

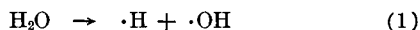
Studies on the γ -Irradiation of Natural Rubber Latex. The Effects of Organic Halogen Compounds on Crosslinking by γ -Irradiation

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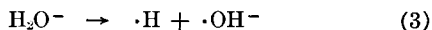
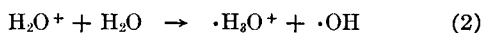
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INTRODUCTION

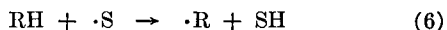
In our previous paper,¹ we reported that vulcanized latex was obtained by γ -irradiation of natural rubber latex. Optimum cure was attained at ca. 2×10^7 r in the case of 40% latex. With water accelerating the reaction, rubber in latex crosslinked more easily than did previously dried latex film, but no appreciable difference was found between latices of various concentrations. The mechanism of acceleration of crosslinking by water has been discussed from various standpoints by different authors, and among other views the following is acceptable. E. J. Hart² found that water was decomposed by γ -irradiation,



and hydrogen and hydrogen peroxide were obtained. The details of this decomposition are not known, but the following elementary reactions can be assumed to take place:



These radicals and ions (although they may be formed in negligible amounts) are considered to attack rubber in latex, and the rubber molecule is then crosslinked in following ways:

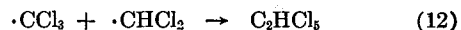
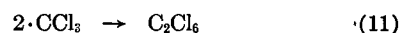
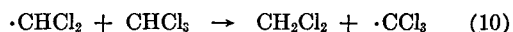
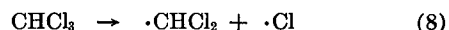


where RH is a rubber molecule and $\cdot\text{S}$ is a radical formed by γ -irradiation, and R—R represents crosslinking.

That the crosslinking is accelerated by small amount of water but that the effect is saturated at

high water content can be attributed to the small affinity between rubber and water. The contact between rubber molecules and water takes place only at the surface of latex particles, and the attack by $\cdot\text{S}$ is restricted.

On the other hand, the numbers of free radicals formed by a given radiation dose were calculated by Chapiro et al.³ for certain organic compounds having intimate affinity with rubber, i.e., benzene, 1,2-dichloroethane, chloroform, and carbon tetrachloride. The numbers of free radicals produced per 100 e.v. in these compounds are shown in Table I. The mechanism of decomposition of these compounds cannot be expressed in general; however, the decomposition of chloroform was studied by F. S. Dainton et al.⁴



It was assumed that these free radicals should accelerate the crosslinking to a greater extent than water. In the present paper, the effect of halogenated compounds on the vulcanization of latex by γ -irradiation will be described.

EXPERIMENTAL

Materials

The properties of the latex used (R.C.M.A. concentrated latex) were as shown in the previous paper.¹ This latex was diluted with distilled water to 50.0% of total solids. The reagents carbon tetrachloride, chloroform, 1,2-dichloroethane, and benzene were redistilled at their boiling points.

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TABLE I
Free Radicals Produced by γ -Irradiation³

Compound	Free radicals/100 e.v.
Benzene	1.8
1,2-Dichloroethane	41.0
Chloroform	59.5
Carbon tetrachloride	(70.0)

Methods

Tensile strength, elongation, modulus, equilibrium swelling ratio, and hardness were measured as described in the previous paper.¹ Since it was already obvious that rubber particles in latex are swollen by these organic solvents, and since the stability of the latex was considered to have been changed by irradiation, the properties of the latex before and after irradiation were not measured.

Calculation of Crosslinking Densities and G_c Values

Crosslinking densities (number of crosslinked units per cm.³ of rubber) were calculated in the manner described in the previous paper.¹ The G value, the amount of the reaction product affected per 100 e.v. of absorbed energy, varies according to whether the energy is assumed to be absorbed by rubber, water, or halides. The practical assumption was made that the energy was absorbed only by rubber, and G_c values of G for crosslinking were calculated on this basis.

