

# DIFFUSION AND THERMODYNAMIC BEHAVIOR OF INSECT REPELLANT AND SUNTAN LOTION IN AUTOMOTIVE LEATHER COATINGS\*\*

by

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## ABSTRACT

The diffusion and thermodynamics of insect repellent and suntan lotion absorption into a series of polyurethane and polyacrylic resins used in leather finishing are examined. Physical testing of these resins applied as crosslinked and uncrosslinked thin-films on leather show that DEET exposure causes drastic reduction in Veslic dry rub fastness (greatly improved with a "desorption period" prior to testing). Reductions in rub fastness of samples exposed to suntan lotion were somewhat less severe than with DEET and were greatly improved by crosslinking, but severe yellowing observed during aging indicates continued degradation by non-volatile penetrants. Effective diffusion coefficients ( $D_e$ ) and saturation weight uptake levels at equilibrium ( $M_{sat}$ ) were calculated from free-film gravimetric sorption experiments. These results indicate very high saturation levels (1000-4000 wt% for DEET absorption, ~200 wt% for suntan absorption) and even total dissolution of uncrosslinked polycaprolactone/polyester-based urethanes in DEET. Interestingly, Deep Woods OFF® (25% DEET in an ethanol/hydrocarbon-based propellant) had identical saturation values as DEET, but with significantly higher diffusion rates - indicating diffusion promotion by highly volatile propellant solvents that do not remain absorbed in the polymer. More fundamentally, both the diffusion and saturation parameters were found to vary with the glass transition temperature,  $T_g$ , where higher  $T_g$  polymers exhibit lower diffusivity but higher equilibrium saturation levels. Calculations of sorption levels in thin-films on leather (using  $D_e$  values from free-film experiments) also reveal that surface wear properties

degrade long before total saturation is achieved.

## INTRODUCTION

The resistance of leather coatings to outdoor personal care products like insect repellent and suntan lotion continues to be a topic of high interest in the leather industry. This interest is at least partially related to increased demand for leather-trimmed vehicles being marketed for outdoor activities. However, while a considerable amount of effort has been invested in developing testing standards for measuring the resistance of leather finishes to insect repellent and suntan lotion,<sup>1</sup> there remains a need for more fundamental knowledge of the mechanisms involved in the degradation of leather coatings by these chemicals. In particular, a better understanding is required as to which specific physical-chemical parameters are most important in the degradation process.

Toward this end, the present study is focused on the measurement of the diffusion and thermodynamic behavior of insect repellent and suntan lotion in resins typically used for leather finishing. The thermodynamic behavior is defined by the ultimate saturation uptake of penetrant at equilibrium, while the diffusion behavior determines the rate at which this equilibrium is achieved.<sup>2-4</sup> Additionally, the resins have been chosen to span a range of polymer behaviors - most notably differentiating between polyacrylic and polyurethane emulsions and also representing a range of glass transition temperatures,  $T_g$  within each subset of polymer types. The effect of crosslinking these resins will also be investigated.

The specific objectives of this investigation are three-fold. First, the absorption behavior of the selected resins toward insect repellent (which is already known to damage polymers such as acetate, rayon, spandex, and others<sup>5</sup>) and suntan lotion will be assessed by applying physical testing methods to exposed samples of the resins coated on leather. In particular, visual inspection and Veslic dry-rub testing

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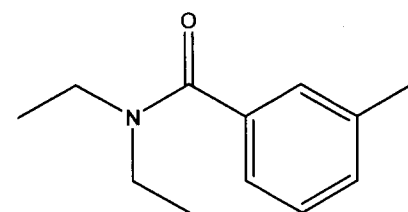
will be used. These data will be compared to results from free-film sorption experiments, where the effective diffusion coefficients and thermodynamic properties are calculated. Second, the key material parameters responsible for the absorption behavior will be identified (acrylic vs. urethane, glass transition temperature, crosslinking, polyol type, etc.). Third, the experimentally-determined diffusion coefficients will be used to calculate the level of absorption of penetrant into the thin films of resin present on the coated leather samples used in the physical testing experiments. This analysis will enable direct comparisons of physical testing results with the actual absorption levels present in the thin films at the time of physical testing.

## EXPERIMENTAL METHODS

### Materials

The sample matrix is presented in Table I along with respective resin properties. All resins are from TFL USA/Canada, Inc. Glass transition temperatures have been determined using differential scanning calorimetry (DSC), and tensile properties have been determined by tensile testing of cast films.

The insect repellants used in the present study include pure N-N-diethyl-m-toluamide (DEET, CAS# 134-62-3, Morflex, Inc.) and Deep Woods OFF® (25% DEET in an ethanol/hydrocarbon-based propellant, S.C. Johnson Wax, Inc.).<sup>5</sup> The chemical structure of DEET is as follows:



N,N-diethyl-m-toluamide  
"DEET"

TABLE I  
Resin Film Properties

Resin	Solids (%)	T <sub>g</sub> (°C)	Tensile Strength (MPa)	Elongation (%)	Film Properties
Acrylic #1	40	-17	1.7	1470	Very Soft, Tacky
Acrylic #2	40	1	6.1	1080	Medium-Soft, Fine Particle Size
Acrylic #3	35	15	1.6	890	Medium-Hard, Tack-free, Self x-linking
Urethane #1	31	-47	60	540	Hard at RT, Soft at 70°C, Fine Part. Size, Polycaprolactone /Polyester Polyol
Urethane #2	15	-47			Urethane #1 cut to 15% solids
Urethane #3	25	-21	35	480	Medium-Hard, Fine Part. Size, Polyether Polyol

NOTE: T<sub>g</sub> for urethanes primarily corresponds to the "soft" polyol-based domains.

