# A Comparative Study of Branched and Linear Dialkyl Phthalate Plasticizer Surface Levels and Their Effects on Adhesive Bonds in Flexible PVC

D. A. ERNES, B. K. GARG, and R. C. WILLIAMS, *B. F. Goodrich Chemical Group, Avon Lake Technical Center, Avon Lake, Ohio 44012*

## Synopsis

A method has been developed to quantitatively measure the surface plasticizer levels present on test plaques made from a plasticized PVC compound. The plaque fabrication conditions have been chosen so that the plaque closely models an extruded flexible PVC profile. The analysis method utilizes sorption of the surface plasticizer on fumed silica, followed by methanol extraction and liquid chromatographic identification and quantitation of the plasticizer. Typical results are presented for a model compound plasticized with either di-2-ethylhexyl phthalate (DOP) or a mixture containing predominantly linear $C_7$, $C_9$, and $C_{11}$ dialkyl phthalates (DHNUP). The effect of compound work level, as measured by Banbury drop temperature and final processing temperature, has also been studied. These results show that, for the model compound studied, the average surface level of DHNUP is always greater than that of DOP. The DOP levels are essentially independent of compound work level. The DHNUP levels generally increase with increasing mold temperatures. Finally, this data has been correlated with a study of the lifetime of a Neoprene-based adhesive bond to DOP- and DHNUP-plasticized flexible PVC in a 100°C oven. These studies clearly show that a one-to-one substitution of DOP for DHNUP will increase the time to adhesive bond failure by a factor of at least 10 with this particular adhesive system and model compound.

## INTRODUCTION

The exudation of plasticizer on the surface of a polymer is a property of major importance to the entire plastics industry, but is particularly crucial in the area of flexible PVC compounds.[1] These materials are used in applications where they must be able to flex and bend without breaking, and, hence, they are usually highly plasticized. However, a large number of applications require that the flexible compound be adhesively bonded to a substrate. In this case, a large amount of plasticizer is a definite disadvantage. If a significant amount of plasticizer exudes to the surface either during processing or later, it can render the part unsuitable for some applications. When the plasticizer content is very high (greater than 40% of the finished compound) even a normally nonexuding plasticizer may cause a problem.

The historical solution to this problem has been to attempt to minimize exudation by appropriate compounding. However, this approach is still essentially empirical. Moreover, the success or failure of a particular recipe may not be known immediately. It may take months or years in the field, to learn whether an unacceptably high loss of adhesion occurs as the product ages. Accelerated aging studies can reduce this time substantially, but even here the times may be too long to allow complete evaluation before deciding to manufacture a product. In short, testing a potential product for loss of adhesion can be ex-
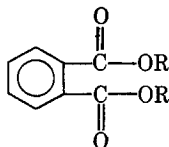
TABLE I
Model Formulation Recipe

| | |
|---|---|
| PVC (Geon 30) | 100 |
| Plasticizer | 60 |
| Secondary plasticizer (epoxidized soya oil) | 5 |
| Stabilizer (barium–cadmium–zinc soap) | 3 |

ceedingly time-consuming, but failure to do so can be very expensive. An alternate approach would be to quantitatively measure the surface level of the plasticizer in a given formulation; this information, combined with a knowledge of the general effects of that plasticizer on adhesion, should allow a compounder to rapidly determine the reliability of a given recipe, and to predict the suitability of a given plasticizer in that recipe. Unfortunately, the existing methods for estimating plasticizer content at a surface are qualitative at best.[1] These range from visual (and hence subjective) evaluation of weathered and heat-aged samples to the visual estimation of exudation when flexible PVC is bent sharply in a loop and aged. A somewhat more quantitative test measures the loss in weight (through migration of plasticizer) of a PVC disk buried in either silica or activated charcoal, which is then heat-aged for several days. None of these tests quantitatively measure surface plasticizer content immediately after molding and/or extrusion. The silica test offers some degree of quantification, but it is questionable how closely PVC buried in heated silica actually models plasticizer level at an adhesive interface. Moreover, several formulations have apparently passed these tests yet failed in actual use.

The purpose of this work was then threefold:

1. to develop a more quantitative method for measuring plasticizer level on the surface of a flexible PVC compound;

2. to use this technique to study several model PVC compounds to determine the effect of work history on surface plasticizer level;

3. to correlate observed adhesive bond lifetimes with measured surface plasticizer levels.

