

# Loss of High Molecular Weight, Sterically Hindered Amines from Polypropylene

A. P. MAR'IN,<sup>1</sup> V. BORZATTA,<sup>2</sup> M. BONORA,<sup>2</sup> L. GRECI<sup>1</sup>

<sup>1</sup> Dipartimento di Scienze dei Materiali e della Terra, Università degli Studi di Ancona, Via Breccie Bianche, I-60131, Ancona, Italy

<sup>2</sup> Ciba Specialty Chemicals, S.p.A., 40044 Pontecchio Marconi, Italy

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**ABSTRACT:** The loss from polypropylene (PP) of sterically hindered amines with molecular weight ranging from 1364 to 2758 in heptane, chloroform, and methanol at room temperature was studied. The additives leak from polymer in heptane and in chloroform and some residual concentration remains in the polymer; the stabilizers show slight migration in methanol. The rate of loss increases with additive concentration in the polymer. The effect of solvent during washing out could be explained by its different solubility in PP resulting in changes in polymer chain mobility and additive migration from the polymer. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 897–903, 2000

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

## INTRODUCTION

Washing out is the principal cause of undesired loss of stabilizers and other additives from polymeric material used outdoors or for the flow of liquids in tubes and containers. The loss of additives in contacting medium like water, oils, and foodstuffs results in their transfer to the surroundings, with consequent pollution and decrease in the life time of the polymer.<sup>1–7</sup> Washing out involves additive diffusion to the surface, its removal from the surface as well as penetration, and dissolution of the liquid inside the polymer. The total process 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</sup> High molecular weight stabilizers are not volatile and their diffusion in the polymer at elevated temperature is very slow; therefore because of their low solubility in the polymer, washing out may be the means that determines their physical loss from the polymer.

In this work, washing out from polypropylene (PP) of sterically hindered amines stabilizers (HAS) with organic liquids (heptane, chloroform, and methanol) carried out at room temperature is described.

## EXPERIMENTAL

### Materials

Polypropylene films 70 and 200  $\mu\text{m}$  were prepared by heating PP powder (Moplen FLF20 Montell) to 200°C. Stabilizers:

*N',N'*-bis(2,2,6,6-tetramethyl-4-piperidinyl)-2,9,15,22-tetrakis(2,2,6,6-tetramethyl-4-piperidinyl), 2,9,11,13,15,22,24,26,27,28-decaazatricyclo[21.3.1.1.10.14]-octacos-

Correspondence to: A. P. Mar'in (alexmarin20@hotmail.com).

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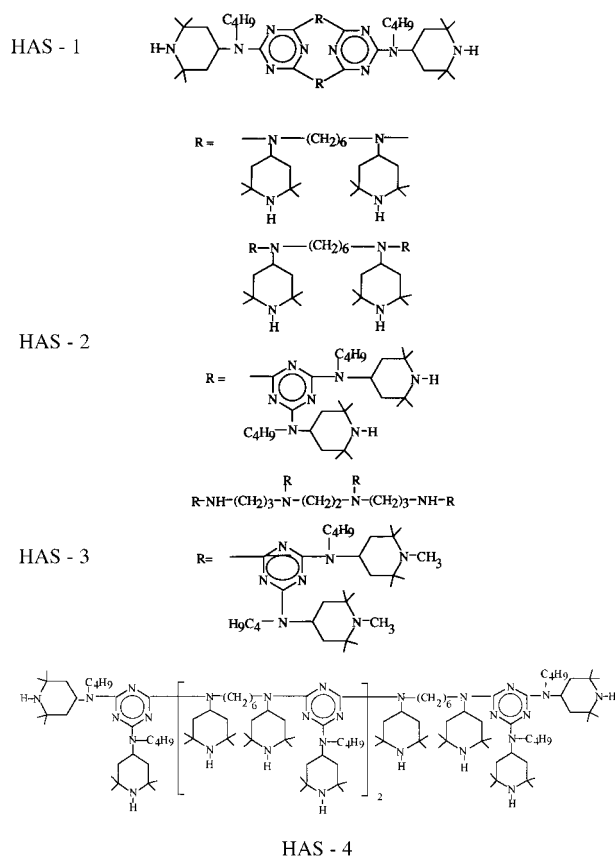
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1(27),10,12,14(28),23,25-hexaene-12,25-dibutylamine (HAS-1), MW 1364. *N,N*-bis[2,4-bis[*N*-(2,2,6,6-tetramethyl-4-piperidiny)butylamino]-1,3,5-triazine-6-yl]-*N,N'*-bis(2,2,6,6-tetramethyl-4-piperidiny)-1,6-hexanediamine (HAS-2), MW 1393.

