$$\frac{[SO_4^{=}]_{\text{surface}}}{[SO_4^{=}]_{\text{solution}}} = K\frac{(x - [SO_4^{=}]_{\text{surface}})}{[C_2O_4^{=}]_{\text{solution}}} \qquad (4)$$

Experiments 5, 6 and 7 given in Table II allow the calculation of the approximate values of K and x. Expressing the number of ions on the surface in micromoles per gram of calcium oxalate monohydrate, and the number of ions in solution in micromoles per liter yields the equations

$$\frac{1.1}{1000} = K\frac{x - 1.1}{105} \qquad (5)$$

$$\frac{2.2}{5000} = K\frac{x - 2.2}{157} \qquad (6)$$

$$\frac{3.6}{20{,}000} = K\frac{x - 3.6}{234} \qquad (7)$$

From (5) and (6): $K = 0.04 \quad x = 3.8$
From (6) and (7): $K = 0.02 \quad x = 5.8$
From (5) and (7): $K = 0.03 \quad x = 5.0$

From the three experiments an average value of K of 0.03 and of x of 5 is found. It is gratifying to find that the number of micromoles of surface oxalate (5) per gram of calcium oxalate monohydrate calculated in this manner is in fair agreement with the value calculated from the microscopic size measurement. From the surface-distribution curve an average particle diameter of 2.4×10^{-4} cm. was calculated. Taking the density of calcium oxalate monohydrate as 2.25 and assuming that the particles are cubical and contain equal amounts of calcium and oxalate ions on the surface, we find the number of micromoles on the surface of 1 g. of the product to be

$$x = \frac{6\left\{\frac{6.06 \times 10^{23}}{146} \times 2.25 \times (2.4 \times 10^{-4})^3\right\}^{2/3}}{2.25 \times (2.4 \times 10^{-4})^3} = 8$$

Although the few experiments reported do not justify a definite conclusion, it seems reasonable to infer that equation (3) expresses the quantitative relation between the exchange of sulfate and oxalate ions on the surface of calcium oxalate monohydrate.

Summary

1. Sulfate, iodate and hydroxyl ions exchange with oxalate, and barium, manganese and probably magnesium exchange with calcium on the surface of calcium oxalate monohydrate. No indication of exchange has been found between sodium, ammonium and hydronium ions, and calcium on the one hand, and of chloride with oxalate on the other on the surface of calcium oxalate monohydrate.

2. The saturated solution of a slightly soluble salt in an electrolyte does not contain equivalent amounts of lattice cation and anion if one of the lattice ions gives an exchange on the surface with one of the ions of the electrolyte. The inequality in the amount of dissolved lattice cation and anion increases with the amount of surface exposed.

3. The mechanism of the exchange has been discussed.

4. A quantitative expression for the distribution of sulfate and oxalate between the surface of calcium oxalate monohydrate and solution has been given and from this the distribution coefficient and the number of moles of surface oxalate per gram of solid have been calculated. The latter value is in reasonable agreement with that calculated from microscopic measurements.

MINNEAPOLIS, MINN. RECEIVED JUNE 1, 1937

[CONTRIBUTION FROM THE JACQUES LOEB LABORATORIES OF STANFORD UNIVERSITY]

Enhanced Polymerization and Depolymerization of Natural Rubber by Quinones and Related Compounds[1]

BY D. SPENCE AND JOHN D. FERRY

Introduction

Oxidizing Agents in Polymerization.—Oxygen and oxidizing agents play a rather puzzling dual role in the chemistry of polyprene substances. Under certain conditions, they cause breakdown and depolymerization of unsaturated hydrocarbon macromolecules. Purified natural rubber, for example, is very susceptible to attack by molecular oxygen, and the absorption of relatively small proportions is sufficient to form a sticky product which lacks tensile strength and dissolves readily in solvents to form solutions of low viscosity.[2] The action of a variety of oxidizing agents, such as potassium permanganate, hydrogen peroxide, and benzoyl peroxide, is similar.[3] On the other hand, the opposite effect, namely, enhanced polymerization by

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[1] The results here recorded form the basis of U. S. Patent applications assigned to The B. F. Goodrich Company.

