[CONTRIBUTION FROM GENERAL LABORATORIES, UNITED STATES RUBBER COMPANY]

The Quantum Yield of Oxidation of Hevea Rubber and GR-S

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I. Introduction

Little previous quantitative work has been reported on the photoöxidation of rubber even though the light aging of rubber products is a serious technological problem. Recently Bateman[1] reported the relative photoöxidation rates of highly purified rubber after fixed oxygen uptake as a function of wave length. The results show a rapid drop in quantum efficiency as the wave length increases above 3000 Å. The considerable amount of qualitative work on the effects of light on rubber, particularly in the presence of air, also show that shorter wave lengths cause more serious oxidation than the longer wave lengths. For example, Raybaud[2] found light below 4000 Å. more effective in deteriorating raw rubber than longer wave lengths, while Yamazaki[3] reports a similar result for vulcanized rubber. According to Asano[4] in the presence of oxygen an insoluble product is formed in raw rubber below 2250 Å. Above this wave length, extending to about 3130 Å., a transparent oxidized rubber resulted.

Quantum yields have been measured for the initial oxidation of rubber following the absorption by the rubber of monochromatic light over the wave length range 2537 to 17,400 Å. Purified Hevea rubber and GR-S (styrene–butadiene copolymer) were investigated.

II. Experimental Details

The quantum yields of oxygen consumption at room temperature (~25°) were obtained by irradiating thin rubber films with monochromatic light. The oxygen absorbed by the rubber was determined by a differential method and compared with the measured amount of absorbed light.

Apparatus for Ultraviolet and Visible.—The light source was either an Hanovia 85-watt H-3 or 100-watt H-4 mercury arc, operated from a stabilized voltage supply. A fused silica jacket was cemented in place of the original glass envelope of the mercury arc for experiments at 3130 and 2537 Å. It was found that filling the silica jacket with nitrogen prolonged the arc life.

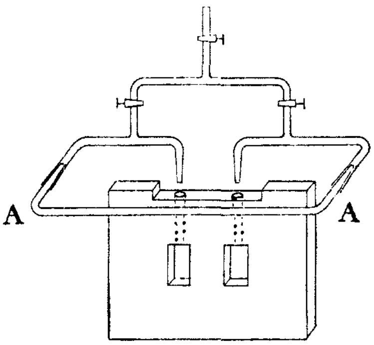

Fig. 1.—Diagram of differential cell for measuring photooxidation rates.

The various mercury lines were isolated by a Gaertner L-234 HT quartz monochromator (F/4 at 2000 Å). However, in one experiment (#15) the light from a portion of an Hanovia SC-2537 tube was focused directly on the rubber film by a quartz lens. This lamp supplies about 90% pure 2537 radiation. The impurity in this light is largely ineffective visible light and so the absorbed intensity was corrected for that fraction of the radiation passed by Pyrex.

The cell of Fig. 1 was placed directly behind the exit slit of the monochromator. This cell consists essentially of an aluminum block with two identical 1 × 2 cm. rectangular holes cut through it. The cavities were closed front and rear with Corning #791 glass windows, sealed with 0.1 mm. polyisobutylene gaskets coated with Apiezon Grease M. The absorption of oxygen by a rubber sample in one side of the cell was followed by the motion of a droplet of Amoil S in a calibrated capillary (~10^{-3} cc./cm.) connecting the two cavities. Barium oxide in each side absorbed any carbon dioxide or water present initially or produced during irradiation.

To measure light intensities an RCA-935 phototube in a Model 510 Electronic Photometer of the Photovolt Corp. was used. Ground quartz screens in front of the photocell diffused the incident light so that uniform response over a 1 × 2 cm. area of the ground quartz was obtained. The Photometer was calibrated against a Gaertner silver-bismuth thermopile L-234 VTBS using the monochromator and H-3 arc. This thermopile had previously been standardized against three National Bureau of Standards lamps. The photometer was corrected for non-linear response by means of an approximate point source and applying the inverse square law as the distance of the photocell from the light source was varied.

To check the photocell calibration, the photocell, H-3 arc and monochromator were used to measure the quantum yield of decomposition in an unstirred uranyl oxalate solution (0.005 M $UO_2C_2O_4$ and 0.025 M $H_2C_2O_4$). We obtained a quantum yield of 0.45 at 3660 Å. while Leighton and Forbes[5] report 0.46 in unstirred solutions of 0.01 M UO_2SO_4 plus 0.05 M $H_2C_2O_4$. According to Forbes and Heidt[6] these two actinometer solutions should give the same quantum yield.

Materials and Preparation of Films.—Deproteinized rubber[7] was prepared by an alkaline hydrolysis method. One liter of triple-creamed Hevea latex (63.3% solids) was diluted with two liters of aqueous 6% sodium hydroxide and heated and stirred eight hours per day at 70°. At night the alkaline latex was allowed to cream and the lower liquid drawn off and replaced with 4% aqueous sodium hydroxide. Ten successive heating and creaming cycles were carried out under oxygen-free nitrogen. The use of carefully purified nitrogen is necessary to avoid oxidation or degradation. After the final creaming, the latex was poured into 60 liters of distilled water and coagulated by adding one liter of 5% acetic acid with continuous stirring. The coagulum was sheeted in a calender between heavy canvas to 0.015″. Acetone extraction under nitrogen for ten days followed by five days of alcohol extraction completed the purification process. The

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[1] L. Bateman, *Trans. Faraday Soc.*, **42**, 266 (1946).

