Technical Report No. LWL-CR-01B71

BARRIER COATINGS FOR SKIN TO BIND DEET

Final Report

by
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February 1972

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U. S. ARMY LAND WARFARE LABORATORY
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ABSTRACT

The purpose of the study presently reported was to examine a variety of skin substantive film-forming polysaccharide esters of fatty acids[1] for their capacity to bind the mosquito repellent, N,N-diethyl-m-toluamide (DEET)[2]. Thus gross physical observations were made of 36 film-forming polysaccharide esters of fatty acids; those that were found to cast good films on the basis of clarity, non-tackiness and pliability were chosen as possible binders for Deet. Their capacity to bind Deet such that perdurability would be imparted to the repellent under both dry and wet conditions was evaluated.

Results indicated that approximately a dozen polymers would be effective in prolonging the efficacy of Deet. These polymer:Deet films slowed down the rate of evaporation of Deet and also protected against the rapid wash-off of Deet.

Representative polymer:Deet formulations were submitted to LWL for lab testing. However, U. S. Army toxicologists considered the solvents initially used for these polymers to be unsafe for human use. These materials were instead subjected to the standard U.S.D.A. stocking test[3]. One of the formulations, containing a polymeric ester with a cellulose backbone was rated more effective than Deet alone.

During the latter part of this work, toxicologically acceptable solvents (duPont's Freon 11 and 21) were found which were compatible with a few of the polymers. Lab testing against mosquitoes was conducted and the first meaningful results from the U.S.D.A. arrived during the last reporting period. Preliminary results did not indicate enhanced efficacy for the polymer:Deet formulations tested. However, differences observed between the various control formulations evaluated suggests reasons for the disappointing efficacy of the polymer:Deet formulations. These unexpected results should be explored further.

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I. INTRODUCTION

Ever since the time of Walter Reed considerable effort has been devoted to control of mosquitos. Long term programs have ranged from destruction of the mosquito's natural habitat to interference with the mating and breeding habits of the species.

A short term solution to the mosquito problem is the use of personally applied repellents[3]. Although many agents have been synthesized and promoted as mosquito repellents, N,N'diethyl-m-toluamide (DEET)[4] has been found to be the most acceptable. However, the efficacy of DEET is short lived. Within 3 to 8 hours subsequent to application, the preparation no longer offers protection. Furthermore, the effectiveness is greatly reduced under humid conditions arising either from the environment or from personal perspiration[3].

The primary objective of Contract No. DAA-D05-71-C-0173 was to utilize skin substantive polysaccharide esters of fatty acids[1] to bind Deet so that the combination would extend the efficacy of the repellent even under humid conditions.

II. EXPERIMENTAL

A. Materials and Apparatus

1. Polysaccharide Esters of Fatty Acids

The majority of the polymeric materials utilized in this study had been previously synthesized in our laboratories.

In that study, corn starch with a molecular weight exceeding 1×10^6 Daltons was esterified with a variety of fatty acids to produce both homologous and mixed starch esters (Table I). Similarly relatively pure amylose (1.5×10^5 Daltons, 800-1000 d.p.) and amylopectin (1×10^6 Daltons, 6,000-9,000 d.p.)were esterified with decanoate to produce the corresponding esters.

TABLE I

POLYSACCHARIDE ESTERS OF FATTY ACIDS

Number	Esters of Starch	Reactant Molar Ratio Polymer:Acid Chloride(s)	% Esterification (Approximate)
1	Starch Butyrate	1:4.60	90
2	Starch Butyrate	1:3.25	76
3	Starch Decanoate	1:4.60	90
4	Starch Decanoate Acetate	1:2:2	83
5	Starch Decanoate Butyrate	1:3:1	83
6	Starch Heptanoate	1:4.60	90
7	Starch Heptanoate	1:3.25	76
8	Starch Hexanoate	1:4.60	90
9	Starch Laurate	1:4.60	90
10	Starch Laurate	1:3.25	76
11	Starch Myristate	1:4.60	90
12	Starch Myristate	1:3.25	76
13	Starch Nonanoate	1:4.60	90
14	Starch Nonanoate	1:3.25	76
15	Starch Octanoate	1:3.25	76
16	Starch Palmitate	1:4.60	90
17	Starch Palmitate	1:3.25	76
	Esters of Amylopectin		
18	Amylopectin Decanoate	1:3.25	76
19	" "	"	70-80
20	" "	"	"
21	" "	"	"
22	" "	"	"
23	" "	"	"
24	Amylopectin Stearate	1:3.25	70-80
25	" "	"	"
	Esters of Amylose		
26	Amylose Decanoate	1:3.25	76
27	" "	1:3.73	79
28	" "	1:3.25	70-80
29	" "	"	"
30	Amylose Stearate	1:3.25	76
	Esters of Cellulose		
31	*Cellulose Acetate		
32	*Cellulose Acetate Butyrate		
33	*Cellulose Acetate Stearate		
34	*Cellulose Tri-Acetate		
35	*Cellulose Tri-Decanoate		
36	*Cellulose Stearate		

*Commercially available.

In most of the esterifications, a reactant molar ratio of polysaccharide: acid chloride of 1:3.25 was used to obtain approximately 76% esterification; 90% esterification was obtained with a polymer:acid chloride reactant molar ratio of 1:4.6.

In some cases the reactant molar ratio was kept constant while the temperature and reaction time were varied. The amylopectin decanoate series illustrates this point (Table I). In these cases the esterification was predicted at 70-80%.

A series of cellulose esters of fatty acid was also utilized in this study. The series of cellulose esters is available commercially and was obtained from the Eastman Organic Chemicals Company (Rochester, New York).

2. Repellent

N,N-diethyl-m-toluamide (DEET) was purchased from the Eastman Chemical Company. Radioactive ^{14}C-Deet was received from Captain Peter Kurtz of the Letterman Army Institute of Research, California.

3. Solvents

The solvents in which the polymeric materials were suspended were 1,1,1-tri-chloroethane, methylene chloride, dioxane, heptane, methanol, ethanol, chloroform and Freon 11, 12, 21, 114B2 and 113 from the duPont Chemical Company.

4. Film Spreader

Experiments designed to measure the release of Deet from films necessitated that the films be of uniform thickness. A Gardner Thin Film Casting Knife (Gardner, Bethesda, Maryland) and a Bird Vacuum Plate (Bird and Sons, Massachusetts) were used in combination to spread films of uniform thickness automatically.

5. Scintillation Counter

Films of polymer: ^{14}C-Deet were used extensively to evaluate the resistance of Deet in films to water and to determine the diffusion of Deet

from these films through the skin. Radioactivity was measured with a Packard Tri-Carb liquid scintillation refrigerated spectrometer equipped with automatic sample changer and printout; the counter operated with a 90% efficiency.

