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PARAQUAT: PENETRATION THROUGH PROTECTIVE
CLOTHING MATERIALS FROM A MALAYSIAN
'GRAMOXONE' FORMULATION

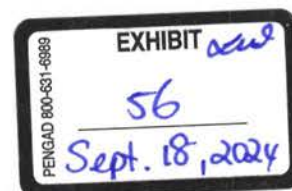
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FROM A MALAYSIAN 'GRAMOXONE' FORMULATION

We, the undersigned, declare that this report constitutes a true record
of the actions undertaken and the results obtained in the above study.

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SUMMARY

To provide information on the efficiency of various protective clothing materials against paraquat penetration from a GRAMOXONE formulation, the penetration rates and break-through times of paraquat have been determined for the following materials:

- a) Polyethylene-coated (yellow) TYVEK
- b) Saran-coated TYVEK
- c) TYVEK
- d) KIMGUARD
- e) COROVIN
- f) Unfinished cotton

GRAMOXONE was applied to these materials as the concentrate (200g paraquat ion/l) and as the spray-strength dilution (2.5g paraquat ion/l).

The two coated TYVEK materials (a and b) were found to have resistance ($<0.05\mu\text{g}$ paraquat ion/ml determined in the receptor solutions) to both GRAMOXONE applications throughout the 6 hour exposure time.

KIMGUARD material (d) had a limited resistance with break-through times of <0.5 hr for the concentrate and <0.5 -4 hrs (mean 2.2 hr) for the spray dilution. The penetration rates were 269 - $924\mu\text{g cm}^{-2}\text{hr}^{-1}$ (mean $608\mu\text{g cm}^{-2}\text{hr}^{-1}$) for the concentrate and 0.08 - $2.43\mu\text{g cm}^{-2}\text{hr}^{-1}$ (mean $1.01\mu\text{g cm}^{-2}\text{hr}^{-1}$) for the spray dilution.

The remaining materials, TYVEK (c) COROVIN (e) and unfinished cotton (f) displayed little resistance to paraquat penetration from either the concentrate or spray dilution.

1. INTRODUCTION

The permeability of 6 different materials (Polyethylene-coated (yellow) TYVEK; Saran-coated TYVEK; TYVEK; KIMGUARD; COROVIN; unfinished cotton) to paraquat has been examined. The materials were mounted in horizontal glass diffusion cells (Fig 1). The GRAMOXONE was applied to the materials both as the concentrate (200g paraquat ion/l) and as the spray strength dilution (2.5g paraquat ion/l) in water.

2. MATERIALS AND METHODS

2.1 Reagents and Test Materials

2.1.1 GRAMOXONE (200g paraquat ion/l; Malaysian formulation, Division ref: SA83/85) was supplied by Plant Protection Division. The formulation was given the Central Toxicology Test Substance code number Y00061/071/001).

2.1.2 Paraquat dichloride analytical standard (99.6% purity) was obtained from Plant Protection Division and given the Central Toxicology Test Substance code number Y00061/010/012.

2.1.3 Samples of protective clothing materials:

- a) Polyethylene-coated TYVEK
- b) Saran-coated TYVEK
- c) TYVEK
- d) KIMGUARD
- e) COROVIN
- f) Unfinished cotton

2.1.4 Sodium dithionite solution: 0.5g sodium dithionite was dissolved in 1M sodium hydroxide (15ml) and made upto 50ml with distilled water.

2.2 Analytical Procedure

2.2.1 Spectrophotometer Conditions:

Instrument : Pye-Unicam SP8-100 UV/visible, double beam, recording spectrophotometer
Scan Range : 420-370nm
Scan Speed : 2nm/sec) 10nm/cm
Chart Speed : 5 sec/cm)
Absorbance Range : 1.0
Band Width : 1nm
Cells : 1cm path length, silica micro-cells

2.2.2 Determination: 50µl of freshly prepared sodium dithionite solution were added to a 0.25ml sample (collected as described in Section 2.3.1). The sample was then transferred to a spectrophotometer cell and its spectrum recorded between 420-370nm, using as a reference 0.25ml 0.9% physiological saline similarly treated with 50µl of sodium dithionite. Where a peak was seen at 396nm, a base line was drawn under the peak and its height at 396nm measured. This peak height was compared against that of a similarly treated standard solution (1µg/ml) to calculate the concentration of paraquat in the sample solution.

The limit of determination using this procedure was 0.05µg paraquat/ml.

2.3 Penetration Measurements

2.3.1 Procedure for all Materials: Glass diffusion cells (Fig 1), in which the material under investigation forms a horizontal membrane separating the "donor" and "receptor" chambers, were used to measure penetration rates. 2.54cm² of the material surface was available for exposure and all experiments were conducted at 22°C ± 1°C.

The receptor chambers were filled with a recorded volume of 0.9% physiological saline which was stirred throughout the experiment.

