

# Reclamation of Vulcanized Rubbers by Chemical Degradation. VIII. Absorption of Oxygen and Degradation of *cis*-1,4-Polyisoprene by Phenylhydrazine–Iron(II) Chloride System

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## Synopsis

Absorption of oxygen and degradation of *cis*-1,4-polyisoprene by the phenylhydrazine–iron(II) chloride system was investigated at 30°C in connection with the mechanism of reclamation of vulcanized rubbers by the system. In the presence of iron(II) chloride, phenylhydrazine rapidly absorbed an equimolar amount of oxygen and evolved an equimolar amount of nitrogen. Gas-chromatographic analysis of the reaction mixture showed the presence of benzene, phenol, and biphenyl in 37%, 35–60%, and 4–8% yields, respectively, based on phenylhydrazine. When *cis*-1,4-polyisoprene was added to the reaction mixture, additional absorption of oxygen was observed. Molecular weight of the polymer decreased during the oxygen absorption, and the scission efficiency (i.e., number of mole scissions/mole oxygen) was 0.14–0.26.

## INTRODUCTION

In a previous paper,<sup>1</sup> we have reported that the phenylhydrazine–iron(II) chloride system is a good catalyst for the reclamation of not only truck tire scrap, but also scrap tire of passenger cars during several hours at room temperature under atmospheric pressure. The system was also shown to be very effective for the reclamation of various types of synthetic rubber vulcanizates.<sup>2</sup> Vulcanization of these reclaims gave useful elastomers. Devulcanization and depolymerization of the new reclamation procedure was shown to result from the oxidative degradation of vulcanized rubbers.<sup>3</sup> In this work, we have investigated the absorption of oxygen and the decrease of molecular weight of *cis*-1,4-polyisoprene by the phenylhydrazine–iron(II) chloride system in connection with the mechanism of the reclamation of vulcanized rubbers by the system.

Mayo and co-workers have investigated oxidations of *cis*-1,4-polyisoprene accelerated by some soluble transition metal salts<sup>4</sup> and hydrazines.<sup>5</sup> However, these workers did not refer to the oxidation of *cis*-1,4-polyisoprene accelerated by the phenylhydrazine–iron(II) chloride system, although they cited a Russian work<sup>6</sup> which reported rate enhancement of butadiene rubber oxidation by phenylhydrazine upon the addition of iron naphthenate. As we have reported previously,<sup>1</sup> individual use of phenylhydrazine and iron(II) chloride was much less effective for the reclamation of vulcanized rubbers. Therefore, oxidation of *cis*-1,4-polyisoprene accelerated by the phenylhydrazine–iron(II) chloride system would have a much different nature when compared with that accelerated by phenylhydrazine alone.

## EXPERIMENTAL

### Materials

*cis*-1,4-Polyisoprene (IR-2200) provided by Japan Synthetic Rubber Co. Ltd. was masticated at room temperature for 20 min and dissolved in benzene. The gel was removed by filtration, and the soluble polymer was recovered by pouring the filtrate into a large excess of methanol and purifying by reprecipitation, followed by drying in vacuo at room temperature. Benzene was purified by washing with concentrated sulfuric acid. After repeated water wash, it was dried with calcium chloride, then refluxed over calcium hydride, and distilled. Specially prepared toluene for gas chromatography provided by Nakarai Chemicals Ltd., Kyoto, was used without further purification. Commercial samples of phenylhydrazine, iron(III) chloride and other chemicals were used without further purification. Thermogravimetric analysis of iron(II) chloride showed the presence of 40.8 wt-% water.

### Procedure

The apparent amount of absorbed oxygen was determined at 30°C under atmospheric pressure with the use of an automated oxygen absorption instrument which was similar to that described by Krueger.<sup>7</sup> The measurements of oxygen absorption were carried out under pressure. Pure oxygen was automatically supplied to the reaction system as gas absorption occurred. Mass spectra were obtained on a Hitachi Model RMU-6 mass spectrometer. Gas-chromatographic analysis was carried out on a Shimadzu Model 4BM gas chromatograph. Viscosity measurements of degraded and undegraded *cis*-1,4-polyisoprene solutions were carried out in benzene at 30°C with an Ubbelohde-type dilution viscometer. Number-average molecular weight of the polymers was determined with a Knauer electronic membrane osmometer in benzene at 25°C. The values for  $K$  and  $a$  in the relationship between the intrinsic viscosity  $[\eta]$  and the number-average molecular weight  $\bar{M}_n$ ,  $[\eta] = K\bar{M}_n^a$ , were determined to be  $2.85 \times 10^{-5}$  and 0.93, respectively, in the range of number-average molecular weights of about 10,000 to 200,000.