NOTE: Urethane "hard" segments are based on aliphatic diisocyanates.

The suntan lotion studied was Coppertone KIDS® SPF 30 sunblock, which contains a very complex mixture of ingredients according to the product label.<sup>5</sup> These ingredients are given in Table II. In fact, it is likely that many of the individual ingredients have some absorption activity in the resins studied but the relative individual magnitudes are not known. Therefore, in the present study the suntan lotion mixture is treated as a single absorbing material with lumped-average "effective" diffusion and thermodynamic properties describing the mixture as a whole.

### Sample Preparation

Samples of resin-coated leather for physical testing were prepared using full-grain, white leather crust that was roll-coated with the resins given in Table I for an application of 15-17 wet-grams/ft<sup>2</sup> (161-183 wet-grams/m<sup>2</sup>), or 4-6 dry-grams/ft<sup>2</sup> (43-65 dry-grams/m<sup>2</sup>). After application, the coated samples were dried at 100 °C for 10 min and then allowed to rest overnight at room temperature (RT) prior to testing. In addition to samples coated with 100% clear resin, other samples were coated with crosslinker in the resin (5 wt. % polyisocyanate crosslinker + 95 wt. % clear resin). Pigmented resins (10 wt.% black pigment + 90 wt. % clear resin) and pigmented resins with crosslinker (5 wt. % polyisocyanate crosslinker + 10 wt.% black pigment + 85 wt. % clear resin) were also applied to additional samples of white crust. The use of black pigmented resins on white crust facilitates easy visual recognition of damage to the coating during wear tests because any exposed white crust is readily visible against the black coating. In the case of clearcoats, the use of white crust promotes easy visual recognition of yellowing/color change within the clear resin.

Free film samples of each resin were prepared by pouring the liquid emulsions into PTFE Petri dishes followed by drying at room temperature for 12 hours before final drying

TABLE II  
List of Ingredients in "Coppertone KIDS® SPF 30 Sunblock"

Active Ingredients	Inactive Ingredients	
Octyl Methoxycinnamate	Water	Methylparaben
Oxybenzone	Sorbitan Isostearate	Joboba Oil
Octyl Salicylate	Sorbitol	Propylparaben
Homosalate	Triethanolamine	Carbomer
Avobenzene (Parsol® 1789 manf. by Givaudan-Roure Corp.)	Octadecene/MA Copolymer	Polyglyceryl-3 Distearate
	Stearic Acid	Fragrance
	Barium Sulfate	Disodium EDTA
	Benzyl Alcohol	Dimethicone
	Aloe Barbadosis Extract	Tocopherol (Vitamin E)

at 70 °C for 30 min. Films were then removed from the dishes and cut into 1 in<sup>2</sup> samples. Film thicknesses were typically in the range of 20-60 mils (0.02 to 0.06 inches), which was necessary to allow for handling of the fragile swollen samples after exposure to insect repellent or suntan lotion. Crosslinked samples (using 5 wt.% polyisocyanate) were prepared in a similar manner, except that final drying was done at 70 °C for 25 hours to ensure full reaction of the crosslinker with the resin. Crosslinked samples are designated with an "xl" suffix in subsequent discussion.

### Physical Testing after 30 min. Exposures

The coated leather samples described above were subjected to 30 min exposures of either insect repellent (100% DEET) or suntan lotion (Coppertone KIDS® SPF 30) at either room temperature or 70 °C. After wiping away the excess penetrant from the surfaces of the exposed samples, evaluations were made to assess visual damage and changes in wear resistance. Specifically, visual assessment of clear coats included observation of any blistering and also evaluation of yellowing (0-to-5 scale; 1=slight yellowing, 5=severe yellowing). Wear resistance of pigmented coats was measured with Veslic dry rubs (number of rubs to cause visible damage using a Giuliani Rub Fastness Tester Model IG/10/MOD with 500 g weight). To study the reversibility of the absorption process, additional samples of coated leather were subjected to the same 70 °C penetrant exposures with wiping of the penetrants from the surface after the 30 min. exposure, but then an additional "desorption period" of 16 hrs. in a 70 °C air environment was allowed to occur prior to conducting the visual and wear testing.

### Diffusion and Saturation Uptake Experiments

Samples of free films (1 in. by 1 in. by ~40 mils) were measured for their planar and thickness dimensions and initial weights (Mettler-Toledo Analytical Balance with 0.0001 g accuracy). The samples were then fully immersed in either insect repellent or suntan lotion and their weights and pla-

nar dimensions were measured as a function of time by periodically removing the samples from the baths to make the measurements. Most importantly, it was necessary to develop a procedure by which the excess surface liquid could be removed from the samples prior to weight measurements. Due to the tackiness of many of the films it was not practical to wipe the excess liquid with a cloth or paper towel because fibers from the cloth or paper towel would stick to the surface of the sample. Instead, the samples were removed from their baths with tweezers and placed on non-stick release paper. Then, the samples were repeatedly flipped and gently wiped across the release paper until the excess liquid was removed and the weight of the sample could be accurately measured (+/- 0.0005 g). Samples were then returned to the baths and periodically re-measured until reaching saturation.