All the materials were exposed to 0.5ml of GRAMOXONE concentrate (200g paraquat ion/l) and spray strength dilution (2.5g paraquat ion/l), which were placed in the donor chamber of the cell.

At recorded intervals duplicate samples (0.25ml) were taken, and replaced by a single addition of saline (0.5ml). The samples were placed in small glass vials and stored at 4°C to await analysis by spectrophotometry.

2.3.2 Procedure used to confirm Break-through Times for TYVEK, COROVIN and Unfinished Cotton: With the above materials the donor applications penetrated too fast to determine break-through times or penetration rates. To attempt an assessment of the break-through time, the test material was laid on top of a filter paper and then clamped between two donor chambers. 0.5ml of either GRAMOXONE concentrate or the spray dilution was applied to each material, and the filter paper below was observed to detect appearance of formulation penetrating the test material; this was therefore a qualitative assessment.

2.3.3 Calculation: The time-course and penetration rate, with correction for the volume of sample removed, were calculated as follows:

Receptor Volume = V

Sample Volume = s

Concentration in samples at: $t_1, t_2, t_3, \dots$
are $c_1, c_2, c_3, \dots$

Thus the amount of paraquat removed from the receptor at:

$t_1 = c_1 s$ etc

The total amount of paraquat having passed through the material at:

$t_1 = c_1 V$

$t_2 = c_2 V + c_1 s$

$t_3 = c_3 V + c_1 s + c_2 s$

$t_4 = c_4 V + c_1 s + c_2 s + c_3 s$

etc

Results were plotted as "the total amount of paraquat ion absorbed versus time".

The slope of the linear region of this plot, corrected for the area of the epidermal membrane, gives the rate of absorption of paraquat ion per cm^2 of material.

The break-through time is not calculated but is defined as the time of the appearance of detectable amounts of paraquat in the receptor chamber.

3. RESULTS

It was intended to run all the experiments for 6 hrs, however, only the Polyethylene-coated TYVEK, Saran-coated TYVEK and KIMGUARD had sufficient resistance to the penetrations of paraquat ion from the formulations to allow the full time course to be sampled. For both the coated TYVEKS, no determinable amounts of paraquat ($<0.05\mu\text{g/ml}$) from either formulation were seen in the receptor solutions after 6 hr. KIMGUARD material displayed break-through times for paraquat of <0.5 hr for the concentrate and between <0.5 -4hr (mean 2.2hr; $\text{SD} \pm 1.8$ hr) for the spray dilution. The penetration rates of paraquat ion through this material were 269 - $924\mu\text{g cm}^{-2}\text{hr}^{-1}$ (mean $608\mu\text{g cm}^{-2}\text{hr}^{-1}$ $\text{SD} \pm 328\mu\text{g cm}^{-2}\text{hr}^{-1}$) from the concentrate and 0.08 - $2.43\mu\text{g cm}^{-2}\text{hr}^{-1}$ (mean $1.01\mu\text{g cm}^{-2}\text{hr}^{-1}$; $\text{SD} \pm 1.25\mu\text{g cm}^{-2}\text{hr}^{-1}$) from the spray dilution.

Both the GRAMOXONE concentrate and its spray dilution penetrated the TYVEK, COROVIN and unfinished cotton almost immediately and thus the penetration rate was too fast to measure apart from one TYVEK sample [with the spray dilution donor which was measurable up to 1 hr ($417\mu\text{g cm}^{-2}\text{hr}^{-1}$)]. This rapid penetration was confirmed by using the second procedure (Section 2.3.2), when the formulations were seen to wet the filter paper immediately they were applied to the material. While the break-through time was almost instantaneous this procedure gave a visible

impression of the penetration rate, indicating that the formulation penetrated the TYVEK at a slightly slower rate than through unfinished cotton, and Corovin showed no apparent resistance with penetration of the formulations occurring immediately after application.

The results for all materials are displayed in Tables 1 and 2.

4. DISCUSSION

No paraquat ($<0.05\mu\text{g}/\text{ml}$) was found to have penetrated polyethylene-coated and Saran-coated TYVEK during the 6 hr exposure time. KIMGUARD material had a short resistance to paraquat ion from the concentrate (mean break-through time $<0.5\text{hr}$; mean penetration rate $608\mu\text{g cm}^{-2}\text{hr}^{-1}$) and the spray dilution (mean break-through time 2.2 hr; mean penetration rate $1.01\mu\text{g cm}^{-2}\text{hr}^{-1}$). TYVEK, COROVIN and unfinished cotton offered little resistance to either formulation, the breakthrough times being immediately after application.