[2] L. Raybaud, *Caoutchouc & Gutta-Percha*, 5736 (1911).

[3] T. Yamazaki, *J. Soc. Chem. Ind., Japan*, **31**, 66B (1927).

[4] K. Asano, *India Rubber. J.*, **70**, 389 (1925).

[5] W. G. Leighton and G. S. Forbes, THIS JOURNAL, **52**, 3139 (1930).

[6] G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

[7] Adapted from procedure of R. Pummerer and H. Pahl, *Ber.*, **60**, 2152 (1927).

purified rubber of osmotic mol. wt. 500,000–1,000,000 analyzed 0.01% nitrogen and 0.03% ash. The high molecular weight indicates little, if any, degradation occurred during purification. The rubber was stored in an evacuated desiccator containing freshly cut sodium.

The fractionation[8] of 20 g. of deproteinized rubber was carried out on a 2.4% solution of rubber in benzene. To this solution methanol was slowly added with stirring until a cloudy precipitate just appeared at room temperature. The first fraction precipitated at a methanol concentration of 17.25 weight per cent. of total solvent. The solution was heated to 45° to redissolve the precipitate and then the solution flask was placed in a thermostat at 30° overnight. The next morning if a fraction of suitable magnitude had settled in the lower layer, the upper layer was carefully decanted. (Otherwise a small amount of benzene or methanol as necessary was added, the precipitate dissolved by warming and the flask returned to the thermostat.) The lower layer was dried by evacuation in a desiccator and the solid rubber fraction obtained was stored *in vacuo* as described above. Additional methanol was added to the decanted upper layer and the fractionation cycle repeated. Redistilled reagent grade methanol and benzene were used, and except during decantation or solvent addition the rubber solution was kept in the dark under nitrogen. In this way the deproteinized rubber was separated into the five fractions of Table I.

TABLE I

YIELDS OF FRACTIONATED RUBBER

Fraction	Wt. of fraction, g.	
I	2.453	Tough
II	8.365	Medium
III	3.642	Soft
IV	2.048	Soft
V	1.820	Very soft

Fraction II resembled the whole rubber, whereas I was practically insoluble and V was yellow and tacky, possibly containing an oxidized fraction. Fraction V was contained in the solution decanted from IV and probably was degraded during the solvent removal. Solvent was removed from fractions I to IV by pumping in evacuated desiccators, while a stream of commercial nitrogen was used to evaporate solvent from Fraction V.

Films of deproteinized rubber were laid down on glass plates by evaporating 5% *n*-hexane solutions under a slow stream of purified nitrogen. The films were stored *in vacuo* in the presence of sodium until used. Fresh films were prepared every two or three weeks.

Antioxidant-free GR-S (75 parts butadiene–25 parts styrene by weight) was prepared by emulsion polymerization by the Naugatuck Chemical Company, using 0.05 part of hydroquinone as shortstop. The polymer was extracted first with cold acetone and then with cold absolute alcohol under nitrogen. GR-S films were deposited from benzene solution on cellophane covered glass plates, since the films could not be removed without tearing or distortion if they were deposited directly on glass.

Linde tank oxygen passed through Dehydrite and Ascarite was used in all photoöxidation experiments.

Procedure.—A polymer film cut to about 3 × 18 mm. was pressed upon a cell window, which was then attached to the rear of one cell cavity. During handling this 3 × 18 mm. section came in contact only with clean glass. Film thicknesses (0.4 to 2.0 mm.) were calculated from the length, width, weight and density of the film. The cell was evacuated and filled with dry oxygen to one atmosphere pressure. The initial dark rate was generally so small it could be taken as zero. During irradiation the light intensity before and behind the cell was determined. Oxygen consumption was followed during and after irradiation. Complete details of all photoöxidation experiments appear in Table II.

Infrared Experiments.—A 1000-watt tungsten filament projection lamp was substituted for the mercury arc described above. The monochromator slit widths corresponded to a range of 0.11μ at 1.74μ and of 0.08μ at 1.0μ. For infrared work, the light in front of the cell but not behind it was measured with the calibrated thermopile. At the end of an experiment the rear window was detached and the film transmission determined.

Calculations.—Quantum yields were calculated in the same manner as those for the actinometer, except that a correction was made for the light reflected at the back of the front window of the cell and at the front surface of the rubber film. The refractive index of rubber from L. A. Wood[9] enabled the latter correction to be made.

The oxygen consumption was never followed beyond a pressure decrease of 1–2%; so the pressure was assumed to be constant at 1 atmosphere in converting volumes of absorbed oxygen to molecules absorbed.

Absorption Spectra.—The absorption spectrum of the purified rubber was photographed on a Baird 3 meter grating spectrograph, using a quartz hydrogen discharge tube as a source of continuous radiation. Optical densities were measured with an ARL–Dietert densitometer and the plates were calibrated by varying the exposure with a rotating sector. Solid films of the purified whole rubber were deposited on thin quartz plates by slow evaporation of rubber–benzene solutions. Film thickness was calculated from the weight and area of the rubber. The absorptions of three of the rubber fractions (II, III and IV) were also determined in chloroform solution. The results are shown in Fig. 2 expressed as the molecular extinction coefficient per double bond.

