

# Migration of Antidegradants to the Surface in NR and SBR Vulcanizates

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**ABSTRACT:** Migration-generating equipment using a vacuum technique was constructed to measure the migration properties of antidegradants to the surface in compounded rubber in a short time. With this equipment, the migration of antidegradants to the surface is accelerated by the fast evaporation of organic molecules on the surface facing the vacuum and the pressure difference applied between two surfaces of the rubber vulcanizate. The effects of initial concentration and temperature on the migration of antidegradants such as 2,6-di-*t*-butyl-4-methyl phenol (BHT), *N*-phenyl-*N*-isopropyl-*p*-phenylenediamine (IPPD), and *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) were investigated with this equipment. The migration rate was found to be independent of the initial concentration of the antidegradants. BHT and IPPD migrate to the surface of an object faster than HPPD, which is due to molecular size. BHT migrates faster than IPPD at a low temperature of 40°C, while IPPD is faster than BHT at a high temperature of 60–100°C. Antidegradants in NR vulcanizates migrate faster than those in SBR ones. This is because interactions of antidegradants with SBR are stronger than those with NR. To explain the difference in rubber base, calculations with molecular mechanics and dynamics were tried, which gave the results that the interaction of IPPD with polystyrene is much stronger than those with *cis*-1,4-polyisoprene and *cis*-1,4-polybutadiene. Activation energies for migration to the surface of NR vulcanizate are 25.8, 30.7, and 38.6 kJ/mol, while those of SBR are 27.6, 36.5, and 51.7 kJ/mol for BHT, IPPD, and HPPD, respectively. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 117–125, 1997

**Key words:** antidegradants; migration; rubber vulcanizate; vacuum technique; molecular simulation

## INTRODUCTION

Ozone attack on rubber compounds causes characteristic cracking perpendicular to the direction of applied stresses. This degradation is caused by reactions of ozone with the double bonds in the rubber molecules. These reactions lead to chain scission and the formation of various decomposition products. Several theories have been discussed in the literature regarding the mechanism

of antiozonant protection. In order to control the effects of rubber ozonation, either paraffin waxes or chemical antiozonants are added to unsaturated rubbers. The most effective antiozonants are *N,N'*-disubstituted-*p*-phenylenediamines, in which at least one of the side groups is alkyl (preferably *sec*-alkyl).<sup>1,2</sup>

There are several theories about the mechanism of protection by chemical antiozonants. The scavenger model states that the antiozonant blooms to the surface and preferentially reacts with ozone so that the rubber is not attacked until the antiozonant is exhausted.<sup>1,3,4</sup> The protective

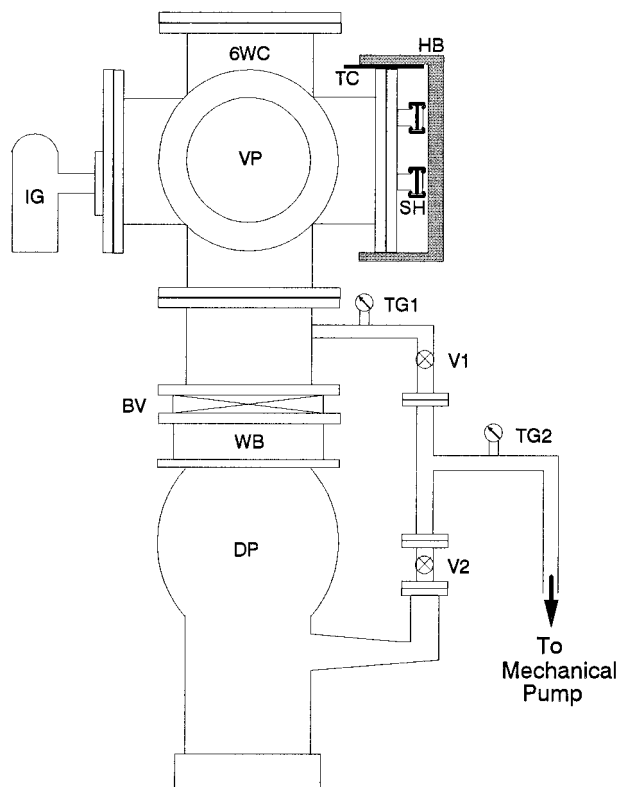
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film theory is similar, except that the ozone-antiozonant reaction products form a film on the rubber surface that prevents (physically and perhaps chemically as well) ozone attack on the rubber.<sup>3</sup> A third relinking theory states that the antiozonant prevents the scission of the ozonied rubber or else recombines severed double bonds.<sup>5</sup> Currently, the most accepted mechanism of antiozonant action is a combination of the scavenger and protective film theories.<sup>6,7</sup>