6. Diffusion Cells and Accessories

Glass diffusion cells[5] were used to study the diffusion of Deet into the skin. Each cell was composed of two L-shaped glass tubes clamped together in a ball-socket union (14/28 joint). A 2.5 cm diameter die was constructed to cut rat skin into circular portions. These pieces of skin were utilized in the diffusion study.

B. Methods

1. Gross Physical Properties of Polymeric Ester Films

Two percent solutions of each polymer were prepared in trichloroethane. In some instances warming to 50-70°C for several minutes was required to solubilize the polymer. Three ml aliquots of each solution were spread on an area of 25 cm^2 of each of three surfaces (glass, Teflon and chrome plates). After the solvent had evaporated, the resulting films were examined for tackiness and general physical appearance. The films were then lifted with a Teflon spatula from the surfaces and examined for their clarity, tack and pliability.

The Teflon surface allowed the removal of the films with ease. This surface was subsequently used whenever films were to be lifted from a surface for evaluation.

2. Gross Physical Properties of Polymeric Ester:Deet Films

Polymeric materials which cast useful films (based on their clarity, non-tack, and pliability) were formulated with Deet such that films cast from these solutions contained 2, 5, 10, 20, 30, 40 and 80% by weight of Deet. Potentially useful polymer:Deet films were chosen based on the parameters mentioned above.

3. Evaluation of Polymeric Ester:Deet Films as Water Barriers

a. Qualitative Evaluation

A series of Polymer:Deet mixtures was made in trichloroethane such that films cast would be 30% by weight of the repellent. A water soluble dye (0.1% aqueous solution of Drug and Cosmetic Red Dye No. 10) was applied to the back of the hand to cover an area 3 cm in diameter. A polymer:Deet mixture was then applied at 0.3 mg Deet per cm^2 of skin to the painted and adjacent areas. The resultant film was examined for tack. The treated area was then washed two times for 30 seconds with warm water and a mild soap and subsequently rinsed for another 30 seconds. The relative resistance of the films to water was estimated from the intensity of dye color remaining. As a control, the procedure was performed on the other hand except that the dye was not protected by a film.

b. Quantitative Evaluation

Polymer: ^{14}C-Deet films containing 20% and 40% Deet and ^{14}C-Deet films were cast on glass plates at a rate of 0.10 to 0.15 mg ^{14}C-Deet/cm^2 of surface. The Gardner casting knife and vacuum plate holder were utilized to produce films of 2 to 3 mils in thickness. Each of the plates was then immersed five times in 200 ml of water for a period of 30 seconds each. Aliquots of 3 ml were withdrawn after each rinse and their radioactivity measured in the scintillation counter. The amounts of Deet which were lost from the polymer: ^{14}C-Deet and ^{14}C-Deet films during the rinses were calculated from the specific radioactivity of the ^{14}C-Deet and the radioactivity of the rinses.

4. Release of Deet from Polymeric Ester:Deet Films

a. Spectrophotometric Method

Uniform thin polymer:Deet films containing 20% to 40% by weight of the repellent were cast in quintruplets on glass plates at 0.15 mg Deet/cm^2 of surface as described previously and incubated at 30°C to simulate skin temperature. At appropriate time intervals films were withdrawn and eluted from the plates with ethanol. Since the polymeric materials were insoluble

in alcohol, the Deet was separated from the polymer by filtration. The amount of Deet present in each plate was determined spectrophotometrically[6].

b. Gravimetric Method

An alternate method for determining the Deet released from films involved the use of a single sample to follow the loss of Deet as a function of time. Films were cast and the solvent was allowed to evaporate. The plates were weighed and subsequently incubated at 30°C. At appropriate time intervals, the plates were weighed. The amount of Deet lost at each time interval was calculated from the original and subsequent weights. A curve was constructed to show μg of Deet lost per cm^2 of surface as a function of time. This relationship was linear between 1 and 5 hours of incubation. The slope of this line (μg of Deet lost/hr/cm^2) was utilized to compare the relative binding capacity of various polymers for Deet.

5. Percutaneous Penetration of Deet

The skins utilized in the diffusion studies were obtained from Sprague-Dawley male rats. The animals were sacrificed, and shaven rapidly. A portion of the back skin was excised and freed of subcutaneous tissues. Circular areas of skin were obtained with a die 2.5 cm in diameter. The skin was draped over the ball end of the diffusion cell[5] so that the epidermis faced outward. The solution under investigation was then applied to the epidermis so that Deet would be applied at a rate of 0.15 to 0.20 mg Deet per cm^2 of skin. The socket end of the cell was joined to the skin-draped ball and the union secured with a clamp. Distilled water at 30°C was placed in the cell to bathe the dermal side of the skin. The epidermis side was left open to the air. The cell was shaken gently in a 30°C constant temperature water bath. At appropriate time intervals aliquots of 3 ml were withdrawn from the dermal side water and mixed with 15 ml of aquafluor. The radioactivity of these samples was measured in the scintillation counter. The amount of Deet diffusing through the skin was calculated from the known specific radioactivity of the ^{14}C-Deet and the radioactivity in the aliquots.

6. Earthworms as Detectors of Deet

Polymer:Deet films and Deet only films were cast on a large surface and allowed to dry for 10 minutes. A mesh wire grid marked in target fashion was placed on the film. Small supports were used to keep the grid 2mm above the film. Earthworms were deposited on ground zero and the time required for 50% of the worms to move off target was recorded. The response of earthworms placed directly on the polymer:Deet and Deet films was also investigated.

III. RESULTS

1. Evaluation of Polymeric Films Without Deet

Considering the number of polymeric materials available for this study, it was decided to determine first the overall gross physical properties of films cast from these polysaccharide esters before proceeding with studies of polymer:Deet mixtures.

Although cosmetic desirability would warrent the use of thin films, thick films were initially cast to facilitate removal from the Teflon surface for evaluation. Three parameters, namely, clarity, tack and pliability were chosen by which to evaluate the films. After the films were cast from 2% solutions on a 25 cm^2 Teflon area and allowed to dry, the degree of tack was estimated by touch. The films were then lifted from the surface and their clarity observed. Pliability was estimated by twisting and pulling the films to the breaking point. Films which were clear, devoid of tack and pliable were considered ideal films. Although very few films performed ideally, several of them were rated potentially useful as binders for Deet (Table II). The best starch ester films were cast from esters whose acid moieties contained six to ten carbon atoms. As the number of carbon atoms in the acid moiety of the esters decreased (butyrate) or increased (laurate, myristate, palmitate and stearate) poor films or no film at all were cast from them. Similarly the amylopectin and amylose esters of stearic acid did not cast films; the decanoic acid esters of these starch components cast fairly good films. Cellulose acetate, cellulose tri-acetate,