The energy deposited in 1 g. of water by 1 r of γ -radiation was taken to be 6.08×10^{13} e.v., and from the ratio of the number of electrons per gram of rubber to the number in water, the energy deposition for rubber was found to be 6.10×10^{13} e.v./g./r. The G value was therefore calculated as

$$G_c = \frac{\text{Crosslinks/g.}}{\text{Energy absorbed (e.v.)/g.}} 100$$

$$= \frac{(v_0/2)}{(\text{Dose})(6.10 \times 10^{13})} 100 \quad (14)$$

RESULTS AND DISCUSSION

Acceleration of Crosslinking by Various Halides

In each case, the required amount of halide was added to latex, and the whole was stirred rapidly in a sealed vessel for one hour at room temperature. Most of the halide added was considered to have entered the rubber phase during the stirring.

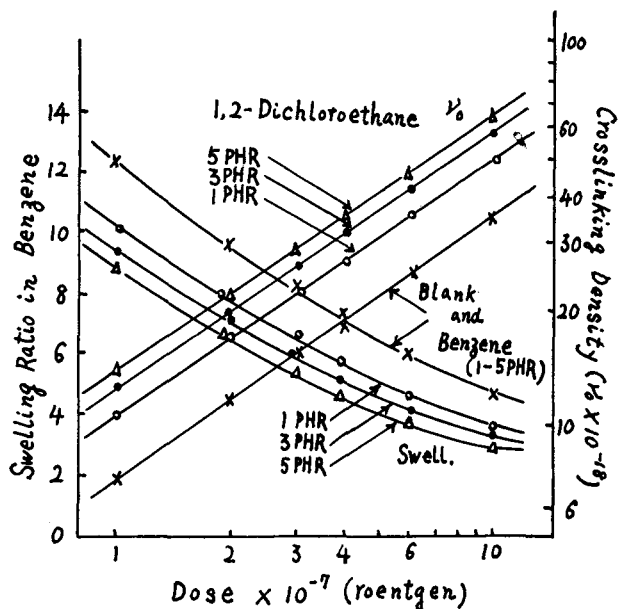


Fig. 1. Swelling ratio in benzene and crosslinking density vs. radiation dose, with 1,2-dichloroethane as accelerator.

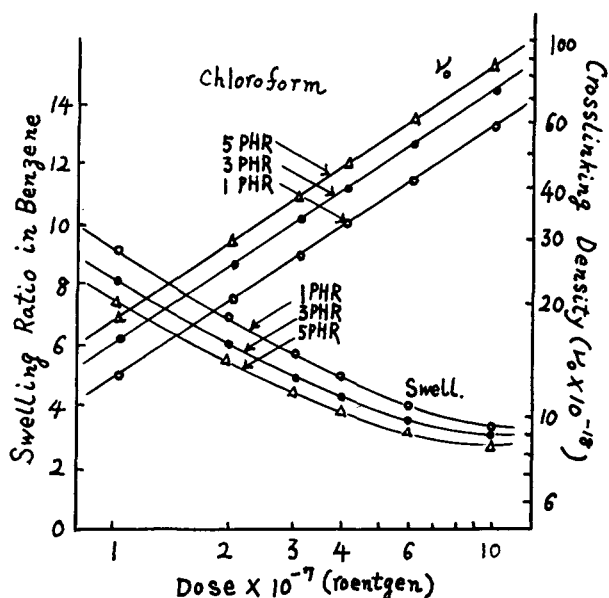


Fig. 2. Swelling ratio in benzene and crosslinking density vs. radiation dose, with chloroform as accelerator.

The latex was then transferred to a standard test tube and irradiated. The irradiated latex was dried to a film on a glass plate and the film was tested. Latices containing chloroform, 1,2-dichloroethane, or no halide were irradiated up to 10^7 - 10^8 r; those containing carbon tetrachloride were irradiated up to 10^5 - 10^7 r. The dose rate was ca. 10^6 r/hr. in all cases. For comparison, latices con-

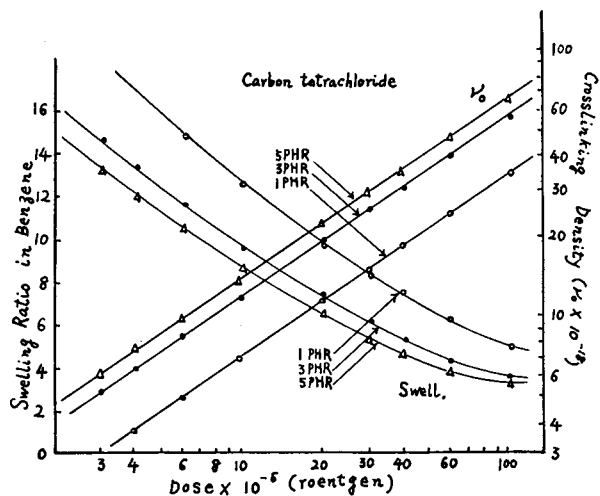


Fig. 3. Swelling ratio in benzene and crosslinking density vs. radiation dose, with carbon tetrachloride as accelerator.

