

APPLICATION OF INTERCALATED COMPOUND OF MONTMORILLONITE AND N, N'-  
DIPHENYL-p-PHENYLENEDIAMINE TO ANTIOXIDANT FOR RUBBER MATERIALS

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**ABSTRACT.** To extend the lifetime of rubber materials, the intercalated compound consisting of N, N'-diphenyl-p-phenylenediamine (DPD) as guest molecule and montmorillonite as host layer was added to chloroprene rubber (CR) and acrylonitrile-butadiene rubber (NBR). These rubber samples were either immersed in a mixture of isooctane and toluene or kept at 140°C in air, and subjected to ozone aging tests. The residual DPD in CR was analysed by high pressure liquid chromatography. Their results were compared with the rubbers of a standard composition, including DPD alone. The solvent-immersed CR containing the intercalated compounds showed more improved ozone-cracking resistance than solvent immersed CR of the standard composition. The residual DPD in CR containing the intercalated compound was more than that in CR of standard composition. However, no significant difference between the specimens containing intercalated compound and those of the standard composition was observed for the solvent-immersed NBR, heat-treated NBR and heat-treated CR.

## 1. INTRODUCTION

Various kinds of antioxidants have been widely used for the purpose of extending the lifetime of synthetic rubbers. These antioxidants react with oxygen or ozone molecules on the surface of rubber materials and, as a consequence, they prevent the aging of rubber materials. As the antioxidants are usually mixed in the rubber matrix, they must migrate from the inner part to the surface. The ideal antioxidants should have the following features which are contradictory to each other; (1) they are easily oxidized, (2) they have a high diffusivity within the rubber materials but (3) they should be neither evaporated from the surface nor extracted by organic solvents such as gasoline before they have worked as antioxidants. In actuality, they are wasted by the evaporation or extraction, then the lifetime of rubber materials is shortened.

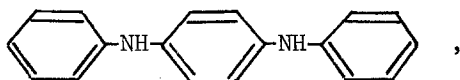
In order to overcome these problems, we attempted to use an intercalated compound of N, N'-diphenyl-p-phenylenediamine (DPD), antioxidant, as a guest material and montmorillonite as a host material. The

montmorillonite has been well known to form intercalated compounds with cations, polar molecules like water or amines or other molecules between the structural layers<sup>(1)</sup>. It was expected that the intercalated compound will release the guest molecule, DPD, gradually and thus the lifetime of rubber materials will be extended.

## 2. MATERIALS AND METHODS

### 2.1. Preparation of intercalated compound

Montmorillonite, which was fractionated from bentonite produced in Yamagata, Japan and is commercially available as KUNIPIA-F<sup>R</sup> from Kuni-mine Industries Co., Ltd., was used as the host material in this study. The cation exchange capacity of the montmorillonite is 119 meq•/100g<sup>(2)</sup> N, N'-diphenyl-p-phenylenediamine (DPD);



was used as the guest molecule. DPD is known to be useful as an antioxidant for chloroprene rubber, but the amount included in rubbers is restricted for its blooming property. The DPD, which is commercially available as NOCRAC-DP<sup>R</sup> from Ouchi-Shinko Chemicals Co., Ltd., was used in this study.

The powder of montmorillonite was vacuum dried at 110°C for 10 hours, followed by mixing with the powder of DPD in a alumina mortar. The mixture of 50g of dried montmorillonite and 10g of DPD was heated in vacuum for 1 hour at 140°C, which is about 5K above the melting point of DPD.

### 2-2. Examination of the intercalated compound

The intercalated compound and the dried montmorillonite were examined by X-ray powder diffraction. The conditions of the diffraction study were as follows; Co-K $\alpha$  ( $\lambda=0.17889\text{nm}$ ) was used as X-ray source, tube voltage was 30kV, tube current was 20mA and scanning speed was 2°(2 $\theta$ )/minute.