TABLE II

GROSS PHYSICAL PROPERTIES OF POLYSACCHARIDE-FATTY ACID ESTER FILMS

Number	Polymeric Esters	Criteria		
		Clarity	Tack	Pliability
1	Starch Butyrate (insoluble)	---	---	---
2	" "	Clear	No Tack	Poor
3*	Starch Decanoate	Clear	No Tack	Good
4	Starch Decanoate Acetate	Clear	No Tack	Poor
5*	Starch Decanoate Butyrate	Very Clear	Slight Tack	Good
6	Starch Heptanoate	Very Clear	No Tack	Good
7*	" "	Clear	Slight Tack	Very Good
8*	Starch Hexanoate	Very Clear	No Tack	Good
9	Starch Laurate	Not Clear	Much Tack	Poor
10	" "	Not Clear	No Tack	Poor
11	Starch Myristate	Clear	Extreme Tack	No Film
12	" "	Clear	Extreme Tack	No Film
13	Starch Nonanoate	Clear	Slight Tack	Good
14*	" "	Clear	No Tack	Good
15*	Starch Octanoate	Clear	No Tack	Good
16	Starch Palmitate	Clear	Extreme Tack	No Film
17	" "	Clear	No Tack	Poor
18*	Amylopectin Decanoate	Clear	Slight Tack	Very Good
19*	" "	Clear	Slight Tack	Very Good
20	" "	Very Clear	Extreme Tack	Good
21	" "	Clear	Slight Tack	Good
22	" "	Very Clear	Much Tack	Fair
23*	" "	Clear	Slight Tack	Good
24	Amylopectin Stearate	Not Clear	No Tack	No Film
25	" "	Not Clear	No Tack	No Film
26*	Amylose Decanoate	Clear	Slight Tack	Fair
27*	" "	Clear	Slight Tack	Fair
28	" "	Clear	Extreme Tack	Good
29	Amylose Stearate	Not Clear	No Tack	No Film
30	Cellulose Acetate	Not Clear	No Tack	No Film
31	Cellulose Acetate Butyrate	Not Clear	No Tack	No Film
32*	Cellulose Acetate Stearate	Clear	No Tack	Very Poor
33	Cellulose Tri-Acetate	Not Clear	No Tack	No Film
34*	Cellulose Tri-Decanoate	Clear	Slight Tack	Good
35	Cellulose Stearate	Not Clear	No Tack	No Film

*Chosen for further study as possible Deet binders.

cellulose acetate-butyrate, and cellulose stearate did not form films. Cellulose acetate-stearate, an ester whose acid moieties have a short (acetate) and long (stearate) alkyl chains did produce, albeit brittle, a clear and non-tacky film.

2. Effects of Deet on Film Properties

It was decided to employ the most abundant and easily accessible ester (No. 32; cellulose acetate stearate) to conduct preliminary investigations on the effect of Deet on the characteristics of the polymer films. Films of cellulose acetate stearate were found to be brittle (Table II). However, when these films were made to contain 10% by weight of Deet, brittleness was lost and the films became pliable. A study was then conducted on the effect of 10, 20 and 30% Deet in films cast from a selected number of polymeric esters.

As shown in Table III, tack increased in these films as a function of Deet-concentration. In addition the pliability of the various polymers increased with increasing Deet. Cellulose acetate stearate (No. 32) a very brittle film became very pliable when the film contained 30% Deet. In some instances 20 and 30% Deet in the films resulted in "gummy films"; these were rated as having poor pliability.

It was observed early in these studies that film thickness had a great influence on the characteristics of the film. Table III shows many films which were cast to a thickness of approximately 20 mils. Preliminary work indicated that if the thickness was reduced to 3 mils, the films could be formulated with as much as 50% Deet without any adverse effects. It was not possible to obtain good films in cases where 70 to 80% Deet by weight was present.

TABLE III

EFFECTS OF DEET ON THE PHYSICAL CHARACTERISTICS OF FILMS[a]

No.	Polymeric Ester	TACK % of Film as Deet				PLIABILITY[b] % of Film as Deet			
		0	10	20	30	0	10	20	30
1	Starch Decanoate	None	Slight	Slight	Slight	Good	Good	Good	Fair
4	Starch Decanoate Acetate	None	Slight	Considerable	Extreme	Good	Good	Poor	Poor
5	Starch Decanoate Butyrate	Slight	Slight	Considerable	Extreme	Good	Good	Poor	Poor
7	Starch Heptanoate	Slight	Slight	Considerable	Extreme	Very Good	Good	Excellent	Poor
8	Starch Hexanoate	None	None	Slight	Considerable	Good	Good	Excellent	Poor
14	Starch Nonanoate	None	None	Slight	Slight	Good	Good	Excellent	Fair
15	Amylopectin Octanoate	None	Slight	Slight	Considerable	Good	Good	Poor	Poor
18	Amylopectin Decanoate	Slight	None	Slight	Considerable	Very Good	Good	Good	Fair
23	Amylopectin Decanoate	Slight	Slight	Considerable	Extreme	Good	Good	Poor	Poor
26	Amylose Decanoate	Slight	Slight	Considerable	Extreme	Fair	Good	Fair	Poor
27	Amylose Decanoate	Slight	Slight	Slight	Slight	Fair	Good	Good	Good
32	Cellulose Acetate Stearate	None	None	None	Slight	Poor	Fair	Good	Excellent
34	Cellulose Tri-Decanoate	Slight	Slight	Considerable	Extreme	Good	Good	Excellent	Poor

a. The thickness of the film was approximately 20 mils.

b. The pliability of films were judged fair or poor if the films tended to be brittle. This characteristic was found in some films with less than 20% Deet. However the pliability of films were also judged fair or poor if the films were oily or gummy. These characteristics were usually observed in films containing more than 20% Deet.

3. Polymeric Ester:Deet Films or Water-Barriers

One of the desirable features of any perdurable mosquito repellent formulation is that the material once applied, be resistant to humid conditions. The resistance of polymer:50% Deet films to wash off with water from the skin was estimated with the aid of a water soluble dye as described in the section on methods. Although none of the films were completely water resistant several were regarded as good water barriers (Table 4). Decanoate esters of amylopectin and amylose and starch nonanoate (No. 14) were rated highly.

TABLE IV

POLYMER:DEET[a] FILMS AS WATER BARRIERS

No.	Materials	Water Resistance[b]
	Deet	0
4	Starch Decanoate Acetate	1
7	Starch Heptanoate	1
8	Starch Heptanoate	2
14	Starch Nonanoate	8
18	Amylopectin Decanoate	5
19	Amylopectin Decanoate	8
26	Amylose Decanoate	4
27	Amylose Decanoate	8
32	Cellulose Acetate Stearate	2
33	Cellulose Tri-decanoate	2

a. All films contained 50% Deet by weight.

