

# Reclamation of Vulcanized Rubbers by Chemical Degradation. V. Degradation of Vulcanized Synthetic Isoprene Rubber by the Phenylhydrazine-Ferrous Chloride System

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## Synopsis

The changes of effective network chain density and soluble fraction were measured for gum vulcanizates of synthetic isoprene rubber (IR) during the degradation by the phenylhydrazine-ferrous chloride system. From the decrease of effective network chain density and the increase of soluble fraction, the network chain was concluded to undergo a severance reaction by the reagents in the following order of ease: polysulfide linkage > monosulfide linkage > carbon-carbon crosslink. Analysis of the relation of soluble fraction with decrease of effective network chain density according to the theory of Horikx indicated that the severance of crosslinks predominated over main-chain scission in the degradation of sulfur vulcanizate by the reagents. The experiments of the degradation of sulfur vulcanizate in sealed vessels in the absence of oxygen indicated that atmospheric oxygen is necessary for the degradation reaction.

## INTRODUCTION

At present, reclaiming processes are well established for natural rubber scrap, and reclaim is accepted in compounding of new rubber products. However, devulcanization and depolymerization of the present reclaiming technology are performed by heating at about 200°C for several hours under pressure in the presence of cheap oil and organic chemicals. The heating at 200°C is economically undesirable. Moreover, the technology has the serious defect of applicability limited only to natural rubber scrap. Since various synthetic rubber vulcanizates are being used, it is important to establish a reclaiming technology for these vulcanizates. Devulcanization and depolymerization, therefore, have to be changed for synthetic rubber scrap. Natural rubber vulcanizates behave well under the present reclaiming conditions, because they soften with heat, and heat alone can give a satisfactory reclaim. On the other hand, it is difficult to reclaim synthetic rubber vulcanizates according to the present reclaiming technology. For example, styrene-butadiene rubber (SBR) vulcanizates, after initial softening with heat, quickly harden on further heating.

In a previous work,<sup>1</sup> we attempted to soften vulcanized rubber by chemical

reactions with use of various chemicals in the presence of atmospheric oxygen in order to simplify the present reclaiming technology and improve the devulcanization and depolymerization stages to be performed at lower temperature. We found that the ferrous chloride–phenylhydrazine system considerably softened pulverized scrap tire composed mainly of natural rubber during several hours under atmospheric pressure at room temperature. The softened rubber easily twined on the roll and showed good properties for processing. The reclaim was revulcanized by press at 140°C with use of sulfur and vulcanization accelerator to afford useful elastomers.

The phenylhydrazine–ferrous chloride system was also shown to be very effective for the reclamation of various types of synthetic rubber vulcanizates.<sup>2</sup> That is, the following ten types of gum vulcanizates were easily softened by treatment with the reagents at room temperature for 4–24 hr: sulfur vulcanizates of styrene–butadiene rubber (SBR), synthetic isoprene rubber (IR), acrylonitrile–butadiene rubber (NBR), ethylene–propylene terpolymer (EPDM), and butyl rubber (IIR); organic peroxide vulcanizates of SBR, chloroprene rubber (CR), and EPDM; SBR vulcanizate prepared with tetramethylthiuram disulfide (TMTD) and zinc oxide; and 2-mercaptoimidazoline vulcanizate of CR. Re-vulcanization of these reclaims gave useful elastomers.

This paper describes a further study on the softening reaction of gum vulcanizates of IR by the phenylhydrazine–ferrous chloride system. We aimed to obtain detailed information on the mechanism of this novel and important degradation of vulcanized rubbers. Scrap tire itself is not adequate for this purpose because it is a composite material consisting of rubber blends, ingredients, reinforcing filler, and various chemicals. Therefore, we studied the degradation of the following three types of gum vulcanizates of IR: sulfur vulcanizate, organic peroxide vulcanizate, and vulcanizate prepared with use of TMTD and zinc oxide.

## EXPERIMENTAL

### Materials

We employed IR-2200 provided by Japan Synthetic Rubber Co. as the starting raw rubber. Commercial samples of rubber chemicals, ferrous chloride, phenylhydrazine, benzene, methanol, and other chemicals were used without further purification. Thermogravimetric analysis of the ferrous chloride indicated the presence of 40.8 wt-% water.

