INCREASED ABRASION AND WASH RESISTANCE OF REPELLENTS WITH ADDITION OF POLYMERS

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ABSTRACT. Repellents applied to skin are lost with sweating, water exposure, or on abrasion with clothes or other body parts. Attempts were made to increase water washability and abrasion resistance of repellents by formulating with a commercially available polymer formulation. Mixing with the polymers improved water washability several fold. Formulation with polymers was most effective with triethylene glycol monohexyl ether and least with dimethyl phthalate. Deet in formulation was improved in water washability 11 times. Formulation with polymers improved abrasion resistance. Deet with polymers resisted abrasion significantly. In four of five tests deet with polymer remained effective for approximately 24 hr. The polymers used appeared innocuous but feel sticky when freshly applied. Improvement is required for cosmetic acceptability.

INTRODUCTION

Mosquito repellents protect best under dry conditions. With heavy sweating or water exposure they fail in minutes. Abrasion with clothing and friction against body parts reduce effectiveness considerably. Under rigorous field conditions (for professional sportsmen, foresters, and military personnel), available repellent formulations often need frequent applications. There is a need to improve abrasion and water-wash resistance of repellents so that a single application may last several hours under demanding field conditions.

We describe the effect of improved abrasion and wash resistance of mosquito repellents by formulating them with a commercially available polymer (Areoplast® dressing, Parke-Davis & Co.) containing co-polymers of hydro-vinyl chloride-acetate and sebacic acid, 8.2%; modified maleic rosin ester, 2.7%; and glycolate plasticizer, 0.6% (total solids 11.5% by weight) in ethyl acetate-acetone solvent.

MATERIALS AND METHODS

The polymer formulation (Aeroplast®) was emptied in a beaker and mixed with an appropriate amount of repellent. All quantities reported in the text pertain to the weight of the solids in the polymer formulations. The solvent was not removed before application. A 5 x 12.5 cm area was marked on the ventral surface of a human forearm and a measured amount of repellent or its formulation with the polymer was applied with a fine pipette, covering the area

several times for uniform application. To test for repellency, a plastic sleeve was rolled over the forearm exposing only the treated surface through a cut-out. A wire clamp held the sleeve in place. The forearm was introduced through a long sleeve in a 1 ft^3 cage containing 500 female *Aedes aegypti* (L.), 6–10 days old, fed on 5% sugar solution. The forearm was exposed for 3 min. The experiment was terminated when a total of 2 bites was obtained. The duration from the time of application to termination was designated as protection time. All tests were performed in a room at 27° C and 55-66% R.H.

WASH RESISTANCE. The area on the forearm coated with the repellent-polymer formulation was washed under flowing water. The flow-rate of water from a faucet was adjusted to 6 L/min. During washing, the water stream touched the forearm 3 cm above the treated area. The forearm was held nearly parallel to the water flow. The treated area was tested against mosquitoes at 30 sec. intervals when repellents only were applied since they washed off within a couple of minutes. With formulations, tests were first done at 5 min. intervals and when mosquitoes started landing the interval between tests was reduced to 30 seconds. The effect of water temperature on washability of repellents was tested in like manner. The temperature tested ranged from 20° to 45°C at 5° intervals.

ABRASION RESISTANCE. This was studied with friction applied to the repellent-treated surface on the forearm. A glass bottle filled with water weighing 1 kg. when stoppered was wrapped with tissue paper (Scott's Microwipes®) and moved or slid (not rolled) down the treated surface. The angle of the forearm to the floor was 45°. The paper wrappings were changed every 50 wipes. Initially, the treated surface was exposed to mosquitoes at 100 wipes intervals; when the mosquitoes were found close to biting, the interval between tests was reduced to 50 wipes. The experiment was terminated when two bites were obtained.

In additional experiments, abrasion was uncontrolled. The subject applied a repellent (1.6 mg/cm^2) on one forearm and its formulation (1.6 mg of repellent + 0.5 gm/cm^2 of polymer) on the other. He allowed abrasion of repellent-treated forearm with clothes, bed sheets, etc. during sleep. The treated surface was tested for mosquito bites at 12 hr intervals (between the previous night and the following day) and at 2 hr intervals during the day until 2 bites were obtained.