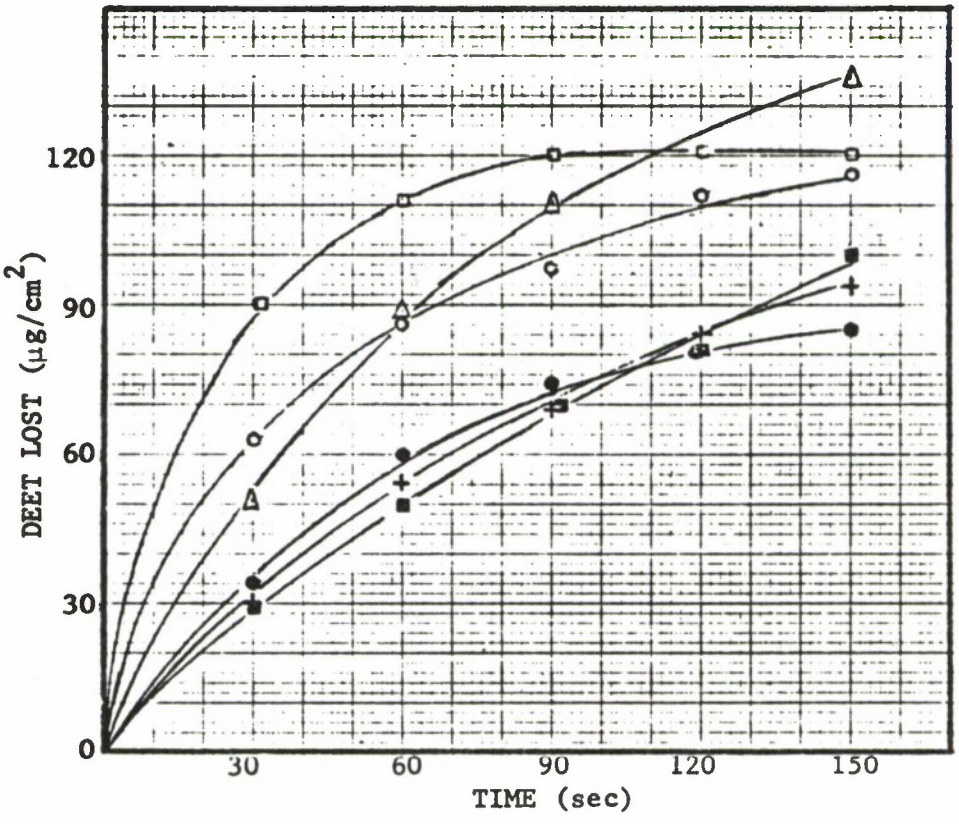
b. Water resistance was rated on a scale of 0 (No resistance) to 10 (Completely resistant).

The use of the water soluble dye provided qualitative information on the water resistance of films under simulated actual-use conditions; another method was chosen to quantitate the films' resistance to water. Polymer: ^{14}C-Deet films were utilized for this purpose. The films contained 20% ^{14}C-Deet by weight and were cast (3 mils thick) on glass plates to cover the surface at a rate of 0.15 mg of ^{14}C-Deet/cm^2. The films were rinsed for 30 seconds each of five times in 200 ml of water (see Methods) and the radioactivity in the rinses (indicative of Deet leached out from the films) was measured. Figure 1 shows curves describing the loss of Deet from representative films as a function of timed rinses. The figure shows that the rate of Deet lost from the pure Deet film was much faster than that lost from polymer:Deet films. In Table V, the actual rates at which Deet was lost from the pure Deet film and polymer:Deet films are presented. Three of these polymers (18, 32 and 34) were each formulated with ^{14}C-Deet to produce polymer:40% ^{14}C-Deet films; polymer No. 32 in addition was also formulated to produce polymer:80% ^{14}C-Deet films. These films were evaluated for their resistance to water.

The data indicate that the polymeric esters imparted a certain degree of protection to Deet from water wash-off. The protection however, was limited. Increasing the Deet content of these films to 40% decreased the protective role of the polysaccharide esters. It appears that increasing the concentrations of Deet in the film prevents the formation of stable films. It has already been indicated that mixtures of polymer:70-80% Deet do not form films. Cellulose acetate stearate:Deet was the only preparation with a polymer:80% Deet formulation evaluated for water resistance. However it is suspected that the other esters when formulated with Deet to produce polymer:80% Deet films do not offer much protection against wash-off.

Figure 1. The Loss of ^{14}C-Deet from Polymer: ^{14}C-Deet Films as a Function of Timed Water Rinses.

The films were cast (3 mils thick) such that 0.15 mg ^{14}C-Deet per square cm covered the surface. The films were subjected to five, 30 second water rinses. The amount of Deet lost during each rinse was calculated from the radioactivity of the rinse and the specific radioactivity of the ^{14}C-Deet.



The films shown in this figure are:

Δ-Δ; No. 14, Starch Nonanoate

□-□; Deet

○-○; No. 27, Amylose Decanoate

■-■; No. 32, Cellulose Acetate Stearate

+-+; No. 4, Starch Decanoate Acetate

●-●; No. 18, Amylopectin Decanoate

TABLE V

DEET-RETENTION BY POLYMER FILMS[a] UNDER WET CONDITIONS

No.	Materials	Rate of Deet Lost (% per sec)[b] 100% Deet Film	80% Deet Film	40% Deet Film	20% Deet Film
	Deet (control)	3.8	----	----	----
18	Amylopectin Decanoate	----	----	1.70	0.80
26	Amylopectin Decanoate	----	----	----	0.60
32	Cellulose Acetate Stearate	----	3.0	0.99	0.65
34	Cellulose Tri-decanoate	----	----	1.83	0.88
7	Starch Heptanoate	----	----	----	1.57
4	Starch Decanoate	----	----	----	0.59

a. The polymer:Deet mixtures were cast such that films covered the surface at 0.12-0.15 mg Deet/cm^2.

b. The rate of Deet lost presented here is the percent of remaining Deet (at any one time) lost per second.

4. Release of Deet from Films

The protection afforded Deet by the polysaccharide esters against water wash-off raised the possibility that the Deet would be entrapped in the polymeric films such that the repellent would not be effectively released. Unfortunately, as will be discussed in a later section, field evaluations could not be carried out to test this possibility. Several *in vitro* methods were therefore attempted to study the release of Deet from polymer:Deet films under dry conditions.

