Diffusion of Amine Stabilizers in Vulcanized Natural Rubber Compositions Used in Tires

DUCLERC F. PARRA, MARIA TERESA DE A. FREIRE, MARCO-A. DE PAOLI

Laboratório de Polímeros Condutores e Reciclagem, Instituto de Química, Unicamp,
C. Postal 6154, 13083-970 Campinas, SP, Brazil

ABSTRACT: The diffusion of amine stabilizers in vulcanized natural rubber formulations used in tires was investigated. Experiments were undertaken using a "sandwich" system composed of a sample disk containing the additive (source disk) between two external disks of nonadditivated rubber (reception disks). Diffusion coefficients (D) were calculated from the experimental migration curves following the Boltzman–Matano model. Theoretical diffusion curves for the additives were obtained according to the limited extension source in an infinite medium. Experimental data showed reasonable fitting with the theoretical curves, suggesting that D does not depend on the additive concentration. Thermooxidative stability data for the vulcanized rubber containing the additives showed no correlation to the diffusion process. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 670–676, 2000

Key words: amine stabilizers; vulcanized natural rubber; diffusion; tires

INTRODUCTION

The tire is a complex system of interacting components including rubber compounds, fabrics, chemicals, and metal, where each component has an specific function in order to provide the desired performance. Rubber compounds are composed of natural rubber, carbon black, antioxidants, and a curing system with a sulfur component. Physical properties of the compound and the final tire performance depend upon processing conditions and the type and ratios of the ingredients that compose each component formula. The compound is formulated to provide good adhesion and tear, fatigue, and aging resistance.[1] Formulations also vary according to the final product geometry and the intended use.

The performance of a tire is evaluated according to the physical characteristics of the vulca-nized compound when exposed to several conditions of temperature, atmosphere, and fatigue. Generally, tests involving traction, compression, and flex fatigue are applied in accelerated aging conditions, giving information on the behavior of the compounds during the tire lifetime.

It has been demonstrated that the reaction between residual nonsaturated bonds of the vulcanized rubber and oxygen and/or ozone produces fatigue when compared to samples submitted only to mechanical deformation under a vacuum or an inert atmosphere.[2,3] The occurrence of fissures in nonadditivated natural vulcanized rubber exposed to an oxidative atmosphere is four times faster when compared to an inert atmosphere (N_2).[4] Oxidation promoted by ozone takes place very quickly, meaning that its penetration in the tire surface is enough to cause fissures even in a small distance. The rate of the reaction of oxygen with rubber is slow, but its diffusion is fast, causing an uniform degradation inside the compound. The flex-fatigue time can be reduced when deformation is applied under a vacuum (10^{-2} Torr).[5]

Some of the additives incorporated into the formulations, such as antioxidants, improve rubber stability, reducing damage of the internal parts of the tire due to mechanical solicitation and local heat dissipation. Flex fatigue of the external elements of the tire, such as the tread and sidewall, promoted by ozone can also be controlled using antioxidants.[2,6,7]

In spite of the benefit of additives in rubber compounds, some researchers have shown that there is a tendency of some stabilizers to distribute among tire parts, reaching an equilibrium concentration. The migration of additives is affected by the polymer structure, presence of fillers, molar mass, and temperature.[8–11] The phenomenon of diffusion in rubber formulations has generated controversy about its consequences for the tire performance. Some authors suggested that the physical properties after aging are not affected by the diffusion of additives.[12] Nevertheless, it has been verified that migration of the stabilizer from a tire element to its outside area, due to the diffusion process, can increase the antioxidant effective concentration, intensifying the resistance to degradation for that region. On the other hand, diffusion through rubber–rubber interfaces can be inconvenient, causing changes in the distribution of the additives, producing stain in colored products, as well as resulting in loss of physical properties, such as adhesion and antidegradation protection.[13–16] Also, antioxidants diffusing to the outer part of the tire can be leached out or be lost by evaporation at sufficiently high temperatures. In addition, storage conditions and time can also affect the functional properties of rubber compounds, since reduction of antioxidant efficiency is related to its participation in oxidation reactions at the surfaces.