Major characteristics required as antiozonant properties are migration to the surface of an object and reactivity with ozone. To measure the migration of organic additives in a rubber compound, various methods such as solvent extraction,<sup>8</sup> the techniques of tagging the additives with a <sup>13</sup>C or a <sup>35</sup>S isotope before mixing it in a compound,<sup>9,10</sup> and compression set plates<sup>11</sup> were used. However, these methods are time consuming or do not consider real tire conditions of inflation. The internal pressure of the tire for a passenger car is about 30 psi in driving conditions, and the pressure difference between inner and outer parts of the tire might be more than twice that value. Recently, the diffusion of antioxidants in rubber using rubber films and ultraviolet analysis was studied, in which rubber compounds without antioxidants were used.<sup>12</sup>

In this study, the migration-generating equipment using a vacuum technique is presented; this technique has the following unique characteristics. First, the pressure difference between the inner and outer parts of a compounded rubber sheet is considered. If the pressure of a vacuum chamber is about  $10^{-6}$  torr, then the pressure difference is about  $10^8$  times that value. Second, organic additives on the surface are well vaporized in vacuum, so migration is accelerated. Third, migration has a direction from atmosphere to vacuum. With this equipment, the effects of migration depending on the initial concentration of the antidegradants and temperature were studied. The dependence of the migration properties on the type of base rubbers such as NR and SBR was also investigated. The migrants 2,6-di-*t*-butyl-4-methyl phenol (BHT), *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine (IPPD), and *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) were used. The interactions of IPPD with polymers such as *cis*-1,4-polyisoprene, *cis*-1,4-polybutadiene, and polystyrene were calculated by molecular mechanics and dynamics to explain the difference of

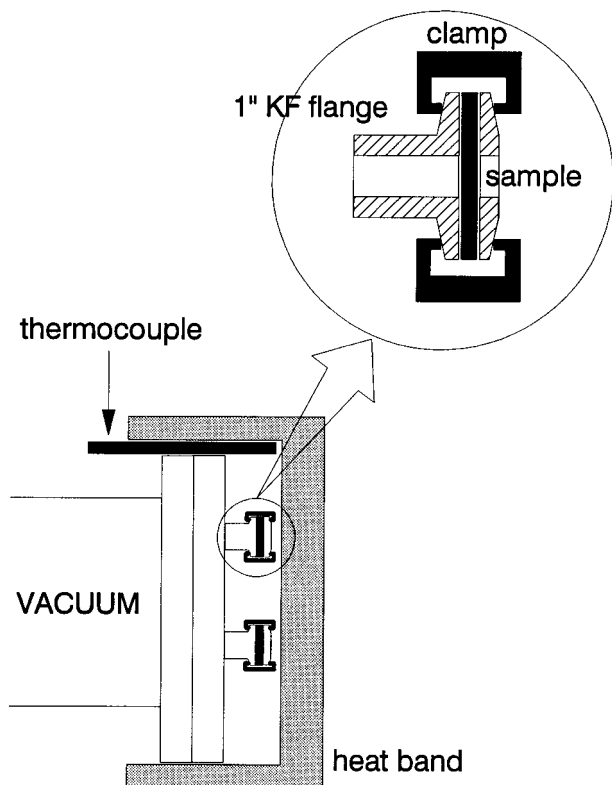


**Figure 1** Migration-generating equipment using vacuum technique. Abbreviations are as follows: (6WC) 8-inch six-way cross, (VP) view port, (TC) thermocouple, (HB) heat band, (SH) sample holder, (IG) ionization gauge, (TG1 and TG2) thermocouple pressure gauge, (V1) roughing valve, (V2) fore-line valve, (BV) butterfly valve, (WB) water baffle, and (DP) diffusion pump.

migration properties between NR and SBR vulcanizates.

