Long Term Oil-Seal Embrittlement

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Synopsis

The effect of antioxidant concentration in mineral oil on polychloroprene rubber vulcanizate, based on different types of carbon black, has been studied. This study shows that, with the increase of antioxidant, the percentage volume swelling of the rubber increases, the hardness of the rubber decreases, and the embrittlement time is prolonged. The properties achieved are important for oil seal manufacturers.

INTRODUCTION

Prevention of embrittlement is very important for oil-seal maintenance. For this reason antioxidants are useful for stabilization. There is always migration of antioxidant from the rubber to the oil. This antioxidant loss causes an increase in rubber hardness, seal shrinkage, and early embrittlement. With oil-containing antioxidant, the diffusing oil will stabilize the antioxidant migration from the rubber to the oil. This maintains low rubber hardness and prolongs the time for embrittlement. The embrittlement of nitrile rubber in mineral oils has been investigated before.[1-5] The objective of this study is to increase the lifetime of chloroprene rubber seal in oil.

MATERIALS AND EXPERIMENTAL PROCEDURE

Rubber Mix Formulation

The mixes that were examined here based on Neoprene WRT elastomer, poly(2-chloro-1,3-butadiene) supplied by E. I. du Pont de Nemours. The basic formulation is given in Table I. Flectol H is a Monsanto product and is used to improve flexing properties of the rubber. The tetramethyl thiourea is a very fast vulcanizing agent. Four types of carbon black were used: thermal medium (MT), semireinforcing furnace (SRF), high abrasion furnace (HAF), and super abrasion furnace (SAF). The properties of the blacks[6] are given in Table II.

Mastication and mixing were carried out on a two-roll mill (300 × 130 mm) operating at a friction ratio of 1.25:1 with water cooling. Vulcanized sheets (from which test pieces were cut) were produced by molding in an electrically heated platen press at 170°C. Rheometer (Monsanto type TM100) tests at 170°C indicated that 90% crosslinking occurs at a cure time of 9 min for all samples.

Antioxidant Preparation

Phenyl-*B*-naphthylamine was prepared using the method reported by Friedlander.[7] The method consists of mixing 10 g of β-naphthol with 12.91 g

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TABLE I
Mix Formulation

Neoprene WRT	100
Flectol H (Monsanto)[a]	1.0
MgO	4.0
Stearic acid	0.75
Zinc oxide	5.0
TMTU[b]	0.75
Carbon black[c]	40

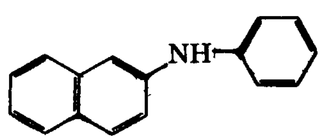
[a]Acetone–aniline products.
[b]Tetramethyl thiourea.
[c]TM, SRF, HAF, and SAF.

TABLE II
Carbon Black Properties

Property	TM	SRF	HAF	SAF
Average particle size (nm)	470	60	29	20
Aggregation structure[a] (cm^3/100 g)	33	65	105	115

[a]Volume of air spaces between carbon black aggregates per unit weight of carbon black.[6]

of aniline and heating the mixture at 280–290°C for 9 h. The brownish-violet mass was cooled, treated with 20 mL of concentrated HCl, heated a further for 1 h, and then cooled. The solid that separated was filtered with hot NaOH solution (10%), and the solid that remained was washed thoroughly with water and crystallized from ethanol to give yellow needles of phenyl-*B*-naphthylamine (108°C mp). The



prepared antioxidant was added to the base oil (containing no additives) at concentrations of 0, 0.125, 0.25, and 0.5%.

Swelling Measurements, Hardness, and Embrittlement Tests

Square-test pieces (15 × 15 × 2 mm) and strip samples (25 × 3 × 2 mm) were immersed in 20 mL of base refinery oil which contain the antioxidant at different concentrations. The swelling and aging tests were carried out in stoppered-glass bottles placed in a fan-assisted air circulating oven at 100°C. The square-test pieces were removed at intervals, weighed, and then reimmersed until constant weight was reached. The volumetric change ΔV was calculated as

$$\Delta V = \frac{(W_4 - W_3) - (W_1 - W_2)}{(W_1 - W_2)}$$

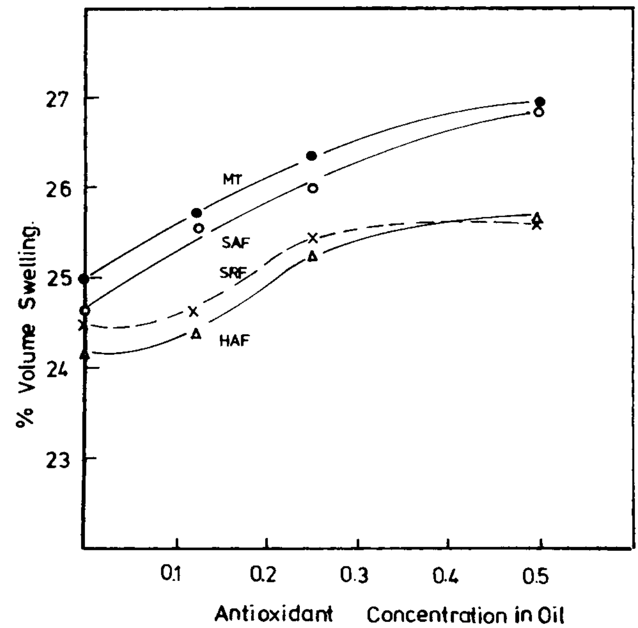


Fig. 1. Relation between the antioxidant concentration and the percentage volume swelling.

where W_1 and W_2 are, respectively, the weight of samples in air and in distilled water before swelling and W_3 and W_4 are the weight of samples in air and distilled water after equilibrium swelling.

