

# Washing Out Oligomeric Triazinic-Hindered Amine from Polypropylene

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**ABSTRACT:** Washing oligomeric and monomeric triazinic sterically hindered amines out of polypropylene (PP) using heptane, dodecane, a mixture of heptane and dodecane, and ethanol was studied at 20°C and 40°C. Stabilizers leaked from the polymer in heptane and dodecane but only slightly in ethanol. Also studied was washing out separate fractions of the oligomeric stabilizer in these solvents. The rate of loss depended on their molecular weight and on their concentration in the polymer. It was learned that the rate of washing out oligomeric stabilizer from PP could be predicted based on its fractions; some discrepancy was observed when most of the additive leaked. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2158–2165, 2000

**Key words:** stabilizers; sterically hindered amines; loss; polypropylene

## INTRODUCTION

The efficiency of polymer stabilization depends not only on the chemical structure of the stabilizers but also on physical factors, including its solubility and mobility, which affect chemical reactions with radicals generating degradation as well as additive loss from the polymer.<sup>1–6</sup> The increase in molecular weight of the stabilizers reduces their loss; but on the other hand it gives rise to a decrease in their solubility inside the polymer. Hindered amine stabilizers (HAS) are widely used for UV and long-term thermal stabilization of polyolefins. High-molecular-weight HAS are not volatile, and their diffusion in the polymer at elevated temperatures is very slow; therefore, washing out may be the only way to achieve their physical loss from the polymer in the case of applications where a contact with specific liquids is involved,

such as pipes or containers for the flow of liquids like water, oils, and foodstuffs.<sup>7–10</sup> The loss of additives in the contacting medium results in their transfer to the surroundings, with consequent pollution and decrease in the lifetime of the polymer. The washing out depends on various factors such as additive solubility inside the polymer and in the surroundings, the diffusion rate of additive in the polymer and in the surroundings, and polymer–solvent interactions.<sup>2,4,6,10</sup> At present little data exist on the loss of heavy HAS from polymers, despite their being the main product on stabilizer market.

Washing oligomeric and monomeric triazinic sterically hindered amines out of polypropylene (PP) using heptane, dodecane, a mixture of heptane and dodecane, and ethanol was studied

This work studied the washing out of oligomeric and monomeric triazinic sterically hindered amines from PP film, using the organic liquids heptane, dodecane, a mixture of the two, and ethanol.

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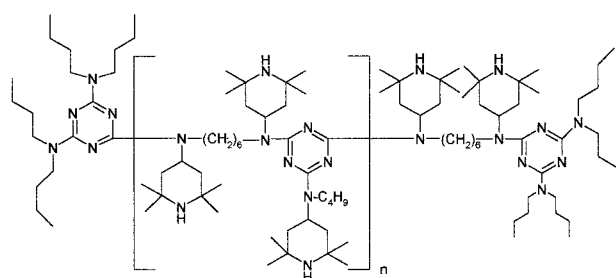
**Table I Characteristics of HAS-1**

| # Fraction | <i>n</i> | $M_{w\text{exp}}$ | $M_{w\text{teor}}$ | % wt |
|------------|----------|-------------------|--------------------|------|
| 1          | 0        |                   | 1352               | 6.4  |
| 2          | 2        | 2308              | 2716               | 35.7 |
| 3          | 4        | 3548              | 4080               | 26.2 |
| 4          | 6        | 5133              | 5444               | 15.3 |
| 5          | 8        | 6172              | 6808               | 8.3  |
| 5          | 10       | 7882              | 8172               | 4.1  |
| 6          | 12       | 9246              | 9536               | 3.4  |

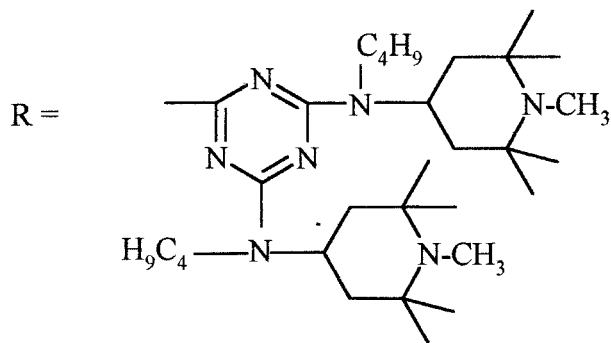
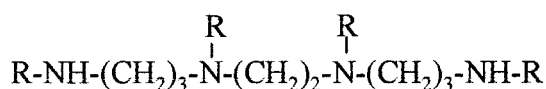
## EXPERIMENTAL

### Materials

Unstabilized PP powder was supplied by Moplen (FLF20 Montell). The following oligomeric stabilizer (HAS-1) and monomeric stabilizer (HAS-2) (MW 2286) were used. HAS-1 characteristics are given in Table I; for comparison, separate fractions of HAS-1, containing  $n = 0, 2, 4, 6,$  and  $8$  were also studied.