1,3,5-Triazine-2,4,6-triamine,*N,N''*-1,2-ethanediybis[*N*-[3-[[4,6-bis(butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino)-1,3,5-triazin-2-yl]methylamino]propyl]-*N',N''*-dibutyl-*N',N''*-bis(1,2,2,6,6-pentamethyl-4-piperidiny) (HAS-3), MW 2286.

*N*<sup>III</sup>,*N*<sup>IV</sup>-bis(2,2,6,6-tetramethyl-4-piperidiny)-*N*<sup>III</sup>,*N*<sup>IV</sup>-bis[*N,N'*-dibutyl-*N*<sup>II</sup>[6-[[4-[butyl(2,2,6,6-tetramethyl-4-piperidiny)-amino]-6-yl-1,3,5-triazine-2-yl]-(2,2,6,6-tetramethyl-4-piperidiny)-amino]-hexyl]-*N,N'*-*N*<sup>II</sup>-tris(2,2,6,6-tetramethyl-4-piperidiny)-1,3,5-triazine-2,4,6-triamine]-1,6-hexanediamine (HAS-4), MW 2758. In some experiments, the ester of 3,5-di-*tert*-butyl-4-hydroxyphenyl propionic acid and pentaertrite (Irganox 1010), and tris(2,4-di-*tert*-butylphenyl) phosphite (Irgafos 168) were also used.



## Introduction of Stabilizers in PP

HAS-1, HAS-2, HAS-4, Irganox 1010, and Irgafos 168 dissolved in heptane were deposited first on one side of the polymer film; after solvent evaporation, the same procedure was repeated on the other side. The PP sample was then sealed under vacuum in a glass tube and kept at 90 and 100°C for different periods of time. Subsequently, the sample was removed from the glass tube and carefully washed with cold heptane; no additive remained on the film surface. HAS-3 was introduced in PP by mixing with PP powder followed by film pressing at 200°C.

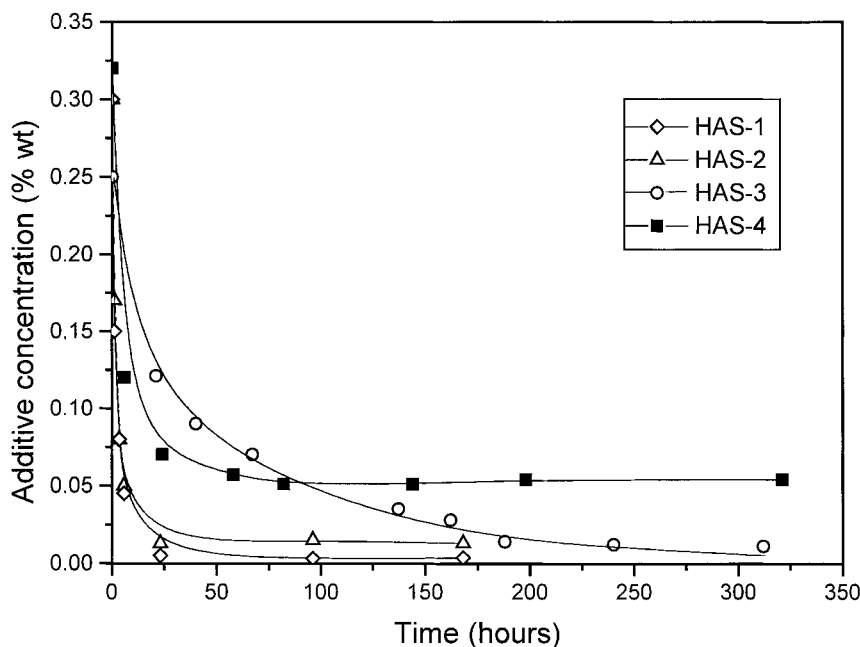
## Washing Out Experiments

Films (20–30 mg) containing additives were kept in solvent (10 mL) at room temperature ( $T = 23$ – $25^\circ\text{C}$ ); the solvent was periodically replaced (once every two days) with a new one. The amount of additive released from the polymer was measured by UV spectroscopy (Uvicom 941 Plus UV-VIS) directly of the film as well as of the solution, throughout the experimental period.