About 10mg of intercalated compound, montmorillonite and a mixture of DPD and alumina powder were examined by differential thermal analysis(DTA) and thermo-gravimetry (TG). The measurements were made in 200cm<sup>3</sup>/min. of nitrogen flow, reference was alumina and heating rate was 5K/min.

### 2-3. Preparation of rubber specimens

Chloroprene rubber (CR) and acrylonitrile-butadiene rubber (NBR) were used in this study. The compositions of the rubbers are shown in Table 1. The standard compositions in Table 1 are those generally adopted for individual rubbers. In the specimens represented by "with talc" in Table 1, talc was mixed instead of montmorillonite. Talc has a layered structure like montmorillonite but does not form intercalated

Table 1. Composition of rubber specimens (by weight).

## (a) Chloroprene rubber (CR)

	Standard	with talc	with intercalated comp.
Raw rubber	100	100	100
Carbon black	29	20	20
Zinc oxide (ZnO)	5	5	5
Magnesium oxide (MgO)	4	4	4
Stearic acid	1	1	1
Vulcanization accelerator	0.5	0.5	0.5
Antioxidant (DPD)	2	2	0
Intercalated compound	0	0	12*
Talc	0	10	0

## (b) Nitrile-butadiene rubber (NBR)

	Standard	with intercalated comp.
Raw rubber	100	100
Carbon black	40	30
Zinc oxide (ZnO)	5	5
Stearic acid	1	1
Vulcanization accelerator	1	1
Sulfur	1.5	1.5
Antioxidant (DPD)	2	0
Intercalated compound	0	12*

\* includes 2 units of DPD

compounds with organic compounds.

Raw rubber and carbon black powders were mixed together with a pressurized kneader. The designated components shown in Table 1 were then mixed with a mixing roll, and the resulting admixture was formed into a sheet of unvulcanized rubber. Thereafter, the unvulcanized rubber sheets were vulcanized at a temperature of 160°C under a pressure of 80 kg/cm<sup>2</sup> for 10 minutes to obtain the rubber sheets of 150 × 150 × 2 mm. From the rubber sheets, dumbbell-shape specimens shown in Figure 1 were stamped out.

## 2-4. Ozone aging test.

Prior to ozone aging tests, some specimens were immersed in a mixture of 60 vol% isooctane and 40 vol% toluene at 40°C for 48 hours, followed by drying for 72 hours at room temperature. Others were kept at 140°C in air for 72 hours.

Thereafter the specimens were elongated by 30% (CR) or 10% (NBR), using test holders. The elongated samples with test holders were hung

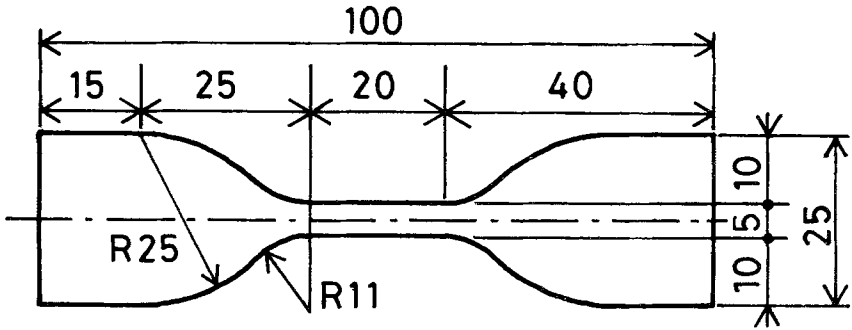


Figure 1. Outline and dimensions of the dumbbell-shaped<sup>(3)</sup> specimen for ozone-aging tests.

in an ozone aging test chamber, in which the concentration of ozone was automatically controlled to be 0.5 ppm and the temperature was maintained at 40°C. The surfaces of these specimens were observed during the aging tests.

#### 2-5. Analysis of residual DPD

The amount of DPD in the unvulcanized CR specimens, vulcanized ones, those immersed in solvent and exposed in 0.5 ppm ozone at 40°C for 1000 hours were analyzed by high pressure liquid chromatography (HPLC).

