

The Surface Migration of Extender Oil in EPDM Vulcanizates

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Synopsis

Extender oil bloomed on the surface of ethylene-propylene-diene rubber (EPDM) vulcanizates has been analyzed by a dissolution/size exclusion chromatographic (SEC) method. Dissolution is here defined as the quantitative and selective removal of bloomed extender oil from the vulcanizates. The rate of migration of three potentially useful extender oils for windshield-wiper materials has been determined by the method. In this work a bloomed oil includes both an excluded oil surfaced during the process of vulcanization and a migrated oil surfaced during the course of aging or weathering. Typical initial rates of oil migration in the presence and absence of an excluded oil on the surface of compression-set EPDM vulcanizates were ca. 0.8 and 2.2 $\mu\text{g}/\text{cm}^2/\text{h}$ at 25°C, respectively. The rate of migration at an attained uniform oil concentration was found to be ca. 0.5 $\mu\text{g}/\text{cm}^2/\text{h}$ for the three extender oils.

INTRODUCTION

As with almost all synthetic elastomers, ethylene-propylene-diene rubber, which bears the ASTM designation EPDM,¹ must be compounded and thermally crosslinked into a final part or product. The capacity of EPDM compounds for extension with large amounts of fillers and petroleum-based oils, while retaining good physical properties, has added a new dimension for low cost compounding in the rubber industry.^{2,3}

Migration of oils, curatives, antioxidants, and other compounding materials in a vulcanized rubber matrix is a general phenomenon of practical importance. A carbon-14 tracer method for measuring the diffusivity and migration of octadecane⁴ and aromatic/polar and paraffinic extender oils⁵ in natural and synthetic rubber has been reported. A subsequent study of oil migration phenomena in an EPDM system has shown that the most basic factor in the rate of Fickian diffusion is the polymer matrix itself and variations in carbon black type and loading levels have no detectable effect at 2% or less oil concentration.⁶ However, increasing the concentration of oil is likely to increase the rate of diffusion in most polymer systems. The rate of oil migration in an EPDM system has been shown to increase 26% over the concentration range of 2–27% at 100°C.⁷

The word "bloom" has been applied for a wide variety of very different surface effects which are conveniently classified into (i) true blooms, (ii) modified blooms, (iii) pseudo blooms, and (iv) surface contamination.⁸ When a compounding ingredient with a limited but appreciable solubility in a rubber vulcanizate is present in excess of this solubility, the true bloom occurs. In this work the bloomed extender oil includes both (i) an excluded oil surfaced during

the process of compression-set vulcanization and (ii) a migrated oil surfaced during the course of aging or weathering.

Extraction has been defined previously as the procedure for removing organic additives from the rubber compounding components without simultaneously removing significant amounts of the polymeric phase, whereas solution and dissolution involve the removal of polymer from the remaining components.⁸ However, "dissolution" is here defined as the quantitative and selective removal of hydrocarbon oils on the surface of oil-extended EPDM vulcanizates. To achieve the above-defined dissolution, hexane is chosen as the solvent on the basis of a preliminary study of oil solubilities at room temperature.

The present paper describes rapid hexane dissolution and size exclusion chromatographic (SEC) determination of bloomed extender oils on the surface of compression-set EPDM vulcanizates at a practical oil loading level to provide oil-migration information correlatable with end-use performance.

EXPERIMENTAL

Materials

Oils A, B, and C evaluated as extender oil were obtained from three different supplier sources. The densities of oils A, B, and C at 15°C relative to water at 4°C were 0.946, 0.868, and 0.874 g/cm³, respectively. Each of three rubber compounds containing an EPDM (40.0%), fillers (30.0%), curatives (7.5%), and an extender oil (22.5% each of oil A, B, or C) was mixed in an internal mixer for 6 min, and then rolled up and pressed out five times on a two-roll mill (20 × 40 cm). The preforms were prepared from the above well-mixed compounds for compression-set molding and vulcanized into 1.24-cm thick by 2.82-cm diameter disks at 160°C and 208 MPa for 29 min (ASTM D-395-82).

The average weights ($n = 6$) of the three sets of compression-set vulcanizates (buttons) with oils A, B, and C were 9.1356, 8.7550, and 8.9319 g, respectively. The relative standard deviation (RSD) of the sample weights for each set of the six buttons was less than 0.2%.