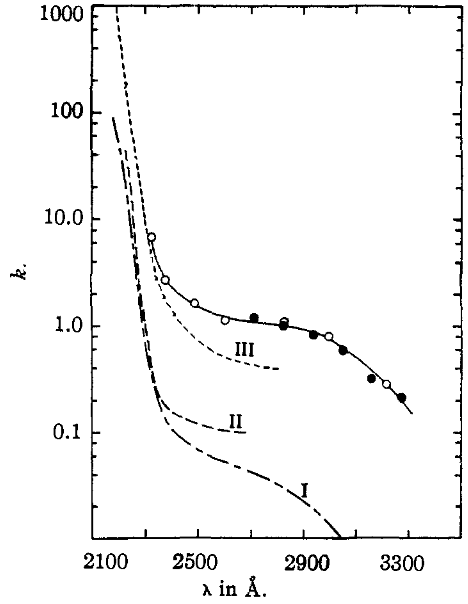

Fig. 2.—The ultraviolet absorption spectra of rubber and related olefins: I, trimethylethylene, ref. 17; II, 2,6-dimethyloctadiene-2,6, ref. 13; III, purified rubber (in cyclohexane + 10% ethyl alcohol) ref. 13; ●, purified rubber fractions II, III and IV (in chloroform)—this paper; ○, purified rubber films—this paper. $K = (1/Cl) \log_{10} (I_0/I)$ = molecular extinction coefficient, where C = moles of $\rangle C{=}C\langle$/liter; l = centimeters depth; I_0 = incident light intensity; I = transmitted light intensity.

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[8] Based on a technique developed by Dr. H. C. Tingey of this Laboratory.

[9] L. A. Wood, *J. Applied Phys.*, **12**, 119 (1941).

TABLE II

PHOTOÖXIDATION OF RUBBER AT ROOM TEMPERATURE AND 760 MM. OXYGEN PRESSURE[a]

Run	Polymer	λ, Å.	Polymer, g.	Thickness polymer, mm.	Light absorbed, %	Quanta absorbed by polymer/sec. × 10^{-13}	Time of exposure, min.	O_2 Absorbed during irrad. % on polymer	Rate of O_2 absorption			Quantum yields	
									Initial, cu. mm./min.	Final, cu. mm./min.	Dark reac. cu. mm./min.	Initial, $O_2/h\nu$	Final, $O_2/h\nu$
8	Rubber	4358	0.1231	2.029	22.8	20.15	211	0.0073	(0–211) 0.015	....	(4048–5498) 0.001	(0–211) 0.03	....
9	Rubber	4358	.0733	1.34	14.5	12.23	2589	0.026	(0–181) 0.0046	(1142–2582) 0.0034	....	(0–181) 0.0146	(1142–2582) 0.012
9	Rubber	3660	.0733	1.34	27.8	18.0	212	0.078	(2600–2812) 0.0674	....	....	(2600–2812) 0.153	....
5	Rubber	3660	.0739	1.29	31.7	17.69	221	0.054	(0–221) 0.0662	....	(1274–1629) 0.006	(0–221) 0.153	....
6	Rubber	3660	.0626	1.08	27.5	14.78	191	0.057	(0–191) 0.0712	....	(1173–1413) 0.0047	(0–191) 0.197	....
7	Rubber	3660	.0584	0.964	23.0	12.27	122	0.025	0.049	....	....	(0–122) 0.163	....
7	Rubber	3130	.0584	0.964	63.1	12.99	60	0.066	0.1305	....	....	(130–190) 0.41	....
7	Rubber	3660	.0584	0.964	22.5	11.97	107	0.109	0.077	....	(1270–1723) 0.0047	(197–304) 0.26	....
1	Rubber	3130	.0296	0.45	40.1	7.26	180	0.46	(0–64) 0.1805	(154–178) 0.337	(1511) 0.0216	(0–64) 1.015	(154–178) 1.896
2	Rubber	3130	.0300	0.48	39.6	6.87	178	0.31	(0–60) 0.1141	(172–177) 0.300	(1226) 0.0225	(0–60) 0.68	(172–177) 1.79
4	Rubber	3130	.0414	0.63	49.7	9.12	180	0.21	(0–53) 0.095	(175–180) 0.28	(1184–1420) 0.0208	(0–53) 0.43	(175–180) 1.25
15	Rubber	2537	.0382	0.53	84.8	18.25	62	0.40	(0–11) 0.237	(51–62) 1.147	(1356–1528) 0.043	(0–11) 0.54	(51–62) 2.50
16	Rubber	2537	.0342	0.51	87.2	13.02	75	0.48	(0–12) 0.2365	(66–75) 0.934	(1283–1661) 0.064	(0–12) 0.78	(66–75) 2.81
19	Frac. II	3130	.0473	0.89	67.3	23.5	180	0.37	(0–22) 0.147	(160–179) 0.584	(1364–1765) 0.0668	(0–22) 0.24	(160–179) 1.095
17	Frac. III	3130	.0656	1.23	72.2	24.3	180	0.23	(0–14) 0.148	(167–179) 0.467	(1363–1682) 0.0298	(0–14) 0.23	(167–179) 0.86
18	Frac. V	3130	.0202	0.33	88.9	30.3	181	0.17	(0–19) 0.0922	(160–180) 0.063	∼0	(0–19) 0.12	(160–180) 0.09
20	Rubber	17400	.0778	1.29	32	166.0	270	<0.005	....	....	None in 16 hrs.	<0.001	....
20	Rubber	10000	.0778	1.29	12	45.3	350	<0.003	....	....	....	<0.002	....
21	GR-S	10000	.0855	1.38	24	81	240	<0.005	....	....	....	<0.004	....
11	GR-S	3660	.0483	0.80	70.2	44.8–38.7	1267	0.37	(0–192) 0.0178	(1147–1265) 0.0872	(1280–1572) 0.035	(0–192) 0.0162	(1147–1265) 0.092
13	GR-S	3660	.0462	0.84	71.3	42.9	214	0.019	(0–208) 0.0162	....	....	(0–208) 0.0155	....
13	GR-S	3130	.0462	0.84	90.2	18.8	75	0.040	(220–295) 0.0497	....	(1273–1560) 0.0019	(220–295) 0.108	....
10	GR-S	3130	0.325	0.47	79.5	14.12	287	∼0.11	(90–165) 0.041	(232–283) 0.071	(1265–1362) 0.005	(90–165) 0.119	(232–283) 0.204
12	GR-S	3130	.0515	0.91	91.7	21.28	283	0.094	(0–67) 0.0249	(223–282) 0.1024	(1345–1574) 0.007	(0–67) 0.05	(223–282) 0.197
12												(90–168) 0.119	
14	GR-S	2537	.0271	0.43	98.9	12.32	150	0.19	(0–28) 0.079	(122–149) 0.1017	(1176–1426) 0.0012	(0–28) 0.29	(122–149) 0.31