TABLE II
Physical Properties of DOP and DHNUP



| DOP | DHNUP |
|---|---|
| | R = mixed $C_7$, $C_9$, $C_{11}$ predominantly linear alkyl (<30% 2-methyl branched) |

| DOP | | DHNUP |
|---|---|---|
| 390 | Mol wt | 414 (avg) |
| −47 | Pour point (°C) | −50 |
| 236 | Boiling point at 10 mm Hg | 252 |
| 1.2 | Vapor pressure at 200°C | 0.4 |
| 348 | Viscosity at 0°C | 183 |

TABLE III
Work Level Study Samples

| Plasticizer | Banbury drop temp (°C) | Mold temp (°C) |
|---|---|---|
| DOP | 168 | Milled only |
| | | 149 |
| | | 174 |
| | | 191 |
| | 177 | Milled only |
| | | 149 |
| | | 174 |
| | | 191 |
| | 188 | Milled only |
| | | 149 |
| | | 174 |
| | | 191 |
| DHNUP | 168 | Milled only |
| | | 149 |
| | | 174 |
| | | 191 |
| | 182 | Milled only |
| | | 149 |
| | | 174 |
| | | 191 |
| | 188 | Milled only |
| | | 149 |
| | | 174 |
| | | 191 |

# EXPERIMENTAL

## The Model Compound and Work History Studies

The primary recipe chosen for this study is shown in Table I. Two model plasticizers were chosen for this study. The first of these was di-2-ethylhexyl phthalate (DOP), a commonly used plasticizer which has been in service for roughly forty years. The second was a commercial mixture of predominantly linear $C_7$, $C_9$, and $C_{11}$ dialkyl phthalates (DHNUP, for diheptyl, nonyl, undecyl phthalate), which has been in use since the early 1970s. Proton and C-13 NMR analysis performed in this laboratory on a typical lot of this material found approximately 30% branched aliphatics. The most usually occurring branch consists of a methyl group attached beta to the ester linkage; this group accounts for better than two-thirds of all the observed branching. These two plasticizers were chosen for the initial study because both of them are commonly used and because we were specifically interested in the effects of $n$-alkyl and 2-ethylhexyl substituents in promoting and/or retarding the presence of plasticizer on the surface. Some significant physical properties of the two materials are shown in Table II.[2]

In an attempt to avoid the variables introduced by extrusion, yet find a model which could be applied to the extrusion process, pressed plaques were chosen. Such plaques are known to have physical properties comparable to those observed for extruded samples; moreover, the temperature control and reproducibility

attained for pressed plaques are excellent (and far better than those commonly obtained in extrusion).   In addition, pressed plaques offer the advantage that they can be prepared more easily than extruded samples because there is less fine-tuning involved.   Lastly, plaques can be prepared more quickly and involve less manpower than extruded samples.   Implicit in this approach is the assumption that variations in the surface plasticizer levels of the model compound plaques will be comparable to those of extrudates.   This assumption seems reasonable, given the known similarity of other physical properties in plaques and extrudates; however, the assumption has not been verified experimentally.

Each formulation was compounded, milled for 15 min at 149°C and pressed for 5 min at 174°C.   The pressed squares, $15.2 \times 15.2 \times 0.24$ cm ($6 \times 6 \times \frac{3}{32}$ in.) were aged for various periods of time in a 100°C oven.   Separate samples of each formulation were removed for analysis of surface plasticizer after the milling, pressing, and various (1, 3, 6, 13, and 25 days) aging stages.   Most flexible PVC formulations use a low level of epoxidized soya oil (ESO) as a secondary plasticizer, in addition to the primary plasticizer, as shown in Table I.   Because it was not clear what effect (if any) ESO would have on either the primary plasticizer or on the analysis itself, additional samples containing DOP and DHNUP were prepared without any ESO.   Thus, a total of four sets of samples were prepared for the initial study.   This study was also used to test the analysis method.

In the subsequent experiment to measure the effect of work history, the processing conditions were varied.   The variables chosen to model work history were the Banbury drop temperature and the press temperature, as shown in Table III.   Samples of the model compound containing either DOP or DHNUP as the primary plasticizer were each divided into three batches.   Each of the three batches used a different Banbury drop temperature.   Each of these samples was roll-milled at 149°C, then further divided into three batches which were pressed at 149°C, 174°C, and 191°C, respectively.   Surface plasticizer analyses were performed on the milled materials and each of the pressed plaques (a total of 12 samples for each of the two model compounds).   All analyses were performed in duplicate.

### Analysis of Surface Plasticizer Levels

Two different methods were used to attempt to measure the surface plasticizer levels.   Both of these were chosen for their ease of use and their ready applicability in minimally equipped laboratories, in contrast to more complex methods of surface analysis, such as electron spectroscopy for chemical analysis (ESCA), secondary ion mass spectroscopy (SIMS), ion scattering spectroscopy (ISS), and Auger spectroscopy.   These latter techniques require expensive and complex instrumentation, along with elaborate sample preparation procedures.   Both of these constraints are major limitations, because many compounders have limited laboratories and because a large number of samples may need to be analyzed on a routine basis.   The first of the two analysis methods we attempted was that of attenuated total reflection (ATR) infrared spectroscopy.[3]   Although this method did yield some valuable qualitative data, quantitation of the surface plasticizer did not seem feasible.   This technique was discarded part way through
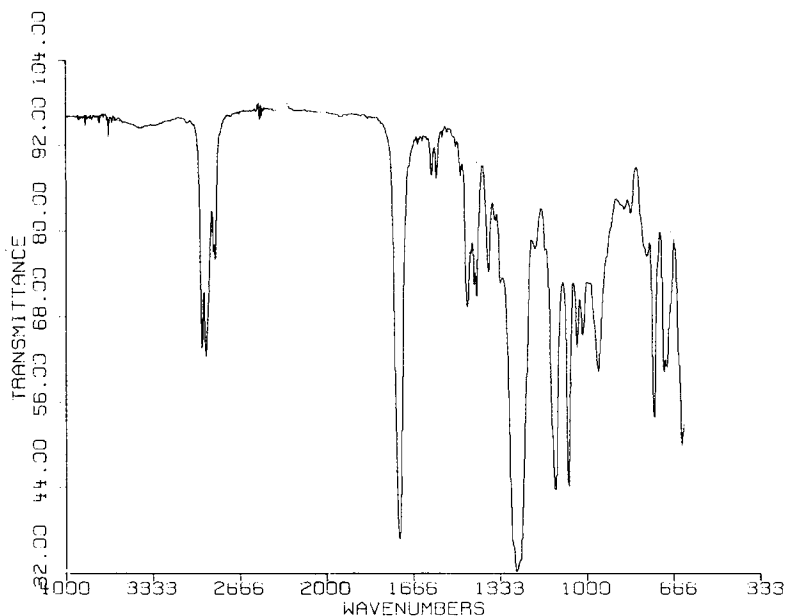
Fig. 1. DOP-plasticized sample, ATR-IR spectrum. Sample 1 (press-mold step)/ATR-ZnSe-45.

