Chemical Protective Gloves for Seven Commercial Herbicides

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The breakthrough times of seven commonly used herbicides through various commercially available protective gloves were determined. Glove samples were challenged with the concentrated herbicide formulations using ASTM Test Method F-739. Based solely on chemical resistance data, the specialty laminate (Silver Shield, 4H) afforded workers the most protection, the longest breakthrough time, against all seven herbicides tested. Nitrile and butyl gloves, based on chemical permeation and chemical degradation, were protective against AATrex-4L (1912249), Dual-8E (51218452), Lasso Micro-Tech (15972608), Sencor-DF (21087649), and Gramoxone-Extra (4685147). However, they were not protective against Judge (15972608) or Treflan-MTF (1582098). Nitrile and butyl glove materials were wrinkled and distorted after 1 hour exposures to Treflan MTF or Judge. The authors note that wrinkled or distorted gloves should be taken as an indicator of a chemical incompatibility between the herbicide and the glove material.

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Abstract

Herbicides are widely used in agriculture to control weed growth and increase crop yields. According to the U.S. Department of Agriculture, there are 3.4 million full-time workers in agriculture, many of whom have exposure to herbicides. The hands are a major route of exposure when workers use herbicides. Many different types of personal protective gloves are worn by applicators and farmers when applying herbicides, but only limited information is available for recommending the appropriate gloves to be worn when using particular herbicides. Selection of inappropriate gloves may result in chemical attack and degradation of the glove material. The objective of this study was to measure the breakthrough time of seven commonly used herbicides through various commercially available protective gloves. This information is used as the basis for recommending the most appropriate gloves to be worn when working with particular herbicides, helping to reduce the exposure of farmers and commercial applicators who use these herbicides. Herbicides, or more appropriately, commercial herbicides, are typically multi-component mixtures. Two important components in these mixtures are active ingredients (AI) and carrier solvents (CS). Active ingredients are chemicals which destroy or inhibit weed

growth--i.e., herbicides. Glove samples were challenged with the concentrated herbicide formulation because pesticide handlers are commonly exposed to the concentrated herbicide during loading and mixing. Test apparatuses to measure permeation were two-chambered cells. Different cells were used in this study depending on the herbicide. The herbicide active ingredient(AI) and carrier solvent(CS) were determined by gas chromatograph. The test method can be used to generate permeation data required by US EPA Worker Protection Standard.

Based solely on chemical resistance data, the specialty laminate (Silver Shield®, 4H®) affords workers the most protection--longest breakthrough time--against all seven herbicides used in this study. Nitrile and butyl gloves, based on chemical permeation and chemical degradation, are protective against AAtrex 4L®, Dual® 8E, Lasso® Micro-Tech®, Sencor® DF, and Gramoxone® Extra®; however, they are unsuitable for use with Judge® or Treflan® MTF$^{(TM)}$. Nitrile and butyl glove materials were wrinkled and distorted after l-hour's exposure to Treflan® MTF$^{(TM)}$ or Judge®. Because of this distortion, it could be inferred that herbicide and test-glove material were chemically incompatible. These gloves should not be used with those herbicides. Evidence of wrinkling or distortion of the glove materials may be used by applicators in the field as a general indicator of chemical incompatibility with particular herbicides. Users must be made aware that wrinkles and distortion may appear after breakthrough has occurred. The manufacturer's recommendations for appropriate selection of gloves and breakthrough time must be followed.

Disclaimer

Introduction

Herbicides are widely used in agriculture to control weed growth and increase crop yields. In the United States, over 90% of all acres planted in corn, soybeans, cotton, and rice are sprayed with herbicides, and over 350 million pounds of herbicides are used on these crops annually.(1,2) According to the U.S. Department of Agriculture, there are 3.4 million full-time workers in agriculture, many of whom have exposure to herbicides, and approximately 200,000 workers who apply herbicides commercially.(3,4)

Dermal Exposure is a major route of herbicide exposure; approximately 80 to 90% of the total herbicide exposure may occur through the hands. Selection of inappropriate glove materials may result in chemical attack, material degradation and in worker exposure to toxic solvents and/or herbicides. In some instances, it may be just as important to protect handlers from the carrier solvent(CS) as the herbicide active ingredient(AI).

The objective of this study was to measure the breakthrough time of seven commonly used herbicides through various commercially-available protective gloves. This information is used as the basis for recommending the most appropriate gloves to be worn when working with particular herbicides, helping to reduce the exposure of farmers and commercial applicators who use these herbicides. Test methods to measure breakthrough time must have physiological significance and industrial hygiene relevance. Worker's gloved hands do perspire. This perspiration does contact the inside of a glove. Assuming water is an acceptable surrogate for perspiration, permeation test methods with water as the collection medium simulate "real life". The collection medium is physiologically significant, and the test method has industrial hygiene relevance. Most herbicide mixtures are not soluble in water so that non-aqueous solvents sometimes are used to collect chemicals permeating protective gloves(See Figure 1). Nonaqueous solvents, the collection liquid, permeate from one side of the test cell into the glove material. At the same time, components of the herbicide mixture permeate into the glove material from the other side. The effect of the non-aqueous solvent permeation on herbicide components permeation is unknown. Many of these same solvents can alter gloves, typically by swelling of the matrix material, such that the permeation of the herbicide components may be affected. These solvents are not physiologically significant. These permeation test methods are not relevant to industrial hygiene. This study used solid sorbent to capture chemical permeants in order to obviate these problems. The solid sorbent simulates dry, intact human skin.