[2] Kohman, *J. Phys. Chem.*, **33**, 226 (1929); Bloomfield and Farmer, *J. Soc. Chem. Ind.*, **54**, 125T (1935).

[3] Harries, *Ber.*, **37**, 2708 (1904); *cf.* Memmler, "Science of Rubber," Reinhold Publishing Corp., New York, 1934, p. 207 ff.

oxidizing agents, has been observed. Thus, a vulcanization of rubber has been effected by benzoyl peroxide and nitrobenzenes,[4] and the authors[5] have successfully employed metallic compounds, such as potassium ferricyanide, to produce enhanced polymerization. Furthermore, in the kinetics of polymerization of dienes and other unsaturated compounds, oxygen[6] and peroxides[7] play important roles, and oxidizing agents are employed as catalysts for such polymerization reactions.[8]

The present paper is a study of the conditions which determine depolymerization or, alternatively, enhanced polymerization. It describes the treatment of natural rubber, in the form of latex and in benzene solution, with several oxidizing agents. Of these, the most completely studied is *p*-benzoquinone; in addition, the action of other quinones, other carbonyl compounds, and other quinonoid oxidants has been investigated. It has been found that enhanced polymerization or depolymerization can be achieved with small proportions of these reagents, depending on the experimental conditions. The results are interpreted in terms of concurrent reactions.

Terminology.—Natural rubber dissolves only partially in such solvents as benzene or ether, leaving a highly swollen residue which disperses extremely slowly, if at all.[9] Although the terms "sol" and "gel" have been used to designate the soluble and insoluble fractions, respectively, some authors[10] have preferred to consider the proportion of soluble to insoluble rubber simply as related to the average degree of polymerization of the material, which may contain fractions of a wide variety of molecular weights rather than two distinct components. In contrast to raw rubber, vulcanized rubber is practically insoluble; in rubber solvents it forms a swollen gel without appreciable solution into the solvent phase.

The term *polymerization* is here employed in its broader sense[11] to include the existence of cross-links between different macromolecules as well as links between the primary units in a straight-chain macromolecule. *Degree of polymerization*, in this respect, may be considered as a measure of the total number of links per unit volume of material; and "enhanced polymerization" and "depolymerization" as creation or destruction, respectively, of such links.[12] Enhanced polymerization of a rubber-like material results in decreased solubility and decreased swelling of the insoluble residue "gel" and in increased tensile strength; depolymerization, the reverse. In vulcanized rubber, for example, the maximum tensile strength occurs at the same degree of vulcanization as the minimum swelling in solvents.[13] Vulcanization may be considered as an enhanced polymerization without specifying whether the latter is "linear" (increase in length of chain molecules) or "random" (cross-linking) or both.

Experimental

Materials.—The material used in most of the experiments was *Hevea* latex buffered at *p*H 6.8–7.1 with dilute phosphate buffers. An ammonia-preserved, centrifuged latex concentrate was furnished through the kindness of The B. F. Goodrich Company. It was purified by dialysis against 0.05 *M* phosphate buffer and subsequently sterilized according to the procedure of Spence and van Niel.[14]

The quinones, aldehydes, and ketones employed were Eastman products, used without further purification. Benzoquinone diimide and benzoquinone dichlorodiimide were prepared by oxidation of *p*-phenylenediamine (Eastman), according to the procedures of Willstätter and Mayer.[15] The "oxidized quinone" was prepared by bubbling air through a slightly alkaline solution of hydroquinone, evaporating the solution to dryness, and heating the mass at 100° to volatilize any remaining hydroquinone and quinone. The involatile, dark brown residue dispersed in water readily.