Mathematical models used to predict diffusion coefficients are generally based on Fick's laws.[17] Research on liquid transport in natural rubber matrices has shown that the sorption equilibrium decreases linearly with the increase in molar mass of the diffusing species.[18] Profiles of the diffusion of solid accelerators in a natural rubber crude matrix indicated that the rate of diffusion decreases with increasing molar mass of the diffusing species. It is also found that temperature activates the phenomenon of diffusion, following the Arrhenius equation.[19]

The aim of this work was to evaluate the diffusion of commercial stabilizers in a vulcanized rubber formulation used in tires and the effects of this phenomenon on the physical properties of the product. In addition, mathematical models applied to the experimental diffusion data are employed to determine the lifetime of the rubber composition.

EXPERIMENTAL

Materials

The natural rubber used was of SMR-L grade. The carbon black was HAF (N110, Coperbo). Commercial amine additives were 3,3′-dioctylphenylamine (OCDP) and 5,5′-dimethyl-5,10-dihydroacridine (ADPA) from Uniroyal; phenyl-2-naphthylamine (PBN) from Bayer; N-isopropyl, N′-phenyl-p-phenylenediamine (IPPD) from Monsanto; N-N′diphenyl-p-phenylenediamine (DPPD) from Bann Quimica; and N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine (HPPD) from Monsanto. The chemical structures and acronyms of the additives are shown in Figure 1.

Formulations

The formulations used for the additive migration experiments are given in Table I. The mixture was processed in two stages in a laboratory Banbury mixer of 2-L capacity. In the first stage, natural rubber, carbon black, and zinc oxide were mixed at a temperature of 140°C for 4 min. In the second stage (ultimate mixing), sulfur, stearic acid, and the stabilizer were added at 90°C for 1 min. The compound containing the stabilizer is described as the source matrix and the others are called the reception matrices. Concentrations of stabilizers in the rubber compound are given in parts per hundred rubber (phr), as routinely used in the tire industry. Disks of 7-mm diameter and 10-mm thickness were vulcanized by pressing at 151°C for 40 min in a laboratory hot press.

Diffusion System

The diffusion system was assembled by placing a source disk between two reception disks. The set was wrapped in aluminum foil and kept under slight pressure at room temperature. After 7, 14, 21, and 28 days, the systems were disassembled and the reception disks were cut into thin slices of an average thickness of 1 mm.

Extraction and Quantification of Additives

The slices were cut into small pieces and stabilizers were extracted with acetone in a Soxhlet am-
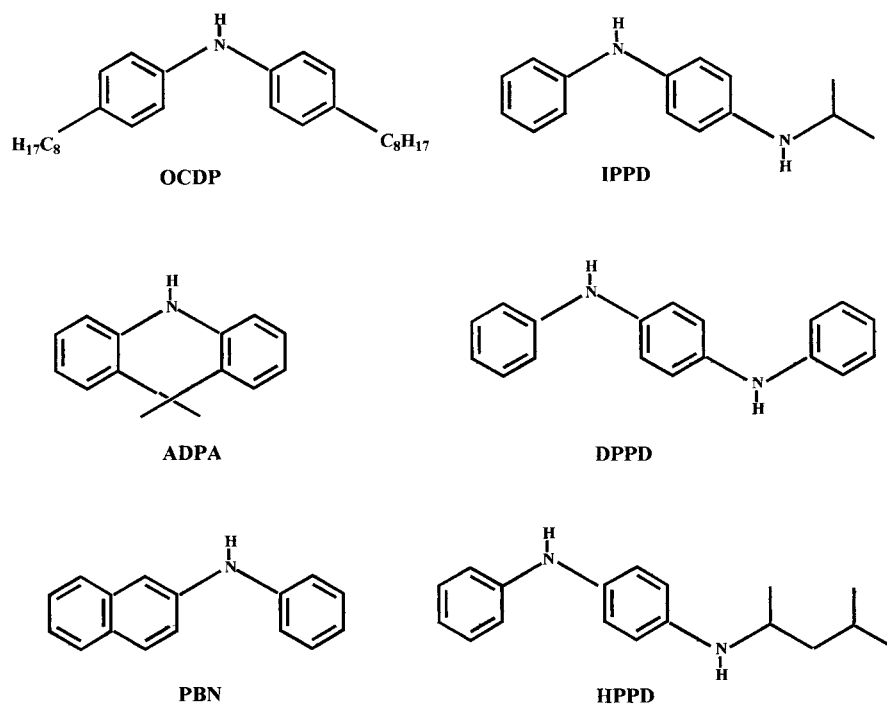
Figure 1   Structure and acronyms of the additives studied in this work.

ber apparatus for 16 h. Stabilizers were quantified by gas chromatography (GC) using an HP5730 instrument coupled to a flame-ionization detector (maintained at 300°C); nitrogen was used as carrier gas at 30 mL/min; the injection port was maintained at 250°C; the column was programmed from 160 to 260°C, with a heating rate of 4°C min^{-1}; an analytical glass column of 2 m × ¼ in.-i.d. was coated with Chromosorb WAW-DMCS and 8% Dehesil 300; and sample injections were of 2 μL.