[a] Figures in parentheses refer to minutes elapsed from start of irradiation.

III. Results

Characteristic oxygen absorption curves as a function of time of irradiation of rubber are given in Fig. 3 for wave lengths 2537, 3130, 3660, and 4358 Å. In every case the intensity of monochromatic light incident on the rubber was kept constant within ±3%. It will be noted that an initial linear absorption occurs at 3130, 3660, and 4358 Å., whereas the absorption at 2537 Å. appears to be sharply autocatalytic from the beginning of irradiation. After about sixty minutes the rate increases autocatalytically at 3130 Å., but the rates remain constant at 3660 and 4358 Å. throughout the periods of observation. As far as the light rates at 2537 and 3130 Å. were followed they continue to increase with time of irradiation.

Fig. 4 in comparison with Fig. 3 shows that in GR-S the initial rates are lower than for rubber at 2537, 3130 and 3660 A. Further, the rates increase with time of irradiation at all these wave lengths, although at 2537 Å. the rate eventually begins to fall off again.

Diffusion of oxygen into the rubber is a factor affecting the rate of oxidation. In rubber at 3130, 3660 and 4358 Å., constant rates of oxygen absorption were apparently attained within a few minutes. However, at 2537 Å. the observed rate increases continually from the onset of irradia-

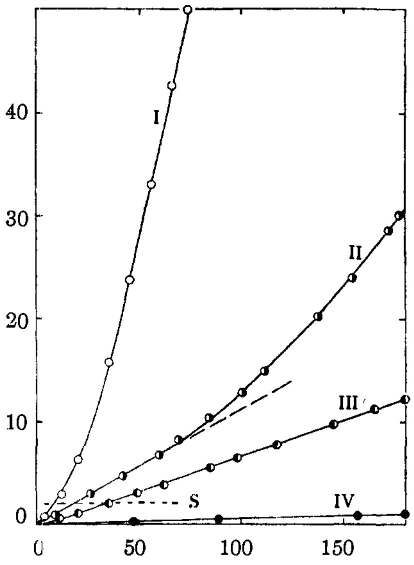

Fig. 3.—Photoöxidation of purified hevea rubber: I, Run 16 at 2537 Å. film 0.51 mm. thick; II, Run 2 at 3130 Å. film 0.48 mm. thick; III, Run 6 at 3660 Å. film 1.08 mm. thick; IV, Run 9 at 4358 Å. film 1.34 mm. thick; S = solubility of oxygen at 1 atmosphere pressure in 0.03 cc. of rubber (0.03 cc. = volume of irradiated rubber film 1.0 mm. thick).

tion, and the question arises whether this is due mostly to true autocatalytic effects or to a time lag in attaining a steady state.

No exact calculation has been made of the time lag required for the diffusion of oxygen into the rubber to attain, for example, 90% of a rate of oxygen consumption equal to that initially measured at 2537 Å. However, the following calculations on experiment 16 have been made:

0.0153 cc.	volume of irradiated rubber
0.00107 cc.	oxygen dissolved in irradiated rubber initially
0.000237 cc.	oxygen absorbed per minute according to initial measurement
0.000054 cc.	oxygen would diffuse into rubber per minute if diffusion occurred only through front irradiated area due to a linear concentration gradient down to zero concentration at the rear of the film.

The rate of diffusion and solubility of oxygen are calculated from the data of Barrer.[10] Comparison of the second and third figures shows that in 4.5 minutes as much oxygen flows into the rubber as was originally dissolved in the irradiated volume. This suggests that the rate of diffusion should approach the rate of reaction within a few minutes after irradiation is begun. Thus, the increasing rate may be attributed chiefly to autocatalytic effects and we will assume that at 2537 Å. also the measured rate corresponds closely to the actual rate of reaction at least in the initial stages of irradiation. Since about half the rubber film surface (including edges) which is in contact with oxygen is irradiated, it is apparent that at least half of the measured oxygen inflow must occur through the irradiated area. Comparing half of 0.000237 (the measured O_2 absorption rate) with 0.000054 (rate of O_2 absorption for linear concentration gradient) it appears that there is a high concentration gradient at the irradiated surface and that the gradient decreases in magnitude toward the rear of the sample.