Treatment of Latex and Removal of Oxygen Therefrom.—In order to heat or irradiate latex with reagents in the absence of oxygen, the latex was freed of air by bubbling through it nitrogen previously passed through alkaline pyrogallol solution. The Pyrex container was finally pumped off to about 20 mm. pressure and sealed. Irradiated samples were suitably agitated during exposure.

Preparation and Testing of Samples.—After treatment of the latex with the various reagents as described below, samples were coagulated either by adjusting the *p*H to 4.8 with 10% acetic acid or by pouring the latex on tiles of unglazed porcelain.[16] The rubber was extracted twice with cold acetone and dried *in vacuo* in the dark. A measure of the degree of polymerization was obtained by determining the solubility and degree of swelling.[17] A portion of rubber was immersed in a volume of benzene (cc.) 100 times its weight (g.). After three days, the solution was decanted from the swollen gel and replaced by its own volume of pure benzene. After fourteen days, this process was repeated. The swelling of the residual gel was

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(4) Ostromislensky, *J. Russ. Phys.-Chem. Soc.*, **47**, 1467, 1885, 1904 (1915).

(5) Spence and Ferry, *J. Soc. Chem. Ind.*, in the press.

(6) Storch, THIS JOURNAL, **56**, 374 (1934); **57**, 2598 (1935).

(7) Conant and Peterson, *ibid.*, **54**, 628 (1932); Houtz and Adkins, *ibid.*, **55**, 1609 (1933).

(8) Heinemann, British Patent 14,041 (1910); Holt and Steimmig, U. S. Patents 1,189,110 (1916), 1,294,662 (1919); du Pont, U. S. Patents 1,950,432 (1934); 1,950,436 (1934); 1,967,865 (1934).

(9) Pummerer and Pahl, *Ber.*, **60**, 2152 (1927).

(10) Whitby, *Trans. Inst. Rubber Ind.*, **6**, 55 (1930).

(11) Carothers, *Trans. Faraday Soc.*, **32**, 39 (1936).

(12) These generalized concepts are aptly expressed by the German terms, *Aufbau* and *Abbau*.

(13) Scott and Webster, *J. Research Assoc. Brit. Rubber Mfrs.*, **4**, 111 (1935).

(14) Spence and van Niel, *Ind. Eng. Chem.*, **28**, 847 (1936).

(15) Willstätter and Mayer, *Ber.*, **37**, 1494 (1904).

(16) Anon., *Vanderbilt News*, **4**, 5, 20 (1934).

(17) Measurements of elongation and tensile strength paralleled the solution and swelling data. Tensile elongation curves of samples subjected to progressive degrees of polymerization resembled those of soft vulcanized rubber. These and other data of technical interest will be published elsewhere.

expressed by the "swelling index"—the volume of gel (cc.) divided by the weight of rubber in it (g.). All operations were conducted in the dark room.

Enhanced Polymerization and Depolymerization with Benzoquinone

Dark Reaction with Benzoquinone.—When benzoquinone is heated in aqueous solution in the absence of air, simultaneous reduction and oxidation occur, with the formation of hydroquinone and a dark brown oxidation product of complex composition.[18] When rubber latex is heated with benzoquinone in solution, a similar reaction apparently occurs, but in addition a substantial enhanced polymerization of the rubber takes place in the absence of air.

Samples of latex of 5% rubber content were heated with *p*-benzoquinone, hydroquinone, and "oxidized quinone" in the absence of air. Data on the resulting rubbers (Table I) show that the hydroquinone and "oxidized quinone" are ineffective in the enhanced polymerization, which must then be due to the quinone itself or an intermediate product in its decomposition.

TABLE I

Latex, 5% rubber content; *p*H 7.0 heated for five hours at 100° in nitrogen: concentration of reagents 0.25%.

Rubber from	Proportion soluble in 14 days	Swelling index
Untreated control latex	0.66	100
Quinone treated latex	.31	38
Hydroquinone treated latex	.74	80
"Oxidized quinone" treated latex	.72	110

When neutral latex was allowed to stand at room temperature (in the dark) for fourteen days with quinone in solution, in the presence of air, the properties of the rubber remained unaltered.