## EXPERIMENTAL

The migration-generating equipment using a vacuum technique is composed of mechanical and oil diffusion pumps, an 8-inch six-way cross, a pressure gauge and controller, a heat band and temperature controller, and a sample holder flange, as shown in Figure 1. The vacuum chamber is evacuated by a Varian VHS-4 oil diffusion pump with a pumping speed of 1,200 l/s for air. The base pressure in the vacuum chamber is typically lower than  $1 \times 10^{-6}$  Torr and rises to about  $5 \times 10^{-6}$  Torr during migration. The sample holder flange has three sample holders made of a 1-inch



**Figure 2** Sample holder region of migration-generating equipment.

KF flange, as shown in Figure 2. The sample holder region is kept in a thermostatically controlled heat band at a constant temperature ( $\pm 1^\circ\text{C}$ ) during the migration time.

The dimension of the test sample is 2.0 mm thick and 4.0 cm in diameter. Migration experi-

ments were carried out at constant temperatures of 40, 60, 80, and  $100^\circ\text{C}$  for 20 h. NR and SBR vulcanizates containing antidegradants such as BHT, IPPD, and HPPD were prepared by curing at  $160^\circ\text{C}$  for 15 min. The formulations are given in Table I. To investigate the effect of the initial concentration of antidegradants on migration to the surface, NR vulcanizates were prepared with an additive of HPPD of 1.0, 3.0, 5.0, 7.0, and 9.0 phr (NR1, NR2, NR3, NR4, and NR5 in Table I, respectively).

The amount of antidegradants that migrated to the surface was determined by the difference in the amounts of antidegradants that remained in the rubber vulcanizates before and after migration. The amount of antidegradants that remained in the rubber vulcanizates was analyzed by gas chromatography after the extraction of the antidegradants with THF. Experiments were carried out three times and averaged.

To explain the difference of migration properties between NR and SBR vulcanizates, the interactions of IPPD with rubbers such as *cis*-1,4-polyisoprene, polystyrene, and *cis*-1,4-polybutadiene were calculated by molecular mechanics and dynamics. The model rubbers were composed of 50 repeat units. The force field used is the CFF91 force field.<sup>13,14</sup> The CFF91 force field uses a quartic polynomial for bond stretching and angle bending and a three-term Fourier expansion for torsions. The out-of-plane coordinate is defined according to Wilson et al.<sup>15</sup> All of the cross terms up through the third order that have been found to be important are also included. The Coulombic interaction between the atomic charges and the van der

**Table I** Formulations

Compound No.	NR1	NR2	NR3	NR4	NR5	NR6	NR7	SBR1	SBR2	SBR3
SMR20	100.0	100.0	100.0	100.0	100.0	100.0	100.0	—	—	—
SBR-1500	—	—	—	—	—	—	—	100.0	100.0	100.0
N351	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Processing oil	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
HPPD	1.0	3.0	5.0	7.0	9.0	—	—	—	—	3.0
BHT	—	—	—	—	—	3.0	—	3.0	—	—
IPPD	—	—	—	—	—	—	3.0	—	3.0	—
Sulfur	1.0	1.0	1.0	1.0	1.0	1.0	1.0	2.0	2.0	2.0
TBBS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	—	—	—
CBS	—	—	—	—	—	—	—	1.7	1.7	1.7

**Table II** Amounts of HPPD Migrated (%) Depending on Initial Concentration and Temperature

Temperature (°C)	Concentration of HPPD				
	1 phr	3 phr	5 phr	7 phr	9 phr
40°	11.2	10.8	11.2	11.2	10.4
60°	22.4	25.4	27.6	20.2	21.1
80°	50.0	47.9	47.5	50.9	47.2
100°	71.8	70.2	72.8	73.2	70.4

Waals interactions using an inverse 9th-power term for the repulsive part are used. The cutoff distance is 1.00 nm, and distance-dependent dielectric constants are used.

The interaction energies of IPPD with rubbers were calculated as follows. First, IPPD and rubber were assembled into one system under constrained conditions to prevent IPPD from separating from the rubber chain. The constrained conditions applied between IPPD and the rubber chain are 0.5 nm of distance and 1,000 N/cm of force constant. Second, the system with constrained conditions was calculated by minimization after molecular dynamics at 900 K for 1,500 fs, and this process was performed 30 times. The most stable system was obtained from the 30 conformers. Third, the most stable system was reminimized without constrained conditions. Finally, interaction energies such as van der Waals and electrostatic energies between IPPD and rubber chain were calculated.

