Wax Barrier Effect on Migration Behaviors of Antiozonants in NR Vulcanizates

Sung-Seen Choi[†]

Kumho Research and Development Center 555, Sochon-dong, Kwangsan-gu, Kwangju 506-040, Korea

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천연고무 가류물에서 왁스막이 오존노화방지제의 이동에 미치는 영향

최 성 신

(주)금호타이어연구소

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ABSTRACT : Waxes compounded into rubber migrate to the surface and form a protection film on the rubber surface. In general, antiozonants were used with wax to protect ozonation of rubber. Influence of wax barrier formed on the surface of a rubber vulcanizate on migration of antiozonants was studied using natural rubber (NR) vulcanizates containing various type waxes. IPPD (N-isopropyl-N'-phenyl-p-phenylenediamine), HPPD (N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine), SBPPD (N,N'-di(sec-butyl)-p-phenylenediamine), and DMPPD (N,N'-di(1,4-dimethylpentyl)-p-phenylenediamine) were employed as antiozonants. Migration experiments were performed at constant temperatures of 60 and 80℃ for 10, 20, 30 days using a convection oven. The migration rates of the antiozonants in the vulcanizate without wax are faster than those in the vulcanizates containing waxes. The antiozonants migrate slower in the vulcanizate containing wax with a high molecular weight distribution than in the vulcanizate with a low one. The migration rates of DMPPD and SBPPD are faster than those of HPPD and IPPD.

요 약 : 고무와 혼합된 왁스는 고무 표면으로 이동하여 방어막을 형성한다. 일반적으로 고무의 오존화를 방지하기 위해 오존노화방지제를 왁스와 함께 사용하고 있다. 다양한 종류의 왁스가 첨가된 천연고무 가류물을 이용하여 왁스막이 오존노화방지제의 이동에 미치는 영향을 연구하였다. 오존노화방지제로 IPPD (N-isopropyl-N'-phenyl-p-phenylenediamine), HPPD (N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine), SBPPD (N,N'-di(sec-butyl)-p-phenylenediamine), 그리고 DMPPD (N,N'-di(1,4-dimethylpentyl)-p-phenylenediamine)를 사용하였다. 노화방지제 이동 실험은 60℃와 80℃에서 10, 20, 30일간 실시하였다. 노화방지제의 이동속도는 고무가류물에 왁스가 없을 때가

[†]대표저자(*e-mail : sschoi@swan.kumho.co.kr*)

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있을 때보다 빨랐으며 분자량이 큰 왁스가 혼합되었을 때가 분자량이 작은 왁스가 혼합되었을 때보다 느렸다. DMPPD와 SBPPD의 이동속도가 HPPD와 IPPD의 이동속도보다 빨랐다.

Keywords : migration, wax barrier, antiozonants, rubber vulcanizate.

I. Introduction

Ozone attack on rubber compounds causes characteristic cracking perpendicular to the direction of applied stresses. This degradation is caused by reaction of ozone with the double bonds in the rubber chains. These reactions lead to chain scission and the formation of various decomposition products. 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 secondary alkyl).[1,2]

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.[1,3,4] The protective 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.[3] The relinking theory states that the antiozonant prevents scission of the ozonized rubber or else recombines severed double bonds.[5] Currently, the most accepted mechanism of antiozonant action is a combination of the scavenger and protective film theories.[6,7]

In the previous works,[8-11] the influences of initial concentrations of antidegradants in a rubber vulcanizate, kinds of rubber, and fillers (silica and carbon black) on the migration behaviors of antidegradants in rubber vulcanizates were studied. Migration of antiozonants to the surface in a rubber vulcanizate is independent of their initial concentrations. Their migration rates in NR vulcanizates are faster than in SBR ones.[8] Migration rates of antidegradants become slower by increasing the filler content in a filled rubber vulcanizate.[9-11] Silica makes migration of the antidegradants slow by intermolecular hydrogen bonds between silica and antidegradants.[9]

It is generally agreed that waxes compounded into rubber are capable of migrating to the surface, thereby providing protection against ozone attack by formation of an impervious barrier. The ability of a wax to migrate to the surface depends upon the wax type, the rubber composition, and the time and temperature before and during exposure to ozone. These parameters influence the solubility and mobility characteristics of each wax.[12] In general, substituted *papa*-phenylenediamine antiozonants were used with wax to protect ozonation of rubber.[13] In this study, the influence of wax barrier on migration of antiozonants to the surface in a rubber vulcanizate was studied with NR vulcanizates containing various type waxes.