Initially identical thin films of a Polymer-Deet solution were cast on a series of glass plates and incubated at 30°C. Plates were withdrawn at appropriate time intervals and their films eluted with alcohol. The amount of Deet in these solutions was measured spectrophotometrically[(6)] to measure

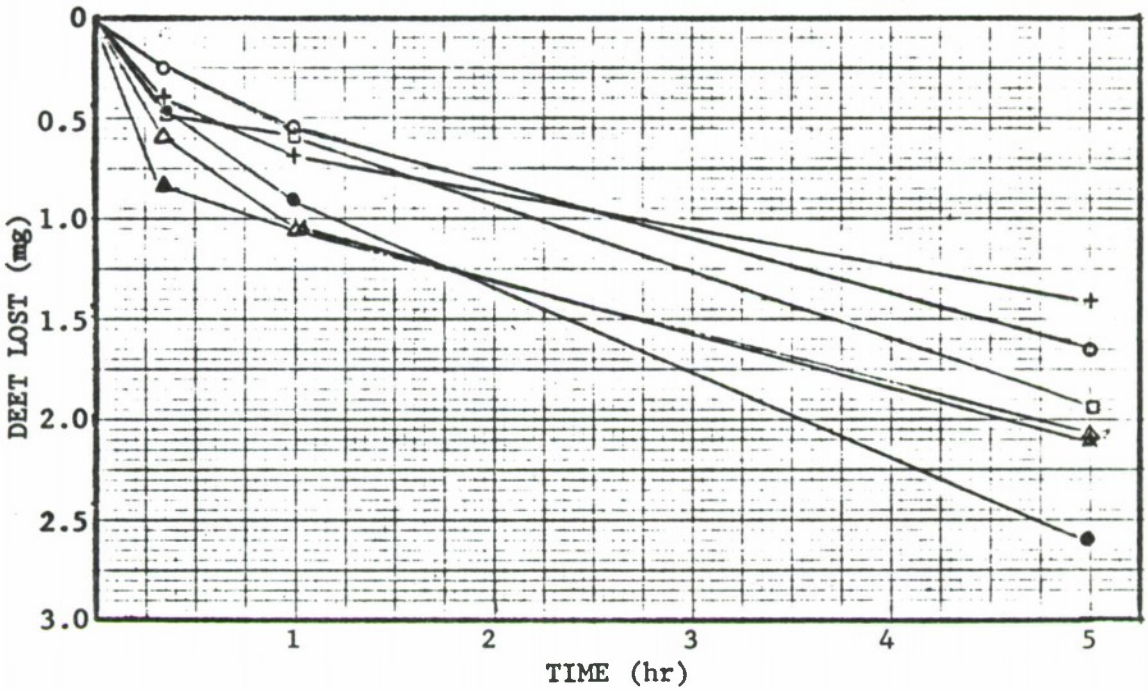
the Deet lost as a function of time. However, it was found that minute amounts of the polymeric materials were soluble in alcohol and interfered with the spectrophotometric determination of Deet.

Molecular sieve chromatography was utilized in efforts to separate the polymeric materials from the Deet. Bio-Glass beads, Bio-Gel-P2 and Bio-Gel A, however were found to adsorb the polysaccharide esters of fatty acids and an effective separation could not be attained. It was therefore decided to determine the rate of Deet lost from polymer-Deet films by the gravimetric method. Since this method was non-destructive, a single polymer:Deet film was used to follow the Deet released over a period of hours.

Films containing 20% to 40% by weight of Deet were thus evaluated for their capacity to hold the repellent. It was found that increasing the Deet concentration (from 20% to 40%) in the films did not influence the capacity of the films to hold the repellent. Figure 2 shows the Deet lost from representative polymer:20% Deet films as a function of time. The results suggest that although these polysaccharide ester films bind Deet in such a way to protect it from water, the binding did not prevent Deet from escaping from the film. On the other hand, inspection of Figure 2 also reveals that the release of Deet from polymer:Deet films was slower than that from pure Deet films. Thus control of Deet release from films was effected by the polymeric esters. The rates of Deet lost from these films were calculated from the slopes of the curves between the first and fifth hour of the experiment. Table VI shows the rates, calculated in this manner, of Deet lost from polymer:20% Deet films. The cellulose esters were found to bind Deet better than did the amylopectin and starch esters.

Cellulose and amylose are both straight-chain polysaccharides; cellulose is composed of β-glucose units while amylose is formed from α-glucose. Amylopectin and starch are both biosynthesized from α-glucose; both are branched polysaccharides. The results seem to indicate that both the degree of branching and the type of acetal linkage found in the polysaccharide contribute to some degree to the capability of the polysaccharide ester film to bind Deet.

Figure 2. The Deet Lost from Polymer:20% Deet and Deet-only Films Under Dry Conditions as a Function of Time.



The films presented in this figure are:

+-+; No. 32, Cellulose Acetate Stearate

O-O; No. 34, Cellulose Tri-decanoate

□-□; No. 27, Amylose Decanoate

Δ-Δ; No. 18, Amylopectin Decanoate

▲-▲; No. 26, Amylose Decanoate

●-●; Deet

TABLE VI

DEET RELEASE FROM POLYMER-DEET FILMS[a]

No.	Films	Deet Lost (μg of Deet/hr/cm^2)
32	Cellulose Acetate Stearate	4.0
34	Cellulose Tri-decanoate	5.8
28	Amylose Decanoate (1354-82)	5.8
27	Amylose Decanoate (1354-79)	6.7
23	Amylopectin Decanoate (1354-102)	6.7
18	Amylopectin Decanoate (12-4)	8.0
7	Starch Heptanoate (1354-71)	8.5
	Deet only	11.2

a. These films contained 20% Deet by weight.

5. The Use of Earthworms as Deet Detectors

Data obtained from the various procedures already discussed provided a great deal of information on the perdurability of polymer:Deet films under dry and wet conditions. However a quick bioassay utilizing a Deet sentitive organism (other than mosquitos) was desirable to correlate the *in vitro* findings with the *in vivo* situation.

It had been suggested in the early phases of this work, that earthworms might respond to Deet and therefore might be used in such a bioassay to detect Deet.

We found that although all worms reacted violently to liquid Deet they varied tremendously in their reaction to Deet vapors (see Materials and Methods). Numerous determinations per film would have to be made with many earthworms to obtain one valid evaluation. Such a bioassay could not be termed a "rapid bioassay."

The search of the literature as well as personal communications with personnel of the U.S.D.A. at Beltsville, Maryland failed to find another suitable biological detector. Our laboratories are not at present equipped to handle the usual Deet-sensitive organisms, namely mosquitoes, ticks, or mites.

6. Percutaneous Penetration of Deet

Maibach and Strauss[7] reported the percutaneous penetration of Deet when the repellent was applied topically to animal skin in vivo. It was possible that the "normal" diffusion of Deet through the skin would increase under the influence of the polysaccharide ester films.