## RESULTS AND DISCUSSION

### Physical Testing of Resin-Coated Leather Samples

The results of the physical testing experiments (using resin-coated leather samples) are presented in Figures 1 and 2 for the Veslic dry-rub data. These figures show that 30 min. exposures to DEET at either 70 °C or at room temperature (RT) both cause an overall and drastic 90% reduction in the rub resistance. The only exception to this trend is for the extremely highly crosslinked Urethane #2xl exposed to DEET at RT, which exhibits a less severe but still significant 60 % reduction in rub fastness. This particular sample has 5 parts of crosslinker to 15 parts resin, compared with the 5 parts crosslinker to ~35 parts resin present in the other crosslinked resins. Nevertheless, even this sample has more than 90% reduction in rub fastness when exposed to DEET at 70 °C. In general, there is significant recovery of rub fastness for DEET-exposed samples tested after a 16 hr desorption period, but complete recovery is only observed for crosslinked Urethane #1xl. Exposure of resin to suntan lotion was slightly less severe, and crosslinked samples gen-

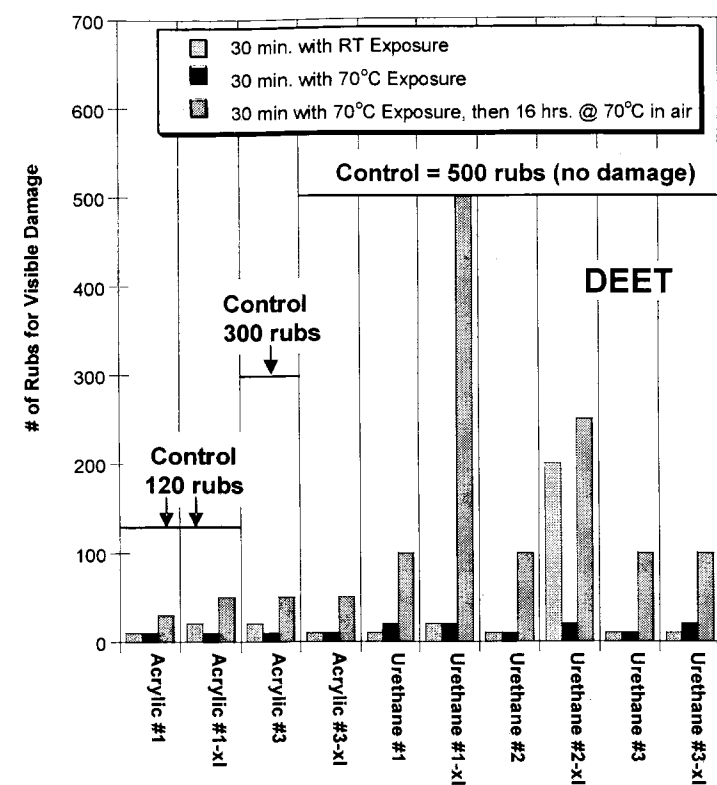


Figure 1. - Physical testing results for Veslic dry-rubs after 30 min exposures to DEET.

erally performed better (especially urethanes, for which crosslinked Urethane #1x1 and crosslinked Urethane #3x1 maintained full rub fastness after RT exposure to suntan lotion). Interestingly, recovery after the 16 hr. desorption period is marginal or even negative for all samples exposed to suntan lotion (except Urethane #1x1), indicating continued degradation and not desorption of penetrant.

Visual assessment of the physical testing samples after 30 min. exposures to DEET did not produce any visible yellowing or blistering at either the RT or 70 °C exposure temperatures. However, the leather samples coated with uncrosslinked Urethanes #1 and #2 appeared to exhibit dissolution of the resins while exposed to DEET and became very tacky, although basic film integrity was regained after drying in the desorption period. Crosslinking significantly reduced this dissolution effect. Exposure to suntan lotion did not cause total film breakdown under any circumstances and no yellowing was observed after 30 min. exposure to suntan lotion at RT. However, 30 min. exposure to suntan lotion at 70 °C did cause slight to moderate yellowing (ratings of 1 to 2, where severe yellowing = 5).

The samples used in these visual assessments were also allowed to age for up to 22 hr. at RT and at 70 °C by wiping excess penetrant from the sample surfaces once their initial

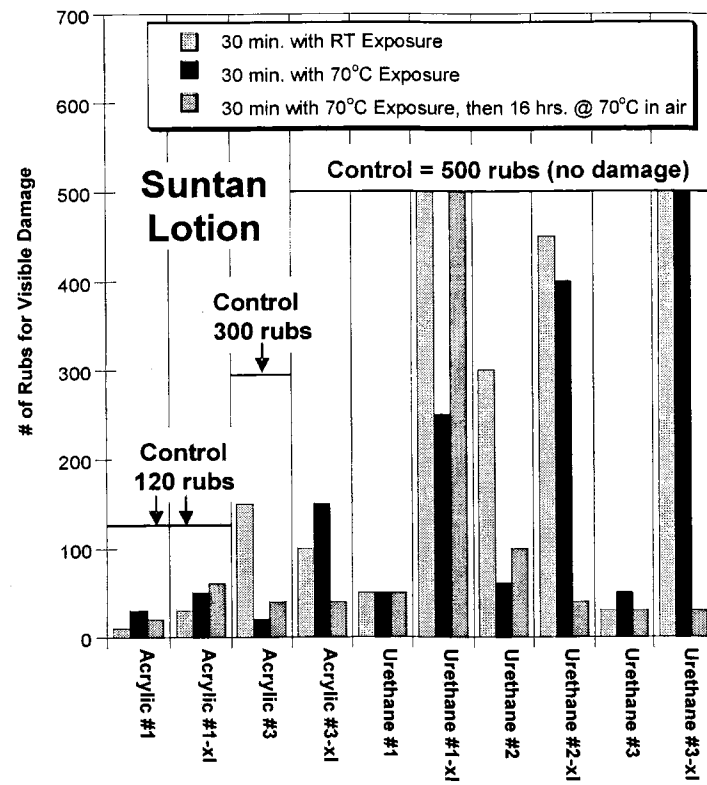


Figure 2. - Physical testing results for Veslic dry-rubs after 30 min exposures to suntan lotion.