II. Experimental

In order to investigate the influence of wax on the migration of antiozonants to the surface in a rubber vulcanizate, sixteen carbon black-filled NR compounds containing three kind waxes were prepared. The waxes have a different molecular weight distribution each other as shown in Figure 1. The Wax-H has a higher molecular weight distribution than the Wax-M and Wax-L. The contents of waxes in the compounds were 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 phr. IPPD (N-isopropyl- N'-phenyl- p-phenylenediamine), HPPD (N-1,3-dimethylbutyl- N'-phenyl- p-phenylenediamine), SBPPD (N,N'-di(sec-butyl)- p-phenylenediamine), and DMPPD (N,N'-di(1,4-dimethylpentyl)- p-phenylenediamine) were used as antiozonants. IPPD and HPPD are the same species of N-alkyl- N'-phenyl- p-phenylenediamines while SBPPD and DMPPD are the same species of N,N'-dialkyl- p-phenylenediamines. Figure 2 shows the structure of the antiozonants. The formulations were given in Table 1. N-tert-Butyl-2-benzothiazole sulfenamide (TBBS) was used as a curing accelerator. The NR vulcanizates were prepared by curing at 160℃ for 15 minutes.

The migration experiments were carried out at constant temperatures of 60 and 80℃ for 10,
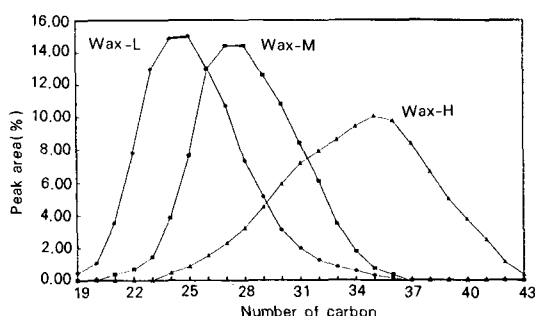

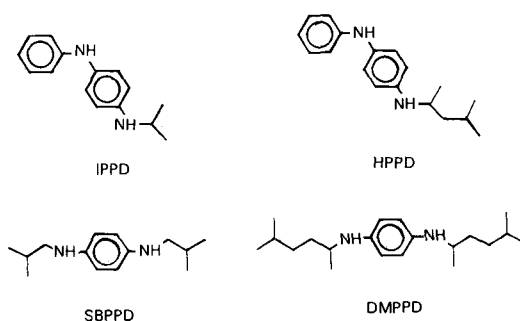Fig. 1. Molecular weight distributions of waxes.

Fig. 2. Formulae of antiozonants.

Table 1. Formulations of Compounds (phr)

Compound No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SMR 20	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
N330	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Wax-L	0.0	1.0	2.0	3.0	4.0	5.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Wax-M	0.0	0.0	0.0	0.0	0.0	0.0	1.0	2.0	3.0	4.0	5.0	0.0	0.0	0.0	0.0	0.0
Wax-H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	2.0	3.0	4.0	5.0
IPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
HPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
SBPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
DMPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	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	2.0	2.0	2.0	2.0	2.0	2.0
TBBS	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

20, and 30 days in a convection oven. The a-
mounts of the antiozonants migrated to the sur-
face in the NR vulcanizate were determined by
the difference between the amounts of the
antiozonants remained in the rubber vulcanizates
before and after migration. The amounts of the
antiozonants remaining in the rubber vulcaniz-
ates were measured by gas chromatography
after extraction of the antiozonants with THF.
The experiments were carried out three times
and averaged.