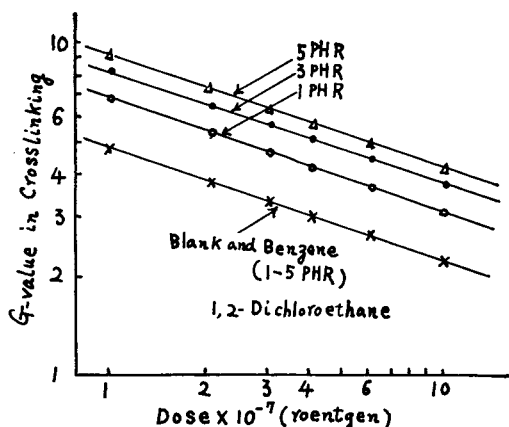


Fig. 4. G_0 for rubber in latex vs. radiation dose, with 1,2-dichloroethane as accelerator.

TABLE II
Relation of Irradiation Dose to Crosslinking Density and G_0 in Rubber with Additives

Additive	Additive content, phr	$k = \nu_0 I^{-2/3} \times 10^{-14}$	$G_0 I^{1/3} \times 10^{-3}$	Irradiation dose I r
None	—	1.15	1.02	10^7-10^8
Benzene	1-5	1.15	1.02	
1,2-Dichloroethane	1	1.66	1.46	
	3	2.00	1.76	
	5	2.24	1.97	
Chloroform	1	2.05	1.81	
	3	2.57	2.27	
	5	2.89	2.55	
Carbon tetrachloride	1	5.37	4.73	10^6-10^7
	3	8.92	7.86	
	5	10.7	9.44	

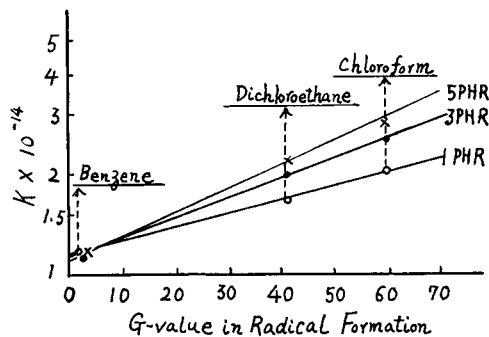


Fig. 5. Coefficient of crosslinking, k , of rubber in latex vs. G_0 , for halides at three concentrations.

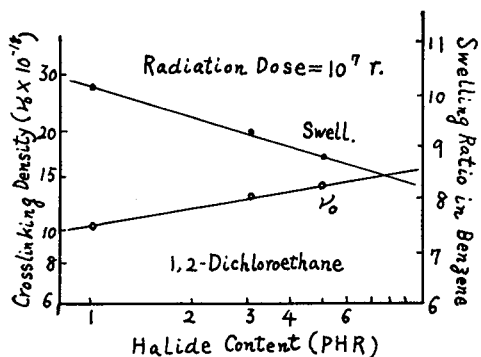


Fig. 6. Crosslinking density vs. content of 1,2-dichloroethane at a dosage of 10^7 r.

taining benzene were also irradiated under the same conditions. The swelling ratios in benzene and crosslinking densities are shown in Figures 1, 2, and 3, and the G_0 values in the case of 1,2-dichloroethane are given in Figure 4.

Rubber in latex containing halides was obviously crosslinked by γ -irradiation in the region of lower dosage ($1-10 \times 10^7$ r), and the crosslinking of rubber in latex containing 1-5 phr benzene was identical, with increasing dosage, with that of the blank sample (see Fig. 4). In order to represent quantitatively the effect of these halides in accelerating crosslinking, these relationships were expressed in the form of an equation. The values of G_0 and ν_0 are given in Table II.