Determination of Diffusion Coefficients

The stabilizer diffusion coefficients were calculated following the Boltzmann–Matano model[20]

Table I   Formulation of Rubber Compounds Studied in This Work

Components	Concentration (phr)
Natural rubber	100
Stearic acid	1.0
Zinc oxide	4.0
HAF carbon black	50.0
Sulfur	2.0
Stabilizer	3.0
MOR[a]	1.0

The reception matrix has the same formulation without the stabilizer. phr, Parts per hundred.
[a] Morpholine benzothiazol sulfenamide.

under the experimental curves of concentration distribution (concentration versus distance from the center of the matrix) and according to eq. (1), where $D(c)$ is the diffusion coefficient at distance x (cm) in cm^2 s^{-1}; t, the diffusion time in s; dc/dx, the concentration gradient at c; and xdc, the area under the diffusion curve limited by the concentration (%) range 0–c:

$$D(c) = \frac{-1\displaystyle\int_0^c xdc}{2t \; dc/dx} \qquad (1)$$

The theoretical curves were calculated following the equations describing the diffusion in a limited extension to an infinite extension model, according to eq. (2), where C_0 is the initial concentration; $2h$, the extension of the matrix; and t, the migration time. The error function erf z is a standard mathematical function, of which extensive tables are available.[21] In this equation, $\eta = \xi/2 (Dt)^{1/2}$. It considers the diffusing substance in an element of width $d\xi$:

$$C(x, t) = \frac{C_0}{2}\left(\text{erf} \, \frac{h - x}{2(Dt)^{1/2}} + \text{erf} \, \frac{h + x}{2(Dt)^{1/2}} \right) \qquad (2)$$

$$\text{erf} \, z = \frac{2}{\pi^{1/2}} \int_0^z \exp(-\eta^2)d\eta \qquad (3)$$

Figure 2 Migration profile for two monoamine additives: (a) ADPA and (b) OCDP after (●) 7, (+) 14, (*) 21, and (□) 28 days.
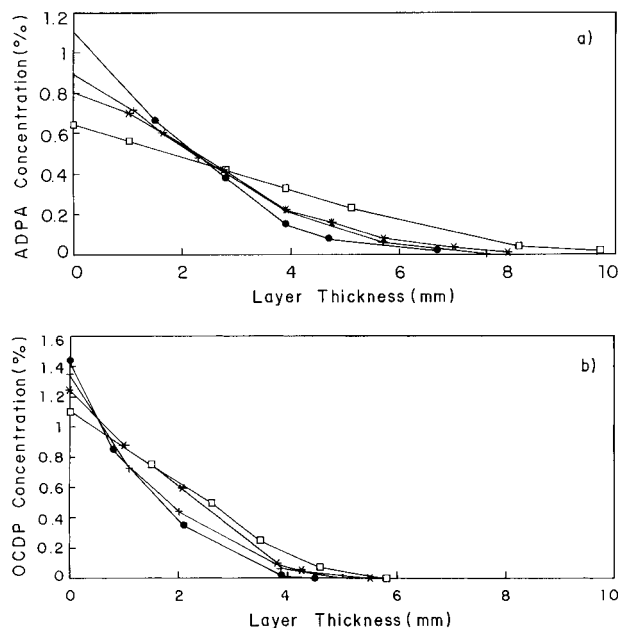

Figure 3 Migration profile for two diamine additives: (a) IPPD and (b) HPPD after (●) 7, (+) 14, (*) 21, and (□) 28 days.