the study when it became apparent that the alternate method (described below) was far better suited to the quantitative application.

The second method utilized silica gel adsorption of surface plasticizer, followed by liquid chromatographic (LC) analysis of a silica gel–methanol extract. [This method differs from the disk test in that (1) the silica is in contact with the PVC for only a short period of time (usually 30 min) and (2) the silica and PVC are maintained at room temperature in this part of the analysis. Thus, the silica is used to measure the surface plasticizer level, but is not present under conditions where it will contribute to plasticizer migration to the surface.]

After molding, each plaque was allowed to stand for 1–3 days in order to condition it. A 7.7 × 15.2 cm (3 × 6 in.) strip of each sample was placed in a 227-mL (8-oz) jar, to which 2.50 ± 0.01 g of silica were added. After a cap was attached, each bottle was rolled to insure intimate contact and complete coverage of the surface with silica. [Geometries of the strip and jar were chosen so that the silica was rolled over both sides of the strip. Specific care was also taken to choose a jar with a radius of curvature sufficiently large (2.5 cm) that stress-induced exudation would be insignificant.] After 30 min of rolling, the silica was recovered and reweighed. A broad-bladed spatula was used to scrape any residual silica from both PVC surfaces, in order to insure maximum recovery of the silica. Recoveries ranged from 94.8% to 98.0%, and averaged 96.7%.

Each silica sample was then suspended in 10 mL of LC-grade methanol (Fisher), filtered, and injected. The chromatograph utilized contained a Waters Associates Model 6000A Pump and $\mu$-Bondapack C18 (3.9 × 30 cm) column equipped with a Model 440 Absorbance Detector. Injection was via a Valco loop injector. Data processing was done on a Waters Model 720 Data Module. Ini-
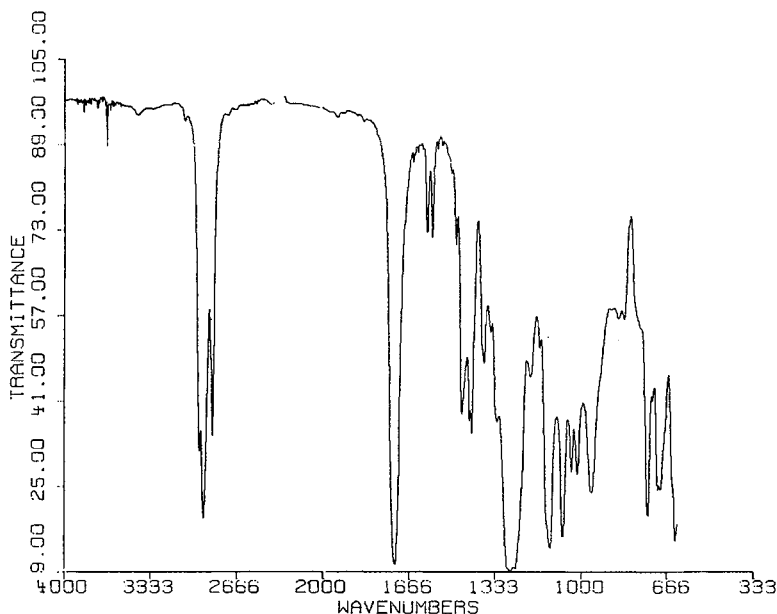
Fig. 2   DHNUP-plasticized sample, ATR-IR spectrum.   Sample 2 (press-mold step)/ATR-ZnSe-45.

tially, an LC profile was obtained for each plasticizer at a sensitivity of 10 ppm. Both plasticizers used in this study could be detected at this level; however, the sensitivity for DHNUP, which is a complex mixture, was less than for DOP, which yields a single LC peak.   Possible partial desorption and/or other interferences from the silica were checked two ways.   10, 20, and 50 ppm spiked solutions of plasticizer in methanol were added to silica, shaken, and analyzed for plasticizer by LC.   Recoveries were in the range 93–104%, which was suitable for this analysis.   Variations were on the order of 1% for the single component plasticizer and ranged from 1% to 5% for the complex mixture.   Calibration curves were established after preliminary analysis of two samples (to determine the appropriate concentration ranges) and were linear over the ranges employed.   In the case of DHNUP, the first peak in the series ($t_R$ = 3.15 min) was used, since it was more symmetrical and better resolved from DOP, in the event of cross contamination.