Comparison of Light and Dark Reactions with Benzoquinone.—The simultaneous oxidation and reduction of quinone in aqueous solution, which occurs slowly at neutrality at room temperature, is greatly accelerated by irradiating with visible and ultraviolet light.[19] Similarly, the enhanced polymerization of rubber in latex by quinone, which has not been detected at room temperature in the dark, is readily effected by irradiation. The results of the reaction in the dark and in diffuse daylight (Pyrex containers) are compared in Table II.

TABLE II

Treatment of latex, 4% rubber content, *p*H 6.2, five hours in the dark and in diffuse daylight, with 0.2% benzoquinone.

Treatment			Proportion soluble in 14 days	Swelling index
Untreated control		...	0.65	111
°C.				
90	Absence of air	Dark	.35	23
90	In air	Dark	.76	..[a]
20	Absence of air	Light	.45	65
20	In air	Light	.50	64
90	Absence of air	Light	.17	22
90	In air	Light	.78	..[a]

[a] Omitted because the amount of residual gel was too small.

At 90°, presence of air causes depolymerization even in the light, and in every case the degree of enhanced polymerization achieved is better when air is excluded. The greatest polymerization occurs at 90° in the light, owing probably to the combined effect of light and dark reactions.

In general, the dark reaction (at elevated temperatures) involves the formation of relatively large amounts of "oxidized quinone," whereas in the reaction in light at room temperature a higher degree of enhanced polymerization may be achieved with very little formation of "oxidized quinone." The remaining experiments cited are devoted to the reaction in light.

Pre-irradiation of Quinone.—In order to show that the enhanced polymerization in the light is a photochemical process and not caused by a stable product of the irradiation of quinone, portions of latex and quinone solution were irradiated separately and mixed in the dark. The results (Table III) show that no enhanced polymerization is caused by this treatment or by irradiation of the latex alone.

TABLE III

Latex, irradiated for five hours in sunlight

Conditions	Proportion soluble in 14 days	Swelling index
Non-irradiated control	0.62	100
Quinone solution and latex, irradiated separately and mixed in dark, standing 16 hours	.62	92
Latex irradiated alone	.69	97
Latex and quinone irradiated together	.18	33

Inhibitors and Light Filters.—It was found (Table IV) that the photochemical polymerization was not inhibited by a twofold excess of hydroquinone. The degree of enhanced polymerization was greatly diminished by an excess of "oxidized quinone"; but this was probably the result of absorption of the actinic light, as the same effect was produced by filtering the light through an aqueous solution of this substance.

TABLE IV

Latex, 10% rubber content, irradiated in sunlight for six hours with 0.1% benzoquinone.

Conditions	Proportion soluble in 14 days	Swelling index
Non-irradiated control	0.33	100
No additional reagent (irradiated)	.10	30
0.2% Hydroquinone added (irradiated)	.10	27
0.2% "Oxidized quinone" added (irradiated)	.28	71
Light filter of "oxidized quinone" (irradiated)	.30	69

Enhanced Polymerization in Solid Rubber.—A film of rubber about 1 mm. thick, prepared by coagulation of latex and subsequent acetone extraction, was dried *in vacuo* and then exposed to the vapor of quinone in the dark at room

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[18] Scheid, *Ann.*, **218**, 227 (1883); Hartley and Leonard, *J. Chem. Soc.*, **95**, 34 (1909).

[19] Ciamician, *Gazz. chim. ital.*, **16**, 111 (1886); Hartley and Leonard, *loc. cit.*; Leighton and Forbes, THIS JOURNAL, **51**, 3549 (1929).

temperature. After it had absorbed about 1% of its weight of quinone, it was placed in the sunlight for two hours. Pieces of commercial "first latex crepe," 1 mm. thick, were treated similarly, one being irradiated dry and the other immersed in water. In each case (Table V), enhanced polymerization occurred, showing the aqueous phase of the latex to be non-essential in this process.