Physical Tests

Thermooxidative resistance of the formulations was measured by means of the oxidation induction time (OIT) using differential scanning calorimetry (DSC)—TA DuPont Model 1090 A. The stabilizer added to crude natural rubber samples (0.5:100) was mixed in a laboratory roll-mill at 20°C. An encapsulated sample of 4–5 mg was then heated in the DSC oven to 180°C under N_2 (40°C/min) and analyzed under an O_2 atmosphere under isothermal conditions. The OIT was the time registered at the onset of the exothermic oxidation reaction.

RESULTS AND DISCUSSION

The diffusion profiles for the monoaminic and diaminic stabilizers are shown in Figures 2 and 3, respectively. There was a migration of the additives along the whole thickness of the reception disks in the 28 days of the experiment. The figures show the expected behavior, with a higher concentration of the additive near the surface of the reception disk after 7 days and an increasing diffusion toward the bulk of the disk, reaching about to 10 mm for ADPA [Fig. 2(a)], 6 mm [Fig. 2(b)] for OCDP (monoaminic stabilizers), 8 mm
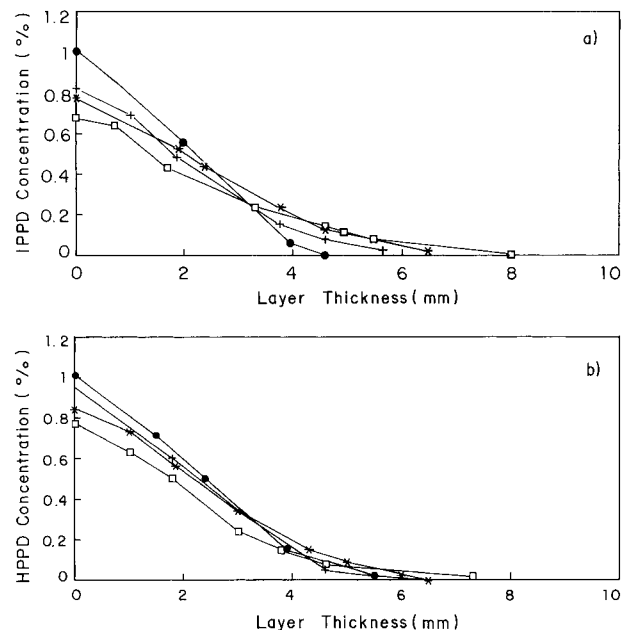
for IPPD [Fig. 3(a)], and 7 mm for HPPD [Fig. 3(b)] (diaminic stabilizers) after 28 days of contact time.

Although the diffusion behavior was similar for all the additives, data obtained for the monoaminic stabilizers show faster migration of ADPA in relation to OCDP, which strongly suggests that the molar mass is the driving force of the diffusion process for these migrating species of similar chemical structures (Fig. 2). A similar trend can be observed between the diaminic stabilizers IPPD and HPPD (Fig. 3). Comparable data were obtained for the diaminic stabilizer IPPD and

Table II   Stabilizers, Molar Mass (MM), Diffusion Coefficients (*D*), and OIT for the Formulations with the Stabilizers Used in This Work (0.5 phr)

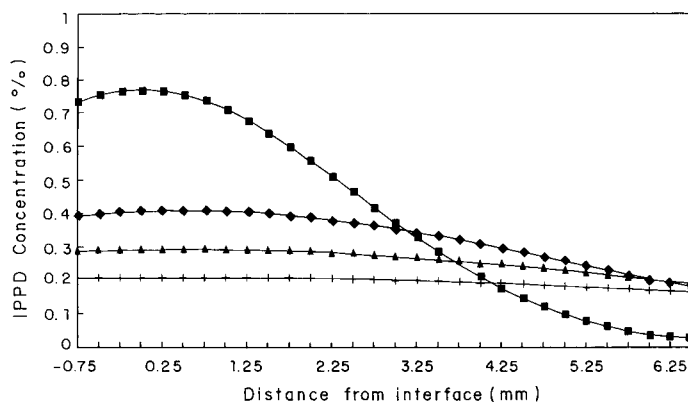| Stabilizer	MM	D (10^{-8} cm^2 s^{-1})	OIT (min)
ADPA	209	1.7 ± 0.2	12.2
PBN	219	1.38 ± 0.03	12.1
OCDP	393	0.65 ± 0.04	9.5
IPPD	226	1.3 ± 0.3	30.8
HPPD	268	1.12 ± 0.07	44.4
DPPD	260	1.15 ± 0.04	65.0
None	—	—	5.5

Figure 4   Calculated curves for diffusion of IPPD in vulcanized rubber after (■) 21, (♦) 90, (▲) 180, and (+) 360 days.

monoaminic stabilizer ADPA with similar molar masses. This is a strong indication that the molar mass more markedly affects the migration of the additive than does the number of amine groups.