## Adhesive Bond Lifetime Study

   Two flexible compounds shown in Table I using either DOP or DHNUP as the primary plasticizer were prepared using compounding techniques listed above.   15.2 × 15.2 × 0.64 cm (6 × 6 × 0.25 in.) plaques were obtained by pressing milled sheets for 5 min at 174°C.   Next 7.6 × 2.5 × 0.64 cm (3 × 1 × 0.25 in.) strips were cut from these plaques.   Half of the total number of strips from each compound were washed with methanol for 5 min and subsequently suspended in air for drying.   All strips were conditioned at 22.2°C and 50% relative humidity for at least 48 h.

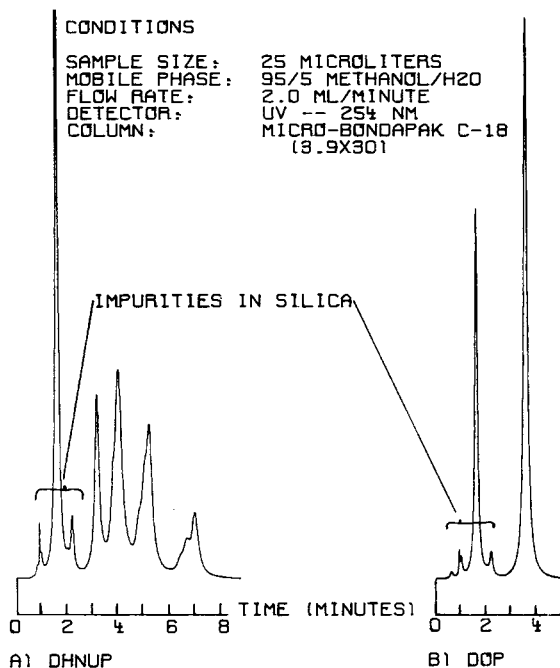   The procedure for preparing composites for testing adhesion was to place a

CONDITIONS

SAMPLE SIZE:      25 MICROLITERS
MOBILE PHASE:     95/5 METHANOL/H2O
FLOW RATE:        2.0 ML/MINUTE
DETECTOR:         UV -- 254 NM
COLUMN:           MICRO-BONDAPAK C-18
                  (3.9X30)

IMPURITIES IN SILICA

TIME (MINUTES)

0   2   4   6   8          0   2   4

A) DHNUP                      B) DOP

Fig. 3. Chromatograms of DHNUP and DOP recovered from silica (figures retraced). Conditions: sample size: 25 μL; mobile phase: 95/5 methanol/H₂O; flow rate: 2.0 mL/min; detector: UV, 254 nm; column: Micro-Bondapak C-18 (3.9 × 30).

strip on a flat metal surface, position a 2.54 × 1.27 cm (1 × 0.5 in.) piece of 4262 Neoprene double face contact adhesive tape (3M Co.) on this strip, and, then, place a second strip on the top of the adhesive tape. Finally, a 1.36 kg (3 lb) weight was placed on the composite for 1 min.

Twenty-seven samples each of four types of composites were prepared. Two sets of composites were prepared from DOP-plasticized PVC using unwashed. and methanol-washed strips. Another two sets of composites were prepared from DHNUP-plasticized PVC using unwashed and methanol-washed strips. All composites were suspended in a 100°C air oven from the short edge of one of the strips in every case. The weight of the other strip was sufficient to cause delamination of composites by creep over various exposure periods. Failure frequency data were collected.

## RESULTS

The ATR-IR spectra of the model compound using DOP and DHNUP as the primary plasticizer are shown, respectively in Figures 1 and 2. These spectra are typical of all the spectra taken, and do confirm that appreciable levels of phthalate plasticizer are present at the surface. Their presence is clearly indicated by the ester bands at 1730, 1270, 1120, and 1080 cm⁻¹ as well as the doublet at 1600 and 1580 cm⁻¹. DOP and DHNUP can be distinguished by the CH band patterns near 2900 cm⁻¹; DOP, in particular, gives a characteristic "double doublet" at 2940 and 2870 cm⁻¹. Spectra of the other samples were all quite

