

# Transport Phenomena into and out of Plasticized PVC Sheets: The Influence of Sample History

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## SYNOPSIS

Diffusional exchanges in plasticized PVC applications comprise a critical aspect of much of the published work, which has been intended to study plasticizer migration into simpler extractants, enabling the various parameters involved in migration to be studied in isolation. In this study the migration of dioctyl phthalate into petroleum oils is investigated with emphasis on prior sample history. Simultaneously, the penetration of the liquid environment into the sheets is monitored. Plasticized PVC samples were prepared containing different amounts of plasticizer. The samples are immersed in paraffin oil until the plasticizer concentration reaches a predetermined value. Afterwards the samples are immersed in white spirit and their migration behavior is compared with that of new samples containing this predetermined plasticizer content, i.e., excluding the prior desorption cycle. Under these experimental conditions the parameters studied include immersion time, immersion temperature, initial plasticizer content and specimen thickness. The results obtained, suggesting considerable restriction of the migration activity for the two-stages specimens, are discussed in terms of surface-depleted concentration profiles and structure rearrangement mechanisms.

## INTRODUCTION

In all applications plasticized poly(vinyl chloride) is in contact with some kind of surrounding medium. The plasticizer may stay in place, or (more usually) it may migrate to the surrounding medium.<sup>1-24</sup> The problem becomes very serious in packaging with plasticized PVC films foodstuffs and pharmaceuticals. These sensitive products are contaminated by the migrating plasticizer, resulting in bad taste and odor especially after storage for prolonged periods of time. Furthermore, because of loss of plasticizer, the polymer deteriorates in its mechanical properties.

The phenomenon becomes more complicated as a liquid environment in contact may migrate into the polymer sheet ("counterdiffusion").<sup>4,6-24</sup> In other words, a simultaneous diffusion of the liquid takes place into, and the previously dispersed plasticizer out of the PVC. The loss in plasticizer is directly

related to the liquid transfer,<sup>7,8,11,14,23</sup> but very often each transfer is studied separately because of the difficulty of the general problem. The plasticizer-liquid medium mixture gradually becomes a non-solvent and then separates as a second phase in the mass.<sup>4,18,19,21-24</sup> The latter phenomenon results also in alteration of the optical properties as the PVC sheets become opaque instead of normally quasi-transparent. On the other hand, such an interaction may result to an ever-thickening layer of mixed polymer and liquid medium, and this case belongs to the general class of diffusion processes with moving boundaries.<sup>25,26</sup>

The extent of migration of a plastics component depends on many variables, but particularly on the density of plastics, the concentration of the component in the plastics, the time of contact between plastics and liquid, the temperature in the system "plastics/liquid," and the physico-chemical properties of the components of the system "polymer/low-molecular plastics component/liquid." Of course, there are similar aspects affecting counterdiffusion. In our laboratory, migration phenomena

into liquid simulants have been studied for many years.<sup>2-5,18,19,21-24</sup> Interest is mainly directed on investigating the influence of the nature of the surrounding medium, immersion temperature, and plasticizer concentration on both migration and counterdiffusion activity up to equilibrium or quasiequilibrium conditions. Also, successful efforts have been made to prevent migration by UV-induced surface crosslinking.<sup>19,23,24</sup>

In this paper, sample history is considered, comprising a very critical aspect as it influences severely the total diffusion behavior.<sup>27-32</sup> It is evident, however, that the prior sorption and thermal history does not affect next sorption cycles in rubbery polymer systems due to their rapid response to changes in ambient conditions.<sup>28,29,32</sup> Previous efforts on history include the investigation of concentration profiles in two-stage plasticizer migration experiments to prove that extraction results in surface-depleted concentration profiles.<sup>16</sup> In both stages the liquid environment employed was *n*-heptane, which, however, readily diffuses into the PVC.<sup>14</sup> In our studies paraffin oil is used instead for the stage of the initial desorption ("first stage"). Paraffin oil comprises a high viscosity medium for which counterdiffusion effects are safely excluded, as experimentally proved in previous papers.<sup>22,23</sup> Therefore, through this choice the plastic sheets initially consist of two basic components (polymer plus plasticizer) instead of three (also liquid counterdiffused), simplifying the problem.