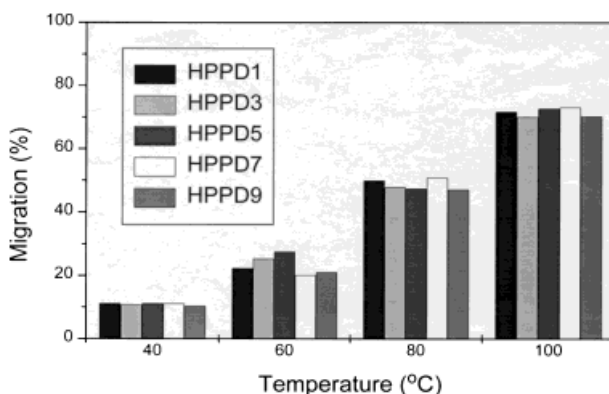
## RESULTS AND DISCUSSION

Using this migration equipment, the migration of antidegradants in rubber vulcanizates to the surface is strikingly accelerated. To investigate the performance of this migration equipment, this migration experiment was compared with a normal thermal aging test under the same conditions of 80°C for 20 h with an NR vulcanizate containing HPPD. The loss of HPPD was about 48% after migration with this equipment, but the loss of HPPD after regular thermal aging was less than 5%.

### Effect of Initial Concentration

NR vulcanizates with added HPPD contents of 1.0, 3.0, 5.0, 7.0, and 9.0 phr corresponding to NR1, NR2, NR3, NR4, and NR5 in Table I, respec-

tively, were prepared to investigate the effect of the initial concentration on migration to the surface of compounded rubber. Migration was carried out at constant temperatures of 40, 60, 80, and 100°C for 20 h. The vacuum pressure for migration was about  $5 \times 10^{-6}$  Torr. The amounts of HPPD that migrated to the surface of an object were determined by the difference of HPPD remaining in the sample before and after migration. The experimental results are represented in Table II. The results listed in Table II are shown in Figure 3 in bar graph form, in which HPPD1, HPPD3, HPPD5, HPPD7, and HPPD9 stand for NR vulcanizates with added HPPD of 1.0, 3.0, 5.0, 7.0, and 9.0 phr, respectively. The amounts of HPPD that migrated at 40, 60, 80, and 100°C were 10.4–11.2, 20.2–27.6, 47.2–50.9, and 70.2–73.2%, respectively, and a specific trend due to initial concentration was not found, as shown in Table II and Figure 3. The migration of HPPD was increased about twice by increasing the temperature from 40 to 60°C and from 60 to 80°C. The fact that the migration is not dependent on the initial concentration of HPPD means that antide-



**Figure 3** Migration of HPPD to the surface of the NR vulcanizate, depending on the initial concentration of HPPD and temperature.

**Table III Migration Rate for HPPD ( $\times 10^6$  %  $s^{-1}$ ) Depending on Initial Concentration and Temperature**

Temperature (°C)	Concentration of HPPD				
	1 phr	3 phr	5 phr	7 phr	9 phr
40°	1.65	1.59	1.65	1.65	1.53
60°	3.52	4.07	4.49	3.13	3.29
80°	9.63	9.06	8.95	9.88	8.87
100°	17.63	16.81	18.08	18.29	16.91

gradants in rubber vulcanizate migrate to the surface by a constant ratio if migration proceeds at the same conditions such as temperature and migration time.

From the fact discussed above, the equation for migration to the surface can be described as follows:

$$C_t = C_0(1 - k)^t \quad (1)$$

where  $C_0$  and  $C_t$  are concentrations of migrant remaining in a sample before and after migration, respectively,  $k$  is the migration rate (%  $s^{-1}$ ), and  $t$  is the migration time in seconds. The migration rates for HPPD obtained from eq. (1) are listed in Table III. The migration rate is increased from 1.53–1.65 to 16.81–18.29  $\times 10^{-6}$  %  $s^{-1}$  by increasing the temperature from 40 to 100°C. This rate,  $k$ , will be used to calculate the activation energy for migration to the surface from the Arrhenius plot.