TABLE V

Photopolymerizatioh by Quinone in Dry Rubber

Material	Treatment	Proportion soluble in 14 days	Swelling index
Latex film	Exposed to quinone vapor but not to light	0.46	107
	Exposed to quinone vapor and irradiated	.12	14
Crepe	Non-irradiated control	Practically complete solution	
	Exposed to quinone vapor, irradiated dry	.26	32
	Exposed to quinone vapor, irradiated in water	.26	30

Irradiation of Rubber Dissolved or Swollen in Benzene.—In contrast with the results in latex or dry rubber, irradiation of benzene solutions of rubber (or benzene-swollen residual gels) with quinone in the presence of air at room temperature leads to marked depolymerization, as evidenced by a rapid fall of viscosity, and dissolution of gel structure. Even the product of enhanced polymerization by quinone, which swells in benzene without dissolving, can be disintegrated rapidly in the swollen state by irradiation with additional quinone provided air is present. The resulting solution has a viscosity differing little from that of the solvent, showing that the macromolecules have undergone marked breakdown. In the absence of light, however, quinone has no effect on the swollen gel rubber.

To show the dependence of the net result of photochemical treatment with quinone upon the degree of swelling (*i. e.*, the dilution) of the rubber, a thin sheet of solid rubber was instilled with quinone vapor in the dark as described above. Pieces swollen in benzene to different extents were then irradiated. The resulting systems (partly swollen, partly dissolved) were freed from benzene by desiccation in the dark at room temperature, and the customary swelling and solution determinations were made on the dried products. The results (Fig. 1) grade uniformly from marked enhanced polymerization for irradiation in the absence of solvent to extensive depolymerization for irradiation of the rubber swollen in a tenfold excess of solvent.

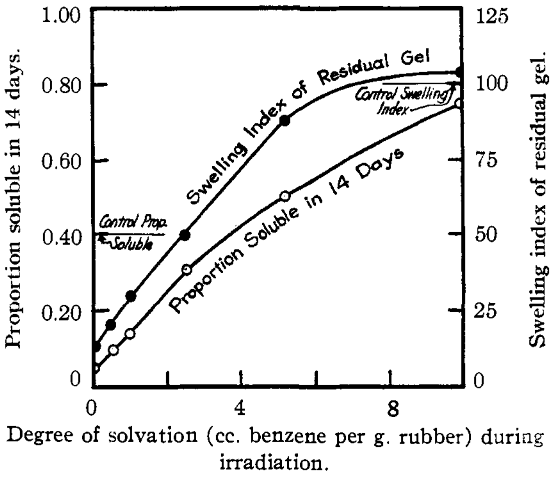

Fig. 1,—Rubber irradiated with benzoquinone while swollen with benzene to different extents: samples desiccated after irradiation and then reimmersed in benzene for solubility and swelling measurements. Proportions of the final products soluble in fourteen days, and swelling indices of the residual gels, plotted against the degree of solvation during irradiation.

Irradiation of rubber in the swollen state with quinone produced depolymerization even when the air was previously removed from the system by evacuation. This does not, however, exclude the possibility that small traces of molecular oxygen are required for the breakdown process.

When a benzene solution of rubber to which quinone has been added is frozen and irradiated at −80°, *enhanced polymerization* occurs. After exposure of the solid solution

TABLE VI

Latex Irradiated with Various Quinones

Rubber content	Time of irradiation, hr.	Quinone	Concentration,[a] %	In air: Proportion soluble in 14 days	In air: Swelling index	In absence of air: Proportion soluble in 14 days	In absence of air: Swelling index
Non-irradiated control				0.39	110	0.39	110
15%	3.5	Benzoquinone	0.07	.18	28		
		1,4 Naphthoquinone	.11	.04	10		
		Chloranil	.17	.25	32		
		Anthraquinone	.15	.61	108	.08	24
10%	2	Benzoquinone	.08			.11	36
		1,4-Naphthoquinone	.115			0	15
		Anthraquinone	.155			.12	29
10%	3	1,4-Naphthoquinone	.12	.18	15	.11	18
		1,2-Naphthoquinone	.12	.24	32	.20	28
		Tolu-*p*-quinone	.09	.20	34	.33	46
		Phenanthrenequinone	.16	.51	57	.14	19

[a] Chosen for equal molecular concentration in comparative experiments.

for an hour to the sunlight (through a bath of alcohol cooled by solid carbon dioxide), warming to room temperature yields not the original solution but a firm gel. This gelation is not produced by the freezing and melting alone nor by irradiation of the solid solution without quinone.