TABLE IV
Plasticizer on Surface of Model Compound

| Plasticizer | Heat history at 100°C (days) | Exudate ($\mu g/cm^2$) | | |
|---|---|---|---|---|
| | | With ESO | Without ESO | Average |
| DOP | Compounding | 6.66 | 16.28 | 11.47 |
| | Mold | 13.10 | 15.17 | 14.14 |
| | 1 | 11.86 | 14.26 | 13.06 |
| | 3 | 9.07 | 8.93 | 9.00 |
| | 6 | 11.70 | 10.82 | 11.26 |
| | 13 | 9.40 | 10.73 | 10.06 |
| | 23 | 9.72 | 8.69 | 9.20 |
| | Average | $10.22 \pm 2.16$ | $12.12 \pm 3.1$ | $11.17 \pm 1.9$ |
| DHNUP | Compounding | 19.74 | 26.80 | 23.27 |
| | Mold | 28.93 | 42.09 | 35.51 |
| | 1 | 23.38 | 29.84 | 26.61 |
| | 3 | 19.13 | 18.07 | 18.60 |
| | 6 | 28.35 | 25.12 | 26.74 |
| | 13 | 15.33 | 20.43 | 17.88 |
| | 23 | 25.90 | 15.64 | 20.77 |
| | Average | $22.97 \pm 5.1$ | $25.43 \pm 8.9$ | $24.20 \pm 6.1$ |

similar, respectively, to either Figure 1 or Figure 2, depending on whether the primary plasticizer was DOP or DHNUP. There were no appreciable differences between spectra of samples which did, and did not contain five parts of epoxidized soya oil as a secondary plasticizer. (Epoxidized soya oil is known to be a relatively weak infrared absorber.) Almost all of the spectra also contained a sharp band near 3670 $cm^{-1}$. This band is usually associated with a hindered phenolic material. Its presence suggests that butylated phenol antioxidant was present in one of the materials used, most probably in the stabilizer.

Typical chromatograms obtained for the samples (reconstructed using a Gaussian curve generator) are shown in Figure 3. Results, calculated as micrograms plasticizer per square centimeter of surface are reported in Table IV and are depicted graphically in Figure 4. Although there is substantial scatter in the data in terms of the level of plasticizer observed, the amount of DHNUP found on the surface was greater than DOP, without exception, for samples with equivalent histories. A statistical analysis of the data indicates that the differences observed are indeed real. The standard errors of the difference of the means (SEDM)[4] of DOP and DHNUP data are 6.09, 3.74, and 5.40, respectively, for trials with ESO, without ESO, and their combined average. A value greater than 2.68 is considered statistically significant ($\alpha = 0.01$, $n = 12$, one-sided). Statistical analysis also suggests that the presence or absence of epoxidized soy oil has little or no effect on the primary plasticizer found on the surface. SEDM's of 1.33 and 0.64, respectively, were calculated for DOP and DHNUP data. Variations smaller than 3.06 are not considered statistically significant ($\alpha = 0.01$, $n = 12$, two-sided). When the results with and without ESO are combined, these results, plotted in Figure 5, clearly show that more than twice as much DHNUP was found on the surface as was DOP. The observed distribution of components in the chromatogram for DHNUP in these analyses was approximately the same as that seen for the virgin material. This indicates that selective fractionation of the mixture has little or no effect on the DHNUP in this system. Some cross
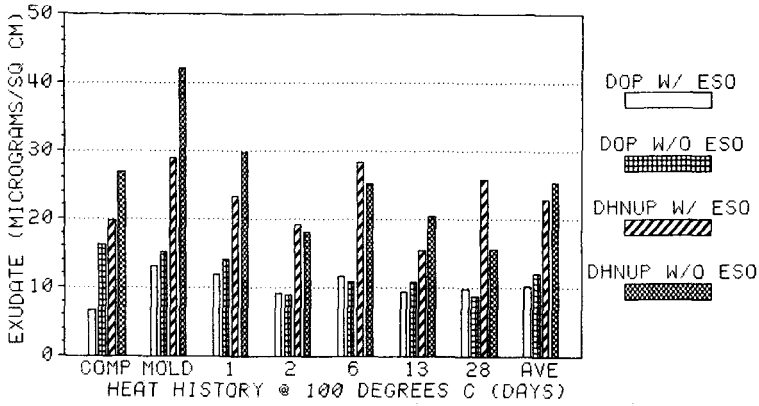
Fig. 4. Plasticizer exudate on Geon 30.

contamination (DOP in DHNUP samples and vice-versa) was noted in several samples. For the few cases observed, contamination was on the order of 2.6–3.5 $\mu g/cm^2$ for both DOP and DHNUP. This contamination is attributed to volatilization/recondensation of surface plasticizer in the 100°C oven. The equivalence of these levels suggests that both materials have approximately the same volatility at 100°C.

The analysis procedure used for the work level study differed from that used in the initial study, in the mesh size of the silica used. Initial studies used 30–60-$\mu m$ silica, while the later study used 200–400 mesh (74–37 $\mu m$). The effect of this change (necessitated because the older 30–60-$\mu m$ material was no longer available) was to increase the average particle size. This, in turn, caused a reduction in the average surface area, which effected the measured level of plasticizer recovered. The magnitude of this effect was found to be comparable for both plasticizers; thus a comparison of the DOP and DHNUP results is still valid.
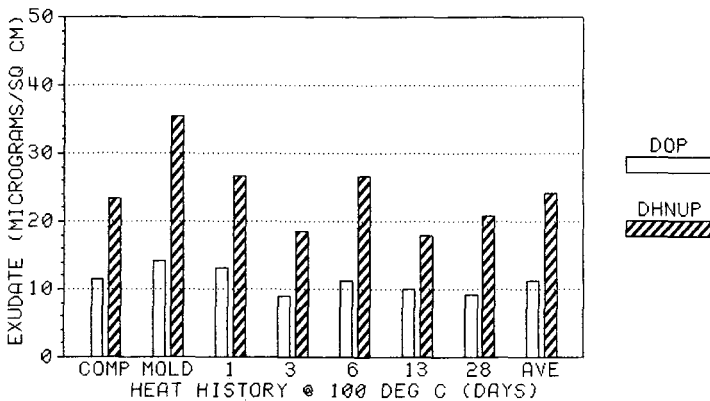