Based on the above considerations, plasticized PVC specimens are prepared, containing different amounts of plasticizer, and then immersed in paraffin oil. Maintenance in this liquid environment is continued until the plasticizer concentration drops to a predetermined value. Afterwards the samples, labeled as "treated samples," are tested against migration in various liquid media ("second stage") as usual. The results obtained are compared with the corresponding ones from new samples ("untreated samples") containing this predetermined plasticizer content, i.e., excluding the prior desorption cycle. In previous work,<sup>32</sup> paraffin oil was employed for prolonged immersion times, also during the second stage. Under these conditions the effect of immersion time on migration performance was examined for different initial plasticizer contents together with the influence of the immersion temperature. A considerable restriction of the migration activity for the two-stage specimens was found. In this paper, while keeping paraffin oil for the first stage to prohibit counterdiffusion, the penetrating white spirit is used for the second stage. The resulting counterdiffusion

process is carefully monitored, simultaneously with the migration process, and the results are compared, as above, for treated and untreated specimens. Furthermore, any conformity to the simple Fickian model has been also considered.

## EXPERIMENTAL

### Reagents

**Polymer.** Suspension PVC, commercial grade, EKO Co., Greece, with a *k* value (a molecular weight index for PVC polymers) equal to 70.

**Paraffin Oil (Also Referred to as White Oil)** (a hydrocarbons mixture in the range C<sub>14</sub>-C<sub>18</sub>, bp 335-440°C), medicinal grade.

**White Spirit.** Technical grade, Fluka AG.

**Diethyl Phthalate, Stabilizer System, Scintillation Solution and also All Reagents Used for the Synthesis of Labeled Diethyl Phthalate.** Proanalysis grade, Fluka AG.

### Synthesis of Labeled Diethyl Phthalate (DOP)

Labeled phthalic anhydride (5.2 g; 7-<sup>14</sup>C; 1 mCi) was transferred to a reaction flask equipped with stirrer, thermometer, N<sub>2</sub> inlet tube, separating funnel, and a side condenser. The reactor was then charged with 2-ethyl hexanol (211 g), phthalic anhydride (80 g), and concentrated sulfuric acid (1.5 mL). The 2-ethyl hexanol was in 50% excess over the theoretical while toluene was also added to the reaction mixture (25% v/v based on the amount of 2-ethyl hexanol). The mixture was heated under stirring in an oil bath for 2 h while the temperature was gradually raised to 170°C. During this period, a slow stream of N<sub>2</sub> was passed and toluene was periodically added to make up for that distilling. After 2 h at 170°C, the mixture was cooled and diluted with 1 L of ether. The ethereal solution was washed with 10% aqueous sodium carbonate solution, then with water, and finally evaporated. The diester obtained was further purified by vacuum distillation. Yield, 89% on phthalic anhydride in labeled DOP. Products with lower radioactivities were obtained by dilution with pure unlabeled DOP.

### Plasticization/Molding

Under our experimental conditions complete fusion of the primary PVC particles is ensured. This is because the preparation of our sheets consists of three distinct stages:

1. Dry blending of the PVC powder, at 80°C, with the calculated amounts of labeled plasticizer and Ba–Cd stabilizer: The concentration of the latter was kept at the level of 3 phr (weight parts of additive per 100 weight parts of polymer) while the plasticizer content was varied between 25 and 90 phr.
2. Melt mixing in an laboratory size internal mixer (Brabender Plasticorder of a 50 cc head): The dry blend was plasticized for 7 min at 170°C and 30 rpm.
3. Hot pressing: The homogenized material was hot pressed to form a sheet of about 1.0 or 0.5 mm thickness. From this sheet, specimens of 20 × 50 mm were cut.