Enhanced Polymerization and Depolymerization with Other Quinones

Comparative Results.—Irradiation of latex with a variety of quinones shows (Table VI) that, as in the case of benzoquinone, enhanced polymerization is produced (even in the presence of air) by tolu-*p*-quinone, chloranil, 1,2-naphthoquinone, and 1,4-naphthoquinone. Two other quinones, anthraquinone and phenanthrenequinone, produce, however, depolymerization in the air, but enhanced polymerization in the absence of air.

Dependence of Enhanced Polymerization upon Concentration and Time.—1,4-Naphthoquinone, as the most effective reagent in enhanced polymerization, was employed to show the effect of concentration and time on the reaction in latex (Table VII). Increase in the quantity of quinone above a small minimum concentration appears to have no effect, nor does prolonged exposure. The minimum concentration for maximum polymerization is for naphthoquinone about 0.4% of the rubber or 1 molecule per 600 isoprene units.

TABLE VII

Latex Irradiated with 1,4-Naphthoquinone

Rubber content, %	Concentration naphthoquinone, %	Time of irradiation, hr.	Proportion soluble in 14 days	Swelling index
Non-irradiated control			0.36	100
20	0.04	4	.08	17
20	.08	4	.06	16
20	.15	4	.06	13
16	.17	2	.07	13
16	.17	2.5	.06	12
16	.17	3	.06	11
10	.50	25	.05	10

Enhanced Polymerization and Depolymerization with Other Carbonyl Compounds

Experiments with benzophenone and benzaldehyde showed that the former resembles the majority of the quinones studied, in effecting enhanced polymerization in latex through irradiation even in the air; the latter, like anthraquinone and phenanthrenequinone, produces breakdown in air but enhanced polymerization in its absence (Table VIII). Benzophenone, like benzoquinone, causes photodepolymerization of benzene-swollen rubber.

TABLE VIII

Latex, 15% Rubber Content, Irradiated in Sunlight with Benzophenone and Benzaldehyde

Reagent	Concn., %	Irradiation	Proportion soluble in 14 days	Swelling index
Non-irradiated control			0.39	111
Benzophenone	0.27	3 hrs. in air	.21	19
Benzaldehyde	.75	3 hrs. in air	Practically complete solution	
Benzaldehyde	.75	3 hrs. in N_2	0.01	9

Enhanced Polymerization with Other Quinonoid Compounds

To show that the oxygen and the carbonyl group in the polymerizing agents described above are not essential to the reaction, latex was treated with quinone diimide and quinone dichlorodiimide (Table IX). The former compound decomposed so rapidly with formation of a black pigment (Bandrowski's base,[15] the analog of the "oxidized quinone" from benzoquinone) that irradiation was not effective. However, polymerization was produced by heating in the absence of air. The dichlorodiimide caused marked enhanced polymerization both by heating and by irradiation.

TABLE IX

Latex, 5% Rubber Content, with 0.25% Quinone Imides

Imide	Treatment	Proportion soluble in 14 days	Swelling index
Untreated control		0.39	111
Quinone diimide	Heated in absence of air $4^1/_2$ hrs.	.24	53
Quinone dichlorodiimide	Heated in absence of air 5 hrs.	0	7
	Irradiated in air 4 hrs.	0.05	13
	Irradiated in absence of air 4 hrs.	0	8

Nature of the Reactions

The results are consistent with the course of two concurrent reactions between the rubber and the polymerizing agent, one leading to enhanced polymerization and the other to depolymerization. The latter process is in every case favored by (a) decreasing the rubber concentration in the reaction system, (b) increasing the temperature, (c) the presence of molecular oxygen.