It is difficult to discuss quantitatively the relationships between G_r , the G value for radical formation in the halide additives (Table I, free radicals/100 e.v.), and the acceleration of the crosslinking, owing to many factors involved, such as the affinity of halides for rubber and water, the range of radiation doses used in the experiment, etc. Some attempts were made, however, and one of the trials is shown in Figure 5 where k , in the

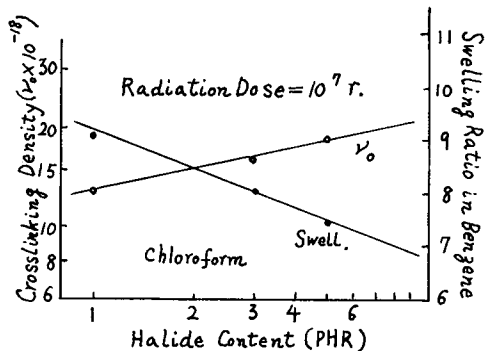


Fig. 7. Crosslinking density vs. content of chloroform at a dosage of 10^7 r.

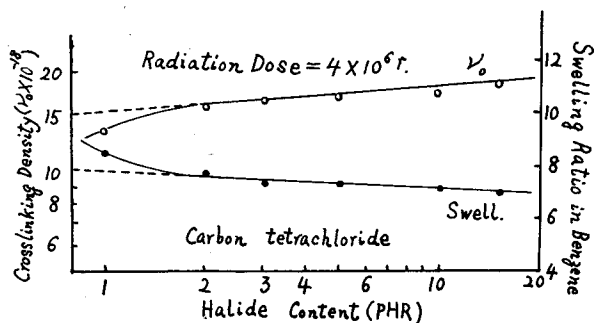


Fig. 8. Crosslinking density vs. content of carbon tetrachloride at a dosage of 4×10^6 r.

following equation relating the crosslinking density to the dose in Table II,

$$v_0 = kr^{2/3} \quad (15)$$

is plotted against the G_r for the halide additive.

The logarithm of k in eq. (15) increased linearly with G_r . From these results, it was assumed that the acceleration of crosslinking by these organic solvents might be due to formation of solvent radicals by γ -irradiation.

The effectiveness of the concentration of these halides in accelerating crosslinking is shown in Figures 6, 7, and 8 for 1,2-dichloroethane, chloroform, and carbon tetrachloride, respectively. The crosslinking density at a given dosage increased with the halide content according to

$$v_0 = A[\text{Ha}]^B \quad (16)$$

where $[\text{Ha}]$ is the content of halide additive in phr, and A and B are constants.

Properties of Latex Films

The 300% moduli and tensile strengths at break are shown in Figures 9-14. The curves representing tensile strength in Fig. 12, for di-

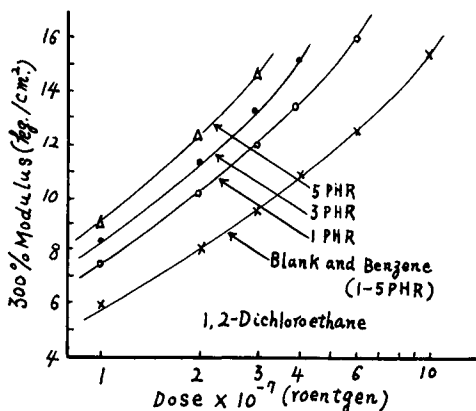


Fig. 9. 300% Modulus vs. radiation dose for dried, cross-linked film, with 1,2-dichloroethane as accelerator.

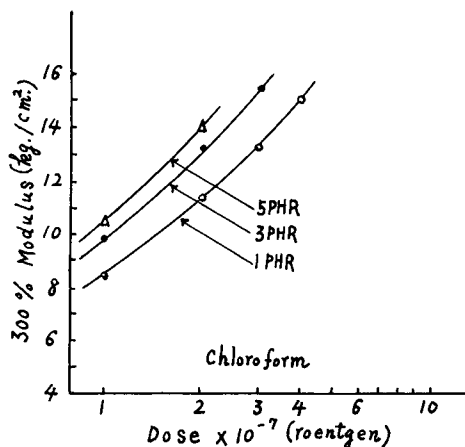


Fig. 10. 300% Modulus vs. radiation dose for dried, cross-linked film, with chloroform as accelerator.