III. Results and Discussion

The amounts of SBPPD migrated to the sur-
face in the vulcanizates at 60℃ for 10 days
are more than 80% and the SBPPD is detected
by trace after the migration at 60℃ for 20
days. The amounts of SBPPD migrated to the
surface in the vulcanizates at 80℃ for 10 days
are above 90% and those of DMPPD migrated
at 80℃ for 20 days are about 99%. Migration
rates of the antiozonants at 80℃ are much
faster than those at 60℃. The migration rates
of the antiozonants are slower in the case of
the vulcanizates contain waxes comparing with
the vulcanizates without wax.

1. Influence of the wax content

Figure 3 shows the variation of the amounts
of HPPD that migrated to the surface at 60
and 80℃ for 20 days with the wax content. A-
mounts of HPPD that migrated to the surface
at 80℃ are much more than those at 60℃ by
above 5 times. However, Figure 3 does not
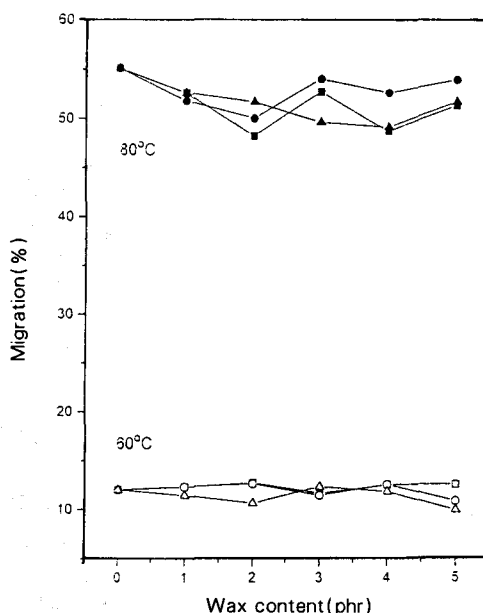show a specific trend depending on the wax

Fig. 3. Variation of amounts of HPPD that migrat-
ed to the surface in the NR vulcanizates at
60 and 80℃ for 20 days as a function of
the wax content. Solid and open symbols in-
dicate 80 and 60℃, respectively. Squares,
circles, and triangles stand for the Wax-L,
Wax-M, and Wax-H, respectively.

content except the Wax-H. The amounts of
HPPD that migrated in the vulcanizates contain-
ing the Wax-H at 80℃ decrease by increasing
the wax content. The migration behaviors of
IPPD in the vulcanizates containing the Wax-H
at 80℃ also show the similar trend. The varia-
tions of the other antiozonants depending on the
wax content also do not show a specific trend.
This may be due to the weak intermolecular in-
teraction of the antiozonants with the wax.

The intermolecular interactions between mi-
grants and matrices of rubber and filler are
principal factors influencing on the migration of
antiozonants in a rubber vulcanizate.[8-11] The mi-
gration rates of migrants become slower and

slower as the intermolecular interactions become stronger and stronger. If the thickness of the wax film affects largely the migration behaviors of the antiozonants, their migration rates will be slower by increasing the content of wax in the vulcanizates from 1.0 to 5.0 phr. But, the migration behaviors do not show a specific trend with the content of the wax as discussed above. Thus, it can lead to a conclusion that the thickness of the wax film hardly affects migration of the antiozonants in the vulcanizates at the high temperatures of 60 and 80 ℃.

2. Influence of the wax type at 60 ℃

The amounts of the antiozonants that migrated in the vulcanizates containing waxes (Compounds 2-16) are, on the whole, less than those in the vulcanizate without wax (Compound 1). Figures 4, 5, and 6 give the variations of amounts of IPPD, HPPD, and DMPPD that migrated in the vulcanizates at 60 ℃ as a function of the migration time. The amounts of the antiozonants migrated increase linearly with an increase of the migration time. The amounts of the antiozonants that migrated in the vulcanizates containing the wax having the high molecular weight distribution are, on the whole, less than those in the vulcanizates containing the wax having the low one. For example, the amounts of IPPD that migrated in the vulcanizates containing the Wax-L, Wax-M, and Wax-H at 60 ℃ for 20 days are 33.6, 32.9, and 31.4%, respectively, those of HPPD are 12.3, 11.9, and 11.2%, respectively, and those of DMPPD are 63.1, 62.5, and 60.9%, respectively.