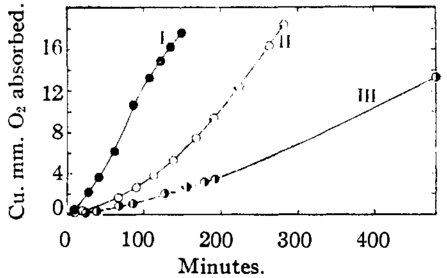

Fig. 4.—Photoöxidation of purified GR-S: I, Run 14 at 2537 Å. film 0.43 mm. thick; II, Run 12 at 3130 Å. film 0.91 mm. thick; III, Run 11 at 3660 Å. film 0.80 mm. thick.

In GR-S the observed rates in the ultraviolet always increased with time. However, since at each wave length the rate of oxygen absorption was considerably less than for rubber, it is likely that the effect of diffusion is less important in the photoöxidation of GR-S.

The quantum yields of oxidation for the measured reaction at various wave lengths of light are summarized in Table III and Fig. 5.

TABLE III

INITIAL AND THREE-HOUR QUANTUM YIELDS FOR DEPROTEINIZED RUBBER AND GR-S

λ (Å.)	Average initial yields Rubber	Average initial yields GR-S	Average three-hour yields Rubber	Average three-hour yields GR-S
2537	0.66	0.29	2.65[a]	0.31
3130	.51	.05	1.66	.16
3660	.17	.016	0.17	.016
4358	.02	...	.02	....
10000	..	...	.002[b]	.004[b]
17400	..	...	.001[b]	....

[a] After 1 hour. [b] Upper limits.

From Table III and Fig. 5 the following conclusions can be drawn: (a) All initial quantum yields are of the order of 1.0 or less, (b) initial and three hour quantum yields are lower for GR-S than for rubber, (c) quantum yields for rubber and GR-S decrease with increasing wave length. The initial quantum efficiency drops rapidly above 3660 Å. for rubber, and in the range above 2800 Å. for GR-S, (d) initial efficiencies are lower than the later (three-hour) yields at 2537 and 3130 Å. for both polymers. Figure 4 also shows that there is actually a slight increase at 3660 Å. for GR-S over this time interval, although the given yield is averaged over the first three hours.

Photochemical reactions in rubber not involving

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[10] R. M. Barrer, *Trans. Faraday Soc.*, **35**, 628 (1939).

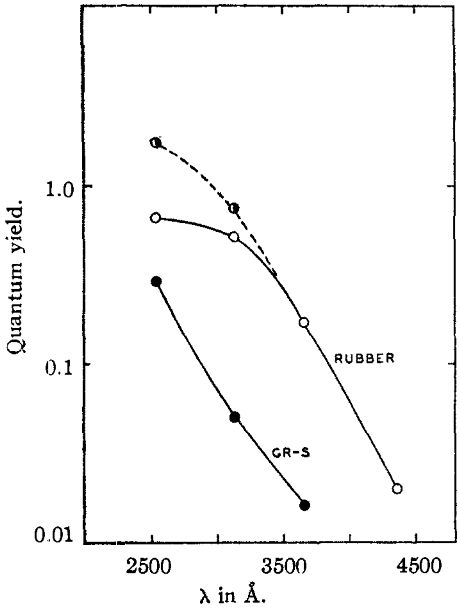

Fig. 5.—Initial quantum yields of photoöxidation as a function of wave length. The dotted line shows our best estimate of the upper limit for the quantum yields if they were measured in extremely thin films to eliminate diffusion effects.

oxygen have been studied by Bateman.[11] He measured the rates of gas formation from thoroughly degassed purified rubber when irradiated *in vacuo* in the wave length range 2300 to 4500 Å. An estimate of 4 × 10^{-4} was made for the quantum yield of non-condensable gas (mostly hydrogen) formation for the wave band 2300–3650. The largest relative yield reported at 2350–2850 Å. was about 2.5 times this so an upper limit of 10^{-3} may be set for the efficiency of non-condensable gas formation. From a typical experiment cited by Bateman (wave length not given), it can be calculated that the number of crosslinks formed is approximately equal to the molecules of non-condensable gas, while the number of double bonds disappearing may be as much as 100 times as large. Thus, the highest quantum yield of chemical change in rubber is not more than 0.1 in the absence of oxygen. If these calculations are permissible, chemical reactions of the rubber not involving oxygen account only in small part for the low quantum yields of oxidation.

The pale blue fluorescence excited in rubber by 3600 Å. light is visually very much weaker than the fluorescence of biacetyl. Since the strong fluorescence of biacetyl has a quantum yield of only 0.03,[12] it is concluded that fluorescence has a negligible effect in lowering the efficiency of the rubber–oxygen reaction.

The results discussed above on rubber have been obtained on unfractionated deproteinized rubber. In order to test the effects due to possible impurities in the rubber, a study was also made on the photoöxidation of Fractions II, III, and V described above under Experimental Details." The results obtained appear in Table IV.

TABLE IV

QUANTUM YIELDS OF OXIDATION OF FRACTIONS OF DEPROTEINIZED RUBBER AT 3130 Å.

Fraction	Quantum yield	
	Initial	3-hour
II	0.24	1.095
III	.23	0.86
V	.12	0.09
Whole	.51	1.66

Fractions II and III comprise two-thirds of the whole rubber and their quantum yields are substantially the same as for the whole rubber. The somewhat lower values obtained for II and III may be partly due to diffusion effects as thicker films were used for II and III than for the whole rubber. In view of this agreement, it is concluded that the suspended and soluble impurities in the whole rubber do not greatly affect the results. The value of the quantum yield for Fraction V appears to be definitely lower than the values obtained for Fractions II and III. Fraction V shows about ten times the absorption of light as Fractions II and III which in turn are identical with the whole rubber. Fraction V therefore increased considerably in extinction coefficient during the fractionation process. The presence of these new chromophoric groups in the rubber may then be responsible for the lower quantum yield of Fraction V.