Fig. 5. Surface plasticizer on PVC (average values on flexible PVC compound).

TABLE V
Effect of Work Level

| Plasticizer | Banbury drop temp (°C) | Mold temp (°C) | Average surface plasticizer ($\mu g/cm^2$) |
|---|---|---|---|
| DOP | 168 | Unpressed | 5.41 |
| | | 149 | 6.28 |
| | | 174 | 7.03 |
| | | 191 | 5.30 |
| | 177 | Unpressed | 7.90 |
| | | 149 | 5.31 |
| | | 174 | 5.66 |
| | | 191 | 5.66 |
| | 188 | Unpressed | 5.34 |
| | | 149 | 5.50 |
| | | 174 | 5.53 |
| | | 191 | 5.09 |
| DHNUP | 168 | Unpressed | 8.65 |
| | | 149 | 8.18 |
| | | 174 | 8.16 |
| | | 191 | 10.70 |
| | 182 | Unpressed | 7.95 |
| | | 149 | 6.20 |
| | | 174 | 8.63 |
| | | 191 | 10.40 |
| | 188 | Unpressed | 6.87 |
| | | 149 | 5.69 |
| | | 174 | 9.07 |
| | | 191 | 10.11 |

However, care must be exercised when comparing the absolute numbers in this work level study with those of the initial study, because the silica surface area (and, hence, amount of plasticizer recovered) in the work level study is approximately half the amount in the initial study.

The work study level results are summarized in tabular form in Table V and in graphical form in Figures 6–8. Figure 6 shows all the data in Table V. A comparison between corresponding bars in several groups (i.e., first bar in group 1, first bar in group 2, etc.) will show the effect of Banbury drop temperature, if any, while a comparison of bars within a given group (i.e., the four adjacent bars in, say, group 6) shows the effect of molding temperature. These effects· are more easily seen in Figures 7 and 8, which are subsets of Figure 6. It is clear from Figure 6, that in general, the Banbury drop temperature does not have a significant effect. The surface plasticizer level observed for the DOP-plasticized material is essentially independent of both Banbury drop temperature and pressing temperature, over the temperature ranges used in this study. The results obtained for the DHNUP-plasticized compound are more complex. When all four plaque types are taken together, there is no clear trend. When they are examined individually, it is clear that the level of surface plasticizer is essentially independent of Banbury drop temperature, for the 174°C and 191°C plaques. There may be a small decrease of surface plasticizer level with increasing drop temperature for the plaques which were milled only and/or pressed at 149°C. When the results for the DOP-plasticized plaques are compared with those from
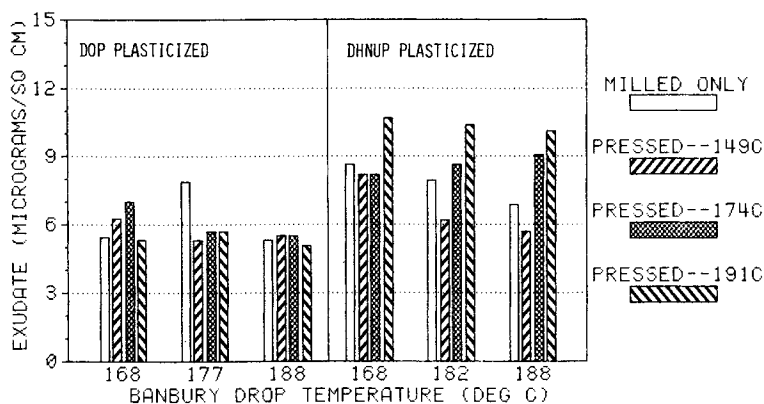
Fig. 6. Exudation study comparison (work level and pressing temperature).

the DHNUP-plasticized plaques, the differences for the milled only and 149°C plaques are not statistically significant (SEDM's of 1.8 and 1.4, respectively). The scatter of the data make it difficult to observe small differences. The absence of statistical significance does not preclude the presence of small, real differences which might become evident when the uncertainty in the measured values is reduced further. For the 174°C and 191°C plaques, the differences in the mean levels of DOP and DHNUP are statistically significant to greater than a 99% confidence limit (SEDM's of 5.6 and 6.1, respectively, vs. a significance criterion of 2.76, one-sided, $n = 10$). These results confirm what is obvious in Figure 8.

