

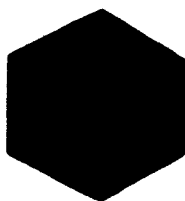
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CENTRAL RESEARCH LABORATORIES
432 WEST 45TH STREET — NEW YORK 36, N. Y.

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RESEARCH REPORT

PROJECT NO: 94022-300

REPORT # 1

**WASHFAST INSECT REPELLENT
FINISH FOR COTTON FABRICS**

GOVERNMENT CONTRACT #:..DA-49-193-MD-2355.

MAY 17, 1963

**JOHN R. ABRAMS
V. LINDSAY CHASE**

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TABLE OF CONTENTS

	Page:
I. INTRODUCTION.....	2
II. SUMMARY.....	2
III. CONCLUSIONS.....	3
IV. EXPERIMENTAL.....	3 - 7.



INTERCHEMICAL CORPORATION

CENTRAL RESEARCH LABORATORIES

FOUR THIRTY-TWO WEST FORTY-FIFTH STREET - NEW YORK 36, NEW YORK

PROJECT NUMBER: 94022-300

DATE: MAY 13, 1963

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SUBJECT.....WASHFAST INSECT
REPELLENT FINISH
FOR COTTON FABRICS

JOHN R. ABRAMS
V. LINDSAY CHASE

ABSTRACT

A stable emulsion system for application of the insect repellent N,N-diethylmetatoluamide (deet), to cotton fabric was developed. Washfastness has not been greatly improved, but "locking" deet in and on the fiber has been achieved. This fixing, however, eliminates the repellency of the treated fabric. The noticeable water solubility of deet makes imparting washfastness to it a quite difficult task. However, there are a number of binder systems and some approaches yet to be evaluated.

DESCRIPTORS:

N,N-DIETHYLMETATOLUAMIDE
emulsification of
trapping in cotton fiber of
binding on " " of
water solubility of
compatibility of
volatility of
washfastness of
INSECT REPELLENCY.

I. INTRODUCTION:

At present N,N - diethylmeta toluamide (deet) is the best practical, general purpose, individual insect repellent known.

It is superior in repellency, resistance to wiping, perspiration, evaporation and rinsing from the skin.

Applied to cotton fabric (sateen used for U. S. Army fatigue uniforms) it withstands one wash sufficiently to remain effective, but not two.

The Army would like to have deet fixed to the sateen so that it will withstand more washing - preferably five washes.

Various binders, binder-absorbent combinations and sealing in the fiber seemed logical approaches to be tried.

II. SUMMARY:

A satisfactory emulsion system for deet was developed.

Various binder systems were tried and tested for washfastness and repellent activity. These were reactive acrylic latex, melamine formaldehyde resin, thermosetting acrylic binder-thickener-latex combination, ethyl cellulose-solvent system, acrylic latex-calcium silicate adsorbent - water system and ethylcellulose-calcium silicate adsorbent - solvent system.

None were washfast - and one, the acrylic latex-calcium silicate adsorbent aqueous system, was not repellent even before washing.

It was found that if water were present during application, deet would be trapped in the cotton fiber upon heating. In that case, even double the quantity normally needed for repellency did not impart repellency. This trapped deet, however, readily washed out with water.

Deet was found to be soluble in water to the extent of 1.2% at room temperature.

III. CONCLUSIONS:

Since deet is appreciably soluble in water, rendering it washfast becomes a difficult task. It would seem that if the deet were locked in /or/ on the binder or fiber, it could resist washing. It would also appear that if deet were thus bound it could be unavailable for repelling insects.

A couple of examples were noted where deet was bound and did not show repellency. In these cases deet was still not washfast.

It is conceivable that the washfastness could be increased without completely masking the repellency. Probably, however, some mechanism would be required to release bound deet after washing to maintain an effective free deet level.

Various binding systems will be tried to find such a compromise as described above.

IV. EXPERIMENTAL:

As the tentative plan of application was the use of emulsion padding, the initial work was on preparation of emulsions.