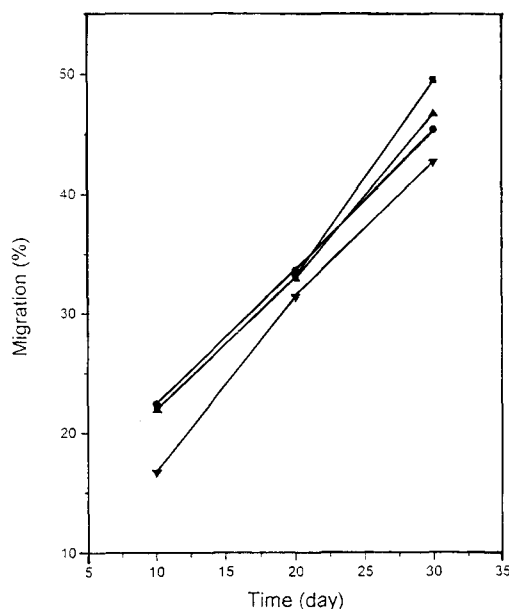The migration rates of the antiozonants in the

Fig. 4. Variation of amounts of IPPD that migrated to the surface in the NR vulcanizates at 60 ℃ as a function of the migration time. Squares, circles, up-triangles, and down-triangles indicate the Non-Wax, Wax-L, Wax-M, and Wax-H, respectively. The values for the Wax-L, Wax-M, and Wax-H are average ones obtained by averaging the amounts of the antiozonant that migrated in the vulcanizates containing the waxes from 1.0 to 5.0 phr.

vulcanizates containing wax are slower than those in the vulcanizates without wax. It may be due to the formation of wax on the sample by blooming. The antiozonants migrate to the surface in the vulcanizate and disappear by reaction with ozone and evaporation. When the wax migrates to the surface in the vulcanizate and make a barrier on the surface, the antiozonants will stay at the interface built between the surface of the rubber vulcanizate and the wax film for some time before migrating to the wax film. The thickness of the wax film formed on a NR vulcanizate containing a paraffin wax
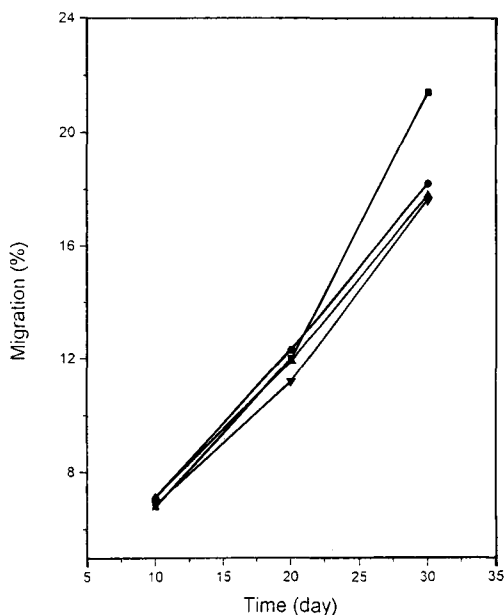
Fig. 5. Variation of amounts of HPPD that migrated to the surface in the NR vulcanizates at 60℃ as a function of the migration time. Squares, circles, up-triangles, and down-triangles indicate the Non-Wax, Wax-L, Wax-M, and Wax-H, respectively. The values for the Wax-L, Wax-M, and Wax-H are average ones obtained by averaging the amounts of the antiozonant that migrated in the vulcanizates containing the waxes from 1.0 to 5.0 phr.
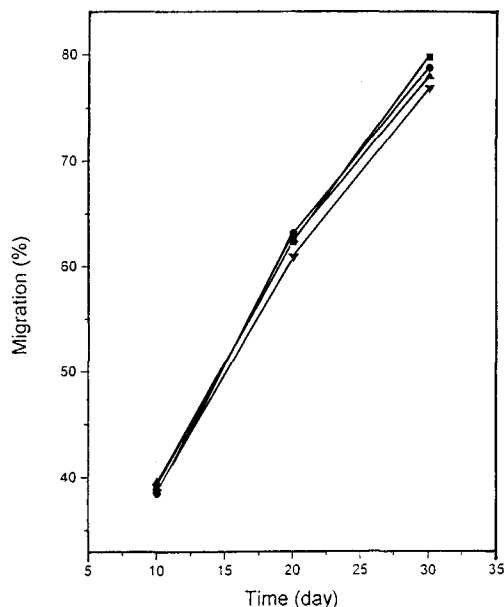
Fig. 6. Variation of amounts of DMPPD that migrated to the surface in the NR vulcanizates at 60℃ as a function of the migration time. Squares, circles, up-triangles, and down-triangles indicate the Non-Wax, Wax-L, Wax-M, and Wax-H, respectively. The values for the Wax-L, Wax-M, and Wax-H are average ones obtained by averaging the amounts of the antiozonant that migrated in the vulcanizates containing the waxes from 1.0 to 5.0 phr.