### Vulcanization

We prepared three types of gum vulcanizates of IR with the ingredients given in Table I. Sulfur vulcanizate was reported to be crosslinked mainly by di- and polysulfide linkage under the vulcanization conditions used in this work<sup>3</sup> and was expressed as IR-S<sub>x</sub> in this paper. Organic peroxide vulcanizate is crosslinked by carbon–carbon single bond<sup>4</sup> and was expressed as IR-S<sub>0</sub> in this paper. The vulcanizate prepared with use of TMTD and zinc oxide was considered to be crosslinked mostly by monosulfide linkage<sup>5</sup> and was expressed as IR-S<sub>1</sub> in this paper.

TABLE I  
Recipe for Vulcanization

Chemicals, phr	IR-Sx				IR-S <sub>1</sub>				IR-S <sub>0</sub>			
	0	1	2	3	0	3	0	3	0	1	2	3
Sulfur	2.3	2.3	2.3	2.3	—	—	—	—	—	—	—	—
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1	1	1	1	1
N-Cyclohexyl-2-benzothiazole sulfenamide	0.9	0.9	0.9	0.9	—	—	—	—	—	—	—	—
Tetramethylthiuram disulfide	—	—	—	—	3	3	—	—	—	—	—	—
Dicumyl peroxide (40C) <sup>a</sup>	—	—	—	—	—	—	10	10	10	10	10	10
Ferrous chloride <sup>b</sup>	0	0.10	0.25	0.50	0	0.50	0	0.50	0	0.10	0.25	0.50
Vulcanization condition	140	140	140	140	150	150	150	150	150	150	150	150
Temperature, °C	20	20	20	20	40	40	40	40	40	40	40	40
Time, min	20	20	20	20	160	160	160	160	160	160	160	160

<sup>a</sup> 40%.

<sup>b</sup> Used as a 20 wt-% solution in methanol.

### Degradation of Vulcanizates

Ferrous chloride was mixed with the rubber prior to the vulcanization. The vulcanizates were extracted with benzene for several days at room temperature and dried in vacuo at that temperature in order to remove the vulcanization residues previous to the experiments of degradation. Degradation of the vulcanizates under air atmosphere was performed at 20°C by soaking in 0.1 or 0.05 vol-% benzene solution of phenylhydrazine.

The degradation in sealed vessels in the absence of oxygen was carried out with use of a vacuum line system. In this case, the vulcanizate and phenylhydrazine were separately placed in a vessel under atmospheric pressure. After phenylhydrazine was frozen by cooling the vessel with Dry Ice and methanol, the vacuum line system was evacuated to  $10^{-4}$  mm Hg, and benzene was added by *trap-to-trap* distillation under high vacuum. In this way, the vulcanizate was soaked in benzene solution of phenylhydrazine in the absence of oxygen. The vessel was cut off from the system and kept at 20°C.

### Physical Properties of Polymers

The number-average molecular weight of raw rubber was determined using a Knauer electronic membrane osmometer. Swelling measurements were carried out by soaking vulcanized rubber samples in benzene at 20°C for 120 hr. After the soaking, the gel was obtained by drying the residual vulcanizates in vacuo at room temperature. The sol was determined as the difference in weight before and after the swelling experiments. The sol fraction was expressed by  $[\text{sol}/(\text{sol} + \text{gel})] \times 100$  (%). Effective network chain density  $\nu_e$  of the vulcanizates was determined using the modified Flory-Rehner equation<sup>6</sup>

$$\nu_e = -\frac{1}{V} \left[ \frac{\ln(1 - v_r) + v_r + \mu v_r^2}{g^{2/3} v_r^{1/3} - \frac{1}{2} v_r} \right] \quad (1)$$

where  $V$  is the molar volume of solvent,  $v_r$  is the volume fraction of rubber in the swollen sample,  $g$  is the volume fraction of gel in the vulcanizate, and  $\mu$  is an interaction parameter between solvent and polymer. The  $\mu$  value for IR determined by the above-mentioned osmometry was 0.427.

Since this network chain density was calculated on the basis of the total number of crosslinks, which includes both chemical crosslinks and entanglements, we evaluated the network chain density on the basis of the actual number of chemical crosslinks according to the procedure of Mullins<sup>7</sup> and expressed as  $\nu'_e$ .