A number of emulsifiers and emulsifier combinations were tried, with blends of nonionics being the best; and Span 60 - Tween 60 blend the best of these.

Even this combination did not give quite stable enough emulsion concentrates at 1:1/deet:water. However, the mixture of deet with the two emulsifiers could be stored and emulsified into water just before use. The dilute emulsions would probably be sufficiently stable for application.

Later it was found that a reactive acrylic terpolymer latex (RL8021) would readily imbibe very large quantities of deet with only hand stirring. Consequently, a small amount of latex was added to the deet emulsion to determine if it would stabilize. It did so.

During the emulsion work it was found that deet is water soluble to the extent of about 1.2% at 25.°C. Thus imparting washfastness where large ratios of water are used becomes extremely difficult.

In determining if there would be excessive losses during a curing of operation at 300°F., it was found that cotton fabric retain from 3.5 and 6% deet regardless of time of heating up to twenty-five minutes.

Since deet evaporates completely from a metal surface, it appears that deet is held in the fiber. The deet, however, is removed by washing. As deet is only slightly soluble in water, the quantity retained by the fiber could not be brought in by water. Water swells the fiber, apparently deet then enters the fiber, heat drives off the water, the fiber shrinks and traps considerable deet. If the deet were thus tenaciously held it might not repel insects.

The U. S. Department of Agriculture Laboratory at Orlando, Florida uses repellent impregnated cotton stockings for testing repellency. The stockings are pulled over the forearm which is then plunged into a cage of four to six day old mosquitos. The number of bites up to ten per minute is counted and repellency rated. Ten or more bites per minute indicates essentially no repellency. No bites indicates good repellency.

A cotton stocking was padded with deet emulsion, air dried and heated to remove excess, leaving *6% deet in the cotton. This was sent to Orlando where it showed essentially no repellency.

*Six percent deet is TWICE as much deet as is needed to give a repellency of NO BITES PER MINUTE.

To check whether the deet was affected by heat, fabric with trapped deet was submitted for analysis. Both infra red and gas chromatographic analysis showed the retained material to be deet. Also, trapped deet which had been extracted from cotton fabric was sprayed and padded on stockings and air dried but not heated. Both of these gave excellent repellency. There was considerable difficulty extracting deet. The solvents were not swelling agents for cotton although miscible with deet so that large volumes and long times were needed.

Water is not satisfactory because large volumes are necessary and deet steam distills during concentration. In one extraction, however, water was used to extract the deet, which in turn was extracted from the water by toluene. This technique also requires large volumes but it does not extract residual sizing or lubricating materials from the fabric.

To check further the assumption that deet enters water wet fibers, it was padded from toluene on fabric that had just been oven dried and on fabric wet with 40 - 50% water. These were air dried and then heated in the oven. The cloth which had been BONE DRY showed no remaining deet whereas the fabric which had been WET WITH WATER showed 4.2% deet retained.

Before the repellency test results were known, a wash and wear treatment - which supposedly cross-links and thus reduces swelling of cotton fibers by water - was applied to deet impregnated fabric to ascertain if washfastness would be improved. No noticeable improvement was observed.

A piece of fabric containing trapped deet was sprayed with water until thoroughly wet. It was then heated. Forty percent of the trapped deet was driven off.

To eliminate the possible effect of emulsifiers on extractability of trapped deet, a water - alcohol solution of deet was padded on cotton. The deet was completely removed by thorough rinsing.

Deet and an acrylic latex were found to be compatible in wet dispersion and in a dried film. An experiment was run on a film cast in a metal container to see if water would extract the deet from the dry film. The deet was extracted essentially quantitatively.

A binder system comprising aqueous alkali soluble thermosetting polymeric, acrylic binder, an acrylic thickener and a reactive acrylic terpolymer latex was padded along with deet on cotton, and over cotton, containing trapped deet. Thorough rinsing was sufficient to remove essentially all deet from both pieces.