In Fig. 2 the extinction coefficient of our rubber appears to be twice that of Bateman and Koch's[13a] at 2537 Å.[13b] If their rubber corresponds to pure polyisoprene, then only half the light in our experiments is absorbed by polyisoprene. If no oxidation results from light absorbed by impurities, then the quantum yield for polyisoprene is double the measured value. If, on the other hand, the light absorbed by impurities causes considerable oxygen reaction, the initial quantum yield of pure polyisoprene may even be lower than found.

The course of the dark reaction following illumination is illustrated in Fig. 6. The dark reaction curve may be divided into three parts: a period of rapid rate decay when light is turned off, a period of apparently constant oxygen absorption, and finally a period when the dark rate begins to show the familiar autocatalysis of olefin oxidation. The initial decay could be due in part to oxidation chains of long life dying away. After irradiation was stopped, the dark rate dropped 60% in experiment 2, 75% in 16, and 50% in 12 in only five minutes and a steady state is achieved in sixty to one-hundred minutes. These results

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(11) L. Bateman, *I. R. I. Trans.*, **21**, 118 (1945).

(12) G. M. Almy and P. R. Gillette, *J. Chem. Phys.*, **11**, 188 (1943).

(13a) L. Bateman and H. P. Koch, *J. Chem. Soc.*, 600 (1944).

(13b) Farmer, Koch and Sutton[13] give a curve for the absorption of the purified hexaisoprene, squalene, which corresponds very closely to that of our purified rubber in the region 2300–2900 Å.

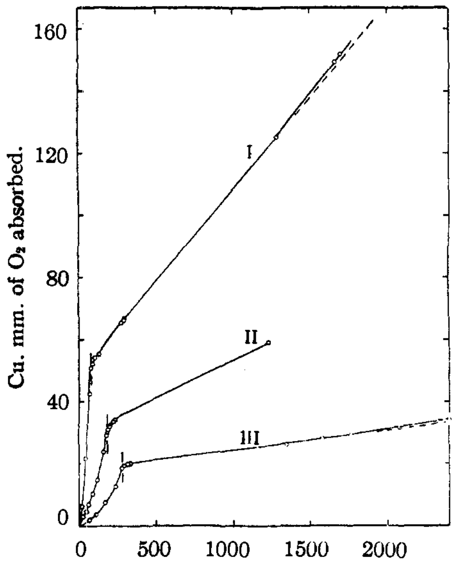

Fig. 6.—Absorption of oxygen by rubber and GR-S during and after irradiation: I, Run 16 rubber at 2537 Å.; II, Run 2 rubber at 3130 Å.; III, Run 12 GR-S at 3130 Å.; vertical lines indicate end of light exposure.

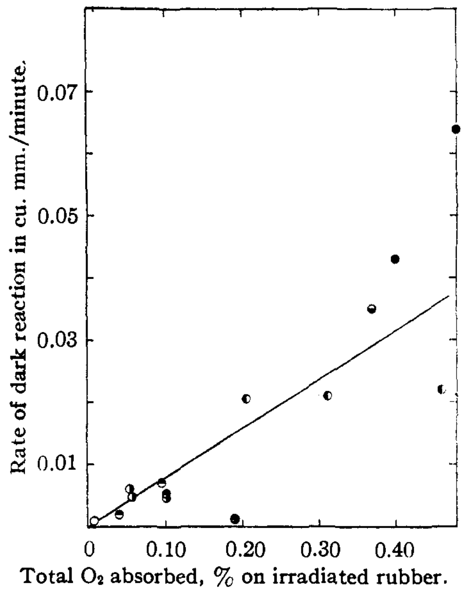

Fig. 7.—Dark reaction rates in rubber and GR-S as a function of the per cent. oxygen absorbed at the end of irradiation:

Rubber	Å.	GR-S
○	4538	
◑	3660	◒
◐	3130	◓
●	2537	⊕

indicate that with the rubber strips used, the major portion of the change in the diffusion rate was achieved in only a few minutes. The steady dark rate after irradiation is 6–8% of the final rate in light, or much too small to account for the oxidation rate increases occurring during irradiation.

The steady dark rate is, as might be expected, approximately proportional to the amount of oxygen absorbed during illumination (Fig. 7). A similar dependence has been found for the dark rate following the chain reaction of later stages of photoöxidation.[1] It has also been found that the thermal rate of autoxidation in ethyl linoleate increases linearly with the extent of oxidation.[14] In Fig. 7, the steady thermal rate is plotted against the per cent. oxygen absorbed by the irradiated portion of the rubber at the end of illumination. This per cent. oxygen is an average value and does not take into account non-uniformity of absorbed light. Oxygen absorbed is greatest at the front surface of the sample, particularly if the extinction coefficient is high. GR-S at 2537 Å. deviates considerably and the reasons for this behavior are discussed later.