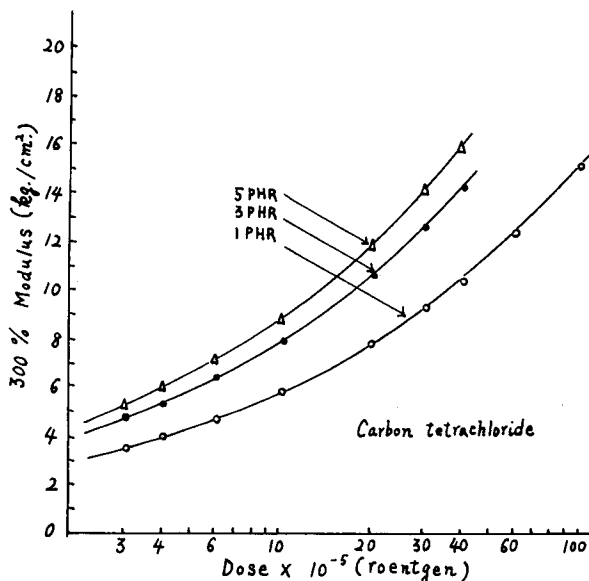


Fig. 11. 300% Modulus vs. radiation dose for dried, cross-linked film, with carbon tetrachloride accelerator.

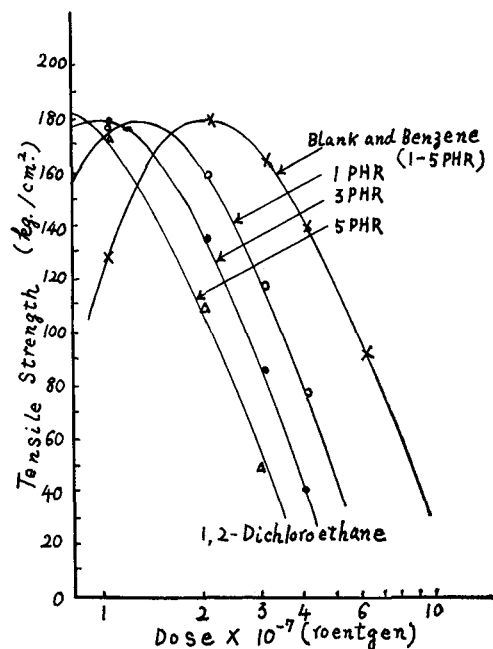


Fig. 12. Tensile strength vs. radiation dose for dried, cross-linked film, with 1,2-dichloroethane as accelerator.

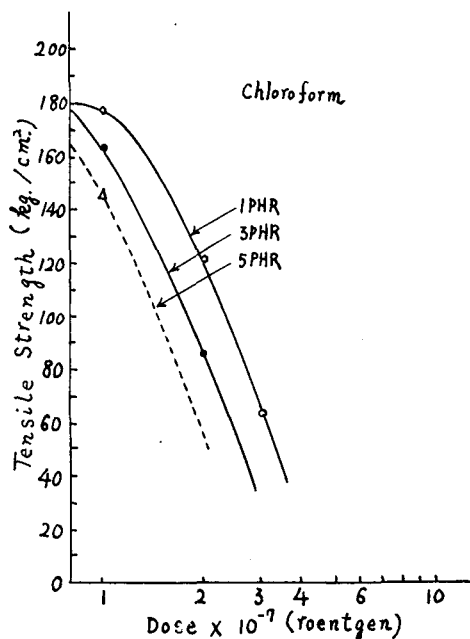


Fig. 13. Tensile strength vs. radiation dose for dried cross-linked, film, with chloroform as accelerator.

chloroethane, and Fig. 13, for chloroform, show only the behavior at the later stage of irradiation, because of the inadequacy of the experimental range of radiation doses; however, from the shape of the curves the tensile strength at the optimum dosage was assumed to be equal to that of the blank

