2H), 4.31 (m, 2H), 7.20 (m, 4H), 7.44 (m, 2H), 7.60 (d, 2H, J=4.51 Hz), 8.33 (m, 4H), 8.43 (m, 2H); ^{13}C NMR ($CDCl_3$/CD_3OD) δ 168.21, 167.97, 167.87, 167.56, 166.54, 165.54, 156.78, 143.23, 141.67, 134.88, 134.56, 134.45, 134.24, 133.56, 133.21, 130.46, 128.97, 127.56, 126.76, 125.09, 119.78, 67.86, 58.03, 57.54, 54.54, 54.09, 53.78, 53.03, 52.98, 47.88 (m), 47.23, 32.65, 31.44, 25.45, 24.76; IR (neat) 3324, 2877, 1685, 1665, 1575 cm^{-1}; MS (FAB) m/z 2591 (M+1).

Typical Procedure of Solid Phase Color Assay. 100 mg (about 10^6 beads) of substrate library was suspended in Eppendorf tube containing 0.5 mL $CHCl_3$ and then added 25 μL of a 0.5 mM $CHCl_3$ solution of dye-linked receptor. After 48 hr of agitation on a wrist-action shaker, about 1% of the beads were stained deep color with more having various lighter colorations.

Decoding Tagged Synthesis Supports. The mostly deep colored beads were selected manually under a 4X microscope, placed individually in separate melting point capilary tubes, and then washed with DMF (2×10 μL). The bead was suspended in 1 μL fresh, pure DMF and the tube was sealed using a flame. Next the bead was irradiated for 3 hr at room temperature at 366 nm with a Model UVL-56 ultraviolet light, and then warmed at 90 °C for 2 hr to complete release of the tag alcohols into solution. The tube was opened and bis(trimethylsilyl)acetamide (0.1 μL) was added for silylation to increase tag volatility. After centrifuging for 2 min, the tag solution (1 μL) over each bead was injected into an electron capture capilary gas chromatograph for tag analysis. The resulting chromatograms showed which tags were present and which were absent. Binary tag code used during library synthesis revealed the structure of each substrate which had been selected by the solid phase binding assay.

Measurement of Binding Energy of Receptor and Substrate Found in Solid Phase Assay. Substrate found in assay was resynthesized on Merrifield synthesis bead using the same methodology to the synthesis of substrate library without the tagging step. Known quantities of dye-linked receptor ($[R]_{total}$) were added to a constant quantity of bead-bound substrate with monitoring of $[R]_{free}$ by UV after 24 hr of equilibration. Because the concentration of bead-bound substrate is unknown, [R] data were collected at two points (A, B) and the two binding equations were solved simultaneously:

$$K=\{[Complex]_B/[R]_{free\text{-}B}-[Complex]_A/[R]_{free\text{-}A}\}/\{[Complex]_A-[Complex]_B\}$$

where $[Complex]=[R]_{total}-[R]_{free}$. Data was collected at three such points, and K's were calculated for each of the three pairs of points. The binding experiment was repeated. The resulting six K's were averaged, and error limits were computed from the different K's as 1 standard deviation.

Acknowledgment. I would like to thank Prof. W. Clark Still for his helpful discussion during this work. Financial support from Ministry of Education (BSRI-97-3416) is gratefully acknowledged.

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Influence of Wax on Migration of Antiozonants in NR Vulcanizates

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Received February 21, 1998

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 chains. These reactions lead to chain scission and the formation of various decomposition products. In order to control the effects of rubber ozonation,

Table 1. Formulations (phr)

Compound	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-A	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-B	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-C	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

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] A third 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,[8-10] the influences of initial concentrations of antidegradants in a rubber vulcanizate, kind of rubber, and fillers (silica and carbon black) on the migration of antidegradants in rubber vulcanizates were studied. Migration of antiozonants to the surface in rubber vulcanizates is independent of their initial concentrations. Migration rates of them in NR vulcanizates are faster than those in SBR ones.[8] Migration rates of antidegradants become slower by increasing the filler content in a filled rubber vulcanizate.[9,10] Silica makes migration of the antidegradants slow by intermolecular hydrogen bonds between silica and them.[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 specific wax type, the rubber composition, and the time and temperature before and during exposure to ozone. These parameters influence the solubility/mobility characteristics of each specific wax.[11] In general, substituted *papa*-phenylenediamine antiozonants were used with wax to protect ozonation of rubber.[12]