Selection of Herbicides

Seven herbicides could reasonably be tested with the resources devoted to this study. Accordingly, these seven herbicides were selected from among the major herbicides used on corn and soybean crops, the crops upon which the greatest volume of herbicides are used.(2)

Herbicides, or more appropriately, commercial herbicides, are typically multi-component mixtures. Two important components in these mixtures are active ingredients (AI) and carrier solvents (CS). Active ingredients are chemicals which destroy or inhibit weed growth--i.e., herbicides. These active ingredients are dispersed in other chemicals or carrier solvents. Material data safety sheets for herbicides should be perused for this information. Table I lists each commercial herbicide used in this study, the major active ingredient, the principal carrier solvent, and the manufacturer. All of these herbicides are considered to have toxic properties, and it is recommended on their product labels that gloves be worn when handling. The U.S. Environmental Protection Agency released PR notice 93-7," Notice to Manufacturers, Formulators, Producers, and Registrants of Agricultural Pesticides" on April 20, 1993. The notice requires labeling changes for many pesticide end-use products. A statement of appropriate glove types to be worn during the handling of products must be included for end-use products of sufficient dermal toxicity to merit a glove requirement on the label. New product labels (effective April 15,1994) that fall within the scope and definitions of the Worker Protection Standard will state the appropriate glove material selection types that are to be used for handling activities for an end-use product. End-use products bearing labels that limit use solely to rangeland, pastures, right-of-ways, and non-crop areas fall outside of the Worker Protection Standard.

Two and one-half gallons of these herbicides were purchased from commercial pesticide application companies. Since these herbicides have toxic properties, and some are considered potential carcinogens, requirements for appropriate handling and storage, as listed on the material safety data sheets, were strictly followed. Waste herbicide and laboratory materials contaminated with herbicide were disposed of as hazardous waste.

Selection of Protective Gloves

Based on previous studies, nitrile and butyl rubber gloves were believed to provide the best protection.(6,7) Therefore, gloves manufactured from these materials were selected for study. In addition, special laminate gloves, consisting of a layer of ethylene vinyl alcohol between two layers of polyethylene, were selected for testing. This special laminate holds promise as an effective protective glove material; however, it has not yet been evaluated for its effectiveness against these pesticides. The laminate gloves are two dimensional, that is, they are created by using radio-frequency radiation or heat seal to fasten the top and bottom portions of the gloves together at a seam. The seam is likely to be the weakest point on the glove representing the area of quickest potential breakthrough. Therefore, the seam was the area of the laminate gloves which was tested.

Brand-to-brand variation in chemical resistance among gloves of the same generic polymer materials has been observed. These variations have been attributed to different manufacturers' processes and polymer formulations. A significant difference in chemical breakthrough times has been found among generically similar products produced by different manufacturers; therefore, to evaluate and control the effect of brand on breakthrough time, two brands of gloves made from butyl rubber, nitrile rubber, and the specialty laminate were evaluated. Each brand of glove was selected to have the same nominal thickness. However, butyl gloves of the same nominal thickness were not available from different manufacturers; therefore, two butyl gloves of different thicknesses were purchased from one manufacturer, and one glove of another thickness was purchased from a second. Table II lists the type of glove material, manufacturer, model name, and nominal thickness.

Glove Samples

The circular glove samples (4.4 mm in diameter) were taken from the back of nitrile and butyl gloves. Those from the laminate gloves were cut from the side so that the seam bisected the sample. The seamed laminate glove specimen did seal well into the test cell, as determined by visual inspection. The thickness of each sample was measured with an Ames micrometer at four equidistant points of the circle and in the center. The five thickness measurements were then averaged and the standard deviation calculated and recorded.

Test Procedures

Chemical permeation of a protective glove material by a herbicide was determined by measuring breakthrough. Chemical breakthrough is defined as elapsed time between initial contact of the challenge chemical with the outside glove surface and the time at which the challenge chemical is detected at the inside surface. Glove samples were challenged with the concentrated herbicide formulation because pesticide handlers are commonly exposed to the concentrated herbicide during loading and mixing. Test apparatuses to measure permeation were two-chambered cells. Different cells were selected depending on the collection medium and herbicide solubility. All of the cells were designed such that a glove sample partitioned one chamber holding a challenge chemical from the other chamber holding a collection medium. A collection medium can be liquid, gas, or solid. A liquid collection medium--water--and a solid collection medium--silicone--were used in this study. The two chambers were assembled so that the outer surface of a glove sample faced toward the challenge chamber, allowing the outside of the sample to be exposed to challenge chemical, then a timer was started to measure elapsed time. For liquid collection, at specified time intervals, a small aliquot of the liquid collection medium, water, was removed and was analyzed for carrier solvent and/or active ingredient. For solid collection, at specified time intervals, the solid collection medium, silicone, was removed, then desorbed by a predetermined technique.