HAS-1



HAS-2

### Introduction of Stabilizers in PP

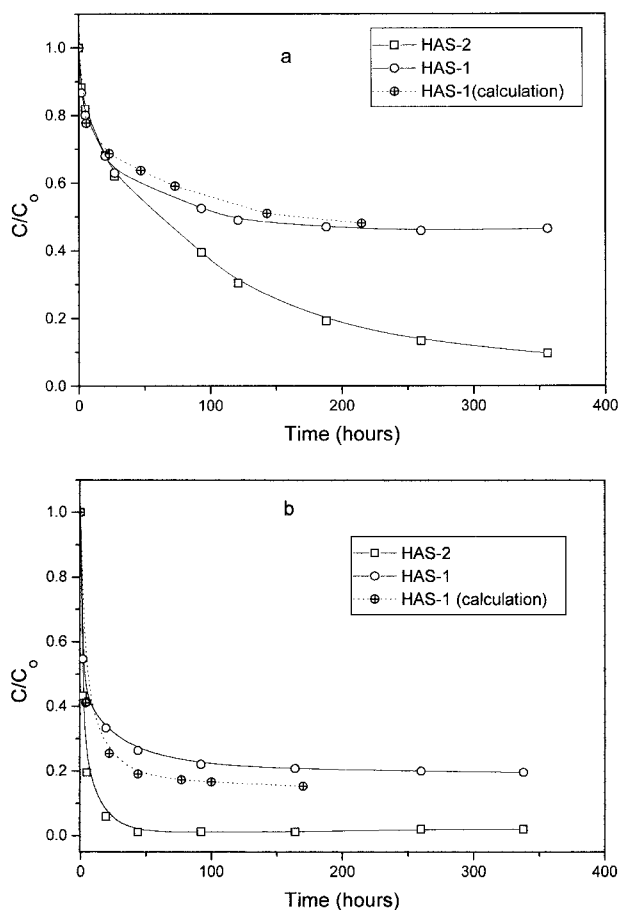
The stabilizers at concentrations of 0.25, 0.5, and 1.0 wt % were mixed with PP powder, followed by extrusion and film pressing (70 and 200  $\mu\text{m}$  thick) at 200°C

### Washing Out experiments

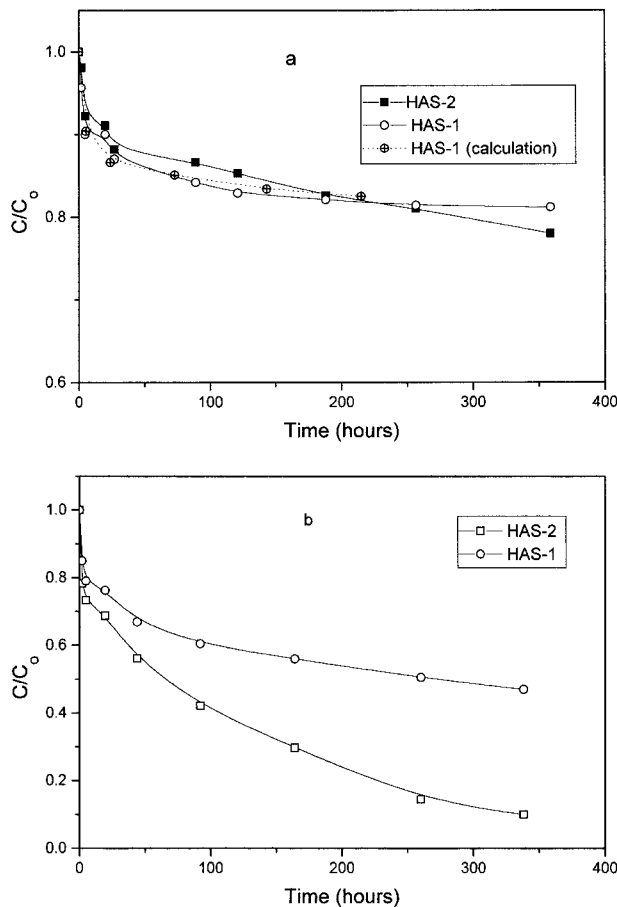
Films (1  $\times$  2 cm) containing additives were kept in solvent (10 mL) at 20°C and 40°C. The solvent was periodically (once every 2 days) replaced with a new one. The amount of additive released from the polymer was measured by UV spectroscopy directly from the film and the solution during the experiment.