The second stage was employed to avoid incomplete fusion and ensure good mixing. Therefore, the morphology of our sheets resembles, at least in terms of homogeneity, those prepared by extrusion, and this has been confirmed also by microscopy observations. On the other hand, the same exactly experimental conditions were always followed, e.g., cooling rate after hot pressing, to exclude interference with processing history effects.

### Immersion

Each of the specimens was immersed in 250 mL liquid contained in a glass-stoppered Erlenmeyer flask of 300 mL. All tests were made in duplicate and the flasks were kept in an oven fixed at 37 or 70°C ( $\pm 1^\circ\text{C}$ ).

### Radioactivity Measurements

The migrating plasticizer can be determined either as the amount leaving the polymer or the amount entering the liquid. A wide variety of experimental methods have been proposed in the literature, including weight loss,<sup>2,3</sup> chromatography,<sup>10-12,14,16</sup> spectroscopy,<sup>17</sup> and radioactivity.<sup>2-5,18,19,21-24</sup> The latter is applied in our studies as follows.

The radioactivity ( $R_t$ , counts per mL per min) of the liquid medium is directly correlated with the amount of the plasticizer migrated at immersion time  $t$ . Divided by the radioactivity of the plasticizer employed ( $R_0 = 1126.9$  counts per mg per min) and reduced per liter of the liquid environment, DOP concentration data (in mg/L or g/L) are provided.

The radioactivity of the liquid medium, at a given time after immersion, was measured by transferring 1.0 mL of the contents of the flasks to a glass measuring vial containing 10 mL of the scintillation so-

lution (5 g of PPO and 0.3 g dimethyl-POPOP in 1 L of toluene), shaking to ensure complete solution, and determination in a Packard 3003 liquid scintillation spectrophotometer over a period of 10 min. From each flask, two samples were taken; thus each quoted result represents the average of four measurements. Before sampling, the contents of the flasks were homogenized by swirling.

### Weight Loss Measurements

To monitor weight changes, the specimens were removed from the liquid environment, wiped gently with a tissue, and immediately weighed.

### History Plan

As mentioned, plasticized PVC specimens of different plasticizer content (60, 75, and 90 phr) were immersed first in paraffin oil. The samples were kept in the liquid environment until the plasticizer concentration dropped to the value of 40 or 25 phr. For the latter case, thinner specimens (of 0.5 mm thickness instead of 1 mm) were employed to reduce the immersion time required.

The immersion temperature for the first stage was kept at the levels of 37 or 70°C. Temperature is closely related with segmental relaxation so that at elevated temperatures one should expect negligible influence of the desorption history.

In the subsequent migration study (second stage), the samples so treated were immersed in white spirit, until quasiequilibrium conditions, at the same temperature as initially. Their migration and counterdiffusion performance was compared with that of new samples, containing from the beginning 40 or 25 phr of DOP, respectively.

## THEORETICAL

Transport processes fall into "Fickian" and "non-Fickian" categories. Depending on the relative rates of penetrant mobility and polymer segment relaxations, Case I (Fickian) and Case II are viewed as the two limiting types of transport processes.<sup>33,34</sup>

Usual assumptions for the treatment of diffusion behavior may not be applicable in solid/liquid plasticizer migration and counterdiffusion especially when these diffusional exchanges occur near the glass transition temperature of the polymer system. When great rates of plasticizer migration are initially encountered, so that nearly all the plasticizer contained is transferred into the surrounding liquid, the

glass transition temperature increases and deviation from Fickian kinetics is expected. On the other hand, no considerable plasticization effect should be expected from the liquid medium penetrated if separation of the latter in a second phase occurs.<sup>4</sup>