RESULTS AND DISCUSSION

Formulating repellents with the polymers improved water washability; without the polymers, repellents failed within minutes (Table 1). Triethylene glycol monohexyl ether was washed most easily and dimethyl phthalate not so easily. With polymer formulation, triethylene glycol monohexyl ether improved the most, lasting 15 min. compared to 0.7 min. without the polymer (21 x increase). Diethyl toluamide (deet) with formulation improved from 1.7 min. to 19 min. (11x). Increases in wash-resistance of other repellents were significant but not as marked.

Water temperature affected wash-resistance significantly when tested against deet and its polymer formulation (Table 2). The correlation between the wash-resistance and the water temperature was inverse and highly significant ($r = -0.9204$, $p < 0.01$). Mixing deet with the polymer improved its abrasion resistance significantly ($p < 0.05$, Table 3). Deet applied at 0.16 mg/cm^2 failed after 750 wipes compared to 1075 and 1200 wipes when formulated

Table 1. Effect of polymer formulation on resistance of repellents to washing with water at 30° C flowing at 6L/min.

	Mean protection time (minutes)				
	Repellent (1.6 mg/cm²)	Repellent (1.6 mg+polymer 0.5 mg/cm²)	Percent increase	Significance "t"	Significance "p"
Deet	1.7	19.0	1.017	8.59	<.005
Ethyl hexane diol	1.4	11.0	685	5.85	<.01
Dimethyl-phthalate	2.2	6.0	172	6.67	<.01
Indalone ®	1.0	8.0	321	10.44	<.005
Triethylene glycol monohexyl ether	0.7	15.0	2.042	15.09	<.001
Hexamethylene butane sulfonamide	2.0	10.0	400	8.58	<.005

with the polymer in two different ratios. The difference between the formulations was not significant.

In uncontrolled abrasion experiments, deet (1.6 mg/cm²) did not last overnight (10–12 hr) in 4 of 5 tests but its polymer formulation remained effective for approximately 24 hr. Triethylene glycol monohexyl ether remained effective for 16–18 hr; its polymer formulations protected for 24–34 hr in 3 replicates and 41–49 hr in 3 others.

Attempts to increase duration of repellent effectiveness have been previously made. Christophers (1947) used materials like China clay, shellac, etc. Smith, Kline and French Laboratories (1951–53) studied formulations of repellents with zinc oxide, antiperspirants, etc. (Smith 1970). Kharitonova and Koshkina (1969) and Koshkina and Kharitonova (1970) tried to prolong effectiveness of insect repellents with compounds like ethyl cinamate, phenyl ethyl benzoate, Peruvian balsam, etc. but without success. Kurtz et al. (1973) combined several acrylic polymers, silicones and polysaccharides with repellents and tested for protection against mosquito bites and effect on water washability. Carboset 526 (B. F. Goodrich Co.) enhanced the protection time of deet by a factor of 1.6. It also increased wash resistance, but the polymer was cosmetically unacceptable.

The polymers reported in this study

Table 2. Effect of water temperature on wash-resistance of deet (1.6 mg/cm²) plus polymer (0.5 mg/cm²).

Water temperature °C	Mean protection time (min)
20	43.0[a]
25	22.4[b]
30	14.4[c]
35	9.3[cd]
40	6.0[d]
45	3.3[d]

Means not followed by the same letter are significantly different ($p<.01$). Water flow was at 6L/min.

Table 3. Analysis of variance of data on abrasion resistance of deet (0.16 mg/cm²) and its formulation with the polymer in two different ratios[a]

Source of variation	df	SS	MS
Total	14	1717500	
Deet (control) vs formulations	1	608400	608400[b]
Among formulations	1	31250	31250
Error	12	1077850	89820

[a] Mean number of wipes to abrade repellent: deet (control)—750 wipes, deet 0.16 mg+polymer 0.98 mg/cm²—1075 wipes, deet 0.16 mg+polymer 0.16 mg/cm²—1200 wipes.

[b] $P<.05$.

mixed with repellents significantly enhanced their abrasion and wash resistance. They are non-irritant (used on burned skin), do not stain, and are permeable to water vapor. They are sticky on application but remain so only a short time. Although these formulations do not meet the ideal requirements of consumer acceptance these may become acceptable in situations of dire need for protection against mosquitoes. Further formulation refinements might improve their physical characteristics and acceptability. Since this study was completed, it has been reported that monomers of vinyl chloride may be unsafe for use on skin. Future studies should include more acceptable compounds.

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