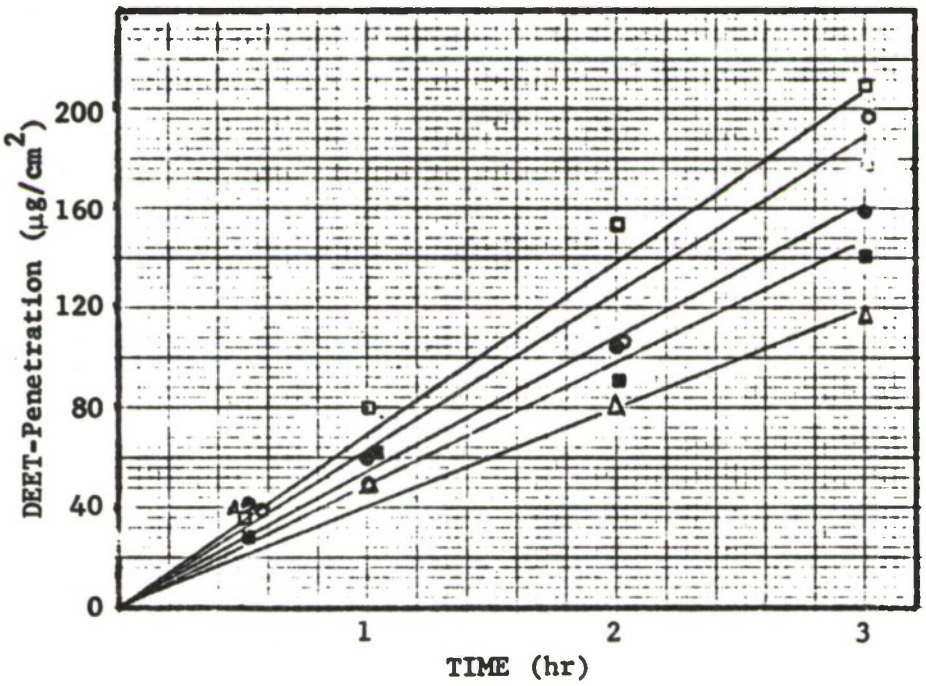
A study utilizing the glass diffusion cells described by Elfbaum and Laden[5] and discussed in the Methods section was undertaken to explore this possibility.

As shown in Figure 3, four polymer:20% ^{14}C-Deet films representative of the starch, cellulose and amylopectin esters were studied. The results indicated that the percutaneous penetration of Deet did not increase when the repellent was present in the polysaccharide ester films. Had the films effected an increase in the percutaneous penetration of Deet, then a pre-film protective barrier would have been necessary to prevent increased Deet penetration. However the data suggested that such a barrier would not be necessary with the films studied.

7. Evaluation of Repellency

A number of polymer:Deet formulations, (Table VII) based on their overall performance in the laboratory, were chosen for laboratory evaluation as mosquito repellents. Formulations in which tri-chloroethane served as the solvent were considered unsafe by U. S. Army toxicologists for human use. The U.S.D.A. (Gainesville, Florida) therefore submitted these formulations to their standard stocking test[3]. Cellulose acetate stearate:Deet films (8-32 and 9-32) were found to be approximately twice as effective as Deet alone. Results obtained with films numbers 1-4, 2-8, 5-23, 6-26, and 7-28 were inconclusive.

Figure 3. Percutaneous Penetration of Deet as a Function of Time.



Films Nos. 7, Starch Heptanoate (O-O);
18, Amylopectin Decanoate (●-●);
34, Cellulose Tri-decanoate (■-■); and
26, Amylose Decanoate (Δ-Δ)
Deet (□-□)

TABLE VII

POLYMER:DEET FILMS SUBMITTED FOR REPELLENCY EVALUATION

Number	Material	Solvent	% Deet
1-4	Starch Decanoate Acetate:Deet	TCE[a]	33
2-8	Starch Hexanoate:Deet	TCE	33
3-14	Starch Nonanoate:Deet	F-11[b]	20
4-14	Starch Nonanoate:Deet	F-11	40
5-23	Amylopectin Decanoate:Deet	TCE	33
6-26	Amylose Decanoate:Deet	TCE	33
7-28	Amylose Decanoate:Deet	TCE	33
8-32	Cellulose Acetate Stearate:Deet	TCE	20
9-32	Cellulose Acetate Stearate:Deet	TCE	40
10-32	Cellulose Acetate Stearate:Deet	F-11	80
11-34	Cellulose Tri-decanoate:Deet	F-11	20
12-34	Cellulose Tri-decanoate:Deet	F-11	40
13-34	Cellulose Tri-decanoate:Deet	F-11	40

a. Tri-chloroethane

b. Freon-11 (duPont)

Despite an intensive search for good and safe solvents only two (Freon-11 and Freon-21) were found which were compatible with a limited number of the polysaccharide esters. Freon 21 was not utilized as a solvent in the formulations submitted for evaluation. This solvent has low boiling point (8.9°C) and therefore requires the use of an aerosol delivery system. Freon 11, whose boiling point is 23.8°C does not require such a system for delivery.

Starch nonanoate, cellulose acetate stearate and cellulose tri-decanoate were found to dissolve in Freon 11. Polymer:Deet mixtures (3-14, 4-14, 10-32, 11-34, 12-34 and 13-34) utilizing these three polysaccharide esters in Freon 11 were submitted for evaluation as mosquito repellents on human skin. Cellulose acetate stearate:80% Deet (10-32) cast from Freon-11 was

found to be as effective as Deet in alcohol; both permitted the first confirmed bite 127.5 minutes subsequent to application. It would be desirable to conduct such an in vivo test (to first bite) and then continue to evaluate the samples for several additional hours. Since in vitro experiments showed a decrease in the rate of Deet released from polymer:Deet films when compared to Deet alone, longer in vivo testing times (e.g., time until third bite) might reveal the prolonged effectiveness of the experimental samples.

Formulations numbers 3-14, 4-14, 11-34, 12-34, and 13-34 (polymer:20%-40% Deet films cast from Freon-11) were found to be less effective than Deet in alcohol.

It would seem from these results that a high concentration of Deet in the films is necessary for effectiveness. However, the reports from the U.S.D.A. also showed that Deet in Freon-11 (our control) was one-half as effective as Deet in alcohol (U.S.D.A. control). Freon-11 is a liquid at room temperature but quickly vaporizes when spread on a large surface area. The disparity in effectiveness between the two Deet samples could be accounted for by an uneven application of the Deet:Freon-11 solution. That is to say, an aliquot intended to cover 100 cm^2 of skin might vaporize before the entire area is covered uniformly. Mosquitoes attacking an inadequately covered area could lower the efficacy reading of the sample. A similar reasoning could be applied to the preliminary tests of the polymer:Deet mixtures in Freon-11.

IV. DISCUSSION

The experimental laboratory work established that several polysaccharide esters bind Deet such that perdurability is imparted to the repellent even under wet conditions. The important question however is "does Deet escape from these films at a rate sufficient enough to repel mosquitoes?" The U.S.D.A. reported that one of the polymers, cellulose acetate stearate, is capable of extending the efficacy of Deet to twice the normal value when evaluated with the standard stocking test.

All of the polysaccharide ester:Deet films evaluated in vivo in the field were cast from the solvent Freon-11. Only one of these preparations received favorable mention in that it was judged just as efficient as Deet in alcohol. However, the reports rated Deet in Freon-11 one-half as effective as Deet in alcohol. The disparity between the two Deet control solutions needs to be resolved, as this could affect results obtained with films cast from Freon-11. Great precautions must be taken when applying Deet or polymer:Deet mixtures in Freon-11. This solvent is extremely volatile and can evaporate before the area to be treated is completely covered. It is suggested that the polymer:Deet mixture in Freon-11 did not fare better due to possible uneven coating of the skin.