## RESULTS AND DISCUSSION

Although Chattaway<sup>8</sup> have indicated that phenylhydrazine was oxidized on exposure to free oxygen, we found that iron(II) chloride considerably accelerated the oxidation. The apparent amount of oxygen absorbed by the phenylhydrazine-iron(II) chloride system was first examined in the absence of *cis*-1,4-polyisoprene. The time dependence of the oxygen uptake is shown in Figure 1. Curve 1 was obtained from an experiment carried out in the absence of iron(II) chloride in an atmosphere of air. Curve 2 was obtained from an experiment carried out in the presence of iron(II) chloride in an atmosphere of air. These two curves show that iron(II) chloride considerably promotes the oxidation of phenylhydrazine. This remarkable effect of iron(II) chloride would be the source of the strong ability of the phenylhydrazine-iron(II) chloride system as a catalyst for the reclamation of vulcanized rubbers. Curve 3 was obtained from an ex-

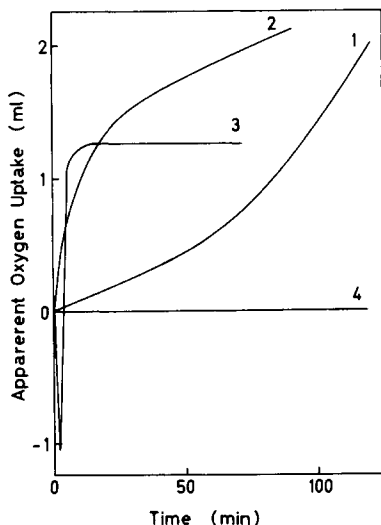


Fig. 1. Time dependence of apparent oxygen uptake by phenylhydrazine-iron(II) chloride system in the absence of *cis*-1,4-polyisoprene at 30°C:

| Run no. | C <sub>6</sub> H <sub>5</sub> NHNH <sub>2</sub> ,<br>mmole | C <sub>6</sub> H <sub>6</sub> ,<br>ml | FeCl <sub>2</sub> ,<br>mmole | CH <sub>3</sub> OH,<br>ml |          |
|---------|------------------------------------------------------------|---------------------------------------|------------------------------|---------------------------|----------|
| 1       | 0.51                                                       | 50                                    | —                            | 1.2                       | air      |
| 2       | 0.51                                                       | 50                                    | 0.13                         | 1.2                       | air      |
| 3       | 0.51                                                       | 48                                    | 0.12                         | 2.0                       | oxygen   |
| 4       | 0.51                                                       | 48                                    | 0.12                         | 2.0                       | nitrogen |

periment carried out in the presence of iron(II) chloride in an oxygen atmosphere. The rate of oxygen uptake was very rapid. Curve 3 also shows that gas evolved vigorously at the early stage of the reaction. Curve 4 was obtained from an experiment carried out in a nitrogen atmosphere. Neither oxygen absorption nor the evolution of gas was observed under these conditions.

As shown above, gas was evolved in the early stage of the reaction of phenylhydrazine with iron(II) chloride in the presence of oxygen. We carried out similar experiments in an oxygen atmosphere and analyzed the reaction products. Mass-spectroscopic analysis of the gaseous product indicated that the evolved gas was pure nitrogen. Based on the apparent amount of absorbed oxygen and the composition of gas, the absolute amounts of absorbed oxygen and evolved nitrogen were calculated. The liquid layer of the reaction mixture was analyzed by gas chromatography. Major products were shown to be benzene, phenol, and biphenyl. Gas-chromatographic analysis also showed the presence of small amounts of unidentified products, and the absence of benzidine, diphenylmethane, diphenylamine, *p*-hydroquinone, *p*-quinone, benzaldehyde, benzyl alcohol, benzyl chloride, and chlorobenzene. Results are given in Table I.