DPD was extracted from each specimen using a Soxhlet's extractor with acetone for 7 hours. After evaporation of acetone, extracted DPD was dissolved in chloroform. Concentrations of DPD in chloroform were analysed by HPLC using the ultraviolet rays of  $\lambda=254\text{nm}$ , with the columns of polystyrene gel; Shodex A801<sup>R</sup> and Shodex A802<sup>R</sup> from Showadenko Co., Ltd., under a flow rate of 1.0 cm<sup>3</sup>/minute.

### 3. RESULTS

#### 3-1. X-ray powder diffraction

Figure 2 shows the results of X-ray powder diffraction of the dried montmorillonite and the heat-treated mixture of montmorillonite and DPD.

The interlayer distances, defined as the *d*-value of (001), were 0.97 nm and 1.22 nm for dried montmorillonite and the mixture, respectively. These results suggested that the montmorillonite and the DPD formed intercalated compound by heating at 140°C.

#### 3-2. DTA and TG

Figures 3 and 4 show the results of TG and DTA of intercalated

compound, mixture of DPD and alumina powder and montmorillonite.

The weight of montmorillonite decreased at about 100°C, accompanied with an endothermic peak in DTA due to evaporation of water molecules adsorbed on the surface or in the interlayer regions. For the intercalated compound, however, weight reduction due to water evaporation was less than 2%, which indicates that the water molecules on the surface or in the interlayer regions of montmorillonite were substituted by DPD molecules.

For intercalated compound and the mixture of alumina powder and DPD, two endothermic peaks were observed at 130~150°C, which is assumed to be the melting point of DPD. At the temperature range from 200°C to 260°C almost all the DPD molecules evaporated from the intercalated compound and from the mixture with alumina powder. The evaporating behavior were similar to each other.

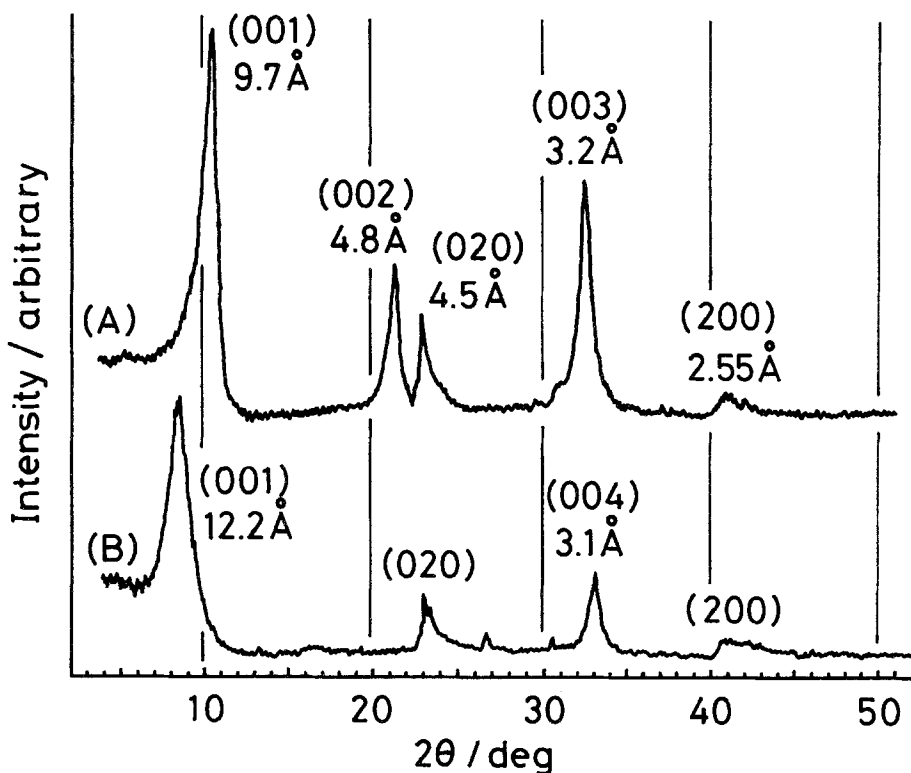


Figure 2. Results of X-ray powder diffraction for (A) the dried montmorillonite and (B) the intercalated compound of DPD and montmorillonite, using Co-K $\alpha$  ( $\lambda = 0.17889$  nm) as an X-ray source.