A standard permeation test method, the American Society of Testing and Materials (ASTM) Test Method F-739, Resistance of Protective Clothing Materials to Permeation by Liquids or Gases,(9) was used as the basis for this study. The method requires a two-chambered permeation cell with a liquid or a gas as the collection medium (Figure 1) and triplicate tests. This cell is commercially available from Pesce Lab Sales, Kennett Square, Pa. Typically, water or air serves as the collection medium. The challenge chamber volume is 90 ml; accordingly, 90 ml of concentrated herbicide would be required to fill the challenge chamber for each permeation test. However, this volume of herbicide poses greater health and safety hazards in the laboratory. Therefore, a smaller volume challenge chamber was selected. [The alternate challenge chamber is discussed later in the text.]

Of the herbicides tested in this study, Gramoxone® Extra® is highly water soluble, therefore the ASTM method and modified permeation cell, with water as a collection medium, was used to evaluate glove permeation. Also, Sencor® DF is slightly soluble in water, so the modified ASTM method and modified permeation cell with water collection was used to evaluate glove permeation. However, Judge®, Dual® 8E, Treflan® MTF(TM), Lasso® Micro-Tech®, and AAtrex 4L® herbicides all have very low vapor pressures and poor solubility in water. Therefore, water or air is an inappropriate collection medium, but a suitable solid collection medium for low vapor pressure or poorly water soluble chemicals has been reported.(10) However, solid collection medium requires additional experiments; that is, active ingredient (AI) and carrier solvent (CS) sorption and desorption efficiency must be determined, and a standard permeation test method using a solid collection medium must also be developed.

A test method developed by Ehntholt et al, for EPA uses a unique test cell and medical grade silicone to collect the permeant.(10) Unfortunately, medical-grade silicone is very expensive ($5/circle); therefore part of this study examined industrial-grade silicone as an inexpensive alternative ($.05/circle) collection medium. In preliminary experiments, both medical-grade silicone, Dow-Corning, Midland, Mi, Silastic sheets, 0.013 mm, and industrial-grade silicone, Unirubber Inc., New York, N.Y., translucent sheets, 0.78 mm thickness, were evaluated as solid absorption media. Circles approximately 4.4 mm in diameter were cut from the silicone sheets. The circles were extracted with 10 ml of 2-propanol in a 50-ml flask with shaking for 30 minutes. A 1-µl aliquot was analyzed by gas chromatography, (GC) to determine if impurities or contaminants were extracted from the silicone sheets. GC conditions are described later. GC analysis demonstrated that medical-grade silicone did not require cleaning to remove trace chemical impurities, whereas industrial-grade silicone had trace amounts of impurities that were extracted in cleaning. Therefore, industrial-grade silicone circles which had been cleaned to remove trace amounts of chemical impurities were used as the solid absorbent in this study.(10) These silicone circles were cleaned by first washing in a Branson 8200 sonic cleaner for 2 hours at 50°C. A 1:1000 solution of water and laboratory cleaner, Micro®, was used for the sonication bath. After drying, the circles were washed again at 50°C, this time using 2-propanol, then air dried.

For permeation experiments using the silicone collection medium, a glove sample was placed in a cell described by Ehntholt.(10) The stainless steel challenge-chamber was fitted with a Luer-loc® for easy filling. The challenge chamber required approximately 10 ml to fill. The collection chamber was a 2-inch glass pipe flared at one end so it could be attached to the cell by a flange. The herbicide was added to the challenge chamber and a timer was started to measure elapsed time. A cleaned silicone circle was quickly placed in the collection chamber and a plunger was placed on top of the silicone circle to assure contact between the circle and the sample. An unassembled test cell is shown in Figure 2. A circle remained in contact with a sample for a specified time interval, then was removed for desorption and analysis.

As stated earlier, additional experiments were conducted to determine herbicide active ingredient, AI, and carrier solvent, CS, sorption and desorption efficiency on silicone. First the solubility of herbicide in organic solvents was crudely evaluated in the laboratory. A known amount of herbicide was placed in a known volume of solvent and agitated. Visual inspection determined miscibility. A solution was miscible if it was homogeneous, without a trace of turbidity when a 100 watt tungsten light was shone through it and inspected at a 90 degree and 0 degree angle to the light beam. Once miscibility had been demonstrated, that solvent was evaluated further. Active ingredient (AI) and carrier solvent (CS) solutions were prepared by dilution of the neat herbicide in that solvent. The density (w/v) and percentage composition given in the material safety data sheet supplied with the herbicide were used to calculate the concentration of AI and CS in neat herbicide mixture. The calculated concentration of AI and CS next was compared to solutions. They did not differ more than 15%. As an additional quality assurance check, the manufacturer of the herbicide mixture was queried as to the composition and percentage of ingredients specific to the batch or lot number of the herbicide mixture used in this study. Based on this information, the decision was made to use the calculated concentration for AI and CS.