The samples used for swelling tests were also used to study the aging effect of the oils on the rubber hardness and the time taken to brittle break. The samples are removed from the oils at given time intervals. The square samples are used to measure the hardness, and the strip samples are used for brittle break (twist test).

RESULTS AND DISCUSSION

The percentage volume swelling of the rubber samples slightly increases with an increase of antioxidant concentration in the oil as shown in Figure 1. The curves show different levels depending on the carbon black particle size. The larger the particle size the higher the percentage volume swelling. The most important conclusion from this curve is that the antioxidant increases the mobility of the oil in the rubber mix.

For engineering application, one very important property is the hardness of the rubber seal in the oil, specially after long immersion. The hardness of all samples was measured after reaching equilibrium volume swelling.

Figure 2 shows plot of hardness versus antioxidant concentration. From this figure, it can be noticed that the samples showed lower hardness as the antioxidant percentage increases and that the hardness of rubber filled with SRF black showed more stability than the three other fillers. The reduction of rubber hardness and increase in volume swelling is an indication of a decrease

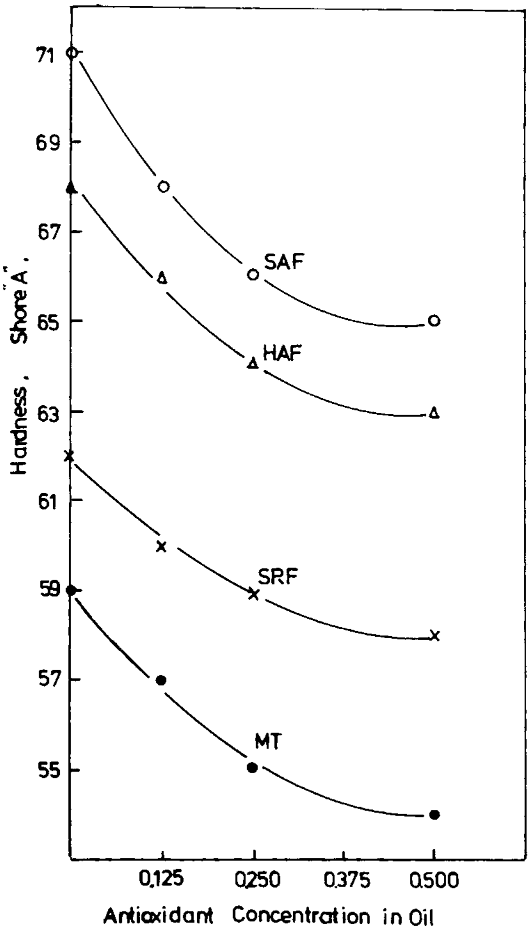


Fig. 2. Relation between the antioxidant concentration and hardness.

in crosslink density. The antioxidant used in both rubber and oils is usually soluble in both phases. This means that during service there is probably a migration of the rubber antioxidant into the oil and vice-versa. During immersion, the oil extracts the soluble ingredients from the rubber, among which is the antioxidant. The oil with antioxidant will diffuse into the rubber. By this way the concentration of the antioxidant in the rubber will maintain high and extend the life of the oil seal. The gained antioxidant lowers the hardness and causes longer time to embrittlement.

Figure 3 shows the plot of antioxidant concentration against the brittle break time expressed in number of days. There are two important aspects that can be shown in this figure: the first is that the antioxidant percentage increases the oil-seal life, the second is that the carbon black has a remarkable effect on the brittle time. Abrasion furnace blacks (SAF and HAF) showed an early brittle followed by the thermal black (TM). The SRF black is the most suitable black because of its moderate particle size and aggregation structure, semireinforcing properties, and relative hardness stability during immersion in the oil.

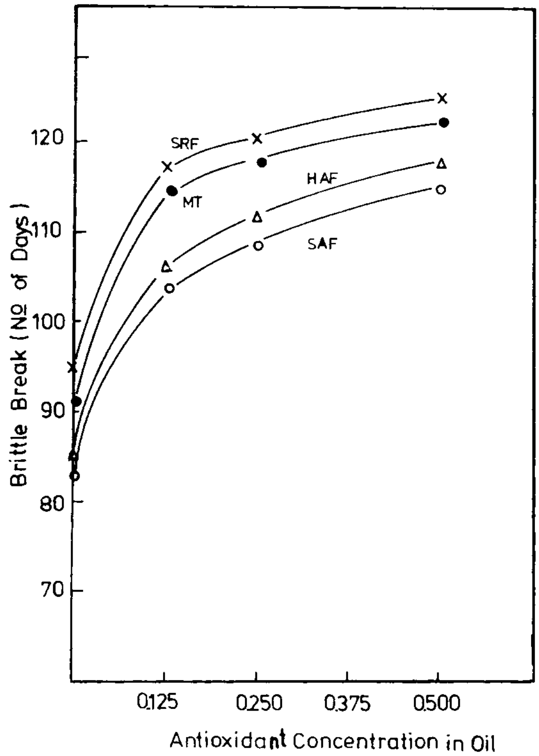


Fig. 3. Relation between the antioxidant concentration and brittle break expressed as number of days.

CONCLUSION

With an increase of antioxidant concentration in oil, the percentage volume swelling increases. This increase in swelling permits more oil, which containing antioxidant, to penetrate through the rubber bulk. The increase of antioxidant in the rubber decreases its hardness and maintains the degree of hardness constant for a long time. This by turn prevents early oil-seal embrittlement. These properties are very important for oil-seal engineering applications.

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