of 1.6 phr after storage at 40℃ for 30 days was about 2μm.[12] Gardiner studied diffusion gradient of curatives in two rubbers.[14] In similar rubbers, curative concentration showed a continuous gradient. But, in dissimilar rubbers, curative concentration showed a discontinuous gradient at the interface. The concentration at the interface was denser than those on the surfaces of the dissimilar rubbers. This may be due to staying of the curatives at the interface. Similarly, the wax that migrated to the surface in the vulcanizate will make the interface between

wax and the NR vulcanizate. Thus, the antiozonants that migrated to the surface in the vulcanizate stay at the interface so that the migration rates of the antiozonants in the vulcanizate containing wax will be slower than those in the vulcanizate without wax.

3. Influence of the wax type at 80℃

Figures 7, 8, and 9 shows the variations of amounts of IPPD, HPPD, and DMPPD that migrated in the vulcanizates at 80℃ as a function of the migration time. The migration behaviors
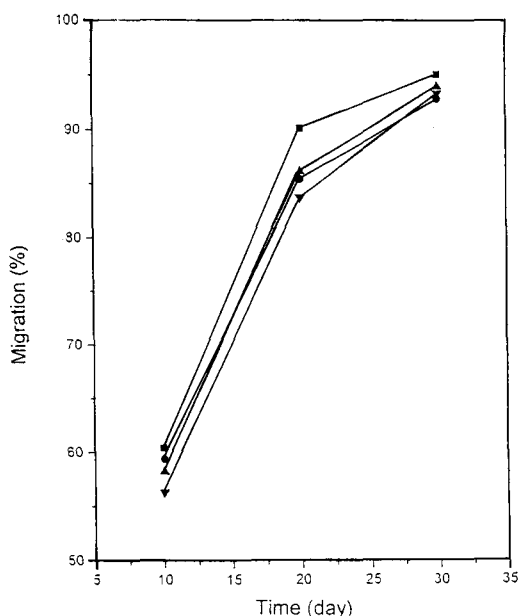
Fig. 7. Variation of amounts of IPPD that migrat-
ed to the surface in the NR vulcanizates at
80℃ as a function of the migration time.
Squares, circles, up-triangles, and down-tri-
angles indicate the Non-Wax, Wax-L,
Wax-M, and Wax-H, respectively. The val-
ues for the Wax-L, Wax-M, and Wax-H
are average ones obtained by averaging the
amounts of the antiozonant that migrated
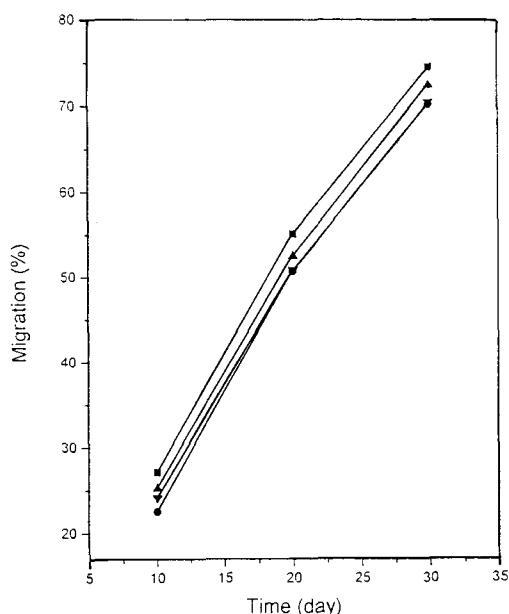in the vulcanizates containing the waxes
from 1.0 to 5.0 phr.