A great amount of research work has been oriented in establishing and solving the corresponding implications of the diffusion mathematics due to the complexity of the total behavior, but the general applicability of some of the models proposed remains limited. Nevertheless, simple migration models are often proposed, based on Fick's law with constant diffusion coefficients, simple boundary conditions, negligible relaxation effects, and constant polymer volume.<sup>35</sup> Thus, in agreement with previous studies on migration phenomena,<sup>10-12,14,16,18,19,21-24</sup> the following well-known Fickian approximation for short times is considered:

$$MS_t/MS_\infty = 2(Dt/\pi l^2)^{1/2} \quad (1)$$

where  $MS_t$  denotes the total amount diffused (of plasticizer migrated or liquid counterdiffused) at time  $t$ ,  $MS_\infty$  the corresponding quantity after infinite time, and  $D$  the diffusion coefficient. The PVC specimens are considered as plane sheets having a thickness  $2l$ .

A plot of  $MS_t/MS_\infty$  against  $2(t/\pi l^2)^{1/2}$  is initially linear and provides the diffusion coefficient for the early stages of the diffusion process. The exact derivation of eq. (1) together with a thorough discussion on all the assumptions required has been given elsewhere.<sup>18,19,21-24</sup>

## RESULTS AND DISCUSSION

### Counterdiffusion Observations

The first evidence for counterdiffusion effects, during the second stage, was based on macroscopic and microscopic observations. The immersed specimens, initially quasitransparent, became opaque as the white spirit diffused into the plastic and eventually was separated in a second phase, in agreement with previous studies.<sup>21-24</sup> This was observed from the early stages of the immersion runs. On the contrary, the high viscosity medium (paraffin oil), during the first stage, did not result in opacity because of very limited counterdiffusion activity as referred already.<sup>22,23</sup>

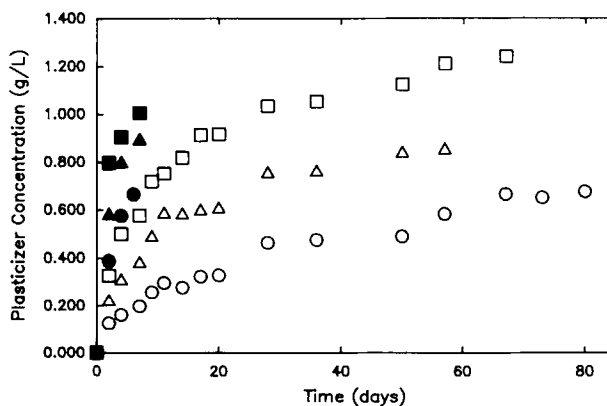
### Prior Desorption (First Stage) Experiments

In Figure 1, corresponding to the temperature levels of 37 and 70°C, curves of plasticizer concentration in paraffin oil versus immersion time are given as a function of the plasticizer content (60, 75, and 90 phr). The samples, of 1 mm thickness here, are immersed up to the point at which the plasticizer content remained in the specimen reaches the value of 40 phr. On the other hand, the same exactly cycle of pretreatment was employed for thinner specimens (of 0.5 mm thickness) at 70°C to effect a lower concluding plasticizer content (25 phr instead of 40 phr) (Fig. 2).

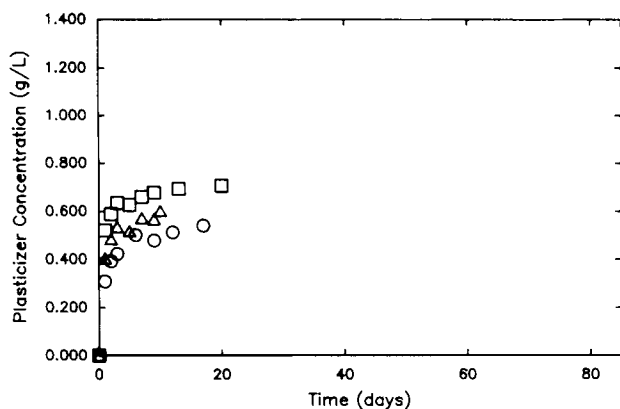
It can be concluded that, for the same plasticizer content, as temperature jumps from the one extreme to the other the migration rate effected increases very significantly (Fig. 1). Furthermore, at the same temperature level, migration increases with plasticizer content (Figs. 1 and 2) while, under the same experimental conditions, when thickness is reduced, migration is boosted (Fig. 1 vs. Fig. 2). It is also useful to mention that plasticizer concentration data based on radioactivity measurements do not deviate from those based on specimen weight loss, since counterdiffusion here is excluded.<sup>22,23</sup>