### RESULTS AND DISCUSSION

We mixed ferrous chloride with rubber prior to the vulcanization. In Figure 1 is shown the relation between  $\nu'_e$  and the content of ferrous chloride of the vulcanizates. The value of  $\nu'_e$  decreased with ferrous chloride content. The result appears to show that ferrous chloride promotes oxidative degradation of rubber to some extent during the vulcanization of IR.

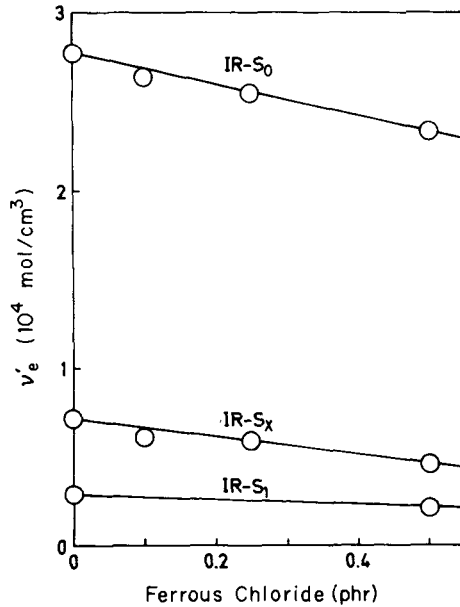


Fig. 1. Effect of ferrous chloride content on effective network chain density  $\nu'_e$ .

Degradation of these vulcanizates was performed by soaking them in 0.1 vol-% benzene solution of phenylhydrazine at 20°C. The ratio of decrease of  $\nu'_e$  to the  $\nu'_e$  before degradation,  $(\nu'_{e0} - \nu'_{e1})/\nu'_{e0}$ , is plotted against the soaking time in Figure 2. The value of  $\nu'_e$  of the sulfur vulcanizate considerably decreased with soaking time without respect to the ferrous chloride content in the vulcanizate. The value of  $\nu'_e$  of the vulcanizate prepared with use of TMTD and zinc oxide decreased to a much lesser extent, and that of organic peroxide vulcanizate decreased very little. These results indicate that the polysulfide linkage undergoes severance reaction by the phenylhydrazine-ferrous chloride system much more easily than the monosulfide linkage and the carbon-carbon crosslink.

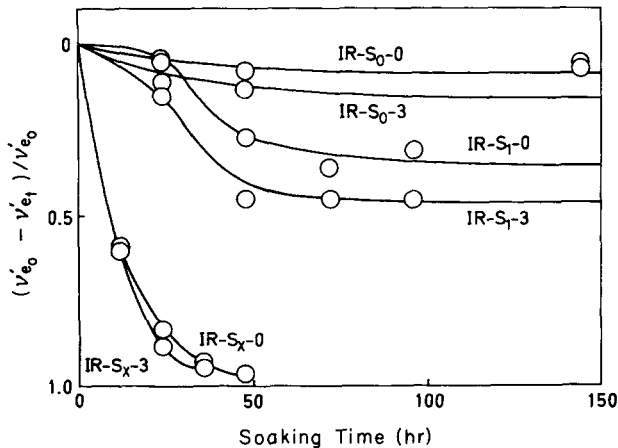


Fig. 2. Effect of soaking time at 20°C in 0.1 vol-% benzene solution of phenylhydrazine on ratio of decrease of effective network chain density to density before degradation.

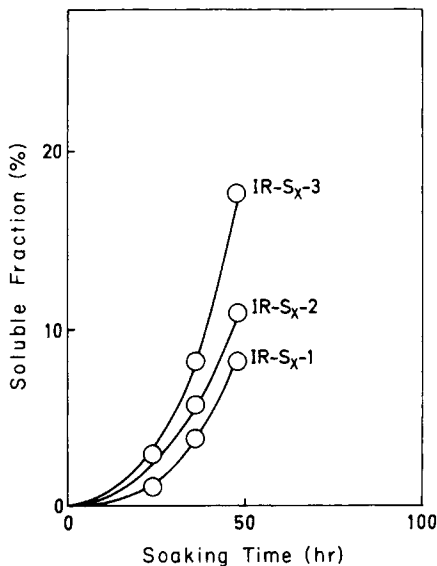


Fig. 3. Effect of soaking time at 20°C in 0.1 vol-% benzene solution of phenylhydrazine upon increase in soluble fraction.