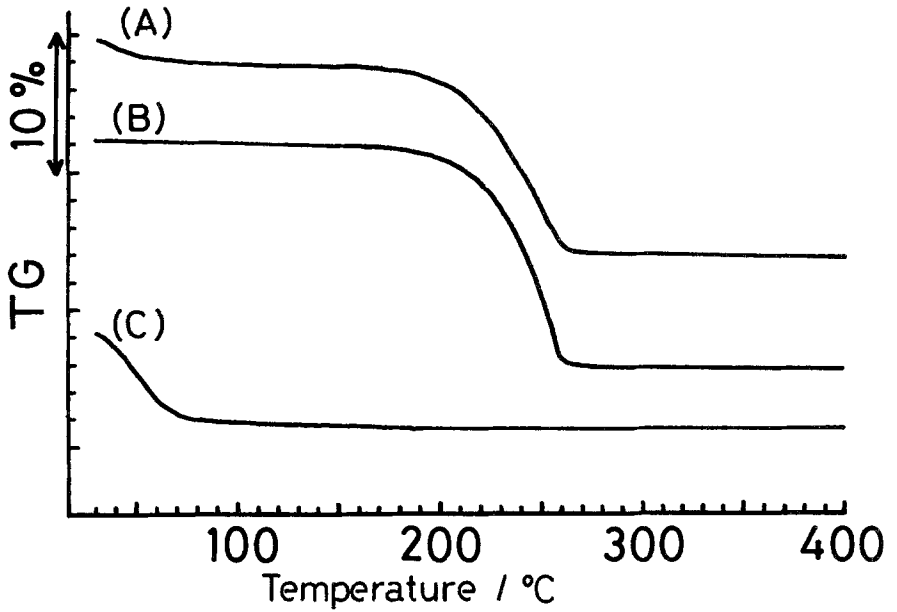


Figure 3. Results of thermo-gravimetry for (A) the intercalated compound, (B) the mixture of alumina powder and DPD and (C) montmorillonite.