In this study, the influence of wax film on migration of antiozonants to the surface in a rubber vulcanizate was studied with NR vulcanizates containing waxes with various kinds and various contents. IPPD (*N*-isopropyl-*N'*-phenyl-*p*-phenyl-enediamine), 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. The experimental results of their migration at 60 and 80 °C for 30 days were given in Tables 2 and 3, respectively. Amounts of the antiozonants that migrated increase by increasing the temperature from 60 to 80 °C. SBPPD was detected by trace after migration at 60 and 80 °C for 30 days. Most DMPPD (over 99.5%) in the vulcanizates migrated after 30 days at 80 °C. Amounts of HPPD that migrated to the surface are much less than those of IPPD and DMPPD. 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. This may be due to the intermolecular interactions of the antiozonants with matrices (rubber and filler). A migrant

Table 2. Amounts of antiozonants that migrated to the surface in the NR vulcanizates at 60 °C for 30 days (%)

Compound No.	IPPD	HPPD	DMPPD
1	49.5	21.4	79.7
2	45.1	19.3	79.4
3	47.8	17.9	79.5
4	45.5	17.9	77.6
5	45.5	17.9	79.2
6	43.0	17.9	77.9
7	43.8	17.5	77.6
8	48.7	19.0	77.9
9	47.3	16.7	77.6
10	46.8	17.9	78.4
11	46.8	18.0	78.1
12	43.6	17.5	77.3
13	44.1	17.7	77.8
14	43.1	18.6	77.5
15	41.5	18.2	76.8
16	41.1	16.2	74.6

Table 3. Amounts of antiozonants that migrated to the surface in the NR vulcanizates at 80 °C for 30 days (%)

Compound No.	IPPD	HPPD	DMPPD
1	95.0	74.6	>99.5
2	93.7	71.9	>99.5
3	93.4	67.5	>99.5
4	93.8	73.2	>99.5
5	92.8	68.1	>99.5
6	93.7	72.6	>99.5
7	94.1	71.1	>99.5
8	94.1	72.4	>99.5
9	93.9	73.3	>99.5
10	93.6	73.7	>99.5
11	94.0	72.2	>99.5
12	94.1	71.6	>99.5
13	93.0	70.7	>99.5
14	93.8	71.7	>99.5
15	91.6	67.9	>99.5
16	93.9	70.7	>99.5

having a strong interaction 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.

Amounts of the antiozonants that migrated in the vulcanizates containing wax (Compounds 2-16) are less than those in the vulcanizates without wax (Compound 1). This may be due to the wax film on the surface. 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 protection film on the surface, the antiozonants will stay at the interface bulit 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 on a NR vulcanizate containing a paraffin wax of 1.6 phr after storage at 40 °C for 30 days was about 2 μm.[11] Gardiner studied diffusion gradient of curatives in two rubbers.[13] 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 that 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.

The migration behaviors of the antiozonants depending on the content of wax (1.0-5.0 phr) in the vulcanizates do not show a specific trend. However, the migration behaviors of the antiozonants depending on the wax type show a specific trend. Amounts of the antiozonants that migrated in the vulcanizates containing the Wax-C at 60 and 80 °C are less than those in the vulcanizates containing the Wax-A and Wax-B. Especially, this trend was observed in migration of HPPD and DMPPD at 60 °C. Amounts of HPPD and DMPPD that migrated in the vulcanizates containing the wax with a high molecular weight distribution are less than those in the vulcanizates containing the wax with a low molecular weight distribution. The average amounts of HPPD that migrated in the vulcanizates containing the Wax-A, Wax-B, and Wax-C at 60 °C are 18.2, 17.8, and 17.6%, respectively, while those of DMPPD are 78.7, 77.9, and 76.8%, respectively.

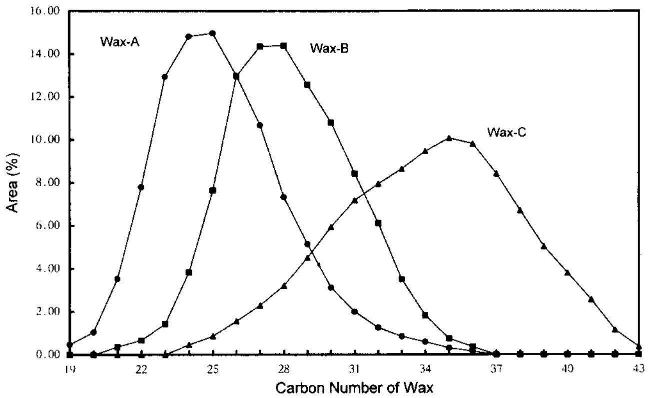

Figure 1. Molecular weight distributions of waxes.