### Second Stage Migration Experiments ("Treated" versus "Untreated" Specimens)

It is simple arithmetic that the total amount  $M_t$  of plasticizer migrated from the immersed PVC sheet



**Figure 1** First stage (1 mm specimens, paraffin oil): Plots of plasticizer concentration versus immersion time, at 37 or 70°C, as a function of the plasticizer content. 37°C: (○) 60 phr; (△) 75 phr; (□) 90 phr. 70°C: (●) 60 phr; (▲) 75 phr; (■) 90 phr.



**Figure 2** First stage (0.5 mm specimens, paraffin oil): Plots of plasticizer concentration versus immersion time, at 70°C, as a function of the plasticizer content. (○) 60 phr; (△) 75 phr; (□) 90 phr.

at time  $t$  to the surrounding liquid can be calculated by the following equation:

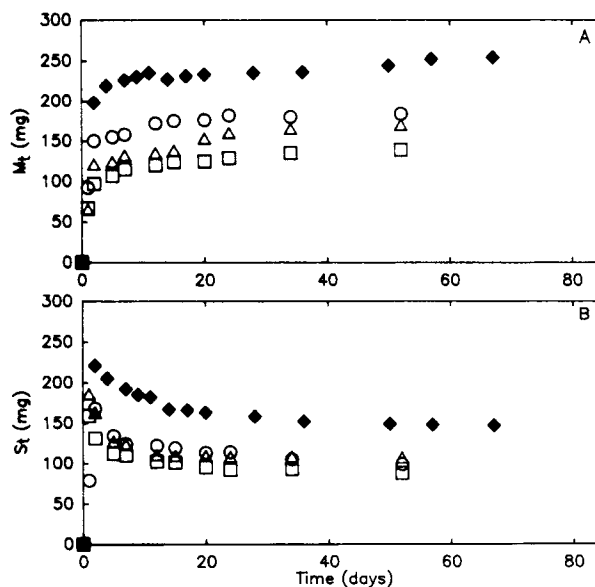
$$M_t = (W_0 - W_t) \quad (2)$$

where  $W_0$  and  $W_t$  represent the weight of the specimen at immersion time 0 and  $t$ , respectively. Of course, this equation is valid if counterdiffusion activity is excluded, otherwise is transformed to the following<sup>23</sup>:

$$S_t = (W_t - W_0) + M_t \quad (3)$$

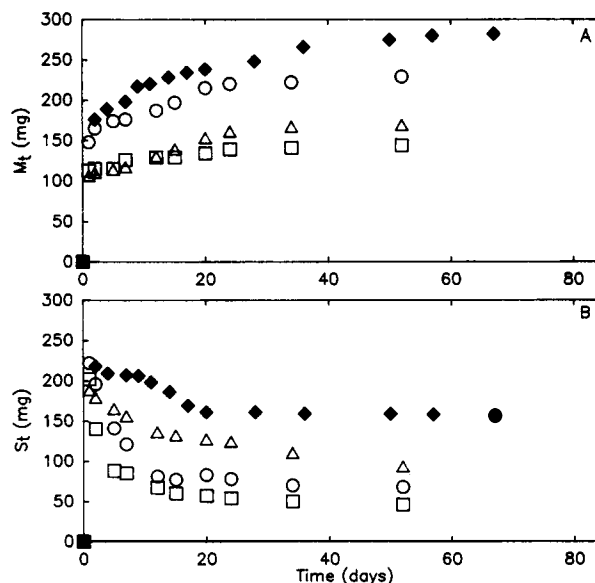
where  $S_t$  represents the total amount of the liquid medium penetrated into the PVC sheet at the same time  $t$ .