To simplify and standardize the rinsing test, a piece of cotton containing trapped deet was soaked for an hour in fifty times its weight of water. By weighing in BONE DRY CONDITION before and after extracting, it was shown that ALL THE DEET WAS REMOVED.

In addition to the trapped deet which was extracted from cotton fabric and applied to a stocking and air dried, several other impregnated stockings were taken along for testing during a visit to the Orlando laboratory:

- (A.) Deet applied from alcohol solution and air dried. The deet should be mostly on the surface.
- (B.) Deet applied from alcohol-water solution, air dried and heated. The deet should be trapped. No emulsifier is present.
- (C.) Deet applied in ethylcellulose solution and air dried. The deet is compatible with ethylcellulose; should be well bound on the fabric but not trapped.

- (D.) Deet adsorbed on calcium silicate (Microcel) which was in turn dispersed in reactive acrylic latex, diluted with water, padded on stocking and air dried. The Microcel might hold the deet sufficiently to improve washfastness.

RESULTS OF REPELLENCY TESTS:

- (A.) EXCELLENT REPELLENCY
- (B.) NO REPELLENCY
- (C.) EXCELLENT REPELLENCY
- (D.) NO REPELLENCY

The extracted and reapplied deet also gave good repellency.

In the deet-Microcel-acrylic latex system, apparently either the water does not dissolve enough deet from the Microcel or the latex solids do not extract enough, or both, to provide repellency.

If the fabric can be brought to the BONE DRY CONDITION before and after washing or soaking, then the amount of deet extracted can be determined by weighing on a torsion balance of 10. mg sensitivity which eliminates the need for quantitative analysis.

However, the heat required to dry the fabric completely will also drive off some deet. If the fabric is conditioned in a temperature and humidity controlled room the same results should be obtained.

Such a room, the Plastics Testing Laboratory, was used to condition the following systems on fatigue uniform sateen:

Deet - ethylcellulose

Deet - reactive acrylic latex

Deet - melamine - formaldehyde resin

Deet - Microcel - reactive acrylic latex

*Deet - Microcel - ethylcellulose

*The last named system was tried because deet is miscible with the solvents, alcohol-toluene, used to dissolve the ethylcellulose and should be removed from the Microcel by the solvents and because deet, bound by ethylcellulose, remains effective as a repellent.

The temperature in the room, however, varies 6 to 7°F. and is occasionally subject to slight variation beyond this range. The control - a piece of untreated fabric - showed an acceptable variation in weight, but a couple of samples gave too large variations.

It became necessary, therefore, to submit these samples for analysis which is now underway. The extraction tests with estimation by weight loss indicate that most, if not all, of the deet is removed.

AMONG TECHNIQUES TO BE TRIED NEXT ARE:

- (1.) Fluorocarbon applied over deet - binder combination to impart water repellency and possibly increase fastness to washing.
- (2.) Silicone resin as binder - possibly less permeable to wash liquor.
- (3.) Molecular sieve to hold deet and bound by polymeric material. Depends on finding a solvent (for the binder) having larger molecular cross section than deet, so that it cannot fit into the molecular sieve and replace the deet.
- (4.) Carboxyl containing polymer on fabric first, then deet. Weak salt forming tendency may hold deet sufficiently to improve washfastness, but not inhibit repellency.
- (5.) Enclose in micro capsules which are then held on with a binder.
- (6.) Deet incorporated in a binder which is then covered with another binder.
- (7.) Vinyl resin with plasticizer and deet - vinyls hold plasticizers tenaciously - may act similarly with deet.
- (8.) Polyethylene emulsion as binder adsorbent - PE adsorbs strongly and while the emulsion is not a true film former, it adheres well.
- (9.) Imine terminated polymers and polyurethanes as binders for room temperature curing.
- (10.) Ascertain if other fiber swelling solvents show same behavior with deet as does water.
- (11.) Fill all reactive sites of the cotton with such materials as urea or citric acid and determine if deet is trapped and active.

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