The diffusion coefficients (D) calculated from the migration experiments are shown in Table II. A log/log plot of D versus the molar mass indicates $D \propto (\mathrm{MM})^{-1.4}$, indicative of the effect of the molar mass of the additive on its migration in the rubber matrix. The table also shows similar diffusion coefficients for monoaminic and diaminic stabilizers with similar molar masses. The calculated data confirm the experimental results, showing the effect of the molar mass upon the diffusion. Theoretical curves for diffusion were obtained from the calculated values of D for a

period of 21 days. The correlation factors between theoretical and experimental curves, calculated using the square method, were higher than 0.96 for all additives tested, suggesting that D is independent of concentration.

Knowledge of the diffusion properties of the additives used in the tire formulations can be very useful to predict the lifetime of the rubber compounds used. Stabilizers with a high diffusion coefficient migrate to the rubber surface, providing protection from ozone and heat. The less mobile stabilizers tend to be retained in the bulk of the rubber matrix, providing long-term stabilization. Nevertheless, long-term storage can reduce the tire lifetime due to losses by volatilization of the high diffusion coefficient additives, especially
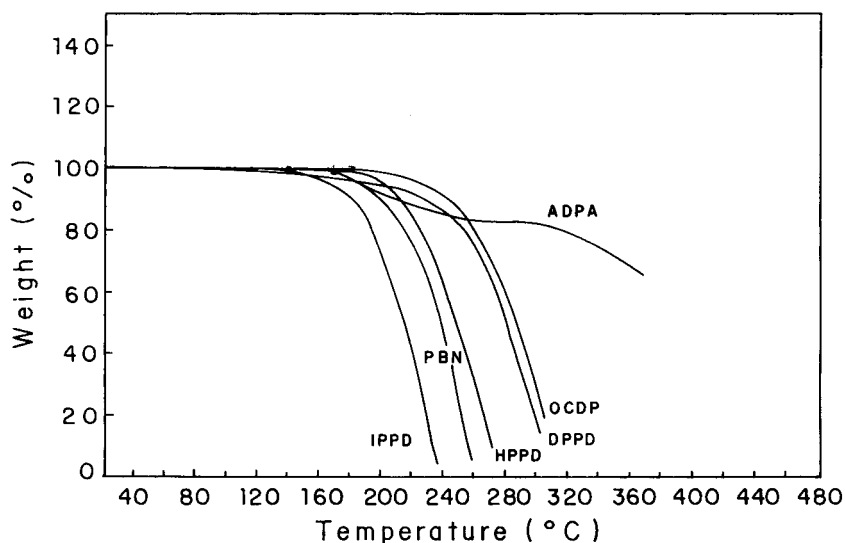

Figure 5   Thermogravimetric analysis for the additives used in the rubber compositions.

Table III   TGA Results for the Stabilizers

Stabilizer	Mass Loss Onset Temperature (°C)
None	153
ADPA	180
OCDP	200
PBN	190
HPPD	214
IPPD	160
DPPD	217

for tires stored in warm warehouses, as normally occurs in tropical and subtropical areas.

The Matano modeling method was employed to predict the diffusion of the stabilizers for long periods of time and the migration profiles were calculated for 360 days. The results obtained for IPPD are shown in Figure 4. The calculated distribution of the stabilizer after 90 days of storage tends to be uniform along 6.3 mm, and after 360 days of storage time, the stabilizer is homogeneously distributed along the rubber matrix. Sim-

ilar profiles were obtained for the other stabilizers used in this work. Despite the amine stabilizer used, storage periods longer than 360 days can lead to losses of additives due to migration to the surface of the rubber compound and volatilization.

Prior to studying the thermal stability of the rubber formulations, we obtained the thermogravimetric curves for the additives in the form of powders (Fig. 5). This was done to determine its onset temperature of thermal degradation (Table III). From Figure 5 and Table III, we observe that all additives are stable up to 150°C under an atmosphere of air. There is no correlation between the thermal stability of the additive and its molar mass or amine group content; however, all additives are stable at the temperature chosen for the OIT determination.