#### Migration in NR Vulcanizate

The migration of antidegradants such as BHT, IPPD, and HPPD in NR vulcanizates (NR6, NR7, and NR2 in Table I, respectively) was carried out for 20 h at  $5 \times 10^{-6}$  Torr of pressure. BHT, IPPD, and HPPD were migrated from 24.1 to 73.8%, from 23.3 to 82.9%, and from 10.8 to 70.2%, respectively, by increasing the temperature from 40 to 100°C. The amount of migration was decreased under the same conditions by increasing the molecular weight of the antidegradant. BHT ( $m/z$  220) and IPPD ( $m/z$  226) migrated more than HPPD ( $m/z$  268), as shown in Table IV. However, IPPD, with a molecular weight heavier than that of BHT, migrated more than BHT, except at 40°C. The increment of migration for HPPD is larger than those of BHT and IPPD by increasing tem-

perature. The amount of HPPD that migrated is increased by 2.35 times, while that of BHT is increased 1.72 times by increasing the temperature from 40 to 60°C. The degree of increment of migrated antidegradants was reduced by increasing temperature. The increments of migration for BHT, IPPD, and HPPD between 40 and 60°C were 1.72, 1.90, and 2.35 times, respectively. When the temperature was increased from 80 to 100°C, those for BHT, IPPD, and HPPD were reduced by 1.24, 1.27, and 1.47 times, respectively.

The migration rates for antidegradants in NR vulcanizate depending on temperature were calculated from eq. (1) and are listed in Table IV. It is very interesting that the differences of migration rates for IPPD and HPPD are big, considering their molecular weights. Both IPPD and HPPD are antidegradants belonging to *N*-phenyl-*N'*-alkyl-*p*-phenylenediamines. Their only difference is that the molecular weight of HPPD is heavier than that of IPPD by  $C_3H_6$ . The migration rate for IPPD was increased from 3.68 to  $24.53 \times 10^{-6}$  %  $s^{-1}$ , while that for HPPD was increased from 1.59 to  $16.81 \times 10^{-6}$  %  $s^{-1}$  by increasing the temperature from 40 to 100°C. The ratio of the migration rate for IPPD to HPPD is 2.3–1.5 at a temperature of 40–100°C, while the ratio of molecular weight for HPPD to IPPD is only about 1.2.

#### Migration in SBR Vulcanizate

SBR vulcanizates SBR1, SBR2, and SBR3 (Table I), with added antidegradants such as BHT, IPPD, and HPPD, respectively, were prepared. BHT, IPPD, and HPPD migrated from 16.1 to 62.4%, from 13.5 to 75.2%, and from 4.5 to 66.3%, respectively, by increasing the temperature from 40 to 100°C, as demonstrated in Table V. The whole trends for the migration properties of antidegradants in SBR vulcanizates were similar to

**Table IV** Amounts of Antidegradants Migrated in NR Vulcanizate (%) Depending on Temperature

Temperature (°C)	Antidegradant		
	BHT	IPPD	HPPD
40	24.1 (3.83)	23.3 (3.68)	10.8 (1.59)
60	41.5 (7.45)	44.2 (8.10)	25.4 (4.07)
80	59.4 (12.52)	65.4 (14.74)	47.9 (9.06)
100	73.8 (18.60)	82.9 (24.53)	70.2 (16.81)

Values in parentheses are migration rates ( $\times 10^6\% \text{ s}^{-1}$ ).

those in NR ones, as discussed above. The migration increments of antidegradants were reduced by increasing temperature. The increments of migration for BHT, IPPD, and HPPD between 40 and 60°C were 1.98, 2.36, and 3.44 times, respectively, while those between 80 and 100°C were 1.34, 1.46, and 1.73 times, respectively. The increment of migration for HPPD is larger than those for BHT and IPPD. The amount of migration was increased at the same conditions by increasing the molecular weight of antidegradant. Similar to the results of NR vulcanizates, BHT (m/z 220) and IPPD (m/z 226) migrated more than HPPD (m/z 268), as shown in Table V. However, IPPD, with a molecular weight heavier than that of BHT, migrated more than BHT, except at 40°C.

The migration rates for the antidegradants depending on temperature were calculated from eq. (1) and are listed in Table V. IPPD also migrated much more than HPPD in SBR vulcanizate, considering that their molecular weights are similar to the results in NR vulcanizate. The migration rates for IPPD were increased from 2.01 to  $19.37 \times 10^{-6} \% \text{ s}^{-1}$ , while those for HPPD were increased from 0.64 to  $15.11 \times 10^{-6} \% \text{ s}^{-1}$  by increasing temperature from 40 to 100°C. The ratio of mi-

gration rate for IPPD to HPPD is 3.1–1.3 at a temperature of 40–100°C, while the ratio of molecular weight for HPPD to IPPD is only about 1.2.