Sorption experiments were conducted first. An exact volume of neat herbicide mixture was placed on a clean glass plate, a cleaned silicone circle was placed on the mixture, and a plunger placed on top of the circle to assure contact. This procedure not only simulated a permeation experiment, but also demonstrated that AI and CS were sorbed onto the silicone circle. The mass range evaluated for AI sorption was between 0.8 mg and 10 mg and for CS sorption between 0.1 mg and 7 mg. After a specified sorption time, usually ½ hour, the silicone circle was removed and desorbed using that solvent. Desorption conditions were varied until only trace amounts of Al and CS remained on the glass plate [desorption conditions are discussed later]. A 1-µl direct injection of the desorption solution was injected into a Perkin-Elmer 8310 automated gas chromatograph, equipped with a J&W Scientific 15-meter DB-5 (1.5 film thickness) glass capillary column, a flame ionization detector, and a temperature program (Oven temperature: 100°C, hold for 3 minutes, increase to 285°C at the rate of 10°C/min., hold for 7.5 minutes. Injector temperature: 285°C, Detector temperature 285°C. Total run time was 29 minutes). The concentration of AI and CS for a herbicide was determined by comparison to standards purchased from Supelco, Bellefonte, Pa. The percentage desorption efficiency was calculated as the quotient of AI or CS concentration in the desorption solution to the concentration of Al or CS in the neat herbicide mixture. Blanks were also determined. A blank was a circle without AI or CS but desorbed as if it had been exposed. Blanks were used to demonstrate that the circles did not introduce other contaminants into these desorption experiments; that is, no extraneous peaks were observed in GC analysis.

AI and CS herbicide desorption conditions from silicone were experimentally determined as a precursor to actual permeation testing. For these tests, an exposed silicone absorbent circle as described previously was placed in a 50-ml flask containing 10 ml of solvent. Optimum desorption conditions--i.e., desorption temperature, desorption time, and flask manipulation--were investigated. These conditions, then, were employed in subsequent permeation tests to desorb AI and CS from the silicone circles. AI and CS were analyzed by GC. The GC was calibrated daily using 1-μl injections of a known concentration of active ingredient and a known concentration of carrier solvent. Peak retention time and area under the curve for active ingredient and carrier solvent were taken from the chromatograms. A chromatogram for each desorbed silicone circle was obtained and compared to the standard chromatograms.

Experiments using Dual® 8E established a 30-minute desorption time at room temperature (ca.23 °C) with intermittent shaking as the optimal desorption conditions. Permeation tests were conducted next. The permeation cell used in these tests is depicted in Figure 2. Silicone circles were changed hourly, desorbed as indicated, then analyzed for AI and CS by GC.

Desorption efficiency of Treflan® MTF$^{(TM)}$ and Judge® demonstrated that a 2-hour desorption time was needed. Additionally, the flasks containing the 2-propanol and silicone circles were mounted on a wrist shaker and continuously agitated to aid desorption. The permeation cell used in these tests is the same as used above. Initially, silicone circles were changed hourly, desorbed as indicated, then analyzed for AI and CS by GC. Additional permeation tests were conducted because breakthrough was observed. Silicone circles were changed at regular intervals much less than 1-hour--usually 15 or 30 minutes--to improve breakthrough time precision. AAtrex 4L® desorption conditions proved that a silicone circle was desorbed by 2-propanol when processed in the sonic bath for 2 hours at 50°C. AAtrex 4L® permeation through glove materials was determined using the same cell and silicone circle changes as were used in Treflan® MTF(TM) experiments. The silicone circles were desorbed as previously described. GC analysis determined presence of AI and CS.

The herbicide Lasso® Micro-Tech®, a water-based suspension, was soluble in 1:1 water and 2-propanol solution. Lasso® Micro-Tech® was desorbed from a silicone circle by using a solution of 5-ml water and 5-ml 2-propanol as the desorbing agent in the sonic bath for 2 hours at 50°C. The cell used in the permeation experiments has been described previously (Figure 2). Lasso® Micro-Tech®-exposed silicone circles were changed hourly then desorbed as stated. The presence of AI and CS were determined by GC.

The percentage desorption efficiency of AI and CS for Dual® 8E and the other herbicides which utilized solid collection medium are listed in Table III. The lower limit of detection, which is defined as a signal greater than three times that of the noise baseline, is a measure of the sensitivity of the analytical method and is included in Table III.

The herbicide Sencor® DF, a granular powder, necessitated a change of test cell and procedure. A concentrated Sencor® DF suspension, 4 grams in 15 ml of distilled water, was assumed to simulate spill conditions which a mixer/loader might encounter. However, Sencor® DF tended to precipitate out of aqueous solution. In order to keep the precipitant in contact with the glove sample, it was necessary to orient the sample horizontally, with the herbicide on top of the sample. A solid sorbent collection chamber was connected to an ASTM collection chamber as demonstrated in Figure 3. Silicone circle and plunger were not used in this configuration. The ASTM collection chamber was connected to a Varistaltic® pump, Junior model, from Manostat Corp., New York, N.Y., and filled with approximately 100 ml of distilled water. The pump flow was 100 ml per minute. A concentrated Sencor® DF suspension, 4 grams in 15 ml of distilled water was added to the solid sorbent collection chamber, which functioned as a challenge chamber for these tests. An aliquot of distilled water from the collection

chamber was withdrawn at specified times and injections made into the GC, for analysis of the active ingredient only.