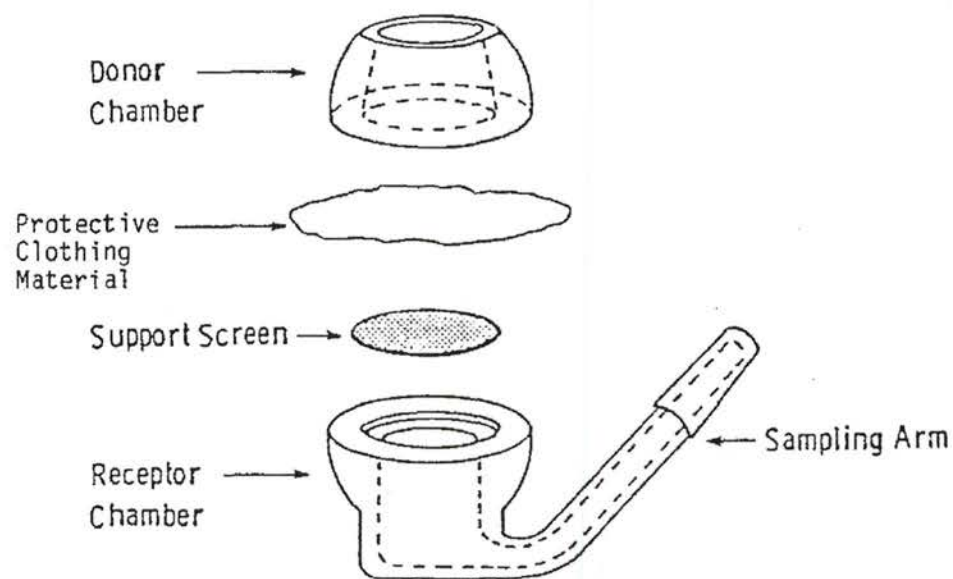
These data would indicate that both polyethylene-coated and Saran-coated TYVEK will offer spray operators protection against both concentrate GRAMOXONE and the spray strength dilution.

From the results obtained, TYVEK, COROVIN and unfinished cotton cannot be recommended for protective clothing for use during the application of GRAMOXONE.

RW/DC/SJS (819)
4.12.85

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FIGURE 1



Diffusion Cell - Horizontal Membrane

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TABLE 1

PENETRATION OF PARAQUAT FROM 'GRAMOXONE' CONCENTRATE (200g Pq^{2+} /l)

Material	Break-through Time		Absorption Rate ($\mu g\ cm^{-2}\ hr^{-1}$)	
	Individual Cell	Mean	Individual Cell	Mean
Polyethylene-coated TYVEK (Yellow)	>6 hr >6 hr >6 hr	>6 hr	ND ND ND	ND
Saran-coated TYVEK	>6 hr >6 hr >6 hr	>6 hr	ND ND ND	ND
TYVEK*	<0.5 min <0.5 min <0.5 min	<0.5 min	Too fast to measure	
KIMGUARD	<0.5 hr <0.5 hr <0.5 hr	<0.5 hr	269 924 633	608 SD 328
COROVIN*	<0.5 min <0.5 min <0.5 min	<0.5 min	Too fast to measure	
Unfinished Cotton*	<0.5 min <0.5 min <0.5 min	<0.5 min	Too fast to measure	

ND = $<0.01\mu g\ cm^{-2}\ hr^{-1}$ based upon the analytical limit of determination
(0.05 μg /ml)

* For TYVEK, COROVIN and unfinished cotton, the dye in the formulation was seen in the receptor immediately after application to the donor and thus the absorption rate was too fast to measure.

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TABLE 2

PENETRATION OF PARAQUAT FROM 'GRAMOXONE' SPRAY
STRENGTH DILUTION ($2.5\text{g Pg}^{2+}/\text{l}$)

Material	Break-through Time		Absorption Rate ($\mu\text{g cm}^{-2}\text{hr}^{-1}$)	
	Individual Cell	Mean	Individual Cell	Mean
Polyethylene-coated TYVEK (Yellow)	>6 hr >6 hr >6 hr	>6 hr	ND ND ND	ND
Saran-coated TYVEK	>6 hr >6 hr >6 hr	>6 hr	ND ND ND	ND
TYVEK*	<15 min < 5 min < 5 min	<15min	417** Too fast to measure	
KINGGUARD	<0.05 hr 2 hr 4 hr	2.2 hr SD ± 1.8	2.43 0.50 0.08	1.01 SD ± 1.25
COROVIN*	<5 min <5 min <5 min	<5 min	Too fast to measure	
Unfinished Cotton*	<5 min <5 min <5 min	<5 min	Too fast to measure	

ND. = $<0.01\mu\text{g cm}^{-2}\text{hr}^{-1}$ based upon the analytical limit of determination
($0.05\mu\text{g/ml}$)

* For TYVEK, COROVIN and unfinished cotton in all, except one TYVEK cell, ** the donor solution had been completely absorbed through the material.

** The donor was completely absorbed at 1 hr therefore only measured upto that time.