IV. Discussion of Results

Before proceeding to a discussion of the significance of these results, it is pertinent to consider the light absorption process. Carr and Walter[15] have shown that in addition to an intense absorption band (*circa* λ = 2000 Å.) unconjugated olefins possess a weak absorption tail extending to longer wave lengths. This long wave length band is shifted to the red by successive alkyl substitutions on the double bond. A simultaneous increase in intensity also occurs. The absorption band at 2000 Å. has been discussed by Mulliken[16] in terms of molecular orbitals, and has been assigned to an N → V transition involving the excitation of an "unsaturation" bonding electron of the double bond to the corresponding antibonding molecular orbital. Since this is a singlet–singlet transition, Snow and Allsopp[17] have suggested that the weak long wave absorption is the analogous singlet–triplet transition, the change in multiplicity thus accounting for the weakness of the absorption.

Ultraviolet absorption curves are shown in Fig. 2 for trimethylethylene, 2,6-dimethyl-octadiene-2,6, and purified rubber corresponding, respectively, to one, two, and many isoprene units per molecule. Mulliken explains the red shifts of olefin spectra on alkyl substitution as due to hyperconjugation.[16,18] It is possible that the differences indicated in Fig. 2 between the spectra of mono-, di- and polyolefins are due to impurities, particularly in the case of rubber. If the differences are not due to impurities, these spectra indicate that, in addition to the alkyl substitution effect, there is an enhancement of absorp-

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[14] J. L. Bolland and G. Gee, *Trans. Faraday Soc.*, **42**, 236 (1946).

[15] E. P. Carr and G. F. Walter, *J. Chem. Phys.*, **4**, 756 (1936).

[16] R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 265 (1942).

[17] C. P. Snow and C. B. Allsopp, *Trans. Faraday Soc.*, **30**, 93 (1934).

[18] R. S. Mulliken, C. A. Rieke and W. G. Brown, This Journal, **63**, 41 (1941).

tion in the singlet–triplet region as the number of isoprene units per molecule increases.

All ultraviolet light absorbed in these photooxidation studies is in the long wave length band region. Therefore, we may tentatively conclude that in the photoöxidation of rubber in this spectral region an unsaturation electron of the double bond is lifted by the absorption of a photon to an antibonding level. Further, this electron is not localized but takes part in considerable hyperconjugation especially with the carbon–carbon bond midway between the double bonds.

Consideration of the absorption phenomenon leads to the question of the mechanism of attack by the oxygen molecule. Farmer[19] has shown that for unconjugated olefins photoöxidation leads at room temperature or lower to very high yields of a hydroperoxide on the carbon adjacent to the unchanged double bond. However, as he points out, this product is the result of a chain reaction and does not necessarily indicate that the initial attack occurs on the α-carbon atom. Farmer[20,21] considers the idea that the oxygen molecule in the initial step of the chain adds at the double bond. The radical resulting abstracts the hydrogen from the α-carbon of another olefin unit. However, Farmer, Koch and Sutton[22] in an earlier paper suggest that molecular oxygen may initiate reaction chains by detaching hydrogen atoms from the α-carbon, at least in 1:4-polyenes.

Farmer and Sundralingam[19b] irradiated a 1% rubber solution in cyclohexane at 12° with a mercury arc. The conditions involve high intensity light with the shortest effective wavelength at about 3130 Å. An induction period of less than one hour was reported and the least oxygen uptake recorded was 0.75%. All of our measurements were taken in the induction period of Farmer and Sundralingam's work and no photoöxidation was carried beyond 0.5% oxygen uptake. Thus, the work reported in this paper is concerned with the initiation of photoöxidation in purified rubber.

The initial quantum yield of 1.0 or less suggests that the primary reaction is not a chain process, but involves the addition of molecular oxygen to an isoprene unit to form a relatively stable intermediate. At 3660 and 4358 Å. where oxidation was carried to slight extents, the quantum yield remained constant during the entire period of irradiation and exhibited none of the autocatalytic character associated with the usual peroxidation of rubber. Thus, at these longer wave lengths the lack of chain character is especially apparent. At 3130 Å. the linear rate of oxidation gives way after about an hour to an autocatalytic effect, and at 2537 Å. the rate increases from the onset of irradiation.

The presence of inhibitors as the cause of low quantum yields is ruled out because of the purity of the rubber used. Furthermore, purification of the deproteinized rubber by fractionation did not appreciably change the quantum yield at 3130 Å. An alternative explanation which we favor is that the original stable intermediate, presumably a hydroperoxide, eventually attains such a concentration that a small but definite fraction of the light is absorbed by the hydroperoxide. This absorbed light decomposes the peroxide into radicals which initiate oxidation chains. This hypothesis is in agreement with linear rates at long wave lengths where a lesser extent of oxidation occurred and an increasing rate at shorter wave lengths where higher percentages of oxygen were absorbed. Further, such an effect could be expected to be more important at shorter wave lengths where peroxides absorb more strongly. In this connection, it was found that observed changes in light absorption during irradiation were small (about 1% or less) for all rubber samples except the fractionated rubbers. At 3130, 3660, and 4358 Å. a small decrease was always observed while in runs at 2537 Å. where the autocatalytic effect was most pronounced the light absorption during irradiation increased slightly.

It seems most probable that the oxygen molecule attacks the α carbon–hydrogen in the initial step to form a relatively stable hydroperoxide. If attack occurs at the double bond, a biradical would be formed which would probably initiate oxidation chains leading to high quantum yields, unless an intramolecular stabilizing reaction generally occurred. Farmer[21] suggests such a reaction leading to an allylic hydroperoxide by double bond displacement. With regard to the energetics of the initial reaction, Bolland and Gee[23] state that either double bond or α-methylene attack by oxygen is possible from thermochemical considerations. The possibility of energy transfer from the double bond to the α-methylene group is supported by the following ideas: (1) Heidt[24] has shown in the irradiation of *d*-glycosides that such transfers are possible, (2) the activated electron is not localized but takes part in hyperconjugation with the α-methylene group, and (3) Bateman[13] has shown that solid purified rubber irradiated *in vacuo* yields a gaseous product, mostly hydrogen, and that the reaction is probably due to dissociation of the α-carbon–hydrogen bond. Thus in the absence of oxygen of sufficient concentration, the photon energy occasionally splits off a hydrogen atom, while in the presence of oxygen a more frequent reaction occurs between the activated group and the molecule of oxygen.