Gramoxone® Extra® presented still another problem. Gramoxone® Extra® is an ionic herbicide and does not elute on the GC column. It was necessary to use an alternative method of analysis, i.e., ultraviolet spectrophotometry. Specifically, a Varian model 2400 ultraviolet/visible spectrophotometer was calibrated at 254 nanometers wavelength (nm) in double-beam mode, 0.2 nanometer slit width, using quartz cuvettes. A stainless steel challenge chamber was connected to an ASTM collection chamber as in Figure 4. The collection chamber was connected to the Varistaltic® pump and filled with distilled water. The herbicide was charged into the challenge chamber, and a timer started. A 1-ml aliquot of the collection medium, water, was withdrawn for analysis at specified time intervals. Analysis of AI was determined by an ultraviolet spectrophotometer calibrated at the maximum absorption peak for AI, 254 nm.

Overnight permeation tests were conducted when protracted test times (18-24 hours) were of interest. However, these permeation tests were not monitored during late night or early morning (1 a.m.-5 a.m.). Additionally, the significance of protracted tests was reconsidered, because gloves would need decontamination if used more than one work day and decontamination was not addressed in this study. Accordingly, midway into this study, permeation test times were reduced to 1 day (5-8 hours).

Results and Discussion

Dual® 8E, evaluated by a minimum of 3 permeation tests, did not permeate any glove materials during the testing period (24-hour test time). Similarly, AAtrex 4L® did not permeate nitrile glove materials in 24 hours, did not permeate butyl glove materials in 6 hours, and did not permeate the specialty laminate glove materials in 24 hours. Lasso® Micro-Tech® did not permeate any glove materials in 8 hours. Sencor®DF did not permeate nitrile glove materials or the specialty laminate gloves in 24 hours, and did not permeate butyl glove materials in 7 hours. Gramoxone® Extra® did not permeate any of the glove materials during the 24-hour test period. Although the carrier solvent in Treflan® MTF$^{(TM)}$ (chlorotoluene) permeated every nitrile and butyl glove tested, the active ingredients did not. Thinner nitrile and butyl gloves exhibited shorter breakthrough times for AI and/or CS, which is consistent with permeation theory.(8) The carrier solvent in Judge®, chlorobenzene, permeated almost every nitrile and butyl glove tested. Again, thinner gloves of the same generic material exhibited shorter breakthrough times.

Chemical permeation data is tabulated only for those herbicides where permeation was observed during the testing period (Tables IV and V). The first column contains glove manufacturer and glove material tested. The second and third columns denote AI and/or CS breakthrough where ND indicates none detected and an "x" indicates breakthrough was observed. Breakthrough time for AI and/or CS and the sampling interval in parenthesis is recorded in the fourth column; total test time is recorded in this column if breakthrough was not detected. The mean sample thickness and standard deviation are listed in the last column.

During the course of each permeation experiment, the glove material was inspected when the silicone absorbent circle was changed. Nitrile and butyl glove materials were very wrinkled and distorted after 1-hour's exposure to Treflan® MTF® or Judge® indicating chemical degradation. A very wrinkled test-glove material made poor contact with a silicone circle. Poor contact varied the amount of AI or CS absorbed on a silicone circle, which in turn caused breakthrough times to vary.

Conclusions

Based solely on chemical resistance data, the specialty laminate (Silver Shield®, 4H®) affords workers the most protection--i.e., longest breakthrough time--against all seven herbicides used in this study. Nitrile and butyl gloves, based on chemical permeation and chemical degradation, are protective against AAtrex 4L®, Dual® 8E, Lasso® Micro-Tech®, Sencor® DF, and Gramoxone® Extra®; however, they are unsuitable for use with Judge® or Treflan® MTF$^{(TM)}$. Nitrile and butyl glove materials were wrinkled and distorted after 1 hour's exposure to Treflan® MTF$^{(TM)}$ or Judge®. Because of this distortion, it could be inferred that herbicide and test-glove material were chemically incompatible. These gloves should not be used with those herbicides. Gloves can be visually inspected for signs of chemical incompatibility by the herbicide applicator. Evidence of wrinkling or distortion of the glove materials may be used by applicators in the field as a general indicator of chemical incompatibility with particular herbicides. Users must be made aware that wrinkles and distortion appear after breakthrough has occurred. The manufacturer's recommendations for appropriate selection of gloves and breakthrough time must be followed.

This test method can be used to generate permeation data for the U.S. Environmental Protection Agency Worker Protection Standard, and to revise material-chemical permeation protocols. During a permeation test, the test material should be visually inspected when the silicone circle is changed. A wrinkled or distorted test material does not provide reliable permeation data; therefore, testing should be terminated and the test protocol should be revised. The revised protocol would test different generic materials with the chemicals rather than test different brands of the generic material which was incompatible with the chemicals.