Taking account of the fact that the conditions adopted to prepare IR-S<sub>1</sub> vulcanizates probably produce networks with not more than 80% monosulfide crosslinks,<sup>8</sup> we cannot determine the relative ease of monosulfide linkage and carbon-carbon crosslink in the severance reaction. However, it would be reasonable to conclude that the monosulfide linkage is more easily severed than the carbon-carbon crosslink, based on the following assumptions: (i) Although the total number of network is altered as shown in Figure 1, the presence of ferrous chloride does not affect the relative proportions of sulfidic crosslinks formed. (ii) The polymer-solvent interaction parameter  $\mu$  is independent of vulcanizate structure and state of oxidation. Nevertheless, a substantial amount of main-chain scission would have been expected in view of the substantial effect of phenylhydrazine and oxygen on the viscosity of polyisoprene solution.<sup>9</sup>

In Figure 3 is shown the relation of the soluble fraction of sulfur vulcanizate to soaking time in 0.1 vol-% benzene solution of phenylhydrazine. Since the soluble fraction of the vulcanizates was once removed previous to the experiments of degradation, the soluble fraction shown in Figure 3 was derived from the degradation of the vulcanizates by the phenylhydrazine-ferrous chloride system. In fact, the vulcanized rubber samples did not give a soluble fraction in the swelling measurements when they were not treated with the benzene solution of phenylhydrazine.

The soluble fraction increased with ferrous chloride content. The vulcanizate prepared with use of TMTD and zinc oxide gave a soluble fraction less than 1% even when the vulcanizate contained 0.5 phr ferrous chloride (IR-S<sub>1</sub>-3) and the soaking time was 96 hr. On the other hand, the organic peroxide vulcanizate did not give a soluble fraction even when 0.5 phr ferrous chloride was mixed before vulcanization (IR-S<sub>0</sub>-3). These results also support the assumption that the network chain of the IR vulcanizate undergoes a severance reaction by the phenylhydrazine-ferrous chloride system in the following order of ease: polysulfide linkage > monosulfide linkage > carbon-carbon crosslink.

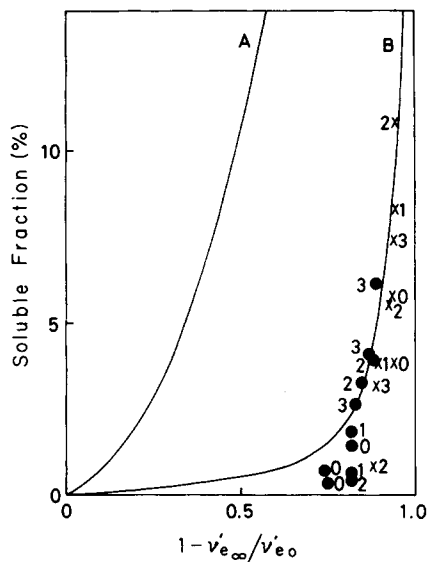


Fig. 4. Plots of soluble fraction vs.  $1 - \nu'_{e\infty}/\nu'_{e_0}$  for the degradation of sulfur vulcanizate of IR by the ferrous chloride-phenylhydrazine system: A and B are theoretical curves for main-chain scission and severance of crosslinks, respectively; (●) and (×) respectively denote degradation in 0.05 and 0.1 vol-% benzene solution of phenylhydrazine; (0) IR-Sx-0; (1) IR-Sx-1; (2) IR-Sx-2; (3) IR-Sx-3. The difference in soluble fraction of samples represented by the same number and symbol is due to the difference in the time of vulcanization.

Horikx<sup>10</sup> derived a relation of soluble fraction with the number of effective chains between crosslinks in a polymer of three-dimensional network undergoing a scission reaction. According to theory, the relation of soluble fraction to effective number of chains between crosslinks is expressed by eq. (2) if chain scission is a random process and the total number of crosslinks is constant during the degradation reaction, i.e., there is no severance of crosslinks but only main-chain scission:

$$1 - \frac{\nu_{e\infty}}{\nu_{e_0}} = 1 - \frac{(1 - S_\infty^{1/2})^2}{(1 - S_0^{1/2})^2} \quad (2)$$

where  $S_0$  and  $\nu_{e_0}$  are the soluble fraction and the effective number of chains between crosslinks in the undegraded crosslinked polymer, respectively; and  $S_\infty$  and  $\nu_{e\infty}$  are the corresponding quantities in the degraded polymer. The relation is expressed by eq. (3) if there is no chain scission but severance of crosslinks:

$$1 - \frac{\nu_{e\infty}}{\nu_{e_0}} = 1 - \frac{\gamma_\infty(1 - S_\infty^{1/2})^2}{\gamma_0(1 - S_0^{1/2})^2} \quad (3)$$

where  $\gamma_0$  and  $\gamma_\infty$  are crosslinking indices of the whole polymer, i.e., average number of crosslinked units per original chain, before and after degradation, respectively.