## RESULTS AND DISCUSSION

Figure 1 shows the migration of HAS-1 and HAS-2 in heptane from PP film 70  $\mu\text{m}$  thick at

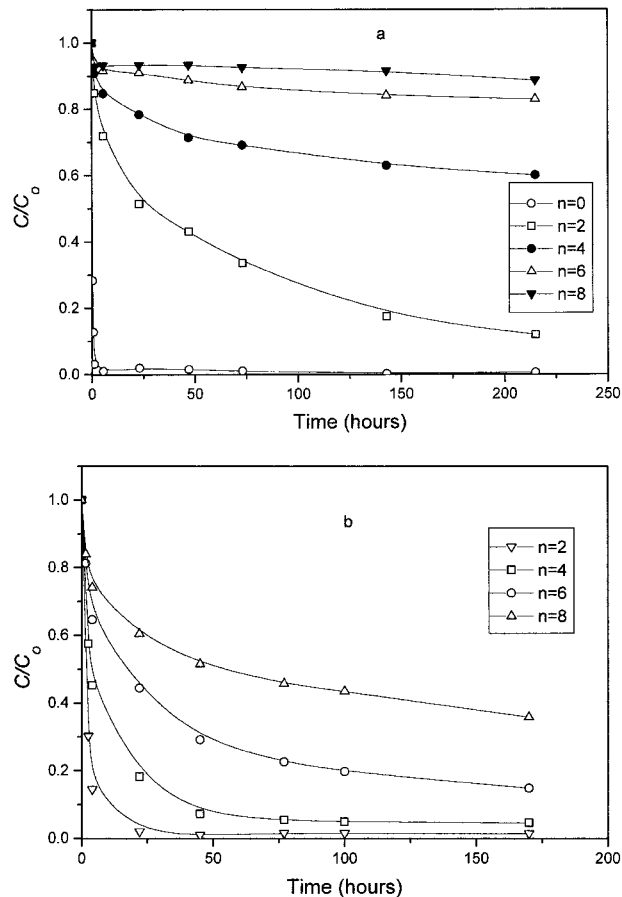


**Figure 1** Loss of HAS-1 and HAS-2 from PP (70  $\mu\text{m}$ ) in heptane at (a) 20°C and (b) at 40°C ; dotted line corresponds to HAS-1 (calculation). The initial concentration of the additives is 0.25 wt %.



**Figure 2** Loss of HAS-1 and HAS-2 from PP film (70  $\mu\text{m}$ ) in dodecane at (a) 20°C and (b) at 40°C; dotted line corresponds to HAS-1 (calculation). The initial concentration of the additives is 0.25 wt %.

20°C and 40°C. The following may be pointed out: (1) the loss of HAS-2 is higher than HAS-1; (2) the rate of release increases with temperature [Fig.



**Figure 3** Loss of the different fractions of HAS-1 from PP in heptane at (a) 20°C and (b) at 40°C; the initial concentration is 0.25 wt %, film thickness 70  $\mu\text{m}$ .

1(a) and (b)]; (3) HAS-1 does not release completely, and a residual concentration (about 0.12 wt % at 20°C and 0.05 wt % at 40°C) remains in the film for a long time. HAS-1 is an oligomeric

**Table II Migration of Stabilizers from PP in Heptane, Dodecane and Ethanol at 20°C (in Nominator) and at 40°C (in Dominator);  $C_o = 0.25\%$  wt, Film Thickness 70  $\mu\text{m}$ ; ( $C/C_o$  is the Part of the Stabilizer Remaining in PP)**

| Stabilizer | Solvent  | $C/C_o$ After |             |            |
|------------|----------|---------------|-------------|------------|
|            |          | 20 h          | 90 h        | 200 h      |
| HAS-2      | Heptane  | 0.68/0.06     | 0.39/0.012  | 0.19/0.012 |
| HAS-1      | Heptane  | 0.68/0.33     | 0.52/0.22   | 0.47/0.20  |
| HAS-2      | Dodecane | 0.91/0.69     | 0.88/0.42   | 0.82/0.20  |
| HAS-1      | Dodecane | 0.94/0.76     | 0.90/0.60   | 0.86/0.54  |
| HAS-2      | Ethanol  | 0.997/0.997   | 0.997/0.950 | 0.995/0.95 |
| HAS-1      | Ethanol  | 1.0/1.0       | 0.99/0.99   | 0.99/0.99  |

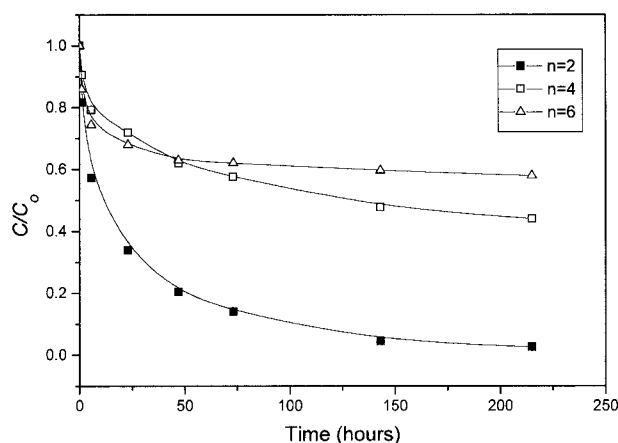
**Table III Migration of Different Fractions of HAS-1 From PP in Heptane at 20°C; Film Thickness 70  $\mu\text{m}$** 