Table I. Test Herbicides

Trade Name	Manufacturer	Active Ingredient	Carrier Solvent
Dual® 8E	Ciba	metolachlor	petroleum solvent
Treflan® MTF$^{(TM)}$	Elanco Products	trifluralin	chlorotoluene
Judge®	Riverside/Tena Corp	alachlor	chlorobenzene
AAtrex 4L®	Ciba	atrazine	ethylene glycol
Lasso® Micro-Tech®	Monsanto Corp	alachlor	water
Sencor® DF	Miles, Inc	metribuzin	none (granular)
Gramoxone® Extra®	ICI Americas	paraquat	water

Table II. Test Materials

Generic Glove Material	Manufacturer	Glove Type Model Name	Nominal Thickness (mm)
Butyl Rubber	North Hand Protection, Inc., Charleston, SC	B-131	0.33
Butyl Rubber	North Hand Protection, Inc., Charleston, SC	B-161	0.41
Butyl Rubber	Best Manufacturing Co., Menlo, GA	878	0.76
Nitrile Rubber	Ansell Edmont Industrial, Inc., Coshocton, OH	Solvex® 37-145	0.28
Nitrile Rubber	Pioneer Industrial Products, Inc.,	StanSolv® A10	0.28
Laminate	Safety 4, Inc., Racine WI	4H®	0.07
Laminate	North Hand Protection, Inc., Charleston, SC	Silver Shield®	0.10

Table III. Herbicide Analytical Limit of Detection

	Active Ingredient		Carrier Solvent	
Herbicide	LOD	Desorption Efficiency	LOD	Desorption Efficiency
Sencor® DF	0.3	n/a	n/a	n/a
Lasso® Micro-Tech®	2.1	43%	n/a	n/a
AAtrex 4L®	1.8	72%	1.11	99%
Judge®	1.9	65%	1.8	99%
Treflan® MTF$^{(\mathrm{TM})}$	4.8	67%	1.5	95%
Dual® 8E	1.0	83%	1.8	97%
Gramoxone® Extra®	8.3	n/a		

LOD = Limit of detection μg/sample
n/a not applicable

Table IV. Permeation Results: Treflan® MTF(TM)

Manufacturer and Material	Breakthrough		Total Test Time (Sample Interval)	Thickness and SD
	AI	CS		
Edmont Nitrile	ND	X	90 min (30)	0.279 ± .008mm
Edmont Nitrile	ND	X	150 min (30)	0.273 ± .016mm
Edmont Nitrile	ND	X	150 min (30)	0.275 ± .010mm
Edmont Nitrile	ND	X	120 min (30)	0.265 ± .028mm
Pioneer Nitrile	ND	X	120 min (60)	0.252 ± .007mm
Pioneer Nitrile	ND	X	110 min (60)	0.260 ± .006mm
Pioneer Nitrile	ND	X	120 min (60)	0.251 ± .017mm
Pioneer Nitrile	ND	X	105 min (15)	0.248 ± .006mm
Pioneer Nitrile	ND	X	90 min (15)	0.259 ± .006mm
North Butyl B131	ND	X	120 min (60)	0.307 ± .007mm
North Butyl B131	ND	X	75 min (15)	0.297 ± .005mm
North Butyl B131	ND	X	105 min (15)	0.298 ± .005mm
North Butyl B161	ND	X	240 min (60)	0.430 ± .010mm
North Butyl B161	ND	X	180 min (30)	0.422 ± .009mm
North Butyl B161	ND	X	165 min (60)	0.433 ± .005mm
North Butyl B161	ND	X	240 min (15)	0.419 ± .014mm
Best Butyl 878	ND	X	240 min (60)	0.705 ± .018mm
Best Butyl 878	ND	X	225 min (15)	0.772 ± .046mm
Best Butyl 878	ND	X	210 min (15)	0.719 ± .021mm

Manufacturer and Material	Breakthrough AI	Breakthrough CS	Total Test Time (Sample Interval)	Thickness and SD
North Silver Shield®	ND	ND	> 7 hours	0.101 ± .001mm
North Silver Shield®	ND	ND	>18 hours	0.111 ± .001mm
North Silver Shield®	ND	ND	>24 hours	0.114 ± .009mm
North Silver Shield®	ND	ND	>24 hours	0.109 ± .010mm
North Silver Shield®	ND	ND	>24 hours	0.104 ± .005mm
Safety 4, Inc. 4H®	ND	ND	>24 hours	0.066 ± .002mm
Safety 4, Inc. 4H®	ND	ND	>24 hours	0.070 ± .002mm
Safety 4, Inc. 4H®	ND	ND	>24 hours	0.069 ± .003mm