In Figures 3, 4, and 5, at the same temperature levels as in the first stage, curves of  $M_t$  versus  $t$  and  $S_t$  versus  $t$  are quoted. Considerable amounts of white spirit penetrate into the immersed specimens. On the other hand, independently of prior sample history, a counterdiffusion activity is encountered that is very similar to that referred in the literature for the system PVC/DOP/benzyl alcohol or ethanol-water<sup>10-12</sup> and also for the system PVC/DOP/petroleum oils<sup>22,23</sup>. The penetration curves are always characterized by a maximum appearing at the very initial stages of the total process. In other words, the amount of white spirit transferred into PVC increases at the beginning of the immersion, rises to a maximum value, and then decreases until equilibrium. Thus, the counterdiffusion process comprises a two-step phenomenon with a liquid transfer into and out of the PVC sheets. However, it has to be admitted that for the sorption stage, even at the lower immersion temperature (Fig. 3),

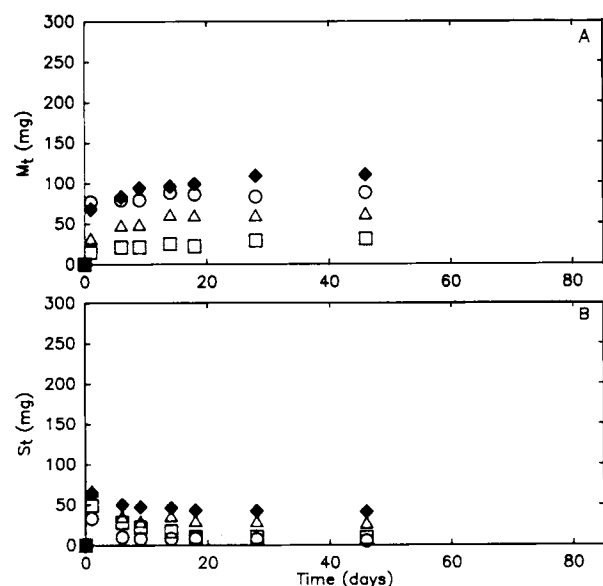


**Figure 3** Second stage (1 mm specimens, all 40 phr plasticizer content, white spirit): Plots of plasticizer loss (A) and penetrant uptake (B) versus immersion time, at 37°C, as a function of the initial plasticizer content (before the commencement of the first stage). (◆) 40 phr (untreated specimens); (○) 60 phr; (△) 75 phr; (□) 90 phr.

our data are not enough to show the maximum discussed. For this reason, uncertainty for its exact value also exists.



**Figure 4** Second stage (1 mm specimens, all 40 phr plasticizer content, white spirit): Plots of plasticizer loss (A) and penetrant uptake (B) versus immersion time, at 70°C, as a function of the initial plasticizer content (before the commencement of the first stage). (◆) 40 phr (untreated specimens); (○) 60 phr; (△) 75 phr; (□) 90 phr.



**Figure 5** Second stage (0.5 mm specimens, all 25 phr plasticizer content, white spirit): Plots of plasticizer loss (A) and penetrant uptake (B) versus immersion time, at 70°C, as a function of the initial plasticizer content (before the commencement of the first stage). (◆) 25 phr (untreated specimens); (○) 60 phr; (△) 75 phr; (□) 90 phr.

Since the appearance of a maximum in the curves  $S_t$  versus  $t$  substantially coincides when high migration rates are obtained, no considerable swelling of the specimens did happen. This also confirms the aforementioned correlation between the penetration ability of a liquid medium into plastics and the migration of low molecular weight components into this liquid.