| $n$     | $C/C_o$ ( $C_o = 0.25\%$ wt) |       |       | $C/C_o$ ( $C_o = 1.0\%$ wt) |      |       |
|---------|------------------------------|-------|-------|-----------------------------|------|-------|
|         | 20 h                         | 90 h  | 200 h | 20 h                        | 90 h | 200 h |
| $n = 0$ | 0.019                        | 0.001 | 0.005 | —                           | —    | —     |
| $n = 2$ | 0.51                         | 0.27  | 0.019 | 0.34                        | 0.1  | 0.03  |
| $n = 4$ | 0.78                         | 0.67  | 0.60  | 0.72                        | 0.55 | 0.44  |
| $n = 6$ | 0.91                         | 0.86  | 0.83  | 0.68                        | 0.61 | 0.58  |
| $n = 8$ | 0.93                         | 0.92  | 0.89  | —                           | —    | —     |

compound, and its average molecular weight is higher than that of HAS-2 (Table I). Partial release of HAS-1 is probably a result of the presence in its composition of high-molecular-weight fractions that leak slightly from the polymer.

A slower migration of the stabilizers from PP in dodecane (Fig. 2) and practically no migration in ethanol was observed (Table II). It is interesting that the rate of loss not only of the oligomeric, HAS-1, but also of the monomeric HAS-2, strongly decreases with time: at 20°C the first 10% of HAS-2 is released in dodecane from PP in 20 h; the following 10% of HAS-2 is released in 200 h (Table II).

To understand better the physical behavior of the oligomeric stabilizer, the washing out of different monomeric fractions of HAS-1 was studied. Figure 3 shows the migration of fractions containing  $n = 0, 2, 4, 6,$  and  $8$  taken at the same initial


**Figure 4** Loss of the different fractions of HAS-1 from PP in heptane at 20°C; the initial concentration is 1.0 wt %, film thickness 70  $\mu\text{m}$ .

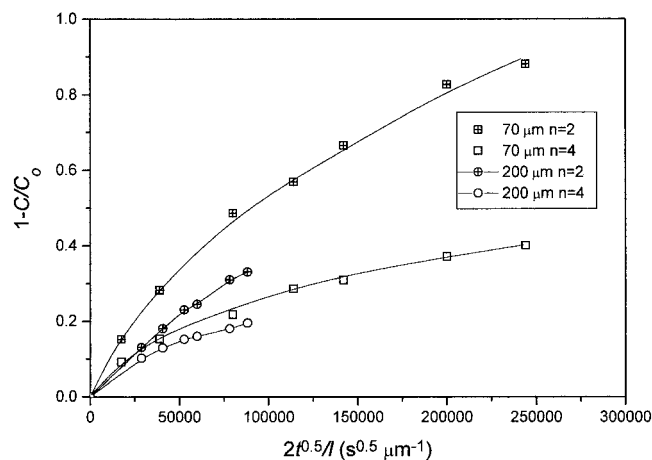
**Table IV Migration of the Fractions of HAS-1 in Heptane; Film Thickness 200  $\mu\text{m}$** 

| Fractions | $C/C_o$ After |       |
|-----------|---------------|-------|
|           | 90 h          | 200 h |
| $n = 2$   | 0.76          | 0.675 |
| $n = 4$   | 0.84          | 0.815 |

concentration (0.25%) in heptane at 20°C and 40°C. As can be seen from Figure 3 and Table III, the fractions containing  $n = 0$  and  $n = 2$  (MW 1062 and 2308) are easily released from the polymer, while the fractions containing  $n = 6$  and  $n = 8$  (MW 5133 and 6172) essentially remain in PP at 20°C but begin to leave at 40°C.

An increase in the initial concentration of the additives results in their fast release from PP (Fig. 4 and Table III): the fractions of HAS-1 with  $n = 2, n = 4,$  and  $n = 6$  taken at the concentration of 1 wt % leak from the PP faster than those taken at 0.25 wt %; besides, the initial rate of release of the fraction with  $n = 6$  (MW 6172) is higher than that with  $n = 4$  (MW 5133). This is probably because the fraction with a higher molecular weight is less soluble in the polymer, forms a metastable phase inside the polymer, and leaks from the polymer more quickly.

An increase in the film thickness results in a decrease of the additive loss that was demonstrated on fractions with  $n = 2$  and  $n = 4$  (Table IV).


**Figure 5** Loss of HAS-1 (fractions:  $n = 2$  and  $n = 4$ ) from PP in heptane at 20°C in coordinates of eq. (1); the initial concentration is 0.25 wt %.