ND Not detected
Total test time in lieu of breakthrough time

Table V. Permeation Results: Judge®

Manufacturer and Material	Breakthrough		Total Test Time (Sample Interval)	Thickness and SD
	AI	CS		
Edmont Nitrile	ND	X	120 min (60)	0.277 ± .011mm
Edmont Nitrile	ND	X	90 min (15)	0.269 ± .008mm
Edmont Nitrile	ND	X	180 min (60)	0.254 ± .012mm
Edmont Nitrile	ND	X	120 min (30)	0.270 ± .003mm
Pioneer Nitrile	ND	X	100 min (40)	0.240 ± .008mm
Pioneer Nitrile	ND	X	75 min (15)	0.243 ± .012mm
Pioneer Nitrile	ND	X	90 min (15)	0.259 ± .009mm
Pioneer Nitrile	ND	X	105 min (15)	0.258 ± .010mm
North Butyl B131	ND	X	90 min (30)	0.322 ± .009mm
North Butyl B131	ND	X	270 min (30)	0.337 ± .016mm
North Butyl B131	ND	X	180 min (30)	0.302 ± .008mm
North Butyl B131	X		60 min (30)	0.310 ± .016mm
		X	210 min (30)	
North Butyl B161	X	X	270 min (30)	0.413 ± .010mm
North Butyl B161		X	270 min (30)	0.389 ± .010mm
	X		210 min (30)	
North Butyl B161	ND	X	270 min (30)	0.394 ± .013mm

Manufacturer and Material	Breakthrough AI	Breakthrough CS	Total Test Time (Sample Interval)	Thickness and SD
Best Butyl 878	ND	ND	> 6 hours	0.779 ± .038mm
Best Butyl 878	ND	ND	> 6 hours	0.747 ± .022mm
North Silver Shield®	ND	ND	> 7 hours	0.104 ± .005mm
North Silver Shield®	ND	ND	> 7 hours	0.105 ± .005mm
Safety 4, Inc. 4H®	ND	ND	> 6 hours	0.072 ± .002mm
Safety 4, Inc. 4H®	ND	ND	> 7 hours	0.070 ± .001mm
Safety 4, Inc. 4H®	ND	ND	> 7 hours	0.070 ± .002mm