For the adhesion study, Table VI and Figure 9 show the failure frequency for DOP- and DHNUP-plasticized model compounds. No additional failures were recorded after 87 days, and testing was suspended after 200 days, at which time the remaining samples were judged to have degraded to the extent that they would no longer be useful in an actual application.

## DISCUSSION

The data in Tables IV and V and Figures 4–8 clearly show that roughly twice as much DHNUP is present on the surface as is DOP, under equivalent conditions. The data also show that the greatest amount of exudation occurred during the pressing step. This, in turn, suggests that under the conditions employed for the initial study, the levels of exudate measured at later times were probably generated during the pressing step. This method could be used to measure plasticizer migration by exposing a fresh surface *after* the press-mold step and measuring accumulation of plasticizer on this surface; in theory, this should ensure a zero (or at least small) surface plasticizer level at time zero. However, since the surfaces of molded parts are not normally swabbed or cleaned, and since methanol swabbing did not materially effect the adhesion study results, these results should accurately reflect actual plasticizer levels seen on molded flexible PVC surfaces, and the implications here are important. Given that roughly twice
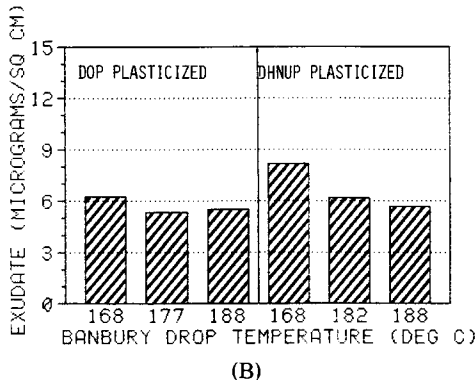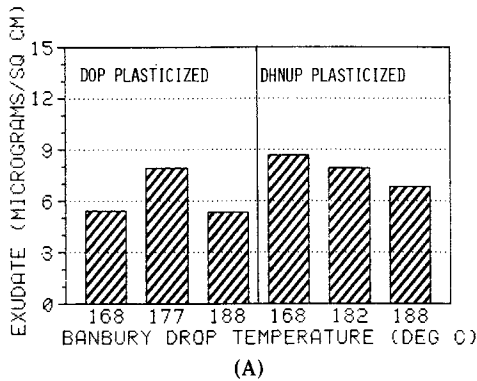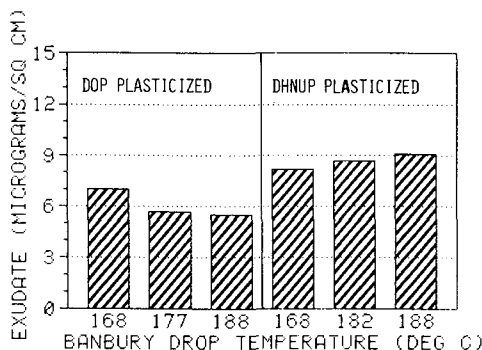
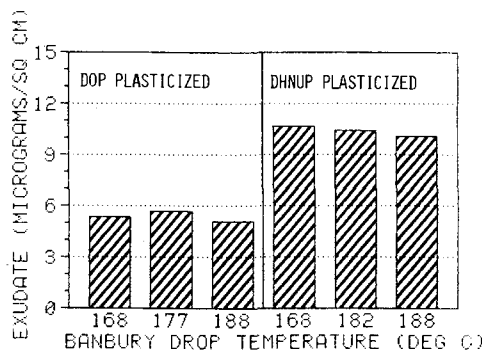Fig. 7. Exudation comparison study (work level and press temperature). (A) Unpressed; (B) pressed at 149°C.

as much DHNUP appeared on a molded surface as did DOP in the initial study, it appears likely that materials made with DHNUP will be more likely to suffer any problems due to the presence of surface plasticizer than will those made from DOP.

In the work level study, the scatter of the data preclude observation of minor effects. However, the trends and conclusions of the initial study are definitely confirmed by the work level results. The absence of a general effect from the variation of Banbury drop temperature is surprising. One possibility is that there is an effect, but it is too small to observe with the present experimental procedure. Additional studies are underway which should improve the experimental procedure and reduce the scatter of the data. A second possibility is that the work level effect is "rezeroed" during the milling procedure—all of these samples were milled at 149°C. If this is the case, then one might expect to see an effect if the samples were milled at their Banbury drop temperatures. Such a procedure, however, would be contrary to standard manufacturing practices. The third, and perhaps most likely, possibility is that the surface plasticizer levels are strongly affected by final processing conditions. The DHNUP data, in particular, suggest that the molding temperature is the dominant mechanism controlling surface plasticizer level for press temperatures of 174°C or greater.