**Table V** Effect of the Additive Concentration and Film Thickness on the Diffusion Coefficient of HAS-1 (Fractions  $n = 2$  and  $n = 4$ ); Heptane, 20°C

| Fractions | Concentration, % wt | Diffusion Coefficient (cm <sup>2</sup> s <sup>-1</sup> ) |                       |
|-----------|---------------------|--|-----------------------|
|           |                     | 70 μm  | 200 μm                |
| $n = 2$   | 0.25                | $1.5 \times 10^{-11}$                                    | $4 \times 10^{-12}$   |
|           | 0.19                | $7 \times 10^{-12}$                                      | $8.4 \times 10^{-12}$ |
|           | 0.17                | $4 \times 10^{-12}$                                      | $2 \times 10^{-12}$   |
|           | 0.1                 | $1.5 \times 10^{-12}$                                    | —                     |
|           | 0.05                | $1.5 \times 10^{-12}$                                    | —                     |
| $n = 4$   | 0.25                | $5.4 \times 10^{-12}$                                    | $2.4 \times 10^{-12}$ |
|           | 0.21                | $7.4 \times 10^{-13}$                                    | $8.6 \times 10^{-13}$ |
|           | 0.2                 | $6 \times 10^{-13}$                                      | $2.8 \times 10^{-13}$ |
|           | 0.16                | $2 \times 10^{-13}$                                      | —                     |

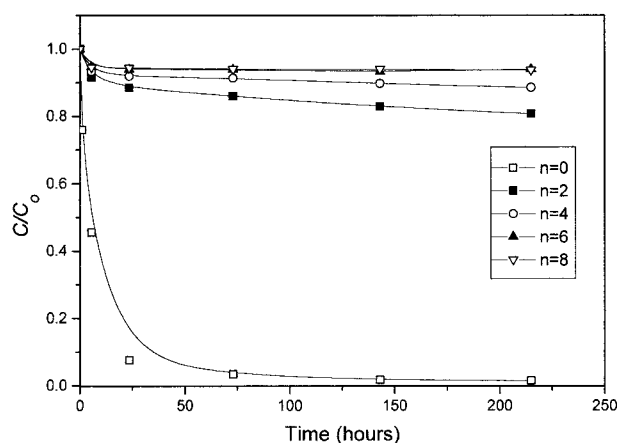
We tried to estimate the apparent diffusion coefficient ( $D$ ) of the fractions of HAS-1 with  $n = 2$  and  $n = 4$  in PP during washing out with heptane. For calculation of  $D$ , eq. (1), obtained from the solution of Fick's second law, was used:<sup>12</sup>

$$D = \frac{(1 - C/C_0)^2}{t} \frac{\pi}{16} \left(\frac{l}{2}\right)^2 \quad (1)$$

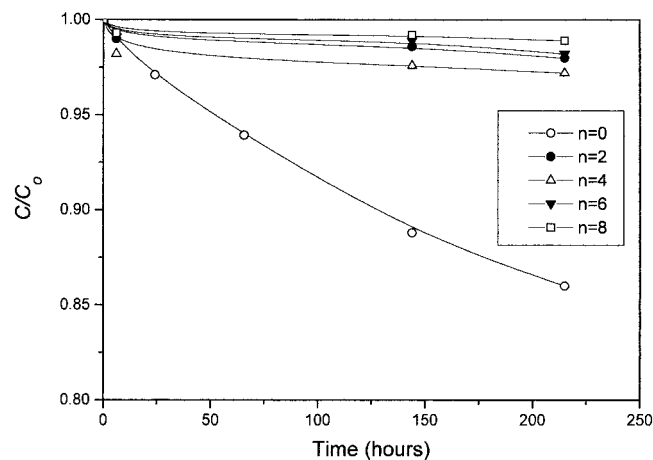
where  $C/C_0$  is the part of additive remaining in the film at time  $t$ , and  $l$  is the sample thickness.

Figure 5 shows the kinetics of the washing out of two fractions of HAS-1 (film thicknesses 70 and 200 μm) in heptane in coordinate  $1 - C/C_0$  versus  $t^{1/2}l^{-1}$ . It is necessary to point out two features: (1) no straight-line dependencies of  $1 - C/C_0$  versus  $t^{1/2}l^{-1}$ , according to eq. (1) are observed; and

(2) the curves corresponding to different thickness do not merge, although they were normalized in accordance with eq. (1). This equation supposes that  $D$  is not concentration dependent. We can approximately estimate the apparent  $D$  assuming that  $D$  does not change in the narrow concentration range. Results of the calculations (Table V) show that the apparent diffusion coefficient of both fractions decreases during their release from the polymer in spite of the fact that the solvent passing into the polymer should facilitate their loss; besides, the changes in  $D$  for the fraction with  $n = 4$  is higher (by a factor of 9) than that for the fraction with  $n = 2$  (by a factor of 2) in the same concentration range (0.2–0.25 wt %). One of the reasons for high diffusion at the initial stages could be connected with the physical state



**Figure 6** Loss of the different fractions of HAS-1 from PP in dodecane at 20°C; the initial concentration is 0.25 wt %, film thickness 70 μm.