Hexane Dissolution of Bloomed Oil

The dissolution of extender oils on the surface of vulcanized buttons into hexane (Burdick & Jackson Laboratories Inc., Muskegon, MI) was performed as follows: Each button was placed in a 30- or 50-mL Pyrex beaker. A 5-mL portion of hexane was poured onto the button, which was immersed completely, and then the beaker was gently swirled. After 20 s from the hexane addition, the solution was decanted into a 10-mL volumetric flask. Then another 5-mL hexane was quickly added to rinse both the beaker and button. The rinsing was combined into the volumetric flask. The described hexane dissolution process required ca. 60 s and the weights of buttons (before and after hexane dissolution) were monitored by an electronic analytical balance (readability: 0.1 mg).

To prove the quantitiveness of the procedure, a series of dissolution experiments were performed: For example, the hexane-rinsed surfaces of three oil-A buttons were smeared with known amounts (5–30 mg) of oil B and then

the oil-B-smear oil-A buttons were immediately subjected to the hexane dissolution. Recovery of the smeared oils was found to be basically quantitative (95+%).

Size Exclusion Chromatography (SEC)

After the evaporation of hexane under a nitrogen flow, the bloomed oils collected into 10-mL volumetric flasks by the hexane dissolution described above were redissolved into "Baker-analyzed" reagent grade tetrahydrofuran (THF; J. T. Baker Chemical Co., Phillipsburg, NJ) and diluted to the mark with the solvent for SEC analysis.

The analysis was performed using a Waters Associates 150C ALC/GPC liquid chromatograph (Milford, MA) equipped with an automatic injector and a differential refractometer (Δ RI). A Waters 730 data module was used for recording of peaks, integration of sliced peak areas (12 s/slice), and calculation of average molecular weights. A 100-Å Ultrastaygel column (30 cm \times 7.8 mm i.d.; Waters Associates, Milford, MA) was used at 30°C with THF as the eluting solvent, flowing at 1.0 mL/min. Injection volumes of 30, 50, and 75 μ L were used for the analysis of bloomed extender oils in the 10-mL THF solutions.

The column was calibrated with a series of *n*-alkanes (C_{12} , C_{16} , C_{22} , C_{28} , C_{32} , and C_{36} ; 99+%; Applied Science Laboratories, Inc., State College, PA) to determine relative number-average molecular weights (\bar{M}_{nrel}) of fresh and bloomed extender oils. The procedure was also calibrated with fresh oils A, B, and C for quantitation of the corresponding bloomed oils.

RESULTS AND DISCUSSION

A SEC molecular-weight calibration curve obtained with a series of *n*-alkanes has been used to calculate \bar{M}_{nrel} of fresh and bloomed extender oils for detecting changes in molecular-size distribution. The standard error of estimate and the correlation coefficient of the curve are 0.0068 and 0.9952, respectively, by a linear regression analysis.⁹ The \bar{M}_{nrel} determined for fresh oils were 282 (oil A), 556 (oil B), and 395 (oil C).

Three comparative chromatograms of the fresh and bloomed extender oils are shown in Figures 1 and 2, in which two arrows indicate their retention-time ranges used for calibration and quantification of each oil. SEC concentration calibration data for fresh oils A, B, and C are listed in Table I. The detector responses per μ g of oil were obtained by using the major portion of sliced peak areas, i.e., 11 slices between the retention times of 7.22 and 9.22 min for oil A, six slices between 6.82 and 7.82 min for oil B, and nine slices between 7.02 and 8.62 min for oil C (cf. Fig. 1), assuming that the Δ RI responses per unit weight are constant over the range of selected slices for each oil.

Infrared spectroscopic examination has revealed that oil A contains the most aromatic components, oil C has significantly less aromatic components than oil A, and oil B is mainly composed of aliphatic hydrocarbons, based on the absorption bands at 1600 and 700–900 cm^{-1} . The relatively low correlation coefficient for oil-A calibration is likely caused by the tailing, lower molecular-weight components (\approx 200).

