. These results are of particular concern in light of the fact that gloves are typically reused at many semiconductor facilities.

Heating exposed nitrile gloves at 70°C overnight restored or nearly restored the permeation resistance of the Nytek gloves against all formulations except the negative photoresist. This procedure could be used to recycle previously exposed gloves to prolong their service life. Vented ovens, such as those used for prebaking coated wafers, might be adapted for this purpose in clean rooms. If thermal decontamination is not feasible, then nitrile gloves should be discarded where exposure to the glove has occurred or is suspected.

ACKNOWLEDGMENT

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