In the adhesion failure study, it is apparent that DHNUP-plasticized materials

Fig. 8. Exudation comparison study (work level and press temperature). (A) Pressed at 174°C; (B) pressed at 191°C.

fail in an average of 18 days of exposure to a 100°C air oven. Methanol washing has had only a minimal effect on reducing the failure rate of DHNUP-based composites. By contrast, the composites obtained from DOP-plasticized PVC did not fail in significant numbers after 200 days of exposure. This shows that DHNUP is at least 10 times more destructive to the Neoprene-based adhesive than is DOP when they are used as primary plasticizers in this model flexible compound. Given the differences in the observed surface plasticizer level, the differences in adhesive bond lifetime are not surprising. However, the magnitude of the difference in surface plasticizer level is surprising, given the similarity of the two materials. If one were to make a guess based strictly on molecular weight, then more DOP would be expected to diffuse to the surface than DHNUP, based on the fact that DOP has a lower molecular weight than the (average) DHNUP value. The only apparent difference in the materials is the considerable steric bulk of the 2-ethylhexyl moiety. These results suggest that the 2-ethylhexyl unit makes a much better steric "hook" which becomes entangled in the PVC matrix and immobilizes the phthalate. Although some of the DHNUP is branched, most of the branching is methyl branching. Since there was no apparent fractionation of the DHNUP, it appears that ethyl (or higher) branching is necessary to effectively reduce the exudation of plasticizer to the surface of this model compound. Conversely, this implies that DOP in high concentration

TABLE VI
Number of Composites Remaining Intact after Various Exposure Periods in a 100°C Oven

| Days at 100°C | DHNUP | | DOP | |
|---|---|---|---|---|
| | Unwashed | MeOH-washed | Unwashed | MeOH-washed |
| 0 | 27 | 27 | 27 | 27 |
| 1 | 25 | | | |
| 13 | 23 | | | |
| 15 | 22 | | | |
| 17 | 16 | 20 | | |
| 18 | 11 | 17 | | |
| 19 | 5 | 8 | 26 | |
| 20 | 4 | 7 | | |
| 21 | | 6 | 24 | |
| 22 | 3 | 4 | | |
| 23 | | 3 | | |
| 24 | 2 | 1 | 23 | |
| 25 | 1 | 0 | | |
| 26 | 0 | | 22 | |
| 42 | | | | 26 |
| 54 | | | 21 | 23 |
| 56 | | | | 22 |
| 62 | | | | 18 |
| 87 | | | | 17 |
| 200 | 0 | 0 | 21 | 17 |

is effectively more compatible with PVC in this model compound than is DHNUP. It is also important to note that the time correlation between the heat-aging adhesion test and "real world" conditions has not been established. It may be that even the shortest failure times correspond to times well in excess of the normal expected product lifetime.

## CONCLUSIONS

An LC-based method has been developed to measure surface plasticizer levels on a flexible PVC compound. For the single model compound used and the
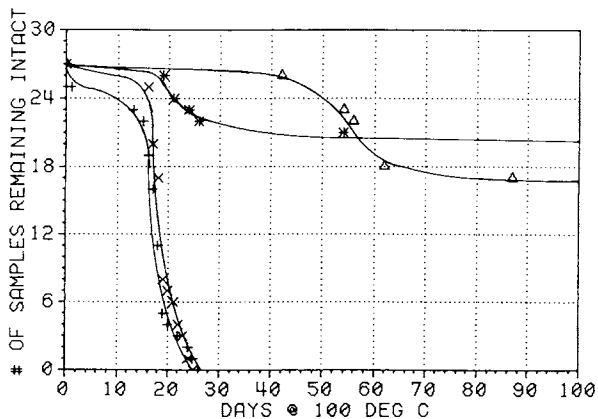


Fig. 9. Effect of oven aging on adhesion (flexible PVC compound). (+) DHNUP/unwashed; (×) DHNUP/washed; (*) DOP/unwashed; (△) DOP/washed.

limited thermal conditions studied, DOP appears to be more compatible than DHNUP in the flexible PVC matrix. Direct measurements show that a one-to-one substitution of DOP for DHNUP leads to a substantially enhanced adhesive bond lifetime, at least with the particular Neoprene-based adhesive and model formulation used in this study. The effect of work level (as modeled by Banbury drop temperature) was not significant, but increasing mold temperature catastrophically increased the surface concentration of DHNUP, but not of DOP. Additional studies with other compound recipes and different adhesive systems would be necessary to determine whether the trends observed are general or unique to the specific system chosen. However, for those applications where adhesive attachment of flexible PVC to a substrate is necessary, this study shows that, in some systems, better performance will be achieved with DOP than with DHNUP as the primary plasticizer.

## CAVEAT

Recognize that the effects of relationships between materials in this work are based on a limited study consisting of one PVC compound, two plasticizers, one adhesive system, and a limited range of thermal conditions. Specific testing programs are required for application to other PVC compounds, plasticizers, or adhesive systems of interest.

## References

1. J. R. Darby and J. K. Sears, in *Encyclopedia of PVC*, L. I. Nass, Ed., Marcel Dekker, New York, 1976, Vol. 1, Chap. 10.

2. L. G. Krauskopf, in *Encyclopedia of PVC*, L. I. Nass, Ed., Marcel Dekker, New York, 1976, Vol. 1, Chap. 11, and manufacturer's data sheets.

3. N. J. Harrick, *Internal Reflection Spectroscopy*, Wiley-Interscience, New York, 1967.

4. J. E. Freund, *Modern Elementary Statistics*, 4th ed., Prentice-Hall, Englewood Cliffs, N.J., 1973, pp. 279–282.