## RESULTS AND DISCUSSION

Figure 1 shows the release of HAS (starting concentrations 0.25–0.33% wt) from PP film in heptane at room temperature. The initial rate of loss may be estimated as the time corresponding to half the initial concentration of the additive in PP ( $\tau_{0.5}$ ). Table I shows the values of  $\tau_{0.5}$  for HAS as well as for Irganox 1010 and Irgafos 168 taken for comparison. The following conclusions may be drawn: (1) all the stabilizers, in spite of their high molecular weights, leak from the polymer; (2) the rate of washing out decreases with increasing additive molecular weight until MW 2286, then it starts to increase; (3) some residual concentration of HAS-3 and HAS-4 remains in the polymer even after a long time.

The diffusion of the studied HAS in PP in the absence of solvents proceeds very slowly, i.e., the diffusion coefficients of HAS-1 and HAS-4 in PP at 70°C are  $4 \times 10^{-12}$  and  $3 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ .<sup>8</sup> Taking into account the high activation energy of the process (49 and 65 kcal mol<sup>-1</sup>, respectively), one should expect no diffusion of the additives at room temperature. One of the reasons for the fast release of the additives is that the solvent facili-



**Figure 1** Loss of the additives from PP in heptane; the initial concentrations of the additives 0.25–0.32% wt, film thickness 70  $\mu\text{m}$ ,  $T = 23\text{--}25^\circ\text{C}$ .

tates the migration of the stabilizers. On the other hand, high molecular weight stabilizers are only slightly soluble at room temperature,<sup>9</sup> so the majority are present in a meta-stable state; alternatively, they can form a separate phase and can be lost rapidly. Experiments show that the solubility of HAS-3 and HAS-4 at room temperature is about  $1 \times 10^{-4}$  and  $3 \times 10^{-5}$  %, respectively.<sup>9</sup> Probably, this is the reason why HAS-4, which is less soluble in PP, leaks faster from PP than HAS-3 does. The residual concentration of HAS-4 remaining in PP is about 0.053% wt for low initial concentrations and slightly decreases to 0.03% wt for high initial ones (Table II, Fig. 2). HAS-3 is practically completely released if low initial con-

centrations are used while a residual concentration (about 0.1%) remains inside the polymer if the additive is added at very high initial concentrations (9% wt) (Fig. 3). It is noteworthy that both compounds are monomeric and the introduction of HAS-4 inside PP was done through its diffusion in the polymer at  $100^\circ\text{C}$ , so the effect observed is not connected with the molecular weight of the stabilizer remaining in the polymer. In addition, it is difficult to expect any chemical interaction between stabilizer and polymer because the additives were introduced in the poly-

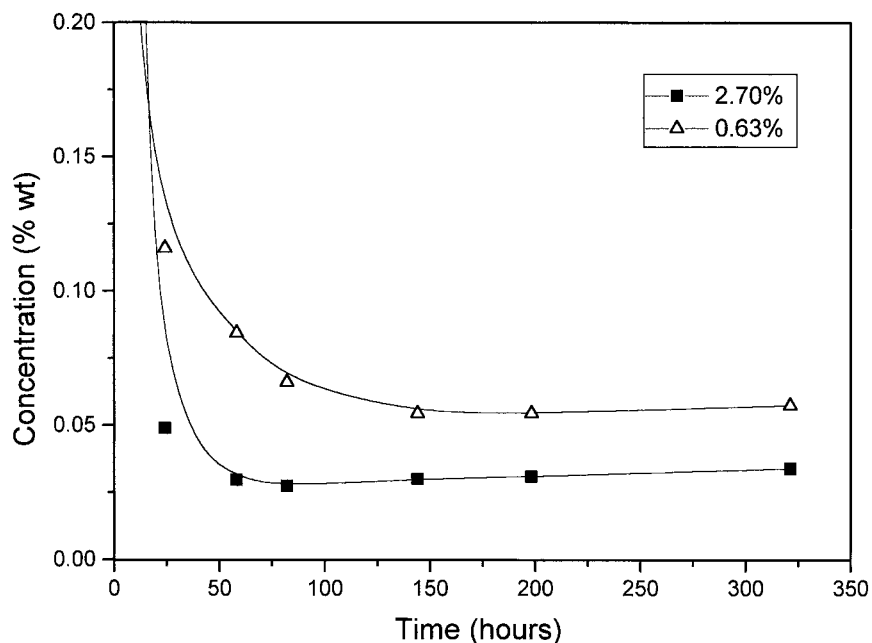
**Table I** Loss of the Additives from PP Film in Heptane;  $C_0 = 0.25\text{--}0.32\%$  wt; Thickness 70  $\mu\text{m}$ ,  $T = 23\text{--}25^\circ\text{C}$