Results of experiments 11 and 14 given in Table I indicate that in the presence of iron(II) chloride under oxygen atmosphere, phenylhydrazine absorbed an equimolar amount of oxygen and evolved an equimolar amount of nitrogen. Result of experiment 13 shows that the decomposition of phenylhydrazine was not complete under the conditions, i.e., during 1 hr in the absence of iron(II) chloride. The result is consistent with the result of the time dependence of the oxygen uptake (curve 1 of Fig. 1.). Experiment 12 shows that in the presence

TABLE I  
Reaction of Phenylhydrazine and Iron(II) Chloride<sup>a</sup>

| Run no.         | Phenyl-<br>hydrazine,<br>mmole | Iron(II)<br>chloride,<br>mmole | Solvent | Absorbed<br>oxygen,<br>mmole | Evolved<br>nitrogen,<br>mmole | Benzene | Phenol | Biphenyl |
|-----------------|--------------------------------|--------------------------------|---------|------------------------------|-------------------------------|---------|--------|----------|
| 11              | 1.06                           | 0.24                           | benzene | 1.07                         | 1.06                          | —       | 0.50   | 0.08     |
| 12              | 1.06                           | 0.24 <sup>b</sup>              | benzene | 1.08                         | 1.01                          | —       | 0.64   | 0.09     |
| 13 <sup>c</sup> | 1.06                           | —                              | benzene | 0.82                         | 0.50                          | —       | 0.40   | 0.04     |
| 14              | 1.06                           | 0.24                           | toluene | 1.17                         | 1.08                          | 0.39    | 0.37   | 0.05     |
| 15 <sup>d</sup> | 1.06                           | 0.24                           | toluene | 1.91                         | 1.00                          | 0.40    | 0.16   | 0.05     |

<sup>a</sup> Reactions were carried out at 30°C for 1 hr under oxygen atmosphere. Iron(II) and iron(III) chlorides were used as solutions in 0.4 ml methanol. Amount of solvent was 9.6 ml.

<sup>b</sup> Anhydrous iron(III) chloride was used instead of iron(II) chloride.

<sup>c</sup> Gas-chromatographic analysis showed the presence of 0.29 mmole unchanged phenylhydrazine in the reaction mixture. In other runs, phenylhydrazine was not detected in the reaction mixture.

<sup>d</sup> The reaction was carried out in the presence of 1.0 g *cis*-1,4-polyisoprene.

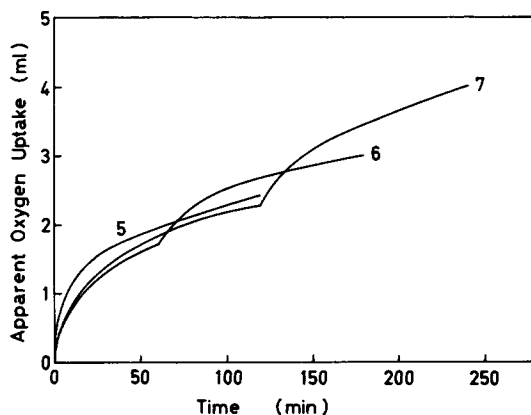


Fig. 2. Time dependence of apparent oxygen uptake by phenylhydrazine-iron(II) chloride system in the presence of *cis*-1,4-polyisoprene under atmosphere of air. Conditions: phenylhydrazine, 0.51 mmole; benzene, 48 ml; iron(II) chloride, 0.12 mmole; methanol, 2.0 ml; *cis*-1,4-polyisoprene, 0.5 g; at 30°C.

of iron(III) chloride instead of iron(II) chloride under oxygen atmosphere, phenylhydrazine also absorbed an equimolar amount of oxygen and evolved an equimolar amount of nitrogen.

In the investigation of the accelerated oxidation of *cis*-1,4-polyisoprene by phenylhydrazine, Mayo and co-workers<sup>5</sup> assumed that one molecule of nitrogen was evolved for each molecule of phenylhydrazine employed. The assumption was, however, based on the experimental results reported by Chattaway,<sup>8</sup> which was carried out in the absence of the polymer and could not always be valid. As shown above, the oxidation of phenylhydrazine by free oxygen was considerably slow in the absence of iron(II) chloride. Results of experiment 15 given in Table I shows that phenylhydrazine also evolved an equimolar amount of nitrogen in the presence of iron(II) chloride and *cis*-1,4-polyisoprene under oxygen atmosphere. The amount of the absorbed oxygen in this experiment was, however, much larger than that of the corresponding experiment carried out in the absence of polymer. The increased amount of oxygen would be consumed by the degradation of the polymer.