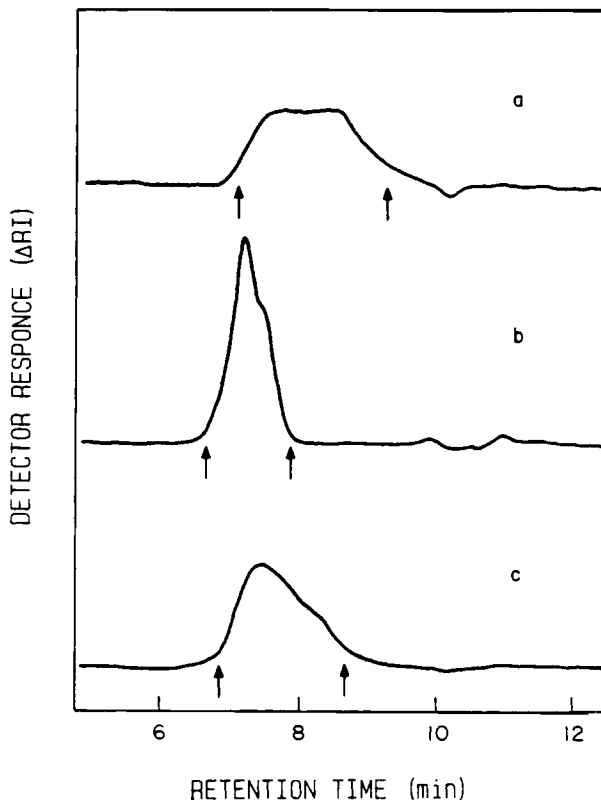


Fig. 1. Chromatograms of fresh extender oils: (a) 130.9 μg oil A ($\bar{M}_{n\text{rel}} = 285$); (b) 190.0 μg oil B ($\bar{M}_{n\text{rel}} = 554$); (c) 163.3 μg oil C ($\bar{M}_{n\text{rel}} = 393$); column, 100-Å Ultrastaygel (30 cm \times 7.8 mm i.d.); solvent, THF; flow rate, 1.0 mL/min (the elution ranges used in the determination of response factors and $\bar{M}_{n\text{rel}}$ are indicated by two arrows).

The relative standard deviations (RSD) determined as a measure of precision for the present SEC concentration analysis of oils A, B, and C, based on the calibration data presented in Table I, were 4.95, 3.00, and 3.18%, respectively ($n = 5$). All chromatograms of the three extender oils exhibit somewhat bimodal molecular-size distributions. The chromatographed bloomed extender oil samples (cf. Fig. 2) were obtained by the second hexane-dissolution of a group of three buttons (one for each oil) with an aging period of 34 days, which was the elapsed time between the first and second dissolutions in a repeated dissolution experiment. Since the excluded extender oil bloomed during the course of compression-set vulcanization had been removed at the first hexane dissolution, the bloomed extender oil on the surface of the buttons during that aging period derived only from the process of diffusive migration.

When the molecular-size distribution of fresh oil A is compared with that of the bloomed oil [cf. Figs. 1 (a) and 2 (a)], the difference in size distribution appears to indicate the molecular-size effect on oil migration in an EPDM system. However, the size distribution and $\bar{M}_{n\text{rel}}$ (257 ± 3) of a series of the bloomed oils obtained from its repeated dissolution of an oil-A button with hexane do not change appreciably from the first to sixth dissolution, i.e., 0 to