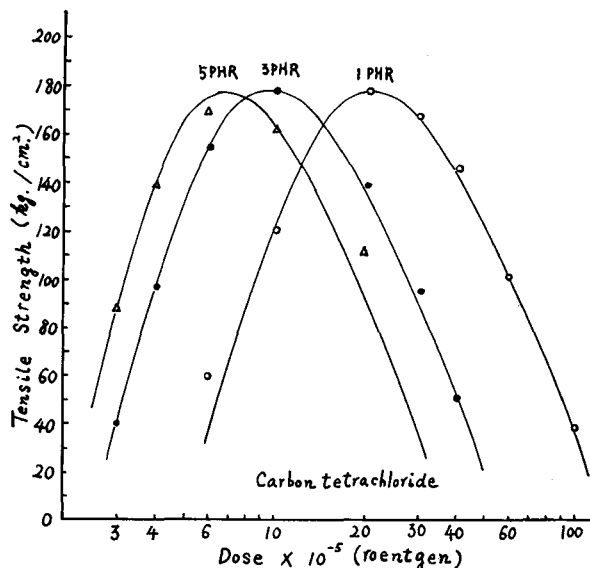


Fig. 14. Tensile strength vs. radiation dose for dried cross-linked film, with carbon tetrachloride as accelerator.

sample or those containing benzene or carbon tetrachloride—i.e., ca. 180 kg./cm.² The optimum dosages were assumed to be 1.17×10^7 , 9.0×10^6 , and 7.6×10^6 r for 1, 3, and 5 phr of dichloroethane, and 8.6×10^6 , 6.2×10^6 , and 5.2×10^6 for 1, 3, and 5 phr of chloroform, respectively, by extrapolation of the straight lines representing crosslinking density versus dosage in Figures 1 and 2. The elongation at break of the film at about the optimum dosage was 950–1000%, and hardness of the same sample was ca. 37° (JIS).

Infrared Spectra Analysis

The crosslinking density as calculated by use of the Flory-Rehner equation is proportional to the $2/3$ power of the dosage, and the G value for crosslinking decreases with the dosage. These facts suggest that decomposition of the rubber molecule occurs under γ -irradiation simultaneously with crosslinking. The extent of decomposition, however, is considered to be the same in the blank sample as in the samples with halide additives, because the powers were the same in all cases. However, since the halides added were decomposed by γ -irradiation into various radicals, it is possible that rubber derivatives were obtained. An infrared spectra analysis was therefore carried out.

G. I. Finch et al.⁵ and D. Stefanescu et al.⁶ reported that hydrochlorinated rubber was obtained by γ -irradiation of rubber solutions in carbon tetrachloride; in the present experiment,