Fig. 8. Variation of amounts of HPPD that migrat-
ed to the surface in the NR vulcanizates at
80℃ as a function of the migration time.
Squares, circles, up-triangles, and down-tri-
angles indicate the Non-Wax, Wax-L,
Wax-M, and Wax-H, respectively. The val-
ues for the Wax-L, Wax-M, and Wax-H
are average ones obtained by averaging the
amounts of the antiozonant that migrated
in the vulcanizates containing the waxes
from 1.0 to 5.0 phr.

at 80℃ of the antiozonants show clearly the dif-
ferences in the amounts of the antiozonants mi-
grated in the vulcanizates with and without
waxes. The amounts of IPPD, HPPD, and
DMPPD that migrated in the vulcanizates cont-
ainig waxes at 80℃ are less than those in the
vulcanizates without wax by about 1-6, 2-5,
and 1-2%, respectively.

For the migration behaviors at 80℃, the
trend of the migration behaviors depending on
the wax type is not clear as shown in Figures
7-9. This may be due to the weak intermolecu-
lar interactions of the wax barrier with the

antiozonants at the high temperature. Since the
chain length of the Wax-H is longer than those
of the Wax-L and Wax-M, the intermolecular
interactions of the Wax-H with the antiozonants
are stronger than those of the Wax-L and
Wax-M. The intermolecular interactions of the
wax barrier with the antiozonants at 80℃ are
weaker than those at 60℃ since the intermolec-
ular interactions become weaker by increasing
the temperature. Thus, the difference of the mi-
gration behaviors with the wax type at 80℃ be-
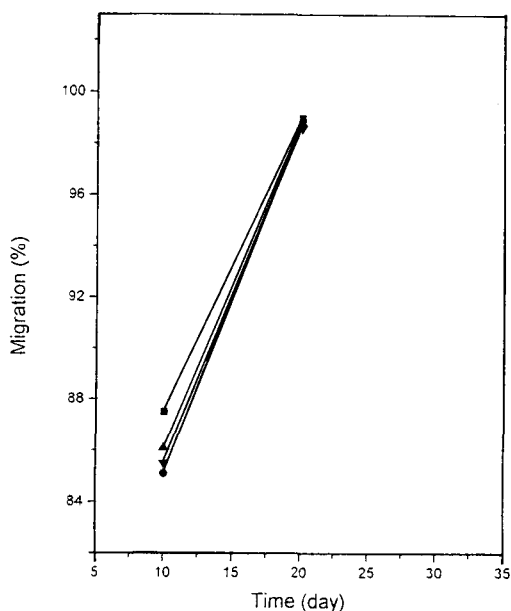come smaller due to the weakness of the
intermolecular interactions.

Fig. 9. Variation of amounts of DMPPD that mi-
grated to the surface in the NR vulcani-
zates at 80℃ as a function of the migration
time. Squares, circles, up-triangles, and
down-triangles indicate the Non-Wax,
Wax-L, Wax-M, and Wax-H, respectively.
The values for the Wax-L, Wax-M, and
Wax-H are average ones obtained by
averaging the amounts of the antiozonant
that migrated in the vulcanizates contain-
ing the waxes from 1.0 to 5.0 phr.