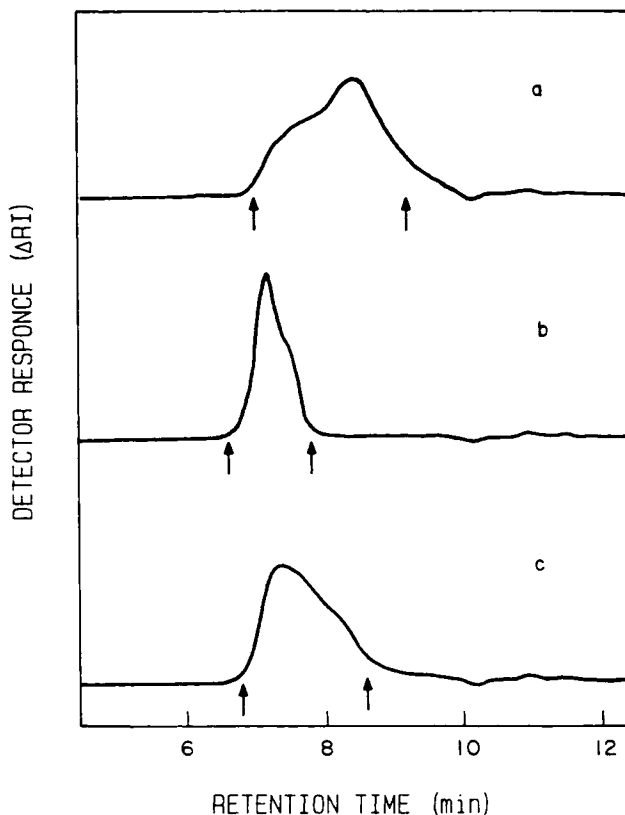


Fig. 2. Chromatograms of bloomed extender oils: (a) 116.0 μg oil A ($\bar{M}_{n\text{rel}} = 253$); (b) 118.0 μg oil B ($\bar{M}_{n\text{rel}} = 552$); (c) 139.5 μg oil C ($\bar{M}_{n\text{rel}} = 377$); SEC conditions are the same as those given in Figure 1.

434 days of the cumulative aging times, probably indicating that a part of the higher molecular-size components of oil A ($\bar{M}_{n\text{rel}} \approx 500$) has been crosslinked into the elastomeric networks during vulcanization. The participation of heterocyclic and aromatic oil components has been reported previously in the crosslinking of EPDM elastomers.¹⁰ In contrast, bloomed oils B and C showed

TABLE I
SEC Concentration Calibration Data for Petroleum-Based Extender Oils^a

Extender oil	Slope (ΔRI response/ μg)	Corr coeff	Std error of estimate ($\times 10^{-2}$)
Oil A	2.501	0.9757	5.740
Oil B	1.404	0.9956	1.151
Oil C	1.872	0.9967	1.603

^a Single 100-Å Ultrastaygel column with a THF flow rate of 1.0 mL/min and refractometer sensitivity at the setting of 32; based on 10 analyses with the concentration range of 40–150 μg per injection ($n = 2$ at each concentration).

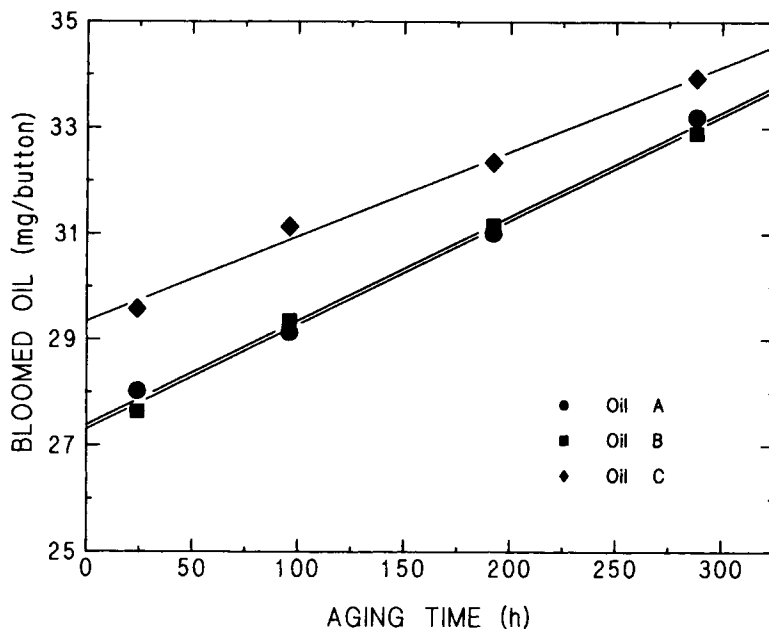


Fig. 3. Plots of bloomed oil vs. aging time (see the consecutive dissolution in the text).

no appreciable changes in size distribution from their corresponding fresh oils [cf. Figs. 1 (b) and 2 (b) and Figs. 1 (c) and 2 (c)], possibly because of very low concentration levels of reactive oil components in the network formation.