A decrease in the rubber concentration is occasioned by presence of a solvent or swelling agent. Latex of any dilution, the rubber particles being on the average about 1 μ in diameter, may be considered as rubber in the undiluted solid phase. The only difference in behavior between solid rubber and latex, in the reactions here discussed, is in accessibility to actinic light. In a thick layer of solid rubber, a large part of the light is absorbed near the surface, shielding the interior, while in latex the individual particles can be brought in turn to the periphery of the vessel and receive irradiation of full intensity. Agitation or circulation of the latex facilitates this result.

The effect of actual dilution of the rubber phase, by a solvent or swelling agent, indicates that the enhanced polymerization process is of higher order than the depolymerization process. The influence of temperature is shown by the enhanced polymerization produced even in dissolved rubber when the solution is illuminated at −80°, as well as by the rapid breakdown of latex in air which occurs at 90° with any of the reagents described. It appears that some step in the depolymerization process involves an activation energy which is high compared with those concerned in the enhanced polymerization. Finally, the influence of molecular oxygen indicates that its presence is necessary for the depolymerization.

Process of Enhanced Polymerization.—The primary photochemical process is not definitely known, but is probably absorption by the quinone, since purified rubber is transparent to light of wave lengths down to 2400 Å.[20] The reaction has not yet been studied in monochromatic light, but is effected by the mercury arc as well as by sunlight. The high efficacy of 1,4-naphthoquinone in enhanced polymerization in the sunlight may be due to its greater absorption in the range of visible wave lengths. Ciamician and Silber[21] described photochemical reactions of benzoquinone, benzophenone, and benzaldehyde with various alcohols. The alcohols were dehydrogenated to aldehydes and ketones, while the light-activated compounds were reduced to hydroquinone, benzopinacone, and hydrobenzoin, respectively. The reaction with rubber is probably similar, the dehydrogenation leading to the formation of new bonds between macromolecules, as suggested by van Rossem, *et al.*, for the vulcanization of rubber by benzoyl peroxide.[22] The quinones are probably reduced to the corresponding hydroquinones and the quinone imides to *p*-phenylenediamine. It is possible that a portion of the reagent may remain in permanent combination with the rubber.

If such cross-linking bonds could be formed at any point along the rubber molecule, one would expect prolonged treatment with a large quantity of reagent to lead to a highly bridged type of three-dimensional polymer which would be hard and inextensible and would not swell at all in solvents. Actually the result of prolonged treatment is a product resembling soft vulcanized rubber, and the maximum amount of reagent effective is very small. This suggests that only the end of the macromolecule forms a complex with the photoactivated quinone or ketone which results in a new link with a second macromolecule. When all the ends have reacted, no amount of further treatment is effective. The mole ratio quoted above for naphthoquinone, 1 per 600 isoprene units, would lead on the above basis to a molecular weight for rubber of 80,000 which is of the order of magnitude suggested by determination of osmotic pressure,[23] viscosity,[24] sulfur addition,[25] and oxygen content.[26] It is possible, on the other hand, that the small number of reactive locations correspond to the active hydrogens found by Midgley, *et al.*,[25] in approximately the same proportion.

Process of Depolymerization.—It seems necessary to postulate another type of complex which a photoactivated quinone or ketone molecule can make at any point along the rubber chain, this complex being oxidizable by molecular oxygen with consequent rupture of the chain. This is supported by the fact that anthraquinone and phenanthrenequinone, which cause depolymerization when irradiated in latex at room temperature, have the lowest reduction potentials of the seven quinones studied, so that their complexes with the rubber molecule would probably be correspondingly more easily oxidized.

The simplest explanation for the predominance of depolymerization in benzene solution is probably that the dilution of the rubber by solvent permits frequent inactivation of terminal quinone complexes before links to neighboring macromolecules can be consummated.