**Figure 7** Loss of the different fractions of HAS-1 from PP in ethanol at 20°C; the initial concentration is 0.25 wt %, film thickness 70 μm.

**Table VI Migration of Fractions of HAS-1 From PP in Dodecane and in Ethanol; 20°C, 70  $\mu\text{m}$** 

|         | $C/C_o$ (Dodecane) |       |       | $C/C_o$ (Ethanol) |
|---------|--------------------|-------|-------|-------------------|
|         | 20 h               | 90 h  | 200 h | 200 h             |
| $n = 0$ | 0.076              | 0.025 | 0.015 | 0.86              |
| $n = 2$ | 0.85               | 0.84  | 0.81  | 0.98              |
| $n = 4$ | 0.92               | 0.90  | 0.89  | 0.97              |
| $n = 6$ | 0.94               | 0.94  | 0.94  | 0.98              |
| $n = 8$ | 0.95               | 0.94  | 0.94  | 0.99              |

of the high-molecular-weight additive present in the polymer, where the initial concentration is higher than its solubility at room temperature. In fact the solubility of HAS-1 in PP at 25°C is very low, about  $1 \times 10^{-4}$  wt %.

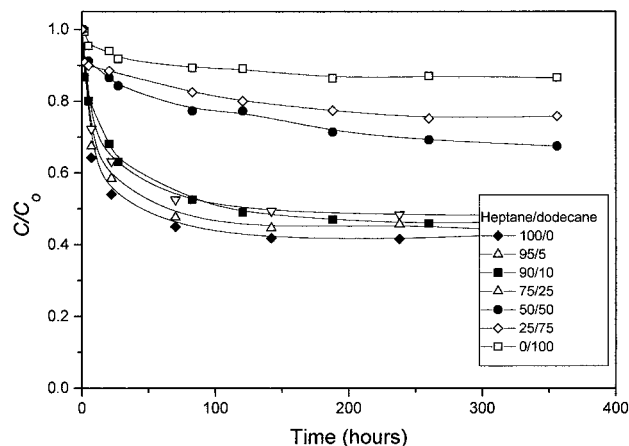
As shown in Table 5, the apparent diffusion coefficient of the additives in thick films is about 2 times less than that in thin ones. Even though it is difficult to find a reasonable explanation for the result obtained, we may suppose that in thin films "swelling effect" by the solvent occurs to a higher extent than that in thick ones.

The migration of fractions of HAS-1 with  $n = 0, 2, 4, 6,$  and  $8$  in dodecane and in ethanol was also studied (Figs. 6 and 7, Table VI). The loss of these fractions in dodecane proceeds considerably slowly compared to heptane: only the low-molecular-weight fraction (MW 1352,  $n = 0$ ) releases completely, while fractions with a higher molecular weight (MW > 2300,  $n = 2$  and higher) release partially (5–20%). Ethanol is able to extract the fractions from PP to a lesser extent than does dodecane (Fig. 7, Table 6).

Based on the data obtained from washing out of different fractions of HAS-1 and taking into account their weight part in the oligomeric HAS-1, we estimated the loss of HAS-1. Results are presented in Figures 1 and 2 (dotted lines). In

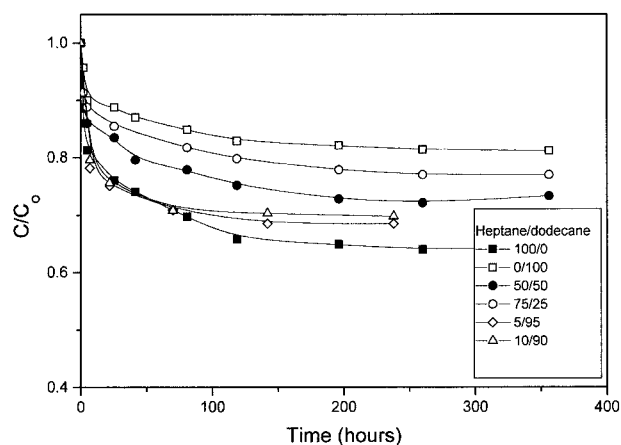
**Table VII Solvent Solubility in PP at 20°C (200  $\mu\text{m}$  Film Thick, 24 h)**

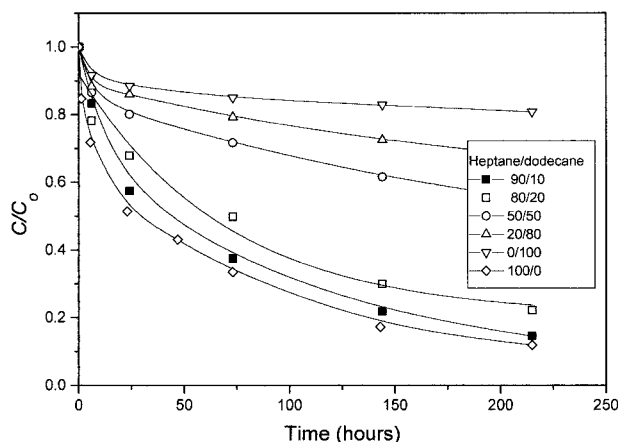
| Solvent  | Solubility |                      |
|----------|------------|----------------------|
|          | % wt       | mol kg <sup>-1</sup> |
| Heptane  | 7.6        | 0.76                 |
| Dodecane | 10         | 0.6                  |
| Ethanol  | 0.015      | 0.033                |