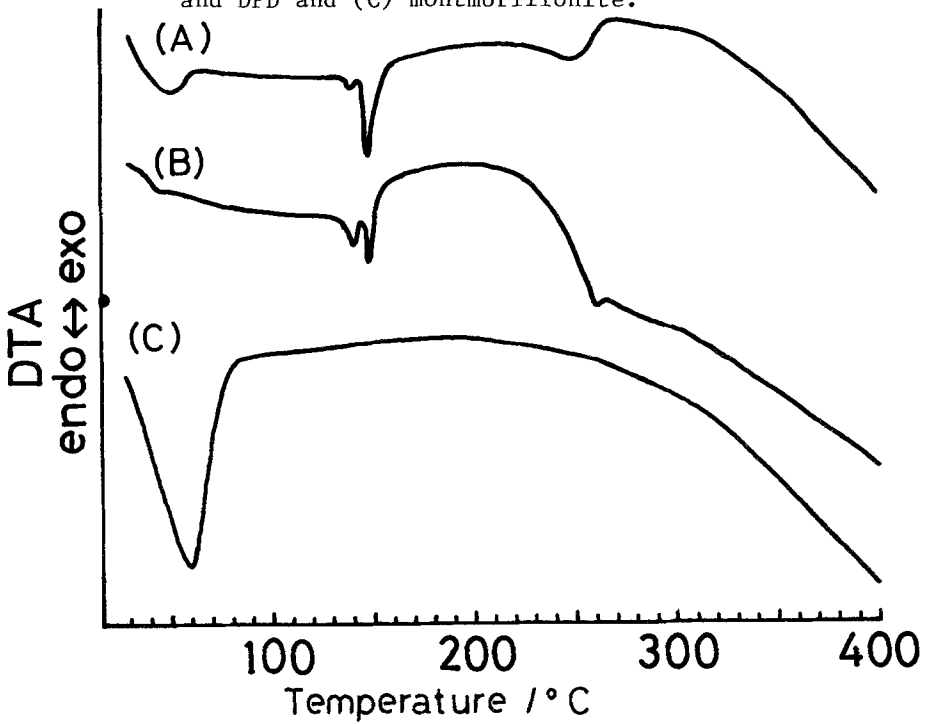


Figure 4. Results of DTA for the (A) intercalated compound, (B) mixture of alumina and DPD and (C) montmorillonite.

### 3-2. Results of ozone-aging tests

The photographs of the surfaces of solvent immersed CR exposed in ozone atmosphere for various periods of time are shown in Figure 5. Cracks appeared in 20 hours of exposure on the specimens of the standard composition and with talc composition, and the cracks were growing gradually. Most solvent immersed CR of the standard and with talc composition were broken down within 1000 hours. On the other hand, no cracks were observed even after 1000 hours on the specimens containing the intercalated compound. Figure 6 shows the crack ranks, specified in JIS (Japanese Industrial Standard)<sup>(4)</sup>, for these samples. The crack ranks indicate the extent of cracks; 0 means that no cracks are observed on the surface, 1 means that very small cracks are observed, and 5 means that fatal cracks are observed or samples are broken down. Figures 7 and 8 show the photographs of the heat treated CR specimens and solvent immersed NBR specimens. Many cracks appeared in short time on the surfaces of both standard samples and those containing the intercalated compound, and the behaviors of crack growth resembled each other.

The heat treated NBR specimens were so degraded that they lost elasticity entirely.

### 3-3. Results of residual DPD analysis

The amount of DPD contained in the CR, expressed in values relative to the initial amount, are shown in Table 2. More DPD remained in the specimen containing the intercalated compound than in that of standard composition at each step.

Table 2. Results of the analysis of residual DPD.

	Specimen including the intercalated compound (%)	Specimen of standard com- position (%)
initial amount	100*	100*
unvulcanized rubber	76	77
after vulcanization	44	32
after solvent immersion	3.5	1.2
after ozone aging test for 1000 hours	1.6	0.8

\* Results expressed in values relative to the initial amount.

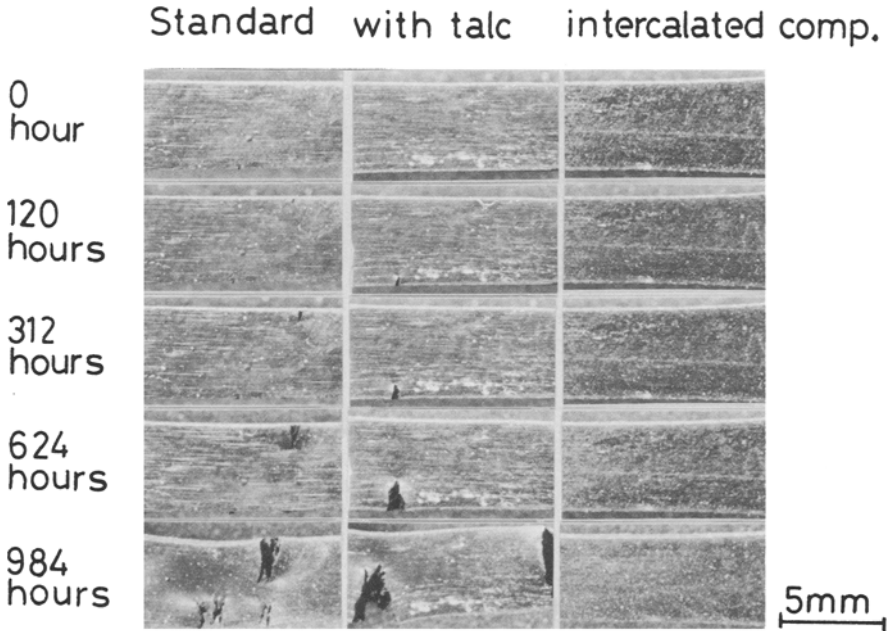


Figure 5. Photographs of the surface of solvent immersed CR exposed in ozone atmosphere for various periods of time.