30 min exposures to DEET or suntan lotion were completed. Visual yellowing/blistering was assessed at regular time intervals and relative to controls that experienced the same heat conditioning but without the initial 30 min exposure to penetrant. In the case of aged DEET-exposed samples, no yellowing/blistering occurred until 6 hr. at 70 °C and the slight yellowing (rating=1) was only observed in a small number of samples and did not significantly worsen even after 22 hrs of aging. Similar aging results were obtained for samples that were initially exposed to suntan lotion at RT. However, the slight to moderate yellowing already observed after the initial 30 min exposures to suntan lotion at 70 °C progressively worsened in the wiped samples used for aging, to the point that all aged samples had severe yellowing (rating = 5) after 22 hrs of aging at this higher temperature. This again indicates that, while DEET appears to significantly desorb from the resins during heat aging, the damage-causing penetrants in suntan lotion are not sufficiently volatile to desorb from wiped samples and instead continue to degrade the resins with time.

#### Free-film Sorption Experiments: Calculation and Trends in $D_e$ and $M_{sat}$

To better understand the diffusion and thermodynamic properties responsible for these observed physical testing results, the penetrant absorption behavior in resin free-films was measured. Figure 3 shows typical data from the free-film

sorption experiments, where the fractional absorption of penetrant relative to maximum uptake is plotted versus time. The rate of absorption may be modeled from this data by assuming that penetrant uptake occurs via molecular diffusion through a plane sheet (i.e., through the faces of the free-film sample squares) with diffusion through the sample edges being negligible.<sup>4</sup> The well-known series solution to the resulting partial differential equation for the concentration dependence of penetrant relative to time and position is as follows:<sup>4</sup>

$$\frac{C_t}{C_{sat}} = 1 - \left\{ \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \sin \left[ \frac{(2m+1)\pi}{L} x \right] \exp \left[ \frac{-(2m+1)^2 \pi^2}{L^2} D_e t \right] \right\} \quad (1)$$

In the above equation,  $t$  is the exposure time to penetrant,  $C_t$  is the concentration of penetrant at time  $t$ ,  $C_{sat}$  is the concentration of penetrant at saturation,  $L$  is the full through-thickness of the sample film,  $x$  is the position within the through-thickness ( $0 \leq x \leq L$ ), and  $D_e$  is the effective diffusion constant of penetrant into the polymer film. Integration of this concentration profile over the through-thickness of the film yields the time-dependence of the total absorption of penetrant into the sample, ( $M_t/M_{sat}$ ), which is the quantity that is actually measured in gravimetric studies:<sup>4</sup>

$$\frac{M_t}{M_{sat}} = 1 - \left\{ \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left[ \frac{-(2m+1)^2 \pi^2}{L^2} D_e t \right] \right\} \quad (2)$$

Two methods are often used to simplify Eq. 2 for the extraction of diffusion coefficients from the experimental data. The first is the "short-time method":<sup>4</sup>

$$\frac{M_t}{M_{sat}} = \frac{4}{L} \sqrt{\frac{D_e t}{\pi}} \quad (3)$$

In the present study, the "short-time" method was found to be very sensitive to both experimental error at short times and also to non-ideal diffusion behavior at longer times, resulting in very poor fit to experimental data at longer times. The second simplified method is called the "half-time technique":<sup>4</sup>

$$D_e = 0.049 \left( \frac{L^2}{t_{1/2}} \right) \quad \text{when} \quad \frac{M_t}{M_{sat}} = 0.5 \quad (4)$$

The diffusion coefficients determined from this method, where the half-times are found graphically from the experimental sorption curves, produced reasonably good fits to experimental data when used directly in Eq. 2. Nevertheless, to obtain the best fit possible, a non-linear least-squares fitting routine was performed using the experimental data and Eq. 2, with the half-time diffusion coefficient serving as the initial guess. Computationally, this was accomplished using Microsoft Excel<sup>®</sup> to calculate ( $M_t/M_{sat}$ ) in Eq. 2 with  $m=50$  and by systematically varying the value of  $D_e$  about the initial guess until the sum of squared errors

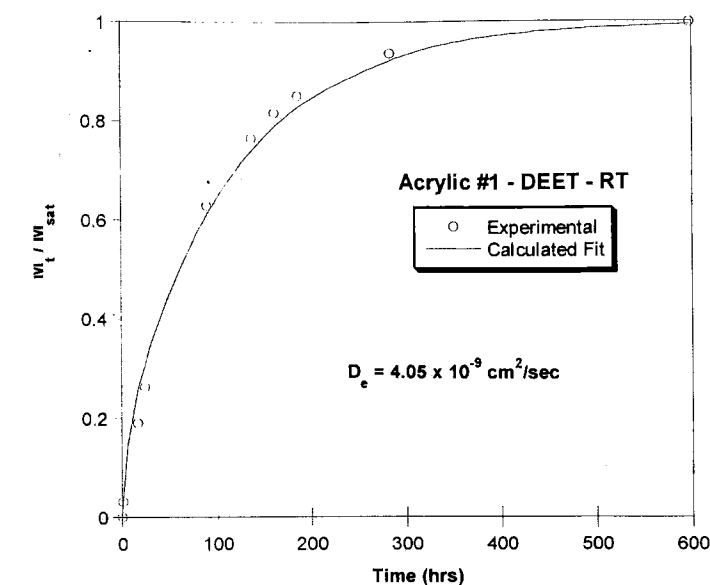


Figure 3. - Typical free-film sorption curve, where both the experimental data and calculated fit are presented for Acrylic #1 after long-term DEET exposure at room temperature (RT).

was minimized. As shown in Fig. 3, generally good fit to experimental data is achieved across the entire curve using this method. It is important to note, however, that diffusion coefficients obtained by this technique are "effective"  $D_e$  values that average over any non-idealities such as experimental scatter, concentration-dependent diffusivity,<sup>6,7</sup> or non-Fickian behavior (not expected for the  $T > T_g$  conditions used in the present study<sup>8,9</sup>).