**Figure 8** Loss of HAS-1 from PP in heptane–dodecane mixture at 20°C; the initial concentration is 0.25 wt %, film thickness 70  $\mu\text{m}$ .

the case of washing out with heptane at 20°C and with dodecane at 20°C and 40°C, a good agreement between experimental and calculated data is observed. Some discrepancy is observed with heptane at 40°C, where the majority of the stabilizer (80%) leaves the polymer: predicted data give rise to faster migration of HAS-1 than the experimental one. This is probably because the initial concentration of the separate fractions taken for the experiments was 0.25 wt %, which is higher than their partial concentrations in oligomeric HAS-1, and so they can migrate faster.

From the results obtained it can be concluded that the efficiency of washing out strongly depends on the type of solvent and it changes in the

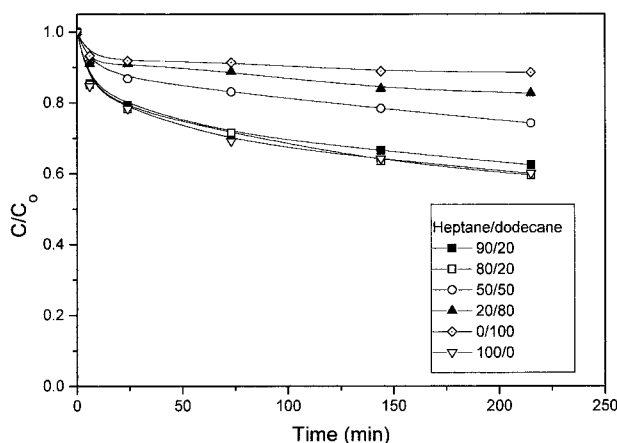

**Figure 9** Loss of HAS-2 from PP in heptane–dodecane mixture at 20°C; the initial concentration is 0.25 wt %, film thickness 70  $\mu\text{m}$ .



**Figure 10** Loss of HAS-1 (fraction containing  $n = 2$ ) from PP in heptane-dodecane mixture at 20°C; the initial concentration is 0.25 wt %, film thickness 70  $\mu\text{m}$ .

order: ethanol  $\ll$  dodecane < heptane. As reported earlier,<sup>10</sup> the solvent molecules passing into the polymers are able to increase the segmental mobility of macromolecules and to facilitate additive migration. The ability of the solvent to escape the additive is connected with the solvent solubility in the polymer: the higher the solvent solubility, the higher the washing out effect. In fact, the solubility of ethanol in PP is considerably lower compared to dodecane and heptane, but only slight differences in solubility between heptane and dodecane in PP are observed (Table 7).

To understand better the differences in behavior between heptane and dodecane, we studied the washing out of HAS-1, HAS-2, and the fractions of HAS-1 ( $n = 2$  and  $n = 4$ ) from PP with a



**Figure 11** Loss of HAS-1 (fraction containing  $n = 4$ ) from PP in heptane-dodecane mixture at 20°C; the initial concentration is 0.25 wt %, film thickness 70  $\mu\text{m}$ .

**Table VIII** The Part of the Stabilizer Remaining in PP ( $C/C_0$ ) After Its Migration in Heptane-Dodecane Mixture at 20°C,  $C_0 = 0.25\%$  wt, Film Thickness 70  $\mu\text{m}$

| Heptane/Dodecane,<br>% vol | HAS-2 |       | HAS-1 |       |
|----------------------------|-------|-------|-------|-------|
|                            | 90 h  | 200 h | 90 h  | 200 h |
| 100/0                      | 0.39  | 0.19  | 0.52  | 0.47  |
| 95/5                       | 0.38  | 0.17  | 0.45  | 0.416 |
| 90/10                      | 0.39  | 0.19  | 0.47  | 0.45  |
| 75/25                      | 0.52  | 0.38  | 0.52  | 0.49  |
| 50/50                      | 0.699 | 0.59  | 0.773 | 0.71  |
| 25/75                      | 0.86  | 0.77  | 0.838 | 0.78  |
| 0/100                      | 0.88  | 0.82  | 0.90  | 0.88  |

heptane-dodecane mixture containing various heptane-dodecane ratios (Figs. 8–11, Tables VIII and IX). The addition of small amounts of either dodecane to heptane or heptane to dodecane (about 25 vol %) does not have much of an influence on the washing out compared to pure solvents, while other heptane-dodecane ratios have a considerable effect on the rate of loss. Figure 12 shows the time corresponding to migration of 20% of the initial amount of the fractions of HAS-1 versus the dodecane-heptane ratio. As can be deduced from Figure 12, a minimal (critical) concentration of heptane in the mixture considerably increases the washing out; this critical concentration depends on the additive molecular weight (20–30 vol % of heptane for fractions with MW 2308 and 80 vol % for fraction with m.w. 3548).