Additive	Molecular Weight	$\tau_{0.5}$ (h)
Irgafos 168	630	<0.5
Irganox 1010	1178	0.5
HAS-1	1364	1.1
HAS-2	1393	1.5
HAS-3	2286	18
HAS-4	2758	4–6

**Table II** Loss of HAS-4 from PP in Heptane at Different Initial Concentrations; Thickness 70  $\mu\text{m}$

Concentration of HAS-4 in PP (% wt)			$W_0/C_0 \times 10^5$ ( $\text{s}^{-1}$ ) <sup>a</sup>
Initial	After 6 h	After 300 h	
0.32	0.12	0.053	2.5
0.63	0.21	0.054	3.1
1.49	0.56	0.050	2.8
2.7	0.22	0.027	4.2
3.0	0.63	0.030	3.7

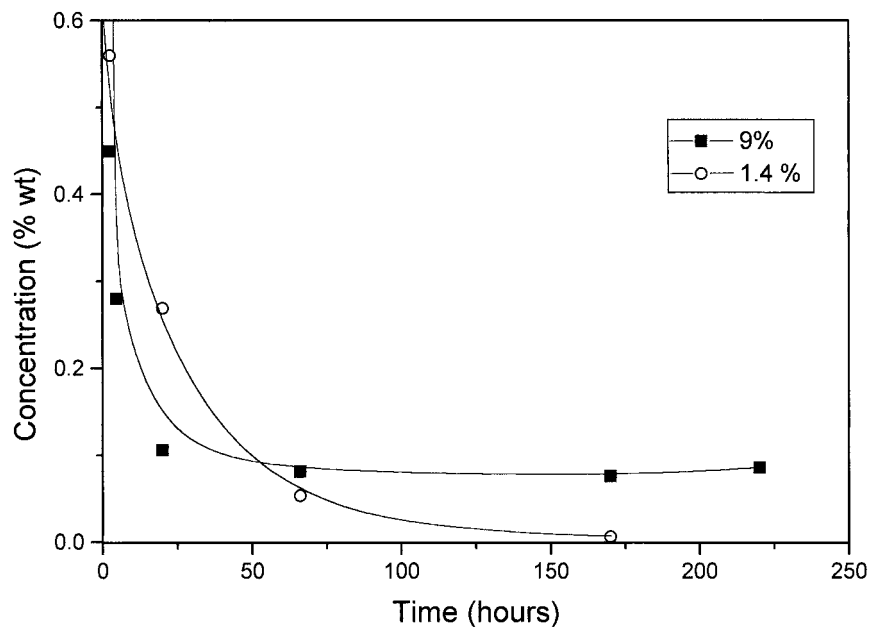
<sup>a</sup>  $W_0$  is the initial loss rate.



**Figure 2** Loss of HAS-4 from PP in heptane; the initial concentrations of HAS-4 are 0.63% and 2.7% wt, film thickness 70  $\mu\text{m}$ ,  $T = 23\text{--}25^\circ\text{C}$ .

mer in the absence of oxygen so oxidation does not occur. Probably, the residual concentration is due to the fact that the dissolved additive changes the polymer structure, making the sorption centers

more convenient for the additive molecules and this process depends on the size of the molecule. This is in agreement with our previous observations that dissolution and migration of these ad-



**Figure 3** Loss of HAS-3 from PP in heptane; the initial concentrations of HAS-3 are 1.4% and 9% wt, film thickness 70  $\mu\text{m}$ ,  $T = 23\text{--}25^\circ\text{C}$ .