We carried out similar experiments of oxygen absorption in the presence of *cis*-1,4-polyisoprene in an atmosphere of air. The results are shown in Figure 2. Curve 5 was obtained from an experiment where the polymer existed from the beginning of the absorption experiment. The intrinsic viscosity of the polymer decreased from 1.95 to 0.34 dl/g during 2 hr. Curves 6 and 7 were obtained from experiments where benzene solution of the polymer was added to the reaction mixture of phenylhydrazine with iron(II) chloride after 1 and 2 hr, respectively, from the beginning of the absorption experiments. As can be seen from curves 6 and 7, oxygen uptake was accelerated by the addition of the polymer solution. In these experiments, the intrinsic viscosity of the polymer decreased from 1.95 to 0.41 and 0.51 dl/g, respectively, during 2 hr after the addition of the polymer solution. Therefore, the reaction product of phenylhydrazine with iron(II) chloride was concluded to have the ability to degrade the polymer even after several hours, although the ability decreases as time passes.

We carried out similar experiments under oxygen atmosphere. Results are

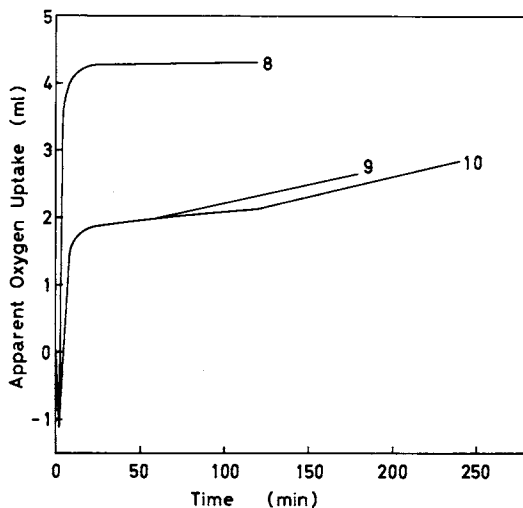


Fig. 3. Time dependence of apparent oxygen uptake by phenylhydrazine-iron(II) chloride system in the presence of *cis*-1,4-polyisoprene under oxygen atmosphere. Conditions: phenylhydrazine, 0.51 mmole; benzene, 48 ml; iron(II) chloride, 0.12 mmole; methanol, 2.0 ml; *cis*-1,4-polyisoprene, 0.5 g; at 30°C.

shown in Figure 3. Curve 8 was obtained from an experiment where the polymer existed from the beginning of the absorption experiment. The intrinsic viscosity of the polymer decreased from 1.95 to 0.27 dl/g during 2 hr. Thus, the oxygen uptake was more rapid and the degradation of polymer was more significant under oxygen atmosphere than those under air atmosphere. Curves 9 and 10 were obtained from experiments where benzene solution of the polymer was added to the reaction mixture of phenylhydrazine with iron(II) chloride after 1 and 2 hr, respectively, from the beginning of the absorption experiments. As can be seen from curves 9 and 10, oxygen uptake was accelerated by the addition of the polymer solution, although the amount of the additional oxygen uptake was smaller than the corresponding amount observed in air. In these experiments, the intrinsic viscosity of the polymer decreased from 1.95 to 1.41 and 1.48 dl/g, respectively, during 2 hr after the addition of the polymer solution. The decrease of intrinsic viscosity of the polymer was not very significant when compared with that of the corresponding experiments carried out in air. Thus, it was concluded that the reaction product of phenylhydrazine with iron(II) chloride loses the ability to degrade the polymer as time passes much more rapidly in an oxygen atmosphere than under air atmosphere.

Degradation of *cis*-1,4-polyisoprene of a number-average molecular weight of 158,500 by the phenylhydrazine-iron(II) chloride system was carried out in benzene. Results are given in Table II. Here, the aging time is the time passed from the beginning of the reaction of phenylhydrazine with iron(II) chloride until the addition of the benzene solution of the polymer to the reaction mixture.