A summary of the calculated diffusion coefficients, as well as the associated thermodynamic saturation values, are presented in Table III and shown graphically in Figures 4 and 5. From Fig. 4 it can be seen that there are no clear distinctions between acrylics versus urethanes in the general magnitudes of the saturation uptake values,  $M_{sat}$  and  $V_{sat}$ . Likewise, these saturation values have no clear trends regarding temperature sensitivity or crosslinking. For example, while  $M_{sat}$  for DEET-exposed Acrylics #1 and #3 increase with temperature, the value of  $M_{sat}$  for DEET-exposed Urethane #3 decreases with temperature. Crosslinking prevents total resin dissolution into DEET for Urethanes #1 and #2 and greatly reduces the saturation uptake of DEET in Acrylic #3, yet the saturation values for Urethane #3 at 70 °C are actually increased slightly by crosslinking. Perhaps the most significant observation concerning the thermodynamic saturation levels is that the total magnitudes in all cases are very large - for DEET exposure the wt.% uptake and sample vol.% at saturation ranges from 1000-4000 % relative to their original values. Saturation levels for suntan lotion exposure are considerably less, but they remain very large at ~200 % relative to original values.

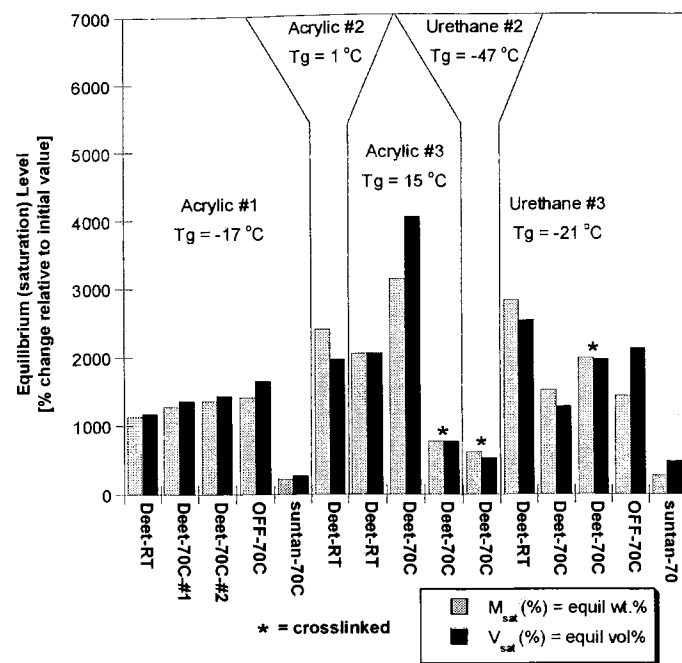


Figure 4. - Thermodynamic saturation levels for free-film samples.

Also of great significance is the fact that saturation uptake levels of Deep Woods OFF® are identical to those of DEET in the same resin. This result applies to both acrylics and urethanes, and indicates that the ethanol/hydrocarbon-based propellant present in Deep Woods OFF® (25 % DEET) is sufficiently volatile that it does not remain absorbed in the resin.

It is also important to note that any attempt to calculate thermodynamic activities or Flory-Huggins interaction parameters<sup>3,6</sup> will require additional data involving saturation levels determined under different partial pressures of penetrant. This is because the very high level of absorption observed in these penetrant-resin systems (saturation wt. fraction of penetrant = 0.7 to 0.97) is well beyond the limit of Henry's Law (wt. fraction < 0.1), which is otherwise a common "one-point" activity model often used to study absorption of dilute penetrants in solids such as polymers.<sup>2,3,6,8,10</sup>

The diffusion behavior across the different resins is illustrated in Fig. 5 and shows that, as with the saturation uptake values, there are no clear distinctions in the magnitudes of the diffusion coefficients between acrylics versus urethanes. However, other relationships are more evident. For example, the diffusion coefficient of DEET in the resins always increases with temperature, as would be expected for a temperature-activated process such as diffusion.<sup>2,3,6,7</sup> Crosslinking has little effect on the diffusion rate of DEET into Urethane #3, but significantly enhances the diffusion of DEET into Acrylic #3. This effect is most likely due to an increase in polar urea-urethane groups introduced by crosslinking, especially in the case of acrylics that have no

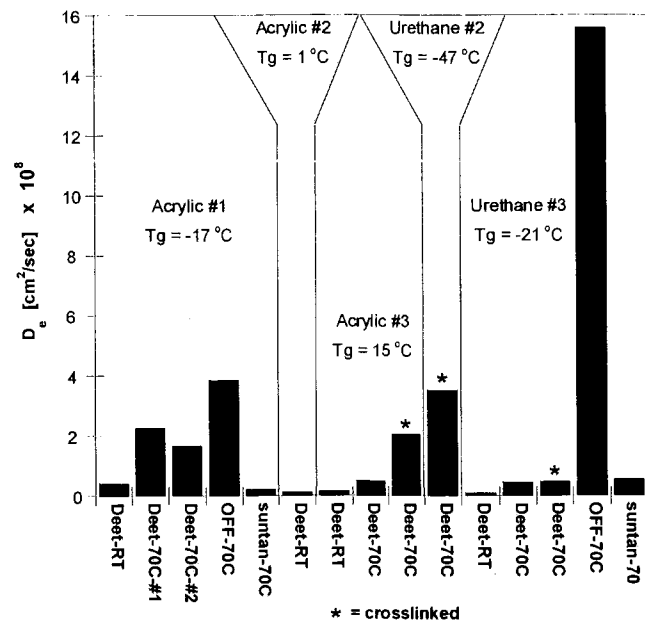


Figure 5. - Diffusion coefficients for free-film samples.