Relationship to Sulfur Vulcanization

Study of the reactions involved in the vulcanization of rubber by sulfur is complicated by the addition of sulfur to the double bonds of the hydrocarbon. After a century of investigation, the relationship, if any, between the enhanced polymerization and this chemical combination of sulfur with the rubber has not been established.

Unpublished work by one of us has shown that when raw rubber is vulcanized in the presence of varying amounts of acetic acid, no enhancement of polymerization occurs if sufficient acid is present, although the rate of sulfur ad-

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[20] Scheibe and Pummerer, *Ber.*, **60**, 2163 (1927).

[21] Ciamician and Silber, *ibid.*, **34**, 1530 (1901).

[22] Van Rossem, Dekker and Prawirodipoero, *Kautschuk*, **7**, 219 (1931).

[23] Fikentscher, *Ber.*, **61**, 1946 (1928); Kroepelin, *Kolloid Z.*, **47**, 294 (1929).

[24] Staudinger, "Die hochpolymeren organischen Verbindungen," Verlag von Julius Springer, Berlin, 1932.

[25] Midgley, Henne, Shepard and Renoll, THIS JOURNAL, **56**, 1325 (1934).

[26] Midgley, Henne, Shepard and Renoll, *ibid.*, **57**, 2318 (1935).

dition remains unchanged. An actual softening (depolymerization) may result by prolonged heating in the presence of acids at the temperature of vulcanization. Furthermore, the well known improvement in physical properties brought about by the presence of small quantities of zinc oxide in vulcanization is not in fact accompanied by any increase in the amount of sulfur which has entered into combination with the rubber.[27] Vulcanizates containing very small proportions of total sulfur to rubber (0.2 to 0.5%), which may be prepared with certain types of ultra-accelerators, are as highly polymerized as those with high sulfur content.[28] Bruni has shown[29] that as little as 0.15% of sulfur is sufficient to give rubber the physical properties characteristic of vulcanization.

There is evidence that, in the total absence of accelerators (including those naturally occurring in raw rubber), the polymerization produced by sulfur is practically insignificant. This is known to be the case for certain synthetic rubbers[30] and for purified natural rubber.[31] It is then possible that in sulfur vulcanization the actual enhanced polymerization is produced by dehydrogenating agents—analogous in their action to those described in the present paper—which are formed by preliminary reactions between sulfur and the so-called "accelerators" present. Such a hypothesis would explain the action of the nitroso compounds[32] as accelerators in vulcanization, and is supported by the fact that certain sulfur containing "accelerators," such as thiuram disulfides—of a structure which might be expected to be effective in dehydrogenation—produce vulcanization in the absence of molecular sulfur.[33] It is hoped that future work may define more clearly the parallelism between oxygen and sulfur in these reactions.

The products of enhanced polymerization here described differ negligibly in chemical composition from natural raw rubber and are entirely free from sulfur. They may prove useful in cases where the presence of sulfur is objectionable in vulcanized rubber.

In both enhanced polymerization and depolymerization, the rubber is oxidized; in the one case presumably by dehydrogenation, and in the other with the introduction of oxygen. Further development of this distinction may offer a clue to the mystery of how the rubber is built up and subsequently broken down in the plant.

Summary

1. The enhanced polymerization or the depolymerization of natural rubber may be effected thermally or photochemically by one and the same reagent.

2. The action of quinones, carbonyl compounds, and other quinonoid compounds in this connection has been studied.

3. Depolymerization is favored by (a) dilution of the rubber by a solvent or swelling agent, (b) increase of temperature, (c) presence of molecular oxygen.

4. The results are interpreted in terms of concurrent reactions.

PACIFIC GROVE, CALIF. RECEIVED MAY 26, 1937

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[27] Experimental data covering these observations will be published elsewhere along with matters of technical importance referred to in this communication.

[28] *Vanderbilt News*, **4**, 4 (1934).

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