The thermal stability for all the rubber formulations, obtained using OIT experiments, after aging the samples at 100°C, is shown in Table II. The onset temperatures of oxidation showed that all the stabilizers improved the thermal resis-
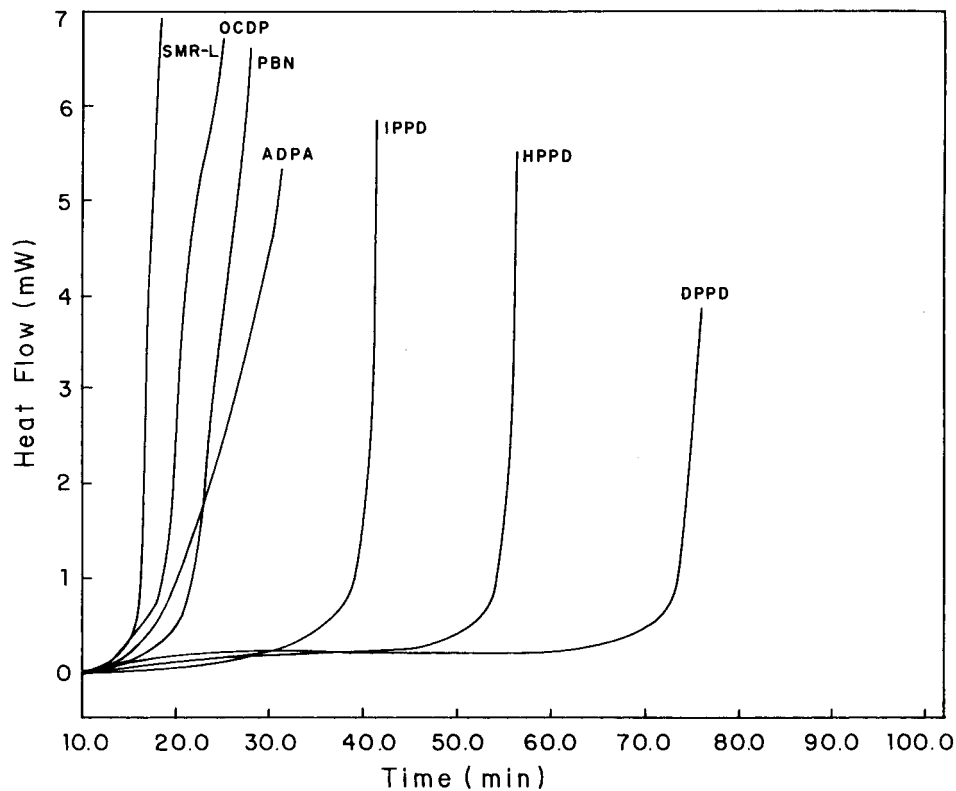

Figure 6   OIT analysis for the different rubber compositions studied in this work. Stabilizer used is indicated in the figure. Curve labeled SMR-L is for a nonstabilized sample.

tance of the vulcanized rubber when compared to a sample formulation without an additive. DPPD was the most effective additive, under the aging conditions studied, with the higher OIT value. OCDP showed an inferior performance in relation to all other additives. The OIT curves (Fig. 6) also show a better performance of diamines (OIT in the range from 30.8 to 65.0 min) in relation to the monoamine stabilizers (OIT in the range from 9.5 to 12.2 min). This behavior is associated to the action mechanism of the amines as radical scavenger stabilizers and hydroperoxide decomposers. Thus, they are considered as chain-terminator agents in a free-radical reaction caused by heat damage and oxidation processes. In addition, the diamines react with end-groups of disrupted chains, promoting regeneration of the chemical bond between chains.[22] Hydrogen bonded to the amine group of the additives can react with the macroradicals; thus, the diamine stabilizers would be expected to be more efficient, as demonstrated by the OIT results.

CONCLUSIONS

The diffusion of stabilizers in the natural rubber-vulcanized matrix exhibited Fickian behavior. The diffusion coefficients did not change with the stabilizer concentration; however, they are related to the molar mass of the stabilizer as $D \, \alpha$ $(MM)^{-1.4}$. Stabilizers providing the same thermoxidative resistance, evaluated according to the OIT determination by DSC analysis, can demonstrate different diffusion-rate values. These results strongly suggest that a comparison between these two variables is important when evaluating stabilizer formulations for vulcanized rubber materials.

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