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[19] (a) E. H. Farmer and D. A. Sutton, *J. Chem. Soc.*, 139 (1942); (b) E. H. Farmer and A. Sundralingam, *ibid.*, 125 (1943); (c) 121 (1942).

[20] E. H. Farmer, *I. R. I. Trans.*, **21**, 122 (1945).

[21] E. H. Farmer, *Trans. Faraday Soc.*, **42**, 228 (1946).

[22] E. H. Farmer, H. P. Koch and D. A. Sutton, *J. Chem. Soc.*, 541 (1943).

[23] J. L. Bolland and G. Gee, *Trans. Faraday Soc.*, **42**, **244** (1946).

[24] L. J. Heidt, *J. Franklin Inst.*, **234**, 473 (1942).

The GR-S was prepared with added hydroquinone as a shortstop. Subsequent acetone and alcohol extractions may not have removed all traces of this inhibitor. It is possible that the presence of hydroquinone or of quinone derived therefrom could vitiate some of the conclusions to be drawn. However, at 2537 Å. calculations using the extinction coefficients of ethyl benzene and *p*-benzoquinone show that the absorption of the phenyl groups in GR-S is many orders of magnitude greater than that of the quinone which would be present even if all of the added hydroquinone were converted to benzoquinone. At 3660 and 3130 Å., one can only say that the highest amount possible of benzoquinone accounts for only a very small fraction of the observed absorption.

The low quantum yield of oxidation of GR-S as in rubber indicates that chains do not immediately follow the primary reaction with oxygen. The phenyl group is the effective absorbing group, and it seems likely that the photon energy is not so readily transferred from the benzene nucleus to the adjacent carbon–hydrogen grouping as from the double bond in rubber. Such an effect would explain the lower quantum yields of GR-S as compared with rubber. At all three ultraviolet wave lengths GR-S shows rates increasing with time of absorption which again may be due to photodecomposition of the peroxide first formed. Due to the high extinction coefficient of GR-S, a large proportion of the oxidation will occur near the front surface of the film and near this surface the per cent. oxygen added will be much higher than the average reported in Table II. Thus sufficient peroxides for autocatalysis may be quickly formed. The discrepancy of the dark reaction in GR-S at 2537 Å. in relation to total oxygen absorbed may be due to the formation of an oxygen-impermeable surface film or to the formation of phenolic type inhibitors during oxidation. Larsen, Thorpe and Armfield[25] have shown that alkyl substituted benzenes form inhibitors during thermal oxidation at 110°.

Summary

The initial quantum yields of photoöxidation for purified Hevea rubber have been measured for various mercury arc lines in the wave length region 2537–17,400 Å. All experiments were carried out at room temperature and at an oxygen pressure of one atmosphere. At the outset of irradiation all quantum yields of combined oxygen are less than unity, although the quantum efficiency rises above 1.0 at 2537 and 3130 Å. as photoöxidation proceeds. The low quantum yield suggests that in its initial stages (less than 0.1% oxygen combined on the rubber) photooxidation is not a chain reaction. It is postulated as the first step in rubber photoöxidation that the light activated rubber group reacts with oxygen to give a relatively stable intermediate which does not immediately dissociate to give a free radical reaction chain.

The quantum yields of photoöxidation of purified GR-S were also measured under the same conditions as used for rubber. At each wave length the quantum yield was lower than for rubber, indicating formation of a stable intermediate in the initial reaction also.

[25] R. G. Larsen, R. E. Thorpe and F. A. Armfield, *Ind. Eng. Chem.*, **34**, 183 (1942).

PASSAIC, NEW JERSEY RECEIVED AUGUST 22, 1947

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies of Retarders and Inhibitors in the Emulsion Polymerization of Styrene. I. Retarders[1a]

BY I. M. KOLTHOFF AND F. A. BOVEY

Typical retarders of polymerization processes are defined as substances which retard the polymerization throughout the entire reaction period, without giving rise to induction periods. On the other hand, ideal inhibitors are defined as substances which cause a well-defined induction period, after which polymerization starts with its normal rate. There are substances the behavior of which is intermediate between that of compounds in either of these two classes.

Inhibitors and retarders both exert their effect by reacting with free radicals to produce reaction products which are either slow in propagating chains (oxygen is an example of this type of inhibitor) or unreactive so far as further chain propagation is concerned. The rate of reaction of inhibitors with free radicals is much greater than that of retarders. Ideal inhibitors react with such a rate that all the free radicals produced in the system are made inactive. Thus a typical induction period is observed, during which the inhibitor is consumed by reaction with the free radicals.

A typical retarder reacts with free radicals with such a rate that only a fraction of the free radicals produced can initiate normal polymerization. In addition, the growing polymer chains can react with the retarder. Thus a retarder acts as a typical chain-breaker. If this concept is correct, a retarder should reduce the molecular weight of the polymer, although this effect may not be large when effective chain transfer agents are present.

[1a] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government's synthetic rubber program.