### Activation Energy

Activation energies for the migration of antidegradants to the surface in rubber vulcanizate were calculated by Arrhenius plot with migration rates. The Arrhenius equation is as shown in eq. (2):

$$k = A \exp(-E_a/RT) \quad (2)$$

where  $k$  is the rate constant,  $A$  is the Arrhenius parameter,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $T$  is the temperature in Kelvin. In this study,  $k$  is the migration rate ( $\% \text{ s}^{-1}$ ), as listed in Tables IV and V. The logarithm of eq. (2) gives

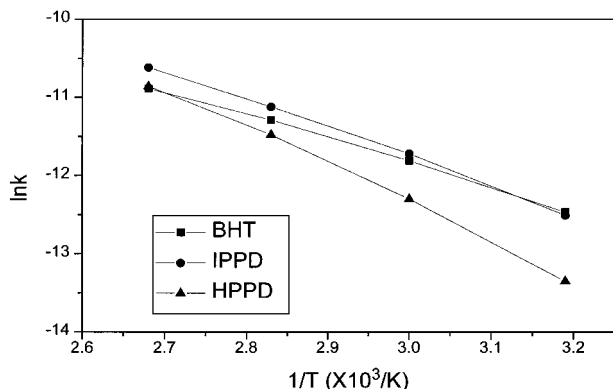
$$\ln k = \ln A - E_a/RT \quad (3)$$

The activation energy can be calculated by multiplying the gas constant to the slope obtained from the Arrhenius plot of  $\ln k$  versus  $1/T$ . Arrhenius plots for the migration of BHT, IPPD, and

**Table V** Amounts of Antidegradants Migrated in SBR Vulcanizate (%) Depending on Temperature

Temperature (°C)	Antidegradant		
	BHT	IPPD	HPPD
40	16.1 (2.44)	13.5 (2.01)	4.5 (0.64)
60	31.9 (5.34)	31.9 (5.34)	15.5 (2.34)
80	46.5 (8.69)	51.5 (10.05)	38.3 (6.71)
100	62.4 (13.59)	75.2 (19.37)	66.3 (15.11)

Values in parentheses are migration rates ( $\times 10^6\% \text{ s}^{-1}$ ).

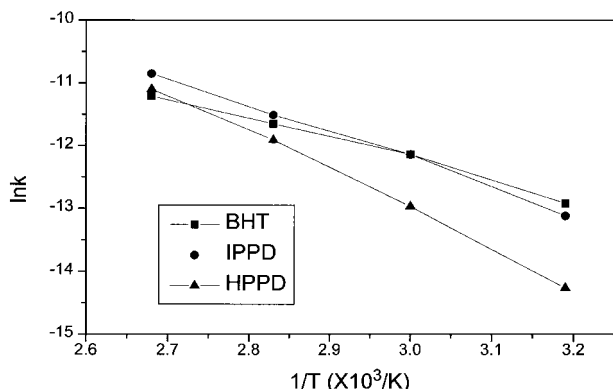


**Figure 4** Arrhenius plot for the migration of antidegradants to the surface in the NR vulcanizate.

HPPD in NR and SBR vulcanizates are graphed in Figures 4 and 5, respectively, and the activation energies calculated from the Arrhenius plot are listed in Table VI. The activation energies for the migration of BHT, IPPD, and HPPD to the surface of the NR vulcanizate were 25.8, 30.7, and 38.6 kJ/mol, respectively, while the activation energies with the SBR vulcanizate were 27.6, 36.5, and 51.7 kJ/mol, respectively. The activation energy for BHT is less than those for IPPD and HPPD. The migrations for BHT, IPPD, and HPPD in the NR vulcanizate require less activation energy than those in the SBR one.

#### Effect of Base Rubber

The migration of antidegradants to the surface in NR vulcanizates was faster than that in SBR ones, as demonstrated in Tables IV and V. The diffusion coefficients of organic additives such as