such groups prior to crosslinking, since these polar amine-based groups should favorably interact with the amide group of DEET to enhance the diffusion rate. The dependence of diffusion rate on the concentration of DEET is again quite startling, since it appears that the ethanol/hydrocarbon-based propellant in Deep Woods OFF® (25% DEET) substantially increases the diffusion coefficient of DEET into the resins even though it later flashes off or is displaced to leave only the DEET at saturation. Interestingly, the diffusion coefficients of suntan lotion are generally comparable to, or only somewhat lower than, the diffusion coefficients of DEET in the same resins - in contrast to the much greater gap in saturation behavior discussed previously between suntan lotion and DEET.

Note also that the diffusion coefficients presented in Table III for the same resins at RT and 70 °C may be fit to an Arrhenius relationship to yield diffusion activation energies,  $E_a$ , and pre-exponential factors, A, according to the equation:<sup>2,3,6,7</sup>

$$D_e = A \exp\left(\frac{-E_a}{RT}\right) ; \quad \ln(D_e) = \ln(A) - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \quad (5)$$

The resulting activation energies, reported in Table IV, are within the range of 5-7 kcal/mol. This is a typical range for diffusion activation energies, since the activation energies for chemical reactions are generally greater than 10 kcal/mol,<sup>6,7,11</sup> and these results provide a measure of confidence in the experimental methods. It is also possible to extract a more quantitative estimate for experimental error using the data for Acrylic #1-DEET-70°C because this resin was tested in replicate (the time-intensive nature of the free film sorption studies prevented additional replicate measurements). The replicate measurements shown in Table III

TABLE III  
Free-Film Sorption Data

Resin	Diffusion Coef.	Thermodynamic Properties	
	$D_e$ (cm <sup>2</sup> /sec)	$M_{sat}$ (wt %)	$V_{sat}$ (vol%)
Acrylic #1-Deet-RT	4.05 e-09	1133	1178
Acrylic #1-Deet-70C-#1	2.25 e-08	1275	1356
Acrylic #1-Deet-70C-#2	1.67 e-08	1358	1438
Acrylic #1-OFF-70C	3.86 e-08	1414	1653
Acrylic #1-suntan-70C	2.05 e-09	225	272
Acrylic #2-Deet-RT	1.28 e-09	2404	1963
Acrylic #3-Deet-RT	1.49 e-09	2058	2055
Acrylic #3-Deet-70C	4.91 e-09	3143	4045
Acrylic #3x1-Deet-70C	2.05 e-08	777	774
Urethane #2x1-Deet-70C	3.52 e-08	614	536
Urethane #3-Deet-RT	9.12 e-10	2829	2535
Urethane #3-Deet-70C	4.51 e-09	1520	1282
Urethane #3x1-Deet-70C	4.67 e-09	1986	1963
Urethane #3-OFF-70C	1.56 e-07	1434	2130
Urethane #3-suntan-70C	5.53 e-09	271	483

NOTE: Urethane #1 and #2 (non-crosslinked, polycaprolactone/polyester polyol) completely dissolved in DEET. Crosslinking prevented dissolution in both cases, but tensile strength of Urethane #1x1 was too fragile to handle after exposure to DEET, so sorption data could not be measured for this sample.

TABLE IV  
Diffusion Arrhenius Parameters

Resin	$E_a$ (kcal/mol)	A (cm <sup>2</sup> /sec)
Acrylic #3 (DEET)	5.00	7.51 e-6
Acrylic #1 (DEET)	6.57	2.94 e-4
Urethane #3 (DEET)	6.70	8.37 e-5

for this resin indicate that the diffusion coefficient has an error of about 15%, while the error associated with the saturation values is less than 5% (errors are calculated as half the total spread relative to the average value of the replicate measurements).

#### Dependence of $D_e$ and $M_{sat}$ on the Glass-Transition Temperature, $T_g$

While the above-cited observations based on Figs. 4 and 5 illustrate a number of important trends, the overall diffusion and thermodynamic behavior of the very different array of resins used in the present study are better understood in the context of fundamental material parameters. For polymers, the most useful material parameter is generally the glass transition temperature,  $T_g$ , which defines the temperature at which the polymer transitions from its higher temperature "rubbery" state to its lower temperature "glassy" state.<sup>3</sup> In the current study, all experiments were performed in the "rubbery" regime well above the resin  $T_g$ , and the departure from  $T_g$  (i.e.,  $\Delta T = T - T_g$ ) determines the amount of free

volume available within the polymer for the temperature-activated processes of diffusion and absorption.<sup>3</sup> The higher the experimental temperature is above the polymer  $T_g$ , the greater the free volume at that temperature.