Very interesting results are obtained when turning to prior desorption history aspects. Independently of immersion temperature or specimen thickness, the treated samples always appear less

susceptible to both migration [Figs. 3(A), 4(A), and 5(A)] and counterdiffusion [Figs. 3(B), 4(B), and 5(B)]. Furthermore, as the "initial plasticizer content" (60, 75, or 90 phr) increases, migration and counterdiffusion values are rather restricted to continuously decreasing levels. Alternatively, this picture is also evident from Table I in which ultimate values of plasticizer migrated and liquid counterdiffused, as a function of the "initial plasticizer content," are tabulated properly reduced.<sup>21-24</sup> From these data it is also shown the influence of reducing the thickness of the specimens at least at the temperature level of 70°C: Migration values increase while those of counterdiffusion are reduced.

### Kinetics Aspects

In agreement with previous studies<sup>10-12,14,16,18,19,21-24</sup> and taking into account the absence of swelling, i.e., good dimensional stability, the short-time approximation of the 1-dimensional, Fick's equation [eq. (1)] can be a good step for trying to fit the experimental data.

Based on the "first stage" data, in Table II the calculated short-time diffusion coefficients are reported for migration at 37°C (1 mm specimens) and 70°C (0.5 mm specimens). The corresponding curves of migration vs. time (Figs. 1 and 2) reveal establishment of equilibrium or quasiequilibrium conditions and, as expected, the values of the diffusion coefficient increase with plasticizer content. Nevertheless, for the thick specimens at 70°C (Fig. 1), no equilibrium is attained, prohibiting any quantitative treatment of the data collected.

We proceeded to the same analysis for the "second stage" data, but the results appear unreliable since the simple Fickian model assumes a uniform

**Table I** Second Stage: Ultimate Values of Plasticizer Migrated<sup>a</sup> and Liquid Counterdiffused<sup>b</sup> as a Function of the Initial Plasticizer Content (i.e. before the Commencement of the First Stage)

	Migration			Counterdiffusion		
	37	70	70	37	70	70
Immersion temperature (°C)	37	70	70	37	70	70
Nominal sheet thickness (mm)	1	1	0.5	1	1	0.5
Real initial plasticizer content (phr)	40	40	25	40	40	25
Initial plasticizer content (phr)						
(Untreated)	74.4	85.4	95.7	12.3	13.4	8.2
60	70.1	76.7	91.1	11.7	8.3	7.7
75	64.0	66.1	72.1	11.5	10.4	6.3
90	62.6	59.9	49.7	11.3	5.5	2.9

<sup>a</sup> All quoted values are expressed as weight percentage of the amount of plasticizer contained at the beginning of the second stage.

<sup>b</sup> All quoted values are expressed on initial (at the beginning of the second stage) weight percentage basis.<sup>22,23</sup>

**Table II First Stage: Correlation and Respective Diffusion Coefficient Data from the Relationship between  $M_t/M_\infty$  and  $t^{1/2}/l$  at 37°C (1 mm Specimens, Fig. 1) and 70°C (0.5 mm Specimens, Fig. 2) During the Initial Stages of the Diffusion Process**

Plasticizer Content (phr)	Immersion Temperature (°C)			
	37		70	
	$r^2$	$D$ (cm <sup>2</sup> /s)	$r^2$	$D$ (cm <sup>2</sup> /s)
60	0.98	$3.52 \times 10^{-10}$	0.99	$1.75 \times 10^{-9}$
75	0.99	$6.07 \times 10^{-10}$	0.98	$1.94 \times 10^{-9}$
90	0.99	$7.99 \times 10^{-10}$	0.97	$2.19 \times 10^{-9}$

concentration of plasticizer throughout the start of the process. At this point, a reference has to be made to a previous paper by Taverdet and Vergnaud,<sup>16</sup> already mentioned in the Introduction. In that study plasticized specimens, of a given plasticizer concentration (35.5% by weight), were soaked in *n*-heptane for a definite short time, at 30°C, and then were extracted and exposed in air to allow evaporation of the liquid previously absorbed by the PVC. The new plasticized PVC thus obtained provided data in complete agreement with the performance encountered now, i.e., low plasticizer transfers were obtained. Their interpretation was based on concentration profiles developed during the first stage extraction. The second stage extraction comprises a desorption process starting with nonuniform, surface-depleted concentration profile which developed during the first stage extraction. In other words, the "young" samples show faster migration because they have a higher plasticizer concentration near the surface than do the previously exposed samples.