It was found that Freon-21 was a good solvent for some of the polysaccharide ester:Deet mixtures. However, due to the low boiling point of this solvent, delivery of these mixtures required an aerosol system. Preliminary work with this system indicated that additional experimentation was needed to obtain the correct size and rate of spray needed for efficient delivery. The solutions to these problems would allow additional polymer: Deet mixtures for evaluation.

During the course of this research several proteinaceous materials capable of forming clear films were examined. Although soluble in water, once such films are allowed to dry they become somewhat resistant to water. Additional insolubility can be imparted to these films by chemical means. Additional work is required to explore the dermophilic properties of these polymers and their capacity to bind Deet.

V. SUMMARY AND CONCLUSIONS

Approximately a dozen skin substantive polysaccharide esters of fatty acids (from an inventory of 36 esters) were chosen, on the basis of their capacity to cast good films, to bind Deet.

Methodology was developed to measure the rate of Deet lost under dry and wet conditions from the selected polymer films. A gravimetric method was employed to measure the loss of Deet from films cast on glass plates as

a function of time. It was found that the release of Deet from polymer:Deet films was lower than that from pure Deet films. Thus control of Deet-release from films under dry conditions was effected by the polymeric esters.

Radioactive Deet was employed to measure the resistance of polymer:^{14}C-Deet films to water. These films were subjected to several water rinses; the amount of Deet which leached out from the films as a function of time was calculated. It was found that the rate of Deet lost from pure Deet films was faster than that lost from polymer:Deet films. The data indicated that the polysaccharide esters of fatty acids imparted a certain degree of protection to Deet from water wash-off.

In view of the results and discussion presented in this report, additional explorations should be carried out in the following areas:

1) Refinement of the aerosol delivery system so that additional polymer:Deet films can be evaluated.

2) Exploration of the skin substantive properties and stability of film-forming proteinaceous materials.

3) Evaluation of preparations as perdurable mosquito repellents under both dry and wet conditions.

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APPENDIX

SUMMARY OF RESULTS OF MOSQUITO REPELLENCY TESTS OF VARIOUS POLYMER-DEET FORMULATIONS

Gillette Research Institute
1413 Research Boulevard
Rockville, Maryland 20850
(301) 424-2000

October 9, 1972

Clyde S. Barnhart, Ph.D.
U.S. Army Land Warfare Laboratory
Aberdeen Proving Ground,
Maryland 21005

Dear Dr. Barnhart:

Enclosed please find six formulations and one control for mosquito repellency testing.

Sample Code	Formulation	Approximate (%)
	(Aerosol System)	
1323-169-1	3g of Cellulose Acetate Stearate (CAS)	3
	45ml DEET	45
	54ml Freon 21	
1323-169-2	6g CAS	5
	50ml DEET	44
	65ml Freon 21	
1323-169-3	10g CAS	9
	24ml DEET	22
	60ml Freon 21	
	24ml Freon 12	
1323-169-4	Control Aerosol Solution	
	50ml DEET	50
	65ml Freon 21	
	(Aqueous Alcohol System)	
1323-169-5	6g CAS	6
	60ml DEET	60
	36ml ethanol	

Sample Code	Formulation (Aqueous Alcohol System)	Approximate(%)
1323-169-6	50ml of Protein solution in alcohol	10(Final Conc.)
	50ml DEET	50
1323-169-8	4g Protein	4
	60ml DEET	60
	40ml 50% aqueous ethanol	

The first three formulations are aerosol systems and must be shaken prior to use. There are difficulties in delivering an exact amount of material as is the case with any aerosol system. However, the evaluators will have to do their best with this type of system. To obtain data on spraying rates and distance from source to target would have drained our financial resources. I thought it best to spend the available funds in obtaining compatible systems. Formulations 5 through 8 are the first non-areosol systems which are compatible with each other and which I am sure the Surgeon General will not object to.

Sincerely,

Angel L. Carrillo

ALC/md

Enclosures

The Gillette Company
Toiletries Division
Gillette Park
Boston, Massachusetts 02106
(617) 268-3200

November 3, 1972

C. S. Barnhart, Ph.D.
U.S. Army Land Warfare Laboratory
Aberdeen Proving Ground
Aberdeen, Maryland 21005

Dear Dr. Barnhart:

Work conducted under Contract No. DAA-005-71-C-0173, "Barrier Coatings for Skin to Bind DEET," for the U.S. Army Land Warfare Laboratory found a limited number of solvents in which the barriers were soluble. However, these were considered hazardous for human use by the Office of the Surgeon General. None the less, the USDA's Agricultural Research Service in Gainesville, Florida, submitted some of these formulations to their standard stocking test. One of these formulations containing cellulose acetate stearate (CAS) and the mosquito repellent DEET in trichloroethane proved to be superior to DEET in alcohol when tested against mosquitos.

Subsequently it was found that CAS and DEET could be formulated in Freon 11 (DuPont). This solvent has a boiling point of 23.8°C and therefore does not necessitate an aerosol system for delivery. This formulation was found to be ineffective as a mosquito repellent when applied to human skin. It was suggested that perhaps the mode of application of materials from Freon 11 was ineffective in giving complete coverage to the test site. We had to consider the possibility of the solvent evaporating before adequate application was made.

At the conclusion of that sutdy it was recommended that further work be conducted to find a better and yet safe way of formulating CAS and DEET so that effective testing could be carried out with the material. In addition we wanted to explore the possibility of formulating CAS and DEET in alcoholic solutions. We had previously attempted such a system and had failed but thought that it could be done by changing the sequence of mixing the ingredients. We had

also suggested the possibility of utilizing proteinaceous materials as the barrier coating. This approach seemed desirable since aqueous alcohol could be used as the solvent.

With this in mind, work under Contract No. DAA 0280 DA 0100 was commenced. Table I lists the samples sent out for testing on June 30, 1972.

Table I

Materials Submitted for Mosquito Repellent Testing

Sample Code	Formulation
1323-150-1	Cellulose tri-decanoate-DEET in Freon 11 5% solution of DEET; 5% Polymer
1323-150-2	Protein polymer alcohol solution containing DEET 5% DEET; 20% Polymer
1323-150-3	5% solution of DEET in Freon 11.
1323-150-4	Cellulose tri-decanoate: DEET 20% DEET; 20% Polymer
1323-150-5	20% DEET solution in Freon 11.
1323-150-6	Protein polymer alcohol solution containing DEET 15% DEET; 15% Polymer

No. 150-1 and its control 150-3 albeit tested previously were included to test out the effectiveness of the mode of application alluded to before. The USDA laboratory in Gainesville chose not to test them because they had been tested before. No. 150-4 which was similar to 150-1 except that the DEET concentration was four times as high was not tested for the same reason. However, cellulose-tri-decanoate formulated with 20% DEET in Freon 11 had never been tested. Solutions No. 150-2 and 151-6 represented initial attempts at formulating proteinaceous material with DEET in a non-Freon system. The advantages of such a system are evident. The solvent is safe and the mode of application presents no problems. Unfortunately, these formulations were ineffective as repellents.