To determine the amount of an excluded oil in bloomed oils and the initial rate of oil migration for an EPDM compounding recipe, three sets of oil-A, oil-B, and oil-C buttons (four each) were prepared and their bloomed oils were collected consecutively at the room-temperature aging times of 24, 96, 192, and 288 h ($t = 0$ at the end of vulcanization). The results of consecutive hexane-dissolution experiments are shown in Figure 3. From the zero aging-time intercept and slope, the amount of an excluded oil and the initial rate of migration (0 to ca. 300 h) for each extender oil have been determined and summarized in Table II.

TABLE II
Determination of the Excluded Oil and Initial Rate of Oil Migration

Extender oil	Excluded oil found		Rate of migration ($\mu\text{g}/\text{cm}^2/\text{h}$)
	(mg/cm^2) ^a	(% w/w) ^b	
Oil A	1.17	1.33	0.84
Oil B	1.16	1.38	0.84
Oil C	1.25	1.46	0.68

^a The average surface area of three sets of buttons was 23.48 cm^2 .

^b Average initial amounts of oils A, B, and C per button were 2,057.1, 1,971.2, and 2,011.3 mg, respectively.

The results indicate that oil C has been excluded slightly more (ca. 7%) than oils A and B during the course of compression-set vulcanization and that the initial rate of migration for oil C is ca. 19% slower than those of oils A and B in the presence of each excluded oil. The bloomed oil, which is defined here as the sum of excluded and migrated oils, reaches an equilibrium amount of $1.41 \pm 0.09 \text{ mg/cm}^2$ beyond 300-h room-temperature aging.

In another series of hexane-dissolution experiments, one of each of oil-A, oil-B, and oil-C buttons was subjected to the hexane dissolution six times at the aging periods of 0–236 days. In Figure 4 are plots of the amount of migrated oils vs. the aging period obtained by the repeated dissolution of bloomed oils on a button for each extender oil. As indicated in the figure, the order of hexane dissolution does not coincide with the length of aging periods. Since the purpose of this series of dissolution experiments was to determine the initial rate of oil migration and the equilibrium amount of migrated oils in the absence of any excluded oil, the amounts of bloomed oils obtained by the first dissolution of the three buttons are not included in the figure. The initial rates of migration determined in the absence of excluded oils for oils A ($2.3 \mu\text{g/cm}^2/\text{h}$), B ($2.1 \mu\text{g/cm}^2/\text{h}$), and C ($2.3 \mu\text{g/cm}^2/\text{h}$) are similar, but two and a half to three times faster than those rates obtained in the presence of excluded oils (cf. Table II). It can be explained on the basis of this data that the reason for the lower initial rate of oil-C migration in the presence of an excluded oil would be the slightly higher excluded-oil concentration on the surface of its EPDM vulcanizates. Also, in the absence of excluded oils, the amounts of migrated oils A, B, and C arrive at their maximum values of 1.12, 1.05, and 1.20 mg/cm^2 at a cumulative aging period of 200–250 days.

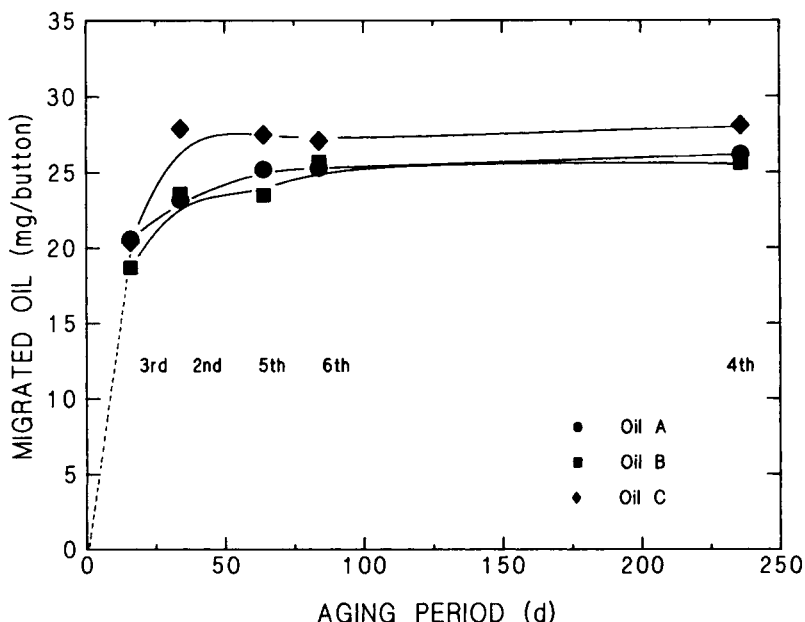


Fig. 4. Plots of migrated oil vs. aging period (the ordinal numbers in the figure are the sequence of hexane dissolution; see the repeated dissolution in the text).