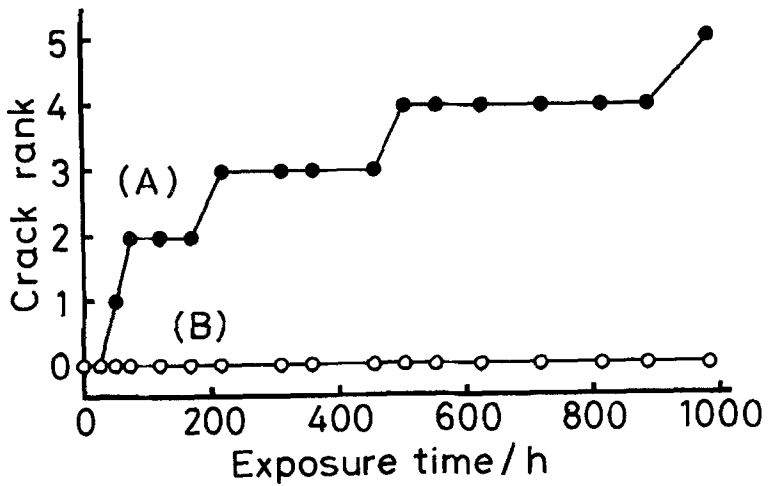


Figure 6. Crack ranks of solvent immersed CR exposed in 0.5 ppm ozone atmosphere for (A) the specimens containing intercalated compounds and (B) those of standard composition.



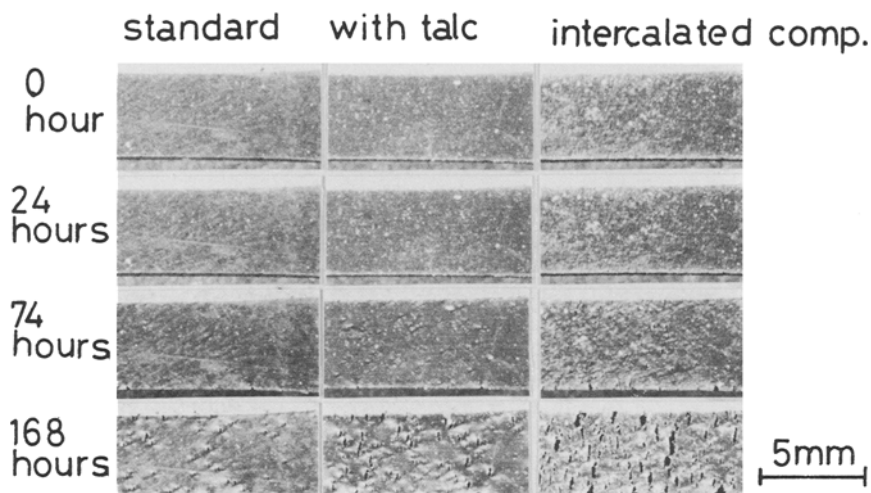


Figure 7. Photographs of the surface of heat treated CR exposed in 0.5 ppm ozone atmosphere for various periods of time.