The following Table 2 lists the second group of formulations sent out for testing.

Table II

Materials for Testing as Mosquito Repellents

Sample Code	Formulation	Approximate Concentration of Polymer and DEET (%)
	(Aerosol System)	
1323-169-1	3 g. of Cellulose Acetate Stearate (CAS)	3
	45 ml DEET	45
	54 ml Freon 21	
1323-169-2	6 g CAS	5
	50 ml DEET	44
	65 ml Freon 21	
1323-169-3	10 g CAS	9
	24 ml DEET	22
	60 ml Freon 21	
	24 ml Freon 12	
1323-169-4	Control Aerosol Solution	
	50 ml DEET	50
	65 ml Freon 21	
	Aqueous Alcohol System	
1323-169-5	6 g CAS	6
	60 ml DEET	60
	36 ml ethanol	
1323-169-6	50 ml of Protein Solution in Alcohol	10 (Final Conc.)
	50 ml DEET	50
1323-169-8	4 g Protein	4
	60 ml DEET	60
	40 ml 50% Aqueous Ethanol	

Ordinarilly, cellulose acetate stearate is not soluble in Freon 21 as was found in the previously reported study. However, it was found that if CAS was first dissolved in DEET, Freon 21 could be added (within limits) without precipitating the CAS. Sample Nos. 169-1 and 169-2 contained approximately the same concentration of DEET (45 and 44%, respectively). However, 169-2 contained almost twice as much CAS. Sample No. 169-3 contained half as much DEET with a greater concentration of CAS. In addition to Freon 11, 169-3 contained Freon 12 to increase pressure needed for delivery of this viscous sample. It was hoped these variations might be reflected in mosquito repellency effectiveness.

Formulation No. 169-5 represented a successful mixing of CAS and DEET in alcohol. This formulation was made by first dissolving the CAS in DEET with subsequent addition of the alcohol.

Sample Nos. 169-6 and 169-8 contained collogenous materials as the protein component. No. 169-6 was similar to 150-6 (Table 1) but contained 50% DEET; the latter contained only 15% DEET.

The collogen component of 169-6 was present as peptides of 1,000 molecular weight; the collogen component of 169-8 was of 20,000 molecular weight.

Result from Gainesville on the efficacy of these materials (Table 2) is forthcoming.

Sincerely,

Angel L. Carrillo, Ph.D.

ALC:lmg

cc: J. Galligan
K. Laden
G. Putterman

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
Insects Affecting Man Research Laboratory
1600 S. W. 23rd Drive
P. O. Box 1268
Gainesville, Florida 32601
Southern Region
Florida-Antilles Area

December 1, 1972

Dr. Clyde S. Barnhart
Biological Sciences Research
U. S. Army Land Warfare Laboratory
Aberdeen Proving Ground, Maryland 21005

Dear Dr. Barnhart:

Enclosed is a report, prepared by this laboratory, on the results of entomological tests with five repellent formulations (1323-169-2 to 6 incl.; OM-2454 to 8 incl.) which were furnished by the Gillette Research Institute through the U. S. Army Land Warfare Laboratory.

Two additional formulations were received, but not tested. Formulations 1323-169-1 and 8 were similar to formulations 1323-169-2 and 6.

We are glad to cooperate in the conduct of these tests and hope that such cooperation will continue to our mutual advantage.

Sincerely,

Donald E. Weidhaas

Donald E. Weidhaas
Investigations Leader

Enclosure - 1

December 1, 1972

Results of Tests with Five Repellent Formulations From the U. S. Army Land Warfare Laboratory

by

Donald E. Weidhaas and Leslie R. Swain, Jr.
Insects Affecting Man Research Laboratory
Gainesville, Florida

References:

Letter from A. L. Carrillo to C. S. Barnhart, October 9, 1972.

Summary of Results:

Protection-time tests were made with 5 repellent formulations from the U. S. Army Land Warfare Laboratory as skin applications against *Aedes aegypti*. The numbers of the formulations are 1323-169-2 to 6 incl. (OM-2454 to 8 incl.).

Slight modifications of the standard methods of testing, as described in the attached procedure sheet, were used. Detailed results of the tests are given in the attached tabulation.

The results show that the standard ethanol solution of deet alone was significantly more effective than the 3 formulations containing deet and cellulose acetate stearate. The formulation containing deet and the protein was about 84% as effective as the ethanol solution of deet; this difference was not significant. The aerosol formula of deet submitted as a control and the ethanol solution of deet were about equal in effectiveness. All test doses were based on equal quantities of deet applied to the skin (see Table 1).

Procedure Sheet
Gainesville, Fla.

Laboratory Tests with Mosquito Repellents Applied to the Skin

One ml. of the repellent, at full strength or in solution, is spread evenly over the forearm of the subject and compared directly with another repellent on the other arm. Each arm is exposed to caged *Aedes aegypti* mosquitoes for 3 minutes at approximately 30-minute intervals. Effectiveness is based on complete protection, that is, the time between treatment and the first confirmed bite (a bite followed by another within 30 minutes). A balanced, incomplete-block experimental design is usually employed. With this design each repellent in the series is paired against each other repellent in the series on the opposite arms of a given number of subjects. Adjusted averages and the least significant difference (0.05 level) between any two repellents are computed.

Table 1. Protection-time tests with 5 repellent formulations of the U. S. Army Land Warfare Laboratory (prepared by Gillette Research Institute) and deet against *Aedes aegypti*. (All experimental formulations and the deet standard were applied at 220 mg/forearm; average of 3 tests.)

Repellent no.	Formulation: Type[a]	Extender[b] and percent	Freon no.	Diluent (AA[c]/A[d])	Percent of deet	Protection time (min): Range	Average	Ratio
OM-2454	Pres.	CAS 5	21		44	30-270	181	0.70
OM-2455	Pres.	CAS 9	21&12		22	30-240	106	.41
OM-2456 (control)	Pres.		21		50	120-360	252	.97
OM-2457	Liq.	CAS 6		AA	60	60-360	166	.64
OM-2458	Liq.	Prot.10		AA	50	90-360	218	.84
ENT-22542	Liq.			A	22	90-390+	260+	1.00
				LSD (0.05 level)			71	

a/ Pres. = Pressurized formulation; Liq. = liquid
b/ CAS = Cellulose acetate stearate; Prot. = protein polymer (Wilson A-200)
c/ AA = Aqueous alcohol
d/ A = An alcohol

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13. ABSTRACT

The purpose of the study presently reported was to examine a variety of skin substantive film-forming polysaccharide esters of fatty acids for their capacity to bind the mosquito repellent, N, N-diethyl-m-toluamide (DEET). Thus gross physical observations were made of 36 film-forming polysaccharide esters of fatty acids; those that were found to cast good films on the basis of clarity, non-tackiness and pliability were chosen as possible binders for DEET. Their capacity to bind DEET such that perdurability would be imparted to the repellent under both dry and wet conditions was evaluated.

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