Indeed, Figure 6 shows that both the diffusion and saturation parameters of uncrosslinked polyacrylates at 70 °C vary with  $T_g$ . Specifically, the highest  $T_g$  resin has the lowest dif-

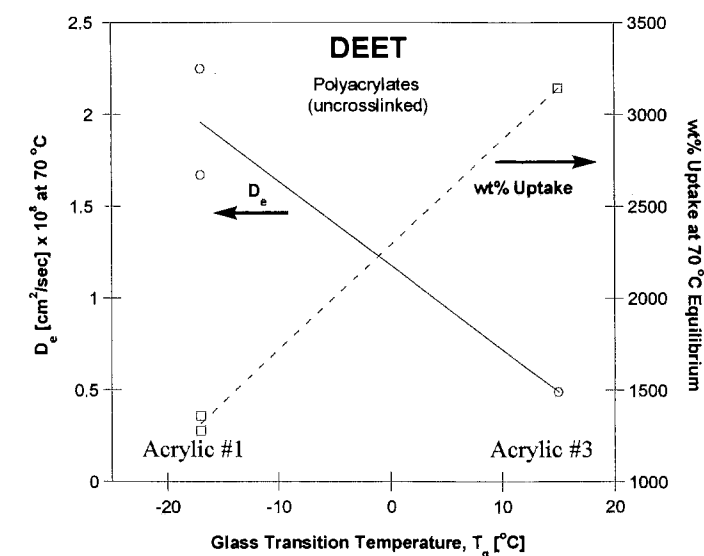


Figure 6. - Dependence of absorption parameters  $D_e$  (data represented as (o)) and wt.% Uptake (data represented as (□)) versus polymer glass transition temperature,  $T_g$ . Note that Acrylic #1 ( $T_g = -17$  °C) has replicate measurements for both  $D_e$  and wt.% Uptake indicated as separate data points.



fusion rate because its departure from  $T_g$  is small - thus it possess a lower polymer free volume and would be expected to have inhibited diffusion. Conversely, this same highest  $T_g$  resin exhibits the highest saturation uptake levels despite its low free volume. This may be explained by considering that the same polar intermolecular interactions responsible for increasing the polymer  $T_g$  will also increase the solubility of polar penetrants like DEET and suntan solvents into the polymer.<sup>3</sup> In this regard, the observed  $T_g$ -dependence of saturation uptake levels may be more related to the enthalpic polymer properties associated directly with  $T_g$  rather than to the entropic free volume as is the case for the  $T_g$ -dependence of diffusivity.

#### Calculation of Sorption Curves for Thin-Film Physical Testing Samples

It is also possible to estimate the actual penetrant absorption into the leather-supported thin-films of resin used in the physical testing experiments by applying Eq. 2 and using the diffusion coefficients obtained from the free-film experiments. Figure 7 shows the calculated sorption curves for these thin-films on leather (note that film thicknesses were estimated from dry coat weights combined with densities obtained from free film measurements; also note that in using Eq. 2, which assumes penetrant diffusion from two faces of a free-film, the values of  $L$  in Fig. 7 calculations were taken as twice the film thickness in order to simulate the single-surface diffusion occurring in the physical testing experiments). Interestingly, only three out of the fifteen analyzed samples reached equilibrium after 30 min exposure to penetrant, although all samples achieved at least 20% saturation after 30 min. Nevertheless, all samples in

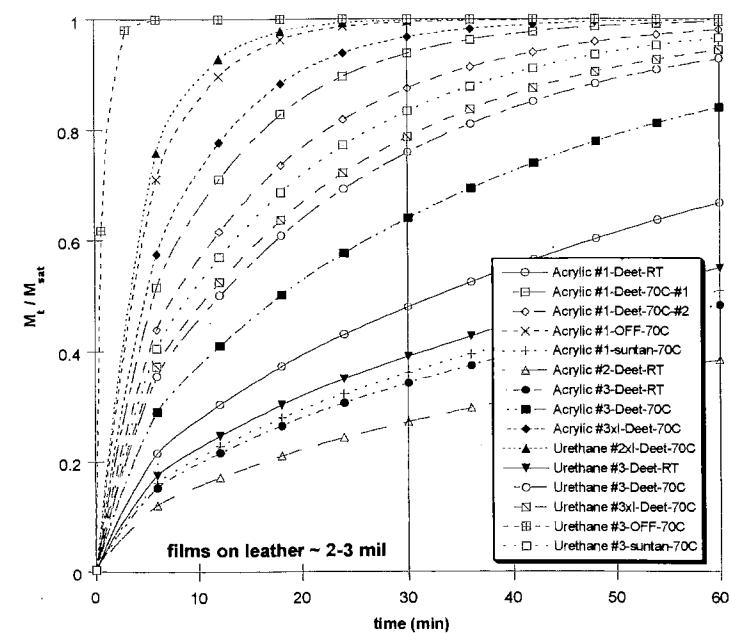


Figure 7. Calculated sorption uptake curves modeling the thin-films of resins present on the physical testing samples. The 30 min sorption levels are denoted by a vertical line.

this analysis exhibited ~90% reduction in rub fastness. This means that surface wear tests (e.g., Veslic rubs) are very sensitive to small amounts of DEET and suntan lotion, degrading long before total saturation is achieved. This conclusion is further supported by Figure 8, which shows the concentration profiles and total absorption of a "slow" penetrant into a thin film physical testing sample that failed Veslic rub after 30 min of exposure to the penetrant. Specifically, it can be seen that total saturation takes about 10 h, and after 30 min there is only about 36% saturation. It is interesting to note, however, that the failure in Veslic rubs at this low total saturation level may be related to the low levels of penetrant that have actually reached the coating-leather interface, as indicated by the 30 min concentration profile.