In Figure 5 are plots of the amount of cumulative migrated oils vs. the cumulative aging periods (Σ six periods = 434 days) in the aging-period sequence of 34 (2nd dissolution), 16 (3rd), 236 (4th), 64 (5th), and 84 days (6th) to determine the rate of oil migration at an attained uniform concentration in the absence of an excluded oil (cf. Fig. 3). The rates of migration calculated from the amounts of migrated oils (slopes) at the cumulative aging periods of 286, 350, and 434 days were 0.48, 0.49, and 0.53 $\mu\text{g}/\text{cm}^2/\text{h}$ for oil A, B, and C, respectively. At the end of the cumulative aging periods, ca. 6.0% of the initially loaded amount of extender oils were bloomed by both exclusion and migration. A uniform oil concentration in the EPDM vulcanizates appears to reach at the room-temperature aging period of 200–250 days, overcoming the higher oil concentration gradient caused by the compression-set oil exclusion at the surface regions. The rates of oil migration determined at the uniform concentration are reduced to about a one-half of those determined at the initial room-temperature aging stage. The results obtained here confirm that the rate of oil migration is largely dependent on the EPDM polymer matrix itself even at very high oil concentration as reported previously.⁶

In conclusion, the present hexane-dissolution/SEC method for the analysis of hydrocarbon-oil blooms on the compression-set surface of oil-extended EPDM vulcanizates described here is relatively simple, requires a short analysis time (ca. 30 min/sample), and is quite precise for the sample matter. RSD of the analysis method is less than 5% in the concentration range of 50–150 μg per analysis and the lower limit of SEC analysis sample sizes is ca. 25–30 μg per injection for the extender oils studied. The method would also be useful in determining the blooming behavior of a variety of hydrocarbon oils in other elastomer systems as a means of predicting the long-term compositional stability.

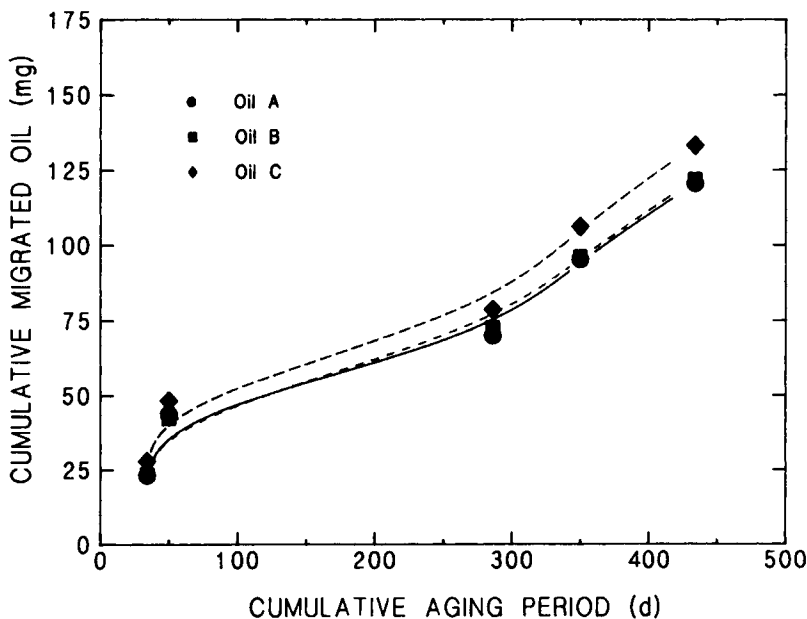


Fig. 5. Plots of the cumulative migrated oil vs. the cumulative aging period.

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