Figure 13 shows the effect of additive molecular weight on washing out with different solvents: ethanol removes the additives well with a molec-

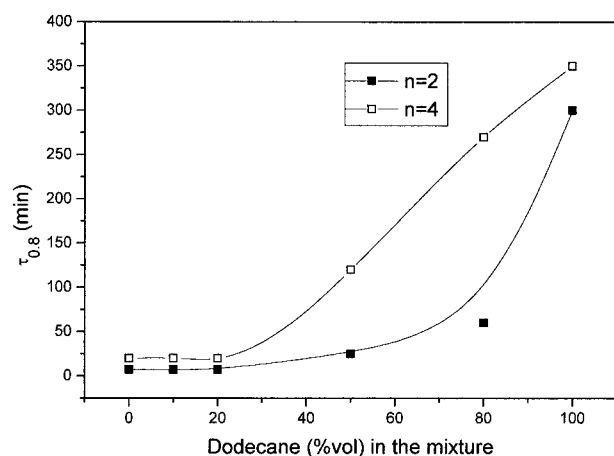
**Table IX** The Part of the Stabilizer Remaining in PP After Its Migration in Heptane-Dodecane Mixture at 20°C; HAS-1, Fractions  $n = 2$  and  $n = 4$ ;  $C_0 = 0.25\%$  wt, Film Thickness 70  $\mu\text{m}$

| Heptane/Dodecane<br>% vol | $C/C_0$ After 90 h |         |
|---------------------------|--------------------|---------|
|                           | $n = 2$            | $n = 4$ |
| 100/0                     | 0.27               | 0.67    |
| 90/10                     | 0.33               | 0.69    |
| 80/20                     | 0.43               | 0.72    |
| 50/50                     | 0.68               | 0.82    |
| 20/80                     | 0.78               | 0.87    |
| 0/100                     | 0.84               | 0.90    |

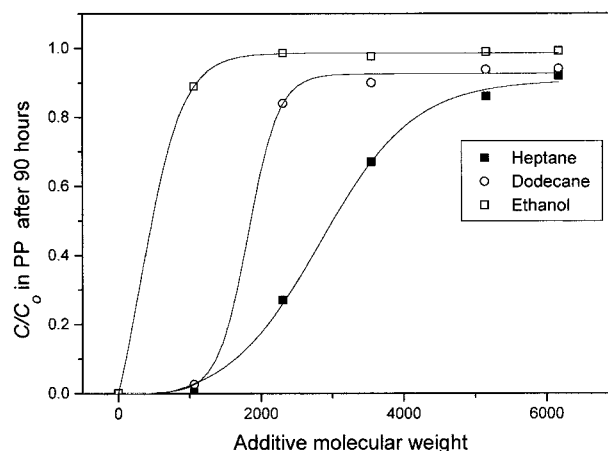
ular weight less than 1000; dodecane, the additives with a molecular weight less than 2000; and heptane, the additives with a molecular weight less than 4000–5000. It is clear that for the additive molecules to escape from the surroundings, excess free volume is required. A solvent, because of its interaction with a polymer, may facilitate the formation of free volume, which depends on the type of solvent and the solvent concentration in the polymer. The additive migration from the polymer should depend on its molecular weight because a different free volume is necessary for each one to escape from the polymer.

## CONCLUSIONS

The high-molecular-weight stabilizers, despite their low diffusion in the polymer, can leak from the polymer in specific solvents at room temperature. The ability of the solvent to facilitate the additive's migration increases with solvent solubility in the polymer. The rate of washing out usually decreases with the additive molecular weight; as a result, low-molecular-weight fractions of oligomeric stabilizers leak from the polymer faster than ones with a high molecular weight. The total loss of the oligomeric stabilizer can be predicted based on the loss of its separate fractions. The apparent diffusion coefficient increases with an increase in the additive concentration in the polymer and with a decrease in the film thickness, indicating a complex diffusion in



**Figure 12** Loss of the fractions of HAS-1 ( $n = 2$  and  $n = 4$ ) from PP in heptane–dodecane mixture: time corresponding to the migration of 20% of the additive versus dodecane content in the mixture; 20°C; the initial concentration is 0.25 wt %, film thickness 70  $\mu\text{m}$ .



**Figure 13** Effect of additive molecular weight on migration from PP in different solvents; 20°C; the initial concentration is 0.25 wt %, film thickness 70  $\mu\text{m}$ .

the presence of a solvent. At higher concentrations the migration also increases, probably because of the low additive solubility in the polymer.

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