**Table III Loss of HAS-3 from PP in Various Solvents at Room Temperature**

$C_0$ (% wt)	Thickness ( $\mu\text{m}$ )	Heptane		Chloroform		Methanol
		$C_1/C_0$	$\tau_{0.5}$ (h)	$C_1/C_0$	$\tau_{0.5}$ (h)	$C_1/C_0^a$
0.25	70	0.48	18	0.37	8	0.98
0.50		0.42	10–15	0.24	3	0.99
1.4		0.2	2	—	—	—
9.0		0.011	<1	—	—	—
0.1	200	0.77	220	0.86	150	0.97
0.25		0.64	120	0.71	45	0.98
0.5		0.68	110	0.66	40	0.98

<sup>a</sup>  $C_1/C_0$  is the part of HAS-3 that remained in PP after 20 h.

ditives in PP at high temperature is accompanied by a strong rearrangement of the polymer structure.<sup>8,9</sup>

The rate of loss increases with increasing additive concentration in the polymer and decreases with sample thickness as observed in the case of HAS-3 and HAS-4 (Tables III and IV). As all the experiments were performed with periodical heptane replacement, we may suppose that the loss of the additive from the film is determined by its migration inside the film. We tried to estimate the apparent diffusion coefficient ( $D$ ) of HAS-4 in PP during its washing out with heptane. For calculation of  $D$ , eq. (1) obtained from the solution of Ficks' law was used<sup>10</sup>:

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

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

Figure 4 shows the kinetics of washing out of HAS-3 from PP films (200  $\mu\text{m}$  thickness) in heptane at different initial concentrations of HAS-3 in PP plotting  $1 - C/C_0$  vs (time)<sup>1/2</sup>. The values of  $D$  calculated from the slopes of the lines in Figure

4 were  $3.2 \times 10^{-12}$ ,  $3.0 \times 10^{-12}$ , and  $4.2 \times 10^{-12}$   $\text{cm}^2 \text{s}^{-1}$  for initial concentrations of HAS-3 0.1, 0.25, and 0.5% wt, respectively. This means that the apparent diffusion coefficient slightly increases with the initial concentration of the additive. It is necessary to point out that the lines on Figure 4 do not start exactly at the beginning of the coordinate axis and this may be due to the fact that faster diffusion takes place at the beginning of the process.

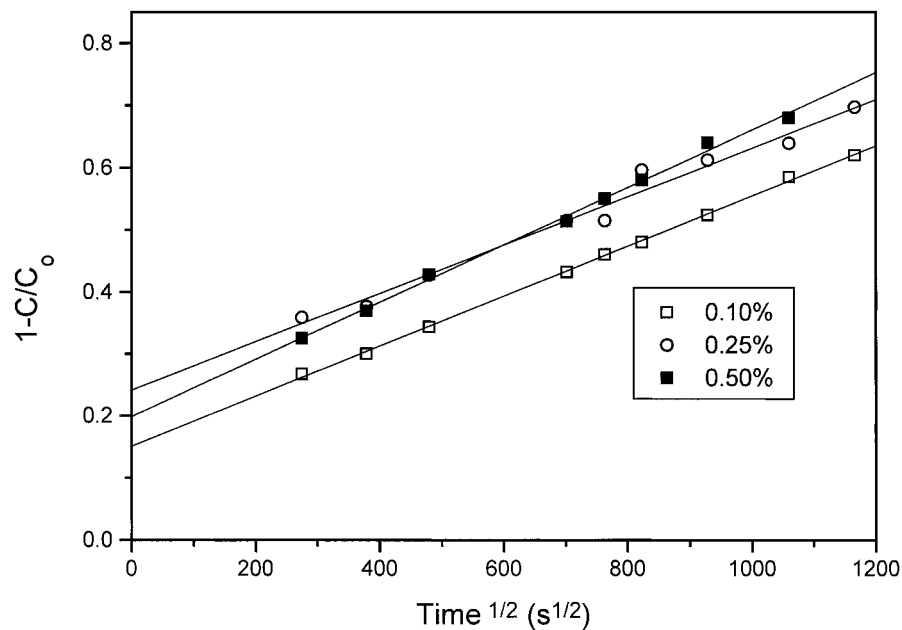
Figure 5 and Table IV show the effect of various solvents on washing out of HAS-3 from PP: the loss of HAS-3 in chloroform occurs faster than in heptane, while that in methanol occurs considerably slower. There are two factors that could influence the migration of stabilizer from the polymer: the solvent solubility in PP and the solubility of the stabilizer in the solvents. Table IV shows that the solubility of HAS-3 in heptane and in methanol is the same, and it is considerably lower than in chloroform, which means that the difference in the solubility of the stabilizer in the solvents may not be the reason for the difference in washing out. On the other hand, the solubility of heptane and chloroform in PP is remarkably higher than that of methanol (Table V).