The intermolecular interactions between migrants and matrices of rubber and filler are principal factors influencing on the migration of antiozonants in a rubber vulcanizate.[8~10] The migration rates of migrants become slower and slower as the intermolecular interaction become stronger and stronger. If the thickness of the wax film affect migration of the antiozonants, their migration rates will be faster 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 depending the content of the wax as discussed above. This may be due to the weak intermolecular interaction of the antiozonants with the wax. Thus, it can lead to a conclusion that the thickness of the wax film hardly affect migration of the antiozonants in the vulcanizates.

Experimental

In order to investigate the influence of wax on migration of antiozonants to the surface in a rubber vulcanizate, sixteen carbon black-filled NR compounds containing three kind waxes were prepared. The three waxes have a different molecular weight distribution each other as shown in Figure 1. The Wax-C has a higher molecular weight distribution than the Wax-B and Wax-A. The contents of waxes in the compounds were from 0.0 to 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 migrants. The formulations were given in Table 1. The NR vulcanizates were prepared by curing at 160 °C for 15 minutes.

The migration experiments were carried out at constant temperatures of 60 and 80 °C for 30 days in a convection oven. The amounts of the antiozonants that migrated to the surface in the NR vulcanizate were determined by the difference between the amounts of the antiozonants that remained in the rubber vulcanizates before and after the migration. The amounts of the antiozonants remaining in the rubber vulcanizates were analyzed using a gas chromatography after extraction of the antiozonants with THF. Experiments were carried out three times and averaged.

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Synthesis of Oxomolybdenum(V) Complexes with Trifunctional ONO-Donor Ligands

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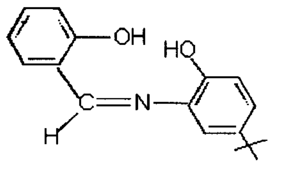
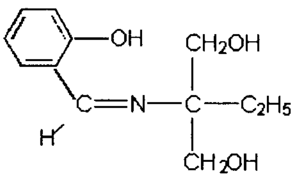
Received March 23, 1998

The chemistry of oxomolybdenum complexes with Schiff base ligands has received intense attention because of its relevance to the active sites of molybdoenzymes.[1] It is well-known[2] that the biological redox process of the molybdoenzymes involves oxidation states, IV-VI. In addition, extended X-ray absorption fine structure (EXAFS) spectroscopic studies have implicated the presence of oxygen and nitrogen atoms at the active sites of oxo-transfer molybdoenzymes.[3]

In this context we have taken up N-salicylidene-2-amino-4-*t*-butylphenol (SabpH_2) and N-salicylidene-2-amino-2-ethyl-1,3-propanediol (SapdH_2) as trifunctional (ONO) dianionic Schiff base ligands. These ligands are of particular interest because chelation may occur either from ON or ONO sites, in principle. It was also reported[4] that functionalities present in the ligands play a vital role in controlling whether the oxomolybdenum complexes are monomers or polymeric species. Thus, with the aim of simulating many characteristic properties for the active sites of molybdoenzymes, we have synthesized the type of complex (PyH)[MoO$(X)_2$(L)] (X=Cl, NCS : L=Sabp, Sapd). In this paper, we report the synthesis, spectral properties, and the electrochemical behaviors of the complexes.



sabpH_2



sapdH_2

Experimental

Materials. Most chemicals used in synthesis were of reagent grade and used without further purification. The complexes (PyH)[$MoOCl_5$] and (PyH)[$MoO(NCS)_5$] as starting materials were prepared by literature methods.[5] All the Schiff bases were prepared by the same method as was published previously.[6] All solvents were dried by standard procedures and distilled before use.

Physical Measurements. Elemental analyses for C, H, N were carried out by the Instrumental Center of Kyungpook National University. The melting point measurements were performed by using a Hakke melting point apparatus. The molar conductivities of the complexes were measured by a YSI conductivity bridge (model 31). The IR spectra of solid samples in KBr were recorded on a Mattson Polaris FT-IR. The ^1H NMR spectra in DNSO-d_6 were recorded on a Varian Gemini 200 spectrometer and referenced to TMS (internal). Electronic spectra were obtained on a Shimadzu 160A UV-visible spectrophotometer. Cyclic voltammograms were recorded on an Electrochemical Research System 270/6/0 (EG&G) consisting of PAR 263 Potentiostat/Galvanostat and an Electrochemical Analysis Software 270. The electrochemical studies were conducted in an oxygen-free DMSO solution containing 0.1 M TEAP (tetraethylammoniumperchlorate) as a supporting electrolyte. We employed a three-electrode cell configuration consisting of a platinum