4. Migration rate depending on the antiozonant type

SBPPD was detected by trace after the mi-
gration at 60 and 80℃ for 20 days. Most DMPPD
in the vulcanizates were consumed after the mi-
gration at 80℃ for 20 days by migration and
evaporation. Amounts of HPPD that migrated
to the surface are much less than those of
IPPD. The amounts of IPPD migrated at 60
and 80℃ are about 2.3-3.2 and 1.3-2.2 times of
those of HPPD, respectively. This is because
HPPD and IPPD are the same species of N-

alkyl-N'-phenyl-p-phenylenediamines and HPPD
is havier than IPPD. Though DMPPD (m/z
304) is much heavier than IPPD (m/z 226),
the amount of DMPPD that migrated in the
vulcanizate is much more than that of IPPD as
well as HPPD. The amounts of DMPPD migrat-
ed at 60 and 80℃ for 20 days are about 1.9
and 1.1 times of those of IPPD, respectively.
This may be due to the intermolecular interac-
tions of the antiozonants with matrices (rubber
and filler). A migrant having a strong interac-
tion with the matrices migrates slower than
that having a weak interaction.[8,9] Thus, it can
be considered that the intermolecular interaction
of DMPPD with the matrices is weaker than
that of IPPD. Figures 10 and 11 show the vari-
ations of amounts of the antiozonants that mi-
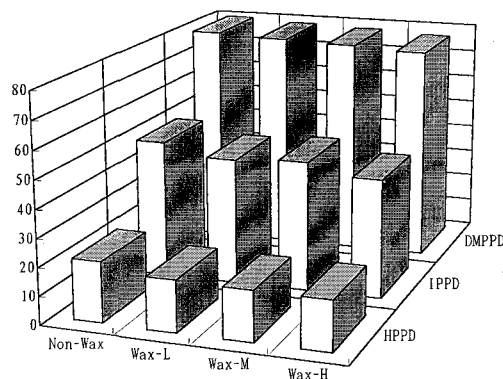grated in the vulcanizates containing the differ-
ent waxes.

Fig. 10. Average amounts of the antiozonants that
migrated in the NR vulcanizates to the
surface at 60℃ for 30 days (%) depend-
ing on the wax type. The values for the
Wax-L, Wax-M, and Wax-H are average
ones obtained by averaging the amounts
of the antiozonants that migrated in the
vulcanizates containing the waxes from 1.
0 to 5.0 phr.

Fig. 11. Average amounts of the antiozonants that migrated in the NR vulcanizates to the surface at 80℃ for 20 days (%) depending on the wax type. The values for the Wax-L, Wax-M, and Wax-H are average ones obtained by averaging the amounts of the antiozonants that migrated in the vulcanizates containing the waxes from 1. 0 to 5.0 phr.
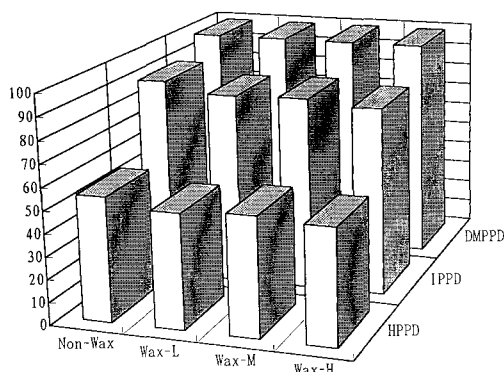
The difference of the migration behaviors depending on the antiozonants is may be due to the intermolecular interactions of the antiozonants with the matrices of rubber and carbon black. The antiozonants interact with the rubber chains and carbon black in the carbon black-filled NR vulcanizates. The intermolecular inet-ractions of the phenyl ring of the IPPD and HPPD with carbon black are mainly π-π interactions, while those of the alkyl groups of the antiozonants with NR chains are mainly σ-σ interactions. The π-π interactions are stronger than the σ-σ interactions. SBPPD and DMPPD have two alkyl groups, while IPPD and HPPD have one alkyl and one phenyl groups. Thus, the migration rates of IPPD and HPPD are slower than those of the SBPPD and DMPPD since the intermolecular interactions of the N-

alkyl-N'-phenyl-p-phenylenediamines with the matrices are stronger than those of the N,N'-dialkyl-p-phenylenediamines at the high temperatures.

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