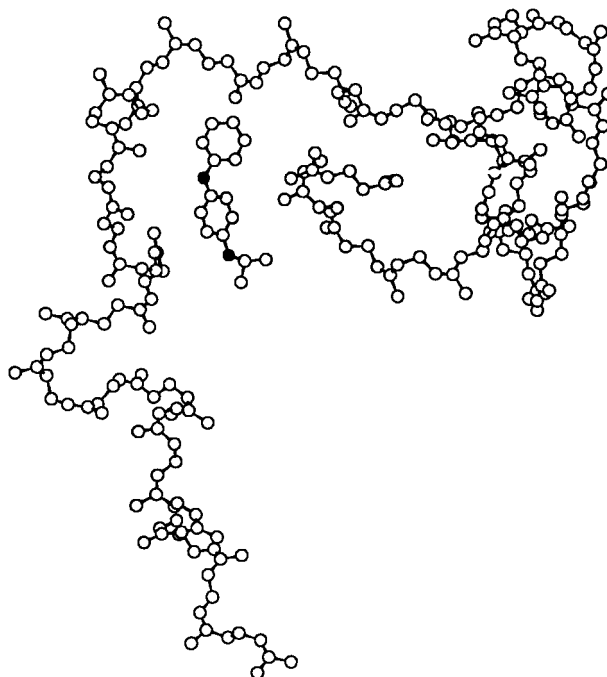
**Figure 5** Arrhenius plot for the migration of antidegradants to the surface in the SBR vulcanizate.

**Table VI** Activation Energy for Migration of Antidegradants in Rubber Vulcanizates (kJ/mol)

Vulcanizate	Antidegradant		
	BHT	IPPD	HPPD
NR	25.8	30.7	38.6
SBR	27.6	36.5	45.3

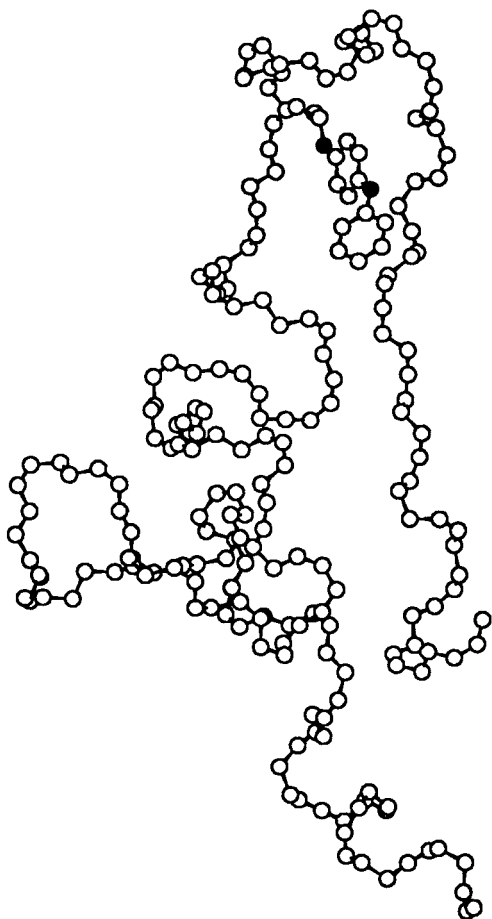
phenolic-type antioxidants and sulfenamide-type accelerators in the NR vulcanizate are larger than those in SBR one.<sup>9</sup> The ratios of migration rates in NR to SBR vulcanizates are 1.18–1.50, 1.10–1.73, and 1.06–2.40 for BHT, IPPD, and HPPD, respectively. The lower the migration temperature, the higher the ratio of migration rates in NR to SBR, because interactions of antidegradants with matrix (rubber, carbon black) are reduced by increasing temperature.

For the elucidation of the difference of migration properties between NR and SBR vulcanizates, the characteristics of NR and SBR poly-