**Table IV Solubility of HAS-3 in Solvents at 20°C**

Solvent	Solubility (% wt)
Heptane	1
Chloroform	20
Methanol	1

## CONCLUSION

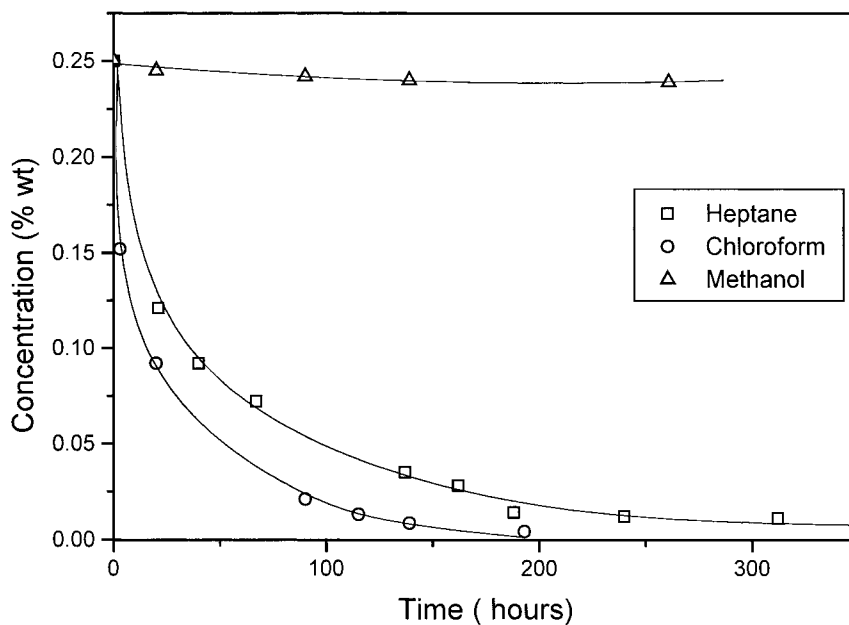
The results obtained indicate that washing activity strongly depends on solvent solubility in the polymer, generally called "swelling" effect. In spite of this fact, the real mechanism of additive migration in the polymer in the presence of the



**Figure 4** Loss of HAS-3 from PP in heptane; the initial concentrations of HAS-3 are 0.10, 0.25, and 0.50% wt, film thickness 200  $\mu\text{m}$ ,  $T = 23\text{--}25^\circ\text{C}$ .

solvent is not clear. Large-sized molecules of stabilizer introduced in PP at high temperature cannot migrate at low temperature because a consid-

erable change in the polymer surroundings is required for this process. Solvent molecules, due to their interaction with polymer chains, can consid-



**Figure 5** Loss of HAS-3 from PP in heptane, chloroform and in methanol; the initial concentration of HAS-3 is 0.25% wt, film thickness 70  $\mu\text{m}$ ,  $T = 23\text{--}25^\circ\text{C}$ .

**Table V Solubility of Solvents in PP Film at 20°C (Time 24 h, Film Thickness 200  $\mu\text{m}$ )**

Solvent	Solubility (% wt)
Heptane	6.5
Chloroform	12
Methanol	0.10–0.15

erably increase the free volume facilitating additive migration. Besides, solvent molecules can substitute additive molecules from sorption centers, increasing their mobility. Another factor affecting additive loss, mentioned above, concerns with the very low additive solubility at room temperature: its release is faster at concentrations higher than its solubility.

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