In Figure 4 the plots of soluble fraction versus  $1 - \nu'_{e\infty}/\nu'_{e_0}$  are shown for the degradation of sulfur vulcanizates of IR by soaking in 0.05 and 0.10 vol-% benzene solution of phenylhydrazine at 20°C for 120 hr. Here, several samples were prepared with variation in curing time but expressed by the same number and symbol in Figure 4. A and B are theoretical curves for the main-chain scission

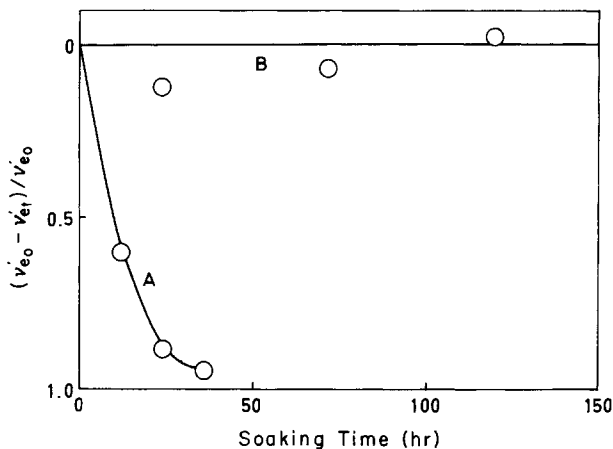


Fig. 5. Effect of oxygen on rate of decrease of effective network chain density of sulfur vulcanizate of IR (IR-Sx-3) caused by soaking in 0.1 vol-% benzene solution of phenylhydrazine. Experiments were carried out (A) under air atmosphere or (B) in the absence of oxygen.

and the severance of crosslinks, respectively. These curves were obtained based on the data of IR vulcanized by sulfur without use of ferrous chloride (IR-Sx-0). As was mentioned above, Figures 2 and 3 support the severance of the network chain of IR vulcanizates by the phenylhydrazine-ferrous chloride system in the following order of ease: polysulfide linkage > monosulfide linkage > carbon-carbon crosslink. Figure 4 shows that the severance of crosslinks predominated over the main-chain scission in the degradation of sulfur vulcanizate of IR by the phenylhydrazine-ferrous chloride system, although a substantial amount of main-chain scission would have been expected.<sup>9</sup>

Sulfur vulcanizate of IR was not degraded by the phenylhydrazine-ferrous chloride system when the experiments were carried out in sealed vessels in the absence of oxygen using a vacuum line system, as shown in Figure 5. The experimental result clearly indicates that atmospheric oxygen is necessary for the degradation of vulcanizates by the reagents.

The result is consistent with our previous findings.<sup>2</sup> That is, infrared spectra of soluble fraction of softened IR-Sx, SBR-Sx, NBR-Sx (sulfur vulcanizate of NBR), and CR-NA (2-mercaptoimidazole vulcanizate of CR) showed the presence of hydroxyl and carbonyl groups in the polymers.<sup>2</sup> Presumably, oxygen participates in the degradation reaction and attached to the degraded polymers. The utility of phenylhydrazine as a peptizer for rubber has long been known.<sup>9,11,12</sup> Decomposition of phenylhydrazine in the presence of oxygen was reported to give benzene and water.<sup>13</sup> Hydrazine was reported to initiate radical polymerization of methyl methacrylate in the presence of oxygen.<sup>14</sup>

These experimental results suggest that the reaction of the phenylhydrazine-ferrous chloride system with atmospheric oxygen may afford hydroperoxide by radical mechanism, and the hydroperoxide would cause main-chain scission and severance of crosslinks of vulcanizates. The presence of ferrous chloride seems to accelerate the decomposition of phenylhydrazine, and the effect is now under investigation.

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