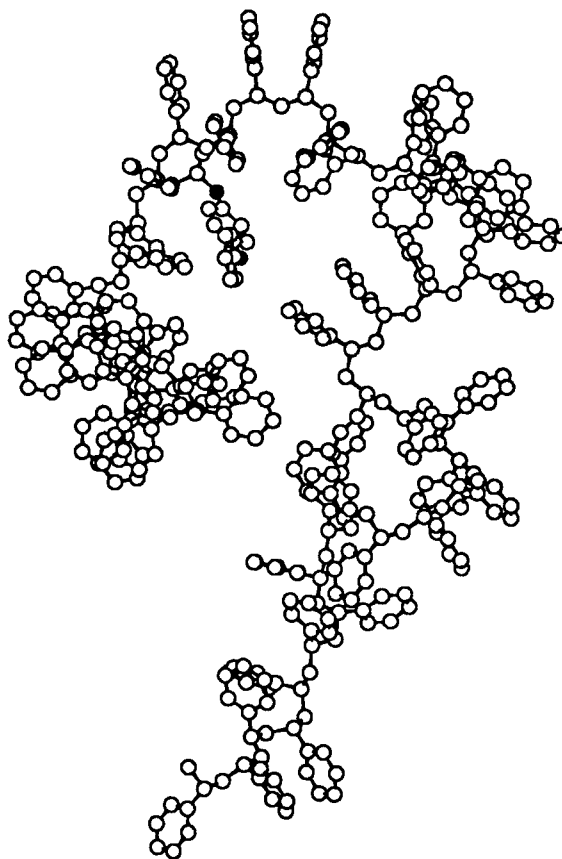


**Figure 6** Interactive skeletal structure of IPPD with *cis*-1,4-polyisoprene, obtained from calculations. Closed circles in IPPD stand for nitrogen atoms. The interaction energy of IPPD with *cis*-1,4-polyisoprene is  $-73.7$  kJ/mol.

mers themselves are considered. Interactions between IPPD and rubbers such as *cis*-1,4-polyisoprene, *cis*-1,4-polybutadiene, and polystyrene were representatively calculated by molecular mechanics and molecular dynamics to explain the difference between NR and SBR vulcanizates, as discussed above. Interactive skeletal structures between IPPD and *cis*-1,4-polyisoprene, *cis*-1,4-polybutadiene, and polystyrene obtained from calculations are shown in Figures 6, 7, and 8, respectively. Closed circles in Figures 6–8 stand for nitrogen atoms of IPPD, which is displayed with only the heavy atoms of carbons and nitrogens. Interaction energies between IPPD and *cis*-1,4-polyisoprene, *cis*-1,4-polybutadiene, and polystyrene are  $-73.7$ ,  $-69.7$ , and  $-148.7$  kJ/mol, respectively. The interaction of IPPD with *cis*-1,4-polyisoprene is stronger



**Figure 7** Interactive skeletal structure of IPPD with *cis*-1,4-polybutadiene, obtained from calculations. Closed circles in IPPD stand for nitrogen atoms. The interaction energy of IPPD with *cis*-1,4-polybutadiene is  $-69.7$  kJ/mol.



**Figure 8** Interactive skeletal structure of IPPD with polystyrene, obtained from calculations. Closed circles in IPPD stand for nitrogen atoms. The interaction energy of IPPD with polystyrene is  $-148.7$  kJ/mol.

than that with *cis*-1,4-polybutadiene (only 4 kJ/mol) but much weaker than that with polystyrene (about 75 kJ/mol). SBR 1500 is composed of 23.5% styrene and 76.5% butadiene by weight. The interaction between IPPD and SBR is stronger than NR because IPPD strongly interacts with styrene; however, the interaction between IPPD and *cis*-1,4-polybutadiene is weaker than *cis*-1,4-polyisoprene. Thus, IPPD in NR vulcanizate migrates faster than in SBR vulcanizate.

## CONCLUSIONS

Migration-generating equipment using a vacuum technique was constructed to measure the migration of antidegradants in rubber vulcanizate in a short time. The migration of antidegradants in rubber vulcanizates to the surface with this equipment is accelerated about 10 times more than that



with a regular thermal aging test. It was found from the results for migration with NR vulcanizates with added HPPD of 1.0, 3.0, 5.0, 7.0, and 9.0 phr that the migration of antidegradants was independent of the initial concentrations of antidegradants. Among the migrations for BHT, IPPD, and HPPD in both NR and SBR vulcanizates, the fastest ones are IPPD at 60–100°C and BHT at 40°C, while the slowest one is HPPD, the migration rate of which is more increased than the other ones by increasing temperature. Activation energies for migration to the surface of NR vulcanizate were 25.8, 30.7, and 38.6 kJ/mol, while those in the SBR vulcanizate were 27.6, 36.5, and 51.7 kJ/mol for BHT, IPPD, and HPPD, respectively. Migration in the NR vulcanizate is faster than in the SBR one. This is because interactions between antidegradants and NR are weaker than those with SBR. The interactions between IPPD and polymers such as *cis*-1,4-polyisoprene, *cis*-1,4-polybutadiene, and polystyrene were calculated by molecular mechanics and dynamics to explain the interactions of antidegradants with rubbers such as NR and SBR. The interaction of IPPD with polystyrene is much stronger than that with *cis*-1,4-polyisoprene and *cis*-1,4-polybutadiene.

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