Turning to the counterdiffusion process appearing to be a two-step phenomenon, i.e., consisting of a sorption step up to a point, followed by a desorption step, the same exact analysis was followed as previously.<sup>11,22,23</sup> Both steps were considered separately and the validity of eq. (1) was tested under the following assumptions: The maximum amount of liquid sorbed has been considered an equilibrium amount. On the other hand, for the desorption step, the same amount was supposed as initially contained in the sheet while the time of its appearance has been defined as starting time ( $t = 0$ ) of the desorption process. Of course, the possible error in determining exactly the position of the peak, i.e., the transition from sorption to desorption it should be emphasized again here.

For the sorption stage, even at 37°C, it is realized that no data exist to test conformity to the Fick's law [Figs. 3(B), 4(B), and 5(B)]. This is because, as referred above, the maximum value is attained early and in future work more emphasis at the very initial stages should be given. On the contrary, for the desorption step, acceptable conformity to eq. (1) was revealed [correlation coefficient ( $r^2$ ) in the range between 0.90 and 0.99], the best fitting obtained for the untreated samples. Nevertheless, a concentration-independent diffusivity remains a particularly questionable assumption.

#### Possible Interpretation: Desorption History versus Structure Rearrangement

According to the literature,<sup>36</sup> the concluding plasticizer level of 40 or even 25 phr at 37 and of course at 70°C corresponds to rubbery behavior for the system PVC/DOP. In other words, during the total course of the first stage, all specimens are maintained above the glass transition temperature, also in agreement with macroscopic observations. Therefore, as mentioned, no differentiation in the second stage should be expected because of this prior desorption history, due to rapid response of the polymer segment to changes at these temperature levels. The fact that there exists such differentiation could be faced as follows:

First it has to be emphasized that the interpretation given by Taverdet and Vergnaud<sup>16</sup> remains reasonable and readily fits the transport phenomena encountered in this study, especially those on migration. Nevertheless, as in Ref. 32, it is claimed another synergistic phenomenon based on the possibility of an alteration of the PVC structure during immersion. Commercial PVC comprises a semi-crystalline polymer and therefore the effect of the extended maintenance of the specimens at the temperature levels examined cannot be ignored (Figs. 1 and 2). A rearrangement of the material morphology to a more ordered and compact scheme is possible, for which the term "annealing" can be used. Such an assumption has been well supported already by plasticizer migration data reported previously.<sup>21-24</sup> In particular, as immersion temperature increases, *long-term* plasticizer migration values pass through a minimum. In other words, the extent of annealing increases, but at the highest temperature tested the effect of immersion temperature on plasticizer migration becomes more pronounced, so that the latter increases again.

Based on the above assumption, the differentiation in migration during the second stage could be

alternatively explained as follows: The specimens maintained for desorption during the first stage become eventually less permeable to both plasticizer and liquid environment, because of prior "annealing" effects. Furthermore, the more the initial plasticizer content, comprising a factor promoting the mobility of the system, closely related with structure transformation, the less the migration and counter-diffusion extent, exactly as the curves of the Figures 3-5 and also Table I suggest. Of course, during the second stage these annealing processes cannot also be excluded.

## CONCLUSION

Under our experimental conditions the prior desorption history results in considerable restriction of both migration and counterdiffusion activity. A rearrangement of the polymer structure during immersion, simply because of extended maintenance at elevated temperatures, is proposed for an interpretation of the total performance while underlining the fact of the nonuniform concentration profiles produced during the initial immersion cycle.

The author wishes to thank Mr. G. Petychakis for his contribution to the experimental part of this study.

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Received December 7, 1990

Accepted May 3, 1991