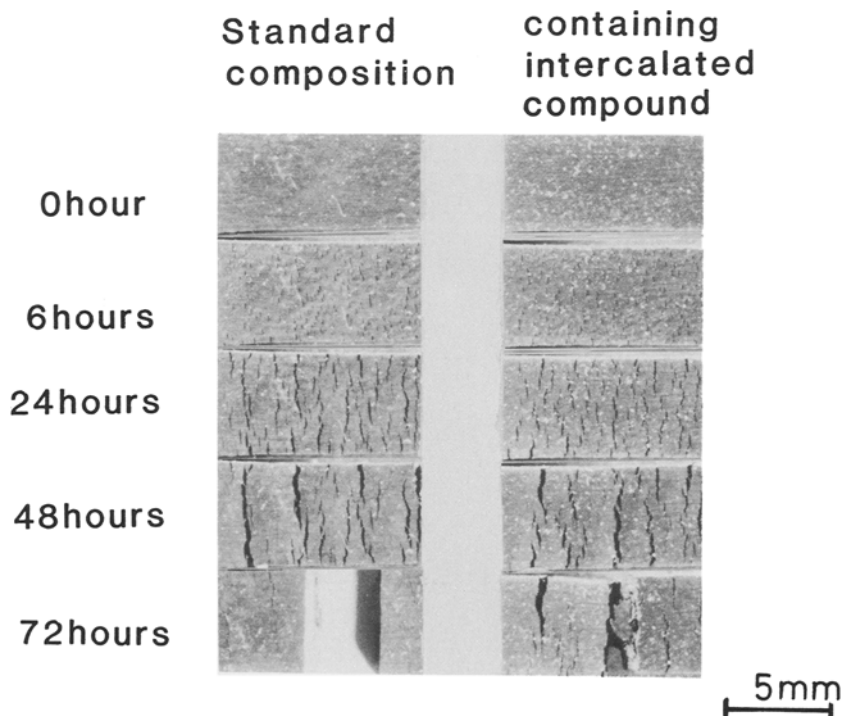


Figure 8. Photographs of the surface of solvent immersed NBR exposed in 0.5 ppm ozone atmosphere for various periods of time.

#### 4. DISCUSSIONS

##### 4-1. Intercalation between montmorillonite and DPD

The behavior of TG curve at about 100°C for montmorillonite and the mixture of montmorillonite and DPD suggested that almost all the water molecules adsorbed on the surface and in the interlayer regions of montmorillonite were substituted by the DPD molecules. This fact and the results of X-ray powder diffraction suggested that montmorillonite and DPD molecules formed the intercalated compound. However, the endothermic peak corresponded to the melting of DPD was observed at 130~160°C for the mixture of DPD and montmorillonite. This result indicated that there was free DPD in the mixture and only partial fractions of DPD formed intercalated compounds with montmorillonite. The interaction between the host layer; montmorillonite, and the guest molecule, DPD, was so weak that the TG curve at about 230°C for the intercalated compound resembled that for the mixture of alumina powder and DPD. This weak interaction is supposed to play an important role in this work.

##### 4-2. Effects of application of intercalated compound

The CR specimens containing intercalated compound which were immersed in organic solvent showed more improved ozone-cracking resistance than that of standard composition and that of "with talc" composition. These results and the result of the analysis of residual DPD indicated that the intercalated compound had an excellent effect on retarding or preventing the dissolution of DPD into the mixture of isooctane and toluene.

The interaction between the montmorillonite and non-polar molecules such as isooctane or toluene is limited, while the interaction between the montmorillonite and polar molecules such as water is very strong. The roles of montmorillonite to prevent access of non-polar solvents, as shown above, and to keep DPD on the surface or in the interlayer region, are considered to prolong the effective life of DPD, thus providing rubbers with good ozone-cracking resistance.

Since the interaction between montmorillonite and DPD, however, was too weak to prevent the evaporation of DPD at high temperatures, the results of DTA and TG at about 230°C for the intercalated compound and ozone-aging test for heat-treated CR containing the intercalated compound did not differ significantly from DPD itself.

As the NBR is rather hydrophilic compared with CR, the interaction between the NBR matrix, intercalated compound and organic solvent might be different from that in CR. In addition to this fact, as NBR have less ozone-cracking resistant than CR, the growth of cracks on the NBR specimens under the conditions in this work is supposed to be too fast to observe the difference between the NBR specimens containing intercalated compound and those of standard composition. These reasons may be responsible for little difference observed between the NBR of the standard composition and that containing intercalated compound.

## 5. ACKNOWLEDGEMENTS

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## 6. REFERENCES

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- (4) JIS, K6301, p.38.