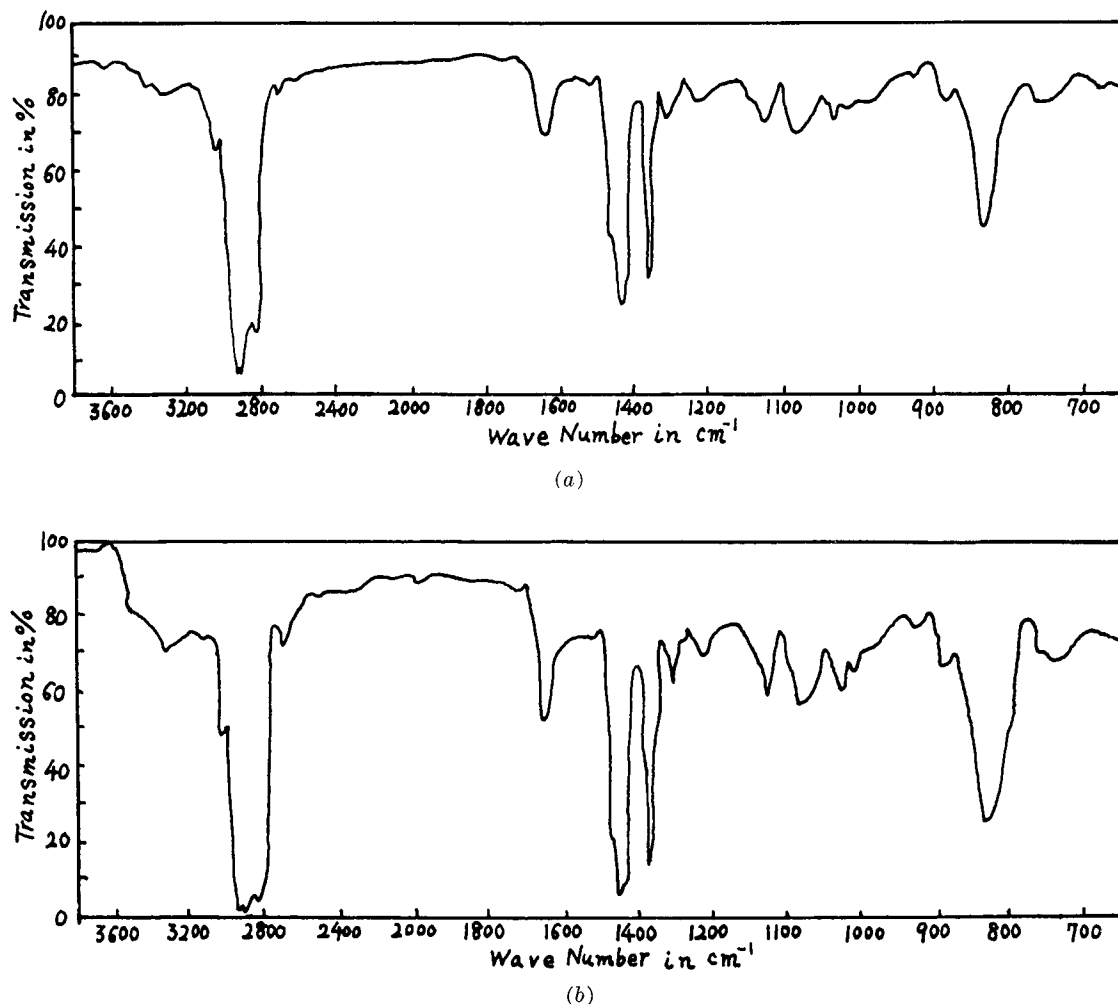


Fig. 15. Infrared absorption spectra of dried films (~ 0.01 mm. thick) of (a) latex irradiated up to 5×10^6 r in the presence of 4 phr carbon tetrachloride, and (b) unirradiated latex.

however, it is obvious that no remarkable change was brought about in the rubber molecule. These different results may be due to the higher concentrations of the solvent and lower concentrations of rubber in the former case. Nevertheless, it was shown by Beilstein tests of the vulcanized latex films we prepared that traces of chlorine were present even after drying *in vacuo* for 24 hr. at room temperature.

CONCLUSIONS

(1) The crosslinking of rubber in natural latex by γ -irradiation was found to be accelerated by the addition of organic halides which have high G values for radical formation by γ -irradiation. Of the halides used here, carbon tetrachloride had the greatest effect.

(2) Tensile properties of dried films obtained

under these accelerating conditions were the same as those of the blank sample reported previously;¹ i.e., at the optimum dosage tensile strength was ca. 180 kg./cm.², the 300% modulus was ca. 8.0 kg./cm.², the elongation at break was ca. 1000%, and hardness was ca. 37° (JIS). The optimum dosages were 2.1×10^6 , 1.0×10^6 , and 7.6×10^5 r for 1, 3, and 5 phr of carbon tetrachloride, and from extrapolation of the plots of crosslinking density versus dosage, were assumed to be 1.17×10^7 , 9.0×10^6 , and 7.6×10^6 r for 1, 3, and 5 phr of 1,2-dichloroethane, and 8.6×10^6 , 6.2×10^6 , and 5.2×10^6 r for 1, 3, and 5 phr of chloroform, respectively.

(3) Side reactions such as the introduction of halogenated radicals into rubber molecules did not occur to the extent that the infrared spectra of latex film were influenced, but Beilstein tests showed

that the films obtained under the accelerating conditions contained traces of chlorine which could not be eliminated by vacuum drying.