In the investigation of the accelerated oxidation of *cis*-1,4-polyisoprene by phenylhydrazine, Mayo and co-workers<sup>5</sup> evaluated the molecular weight of the degraded polymer from the reduced relative flow time of the polymer solution, and the viscosity to molecular weight relation was uncertain. We determined

TABLE II  
 Degradation of *cis*-1,4-Polyisoprene by the Phenylhydrazine-Iron(II) Chloride System<sup>a</sup>

| Run no. | Aging time,<br>hr | Atmosphere | Absorbed oxygen, mmole<br>Total | With polymer         | $\bar{M}_n$ | Number of<br>scissions,<br>mmole | Scission<br>efficiency, <sup>c</sup><br>% |
|---------|-------------------|------------|---------------------------------|----------------------|-------------|----------------------------------|-------------------------------------------|
| 5       | 0                 | air        | 0.611                           | (0.101) <sup>b</sup> | 24200       | 0.017                            | (17) <sup>b</sup>                         |
| 6       | 1                 | air        | 0.631                           | 0.052                | 29600       | 0.014                            | 26                                        |
| 7       | 2                 | air        | 0.671                           | 0.072                | 37500       | 0.010                            | 14                                        |
| 8       | 0                 | oxygen     | 0.683                           | (0.173) <sup>b</sup> | 18900       | 0.023                            | (13) <sup>b</sup>                         |
| 9       | 1                 | oxygen     | 0.601                           | 0.028                | 111800      | 0.001                            | 5                                         |
| 10      | 2                 | oxygen     | 0.625                           | 0.026                | 117800      | 0.001                            | 4                                         |

<sup>a</sup> Reactions were carried out with 0.5 g *cis*-1,4-polyisoprene of number-average molecular weight of 158500, 0.51 mmole phenylhydrazine, 0.12 mmole iron(II) chloride in 2.0 ml methanol, and 48.0 ml benzene at 30°C for 2 hr.

<sup>b</sup> Calculated based on the assumption that an equimolar amount of oxygen to phenylhydrazine was consumed by the reaction with phenylhydrazine and iron(II) chloride, and the other part of oxygen was consumed by the degradation of the polymer.

<sup>c</sup> Calculated as (number of mole scissions/mole oxygen) × 100. Here, the mole oxygen was the molar amount of oxygen absorbed after the addition of the polymer solution.

the number-average molecular weight of the degraded polymer and calculated the scission efficiency.

The scission efficiency was calculated based on the assumption that the absorbed oxygen after the addition of *cis*-1,4-polyisoprene was completely consumed by and only for the degradation of the polymer. Comparison of the results of experiments 5, 6, and 7 shows more definitively that the reaction product of phenylhydrazine with iron(II) chloride loses the ability to degrade the polymer as time passes. The scission efficiency also decreased as time passes. Comparison of the results of experiments 8, 9, and 10 also shows more definitively that the reaction product of phenylhydrazine and iron(II) chloride loses the ability to degrade the polymer much more rapidly under oxygen atmosphere than under air. The reaction with oxygen seems to be the cause of the loss of the ability of the phenylhydrazine-iron(II) chloride system to degrade the polymer.

In the autoxidation of natural rubber, scission efficiency was reported to be 9.7% and 16% at 130° and 150°C, respectively.<sup>9</sup> On the other hand, scission efficiency would be higher than 26% even at room temperature in the degradation of *cis*-1,4-polyisoprene by the phenylhydrazine-iron(II) chloride system when carried out in air. This high scission efficiency would be the source of the strong ability of the phenylhydrazine-iron(II) chloride system as a catalyst for the reclamation of vulcanized rubbers.

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### References

1. S. Yamashita, N. Kawabata, K. Mori, and T. Fujii, *J. Soc. Rubber Ind., Jpn.*, **49**, 360 (1976).
2. S. Yamashita, N. Kawabata, and K. Hayashi, *J. Soc. Rubber Ind., Jpn.*, **49**, 420 (1976).
3. S. Yamashita, N. Kawabata, S. Sagan, and K. Hayashi, *J. Appl. Polymer Sci.*, **21**, 2201 (1977).
4. F. R. Mayo, K. Egger, and K. C. Irwin, *Rubber Chem. Technol.*, **41**, 271 (1968).
5. F. R. Mayo, J. Heller, R. L. Walrath, and K. C. Irwin, *Rubber Chem. Technol.*, **41**, 289 (1968).
6. E. I. Tinyakova, B. A. Dolgoplosk, and V. N. Reikh, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1135 (1957).
7. R. A. Krueger, *J. Appl. Polymer Sci.*, **17**, 2305 (1973).
8. F. D. Chattaway, *J. Chem. Soc.*, **91**, 1323 (1907).
9. E. M. Bevilacqua, *Rubber Chem. Technol.*, **29**, 583 (1956).

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