#### CONCLUSIONS

The diffusion and thermodynamic behavior of leather finishing resins toward insect repellent and suntan lotion have

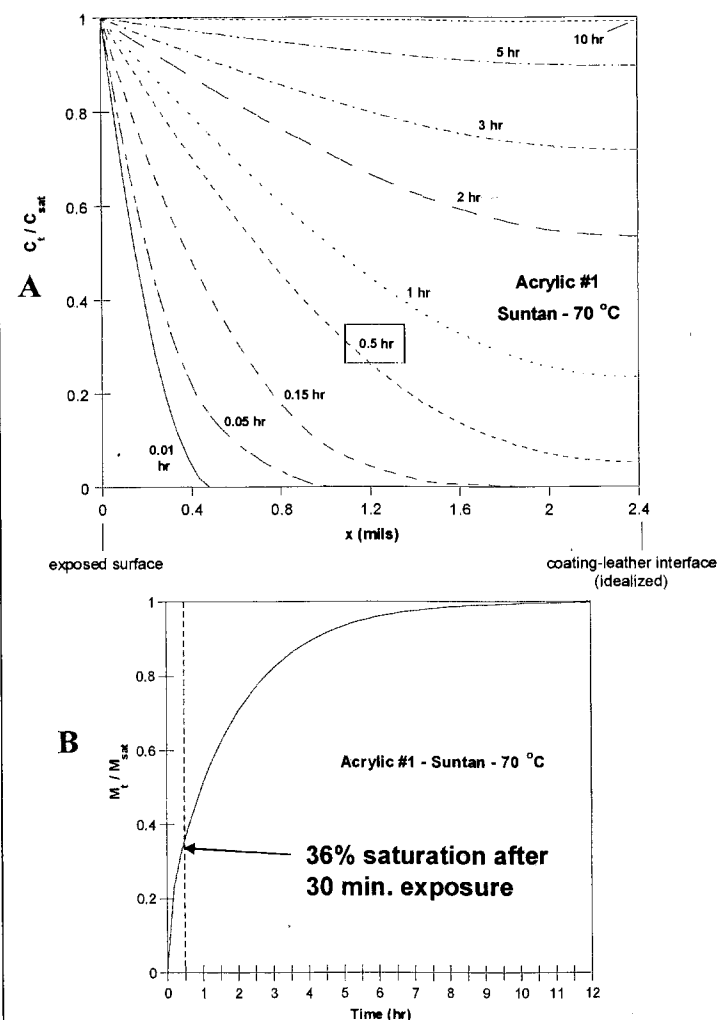


Figure 8. - Calculated sorption curves modeling a "slow" penetrant-resin system (Acrylic #1 exposed to suntan lotion at 70 °C). A) Calculated concentration profiles. B) Calculated sorption uptake curve. Note that the 30 min exposure data is specially denoted in both sub-figures.

been studied by physical testing (Veslic dry rub, visual color change after 30 min exposures) and free-film sorption methods. DEET exposure was found to reduce resin rub fastness by ~90% on both acrylics and urethanes, although no color change was observed. While even severe crosslinking imparted only a slight improvement in samples tested immediately after exposure to DEET, partial-to-complete recovery is possible by desorbing the DEET in air at elevated temperature. Suntan Lotion exposure resulted in somewhat less severe degradation in rub fastness, with crosslinking providing a major improvement (crosslinked urethanes exhibited almost no loss in rub fastness when exposed to suntan lotion for 30 min). However, unlike DEET exposure, recovery during a "desorption period" was marginal to negative and was also accompanied by severe yellowing at longer aging times due to continued degradation by non-volatile penetrants present in the suntan lotion. Based on these results, surface wear properties for DEET exposure are most improved by providing a desorption period prior to rubs, but for suntan lotion the most beneficial effect comes from crosslinking the resins.

Calculation of diffusion coefficients and saturation uptake levels from free-film sorption curves indicate that resin saturation levels at equilibrium are very high - between 1000 - 4000 % relative to initial weight and volume for DEET absorption, and ~200 % relative to initial weight and volume for suntan lotion. Calculated diffusion coefficients ranged from  $10^{-10}$  to  $10^{-7}$  cm<sup>2</sup>/s, with diffusion activation energies of 5-7 kcal/mol. It was also discovered that polycaprolactone/polyester-based urethanes with low  $T_g$  dissolve completely in DEET unless crosslinked, although polyether-based urethanes with higher  $T_g$  and all acrylics did not dissolve in this harsh penetrant. Crosslinking reduced the saturation uptake,  $M_{sat}$ , of DEET in acrylics and urethanes, but also enhanced diffusion,  $D_e$ , (especially in acrylics) by generating additional urea/urethane groups that can attract polar penetrants. The effect of resin crosslinking on the absorption of suntan lotion appears to be quite significant based on Veslic rub data, but additional free-film tests are required before an assessment can be made regarding its specific effects on  $D_e$  and  $M_{sat}$ . Interestingly, Deep Woods OFF® (25% DEET in an ethanol/hydrocarbon-based propellant) had identical saturation values as DEET, but with significantly higher diffusion rates. This indicates diffusion promotion by highly volatile propellant solvents that do not remain absorbed in the polymer. More fundamentally, both the diffusion and saturation parameters were found to vary with the glass transition temperature,  $T_g$ . Diffusion rates are lower for higher  $T_g$  polymers, whereas saturation levels are higher for higher  $T_g$  polymers.

Predictions of sorption levels in thin-films on leather sub-

strates were calculated using the free-film diffusion coefficients in order to investigate the actual absorption behavior of the samples used in physical testing experiments. These calculations reveal that surface wear properties degrade long before total saturation is achieved, so the ultimate thermodynamically-determined saturation level is only significant in so far as it affects the diffusion rate. Improvements in the resistance of leather finishing resins to insect repellent and suntan lotion should focus on slowing the diffusion rate of these penetrants into the resins, e.g., through the use of higher  $T_g$  resins, because even a small amount of absorption causes significant performance degradation.

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