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Synopsis

As the accelerating effect of water in the crosslinking reaction of rubber in natural latex by γ -irradiation was assumed to stem from the decomposition of water into radicals by γ -irradiation, more effective reagents were sought among the organic halides which have greater G values for radical formation by γ -irradiation and, simultaneously, an affinity for rubber greater than that of water. 1,2-Dichloroethane, chloroform, carbon tetrachloride, and benzene (for comparison) were tested, and these compounds, except for benzene, were found to accelerate the reaction in proportion to their G values for radical formation. Benzene was found to have no effect, in concentrations between 1 and 5 phr. The optimum dosage was decreased to 2.1×10^6 , 1.0×10^6 , and 7.6×10^5 r by the addition of 1, 3, and 5 phr of carbon tetrachloride, respectively, and was assumed to have decreased to 1.17×10^7 , 9.0×10^6 , and 7.6×10^6 r with 1, 3, and 5 phr of 1,2-dichloroethane, and to 8.6×10^6 , 6.2×10^6 , and 5.2×10^6 r with 1, 3, and 5 phr of chloroform, respectively. The physical properties of the films obtained at the optimum dosages under these accelerating conditions were equal to those of the latex irradiated up to the optimum dosage with no addition of halide. No side reactions occurred during the halide-accelerated crosslinking that were sufficiently extensive to influence the infrared spectra.

Résumé

Comme l'effet accélérateur de l'eau dans la réaction de pontage du caoutchouc dans le latex naturel par irradiation

γ était supposé provenir de la décomposition de l'eau en radicaux par l'irradiation γ , des réactifs plus effectifs ont été recherchés parmi les halogénures organiques qui ont de plus grandes valeurs G dans la formation de radicaux par irradiation γ et simultanément une plus grande affinité vis à vis du caoutchouc que l'eau. Le 1,2-dichloro-éthane, le CHCl_3 et le CCl_4 , et le benzène (pour comparaison) ont été essayés et ces composés à l'exception du benzène accélèrent la réaction en accord avec leur valeur G dans la formation de radicaux. On a trouvé que le C_6H_6 n'avait pas d'effet à une teneur situé entre 1 et 5 PHR. La dose optimum diminue jusqu'à 2.1×10^6 , 1.0×10^6 et 7.6×10^5 roentgen pour 1, 3 et 5 PHR de CCl_4 et elle était supposé diminuer jusqu'à 1.17×10^7 , 9.0×10^6 et 7.6×10^6 roentgen pour 1, 3 et 5 PHR de 1,2-dichloro-éthane et finalement jusqu'à 8.6×10^6 , 6.2×10^6 et 5.2×10^6 roentgen pour 1, 3 et 5 PHR de CHCl_3 . Les propriétés physiques de films à dose maximum obtenus dans ces conditions d'accélération sont égales à celles du latex irradié jusqu'à la dose optimum en absence d'halogénure, et aucune réaction secondaire ne se produit au point d'influencer les spectres infrarouge.

Zusammenfassung

Entsprechend der Annahme, dass die beschleunigende Wirkung von Wasser bei der Vernetzung von Kautschuk in natürlichem Latex durch γ -Bestrahlung auf der Zersetzung von Wasser durch γ -Strahlen in Radikale beruht, wurden wirksamere Reagenzien unter den organischen Haliden gesucht, welche grössere G -Werte bei der Radikalbildung durch γ -Strahlung und zugleich eine grössere Affinität zu Kautschuk als Wasser besitzen. 1,2-Dichloräthan, Chloroform, Tetrachlorkohlenstoff und Benzol (zum Vergleich) wurden untersucht und mit Ausnahme von Benzol beschleunigten alle Verbindungen die Reaktion entsprechend ihrem G -Wert bei der Radikalbildung. Benzol hatte bei einem Gehalt zwischen 1-5 PHR keine Wirkung. Die optimale Dosis wurde für 1, 3 und 5 PHR Tetrachlorkohlenstoff und $2,1 \times 10^6$, $1,0 \times 10^6$ und $7,6 \times 10^5$ Röntgen herabgesetzt. Es wurde angenommen, dass sie für 1, 3 und 5 PHR Dichloräthan auf $1,17 \times 10^7$, $9,0 \times 10^6$ und $7,6 \times 10^6$ Röntgen und für 1, 3 und 5 PHR Chloroform auf $8,6 \times 10^6$, $6,2 \times 10^6$ und $5,2 \times 10^6$ Röntgen herabgesetzt wurde. Die physikalischen Eigenschaften der unter diesen Beschleunigungsbedingungen bei der optimalen Dosis erhaltenen Filme waren die gleichen wie bei Filmen aus, ohne Anwesenheit von Haliden, mit der optimalen Dosis bestrahltem Latex; es traten keine Nebenreaktionen auf die zu einem im Infrarotspektrum merklichen Effekt geführt hätten.

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