ND Not detected
Total test time in lieu of breakthrough time

Figure 1 ASTM Test Method 739 Permeation Cell

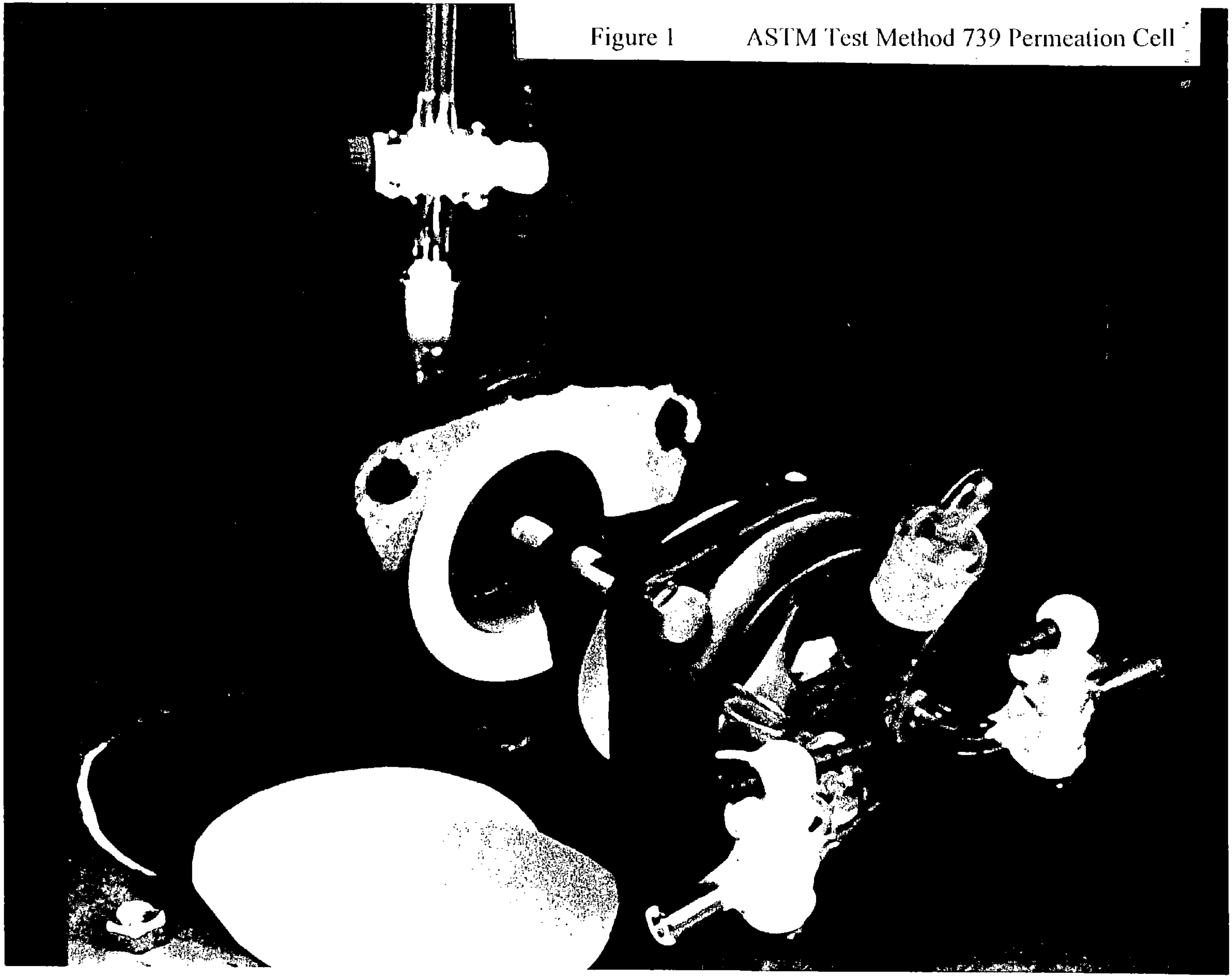

Figure 2 Ehntholt-EPA Permeation Cell

Figure 3 Permeation Cell - Sencor® DF

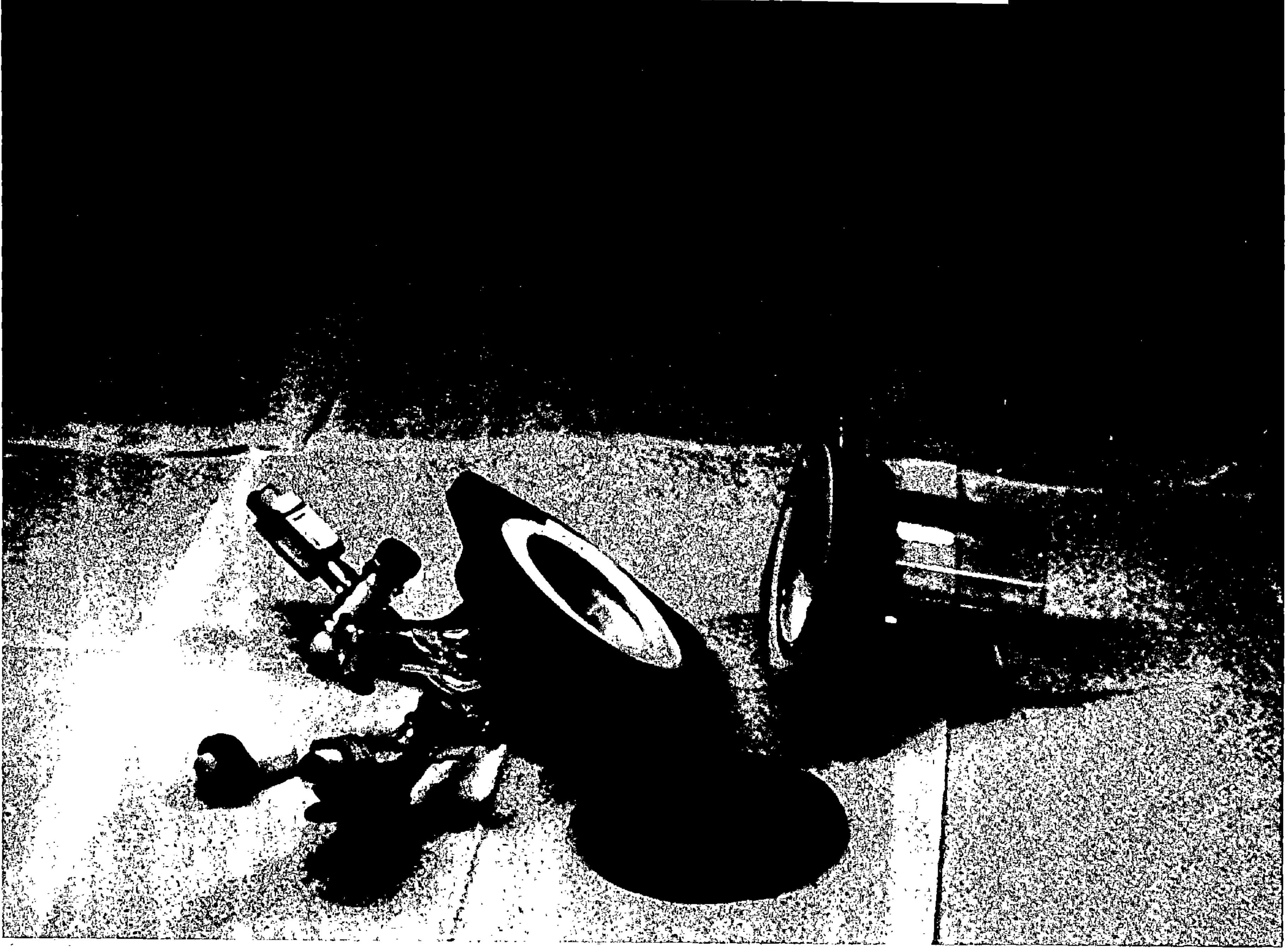

Figure 4 Permeation Cell - Gramoxone® Extra®

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